Lecture Atmospheric Chemistry

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Contents:

Literature for the lecture

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

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

Colin Baird, Environmental Chemistry, Freeman and Company, New York, 1995

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

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

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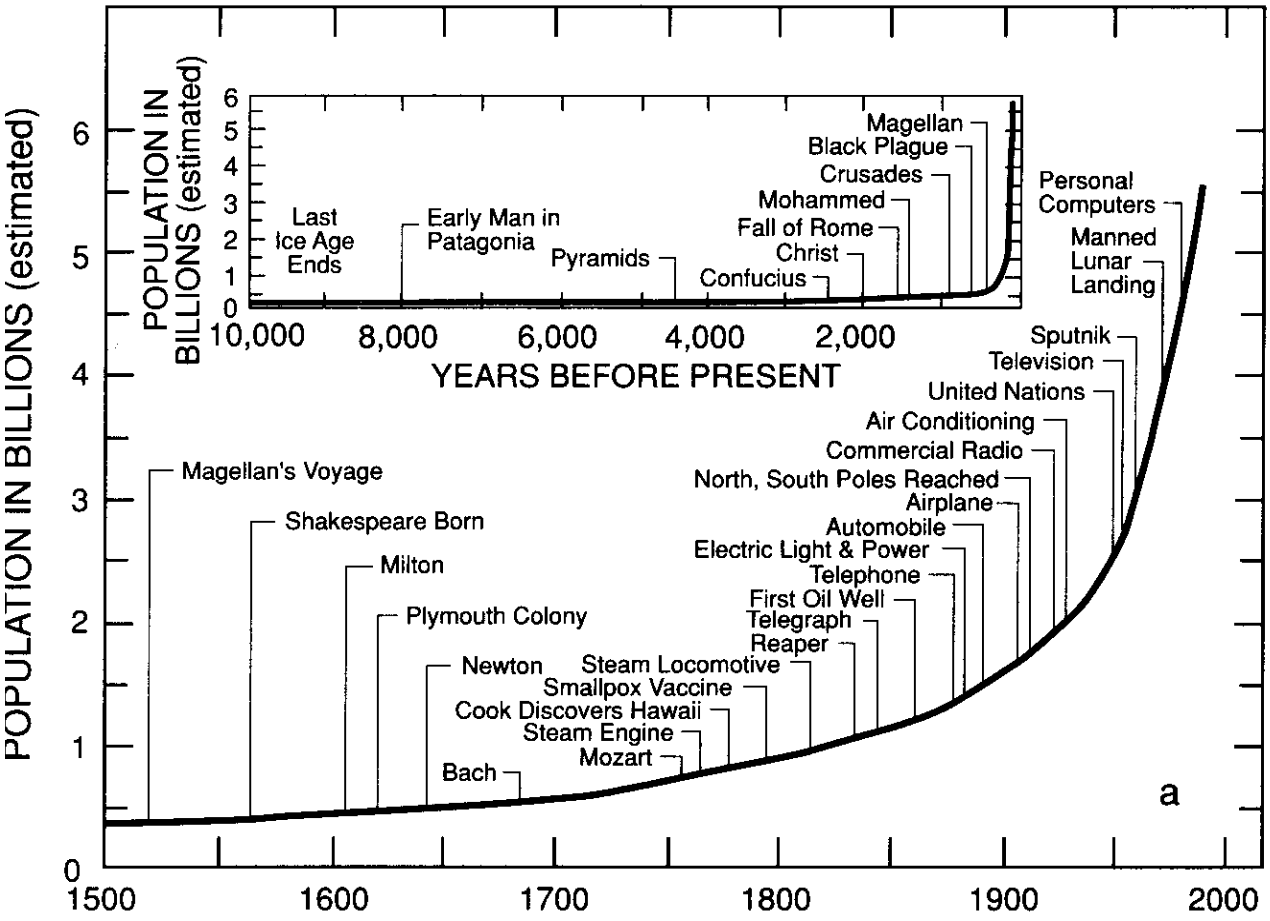
Why should we care about Atmospheric Chemistry?



- population is growing
- emissions are growing
- changes are accelerating

Why should we care about Atmospheric Chemistry?

- scientific interest
- atmosphere is created / needed by life on earth
- humans breath air
- humans change the atmosphere by
  - air pollution
  - changes in land use
  - tropospheric oxidants
  - acid rain
  - climate changes
  - ozone depletion
  - ...
- atmospheric chemistry has an impact on atmospheric dynamics, meteorology, climate

The aim is

1. to understand the past and current atmospheric constitution
2. to predict future atmospheric constitution
3. to provide input for political decisions affecting atmospheric constitution

What are the Questions in Atmospheric Chemistry?

