Environmental Chemistry

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Overview

Lecture	Topic
1	Introduction / Organisation
2	Thermodynamic
3	Thermodynamic
4	Chemical Equilibrium
5	Photochemistry
6	Photolysis rate, frequency
7	Chemical lifetime
8	Heterogenous Reactions
9	Chemistry of the upper atmosphere
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11	Ozone Hole
12	Tropospheric chemistry
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14	Tropospheric chemistry

Introduction

Organisation:

Exercises: start next week

1st Ex.-Paper this week via e-mail

deadline: Monday or Tuesday next week

Introduction

Introduction

Literature:

P.W.Atkins, Physical Chemistry, Oxford University Press, 1990

Colin Baird, Environmental Chemistry, Free-man and Company, New York, 1995

Guy Brasseur and Susan Solom, Aeronomy of the Middle Atmosphere, D. Reidel Publishing Company, 1986

Guy P. Brassuer, John J. Orlando, Geoffrey S. Tyndall (Eds): Atmospheric Chemistry and Global Change, Oxford University Press, 1999

Finlayson-Pitts B. J. and J. N. Pitts, Atmospheric Chemistry

Richard P. Wayne, Chemistry of Atmospheres, Oxford university Press, 1991

Introduction

Chemical constituents of the Atmosphere

- Protons and electrons: come from the Sun and created in the atmosphere

- Ion: any species with/without electron

- Atoms: the smallest elemental molecules

- Free radicals: very reactive particles and have at least 1 unpaired electron

- Free radical ions: has electric charge, produce electrical field and can pull other molecules from the distance

- Particles
- Clusters
- Aerosols
- Cloud droplets

Introduction

The evolution of the atmosphere

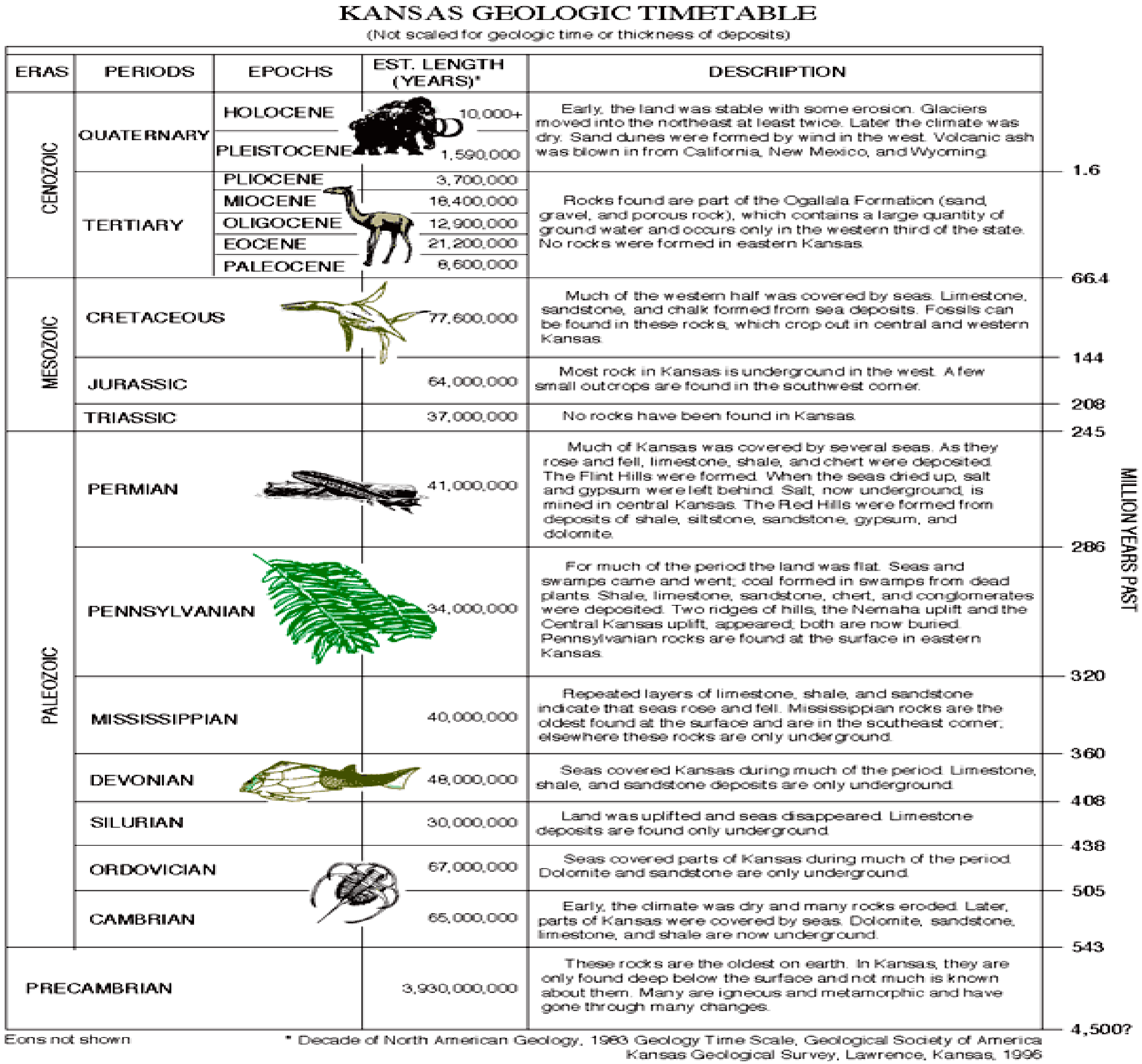
The atmosphere compositions were created from the earliest processes in the formation of the solar system and the planets.

The Big Bang created the Universe ~$15*10^9$ years

The solar system is $4.6*10^9$ years (and the Earth was formed), based on the radioactive dating of meteorites.

The evolution of Earth see from the geological table:

Introduction



KANSAS GEOLOGIC TIMETABLE

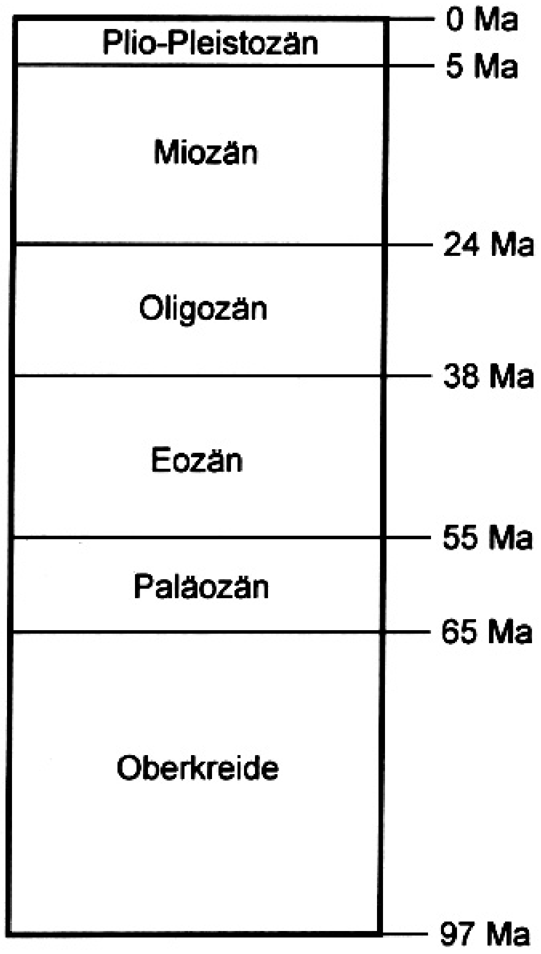
(Not scaled for geologic time or thickness of deposits)

ERAS	PERIODS	EPOCHS	EST. LENGTH (YEARS)*	DESCRIPTION	MILLION YEARS PAST
CENOZOIC	QUATERNARY	HOLOCENE	10,000+	Early, the land was stable with some erosion. Glaciers moved into the northeast at least twice. Later the climate was dry. Sand dunes were formed by wind in the west. Volcanic ash was blown in from California, New Mexico, and Wyoming.	
		PLEISTOCENE	1,590,000		1.6
	TERTIARY	PLIOCENE	3,700,000	Rocks found are part of the Ogallala Formation (sand, gravel, and porous rock), which contains a large quantity of ground water and occurs only in the western third of the state. No rocks were formed in eastern Kansas.	
		MIOCENE	18,400,000		
		OLIGOCENE	12,900,000		
		EOCENE	21,200,000		
		PALEOCENE	8,600,000		66.4
MESOZOIC	CRETACEOUS		77,600,000	Much of the western half was covered by seas. Limestone, sandstone, and chalk formed from sea deposits. Fossils can be found in these rocks, which crop out in central and western Kansas.	144
	JURASSIC		64,000,000	Most rock in Kansas is underground in the west. A few small outcrops are found in the southwest corner.	208
	TRIASSIC		37,000,000	No rocks have been found in Kansas.	245
PALEOZOIC	PERMIAN		41,000,000	Much of Kansas was covered by several seas. As they rose and fell, limestone, shale, and chert were deposited. The Flint Hills were formed. When the seas dried up, salt and gypsum were left behind. Salt, now underground, is mined in central Kansas. The Red Hills were formed from deposits of shale, siltstone, sandstone, gypsum, and dolomite.	286
	PENNSYLVANIAN		34,000,000	For much of the period the land was flat. Seas and swamps came and went; coal formed in swamps from dead plants. Shale, limestone, sandstone, chert, and conglomerates were deposited. Two ridges of hills, the Nemaha uplift and the Central Kansas uplift, appeared; both are now buried. Pennsylvanian rocks are found at the surface in eastern Kansas.	320
	MISSISSIPPIAN		40,000,000	Repeated layers of limestone, shale, and sandstone indicate that seas rose and fell. Mississippian rocks are the oldest found at the surface and are in the southeast corner; elsewhere these rocks are only underground.	360
	DEVONIAN		48,000,000	Seas covered Kansas during much of the period. Limestone, shale, and sandstone deposits are only underground.	408
	SILURIAN		30,000,000	Land was uplifted and seas disappeared. Limestone deposits are found only underground.	438
	ORDOVICIAN		67,000,000	Seas covered parts of Kansas during much of the period. Dolomite and sandstone are only underground.	505
	CAMBRIAN		65,000,000	Early, the climate was dry and many rocks eroded. Later, parts of Kansas were covered by seas. Dolomite, sandstone, limestone, and shale are now underground.	543
PRECAMBRIAN			3,930,000,000	These rocks are the oldest on earth. In Kansas, they are only found deep below the surface and not much is known about them. Many are igneous and metamorphic and have gone through many changes.	4,500?

Eons not shown

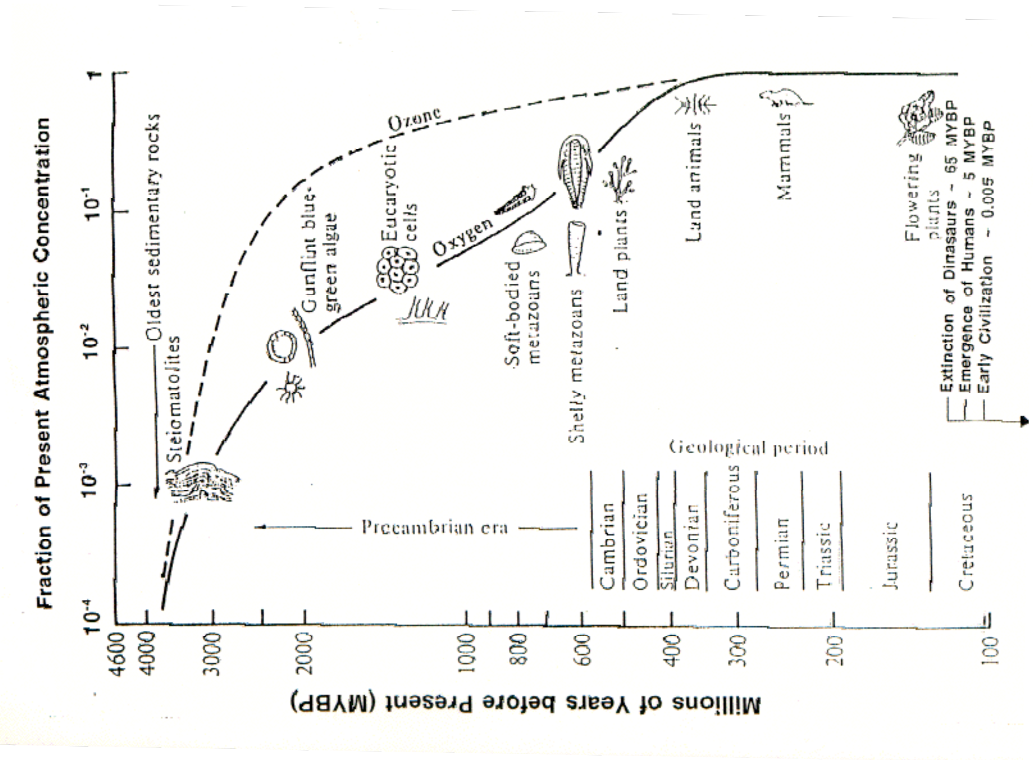
* Decade of North American Geology, 1983 Geology Time Scale, Geological Society of America

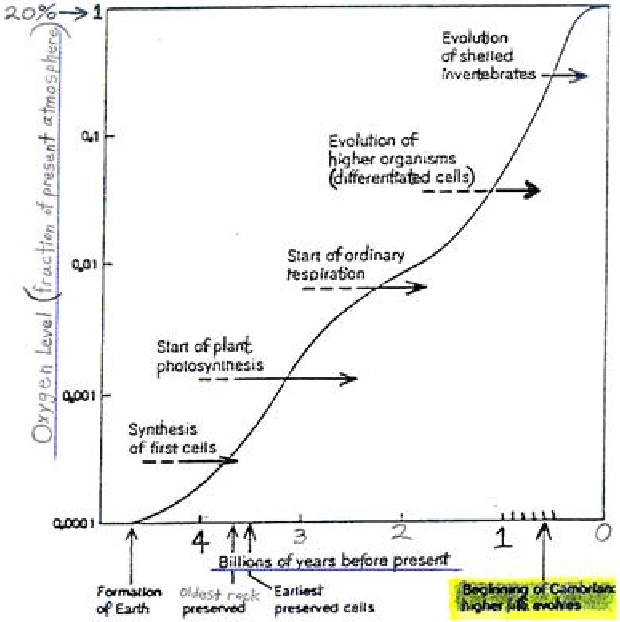
Kansas Geological Survey, Lawrence, Kansas, 1996



Introduction

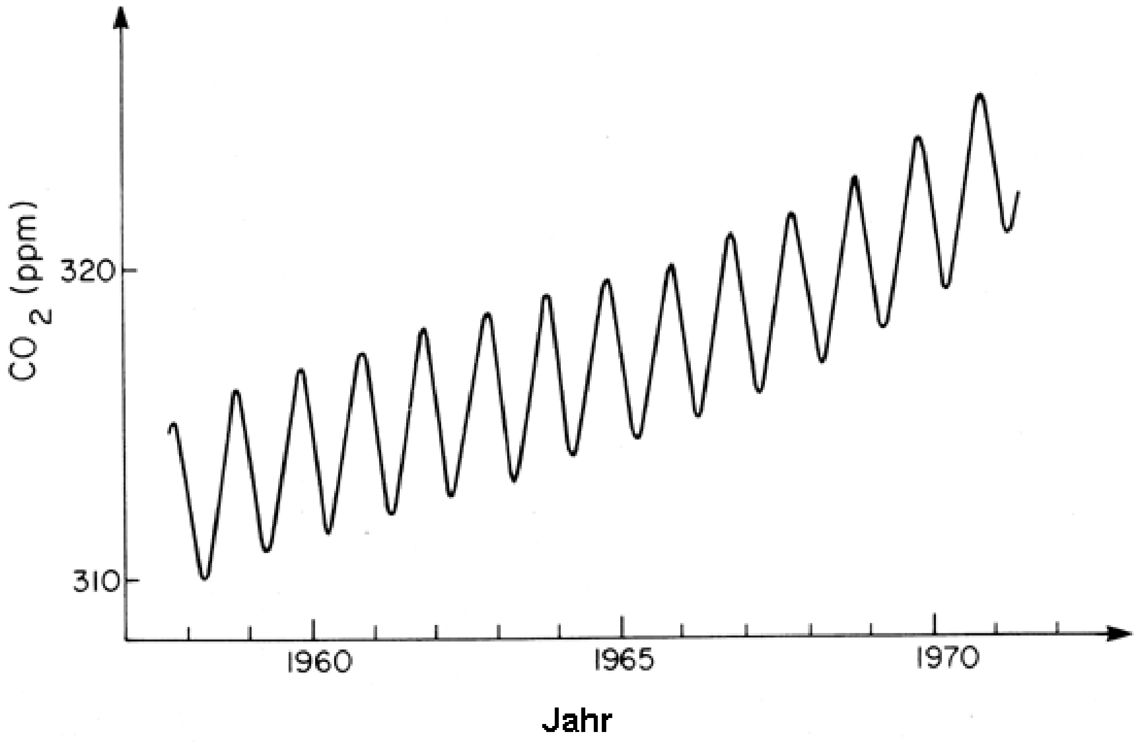
Evolution and changes in atmosphere and climates were modified by the





Introduction

The changing of population and standard of life lead to the CO_2 rising as shown below



Introduction

The evolution of the atmosphere

Sun system is ~ 4,6× 10^9 years old

At the beginning only a solar haze exists (a cloud with gas, particles and ice)

This cloud was compressed including temperature increase (from 2-3 K to 2000 – 3000 K at the end of compression)

→ all compounds evaporated

Inner planets: Venus, Earth, Mars only H_2, He, C, N_2 and oxygen combined with Si, Fe, Al and Ca

after 10^7 years planets exist but without atmosphere

Introduction

The evolution of the atmosphere

Primordialatmosphere

Oxygen was combined → so first a reduction of gases in the 1st atmosphere

1st atmosphere: CH_4, NH_3, H_2, H_2O

(in the liquid planets: NiO, FeO to Ni and Fe reduced)

→ earth‘s core

Consequently: O_2 was produced

→ water vapor, CO_2, N_2 (probably similar to the atmosphere of the vulcanoes today)

Introduction

H_2O	80%
CO_2	10%
H_2S	7%
CO	0.5%
CH_4	In traces
NH_3	In traces

Introduction

Atmosphere today:

Production of:

Hydrosphere: H_2O

Lithosphere: carbonates

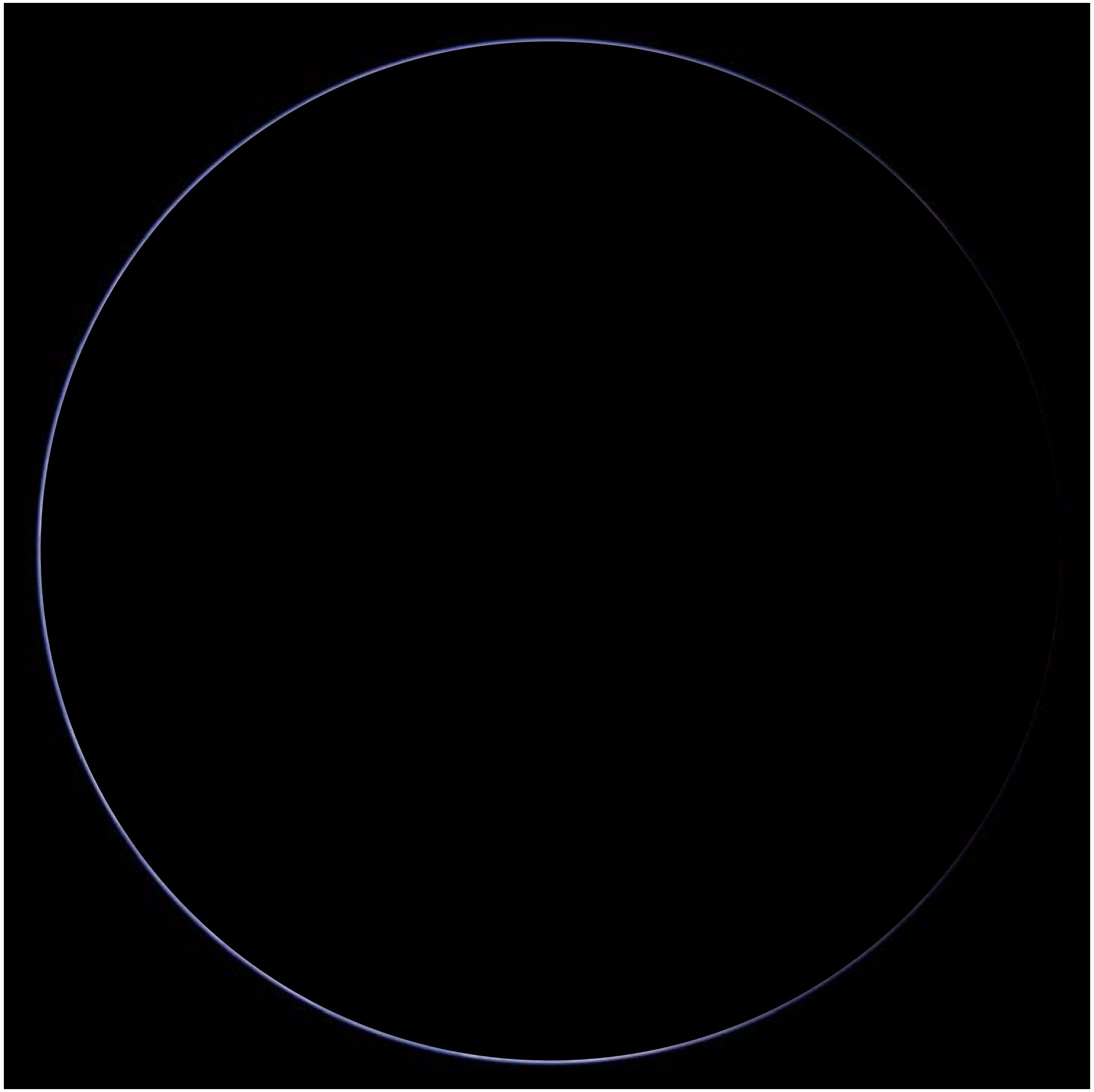
Biosphere: (O_2 was produced)

$2\ CO_2 + \text{UV-radiation} \rightarrow CO + O_2$

$2\ H_2O + \text{UV-radiation} \rightarrow 2\ H_2 + O_2$

$6\ CO_2 + 6\ H_2O + h\nu + \text{Chlorophyll} \rightarrow C_6H_{12}O_6 + 6\ O_2$

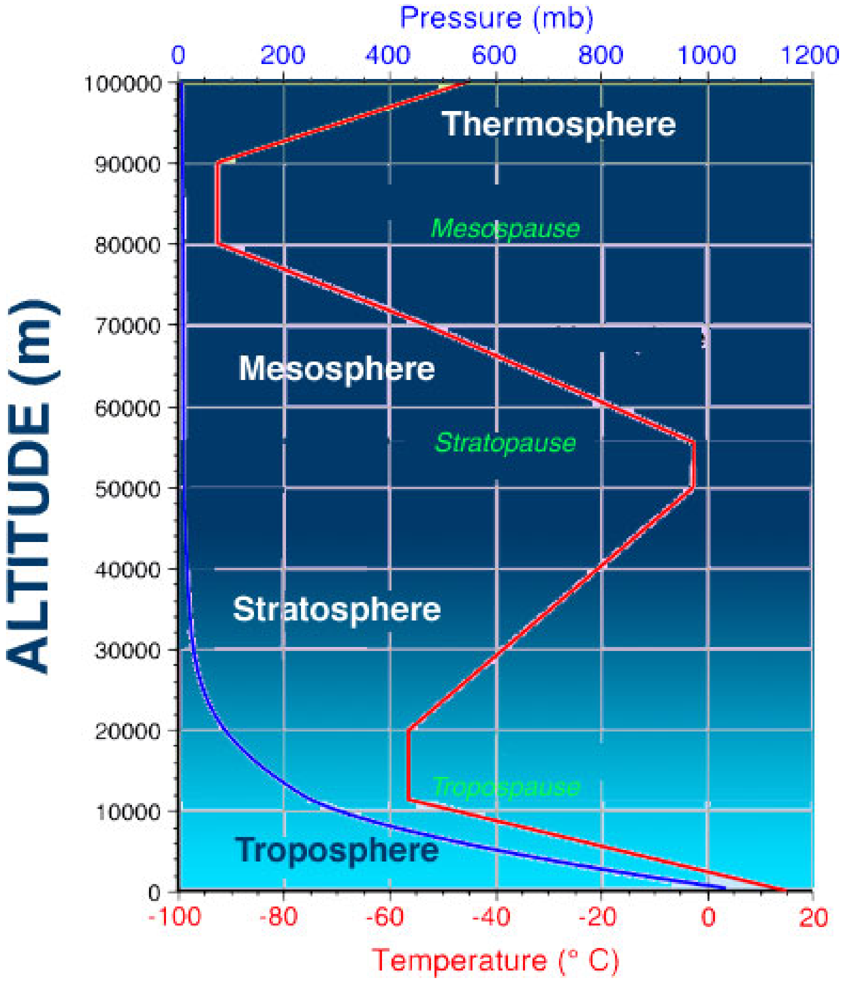
Atmosphere – a thin cover



~ 98% of total atmospheric air masses within the lower 30 km

Introduction

Atmosphere today:



Thermodynamic

Thermodynamic

Ideal Gas

Assumptions:

- ensemble of individual molecules
- no interaction apart from collision
- no chemical reactions
- no appreciable volume of individual molecules

State properties of a gas: p, T, V, and n

Equation of state for the ideal gas:

$$pV = nRT$$

or

$$pV = NkT$$

p = pressure, V = volume, n = number of moles,
N = number of molecules, R = universal gas constant,
k = Boltzman constant, T = temperature

Thermodynamic

Pressure:

1 Pa = 1 N/m^2
1 bar = 100 kPa
1 atm = 101.325 kPa = 760 Torr

Pressure of atmosphere is measured with a **barometer**

Temperature:

Temperature tells us about the flow of energy

energy flows from A to B: A has higher temperature

Energy doesn‘t flow: A and B have the same temperature (thermal equilibrium)

Thermodynamic temperature scale: 0°C = 273.15K

Thermodynamic

Gas constant R:

$R = 8.314\ J\ K^{-1}\ mol^{-1}$

Boyle's law:
If n, T = constant (isotherm)

$$pV = \text{constant}$$

$$p_2V_2 = p_1V_1$$

Gay-Lussac's law:
If n, p or if n, V = constant (isobar, isochor)

$$V_1/V_2 = T_1/T_2$$

$$p_1/p_2 = T_1/T_2$$

Thermodynamic

Ideal Gas

All gases act as ideal gases at very low pressure;

to good approximation, gases in the atmosphere can be treated as ideal gases with the exception of water vapour (phase changes)

Thermodynamic

Mixtures of Ideal Gases

Dalton's law:

The pressure exerted by a mixture of perfect gases is the sum of the pressures exerted by the individual gases occupying the same volume alone or

$$p = p_A + p_B$$

(air: N_2: 78.08%, O_2: 20.95%, CO_2: 0.04%.
These add up to 100% of dry air, so there are almost no other gases (really, 0.002%)(.

Mole fraction:

The mole fraction of a gas X in a mixture is the number of moles of X molecules present (n_X) as a fraction of the total number of moles of molecules (n) in the sample:

$$x_x = \frac{n_x}{n}$$

with

$$n = n_A + n_B + n_C + \ldots.$$

Thermodynamic

Partial pressure:

The partial pressure of a gas in a mixture is *defined* as the product of mole fraction of this gas and total pressure of the gas:

$$p_x = x_x p$$

Thermodynamic

Units

Quantity	Name	Units
Number of molecules	N	mol = 6.022 x10^{23}
Density	N	particles / m^3
Mass	ρ	kg / m^3
Volume mixing ratio	μ	ppmV = 10^{-6} ppbV = 10^{-9} pptV = 10^{-12}
Mass Mixing ratio	μ	ppmm =10^{-6} ppbm =10^{-9} pptm = 10^{-12}
Different column definition		molec/cm^2 DU = 10^{-3} cm at STP

Thermodynamic

Excursion: Ideal Gas Law

The ideal gas law can be expressed in molecules or moles:

$$pV = nRT$$

or

$$pV = NkT$$

R or R* = **Universal gas constant** = 8.314 J mol^{-1} K^{-1}

k = **Boltzmann's constant** = 1.381 10^{-23} J molec^{-1} K^{-1}

N_A = **Avogadro's number** = 6.022 10^{23} mol^{-1}

Molar quantity:

$$n = \frac{N}{N_A}$$

$$V = \frac{V}{n}$$

$$M = \frac{m}{n}$$

Thermodynamic

$$R = N_A k$$

Number density:

$$\frac{N}{V} = \frac{p}{kT}$$

Mass density:

$$\rho = \frac{m}{V} = \frac{Nm_x}{V} = \frac{m_x p}{kT} = \frac{M_x p}{N_A kT} = \frac{M_x p}{RT}$$

m_x = Mass of one molecule x, M_x molar mass of x

In some books, individual gas constants are defined for each gas:

$$MR_x = \frac{R}{M_x}$$

Thermodynamic

Real Gas:

Interactions between molecules are taken into account

Moving in a Volume (V) - smaller volume (V - nb)

With nb: total volume taken by the molecules themselves

Pressure depends on frequency of collisions with walls and the force of each collision - reduction of pressure -a (n/V)²

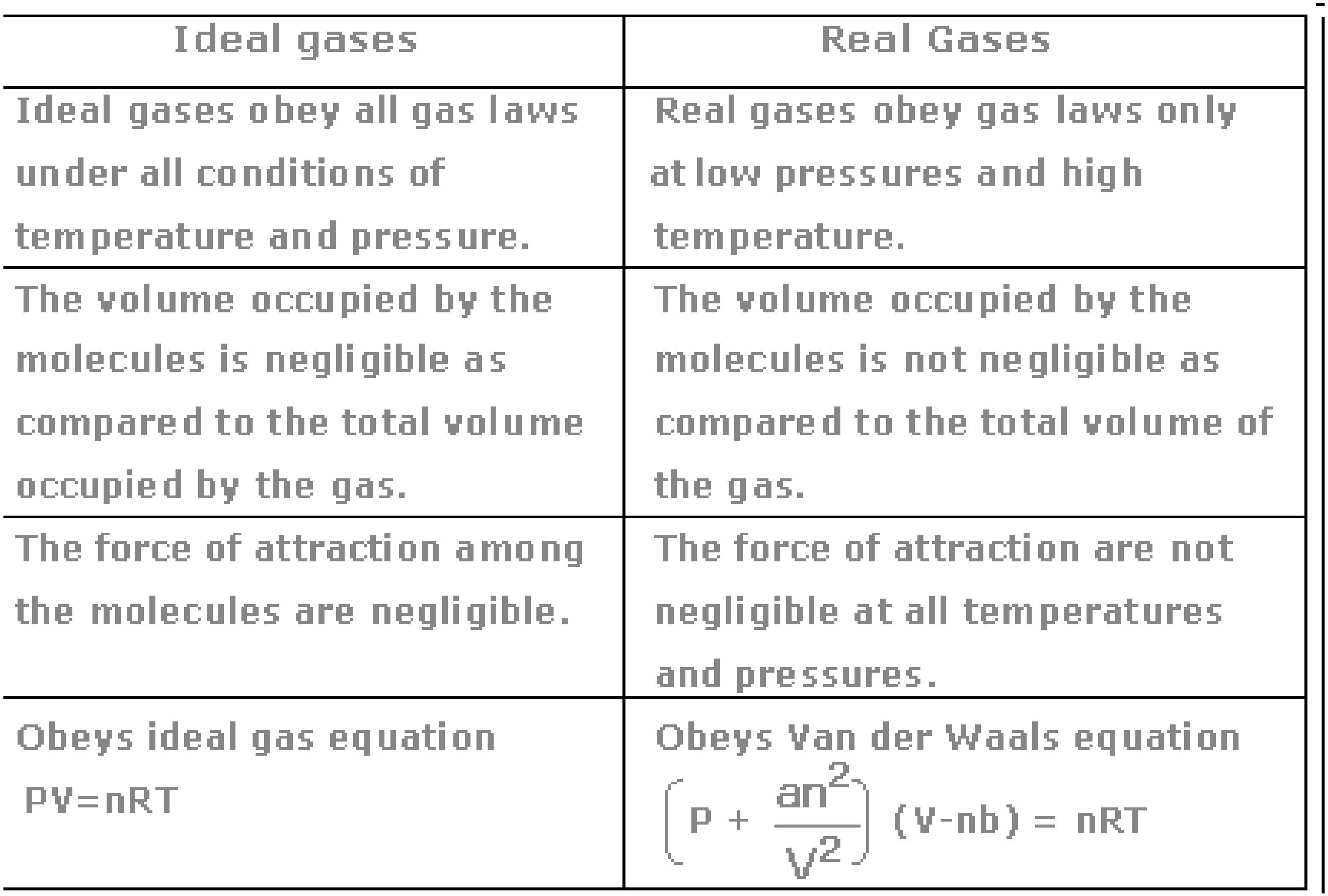
$$p = \frac{nRT}{V - nb} - a\left(\frac{n}{V}\right)^2$$

Often written like V_m = V/n where a/V_m^2 = internal pressure

$$p = \frac{RT}{V_m - b} - \frac{a}{V_m{}^2}$$

$$\left(p + \frac{an^2}{V^2}\right)(V - nb) = nRT$$

Thermodynamic



Ideal gases	Real Gases
Ideal gases obey all gas laws under all conditions of temperature and pressure.	Real gases obey gas laws only at low pressures and high temperature.
The volume occupied by the molecules is negligible as compared to the total volume occupied by the gas.	The volume occupied by the molecules is not negligible as compared to the total volume of the gas.
The force of attraction among the molecules are negligible.	The force of attraction are not negligible at all temperatures and pressures.
Obeys ideal gas equation $PV=nRT$	Obeys Van der Waals equation $\left(P + \frac{an^2}{V^2}\right)(V-nb) = nRT$

Thermodynamic

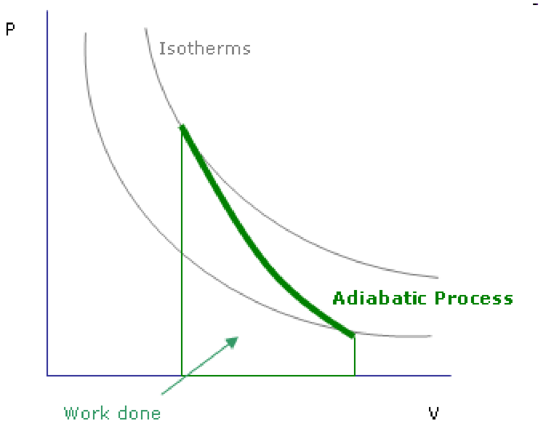
Work, heat, energy are basics of thermodynamic, the most fundamental is work

Work is done by the system to bring a change

Energy is the capacity of a system to do work

Energy changes as a result of temperature difference - energy has transferred as heat

Adiabatic:	walls do not permit energy transfer
Exothermic:	processes realising energy as heat
Endothermic:	processes absorbing energy as heat



Thermodynamic

1st Law of Thermodynamic

example: increase the temperature of 1kg H_2O from 14°C to 15°C, the work of 4.18 kJ has to be carried out

no energy is lost, it is only exchanged from one to the other (work – heat)

in the case heat is coming to a system → variation in volume, pressure, content, temperature = internal energy (total energy of a system) is changing
Each system has an internal energy U, which is only changing when heat (Q) or work is changing

$$U_2 - U_1 = W + Q = -pdV + Q = \Delta U = \int dU$$

W can be electrically or mechanically

for V = constant (isochor) dV =0

$$(dU)_V = dQ$$

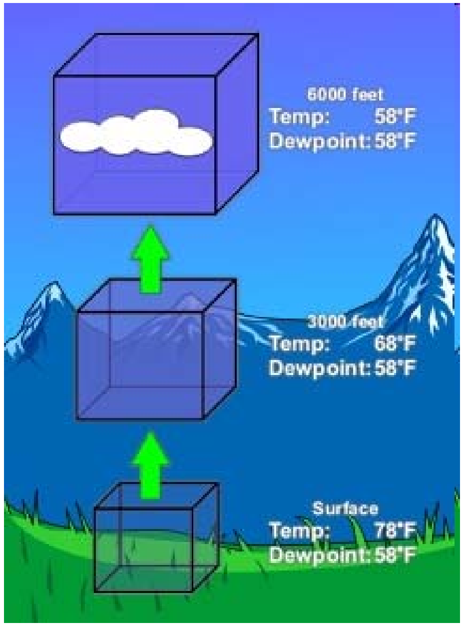
as follows:

$$(U_2 - U_1)_V = Q$$

Thermodynamic

Adiabatic process:

$$W_{ad} = U_2 - U_1 = \Delta U$$



Mechanical work: work (compression or expansion) is done by moving an object a distance dz against a force - internal energy will decrease (negative value)

$$dW = -Fdz$$

$$W = -\int_{z1}^{z2} Fdz = -(z_2 - z_1) = -mgh$$

g: 9.81 m s^{-2}

Thermodynamic

Compression, expansion: isothermal

$$W = -\int_{V1}^{V2} p dV = -nRT \int_{V1}^{V2} \frac{dV}{V} = -nRT \ln \frac{V_2}{V_1}$$

Internal energy, heat, work heat have the same unit: Joule (J)

$1 J = 1\ kg\ m^2\ s^{-2}$

1st law: U of a system is constant unless it is changed by doing work or by heating

Thermodynamic

in a closed system the variation of the internal energy is equal to the exchange of heating with the environment when dV = 0

if dp = 0 (isobar)

$$U_2 - U_1 = Q - p(V_2 - V_1)$$

$$(U_2 + pV_2) - (U_1 + pV_1) = Q$$

as follows: the exchange of heat is not now the variation of internal energy it is

$$U + pV = H$$

H = Enthalpy

Thermodynamic

$$(H_2 - H_1) = Q$$

$$H = f(T, p, n_1, n_2, \dots n_k)$$

differential

$$dH = \left(\frac{\partial H}{\partial T}\right)_{p,n} dT + \left(\frac{\partial H}{\partial p}\right)_{T,n} dp + \left(\frac{\partial H}{\partial n_1}\right)_{T,p,n_j} dn_1 + \dots$$

$$dU = \delta Q + \delta W = \delta Q - pdV = \left(\frac{\partial U}{\partial T}\right)_V dT + \left(\frac{\partial U}{\partial V}\right)_T dV$$

$$dH = d(U + pV) = dU + pdV + Vdp = \left(\frac{\partial H}{\partial T}\right)_V dT + \left(\frac{\partial H}{\partial p}\right)_T dp$$

Thermodynamic

molar heat capacity for isochor and isobar work:

$$c_V = \left(\frac{\partial Q}{\partial T}\right)_V = \left(\frac{\partial U}{\partial T}\right)_V$$

$$c_p = \left(\frac{\partial Q}{\partial T}\right)_p = \left(\frac{\partial H}{\partial T}\right)_p$$

relation between c_V and c_p:

$$c_p - c_V = \left(\frac{\partial H}{\partial T}\right)_p - \left(\frac{\partial U}{\partial T}\right)_p$$

$$H = U + pV = U + nRT$$

$$c_p - c_V = \left(\frac{\partial U}{\partial T}\right)_p + nR - \left(\frac{\partial U}{\partial T}\right)_p = nR$$

Thermodynamic

work of adiabatic expansion: as $c_V = \frac{dU}{dT}$

$$W = \int dU = \int c_V \, dT = c_V (T_2 - T_1) = c_V \Delta T$$

Special cases:

irreversible adiabatic expansion:

$$\Delta T = \frac{-p_{ex} \Delta V}{c_V} \qquad pV = nRT$$

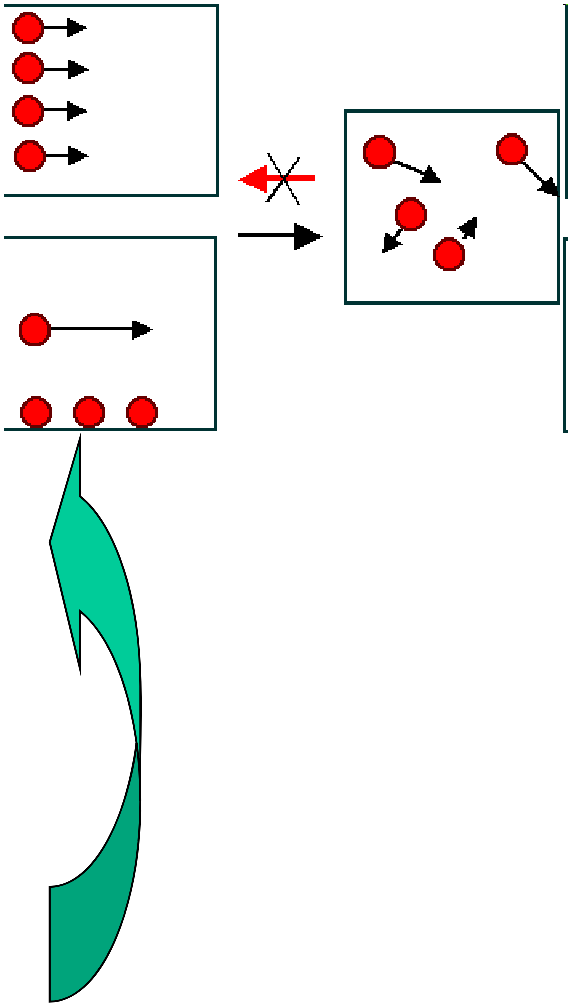
irreversible adiabatic expansion:

$$c_V dT = -p dV \Rightarrow \frac{c_V dT}{T} = \frac{-nR dV}{V}$$

Thermodynamic

it is impossible that heat is converted to mechanical energy (work) and we have to find solutions for irreversible processes as follows:

2nd Law of Thermodynamic



new function is introduced: Entropy S

$$\frac{dQ_{rev}}{T} = dS = S_2 - S_1 = nR\ln(\frac{V_2}{V_1})$$

Because isotherm → dT =0 reversible

$$dU = dQ - pdV = (\frac{\partial U}{\partial T})_V dT = 0$$

$$dU = dW + dQ$$

$$-dQ = dW = nRT\ln\left(\frac{V_2}{V_1}\right)$$

Thermodynamic

$$\frac{dQ_{rev}}{T} = dS = S_2 - S_1 = nR\ln(\frac{V_2}{V_1})$$

$$dS = \frac{dQ_{rev}}{T} = (\frac{\partial S}{\partial T})_V dT + (\frac{\partial S}{\partial V})_T dV$$

dependent of T and V

$$dS = \frac{dQ_{rev}}{T} = (\frac{\partial S}{\partial T})_p dT + (\frac{\partial S}{\partial p})_T dp$$

dependent of T and p

Reversible exchange of heat with environment

$$dS = \frac{dU + pdV}{T} = \frac{1}{T}\left[(\frac{\partial U}{\partial T})_V dT + (\frac{\partial U}{\partial V})_T dV + pdV\right]$$

$$dS = \frac{dH - Vdp}{T} = \frac{1}{T}\left[(\frac{\partial H}{\partial T})_p dT + (\frac{\partial H}{\partial p})_T dp - Vdp\right]$$

Thermodynamic

$$dS = \frac{dQ_{rev}}{T} = \left(\frac{\partial S}{\partial T}\right)_p dT + \left(\frac{\partial S}{\partial p}\right)_T dp = \frac{dU + pdV}{T} = \frac{dH - Vdp}{T}$$

As follows:

$$dS = \frac{c_V}{T} dT + \frac{1}{T}\left[\left(\frac{\partial U}{\partial V}\right)_T + p\right] dV$$

$$dS = \frac{c_p}{T} dT + \frac{1}{T}\left[\left(\frac{\partial H}{\partial p}\right)_T - V\right] dp$$

in the case of changing the phase (e.g. liquid – solid) reversible: entrophy of changing is used

$$dS = \frac{dQ}{T} = \frac{dH - Vdp}{T}$$

For isobar and isotherm:

$$\Delta S = \frac{\Delta H}{T}$$

Thermodynamic

Normally all reactions are irreversible but in the case of equilibrium - changing the phase:

$$\Delta S = \frac{\Delta H}{T} \Rightarrow TdS = dH$$

$$dS = 0$$

Thermodynamic

in the case of a closed system and using the 1st law of thermodynamic:

$$dS - \frac{dU}{T} \geq 0 \Rightarrow \quad \text{(V, T = constant)}$$

$$dS - \frac{dH}{T} \geq 0 \Rightarrow \quad \text{(p, T = constant)}$$

now with Helmholtz (free energy A) and Gibbs (free enthaphy G) new functions are introduced:

$$A = U - TS$$

$$G = H - TS$$

$$\Delta A = \Delta U - T\Delta S$$

$$\Delta G = \Delta H - T\Delta S$$

in the case G is positiv the reaction is not spontaneous and in contrast if G is negativ the reaction is spontaneous

Thermodynamic

4 thermodynamic functions: U, H, A, G
Closed system, homogenic compound
Work only as so called “volume-work”

Internal energy following the 1st law and replacing dQ with entropy and dW with “volume-work”:

$$dU = dQ + dW = TdS - pdV$$

Enthalphy: H = U + pV, dH = dU + pdV + Vdp

$$dH = TdS + Vdp$$

dA = dU - TdS - SdT

$$dA = -SdT - pdV$$

$$dG = -SdT + Vdp$$

Thermodynamic

⇨Guggenheim scheme:

	S	U	V	
+	H		A	-
	p	G	T	

$$T = \left(\frac{\partial U}{\partial S}\right)_V = \left(\frac{\partial H}{\partial S}\right)_p$$

$$p = -\left(\frac{\partial U}{\partial V}\right)_S = -\left(\frac{\partial A}{\partial V}\right)_T$$

$$S = -\left(\frac{\partial A}{\partial T}\right)_V = -\left(\frac{\partial G}{\partial T}\right)_p$$

$$V = \left(\frac{\partial H}{\partial p}\right)_S = \left(\frac{\partial G}{\partial p}\right)_T$$

Thermodynamic

Definitions:

Adiabatic:	no exchange of energy (walls do not permit energy transfer)
Diathermic:	contrast to adiabatic
Exothermic:	process when heat (energy) is released
Endothermic:	contrast to exothermic (absorbing of energy)

Thermodynamic

Thermodynamics of mixture

Partial molar volumes of the components of a mixture

$$V_j = \left(\frac{\partial V}{\partial n_j} \right)_{p,T,n'}$$

n_j are the numbers of moles
the composition of the mixture (e.g. H_2O and C_2H_5OH) is changed by the addition of e.g. dn_A of A)

$$dV = \left(\frac{\partial V}{\partial n_A} \right)_{p,T,n_B} dn_A + \left(\frac{\partial V}{\partial n_B} \right)_{p,T,nA} dn_B = V_A dn_A + V_B dn_B$$

in the case we know the partial molar volumes then the total volume

$$V = n_A V_A + n_B V_B$$

Thermodynamic

partial molar quantity can also be expressed by the partial molar Gibbs function

$$\mu_j = \left(\frac{\partial G}{\partial n_j} \right)_{p,T,n'}$$

→ total Gibbs function

$$G = n_A \mu_A + n_B \mu_B$$

μ_A μ_B are the chemical potentials (or molar free enthaphy) at the composition changing

$$dG = n_A d\mu_A + n_B d\mu_B$$

at constant pressure and temperature

$$n_A d\mu_A + n_B d\mu_B = 0$$

$$\sum n_j d\mu_j = 0$$

two gases at a temperature and a pressure

Thermodynamic

→ Gibbs function of mixing

$$\Delta G_{mix} = n_A RT \ln \frac{p_A}{p} + n_B RT \ln \frac{p_B}{p}$$

other thermodynamic mixing functions

$$-S = \frac{\partial G}{\partial T}_{p,n}$$

a mixture of a perfect gas

$$\Delta S_{mix} = -\left(\frac{\partial \Delta G_{mix}}{\partial T}\right)_{p,n_A,n_B} = -nR\left(x_A \ln x_A + x_B \ln x_B\right)$$

since $\ln x < 0 \rightarrow \Delta S_{mix} > 0$

the enthalpy of mixing is then:

$$\Delta G = \Delta H - T\Delta S$$

Thermodynamic

Chemical equilibrium:

$$\left(\Delta G\right)_{p,T} = 0$$

Chemical reaction, if the chemical potential is decreasing:

$$\left(\Delta G\right)_{p,T} < 0$$

Thermodynamic

For isothermal processes $\Delta T = 0$

and $\Delta H_{mix} = 0$ (constant p, T)

The chemical potential of liquids :

At equilibrium:

$$\mu = \mu^{\Theta} + RT \ln = \left(\frac{p}{p^{\Theta}} \right)$$

with the chemical potential

$$\mu = \left(\frac{\partial G}{\partial n} \right)_{p,T}$$

Thermodynamic

Ideal solution:

The chemical potential of pure liquid A is $\mu^*_A(l)$

The vapor pessure is then: p^*_A

Chemical potential in vapor is:

$$\frac{p^*_A}{p^\Theta}$$

$$\mu_A^\Theta + RT\ln$$

Thermodynamic

the both chemical potential are equal at equilibrium:

$$\frac{p*_A}{p^{\Theta}}$$

$$\mu_A*(l) = \mu_{A^{\Theta}}* + RT\ln$$

in addition an other substance is present then:
The chemical potential of A in the liquid is $\mu_A(l)$ and its vapor pessure is then: p_A

In this case:

$$\mu_A(l) = \mu_A{}^{\Theta} + RT\ln\left(\frac{p_A}{p^{\Theta}}\right)$$

to eliminate the standard potential of the gas the eqn. are combined

Thermodynamic

Henry’s Law

With x_B (mole fraction of solute) and K_B is a constant (with dimensions of pressure)
Spontaneous chemical reactions

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

A,	Reaction completed:	all the transformed to products
B,	reaction partially:	equal A + B and C + D
C,	no reaction:	only reactants

$$A \rightarrow B$$

Thermodynamic

perfect gas equilibrium: A ↔ B equilibrium

$$\Delta G = \mu_B - \mu_A = \left(\mu_B{}^{\Theta} + RT \ln \frac{p_B}{p^{\Theta}} \right) - \left(\mu_A{}^{\Theta} + RT \ln \frac{p_A}{p^{\Theta}} \right)$$

$$\Delta G = \Delta G^{\Theta} + RT \ln \frac{p_B}{p_A}$$

the ratio of the partial pressures is an example of reaction quotient Q_p

$$\Delta G = \Delta G^{\Theta} + RT \ln Q_p$$

at equilibrium $\Delta G = 0$, the value of the reaction quotient = equilibrium constant K_p

$$K_p = (Q_p)_{equilibrium} = \left(\frac{p_B}{p_A} \right)_{eq}$$

then with $\Delta G = 0$, $Q_p = K_p$

$$RT \ln K_p = -\Delta G^{\Theta}$$

Thermodynamic

e.g $2A + 3B \rightarrow C + 2D$

$$\Delta G^{\Theta} = -2\mu_A{}^{\Theta} - 3\mu_B{}^{\Theta} + \mu_C{}^{\Theta} + 3\mu_D{}^{\Theta}$$

$$K = (Q)_{equilibrium} = \left(\frac{a_C a_D{}^2}{a_A{}^2 a_B{}^3} \right)_{eq}$$

Chemical Equilibrium

Chemical Equilibrium

Gibbs-Energy is defined: $G = U + pV - TS$

As $H = U + pV \quad \rightarrow \quad U = H - pV$

$$G = H - pV + pV - TS = H - TS$$

With U, V, S and H

Often the differential form is used:

$$dG = dU + d(pV) - d(TS) = dQ + dW + d(pV) - d(TS)$$

And $dS = \dfrac{dQ}{T} \quad \rightarrow \quad TdS = dQ$

$$dG = TdS - pdV + pdV + Vdp - TdS - SdT = Vdp - SdT$$

Chemical Equilibrium

If the number of moles are not const:

$$dU = TdS - pdV + \Sigma \mu_i dn_i$$

$$dG = -SdT + Vdp + \Sigma \mu_i dn_i$$

At the equilibrium, the term of Gibbs energy equal zero, .

$$dG = 0$$

Chemical Equilibrium

Any reactions try to move toward the equilibrium in both reactant and product and time is needed to reach the equilibrium e.g. in the atmosphere at the present time, CO_2 is rising to reach the equilibrium temperature.
Chemical Equilibrium: the state in which the chemical activities or concentrations of the reactants and products have no net changed over time. The reaction rates of the forward and reverse reactions are generally not zero but, being equal, there are no net changes in any of the reactant or product concentrations. This process is called dynamical euqilibrium

In this path, we will use the thermodynamics to describe the equilibrium under the reaction conditions. In term of Gibbs energy for the perfect (ideal) gas,

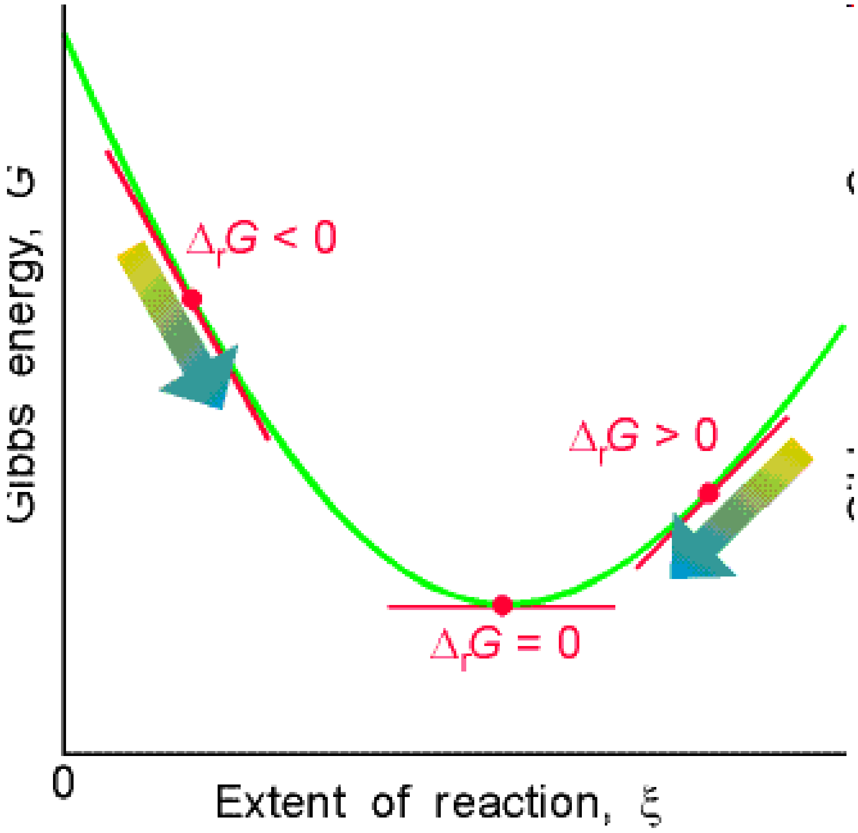
$$\Delta G = \Delta G^{\Theta} + RT \ln \frac{p_A}{p_B}$$

as p_A is the partial pressure of reactant A and p_B is the partial pressure of product B.

Chemical Equilibrium

At the equilibrium, the term of Gibbs energy equal zero, .

$$\Delta G = 0$$



Chemical Equilibrium

Let consider the reaction;

$$\nu_A A + \nu_B B \Leftrightarrow \nu_C C + \nu_D D$$

in term of the reaction activity, we define the ratio of partial pressures at equilibrium as the thermodynamic equilibrium constant (as denoted K_p). Thus the Gibbs energy of the standard state can be written as:

$$-\Delta G^{\Theta} = RT \ln K_p \qquad K_p = \frac{a_C{}^{\nu_C} a_D{}^{\nu_D}}{a_A{}^{\nu_A} a_B{}^{\nu_B}} = \prod_J a^{\nu}{}_J$$

$$-\Delta G^{\Theta} / RT = \ln K_p$$

$a^{\nu_i}{}_J$ is the partial pressure of substance J having mole. ν_i

The equilibrium constant can be defined in term of concentration, K_c.

$$K_C = \frac{[D]^{\nu_D} [C]^{\nu_C}}{[A]^{\nu_A} [B]^{\nu_B}}$$

Chemical Equilibrium

Example: combustion process in motor:

$$N_2 + O_2 \Leftrightarrow 2NO$$

$$K = \frac{k_{forward}}{k_{backward}} = \frac{[NO]^2}{[N_2][O_2]}$$

The rate constants and the concentration of the reactants and products are considered in the equilibrium constant

Chemical Equilibrium

The relationship between equilibrium constants in terms of partial pressure (K_P) and concentration (K_C) can be determined by using the ideal gas law.

$$p = \frac{nRT}{V}$$

$$K_P = \frac{a_C^{\nu_C} a_D^{\nu_D}}{a_A^{\nu_A} a_B^{\nu_B}} = \frac{\left(\frac{\nu_C}{V} RT\right)^{\nu_C} \left(\frac{\nu_D}{V} RT\right)^{\nu_D}}{\left(\frac{\nu_A}{V} RT\right)^{\nu_A} \left(\frac{\nu_B}{V} RT\right)^{\nu_B}} = \frac{[C]^{\nu_C} [D]^{\nu_D}}{[A]^{\nu_A} [B]^{\nu_B}} (RT)^{\Delta \nu_j}$$

$$K_P = K_C (RT)^{\Delta \nu_j}$$

Chemical Equilibrium

How equilibria respond to pressure?

Henry’s law (real solution)

For the real solutions at low concentration, the proportional of its mole fraction (X_B) and the vapour pressure of the pure substance (P_B) is constant (K_B).

$$p_B = X_B K_B$$

Or the concentration of a gas in a solution is direct proportional to the partial pressure of the gas over the solution. The propornality is difined by K (Henry's law coefficients representing solubility (i.e. aqueous-phase composition divided by gas-phase composition) . This law is mostly used to understand the real atmosphere, for example the reaction:

$$N_2O_5\ (g) + H_2O\ (l) \rightarrow 2HNO_3$$

in form of stick to N_2O_5 (g) stick to the surface of H_2O (l)

Chemical Equilibrium

Additional superscripts denote which properties are used for Henry‘s law:

symbol	**definition**	**description**	**unit(s)**
k_H^{cp}	c/p	aq-concentration / partial pressure	[mol/(m^3*Pa)] or [M/atm]
k_H^{cc}	c/c	aq-concentration / gas-concentration	dimensionless
k_H^{bp}	b/p	molality / partial pressure	[mol/(kg*Pa)] or [mol/(kg*atm)]
k_H^{xp}	x/p	molar fraction / partial pressure	[1/atm]
$k_{H,inv}^{px}$	p/x	partial pressure / molar fraction	[atm]
$k_{H,inv}^{pc}$	p/c	partial pressure / aq-concentration	[m^3*Pa/mol]
$k_{H,inv}^{cc}$	c/c	gas-concentration / aq-concentration	dimensionless

Chemical Equilibrium

Raoult's law (ideal solution)

The ratio of the partial pressure of each component to its vapour pressure as a pure liquid

$$\frac{p_A}{p_A*}$$

is approximately equal to the mole fraction of A in the liquid mixture.
p_A: partial pressure over liquid, p_{A*}: partial pressure of liquid

$$p_A = X_A p_A *$$

Example:

$$A \Leftrightarrow 2B$$

The reaction:

at t=0 the molar reactant A = n and the product B = 0

at t=t the molar reactant A = n(1-α) and the product B = 2nα

Chemical Equilibrium

the mole fraction $$x_A = \frac{(1-\alpha)n}{(1-\alpha)n + 2n\alpha} = \frac{1-\alpha}{1+\alpha}$$

the mole fraction $$x_B = \frac{2n\alpha}{(1-\alpha)n + 2n\alpha} = \frac{2n}{1+\alpha}$$

$$K_P = \frac{\left(\frac{p_B}{p_\Theta}\right)^2}{\left(\frac{p_A}{p_\Theta}\right)} = \frac{\left(\frac{x_B p}{p_\Theta}\right)^2}{\left(\frac{x_A p}{p_\Theta}\right)} = \frac{x_B{}^2 p}{x_A p_\Theta} = \frac{4\alpha^2 p}{(1-\alpha)p_\Theta}$$

$$\alpha = \left(\frac{K_p}{K_p + 4\frac{p}{p_\Theta}}\right)^{\frac{1}{2}}$$

Chemical Equilibrium

It shows that the amounts of A and B depend on pressure. For example, if P is increased, the amount of α will decrease to reach the new equilibrium, (the equilibrium constant, K_p, is independent of pressure.

$$\left(\frac{\partial K}{\partial p}\right)_T = 0$$

This corresponds to Le Chetalier's principle.

Le Chetalier principle

"A system at equilibrium, when subjected to a disturbance, responds in a way that tends to minimize the effect of the disturbance."

e.g. if you want to have more products → change:

1. T or/and p
2. Increase concentration of reactants or decrease the concentratopn of product continously
3. An additional catalysator

Chemical Equilibrium

How equilibria respond to temperature?

From the Gibbs energy of the standard state at the equilibrium;

$$-\Delta G^{\Theta} = RT \ln K_p$$

$$\ln K_p = -\frac{\Delta G^{\Theta}}{RT}$$

$$\frac{\partial}{\partial T} \ln K_p = -\frac{1}{R} \frac{\partial}{\partial T} \frac{\Delta G^{\Theta}}{T}$$

Gibbs-Helmholtz-Equation

connection *G*, *H*, *TS*:

$$G = H - TS$$

Isobare modication of *G with T*:

$$\left(\frac{\partial G}{\partial T}\right)_p = -S$$

Replacement of *S*:

$$\left(\frac{\partial G}{\partial T}\right)_p = -\frac{H - G}{T}$$

All *G* on left side:

$$\left(\frac{\partial G}{\partial T}\right)_p - \frac{G}{T} = -\frac{H}{T}$$

Division by *T*:

$$\frac{1}{T}\left(\frac{\partial G}{\partial T}\right)_p - \frac{G}{T^2} = -\frac{H}{T^2}$$

Gibbs-Helmholtz-Equation

$$\frac{1}{T}\left(\frac{\partial G}{\partial T}\right)_p - \frac{G}{T^2} = -\frac{H}{T^2}$$

Summary on right side:

$$\frac{\partial}{\partial T}\left(\frac{G}{T}\right)_p = -\frac{H}{T^2}$$

Product law:

$$\frac{\partial}{\partial T}\left(\frac{G}{T}\right)_p = \frac{\partial}{\partial T}\left(G\cdot\frac{1}{T}\right)_p = \frac{\partial}{\partial T}(G)_p\cdot\frac{1}{T} + G\cdot\left(-\frac{1}{T^2}\right)$$

Gibbs-Helmholtz-Equation

$$\boxed{\frac{\partial}{\partial T}\left(\frac{G}{T}\right)_p = -\frac{H}{T^2}}$$

Connection of temperature dependency of Gibbs-Potential and Enthalpy

$$\frac{\partial}{\partial T}\left(\frac{\Delta G}{T}\right)_p = -\frac{\Delta H}{T^2}$$

van‘t Hoff‘
Reaction isobare

$$\boxed{\left(\frac{\partial \ln K}{\partial T}\right)_p = \frac{\Delta H^\circ}{RT^2}}$$

Chemical Equilibrium

Use the Gibbs-Helmholz equation:

$$\frac{\partial}{\partial}\left(\frac{\Delta G^{\Theta}}{T}\right) = -\frac{\Delta H^{\Theta}}{T^{2}}$$

Therefore,

$$\frac{\partial \ln K_p}{T^{2}\partial\left(1/T\right)} = \frac{\Delta H^{\Theta}}{RT^{2}}$$

$$\frac{\partial \ln K_p}{\partial\left(1/T\right)} = \frac{\Delta H^{\Theta}}{R}$$

and

$$\frac{\partial \ln K_p}{\partial T} = \frac{\Delta H^{\Theta}}{RT^{2}}$$

These are the simplifies of the van ‘t Hoff equations, which show the changing of temperature in equilibrium is dependence on the changing of enthalpy.

Photochemistry

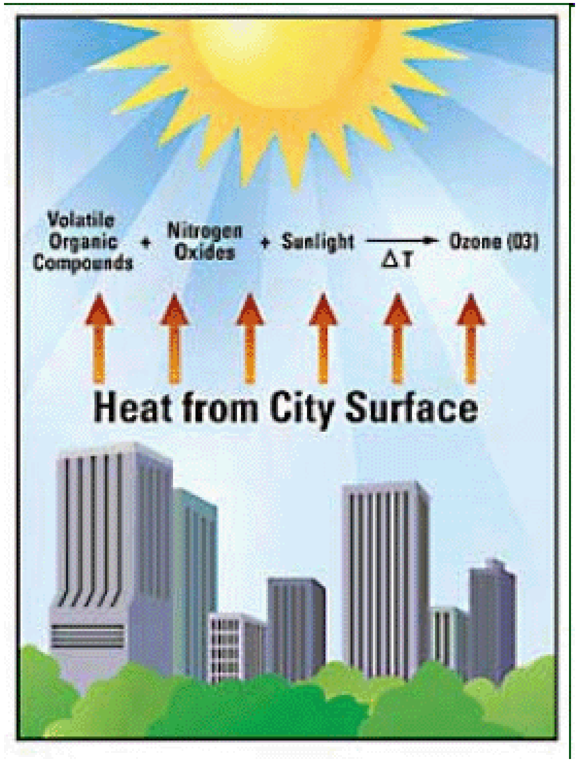
Photochemistry

Photochemistry

Photochemisty: chemical reactions initiated by light

Conditions: absorption of light of the molecule which reacts in a wavelenght region of the incoming light

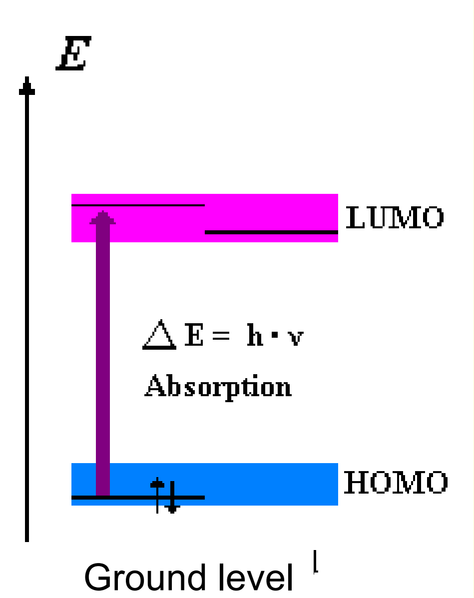
Absorption of light leads to an energetic exited level of a molecule



This additional energy can be lost by emission (singulet-level = flourescence) or triplel-level = phosphorescence)

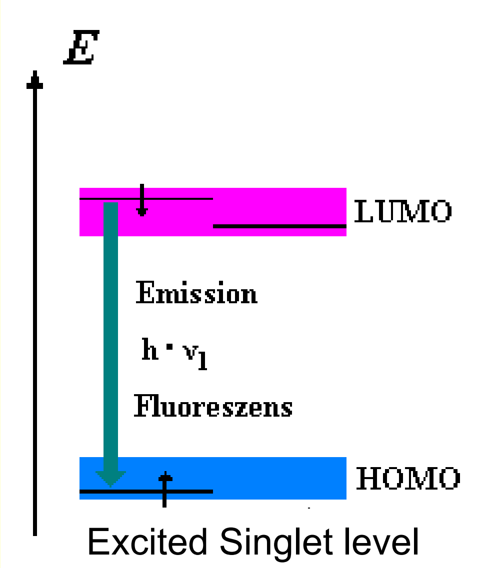
Or without radiation = collision, chemical reaction

Photochemistry



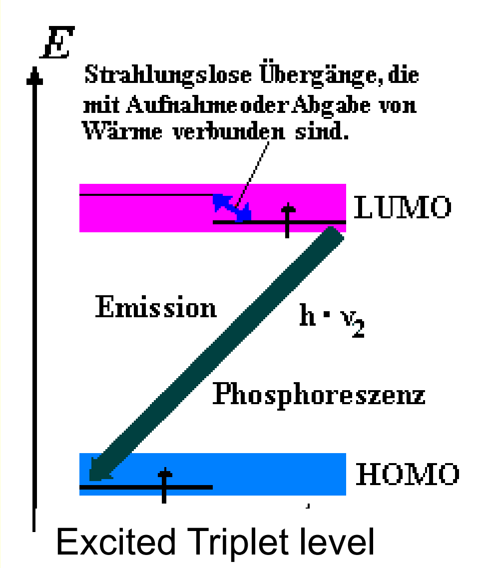
Ground level

Abb. 1



Excited Singlet level

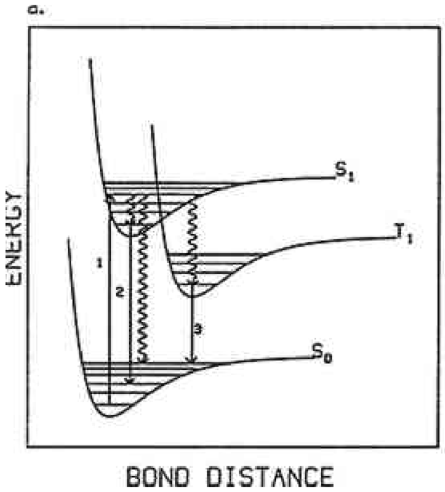
Abb. 2

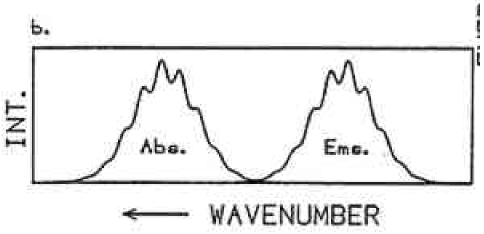


Excited Triplet level

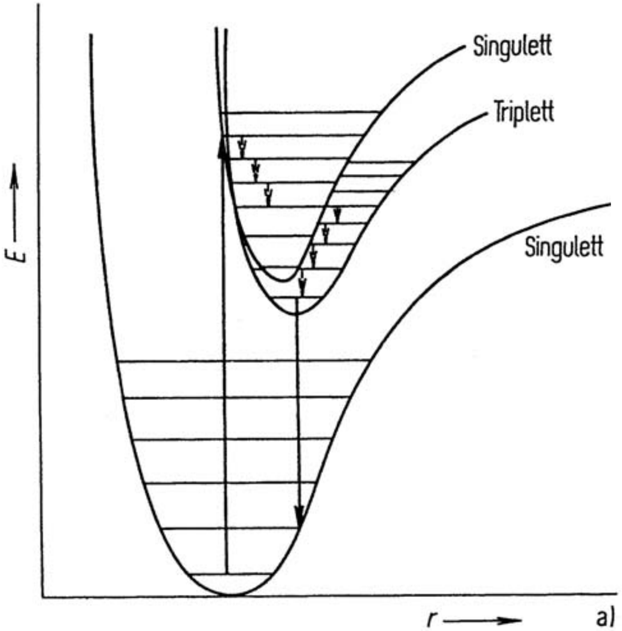
Abb. 3

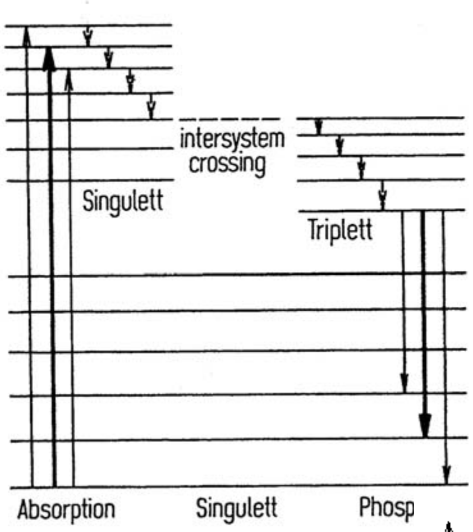
Quelle: Lit. [4], S. 299

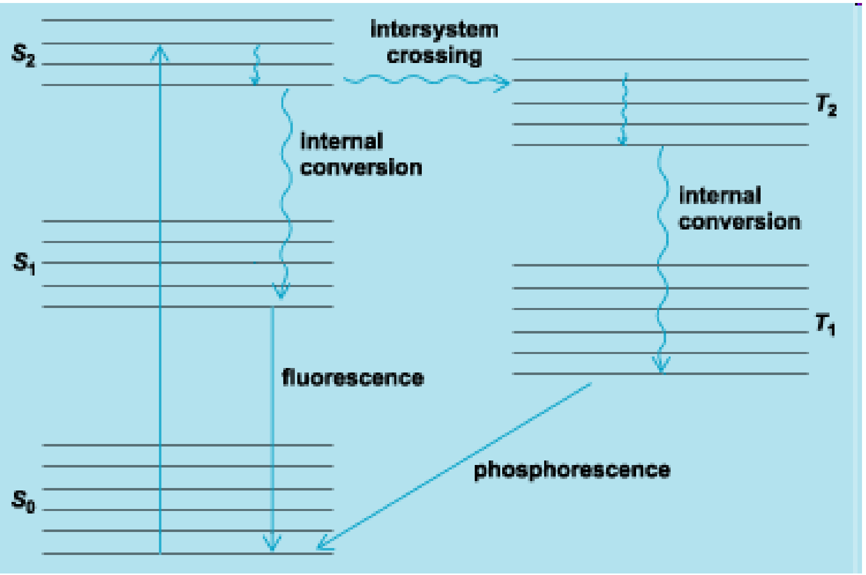


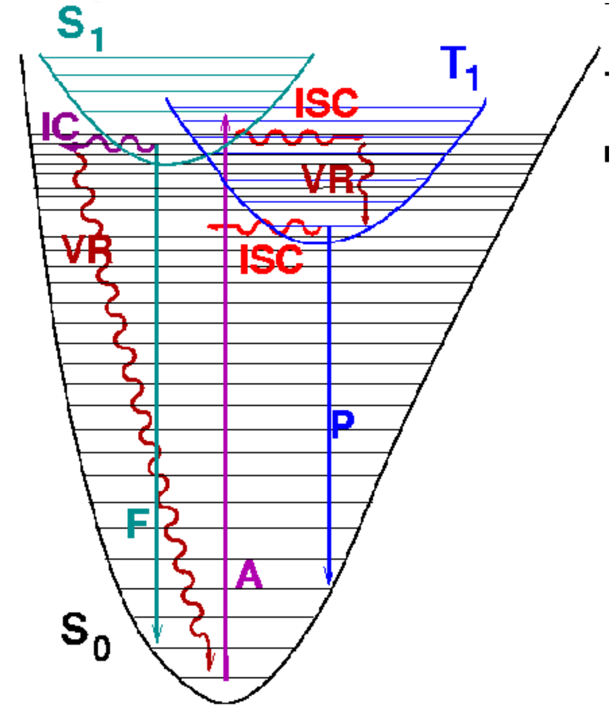


Photochemistry

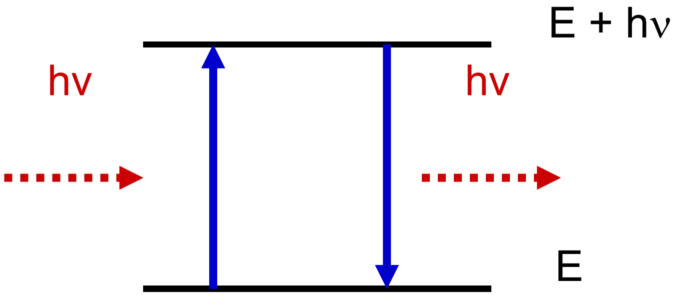




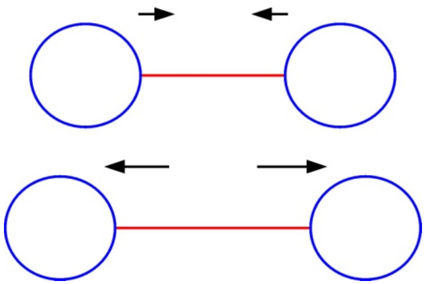




Photochemistry



$$\Delta E = E_j - E_i = h\nu$$



Rotation levels:	10^{-4} eV
Vibration levels:	$5*10^{-2}$ eV
Electronic levels:	3.00 eV

Lifetime: crossing from one to the other level, stay on an exited level (eletronic: in VIS-wavelenght region = 10^{-9}s
rotational: in mirco wave region = 10^{3}s)

Photochemistry

Photochemistry

Most chemical processes in the atmosphere are initiated by photons. The general reaction:

$$ABC + h\nu \rightarrow product$$

The rotational energy

At low energy:

in microwave or FIR wavelengths) : $\lambda > 25\ \mu m$

$$ABC + h\nu \rightarrow ABC^*$$ (rotation excited)

Molecules will be emitted or collided the original molecule itself.

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

or

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

Photochemistry

The rotational energy is E_J :

$$E_J = BJ(J+1)$$

J= constant rotational number

$$B \approx \frac{1}{I} \qquad I = \mu r^2$$

$$\mu = \frac{m_1 m_2}{m_1 + m_2}$$

= reduced mass

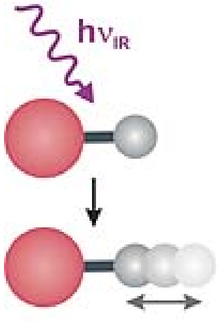
For example: I_{HCl} = 1 and I_{Cl2} = 1/37 ,

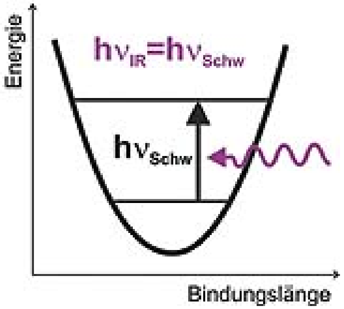
The small value of I has large B, it introduces to the large energy E_J value, therefore .

$$\boldsymbol{E_{J,Cl_2} > E_{J,HCl}}$$

Photochemistry

The vibrational energy





At higher energy:

in thermal IR wavelength, 2.5 μm < λ < 25 μm.