- which species are relevant for the atmosphere?
- what are the concentrations / mixing ratios for these species at different locations, altitudes and times?
- which reactions are in principle possible between the atmospheric constituents?
- how fast do these reactions proceed?
- what are the dependencies on pressure and temperature?
- what is the impact of sun light on these reactions?

- what are the life times of species in the atmosphere?
- what are the sources and sinks of the species
- what impact have human activities?

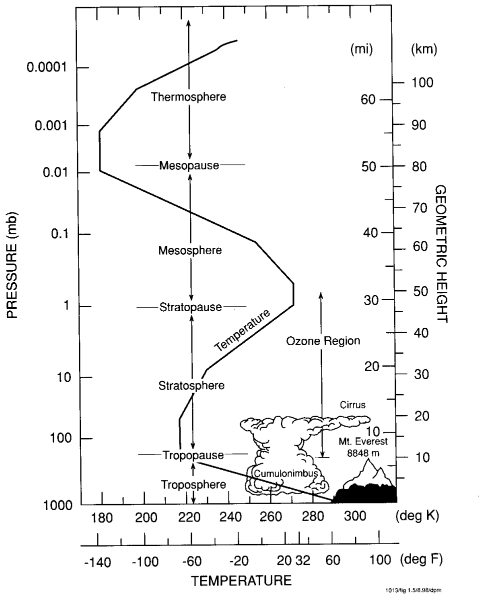
What is Special about Atmospheric Chemistry?

- temperature range -80°C ... +30°C
- pressure range 0...1000 mbar
- mixture of many reactive species
- energy input from the sun
- day - night changes
- large inhomogeneities in time and space
- system is not in equilibrium
- impact of transport
- impact of biology
- impact of sources and sinks
- impact of ocean
- impact of human activities

Vertical Structure of the Atmosphere

Atmospheric Chemistry and Global Change 7

Figure 1.5. *Vertical profile of the temperature between the surface and 100 km altitude as as defined in the U.S. Standard Atmosphere (1976) and related atmosphere layers. Note that the tropopause level is represented for midlatitude conditions. Cumulonimbus clouds in the tropics extend to the tropical tropopause located near 18 km altitude.*



Reasons for the temperature profile:

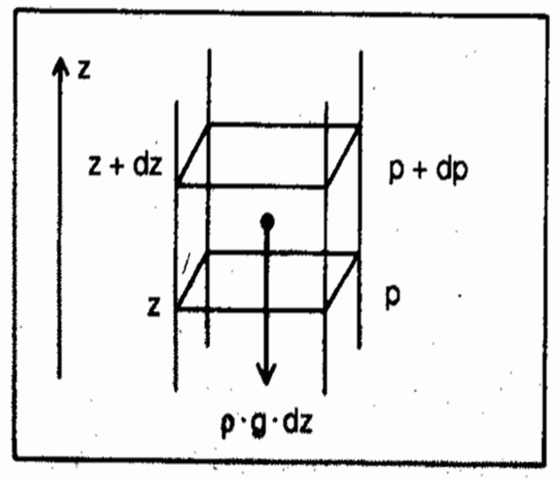
- adiabatic vertical transport
- radiative cooling by water vapour
- absorption in the ozone layer
- oxygen absorption in the thermosphere

Consequences of the temperature profile:

- strong mixing in the troposphere
- low vertical mixing in the stratosphere
- very low humidity in the stratosphere (tropopause acts as a cooling trap)

Barometric Equation

$$dp = -\rho \cdot g \cdot dz$$



Ideal gas (1 mol)

$$p \cdot V = R \cdot T$$

Definition of density:

$$\rho = \frac{M}{V} = \frac{M \cdot p}{R \cdot T}$$

Insert:

$$dp = -p \cdot \frac{M \cdot g}{R \cdot T} \cdot dz$$

Integrate:

$$p = p_0 \exp\left(-\frac{M \cdot g}{R \cdot T} \cdot z \right)$$

p = pressure M = molar mass, g = gravitational acceleration,
R = universal gas constant, T = temperature, z = height,
V = volume, ρ = density

Layers in the Atmosphere

Troposphere	Stratosphere
unstable, vertical mixing	stable, stratified
high pressure	low pressure
warm	cold
moist	dry
clouds	clouds only under special conditions
rain, ice, phase changes	
little UV radiation	lots of UV radiation
large biological impact	
large aerosol load	high aerosol load only after volcanic eruptions
many surfaces	few surfaces
deposition as sink	sedimentation as sink
OH, NH_3, O_3, NO_2	O, O_3, NO_2