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

(vibrational excited)

or

$$ABC + h\nu \rightarrow ABC^* \rightarrow ABC + h\nu''$$

emit

collision

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

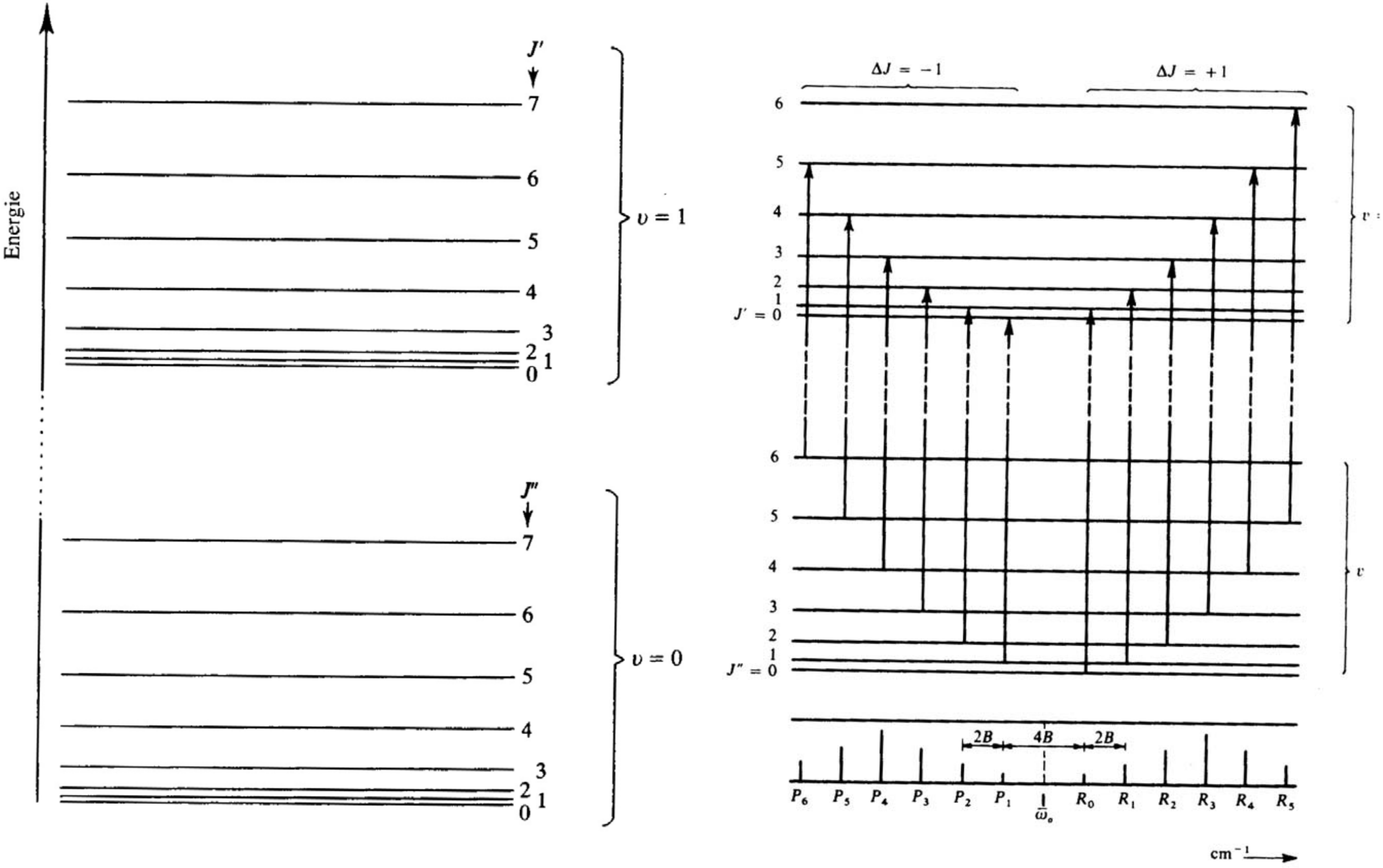
Molecules will be collided or emitted the original molecule itself with the vibrational energy E_ν :

$$E_\nu = h\nu_0\left(\nu + \frac{1}{2}\right) \qquad \nu_0 = \frac{1}{2\pi}\sqrt{\frac{k}{\mu}} \qquad \mu = \frac{1}{\mu_1} + \frac{1}{\mu_2}$$

ν= constant vibrational number

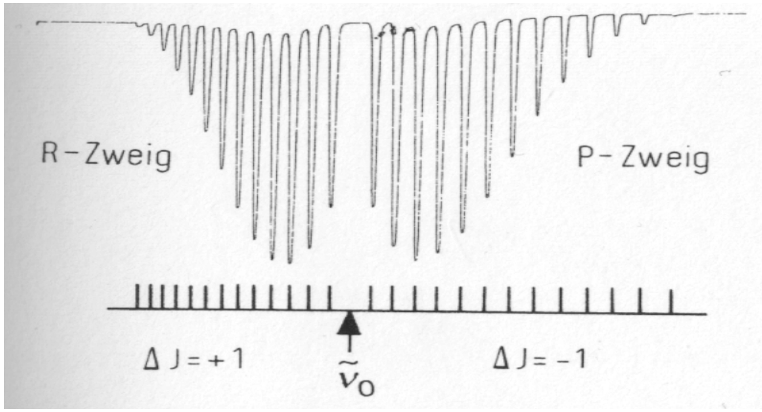
Photochemistry

Combination of rotation and vibration

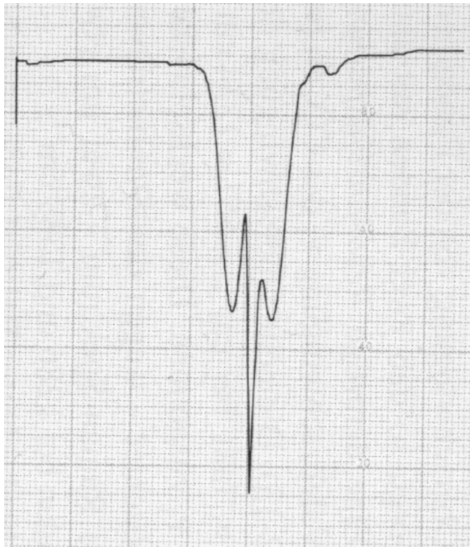


Photochemistry

Combination of rotation and vibration (spectrum)



Spectrum of benzene

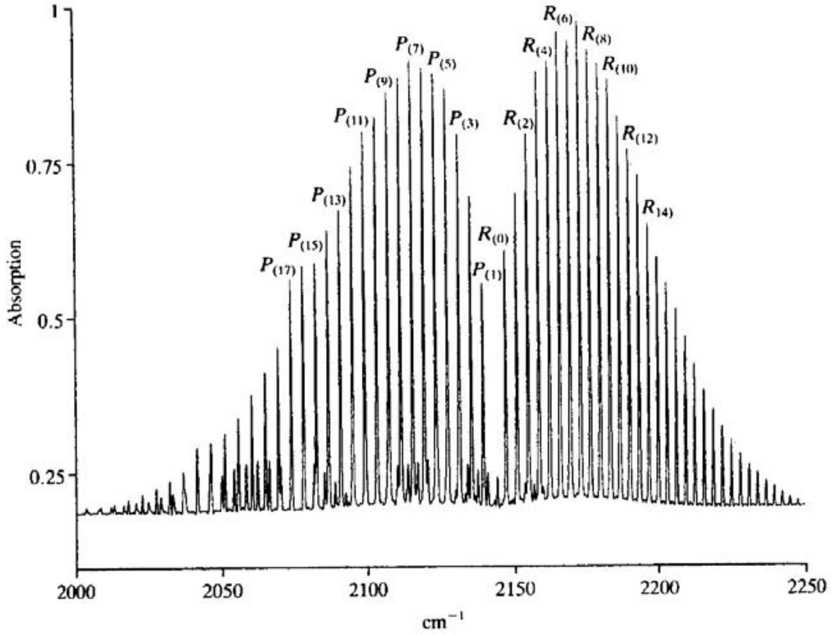


gas phase

liquid

Photochemistry

Spectrum of CO



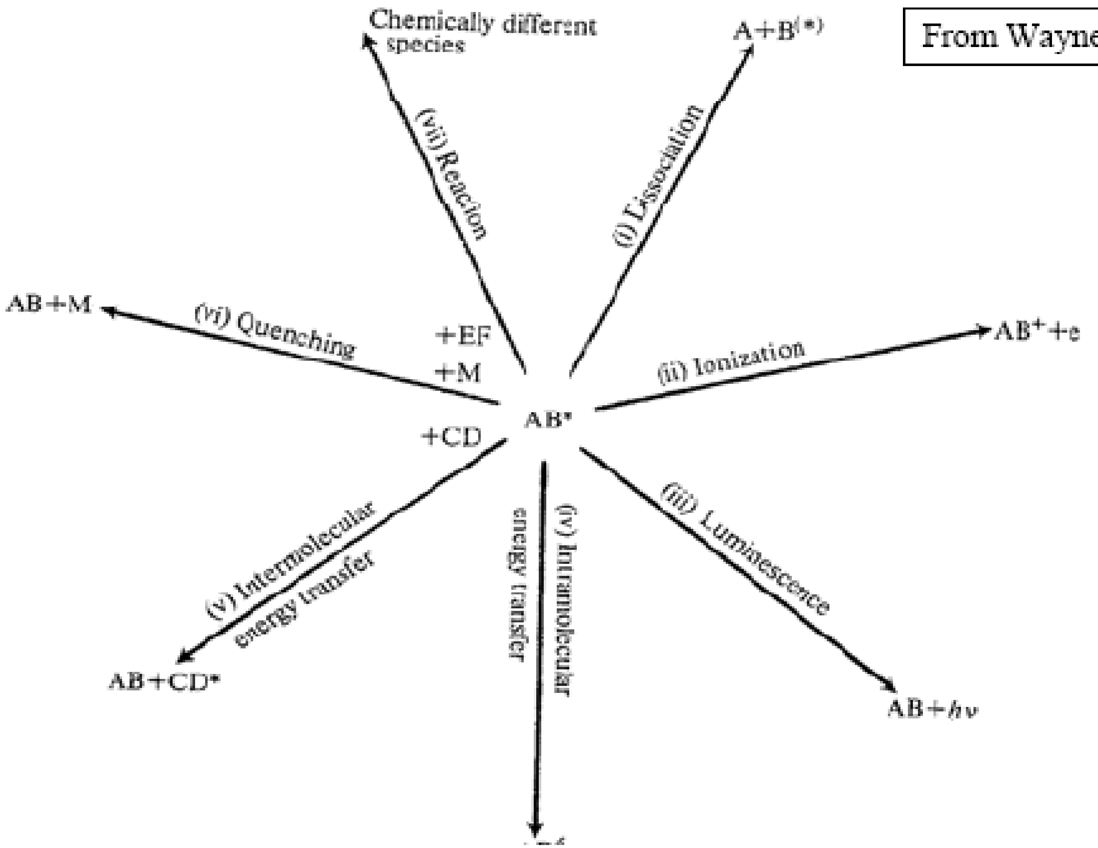
Line	$\tilde{\nu}$	$\Delta\tilde{\nu}$	*Line*	$\tilde{\nu}$	$\Delta\tilde{\nu}$
$P(1)$	2139.43		$R(0)$	2147.08	
		3.88			3.78
$P(2)$	2135.55		$R(1)$	2150.86	
		3.92			3.73
$P(3)$	2131.63		$R(2)$	2154.59	
		3.95			3.72
$P(4)$	2127.68		$R(3)$	2158.31	
		3.98			3.66
$P(5)$	2123.70		$R(4)$	2161.97	

$\Delta\nu=\nu_0-2BJ$ $\Delta\nu=\nu_0+2B(J+1)$

Photochemistry

The electronic energy

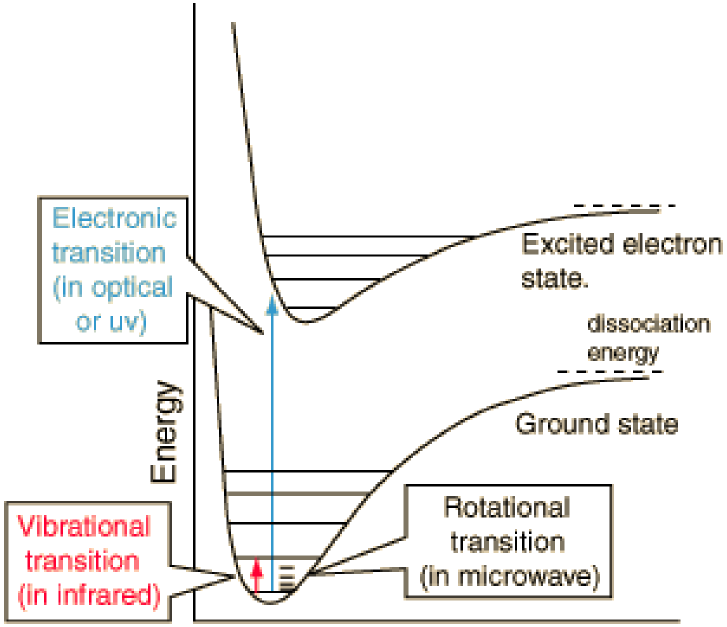
At high energy: in UV and visible wavelengths, molecules will be vibrated, rotated and have electronic transition. In the physical processes lead to emission of radiation and energy is converted to heat. In the photochemical processes lead to the several pathways as shown in the figure.



From Wayne

Fig. 3.1. Pathways for loss of electronic excitation that are of importance in atmospheric chemistry. The use of the symbols * and § illustrates the presence of electronic excitation: the products of any of the processes may be excited. With the exception of pathways (i) and (iv), excited atoms can participate as well as excited molecules.

Photochemistry



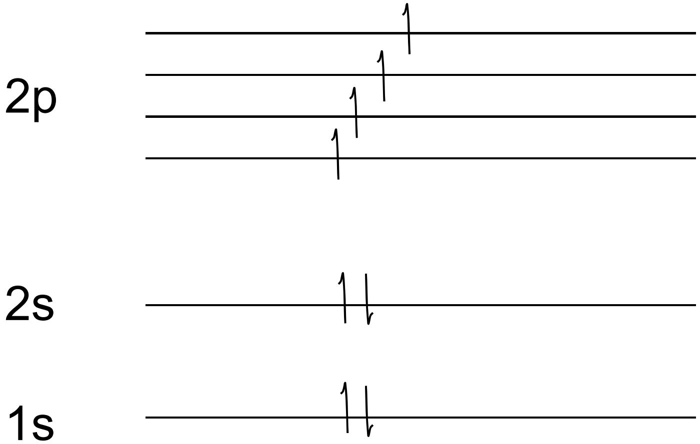
Atomic and molecular spectroscopy:

In general, an atomic term symbol is of the form $^{2S+1}L_J$,

where 2S+1 represents the spin multiplicity of the atom,

L represents the orbital angular momentum of the atom and J represents the total quantum number, J = L+S.

Example

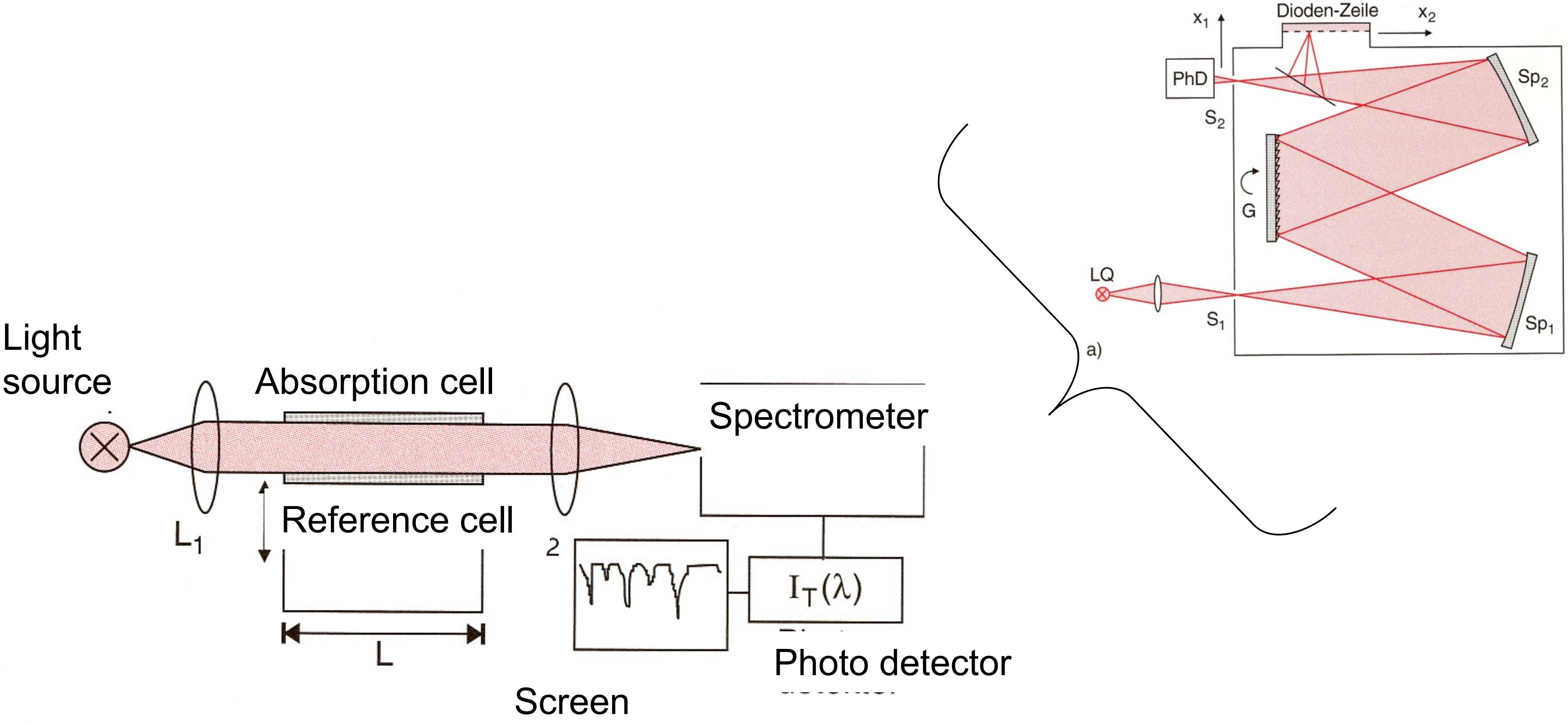


Oxygen atom

Electronic configuration is $1s^2\ 2s^2\ 2p^4$.

Atomic term symbol at ground state is $^3P_2$.

Photochemistry



Light source

Absorption cell

Reference cell

Spectrometer

Screen

Photo detector

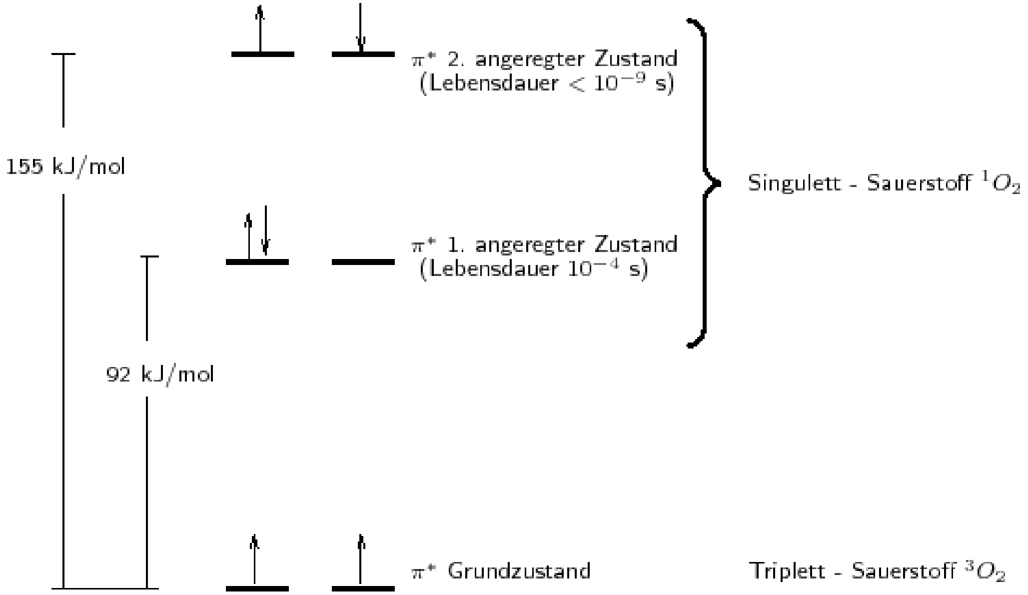
Photochemistry

Oxygen molecule

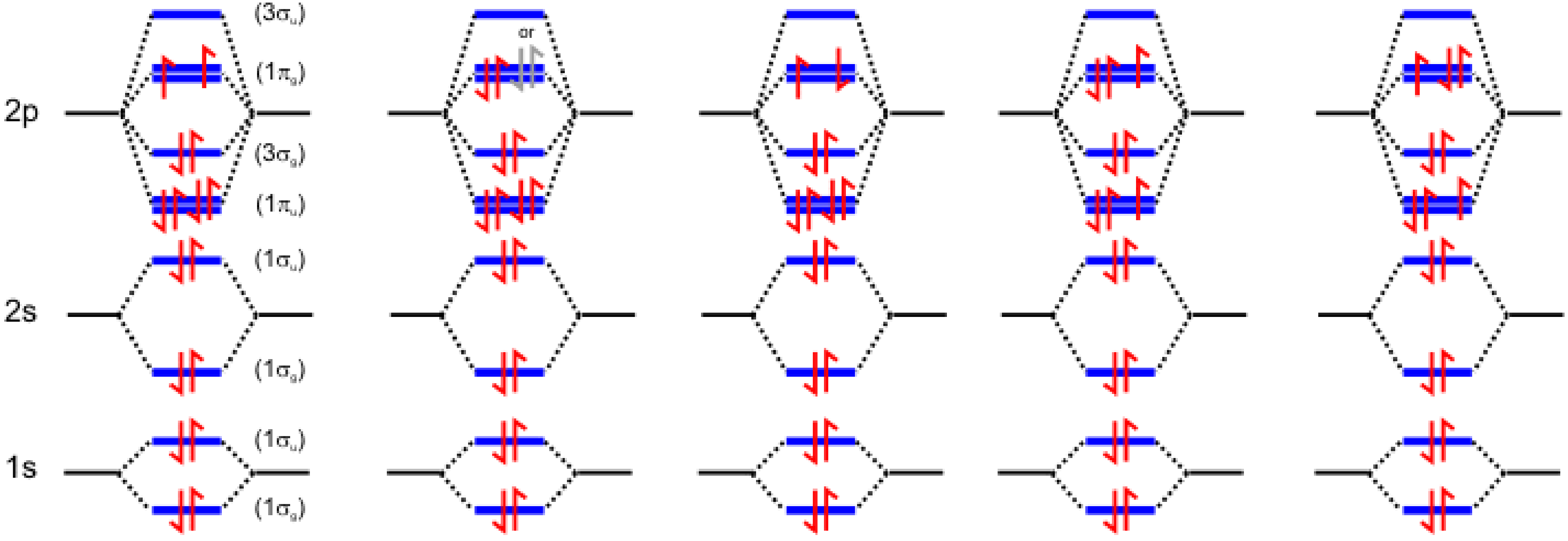
In atmosphere, the oxygen molecule is formed by photolysis of ozone.

$$O_3 + h\upsilon \longrightarrow O_2(^3\Sigma_g^-) + O(^3P)$$ triplett

$$\longrightarrow O_2(^1\Delta_g^-) + O(^1D)$$ singulett



Photochemistry



Ground State	**Excited State**	**Excited State**	**Excited State**	**Excited State**
($^3\Sigma_g^-$)	($^1\Delta_g$)	($^1\Sigma_g^+$)	($^3\Sigma_u^+$)	($^3\Sigma_u^-$)
0 eV	**1268 nm**	**762 nm**	**280 nm**	**202 nm**
	(0.9772 eV)	**(1.6266 eV)**	**(4.4278 eV)**	**(6.1202 eV)**

Photolysis rate, frequency

Photolysis rate, frequency

Photolysis rates and frequency

The general reaction:

$$AB + h\nu \rightarrow product$$

The photolysis rate from the reaction is

$$\frac{d}{dt}[AB] = -J_1[AB]$$

where as [AB] = concentration of AB substance

$\frac{d}{dt}[AB]$ = photolysis rate

J_1 = photolysis frequency (similar to k → $\tau = 1/J$ with J in [s^{-1}])

Photolysis rate, frequency

J: Integration of product of spectral actinic flux I (intensity of light), spectral absorption coefficient σ [cm^2](area in which one photon is absorbed) and relative quantum yield (Ø [cm^{-2} s^{-1}])

$$J_1(\lambda, T) = \int_{\lambda_{\min}}^{\lambda ax} I(\lambda)\sigma(\lambda, T)\Phi(\lambda, T)\,d\lambda$$

Photons can arrive from all directions on the molecule → spheric flux has to be considered

$$I(\lambda) = \int_0^{2\pi}\int_0^{\pi} R(\lambda, \theta)\,d\Omega$$

$$d\Omega = \sin\theta\, d\theta\, d\varphi$$

$d\Omega$	infinitesimal solid angle
Φ	azimuth
Θ	solar zenith angle

Photolysis rate, frequency

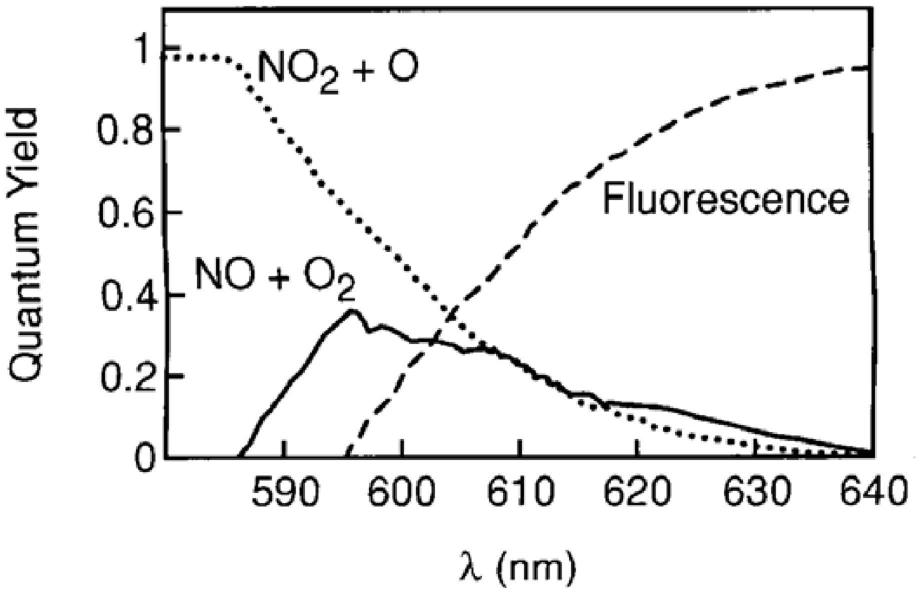
Quantum yield (Ø) is the relative efficiency of various photophysical and photochemical processes.

$$\phi = \frac{\textit{number of molecule photolysed by the chemical process}}{\textit{total number of photo absorbed}}$$

For example: $O_2 + h\nu \rightarrow O + O$

Φ is wavelength dependent, all important at different λ.

Photolysis rate, frequency



Quantum yields for NO_3 photolysis: (dotted line) $$NO_3 \rightarrow NO_2 + O$$

(solid line) $$NO_3 \rightarrow NO + O_2$$

(dashed line), fluorescence quantum yield (From F-P&P)

Photolysis rate, frequency

J depends on

– Light intensity from all directions *“Actinic flux”*

– Absorption cross section (σ)

– Quantum yield for photodissociation (Φ)

– All are functions of wavelength

$$J = \int_{\lambda_1}^{\lambda_2} I_\lambda \sigma(\lambda) \phi(\lambda) d\lambda$$

Photolysis rate, frequency

e.g. Destruction and production of O_3

O_3 + hv (l< 310 nm) → O + O_2 J_1

O + O_2 + M → O_3 + M k_3

Productionrate:

$d [O_3]/dt = k_3 [O][O_2][M]$

Both processes production and destruction are very fast → equilibrium:

Production = destruction

$J_1 [O_3] = k_3 [O][O_2][M]$

$$[O]/[O_3] = J_1/k_3[O_2][M]$$

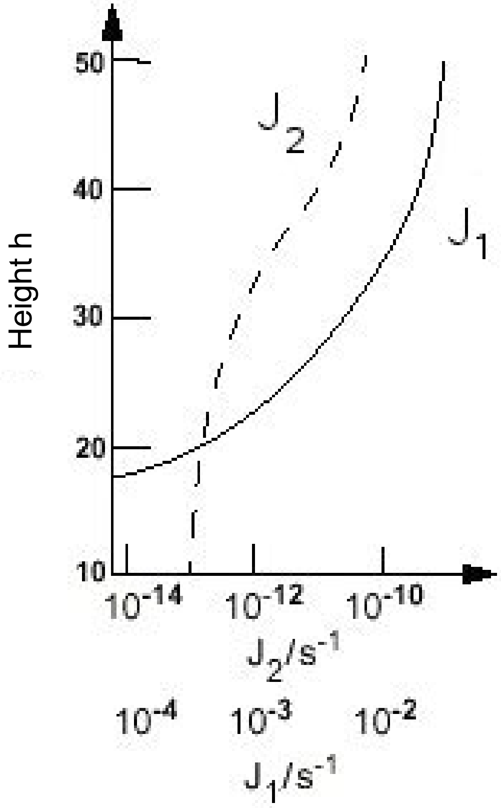
As $[O_2]$ and [M] decrease with increasing height ⟶ $[O]/[O_3]$ increase

Photolysis rate, frequency

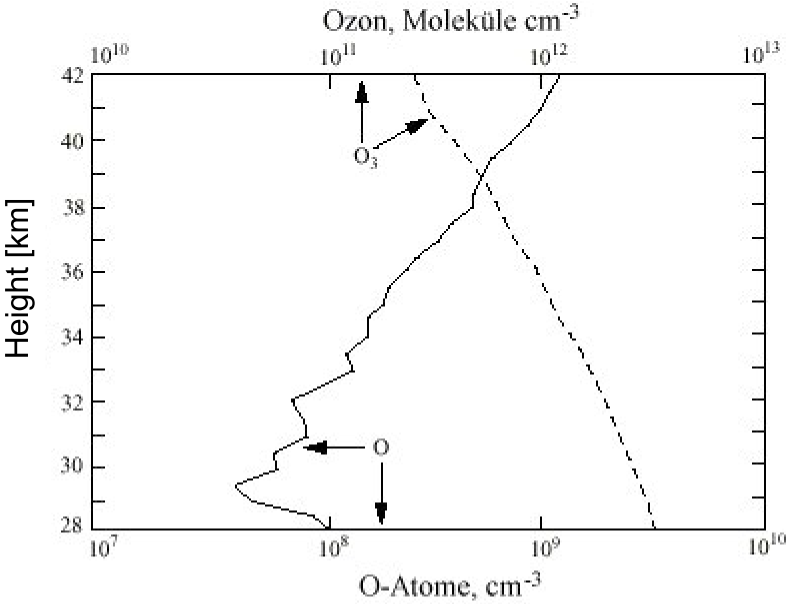
In addition O is produced by the photolysis of O_2

O_2 + hv (λ< 230 nm) → O + O J_2

d [O]/dt = J_2 [O_2]



Photolysis rates of O_2 (J_2) and O_3 (J_1) at different heights h.



Measurements at the same time of ozone over Texas

Photolysis rate, frequency

Kinetics

Order of reaction:

Overall = sum of more than one elementary reaction

The order with respond to the individual reactant

First order reaction

$$A \rightarrow B$$

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

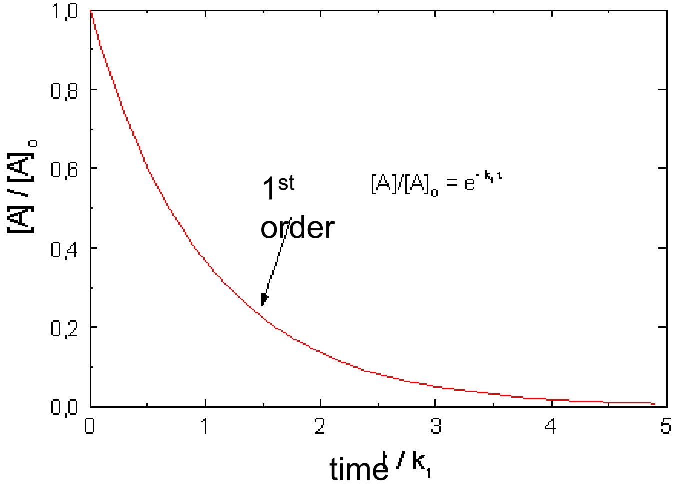
$$-\frac{d[A]}{[A]} = kdt$$

Photolysis rate, frequency

$$-\frac{d[A]}{[A]} = kdt$$

$$\int_{[A]_0}^{[A]} \frac{d[A]}{[A]} = -\int_0^t kdt$$

$$\ln\frac{[A]}{[A]_0} = -kt \longrightarrow [A] = [A]_0 \exp(-kt)$$



$$[A] = \frac{1}{2}[A]_0$$

$$\ln\frac{\frac{1}{2}[A]_0}{[A]_0} = \ln\frac{1}{2} = -kt_{\frac{1}{2}} \longrightarrow t_{\frac{1}{2}} = \frac{\ln 2}{k}$$

Photolysis rate, frequency

1st order: $A \rightarrow C + D$

2nd order: $A + B \rightarrow C + D$

3rd order $A + B + M \rightarrow C + M$

Molecularity of Reactions

- Unimolecular: overall is first order.

$$AB \rightarrow A + B$$

- Bimolecular: overall is second order, two body reactions

$$A + BC \rightarrow AB + C$$

Photolysis rate, frequency

- Termolecular: overall is third order, three body reactions, association reactions. example

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

M = usually N_2 or O_2 for atmosphere

The general reaction: $$aA + bB \rightarrow cC + dD$$

Rate of reaction $$= \frac{d[A]}{dt} = \frac{d[B]}{dt} = -\frac{d[C]}{dt} = -\frac{d[D]}{dt}$$

Rate of reaction in terms of concentrations can be written:

Photolysis rate, frequency

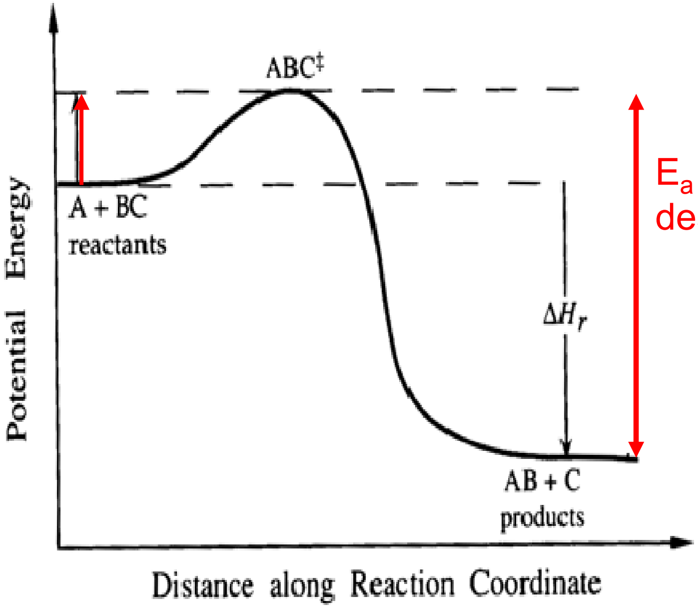
Rate of reaction, = $k[A]^a[B]^b$ where as k is rate constant.

For elementary reactions ($a + b \leq 3$), the Arrhenius equation can be apply to calculate the rate constant k

→ temperature dependence of rate constant is given by Arrhenius equation

$$k = A\exp\left(-\frac{E_a}{RT}\right)$$

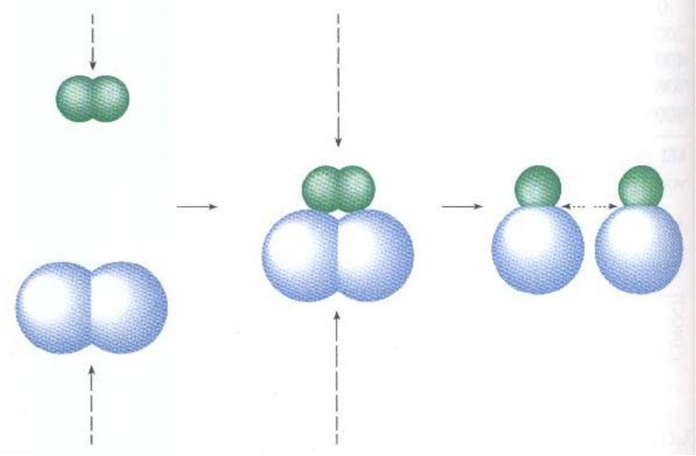
E_a for the production



E_a for the destruction

where as A = pre-expectation factor
E_a = Activation energy

Photolysis rate, frequency



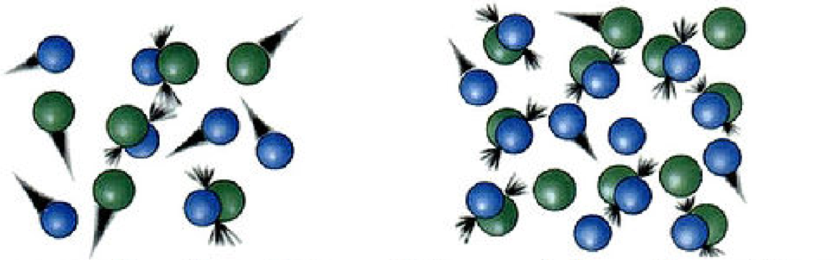
The collision theory

$$A + BC \rightarrow [ABC]$$

Collision rate for molecules A and BC = $\frac{n\bar{c}}{4}$

where as n = number of molecular density (concentration) and

$\bar{c}$ = mean velocity



Low concentration = Few collisions

High concentration = More collisions

$$-\frac{d[A]}{dt} = [A][BC]\sigma\bar{c}$$

when no reaction occurs.

Photolysis rate, frequency

$$-\frac{d[A]}{dt} = [A][BC]\sigma\bar{c}\exp\left(-\frac{E_a}{RT}\right)$$

when reaction occurs.

$$\bar{c} = \sqrt{\frac{8kT}{\pi\mu}}$$

k = Boltzmann constant

μ = reduced mass

$$\sigma = \pi(r_A + r_{BC})^2$$

= collision cross section

Therefore, in collision theory:

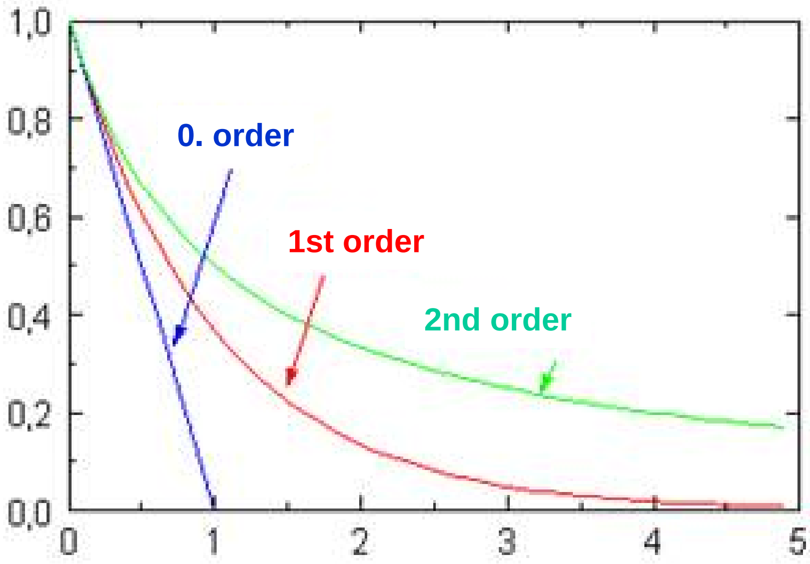
$$k_C = \sigma\bar{c}\exp\left(-\frac{E_a}{RT}\right)$$

Chemical lifetime, chain reaction

Chemical lifetime, chain reaction

Chemical lifetime

First order reaction: $$A \rightarrow product$$

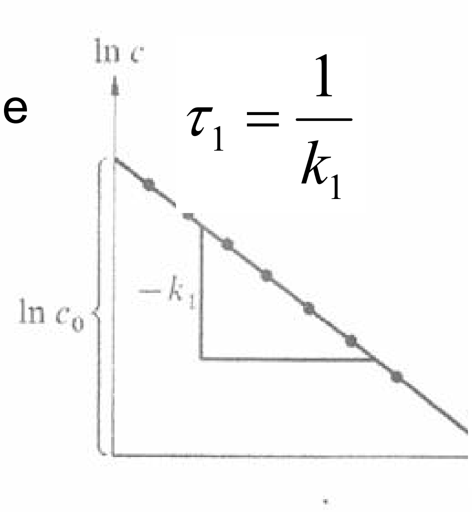


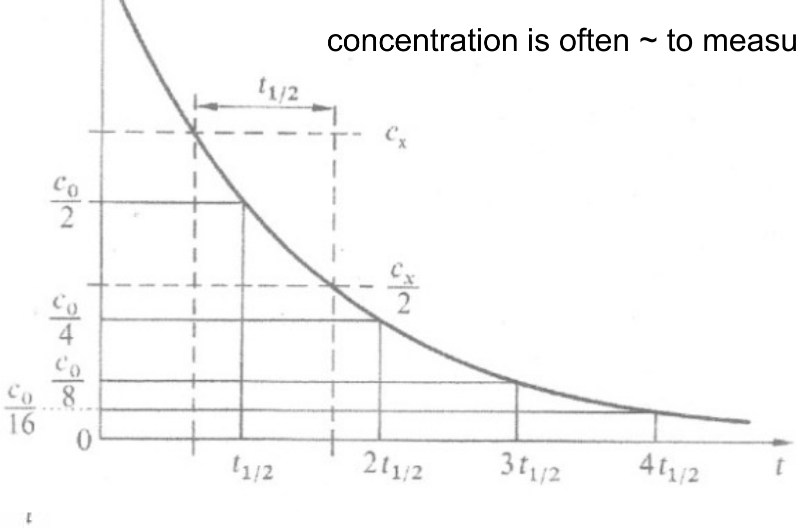
concentration is often ~ to measured reaction rate

Rate of reaction $$\frac{d}{dt}[A] = -k_1[A]$$

Unit of $k_1 = s^{-1}$

Chemical lifetime $$\tau_1 = \frac{1}{k_1}$$





Unit of τ_1 = s

Chemical lifetime, chain reaction

Second order reaction: $A + BC \rightarrow product$

Rate of reaction: $\frac{d}{dt}[A] = -k_2[A][BC]$

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

The true rate law is forced to be first-order form, called a pseudo-first-order rate law and

$$k = k_2[A]$$

Unit of k:= cm^3 $molecule^{-1}s^{-1}$

Chemical lifetime

$$\tau_1(A) = \frac{1}{k} = \frac{1}{k_2[BC]}$$

Chemical lifetime, chain reaction

$[OH]_{global}$ = $5x10^5$ molecule cm^{-3}

1st example: $OH + CH_4 \rightarrow CH_3 + H_2O$

$$k_{CH_4}(298K) = 1x10^{-14} cm^3 molecules^{-1} s^{-1}$$

$$\tau_{1(CH4)} = \frac{1}{k_3[OH]} = 2x10^8 s \cong 10 years$$

2nd example: $OH + CO + M \rightarrow CO_2 + H + M$

$$k_{CO}[M] \cong 1x10^{-13} cm^3 molecules^{-1} s^{-1}$$

$$\tau_1(CO) = \frac{1}{k[OH]} \cong 2x10^7 s \cong 8 months$$

3rd example: $OH + NO_2 + M \rightarrow HNO_3 + M$

$$k_{NO_2}[M] \cong 1x10^{-11} cm^3 molecules^{-1} s^{-1}$$

$$\tau_1(NO_2) = \frac{1}{k[OH]} \cong 2x10^5 s \cong 2.3 days$$

Chemical lifetime, chain reaction

In equilibrium (or stationary state or steady state), the production rate (P) and loss rate (L) are equal.

$$\frac{d}{dt}[A] = 0 = P - L$$

Example: For equilibrium reaction:

$$NO_2 + NO_3 + M \leftrightarrow N_2O_5 + M$$

$$\frac{d[N_2O_5]}{dt} = 0 = P - L = k_+[NO_2][NO_3] - k_-[N_2O_5]$$

$$K = \frac{k_-}{k_+} = \frac{[NO_2][NO_3]}{[N_2O_5]}$$

Chemical lifetime, chain reaction

For the termolecular (3rd order) reaction:

$$A + BC \rightarrow ABC^* \qquad k_1$$

$$ABC^* \rightarrow A + BC \qquad k_2$$

$$ABC^* + M \rightarrow ABC + M \qquad k_3$$

$$\frac{d[ABC]}{dt} = 0 = k_1[A][BC] - k_2[ABC^*] - k_3[ABC^*][M]$$

Assume that [ABC*] is in the steady state:

$$\frac{d[ABC]}{dt} = k_1[A][BC] - (k_2 + k_3[M])[ABC^*]$$

Chemical lifetime, chain reaction

$$\frac{d[ABC]}{dt} = k_1[A][BC] - (k_2 + k_3[M])[ABC^*]$$

$$[ABC^*] = \frac{k_1[A][BC]}{k_2 + k_3[M]}$$

$$\frac{d[ABC]}{dt} = -\frac{d[A]}{dt} = -\frac{d[B]}{dt} = k_3[ABC^*][M]$$

$$\frac{d[ABC]}{dt} = k_3 \frac{k_1[A][BC]}{k_2 + k_3[M]}[M] = k'''_{complex}[A][BC]$$

$$k'''_{complex} = \frac{k_1 k_3[M]}{k_2 + k_3[M]}$$

Chemical lifetime, chain reaction

At low pressure $k_2 > k_3[M]$

$$k'''_{complex,lowP} = \frac{k_1 k_3[M]}{k_2}$$

$$k'''_{complex,lowP} = \frac{A_{3[}\exp(-\frac{T_3}{T})A_1\exp(-\frac{T_1}{T})[M]}{A_2\exp(-\frac{T_2}{T})} = \frac{A_1 A_3}{A_2}[M]\exp-(\frac{T_3+T_1-T_2}{T})$$

$$k'''_{complex,lowP} = A\exp(-\frac{T_a}{T})[M]$$

$$T_i = \frac{E_a}{R}$$

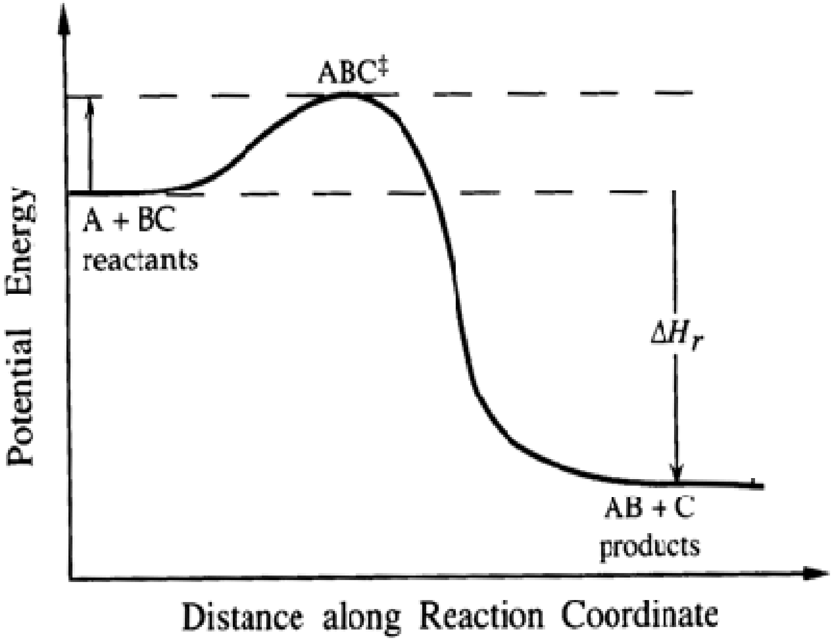
Chemical lifetime, chain reaction

At high pressure $k_3[M] > k_2$

$$k'''_{complex,highP} = k_1 = A_1 \exp(-\frac{T_1}{T})$$

Complex Reaction:

$$A + B \Leftrightarrow ABC \rightarrow AB + C$$



- ABC is complex formed at top of energy hill.

- It referred to as transition state.

- Ter-molecular is just one good example of the complex elementary reaction, when the transition state of elementary reaction has a living long enough.

Chemical lifetime, chain reaction

Chain reaction:

Initiation: $$A_2 + h\nu \rightarrow 2A$$ k_1

Propagation: $$A + BC \rightarrow AB + C$$ k_2

$$AB + D \rightarrow DB + A$$ k_3

Termination: $$A + AB \rightarrow A_2B$$ k_4

Chain Length: CL

$$CL_A = \frac{k_2[BC][A]}{k_4[A][AB]} = \frac{k_2[BC]}{k_4[AB]}$$

A and AB are chain carriers

$$\frac{1}{CL} = \frac{1}{CL_A}\frac{1}{CL_{BC}}$$

Chemical lifetime, chain reaction

Chain reaction: Example

Initiation:

$$CH_4 + O_2 \rightarrow CH_3 + HO_2$$

Propagation:
1st reaction

$$CH_3 + O_2 \rightarrow CH_2O + OH$$

$$OH + CH_4 \rightarrow H_2O + CH_3$$

2nd reaction:

$$OH + CH_2O \rightarrow H_2O + CHO$$

$$CHO + O_2 \rightarrow HO_2 + CO$$

$$HO_2 + CH_2O \rightarrow H_2O_2 + CHO$$

Chemical lifetime, chain reaction

Intersection: $$H_2O_2 + M \rightarrow 2OH + M$$

Propagation:
3rd reaction

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

$$H + O_2 + M \rightarrow HO_2 + M$$

$$HO_2 + CO \rightarrow CO_2 + OH$$

Termination:

$$OH + HO_2 \rightarrow H_2O + O_2$$

$$HO_2 + HO_2 \rightarrow H_2O_2 + O_2$$

Heterogenous Reactions

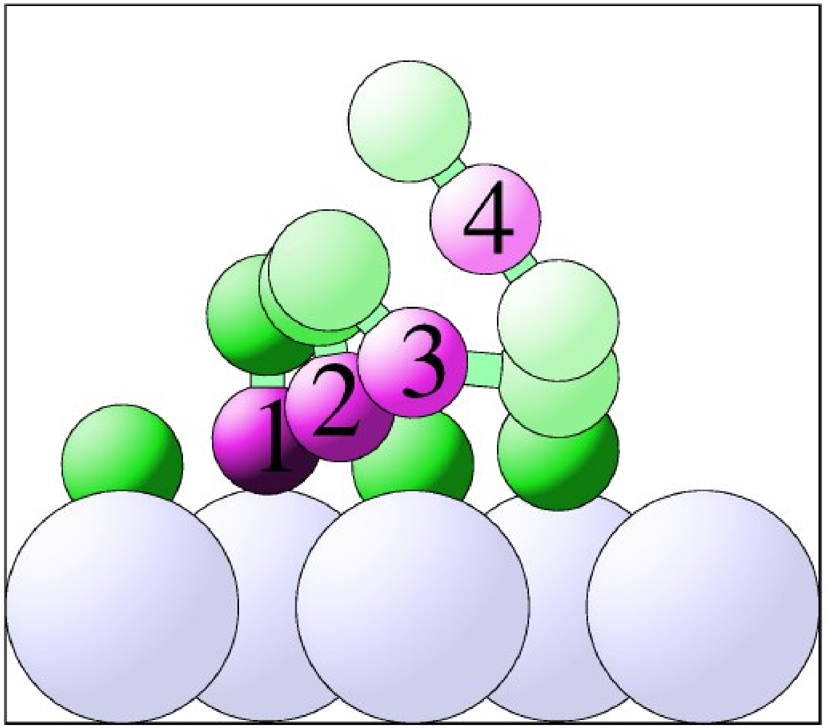
Heterogenous Reactions

Heterogeneous reactions

Homogeneous reactions: reactants are in the same phase, reactions between two gases, two liquids or two solids

Heterogeneous reactions: reactants are in two or more phases and/or reactions on the surface of a catalyst of a different phase

(manufacturing engineers have used surface reactions for synthesis of micro and nanoscale features in biomedical devices)

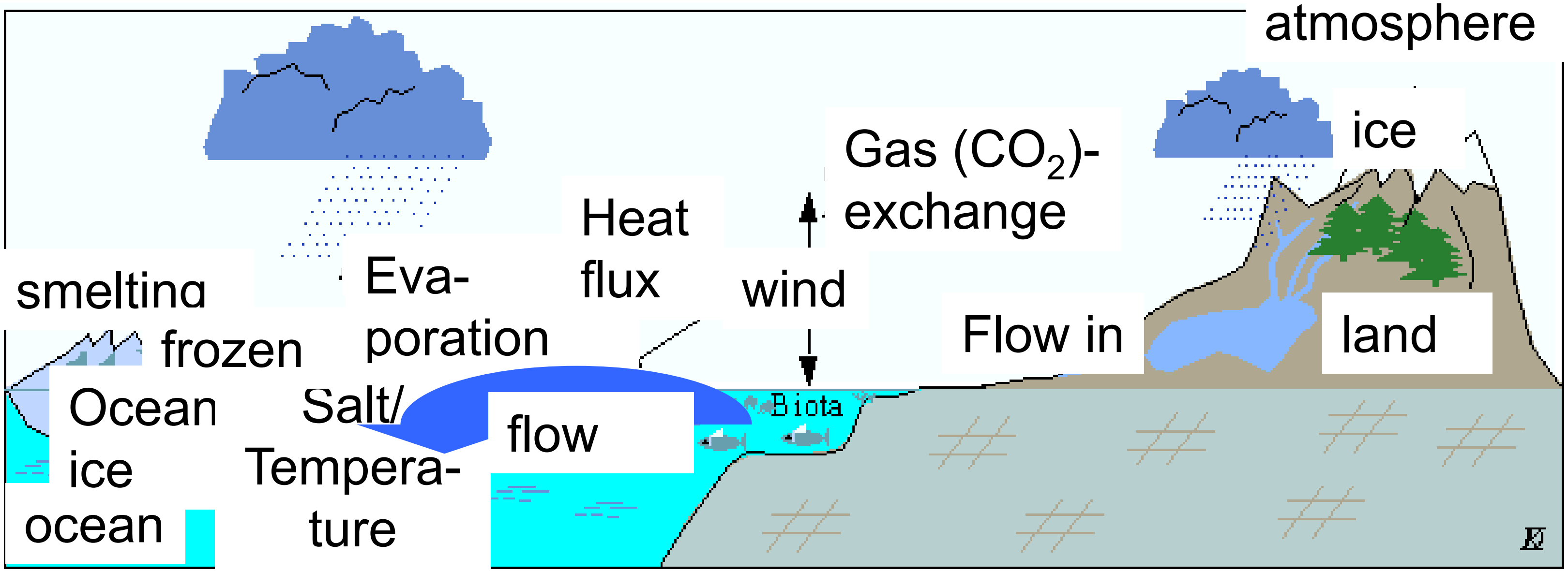


CO_2 formation

Heterogenous Reactions

- The heterogeneous interaction of HCl with chlorine containing reservoir molecules (e.g. $ClONO_2$ and HOCl on low-temperature ices leads to the release of Cl_2 → effect on atmospheric chemistry in the polar regions ("ozone hole“)

- heterogeneous reactions of NO_x leading to N_2O in the presence of SO_2 and airborne particles→ heavily polluted environments (power stations)



atmosphere

ice

Gas (CO_2)-exchange

Heat flux

wind

smelting

Evaporation

frozen

Flow in

land

Ocean ice

Salt/ Temperature density

flow

ocean

Heterogenous Reactions

5 examples for heterogenous reactions:

- interaction of atmospherically relevant molecules (e.g. H_2O and NO_2 with combustion aerosol (soot) particles

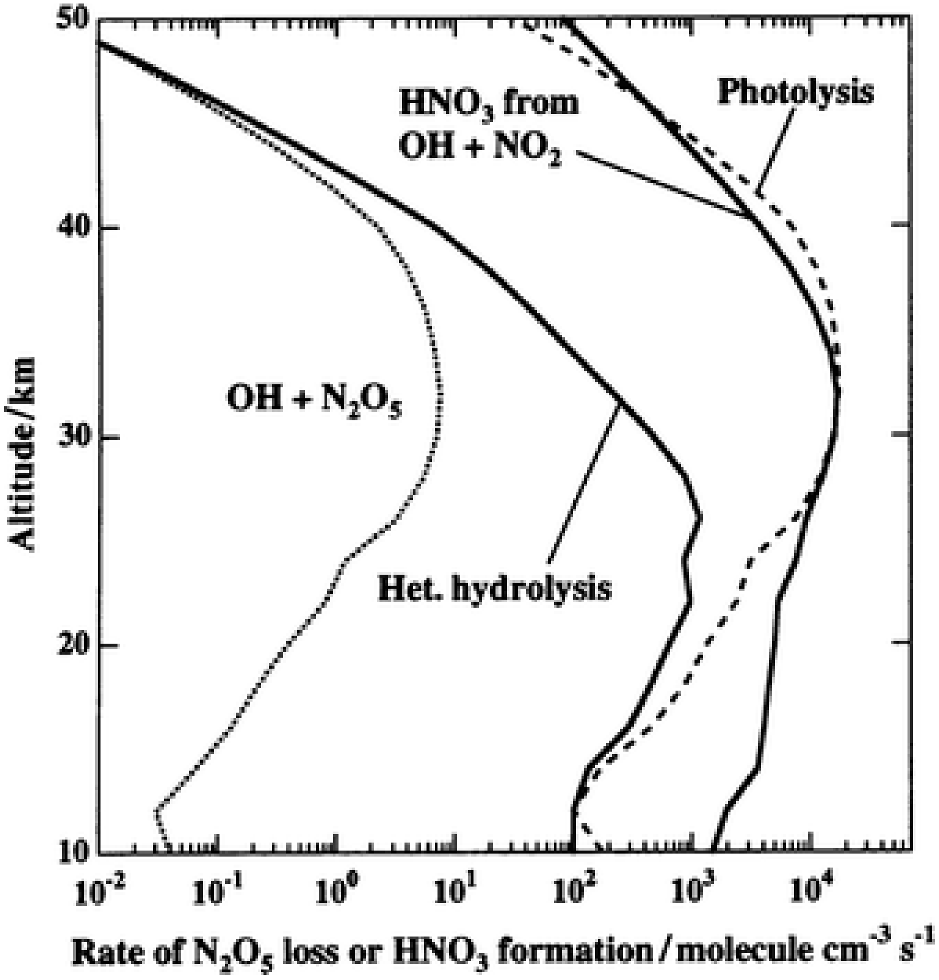
  → important in the planetary boundary layer and upper troposphere in relation to aircraft-induced Cirrus cloud formation

- NO_2 in a chemical oxidation-reduction reaction on soot result in HONO or in NO (depending on type of soot)

  → HONO important OH source early in the morning which controls the development of photochemical smog

- heterogeneous interaction of HX (X=Cl, Br) on ice reveals that an interface region of approximately 100-200 nm thickness (depending on type of ice, the HX/ice interface controls a large extent the kinetics of effective bimolecular reactions with reservoir molecules e.g. $ClONO_2$ and HOCl)

Heterogenous Reactions



Heterogenous Reactions

Heterogeneous condensed surface phase reaction

Multiphase reactions, for example, SO_2 and H_2O_2 diffuse to the cloud droplet.

$$SO_2(g) \xleftrightarrow{H_2O} SO_2(l)$$

$$SO_2(l) \xleftrightarrow{H_2O} HSO_3^{\,-} + H^+$$

$$HSO_3^{\,-} + H_2O_2 \rightarrow SO_4^{\,2-} + H_2O + H^+$$

In stratosphere,

$$ClONO_2 + HCl(l) \rightarrow Cl_2 + HNO_3(l)$$

It occurs in flog, aerosol, surface of ocean, plants or PSC.

Heterogenous Reactions

Liquid phase reaction : diffusion controlled kinetic behaviour.

The diffusion-controlled rate constant (k_D) is $k_D = 4\pi r_{AB} * D_{AB}$, where as D_{AB} is the diffusion coefficient for the reaction.

The example is Na^+ in H_2O.

$$Na^+ + H_2O \rightarrow NaOH + H^+$$

$$D_{AB} = 1.3 \times 10^{-9} m^2 s^{-1}$$
$$r_{AB} = 0.5 nm$$

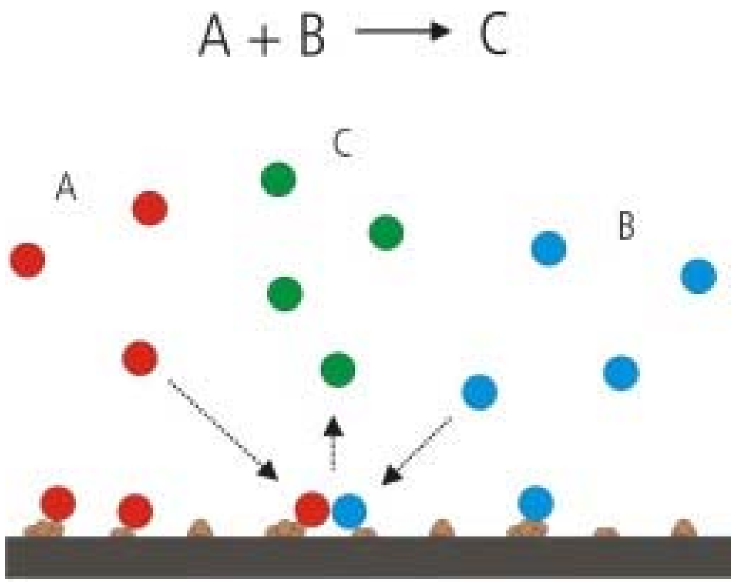
$$k_D = 4\pi r_{AB} \cdot D_{AB} \cong 8 \times 10^{-12} cm^3 molecule^{-1} s^{-1}$$
$$\cong 6.02 \times 10^{23} \cdot 8 \times 10^{-12} \cdot 10^{-3} \cong 5 \times 10^9 dm^3 mol^{-1} \cdot s^{-1}$$

Heterogenous Reactions

In general, the rate constant of the gas phase(k_G)

$k_G \equiv 2{*}10^{11}$ dm³ mol⁻¹ s⁻¹

Therefore, $k_D \equiv 400\ k_G$ faster than gas phase reaction.



Catalytic active surface

Liquid phase reaction

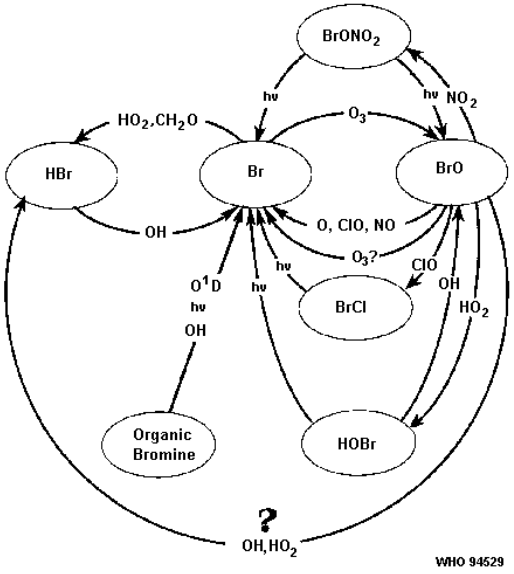


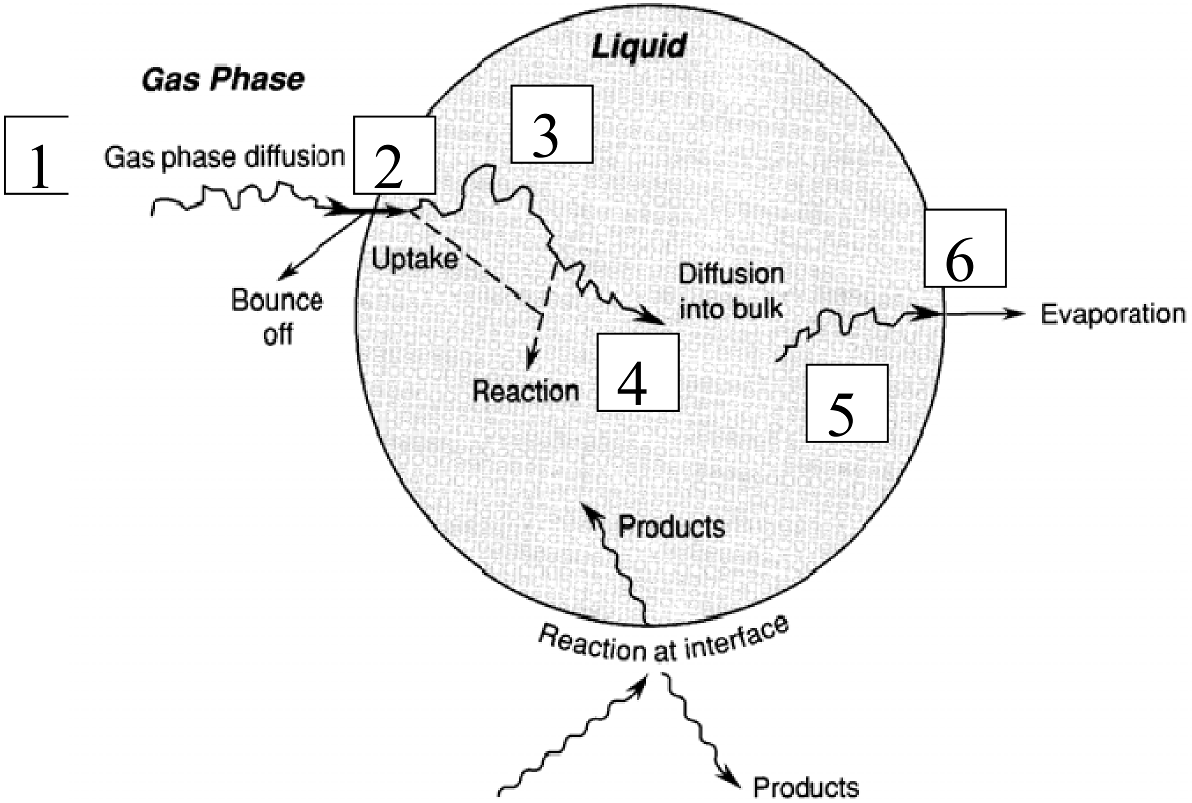
Fig. 2. Gas phase bromine cycle[a]

[a] Adapted from UNEP (1992).
Note that methyl bromide constitutes 55% of the atmospheric organic bromine (Schauffler et al., in press).
O^1D denotes electronically excited oxygen atom. A profit of O^1D can be found in NASA (1992).

Heterogenous Reactions

Multiphase reactions

1. Gas diffusion
2. Absorption
3. Diffusion into the surface (not so fast)
4. Chemical reaction in liquid
5. Diffusion of products to the surface
6. Desorption of products to the surface



Heterogenous Reactions

Uptake coefficient, γ, is the ratio of molecules lost to a surface to the number of gas-surface collisions.

The rate of collision of a molecule X with an area A of the surface is ω then the rate of loss of X per unit volume (V) is equal to

. ,

$$\gamma \frac{\omega}{V}$$

$$\frac{d[X]}{dt} = \frac{\gamma\omega}{V} = \frac{\gamma \bar{c} A[X]}{4V}$$

therefore,

$$k_s = \frac{\gamma \bar{c} A}{4V}$$

Heterogenous Reactions

The partitioning of molecules between gaseous and liquid phases, the solubility of gas at low solute concentration obeys the Henry's law.

$$[X_s] = H_x P_x$$

where $[X_s]$ is the concentration of X in the solution, p_x is the pressure in the gas phase and H_x is the Henry's law coefficient.

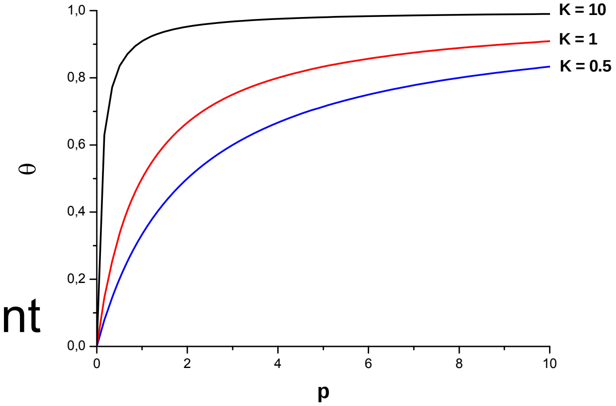
The uptake coefficients at time t is

$$\frac{1}{\gamma_t} = \frac{1}{\gamma_0} + \frac{\pi^{1/2}\bar{c}}{4H_x RTD^{1/2}} t^{1/2}$$

Heterogenous Reactions

Consider reaction on the surface of atmospheric particles. The Langmuir adsorption isotherm is the simplest of equation to express the partitioning of gas between surface and gas phase. The surface coverage (θ_x) is ,

$$\theta_x = \frac{bp_x}{1 + bp_x}$$

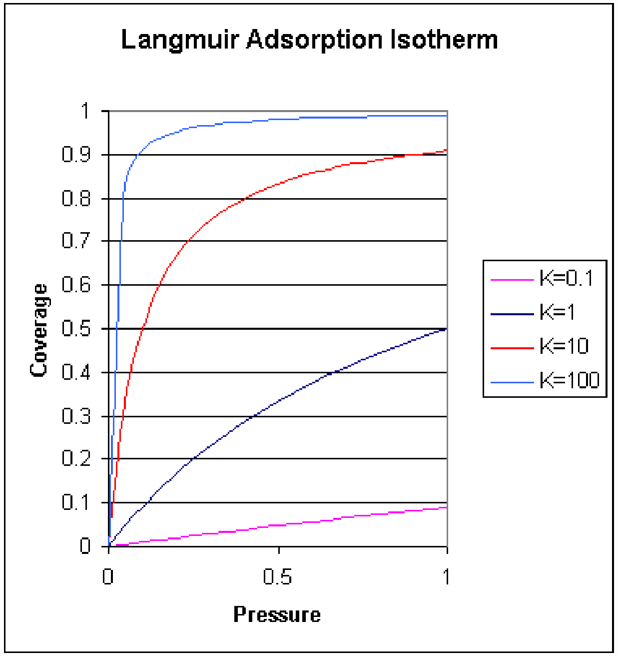


where b is a constant equal to the ratio of rate coefficient for adsorption onto the surface and its desorption.
The kinetics of reaction for a single reactant are developed by including a loss of the adsorbed molecule, the rate coefficient for this first-order loss process is k_L. The chemical rate change is

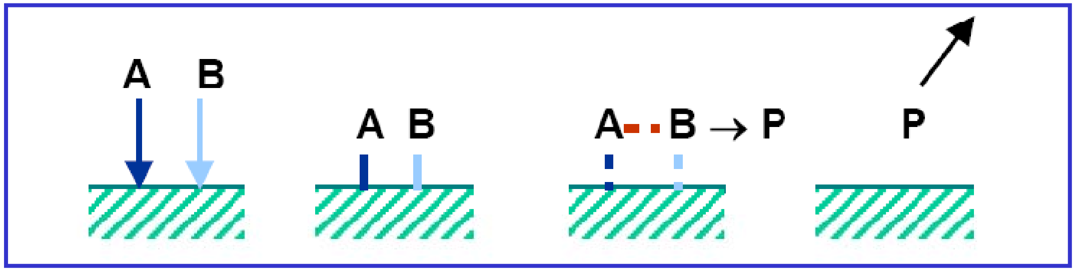
.

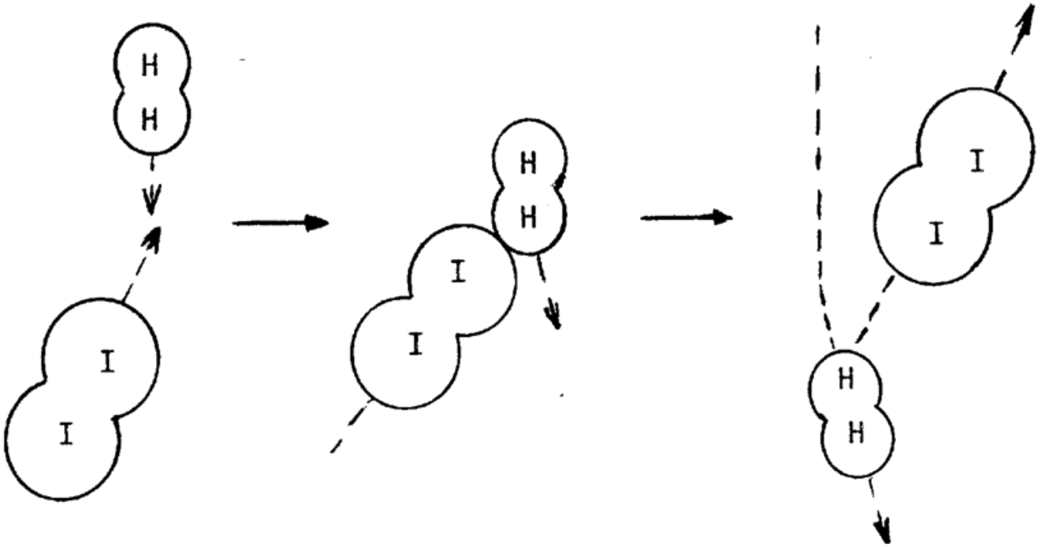
$$Rate = k_L \theta_x = k_L b_x p_x$$

Heterogenous Reactions



$$A + B \xrightarrow{k} P \;; \quad v = k\,\theta_A\theta_B$$





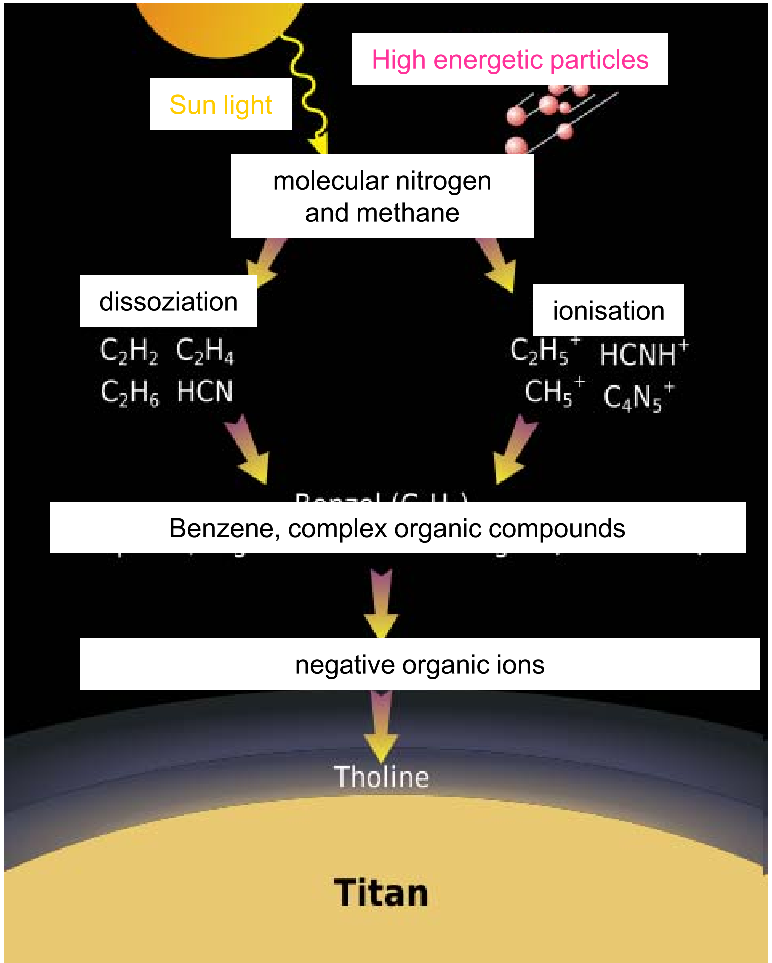
Chemistry of the upper atmosphere

Chemistry of upper atmosphere

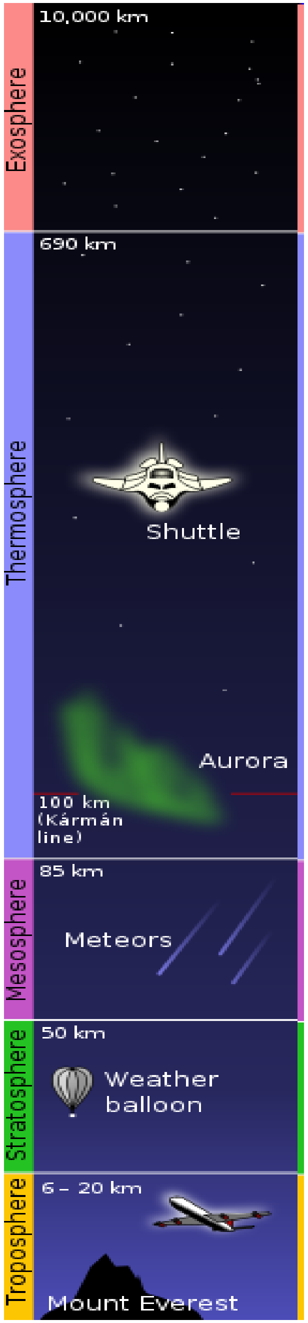
Chemistry of the upper atmosphere

Energy source:	Solar radiation, in short wavelength (UV-Vis) associate with the absorption of molecule by electronic transition.
Photolysis:	Chemical changing and transition energy heat clumped into the atoms.
At the surface:	absorption of visible energy leads to biological mechanism.