Composition of the Atmosphere I

- N_2 (78.09%) and O_2 (20.95%)
- noble gases
- water: all three phases (solid,, liquid, gaseous), very variable (0..2%), strong absorption, relevant for climate, clouds, rain, aerosols and chemistry
- trace species: relevant for chemistry, climate and aerosols, e.g.
    - CFC
    - halogen oxides
    - ozone
    - halo carbons
    - nitrogen oxides
    - sulphur compounds

Composition of the Atmosphere II

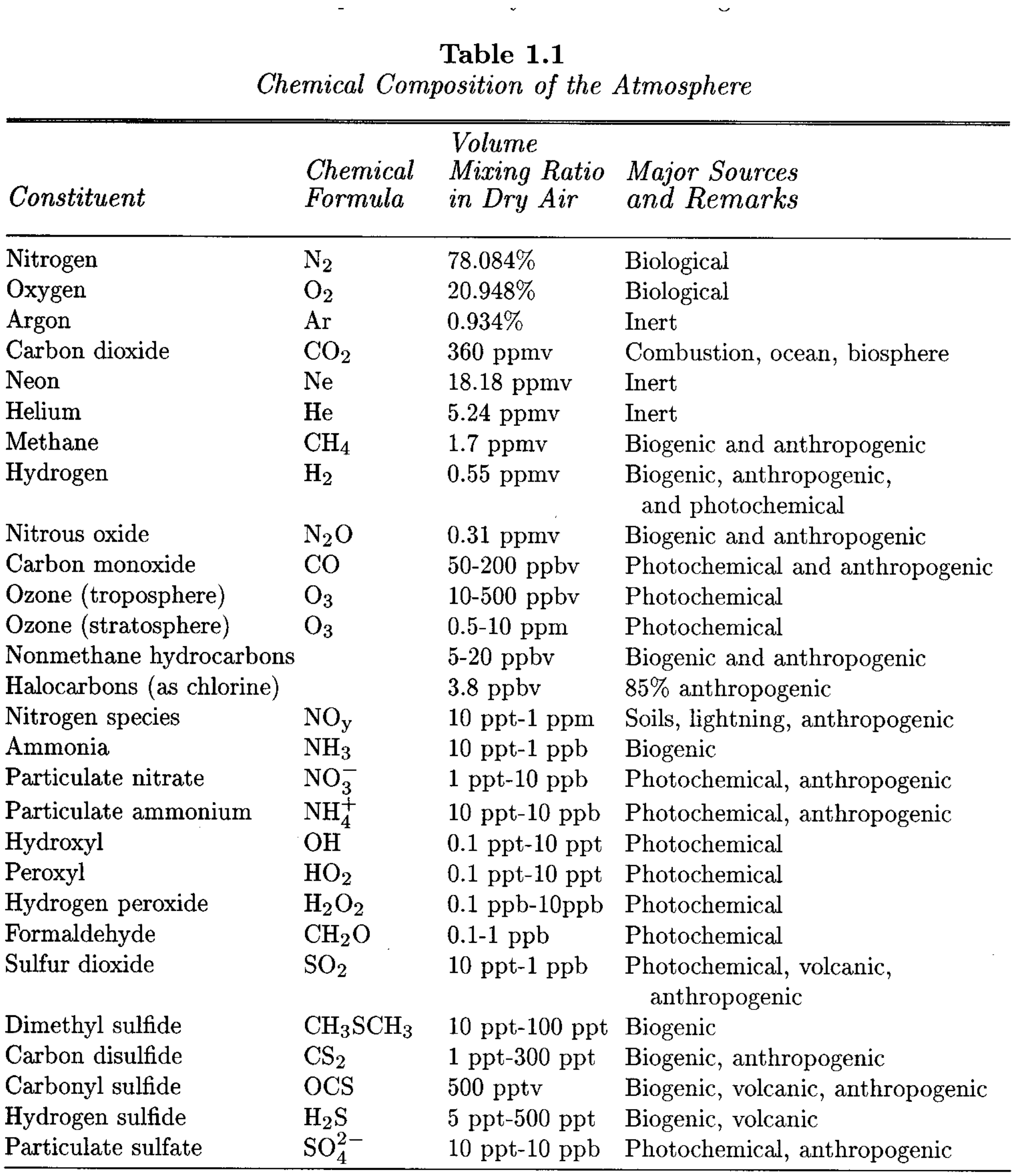


Table 1.1
Chemical Composition of the Atmosphere

Constituent	*Chemical Formula*	*Volume Mixing Ratio in Dry Air*	*Major Sources and Remarks*
Nitrogen	N_2	78.084%	Biological
Oxygen	O_2	20.948%	Biological
Argon	Ar	0.934%	Inert
Carbon dioxide	CO_2	360 ppmv	Combustion, ocean, biosphere
Neon	Ne	18.18 ppmv	Inert
Helium	He	5.24 ppmv	Inert
Methane	CH_4	1.7 ppmv	Biogenic and anthropogenic
Hydrogen	H_2	0.55 ppmv	Biogenic, anthropogenic, and photochemical
Nitrous oxide	N_2O	0.31 ppmv	Biogenic and anthropogenic
Carbon monoxide	CO	50-200 ppbv	Photochemical and anthropogenic
Ozone (troposphere)	O_3	10-500 ppbv	Photochemical
Ozone (stratosphere)	O_3	0.5-10 ppm	Photochemical
Nonmethane hydrocarbons		5-20 ppbv	Biogenic and anthropogenic
Halocarbons (as chlorine)		3.8 ppbv	85% anthropogenic
Nitrogen species	NO_y	10 ppt-1 ppm	Soils, lightning, anthropogenic
Ammonia	NH_3	10 ppt-1 ppb	Biogenic
Particulate nitrate	NO_3^-	1 ppt-10 ppb	Photochemical, anthropogenic
Particulate ammonium	NH_4^+	10 ppt-10 ppb	Photochemical, anthropogenic
Hydroxyl	OH	0.1 ppt-10 ppt	Photochemical
Peroxyl	HO_2	0.1 ppt-10 ppt	Photochemical
Hydrogen peroxide	H_2O_2	0.1 ppb-10ppb	Photochemical
Formaldehyde	CH_2O	0.1-1 ppb	Photochemical
Sulfur dioxide	SO_2	10 ppt-1 ppb	Photochemical, volcanic, anthropogenic
Dimethyl sulfide	CH_3SCH_3	10 ppt-100 ppt	Biogenic