The first protection layer absorption are O, N, H-α band, N_2, it leads to the chemistry of ions and molecule in the heterosphere (ionosphere+ thermosphere, > 80 km).



Chemistry of upper atmosphere



The atmosphere is divided into 5 layers.

Troposphere is the first layer above the surface and contains half of the Earth's atmosphere. Weather occurs in this layer.

Stratosphere: Many jet aircrafts fly in this layer because it is very stable. Also, the ozone layer absorbs harmful rays from the Sun

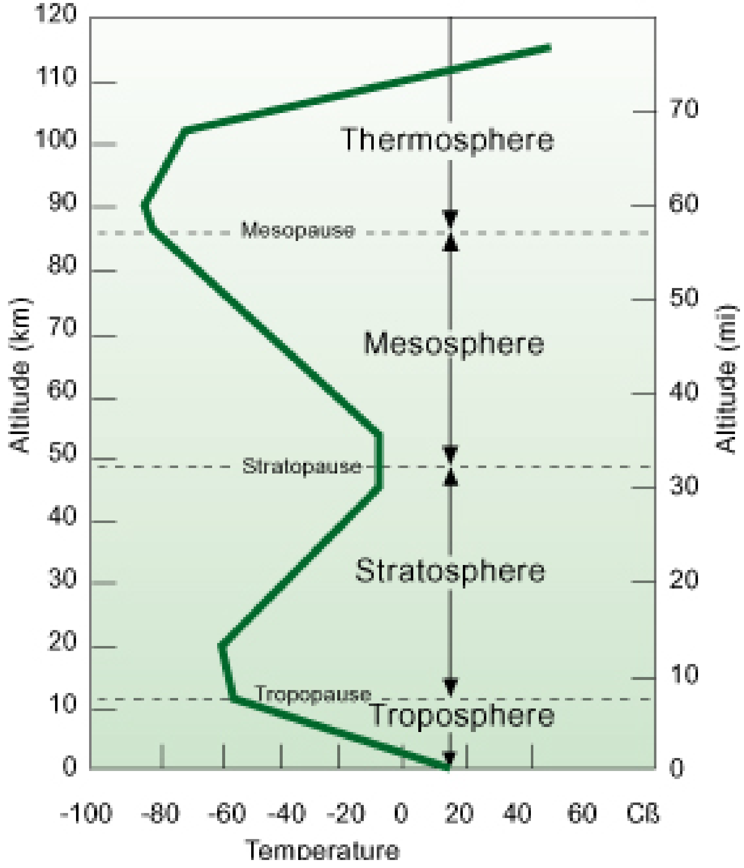
Mesosphere: Meteors or rock fragments burn up in there; the atmosphere reaches its coldest temperature of around -90°C in the mesosphere.

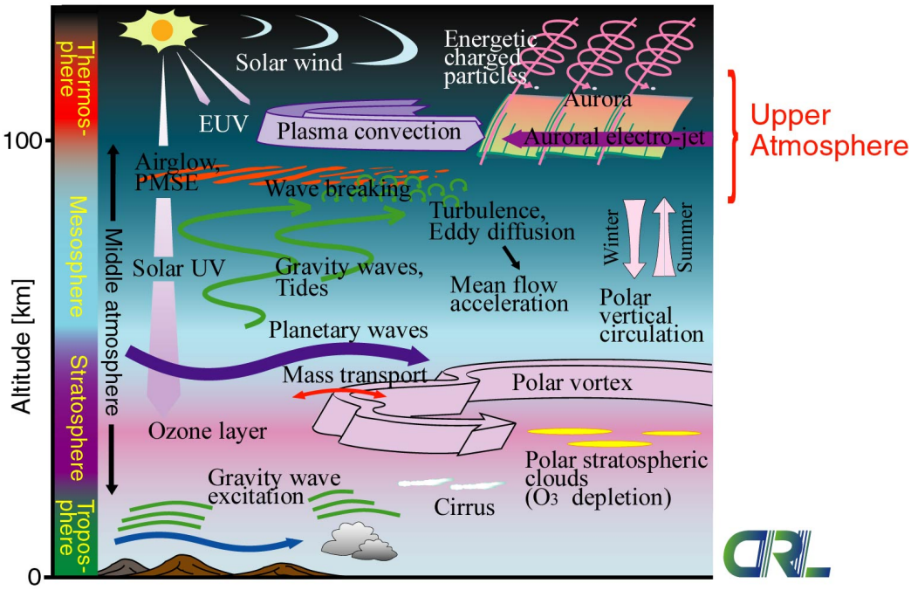
Thermosphere layer with auroras, space shuttle orbits, the air is thin, small change in energy - large change in temperature (solar activity heat up to 1,500° C or higher)

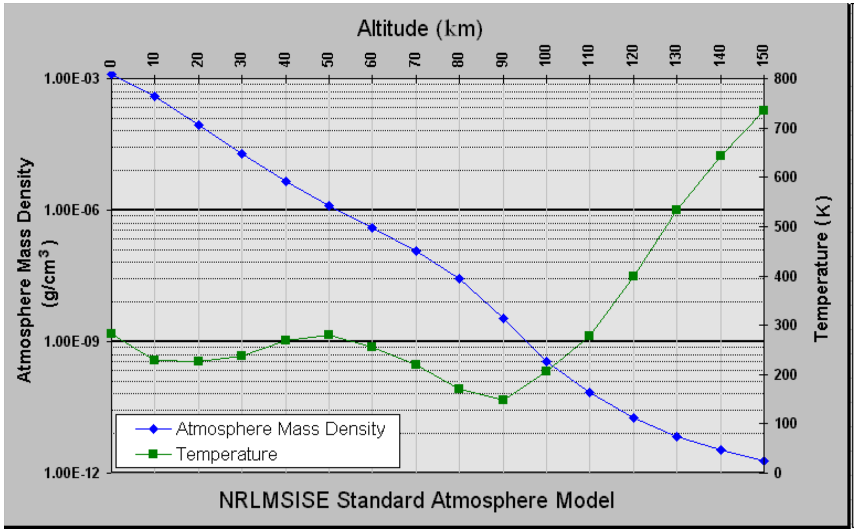
Ionosphere an extension of the thermosphere, less than 0.1% of the total mass of the Earth's atmosphere (ionisation by solar radiation)

Exosphere: The region where atoms and molecules escape into space is referred to as the exosphere. The atmosphere merges into space in the extremely thin exosphere. This is the upper limit of our atmosphere.

Chemistry of upper atmosphere




Atmospheric phenomena characterizing in the Arctic middle atmosphere



NRLMSISE Standard Atmosphere Model

Chemistry of upper atmosphere

The second protective layer is hν (100 < λ < 200 nm). NO_2 source is transported from the troposphere, where is processed in soil (NO, N_2O)

$$N_2O + h\nu \rightarrow NO + N$$

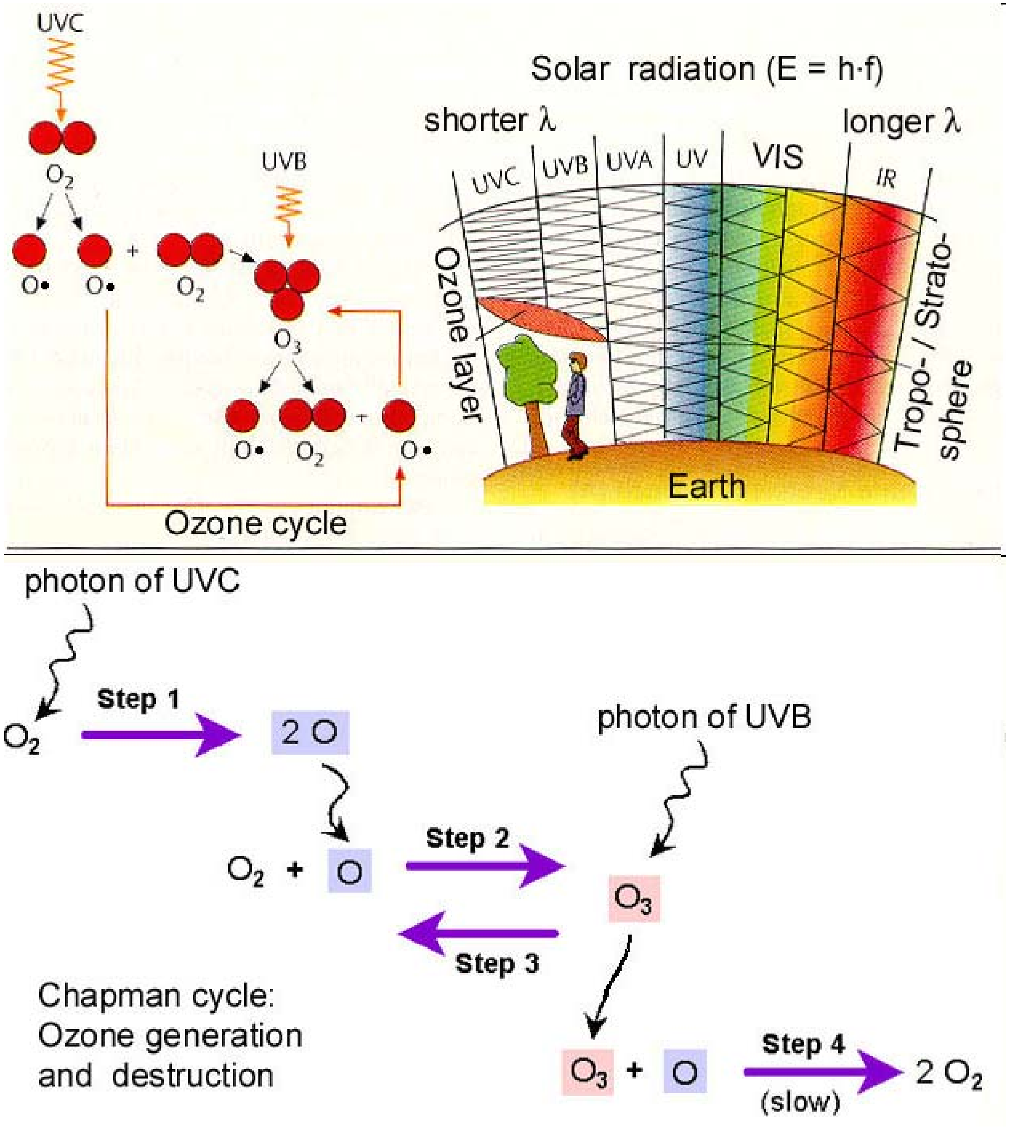
$$N_2O + h\nu \rightarrow N_2 + O$$

The third protective layer is the massive absorption from:

$$O_2({}^3\sum\nolimits_g^-) + h\nu \rightarrow O + O$$

Chemistry of upper atmosphere

In 1929, Chapman proposed the Chapman cycle:



Chemistry of upper atmosphere

In 1929, Chapman proposed the Chapman cycle:

Production: $$O_2 + h\nu \rightarrow O + O$$ *(1)*

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

Loss: $$O + O_3 \rightarrow O_2 + O_2$$ (3)

$$O_3 + h\nu \rightarrow O + O_2$$ (4)

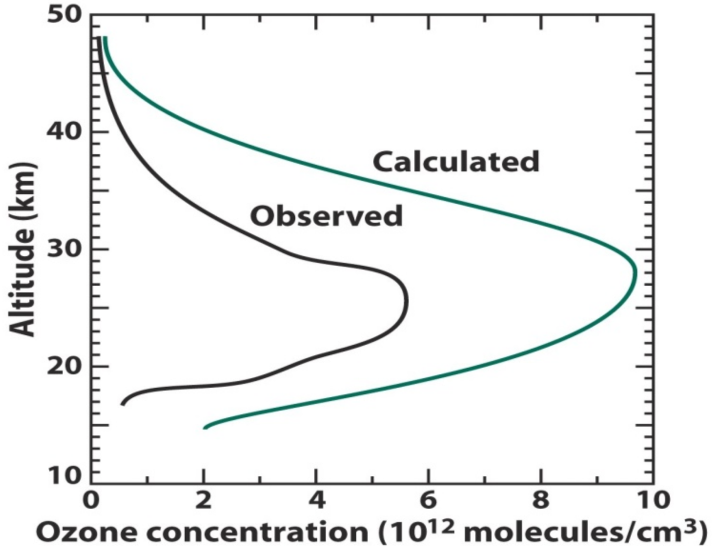


Figure 1-14
Environmental Chemistry, Third Edition
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- Chapman-Cycle: explain qualitative the observed stratospheric O_3
- but: concentrations too high (factor 2), maximum too high
- uncertainties in measurements can not explain the deviations

→ loss process in addition …

Chemistry of upper atmosphere

In 1950-1960, using the Flash photolysis proved that k3 is slow, therefore it should be something going on in this region.

In 1940, Meinel observed the OH emission.

In 1952, Bates and Nicolet suggested odd oxygen cycles.

Cycle:1

$$H + O_3 \rightarrow OH + O_2$$

$$\acute{O}H + O \rightarrow H + O_2$$

Net:

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

Cycle: 2
(35-60 km)

$$OH + O_3 \rightarrow HO_2 + O_2$$

$$HO_2 + O \rightarrow OH + O_2$$

Net:

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

<u>OH-source:</u>

$$H_2O + h\nu \rightarrow OH + H$$

<u>H_2O-source in the stratosphere:</u>
(Oxidation of CH_4, not direct injection of H_2O from troposphere)

Chemistry of upper atmosphere

The NO_x cycle: in 1979, aircraft emission from NO_x was found.

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

$$NO_2 + O \rightarrow NO + O_2$$

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

<u>NO_x -source:</u> from active $O(^1D)$

$$O_3 + h\nu \rightarrow O(^1D) + O_2(^1\Delta)$$

$$O(^1D) + N_2O \rightarrow N_2 + O_2$$

$$O(^1D) + N_2O \rightarrow NO + NO$$

from NO_x ion molecule down welling from the thermosphere and mesosphere.

- HO_x, NO_x and Chapman-cycle together agree with measured stratospheric O_3
- ⟶ Nobel prize 1995 (Paul Crutzen)

Chemistry of upper atmosphere

<u>NO_2 -source:</u> from troposphere => NO_3^- >> N_2O, N_2, NO

=> NH^+_4

Loreloch measured the troposphere and found CFC’s [CFC-11 (CF3Cl) and CFC-12(CF2Cl2)]. CFC is hanged around the atmosphere.

Rowland and Molina, in 1974, said CFC in the troposphere transports to the stratosphere.

In addition: Cl and Br → changing in the concentration of stratospheric O_3

Chemistry of upper atmosphere

ClO_x-cycle: (source: CFC-12: CF2Cl2 + hν → CF2Cl + Cl)

$$\begin{aligned} Cl + O_3 &\rightarrow ClO + O_2 \\ ClO + O &\rightarrow Cl + O_2 \\ \hline \text{net}: O_3 + O &\rightarrow 2O_2 \end{aligned}$$

Termination (formation of reservoirs):

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

$$ClO + NO_2 + M \rightarrow ClONO_2 + M$$

Re-release of Cl:

$$HCl + OH \rightarrow Cl + H_2O$$

$$ClONO_2 + h\nu \rightarrow Cl + NO_3$$

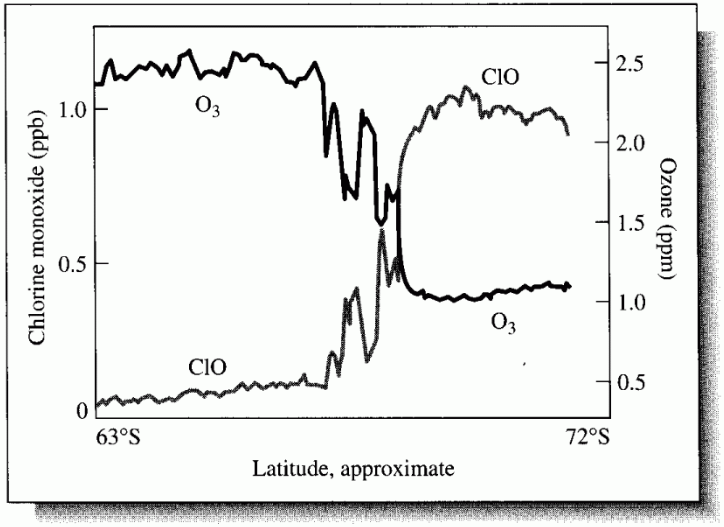
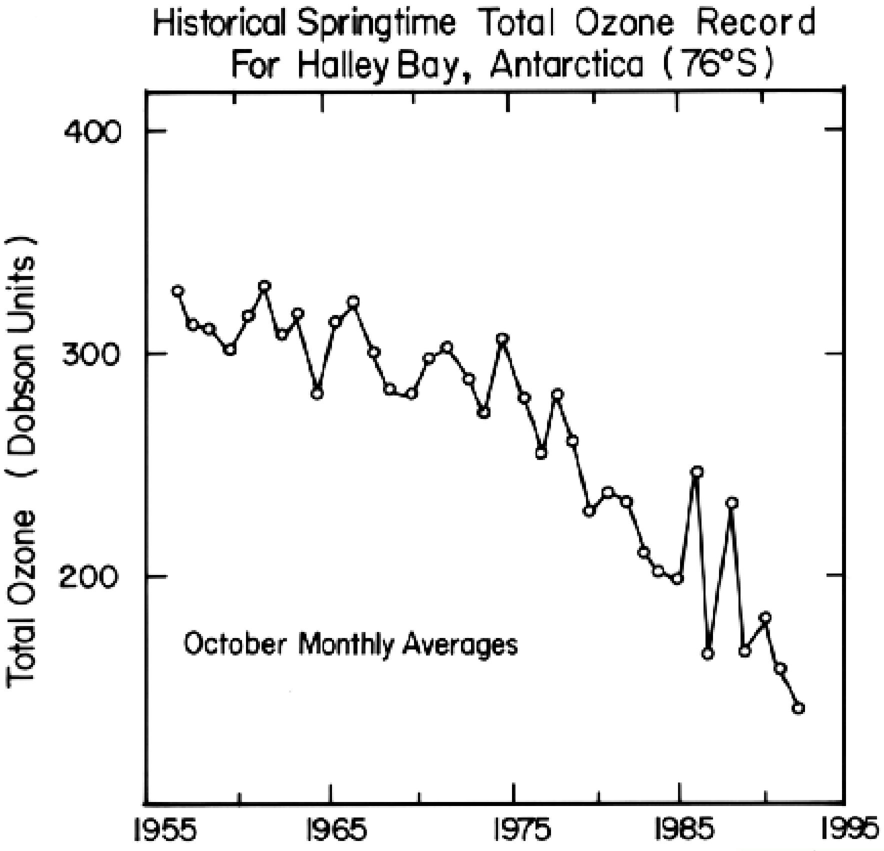


FIGURE 2-14
Ozone and chlorine monoxide concentrations versus latitude near the South Pole on September 16, 1987. (Source: Reprinted with permission from P. S. Zurer, *Chemical and Engineering News* (May 30, 1988): 16. Copyright 1988 by American Chemical Society.)

Chemistry of upper atmosphere

1985: scientists analysed an O_3 decrease in polar regions



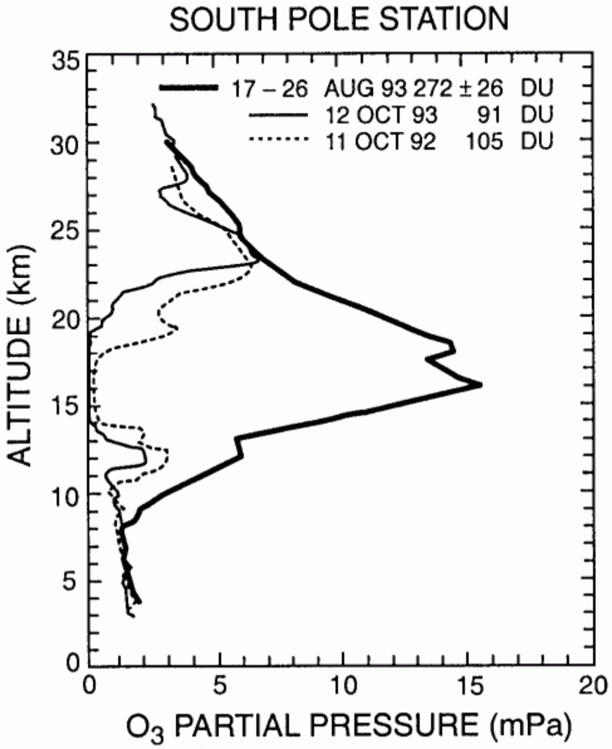


Figure 10-10 Vertical profiles of ozone over Antarctica measured by chemical sondes. In August the ozone hole has not developed yet, while in October it is fully developed. From Harris, N.R.P., et al., Ozone measurements, in WMO, op. cit..

Chemistry of the stratosphere

Loss process

Chemistry of the stratosphere

In upper and middle of the stratosphere, HO_x, NO_x, ClO_x, FO_x and BrO_x are involved.

(x=H, OH, NO, Br and Cl)

$$X + O_3 \rightarrow XO + O_2 \qquad k_1$$

$$XO + O \rightarrow X + O_2 \qquad k_2$$

$$O + O_3 \rightarrow O_2 + O_2 \qquad \text{Net.}$$

$$\frac{d[X]}{dt} = -k_2[X][O_3] + k_2[XO][O] = 0$$

Removal O_3

X	Life time of O_3 ($k_{X+O3}[X]$)
H	$k_{H+O3}[H]$
OH	$k_{OH+O3}[OH]$
NO	$k_{NO+O3}[NO]$
Cl	$k_{Cl+O3}[Cl]$
Br	$k_{Br+O3}[Br]$
F	$k_{F+O3}[F]$

Chemistry of the stratosphere

Source of OH and H (dominate in Mesosphere and upper stratosphere)

$$CH_4 + h\nu \rightarrow\rightarrow\rightarrow H_2O$$

$$H_2O + h\nu \rightarrow H + OH$$

Source of NO_x (dominate in Stratosphere)

$$N_2O + O(^1D) \rightarrow NO + NO$$

$$(N_2O + h\nu \rightarrow N + NO)$$

Source of Cl

$$O(^1D) + Cl - CF_3 \rightarrow ClO + CF_3$$

Chemistry of the stratosphere

CH_4 in Stratosphere oxidation

$$O_3 + h\upsilon \rightarrow O(^1D) + O_2$$

$$\rightarrow O(^3P) + O_2$$

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

$$O(^1D) + CH_4 \rightarrow OH + CH_3$$

$$OH + CH_4 \rightarrow H_2O + CH_3$$

$$O_2 + CH_3 + M \rightarrow CH_3O_2 + M$$

$$CH_3O_2 + NO \rightarrow CH_3O + NO_2$$

$$CH_3O + O_2 \rightarrow HCHO + HO_2$$

$$HCHO + h\upsilon \rightarrow H + HCO$$

or

$$OH + HCHO \rightarrow H_2O + HCO$$

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

$$HCO + O_2 \rightarrow HO_2 + CO$$

$$HO_2 + OH \rightarrow H_2O + O_2$$

$$CO + OH + O_2 \rightarrow CO_2 + HO_2$$

$$\underline{CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O} \qquad \underline{Net}$$

Chemistry of the stratosphere

How do they remove the ozone destroying?
<u>HOx</u>

$$H_2O \rightarrow H_2 + O$$

escape to the space

Termination

$$H, OH, HO_2 \Rightarrow OH + HO_2 \rightarrow H_2O + O_2$$

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

HNO_3 and H_2O are temporary reservoir of HO_x.

$$HNO_3 + h\nu \rightarrow H_2O + NO_2$$

$$H_2O + h\nu \rightarrow H + OH$$

Chemistry of the stratosphere

Temporary reservoir of NO_x

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

$$at\ \ night: \quad NO_2 + O_3 \rightarrow NO_3 + O_2$$

$$NO_3 + h\upsilon \rightarrow NO_2 + O$$

$$\rightarrow NO + O_2$$

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

Temporary reservoir of ClO_x

$$ClO + NO_2 + M \rightarrow ClONO_2 + M$$

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

$$HO_2 + ClO \rightarrow HOCl + O_2$$

What remove the temporary reservoirs?

$$ClONO_2 + h\upsilon \rightarrow Cl + NO_3$$

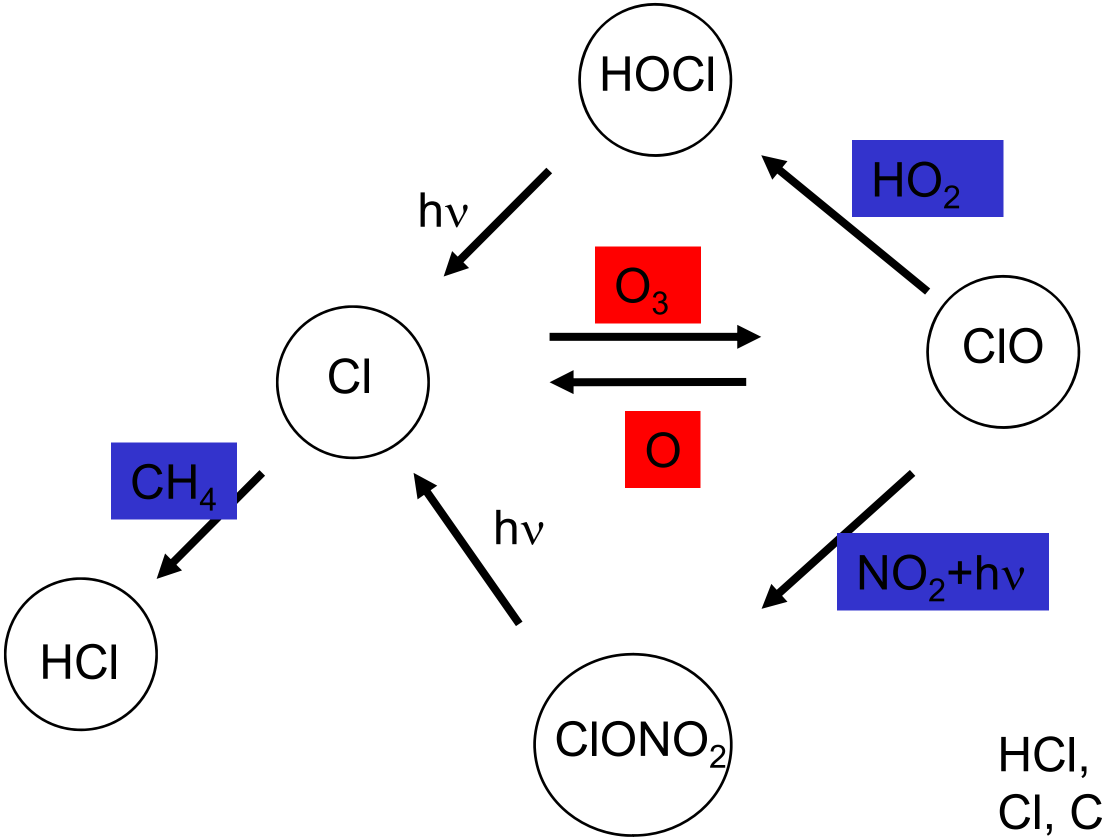
$$\rightarrow ClO + NO_2$$

$$HCl + h\upsilon \rightarrow Cl + H$$

Chemistry of the stratosphere

ClOx

Note: Highlight => propagation and termination

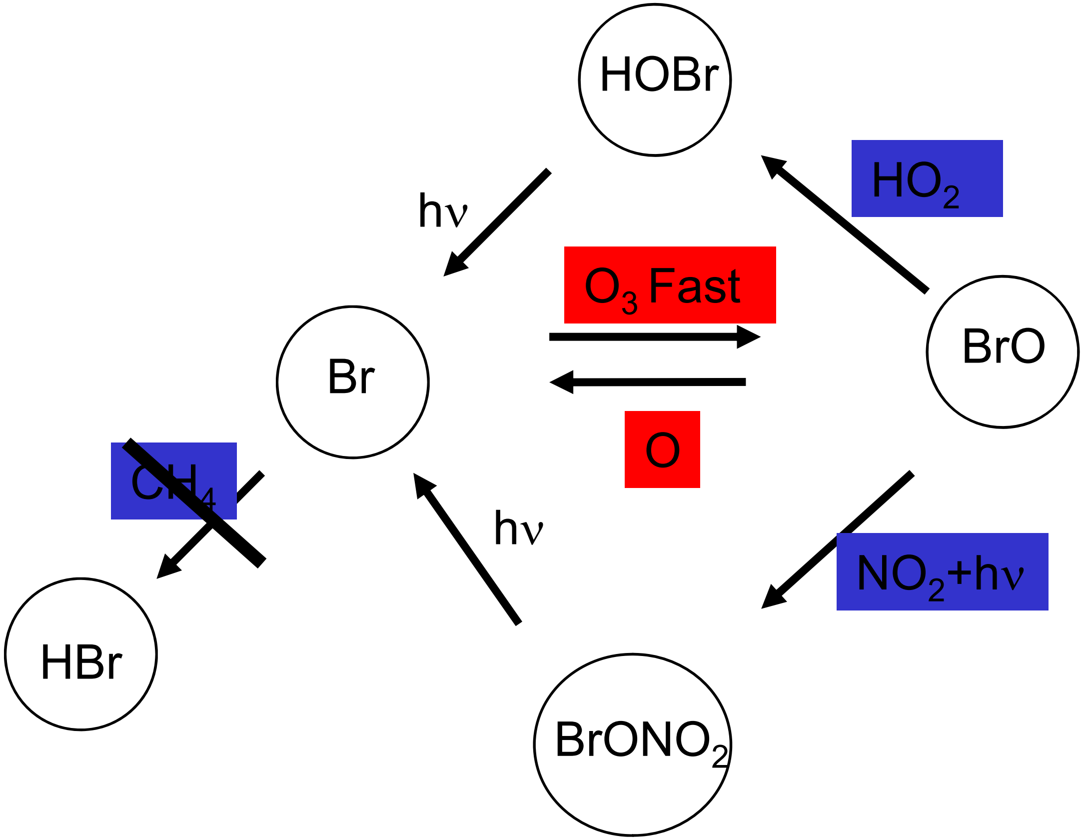


HCl, ClNO are non-active reservoirs
Cl, ClO are active reservoirs.

Chemistry of the stratosphere

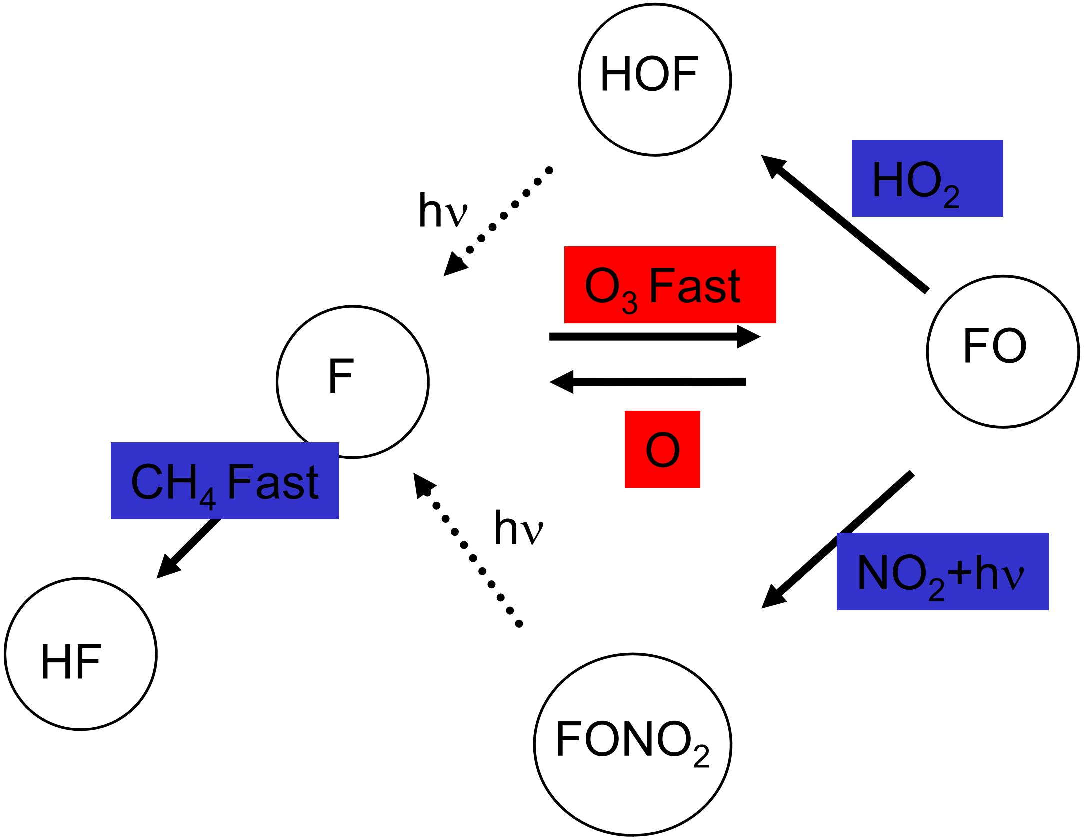
BrO_x from $CFCl_2Br$ (Halons)

In atmosphere, we have less Br than Cl.
Br is heavy molecule and high vibrational energy.



Chemistry of the stratosphere

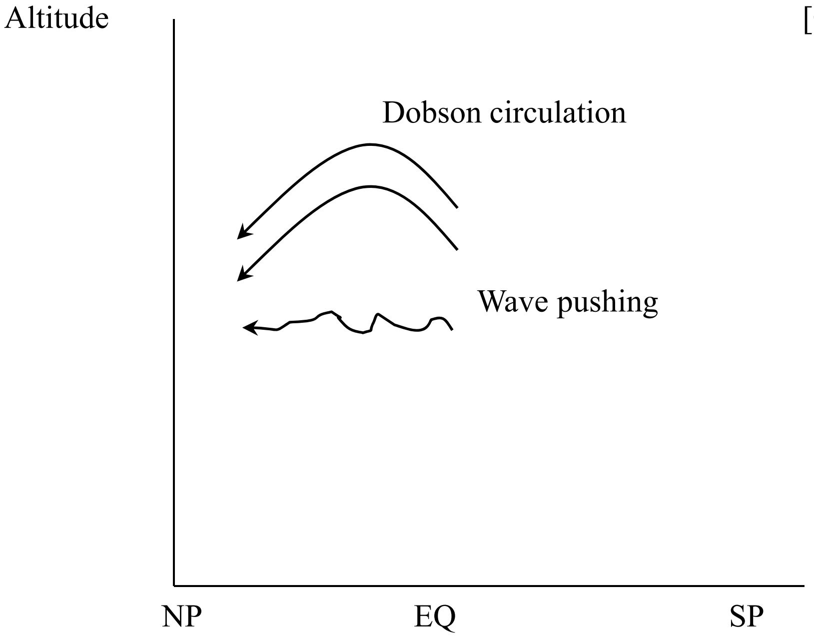
FO_x

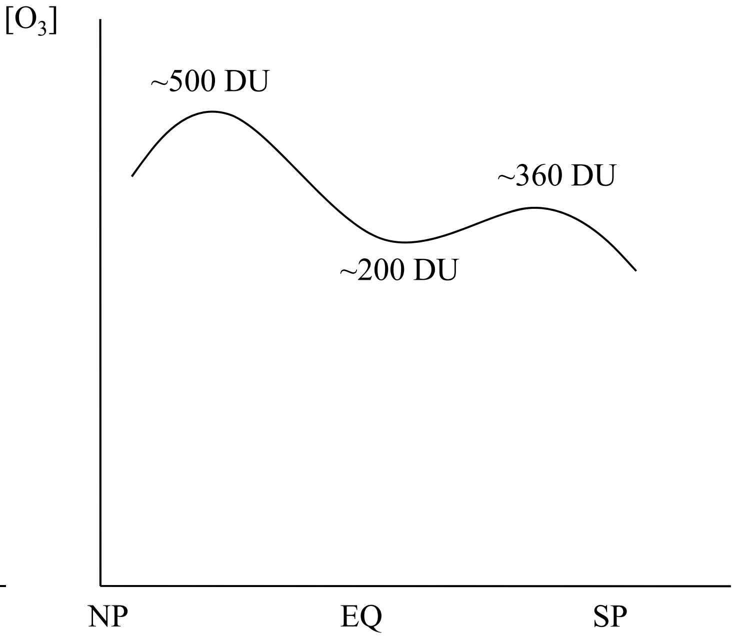


Chemistry of the stratosphere

Ozone is high produced in tropic region but amount of ozone is high in Poles.

During Summer





Chemistry of the stratosphere

1975: (IGY: International Geophysics Year) – Dobson network is set for ozone measurement.

1985: Farmad proposed paper and we know the ozone hole.
The explanation in the polar night

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

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

$$NO_2 + NO_3 + M \Leftrightarrow N_2O_5 + M$$

In polar night, polar stratospheric clouds (PSCs) type I are formed.

$$N_2O_5(s) + H_2O(l) \rightarrow 2HNO_3$$

$$nHNO_3 + 3nH_2O \rightarrow' n(HNO_3 \bullet 3H_2O)(NAT)$$

Chemistry of the stratosphere

Ozone destruction processes:

1. Winter polar vortex
2. $N_2O_5(s) \rightarrow NAT$
3. PSC formation (no photolysis)
4. Production of PSC product

$$\mathbf{ClONO_2(s) + HCl(s) \rightarrow Cl_2 + HNO_3}$$

$$\mathbf{N_2O_5 + HCl \rightarrow ClONO + HNO_3}$$

or

$$\mathbf{HOCl + HCl \rightarrow H_2O + Cl_2}$$

Chemistry of the stratosphere

5. During Spring

$$Cl_2 + h\upsilon \rightarrow Cl + Cl$$

$$ClONO + h\upsilon \rightarrow ClO + NO$$

6. Ozone destruction

$$2\{Cl + O_3 \rightarrow ClO + O_2\}$$

$$ClO + ClO + M \rightarrow Cl_2O_2 + M$$

$$Cl_2O_2 + h\upsilon \rightarrow Cl + ClOO$$

$$ClOO + M \rightarrow Cl + O_2 + M$$

$$\underline{2O_3 \rightarrow 3O_2} \qquad \underline{Net}$$

Stratospheric O_3

Polar stratospheric clouds (PSC) heterogenous reactions

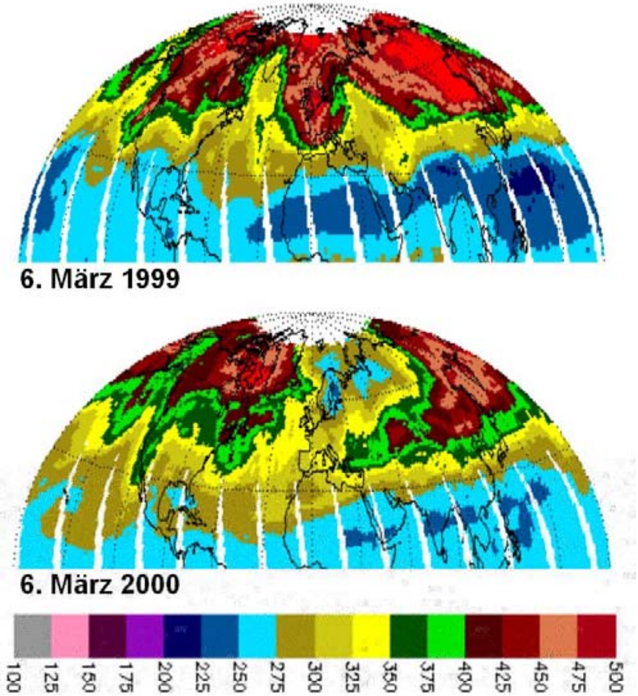
$$ClONO_2 + HCl \xrightarrow{PSC} Cl_2 + HNO_3$$

$$ClONO_2 + H_2O \xrightarrow{PSC} HOCl + HNO_3$$

$$HOCl + HCl \xrightarrow{PSC} Cl_2 + H_2O$$

$$N_2O_5 + HCl \xrightarrow{PSC} ClNO_2 + HNO_3$$

$$N_2O_5 + H_2O \xrightarrow{PSC} 2HNO_3$$

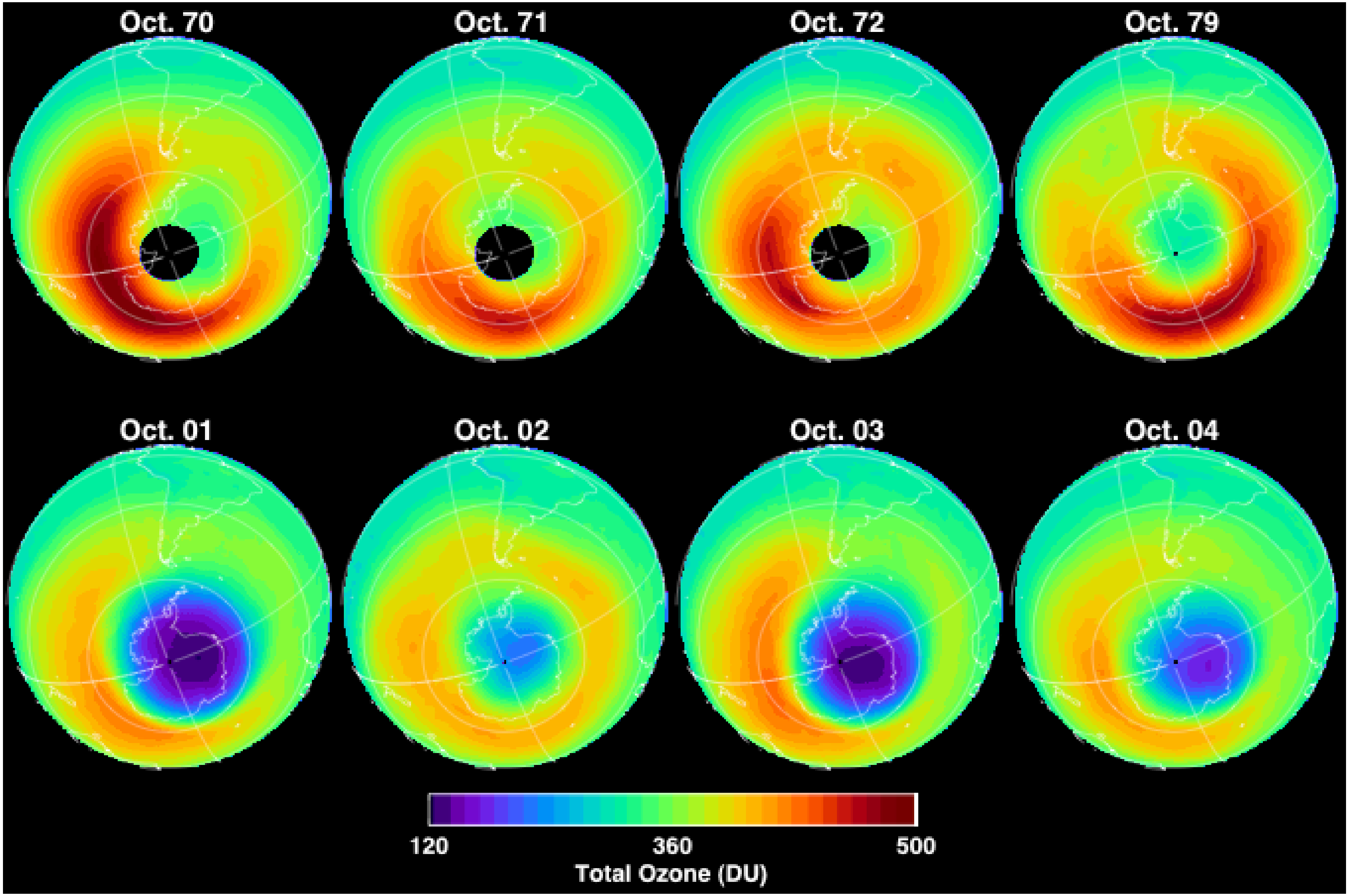


Result: ClO_x from reservoir and $NO_x \rightarrow HNO_3$ (**Denoxification**).

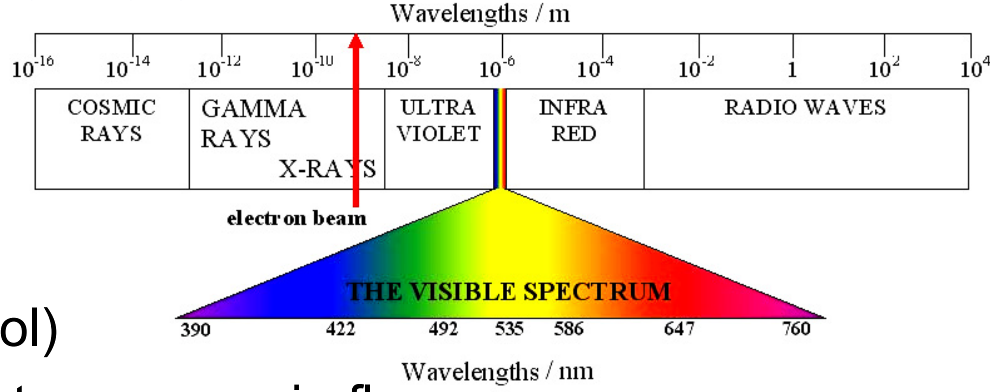
Stratosphere (dry) → low temperatures (185K - 190K) are needed for condensation

Ozone hole

Ozone Hole

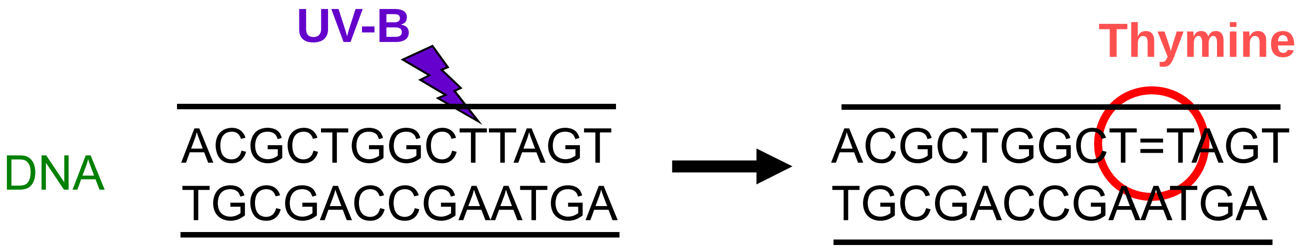

Oct. 70
Oct. 71
Oct. 72
Oct. 79
Oct. 01
Oct. 02
Oct. 03
Oct. 04
120
360
500
Total Ozone (DU)

Ozone Hole



- UV light can have beneficial effects too
- It stimulates the transformation dietary steroids into Vit D (calciferol)
- Insects use it to guide them to nectar sources in flowers
- UV light is high energy light
- When it strikes molecules it can cause them to beak into ions or free radicals
- The free radicals in turn damage large molecules such as proteins and DNA - causes mutations - lead to cancer

UV-B has a direct effect on DNA, DNA absorbs UV light of 260nm, the action of UV forms thymine dimers, this can cause a gene mutation when the DNA replicates



UV-B

Thymine dimer

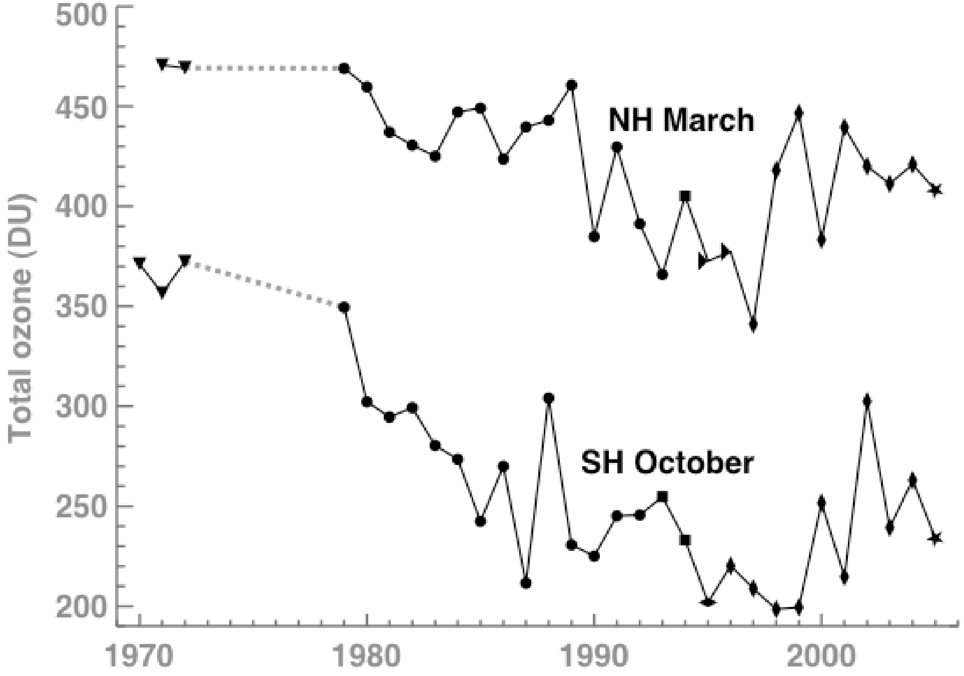
DNA

ACGCTGGCTTAGT
TGCGACCGAATGA

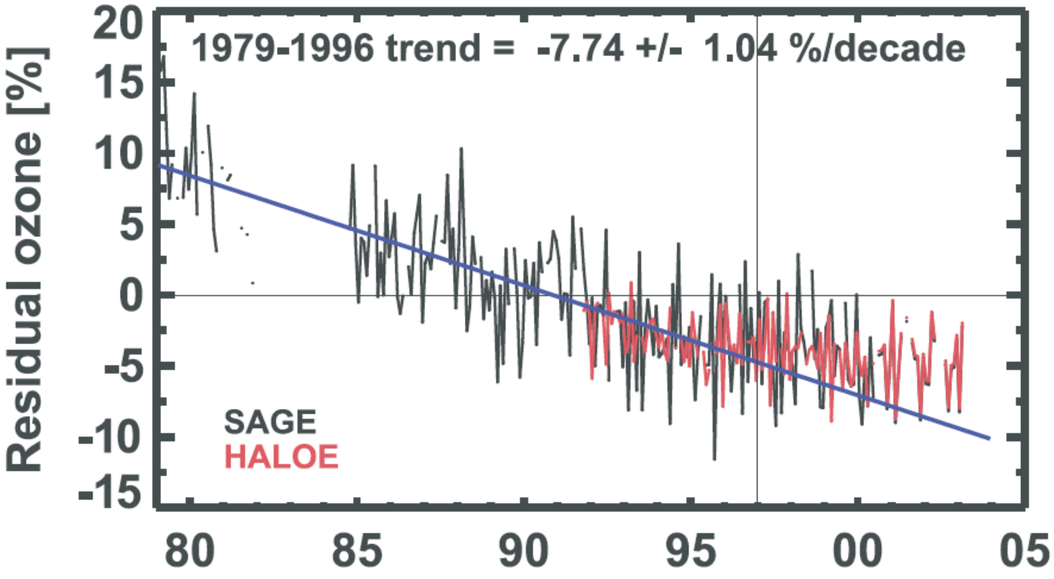
→

ACGCTGGCT=TAGT
TGCGACCGAATGA

Arctic & Antarctic Trends



- Substantial losses have occurred in the Arctic
- Arctic levels are naturally higher because of the structure of the NH

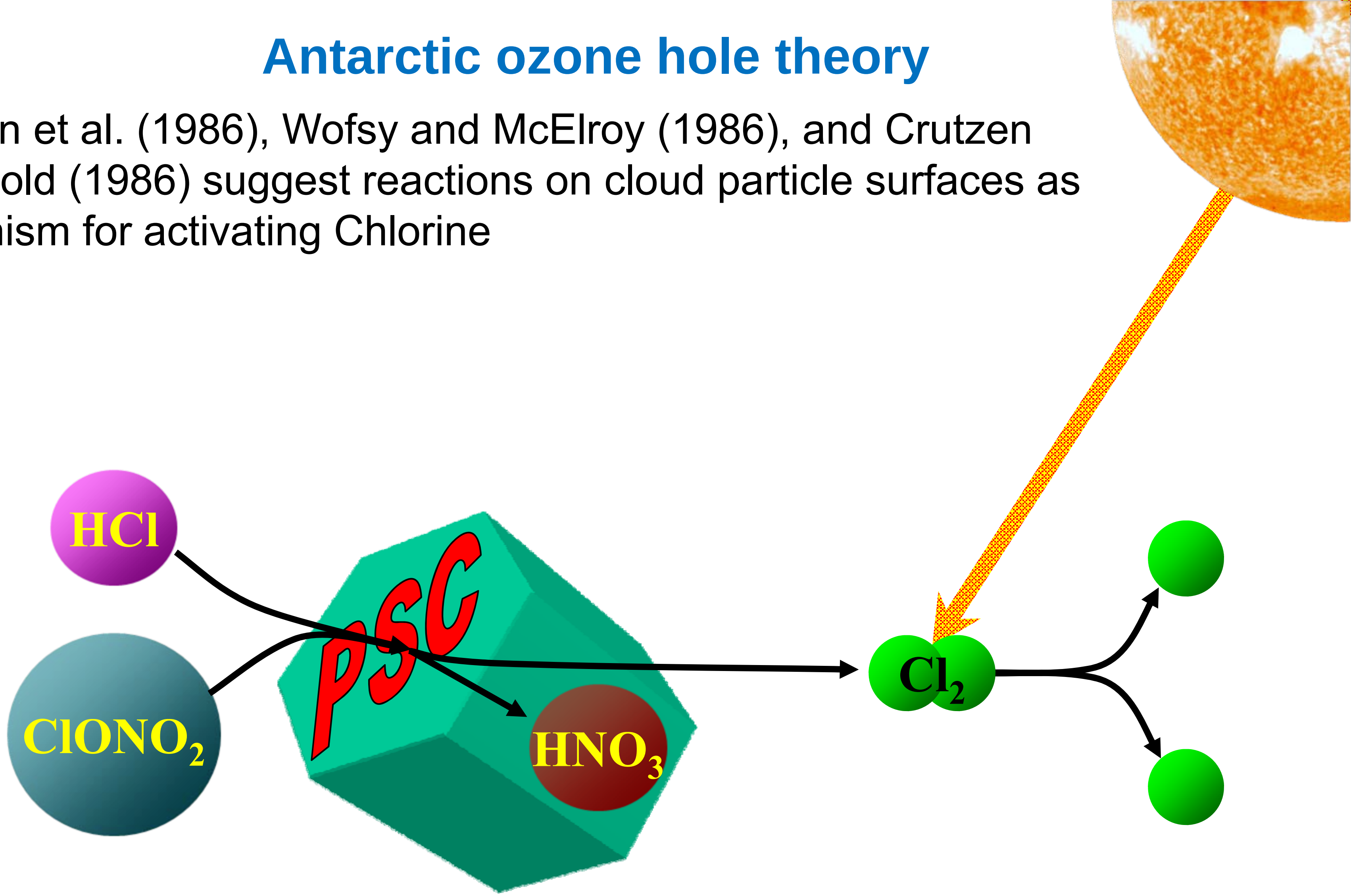


- 35-45 km, 30-50˚N ozone
- Note that the later year (post 1997) are above the downward slope
- **Ozone is no longer decreasing** (1st step in the recovery process)

Newchurch et al. (2003)

Antarctic ozone hole theory

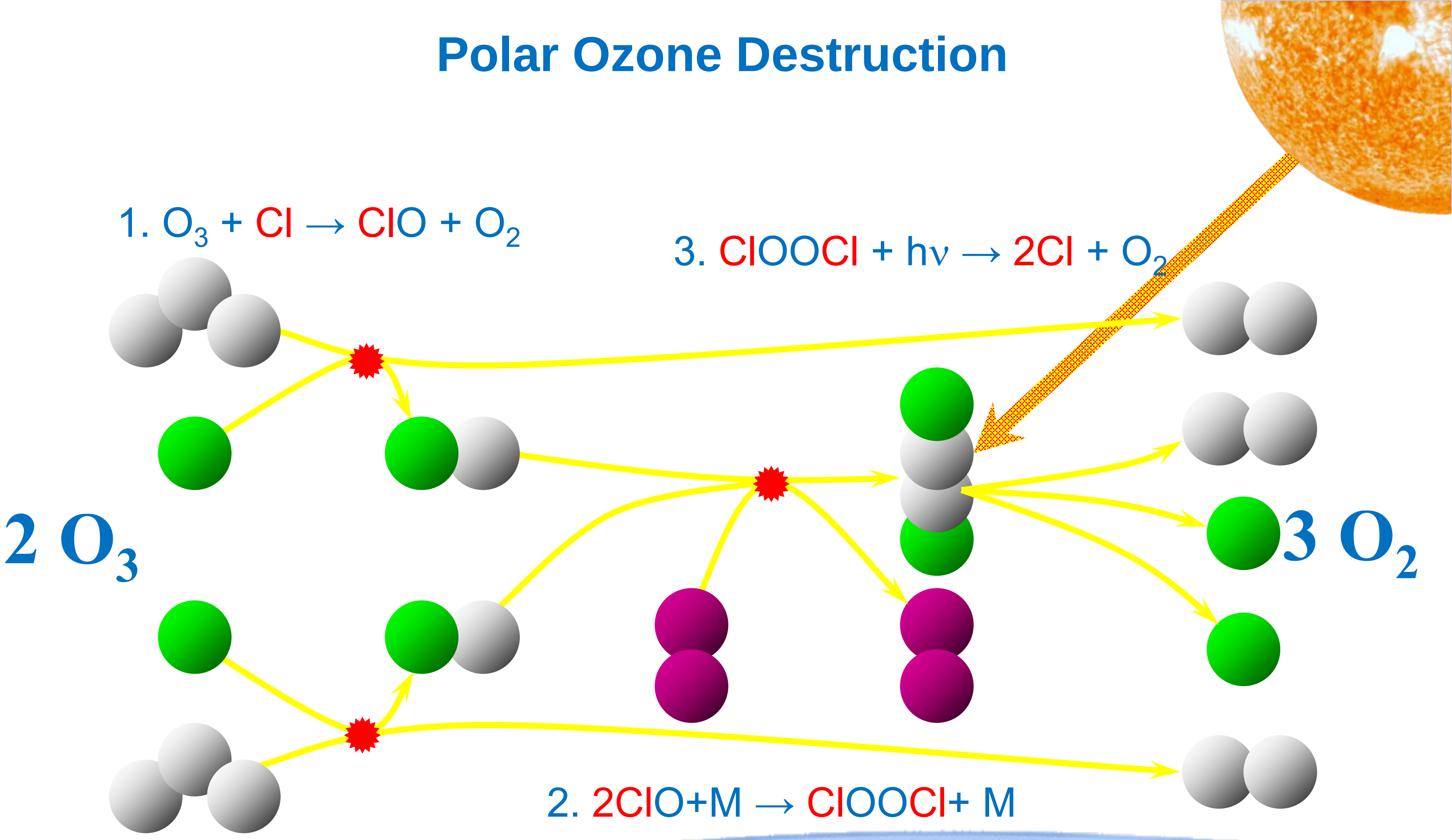
Solomon et al. (1986), Wofsy and McElroy (1986), and Crutzen and Arnold (1986) suggest reactions on cloud particle surfaces as mechanism for activating Chlorine



Cl_2 is easily photolyzed by UV & blue/green light

HNO_3 is sequestered on PSC

Polar Ozone Destruction



1. $O_3 + Cl \rightarrow ClO + O_2$

3. $ClOOCl + h\nu \rightarrow 2Cl + O_2$

$2\ O_3$

$3\ O_2$

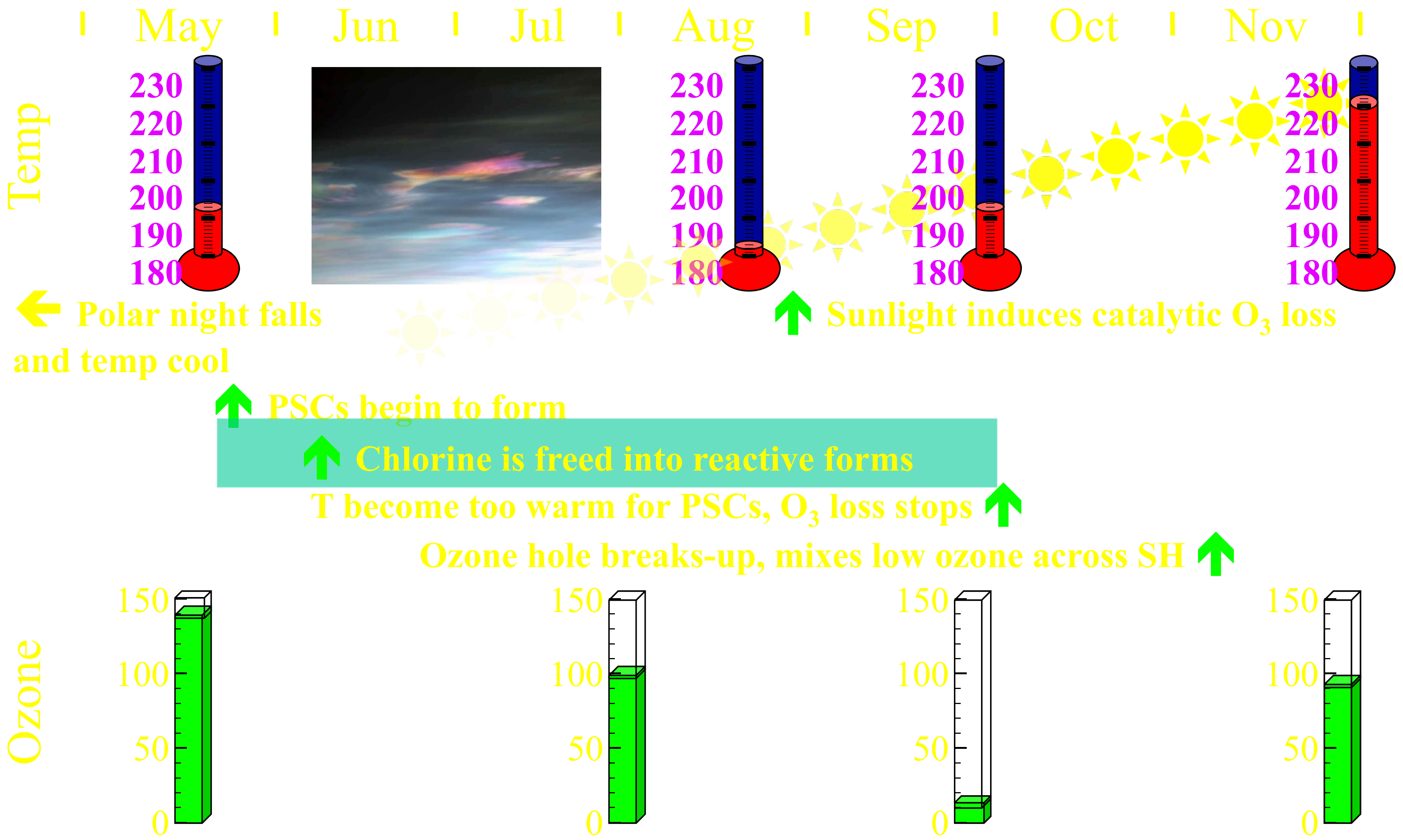
2. $2ClO + M \rightarrow ClOOCl + M$

Only visible light (blue/green) needed for photolyzing ClOOCl

No oxygen atoms required

Net: $2\bullet O_3$ + solar photon → $3\bullet O_2$

Ozone Hole timeline



Polar night falls and temp cool

Sunlight induces catalytic O_3 loss

PSCs begin to form

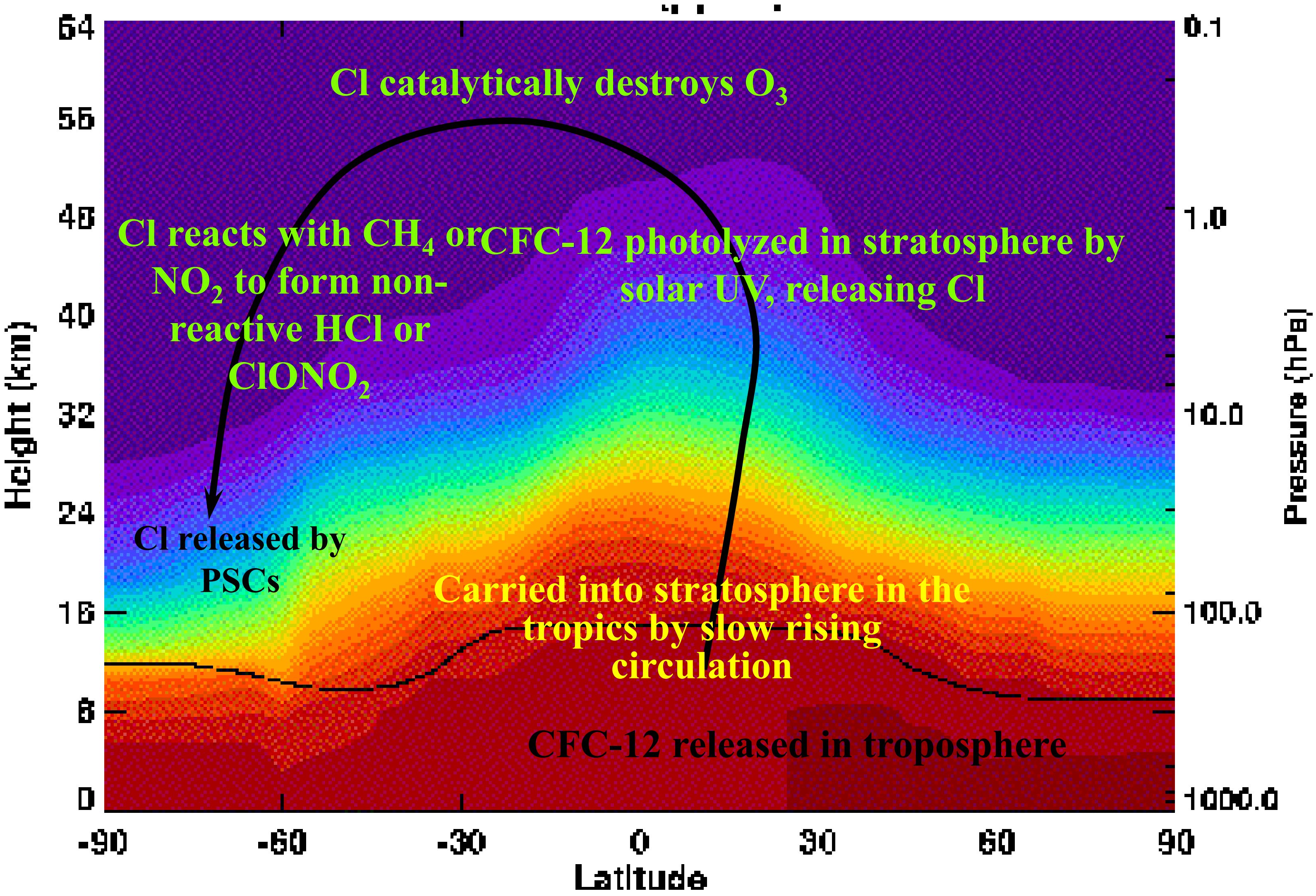
Chlorine is freed into reactive forms

T become too warm for PSCs, O_3 loss stops

Ozone hole breaks-up, mixes low ozone across SH

Cold T → PSCs + high Cly → het reactions → Large catalytic loss

How does chlorine get from our refrigerators to the Antarctic stratosphere?



Cl catalytically destroys O_3

Cl reacts with CH_4 or NO_2 to form non-reactive HCl or $ClONO_2$

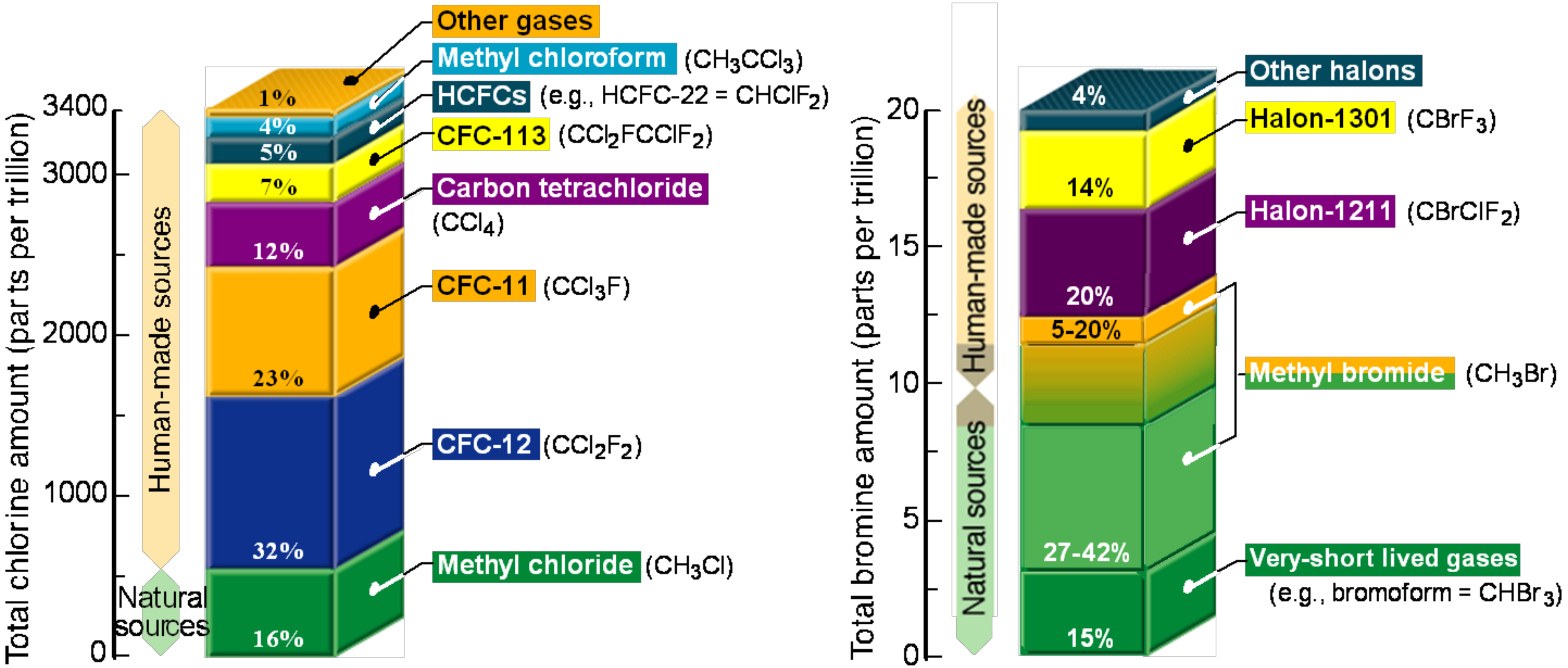
CFC-12 photolyzed in stratosphere by solar UV, releasing Cl

Cl released by PSCs

Carried into stratosphere in the tropics by slow rising circulation

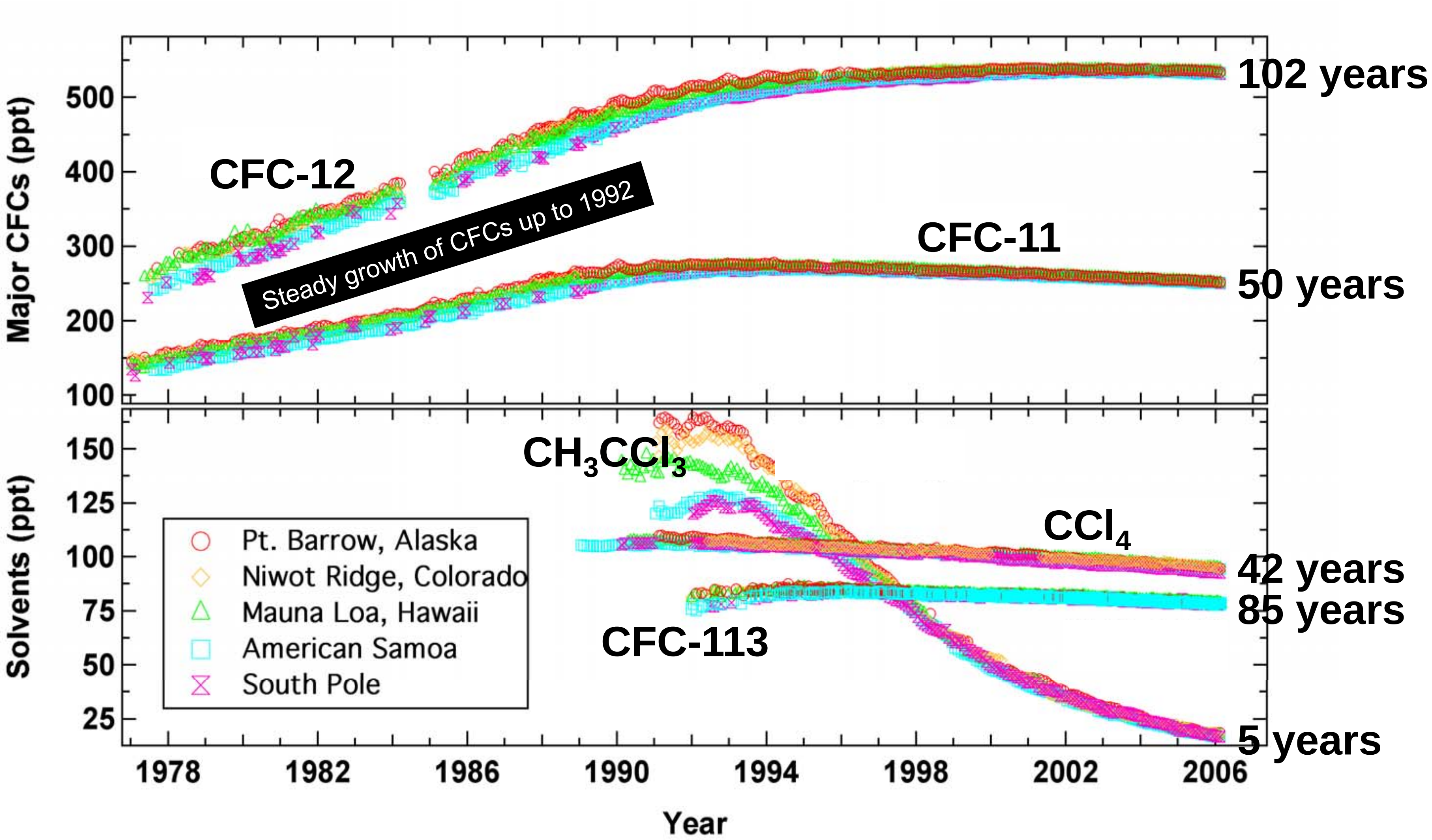
CFC-12 released in troposphere

Source Chemicals



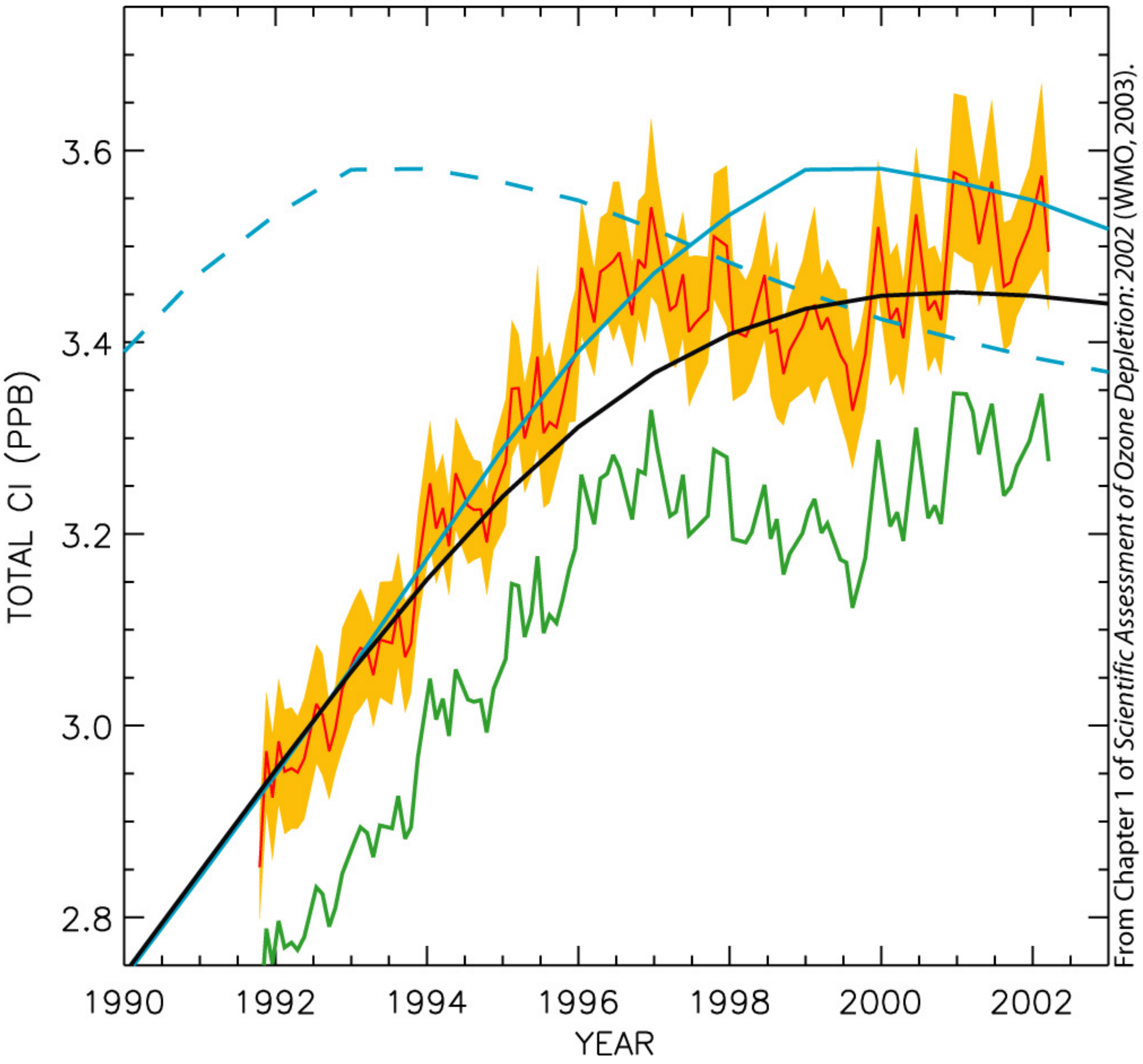
- Cl is much more abundant than Br
- Br is about 50 times more effective at O_3 destruction

Atmospheric Chlorine Trends from NOAA/ERL – Climate Monitoring Division



Updated Figure made by Dr. James Elkins from Trends of the Commonly Used Halons Below Published by Butler et al. [1998]**,** All CFC-113 from Steve Montzka (flasks by GC/MS), and recent updates of all other gases from Geoff Dutton (in situ GC).

Global Stratospheric Chlorine trends



From Chapter 1 of *Scientific Assessment of Ozone Depletion: 2002* (WMO, 2003).

Time evolution of chlorine

From WMO (2003) - Figure 1-7

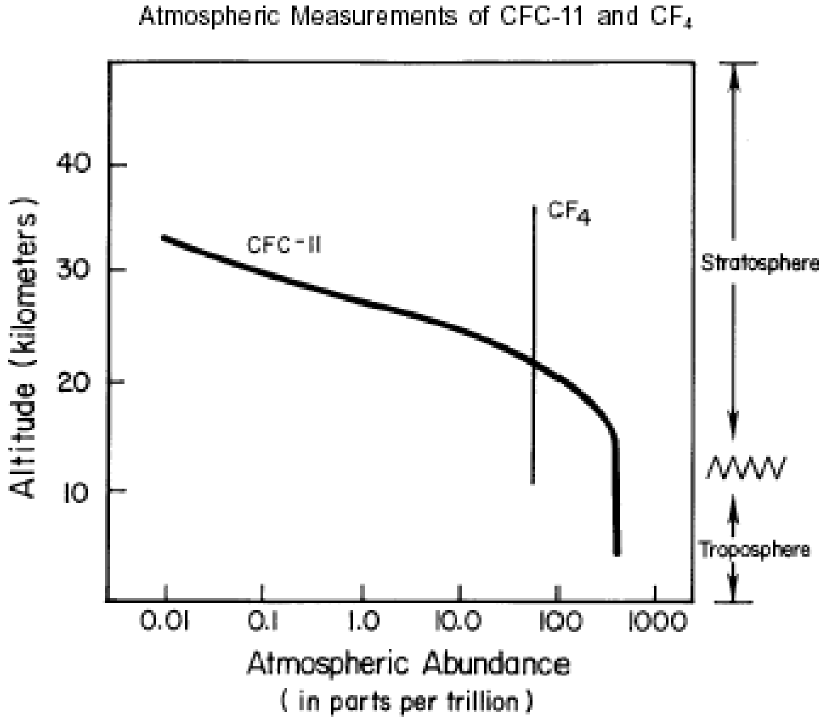
Ozone Hole

How do CFCs arrive the stratosphere?

- CFCs have more weight than „air“

- CFCs are stabil in the troposphere and therefore well mixed

- from observations we know that CFCs arrive in the stratosphere but the concentration decrease with increasing height (photolysis)

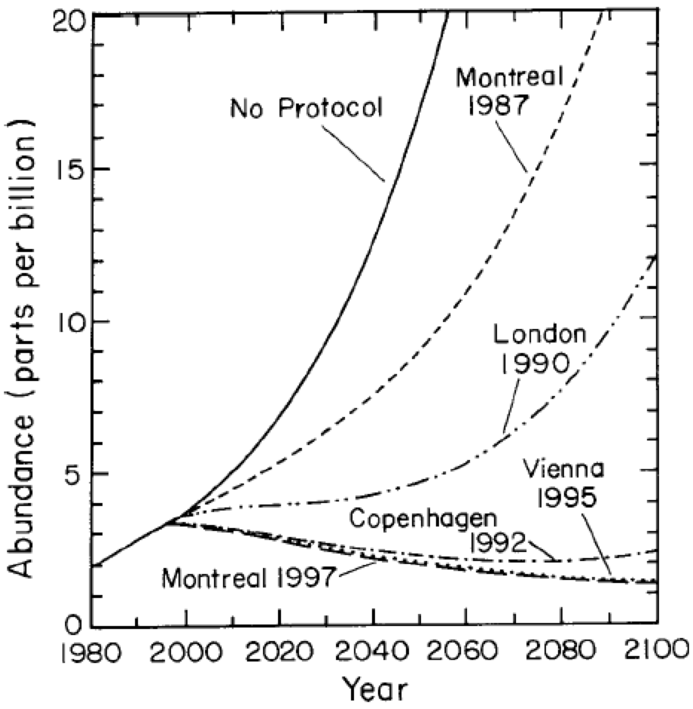


Ozone Hole

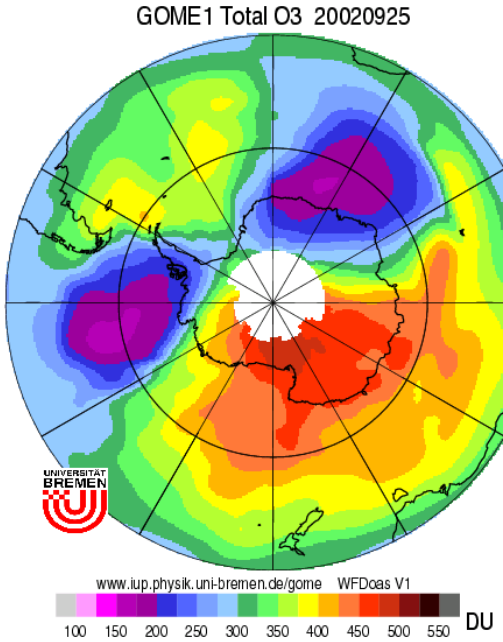
Source: CFC-12: $CF_2Cl_2 + h\nu \rightarrow CF_2Cl + Cl$

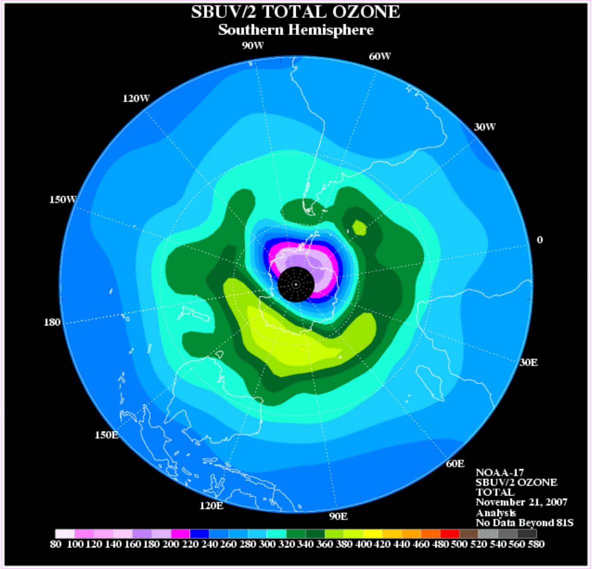
→ Montreal protocol and international appointments should prohibit or minimize the use of CFCs until 1996

Effect of the International Agreements on Ozone-Depleting Stratospheric Chlorine/Bromine



Ozone Hole





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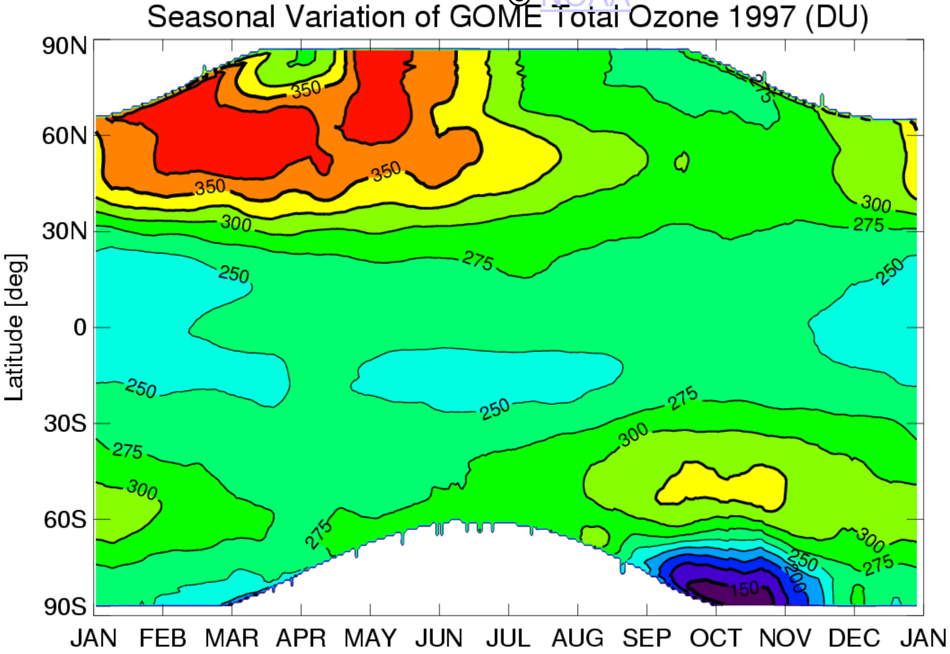


Ozone Hole

Correlation of ozone concentration - global warming?

Ozone absorbs UV-radiation, increase of temperature in stratosphere→ less ozone lower temperature in stratosphere

Greenhouse gas absorbs IR radiation from the surface, increase of temperature in lower atmosphere but cooling of upper atmosphere → global warming leads to cooler stratosphere

Reduction of stratospheric temperature, increase of PSC a in spring reduction of ozone, increase of heterogenous processes in mid-latudues possible

Ozone Hole

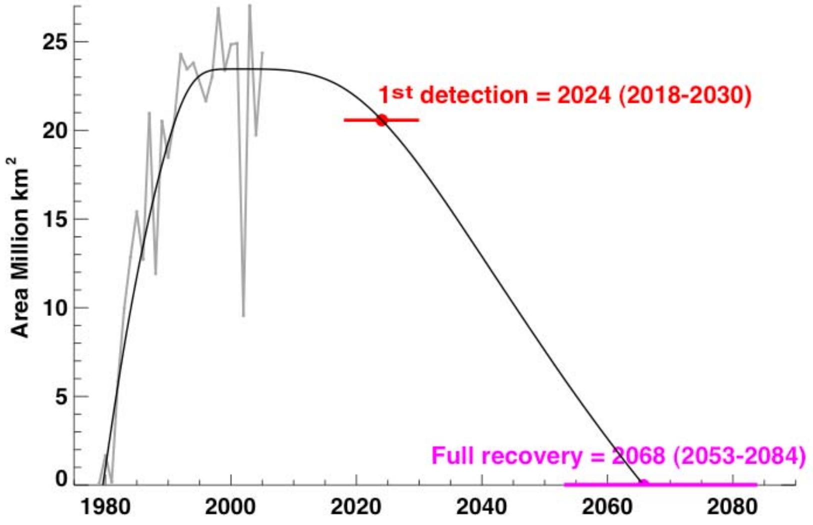
What about the future of ozone reduction?

Global reduction -5% since 1965

- 10% reduction in mid-latitude winter/spring
- 60% reduction in antarctic spring
- 5-30% reduction in arctic spring

up to 20% reduction after volcanic eruption of Pinatubo (Philippines)

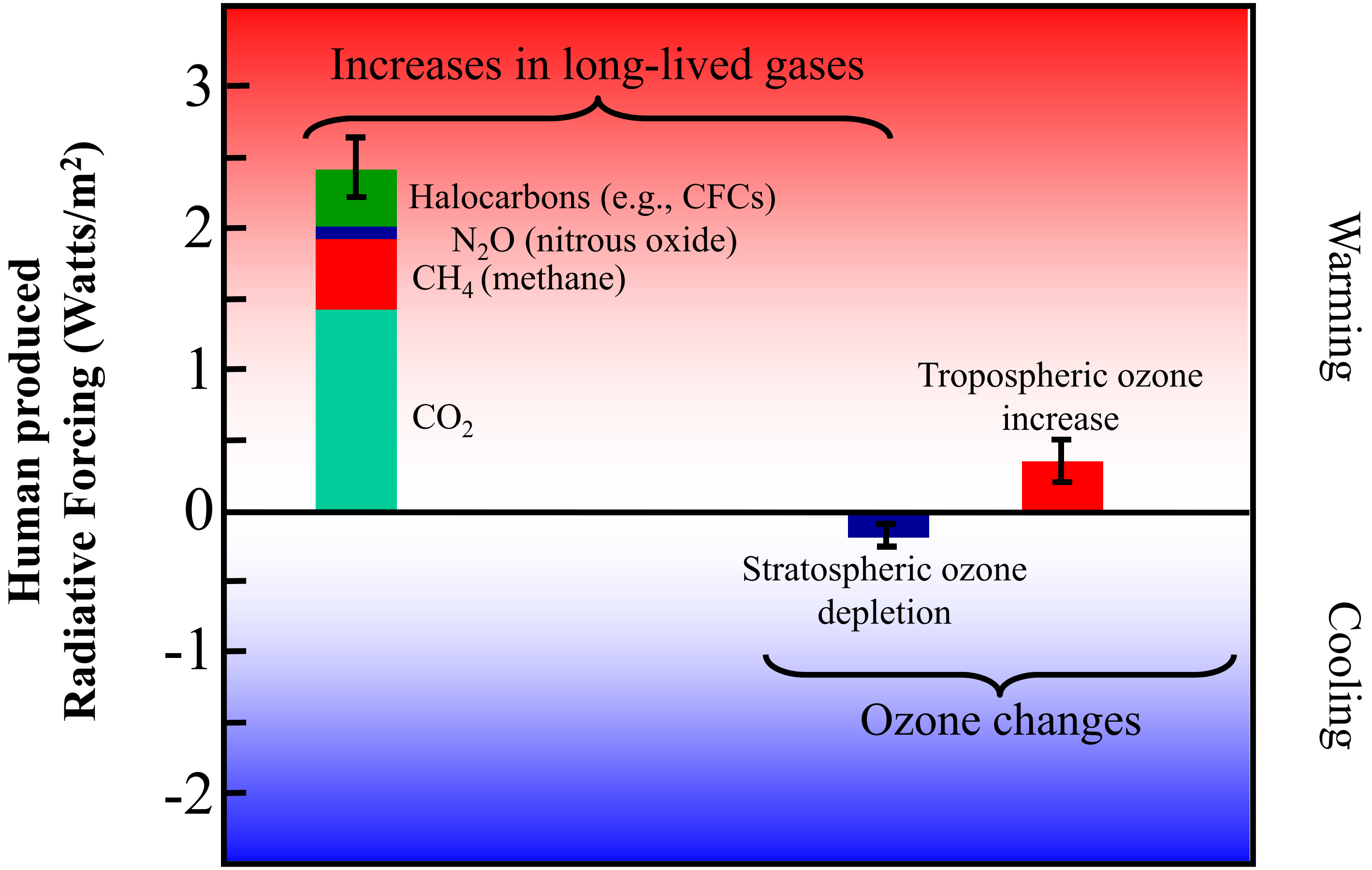
- Maximum of stratospheric Cl now reached ?
- back to „normal situation“ in 2100 ?



1st detection is the approximate year that we’ll be able to say that the ozone hole is improving.

Full recovery is the year when the ozone hole size is zero.

Ozone and climate change



Ozone change is not a primary cause of climate change.

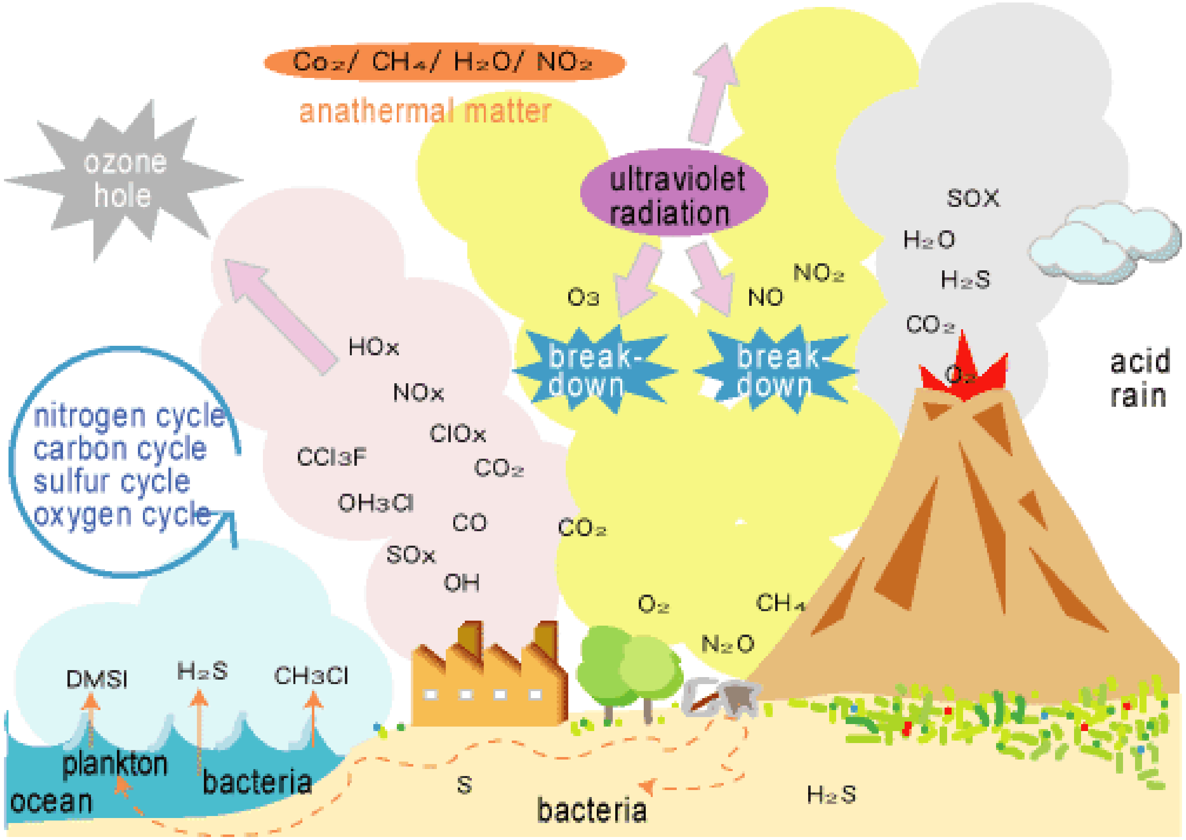
- Ozone depleting substances contribute to climate change.
- Ozone changes causes a climate response that is generally larger than the Halocarbon response.
- Climate change may seriously impact ozone levels.

Tropospheric Chemistry

Tropospheric Chemistry

Stratosphere	**Troposphere**
Low pressure	High pressure
Low temperature	High temperature
Some sinks	Many sinks
Some sources	Many sources
No biological emissions	Biological emissions
Less anthropopgenic input	Many anthropopgenic input
Less vertical mxing	More vertical mixing
Low humidity	High humidity

Emissions in Troposphere



Tropospheric Chemistry

- Many different trace gases in troposphere, Complex reaction chains
- Life times from seconds to years, Transport from source to sink

Life time of trace gases

- source → sink
- dry deposition: gases are absorbed
- irreversible at the surface, Ocean and plant-surfaces
- wet deposition: compounds are implemented in clouds, aerosols, rain droplets
- emit and remove from atmosphere
- Transport: vertical und horizontal
- Source → Sink = Life time

Tropospheric Chemistry

Mixing time: τ_M

Vertical mixing: ~ 1 week (surface → tropopause)

Horizontal mixing: ~ 1 year (around the globe)

e.g. CH_4 (by physical processes and oxidation → slowly oxidydised τ = some years), HCHO (intermediate during oxidation, fast photolysed τ = some hours)

- H_2 τ = some years CO τ = some months
- natural gases: biogenic sources, reduced form (CH_4, terpenes, H_2S, ..) or only oxidised (CO, N_2O) = mainly solute in water

"anthropogenic gases": higher oxidised (CO_2, NO_2, SO_2) easy soluble

- only some are directly deposited

Tropospheric Chemistry

Dry deposition = SO_2, O_3, CO_2, SO_3

- Micro biological sinks = CO, H_2
- fast soluble = HCl, HF, HNO_3
- Wet deposition, after arriving in aerosols = NH_3, SO_2, NO_x
- Inert (physical and chemical) = NO_x, Carbonyl, Sulfids (COS), CFCs
- all others = photochemical reactions with OH, or direct photolysis (O_3, NO_2, HCHO)
- near the surface: many turbulences, mixing (0.5-2 km during day and less during night)
- time scale:

Tropospheric Chemistry

days:	some compounds, atmospheric circulation, transport
Free troposphere:	transport over long distances near surface
Wind speed:	10-30 ms^{-1} in E-W direction, less in N-S and vertical direction (mid latitude)

Air masses are moving in circles along latitudes in 10s of days

Movings in N-S directions slower, transport between hemispheres not allowed, only during defined seasons (N →S in upper troposphere and S →N in lower troposphere (1 year)

E-W averaging (tropospheric mixing $\tau = 1$ month (2-dimensional model (height, latitude)

Tropospheric Chemistry

Many compounds:

- 1940: ~24 different chemical compounds were known
- 1950: known scientists begun the resarch on chemical and biological compounds of atmoshere, less than 100 compounds were known
- today: 3000 compounds are known
- some in atmospheric gases, aerosol particles, (small and big), in rain snow, fog, in reservoirs
- natural and anthropogenic sources, pre-industrial atmosphere
- more or less reactive compounds (CH_4 = 1.7-1.8 ppmv)
- 4 times more reactive are organic than inorganic compounds

Tropospheric Chemistry

Many compounds:

- organic: HC (solutions, industrial chemicals, combustion processes)
- reaction to oxidised products (moving faster than precursors)

Tropospheric Chemistry

- every element of periodic system is in atmosphere
- a small number of groups of compounds:
- **sulfur compounds**
- **nitrogen compounds**
- **HC compounds**
- **Halogen compounds**
- **with and without HC**

Emission of compounds which are removed →
cycles of elements (*bio geo chemical cycles: e.g. B.* H_2O)

Transport: within the atmosphere, ocean, biosphere, continent

- "Elements of life": C, O, N, S, P with reservoir substances, within the atmosphere, ocean, organism

Tropospheric Chemistry

- many source gases partiell oxidized (CO, SO_2) or reduced (H_2S, NH_3)
- in the troposphere they are not directly oxidized by O_2
- first reaction is with hydroxy radical **OH (**atmospheric cleaning substance)
- <u>example:</u>
- $CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O$
- Oxidation follows many reaction steps and produce redicals as function of photolysis (OH-concentration, other radicals and NO_x).

Tropospheric Chemistry

- OH is the most important radical in troposphere
- many tropospheric reactions start with OH (life time$_{OH}$ ~ 1 s, low concentration ~10^6 molec/cm^3)
- concentration variable dependent of: photolysis, O_3- and H_2O-concentration and other radicals

<u>Sources of OH:</u>

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

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

Tropospheric Chemistry

Photolysis of HCHO:

$$CH_2O + h\nu \rightarrow H + HCO$$

$$\rightarrow H_2 + CO$$

$$HCO + O_2 \rightarrow HO_2 + CO$$

$$H + O_2 + M \rightarrow HO_2 + M$$

under clean air situation no NO:

$$HO_2 + O_3 \rightarrow OH + 2O_2$$

$$HO_2 + NO \rightarrow OH + NO_2$$

2. Reaction of O_3 with alkenes
3. Reaction of NO_3 with aldehyds or alkens during night

Tropospheric Chemistry

- Sinks for OH:

1. Direct key reactions:

$HO_2 + HO_2 \rightarrow H_2O_2 + O_2$

$OH + HO_2 \rightarrow H_2O + O_2$

2. Formation of stabil peroxiyds

$CH_3O_2 + HO_2 \rightarrow CH_3OOH + O_2$

3. Reaction with NO_2 & HNO_3 in polluted areas

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

$OH + HNO_3 \rightarrow H_2O + NO_3$

Tropospheric Chemistry

A: Reaction with OH

· $SO_2 + OH \rightarrow OSOOH$

$CO + OH \rightarrow HOCO$

$CH_4 + OH \rightarrow CH_3 + H_2O$

$NH_3 + OH \rightarrow NH_2 + H_2O$

$H_2S + OH \rightarrow SH + H_2O$

$CH_3Cl + OH \rightarrow CH_2Cl + H_2O$

B: Photolysis

$HCHO + h\nu \rightarrow H + HCO$ ($\lambda < 338$ nm)

C: Reaction of radicals with O_2

$CH_3 + O_2 \rightarrow CH_3OO$

Tropospheric Chemistry

D: Reaction of Peroxy-Radicals with NO

$HOO + NO \rightarrow OH + NO_2$

$CH_3OO + NO \rightarrow CH_3O + NO_2$

E: Abstraction of H by O_2:

$CH_3O + O_2 \rightarrow CH_2O + HO_2$

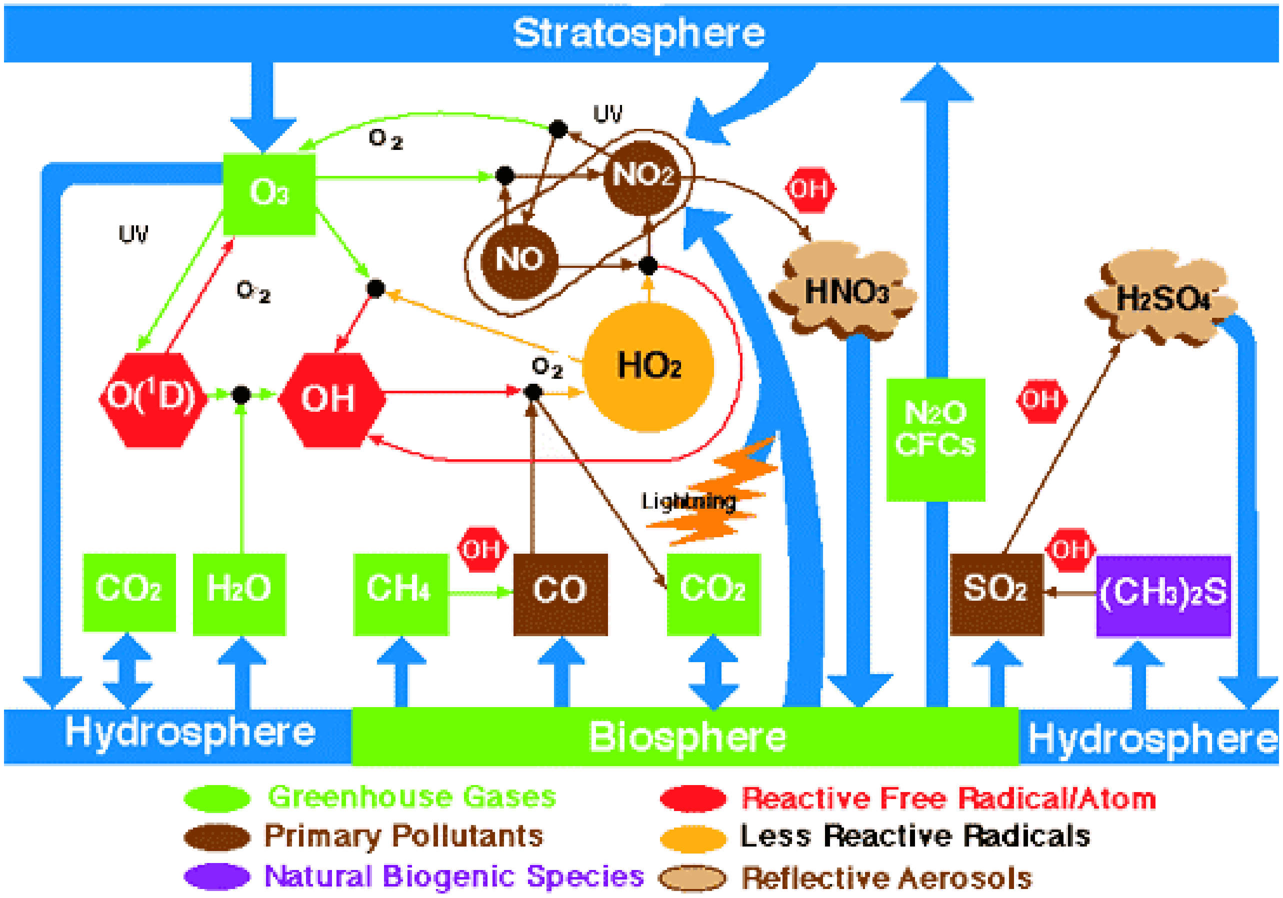
$HOCO + O_2 \rightarrow OCO + HO_2$

$HCO + O_2 \rightarrow CO + HO_2$

F: Addition von O_2:

$RCO + O_2 \rightarrow ROCOO$

Tropospheric Chemistry



Tropospheric Chemistry

$$NMHC + NO + h\nu \rightarrow NO_2 + \mathrm{Pr}\,odukte$$ R1

$$NO_2 + h\nu(\lambda \leq 410nm) \rightarrow NO + O$$ R2

$$O + O_2 + M \rightarrow O_3 + M$$ R3

$$NO + O_3 \rightarrow NO_2 + O_2$$ R4

equilibrium:

$$\frac{[NO_2]}{[NO]} = \frac{k_{R4}[O_3]}{j_{R2}}$$

Tropospheric Chemistry

$$O_3 + h\nu(\leq 310nm) \rightarrow O(^1D) + O_2$$

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

$$RH + OH \rightarrow R + H_2O$$

$$R + O_2 + M \rightarrow RO_2 + M$$

$$RO_2 + NO \rightarrow NO_2 + RO$$

Methan-Oxidation

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

wavelenght: < 310 nm

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

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

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

Regeneration of O_3

Oxidation steps:

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

$$OH + CH_4 \rightarrow CH_3 + H_2O$$

$$H + O_2 \rightarrow HO_2$$

$$CH_3 + O_2 \rightarrow CH_3O_2$$

Methan-Oxidation

$$CH_3O + O_2 \rightarrow HCHO + HO_2$$

$$HCHO + h\nu(\lambda \le 330nm) \rightarrow H + HCO$$

$$HCO + O_2 \rightarrow CO + HO_2$$

$$H + O_2 + M \rightarrow HO_2 + M$$

3[$H + O_2 + M \rightarrow HO_2 + M$]

4[$NO_2 + h\nu(\lambda \le 410nm) \rightarrow NO + O$]

3[$O + O_2 + M \rightarrow O_3 + M$]

Net: $CH_4 + 8O_2 + 5h\nu \rightarrow CO + 4O_3 + 2OH + H_2O$

CO-Oxidation

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

$$H + O_2 + M \rightarrow HO_2 + M$$

$$NO_2 + h\nu(\lambda \leq 410nm) \rightarrow NO + O$$

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

Net: $$CO + 2O_2 + h\nu \rightarrow CO_2 + O_3$$

Ozon-Production in Troposphere

high NO_x – production of O_3:

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

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

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

$$H + O_2 + M \rightarrow HO_2 + M$$

$$HO_2 + NO \rightarrow OH + NO_2$$

Netto:

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

Ozon-Destruktion in der Troposphäre

low NO_x – destruction of O_3:

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

$$H + O_2 + M \rightarrow HO_2 + M$$

$$HO_2 + O_3 \rightarrow OH + 2O_2$$

Netto: $$CO + O_3 \rightarrow CO_2 + O_2$$

Methan-Oxidation

Production of peroxy radicals:

$$H + O_2 + M \rightarrow HO_2 + M$$

$$CH_3 + O_2 + M \rightarrow CH_3O_2 + M$$

low NO_x – production of acids:

$$HO_2 + HO_2 \rightarrow H_2O_2 + O_2$$

$$CH_3O_2 + HO_2 \rightarrow CH_3OOH + O_2$$

high NO_x – production of NO_2:

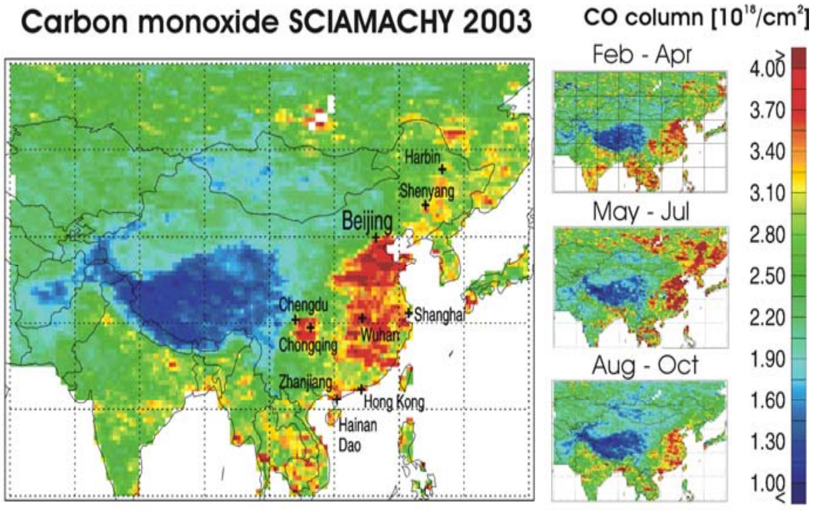
Regeneration of OH:

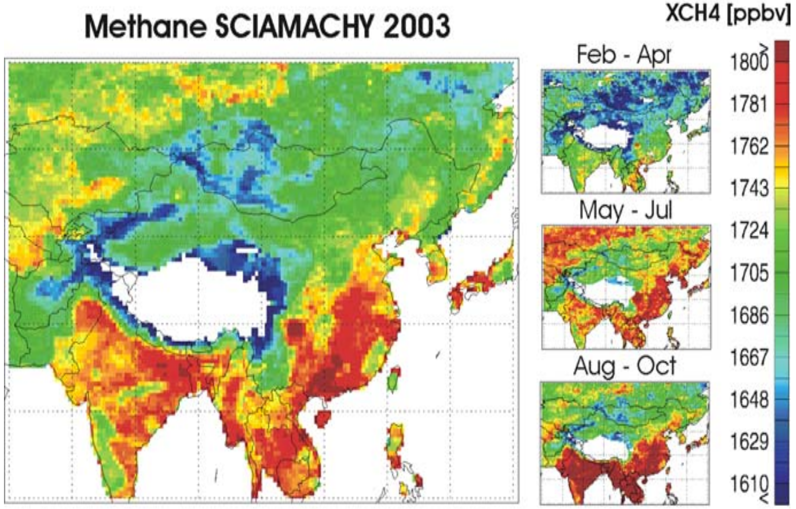
$$HO_2 + NO \rightarrow OH + NO_2$$

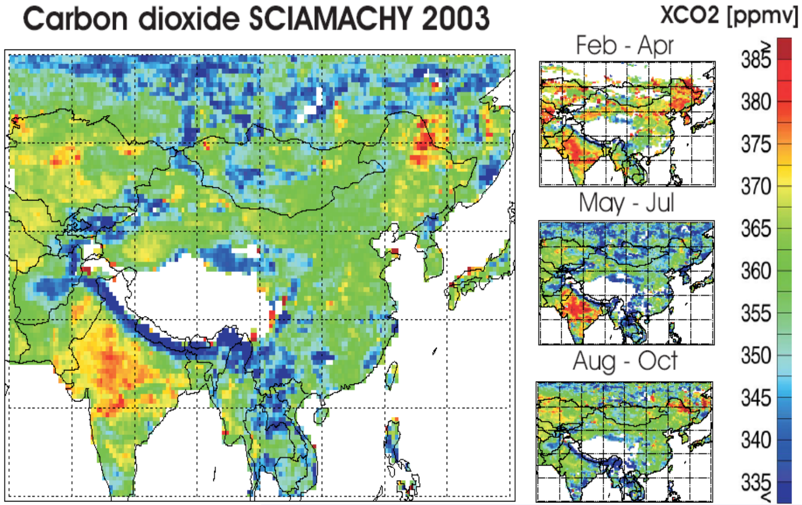
Or production of Methoxy-Radical:

$$CH_3O_2 + NO \rightarrow CH_3O + NO_2$$

CO, CO_2, und CH_4 Messungen von SCIAMACHY



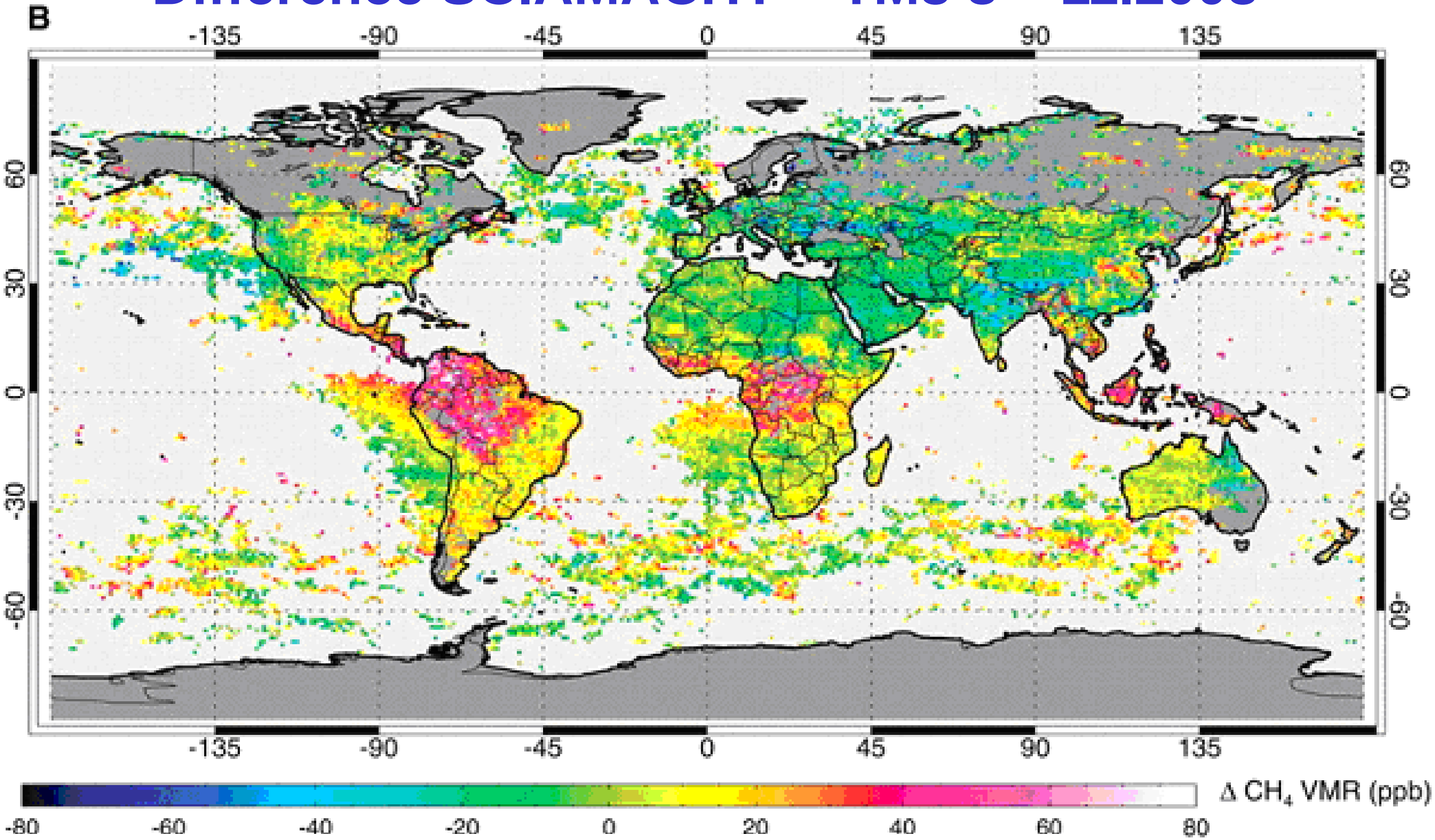




Buchwitz et al., de Beek et al., ACPD, 2005, ACPD 2006

CH_4 Messungen von SCIAMACHY

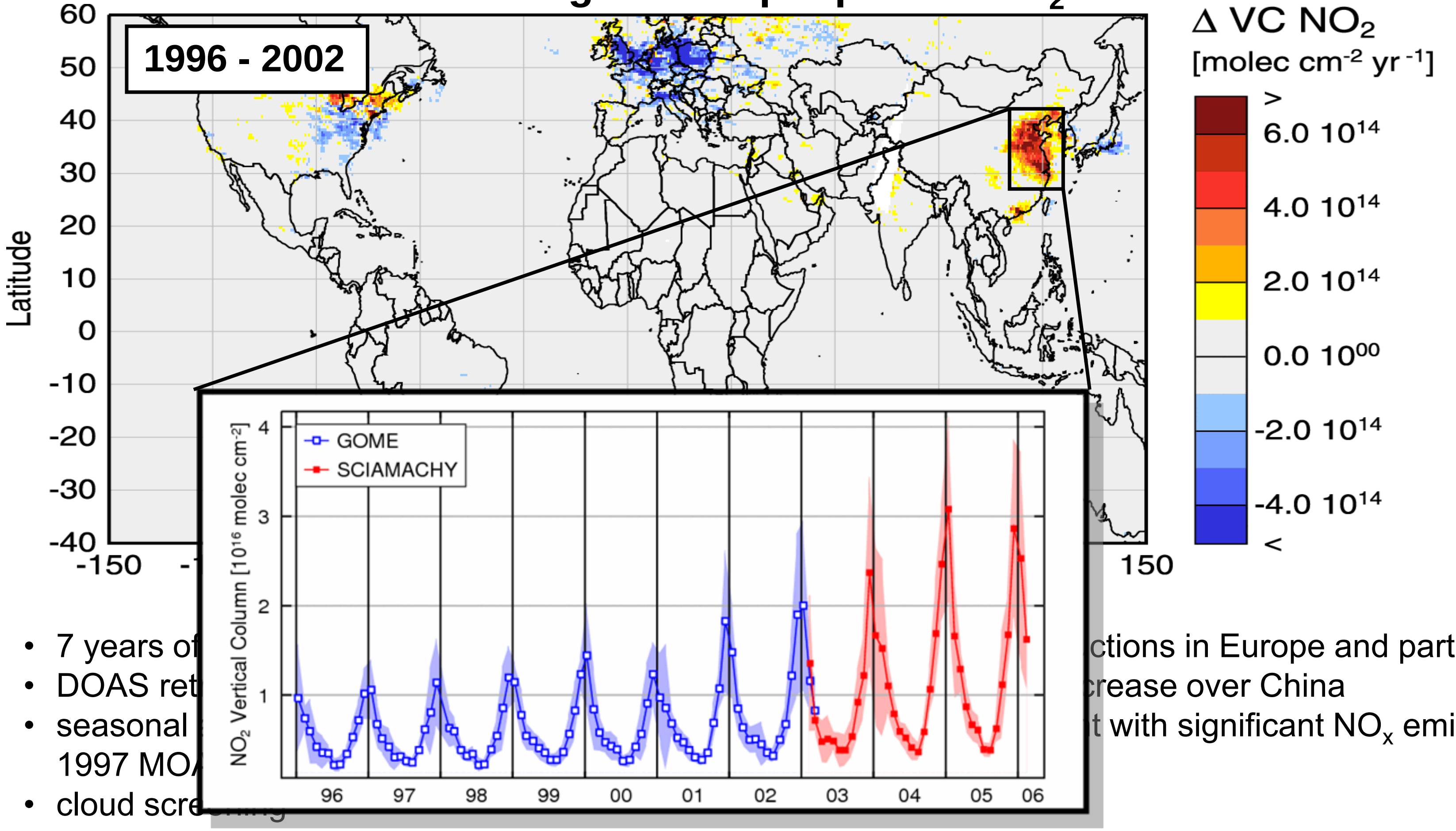
Difference SCIAMACHY – TM3 8 – 11.2003



Frankenberg, C.,et al., Assessing methane emissions from global space-borne observations. *Science*, **308** (2005), 1010-1014.

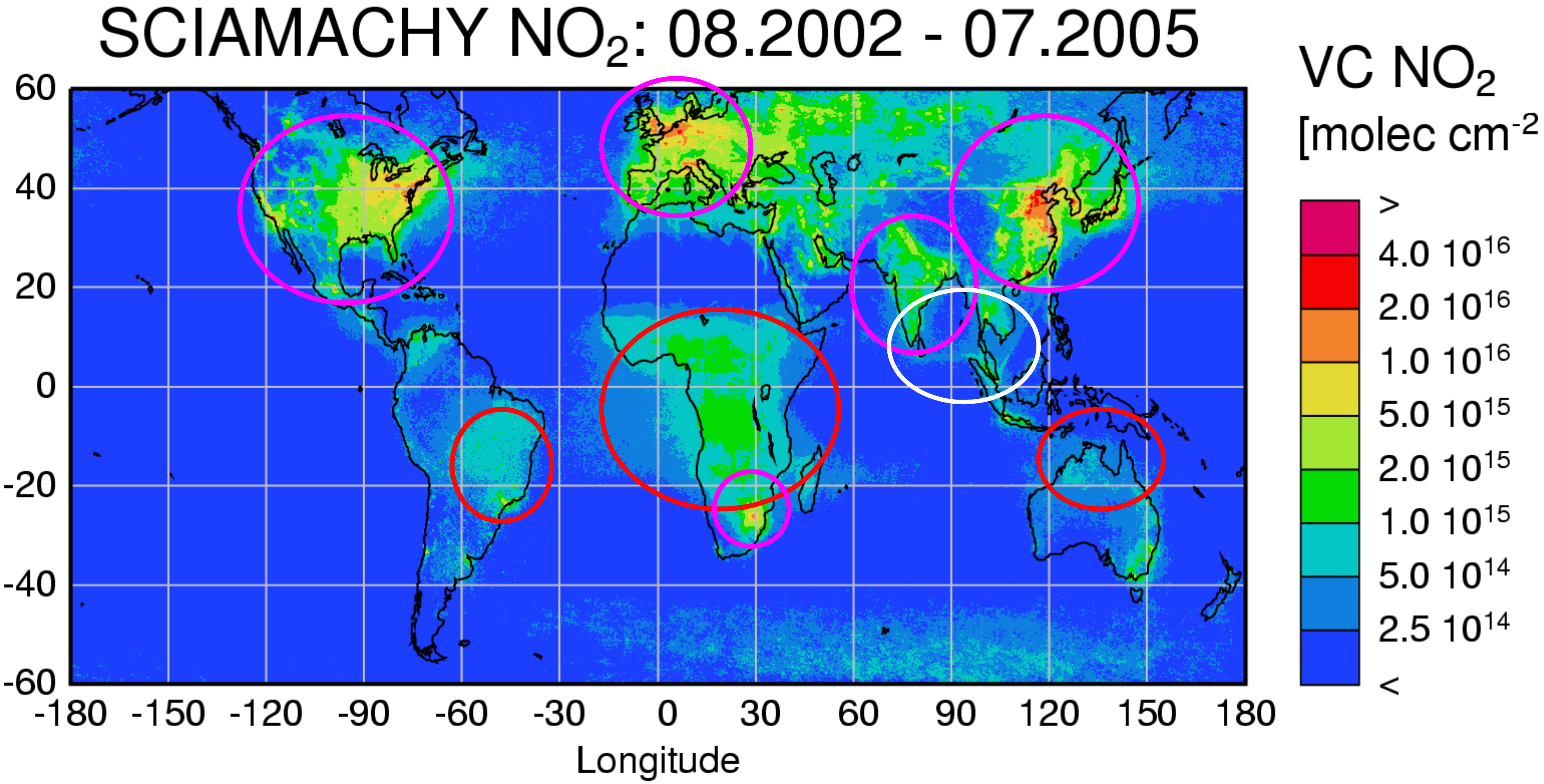
© C. Frankenberg et al., Univ. of Heidelberg

GOME annual changes in tropospheric NO_2



- 7 years of … ctions in Europe and parts of the US
- DOAS ret … crease over China
- seasonal … t with significant NO_x emission
  1997 MO…
- cloud scre…

A. Richter et al., Increase in tropospheric nitrogen dioxide over China observed from space, *Nature*, **437** 2005

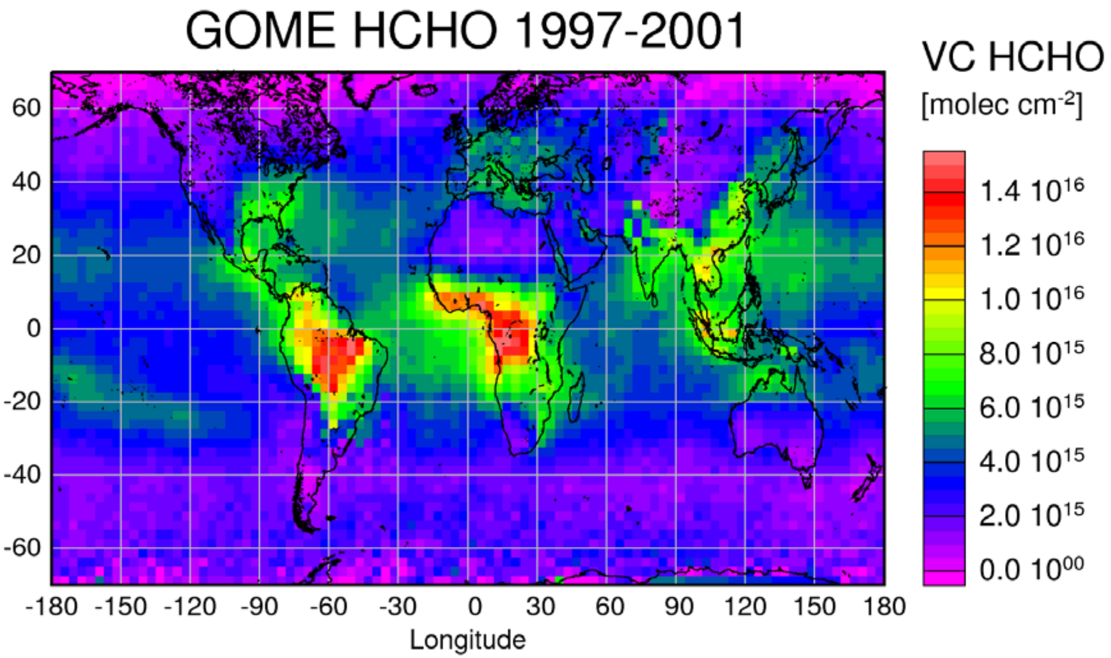


pollution

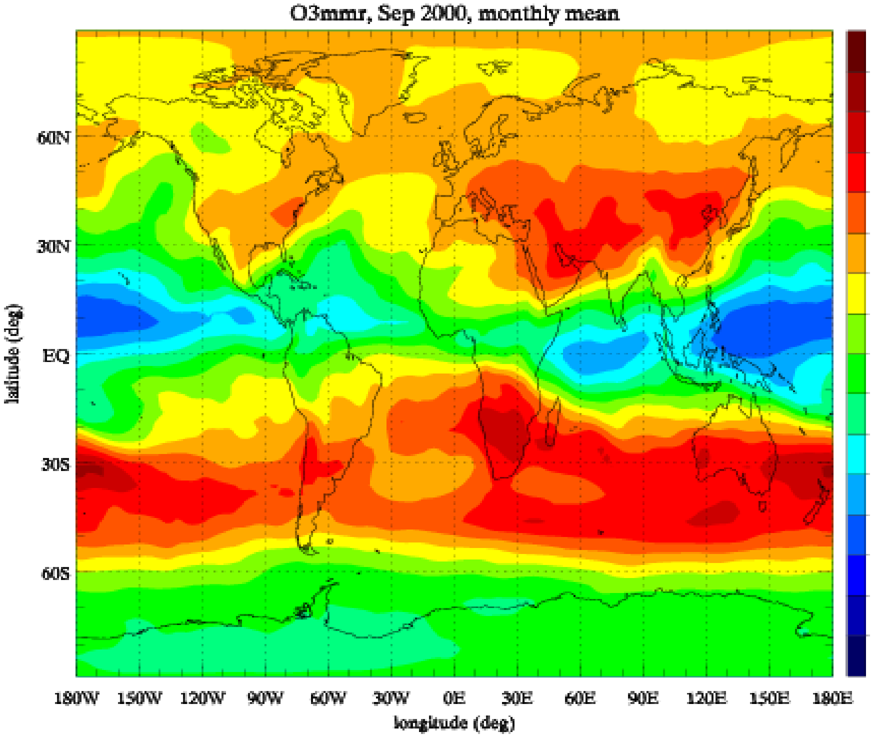
biomass burning

Courtesy of Andreas Richter

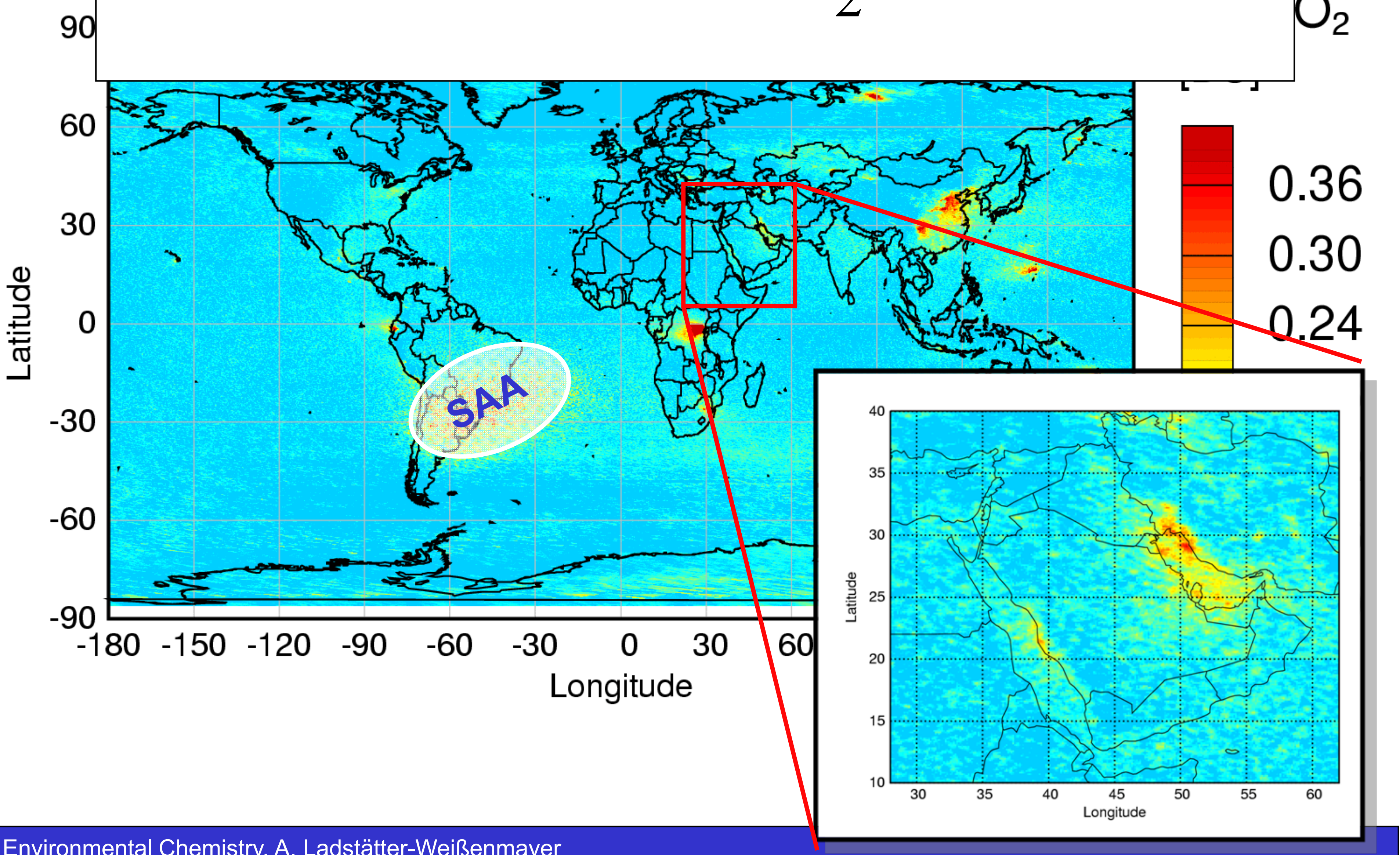
HCHO Messungen von GOME



Troposphärische O_3 Messungen von GOME



SCIAMACHY SO_2:Pollution



Anorganic Chemistry

$$HSO_3^- + H_2O_2 \rightarrow HSO_4^- + H_2O$$

$$HSO_3^- + O_3 \rightarrow HSO_4^- + O_2$$

$$H_2SO_4 \leftrightarrow H^+ + HSO_4^-$$

$$HSO_4^- \leftrightarrow H^+ + SO_4^{2-}$$

$$HNO_3 \leftrightarrow H^+ + NO_3^-$$

Photochemistry – Organic Chemistry

$$H_2O_2 + h\nu(\lambda \leq 380nm) \rightarrow 2OH$$

$$RCHO_{(aq)} + OH \rightarrow RC(O)OH_{(aq)}$$

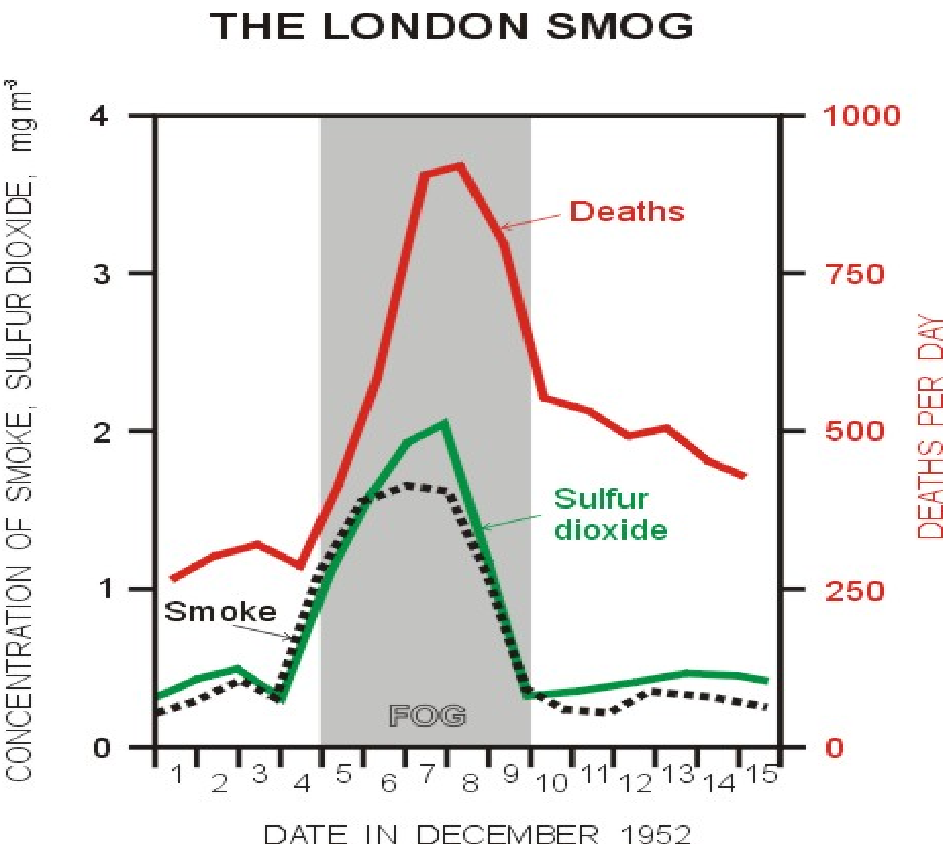
$$RC(O)OH \leftrightarrow H^+ + RC(O)O^-$$

Air pollution

- compounds caused by antropogenic activities
- concentrations high above normal
- → human influence, animals, veetation and material
- mainly: in urban and industrialised regions
- 1. Typ: (SO_2 and Sulfate), particles from combustion
- cold regions: heating – Emissions
- 2. Gas and Benzene (Los Angeles, Tokyo, Athens, Mexico City, Sao Paulo, Brazil)

Air pollution

1952: London view less than some m for 1 week



Air pollution

- Smog (photochemical Smog)

  Smog: NO_x, organic compounds, O_3 (nitrats, oxidised HC, photochemical aerosols)

- O_3 normal: 20-60 ppb
- O_3 urban: 500 ppb
- Natural and anthropogenic processes (started mainly with OH)
- High reactivity → Oxidation and chemische reaction
- Free Radicals - chain reactions: Oxidation of H_2, CH_4, other HC, CO to CO_2 and H_2O

other gases like NO_x and sulfur compouds modify the „way of combustion process“

Air pollution

surface as source of compounds

- NO_x and CO produced in sand storm
- surface emission: natural and anthropogenic sources
- High concentration in urban and industrial regions (NH)
- Stratospheric O_3 limits sun radiation at surface → wavelenght > 280 nm
- Photochemical labill > 280 nm: O_3, NO_2, HCHO
- All 3 gases (O_3, NO_2, HCHO) → OH (oder HO_2 production) → start of oxidation chain

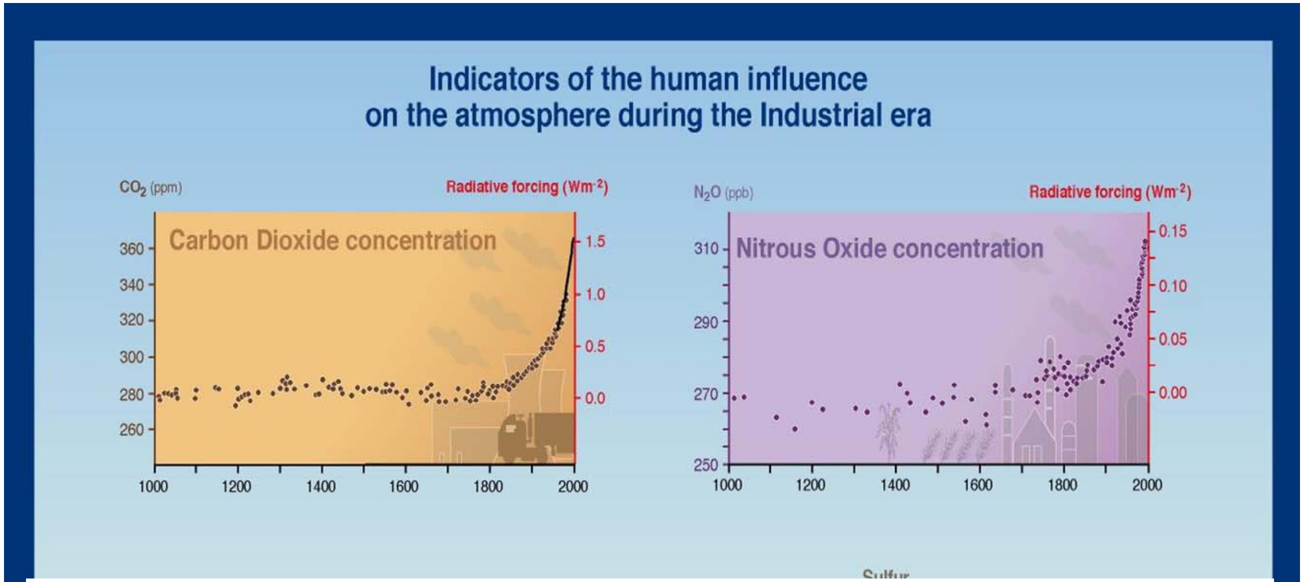
Air pollution

- 10% of total O_3 in troposphere
- natural atmosphere: all reactions start with O_3
- Source of O_3 is important
- O_3 formation in low altitude (dependent of hydrocarbons and NO_x)
- O_3 Transport (Stratospheric – Tropospheric - Exchange)

Air pollution

- OH influence during day (stratosphere and troposphere)
- NO_3 influence during night
- NO_3 less reactiv than OH
- diurnal variation different (OH and NO_3)
- OH photolysed (during day)
- NO_3 photolysed during day (present during night)
- 90% of total atmospheric mass stays in troposphere (main part of gases of combustion processes)

Greenhouse gases

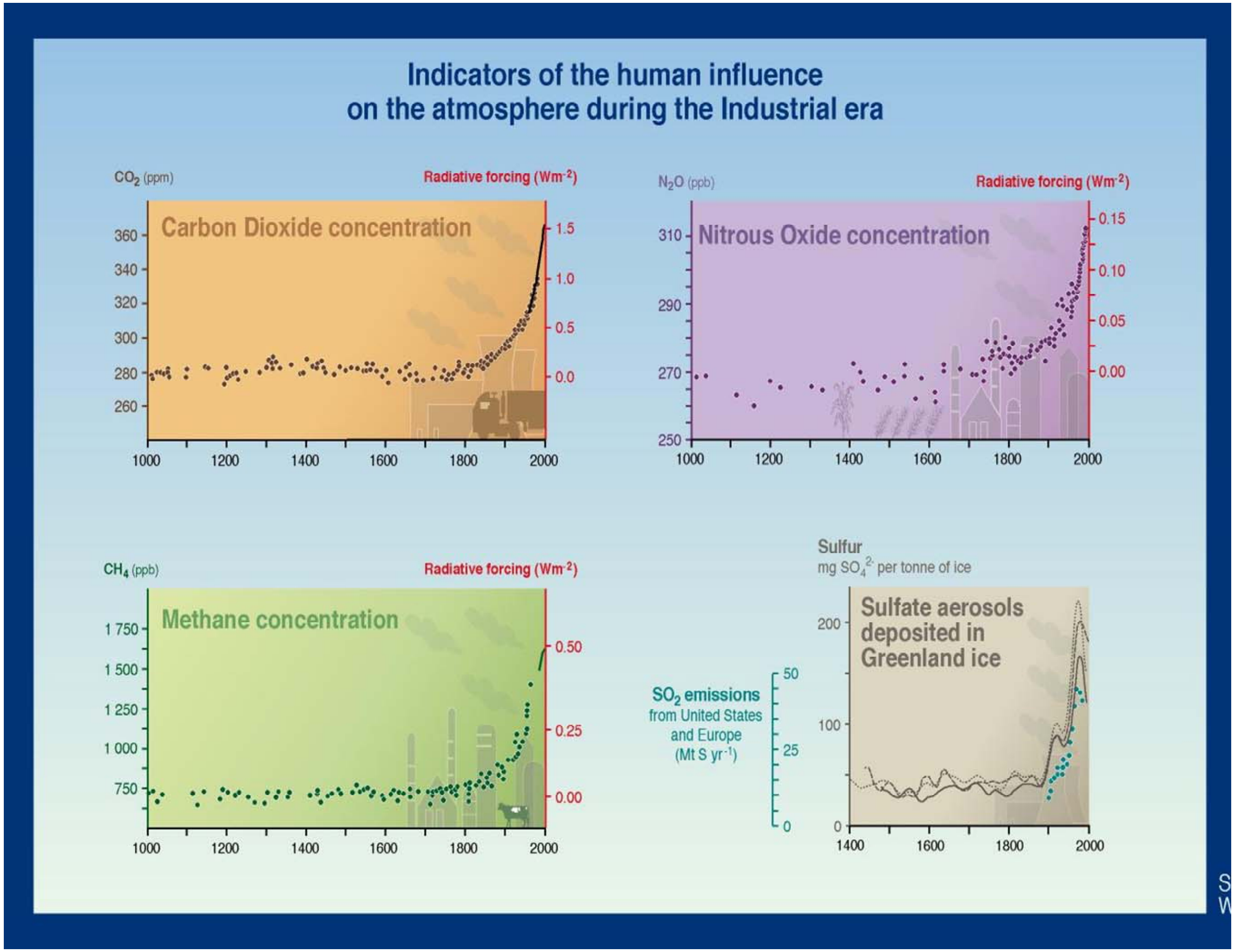


- 1750-2005: increase of CO_2~ 35%
- increase of CO_2 the last 10 years > than the last 50 years
- today: Maximum in the last 650.000 Jahren

- ➢ 78% of increase (← use of fossil fuel)
- ➢ 22% of increase (← land use)

IPCC 2007

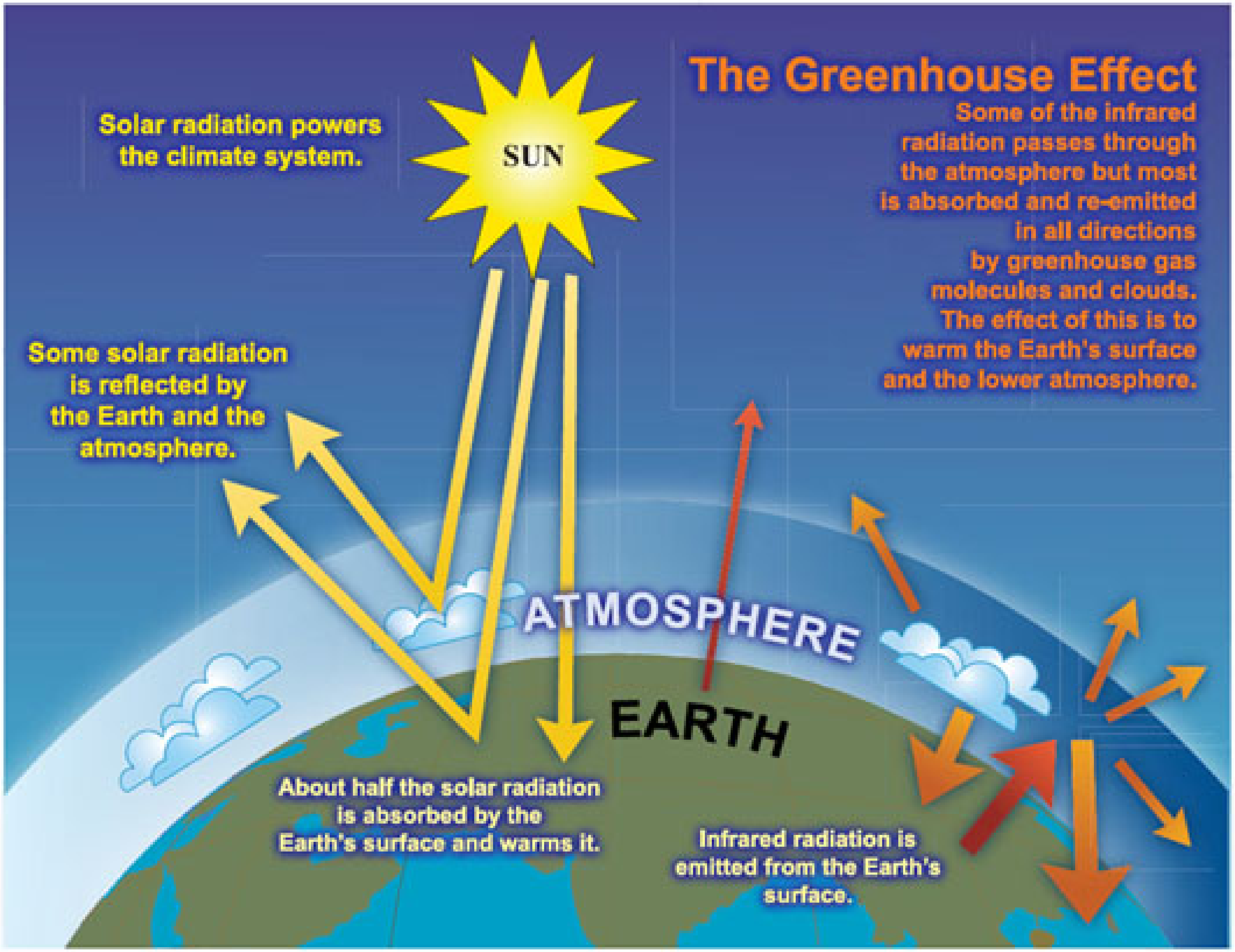
Greenhouse gases



IPCC 2007

- since 1750: CH_4- and N_2O- increase ~148% respectively ~ 18 %

Greenhouse gases



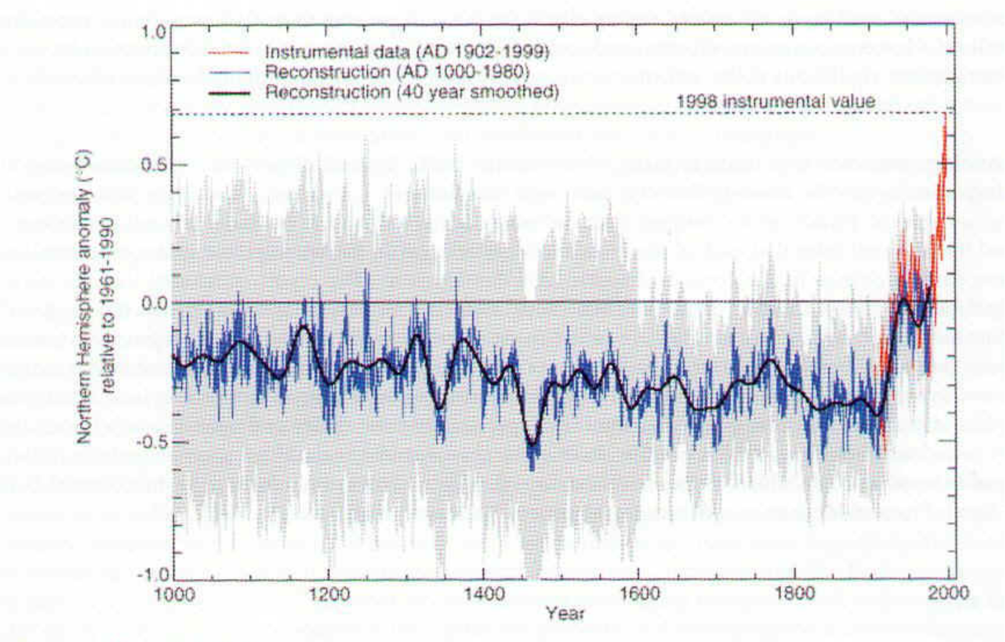
Greenhouse gases

- GHG: H_2O, H_2, CO_2, O_3, N_2O, CH_4.
- important for climate change caused by physical and chemical features
- GHG are gases in an atmosphere that absorb and emit radiation within the thermal infrared range. This process is the fundamental cause of the greenhouse effekt
- GHG warm the atmosphere by efficiently absorbing thermal infrared radiation emitted by the Earth‘s surface, by the atmosphere itself, and by clouds. As a result of its warmth, the atmosphere also radiates thermal infrared in all directions, including downward to the Earth’s surface. Thus, greenhouse gases trap heat within the surface-troposphere system.

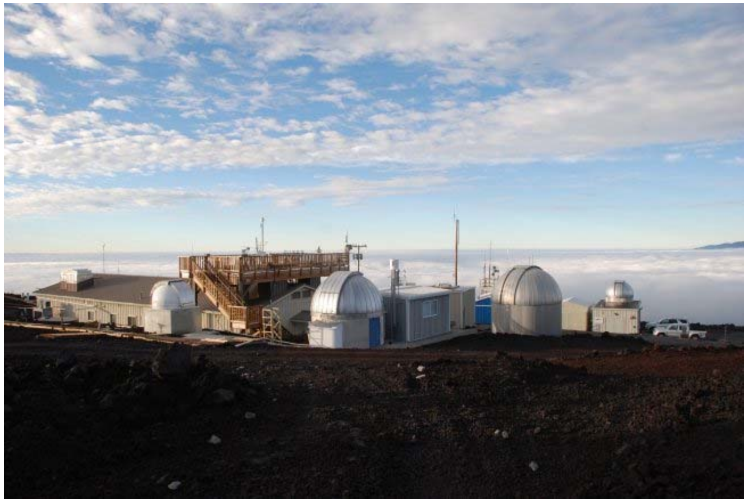
Greenhouse gases

- in addition anthropogenic synthetic gases (halogen compounds) are emitted → climte change
- the measured value: „Global Warming Potential“ (efficiency of a gas over 100 years is observed, fficiency of CH_4 is 21 time higher than CO_2)
- if the concentration of emitted gases is known → Global Warming Potential can be calculated
- More GHG more climate change

Tropospheric Chemistry



Source: Mann et al. 1999.



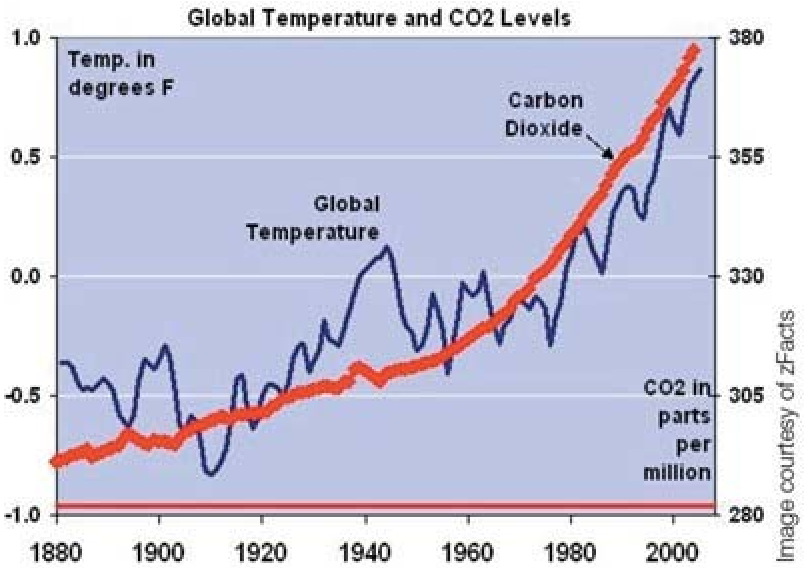


Image courtesy of zFacts