Carbon disulfide	CS_2	1 ppt-300 ppt	Biogenic, anthropogenic
Carbonyl sulfide	OCS	500 pptv	Biogenic, volcanic, anthropogenic
Hydrogen sulfide	H_2S	5 ppt-500 ppt	Biogenic, volcanic
Particulate sulfate	SO_4^{2-}	10 ppt-10 ppb	Photochemical, anthropogenic

Abundance Units in Atmospheric Chemistry

quantity	name	units
number of molecules	N	mol = 6.022×10^{23}
number density	n	particles / m^3
mass density	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}
column abundance		molec/cm^2 DU = 10^{-3} cm at STP

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:

$$pV = nRT \quad \text{or} \quad pV = NkT$$

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

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)

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

$$p = p_A + p_B$$

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:

$$x_X = \frac{n_X}{n} \text{ with } n = n_A + n_B + n_C + ...$$

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:

$$p_x = x_X p$$

Real Gases

- molecules interact which each other
- at large distances, the interactions can be neglected (=> ideal gas)
- at intermediate distances, the forces are attractive
- at small distances, the forces are repulsive

van der Waals equation of state for a real gas

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

nb = volume taken by the molecules,
a = gas specific constant for intermolecular forces

Virial equation of state for a real gas

$$pV = nRT(1 + Bp + Cp^2 + ...)$$

B, C, D, ... virial coefficients

Real gases show

- deviation from the ideal gas laws
- condensation, sublimation

State Functions: Examples

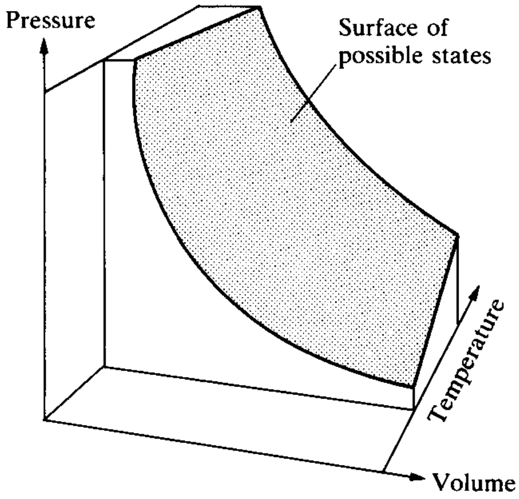


Fig. 1.4 A region of the p, V, T surface of a fixed amount of perfect gas. The points forming the surface represent the only states of the gas that can exist.

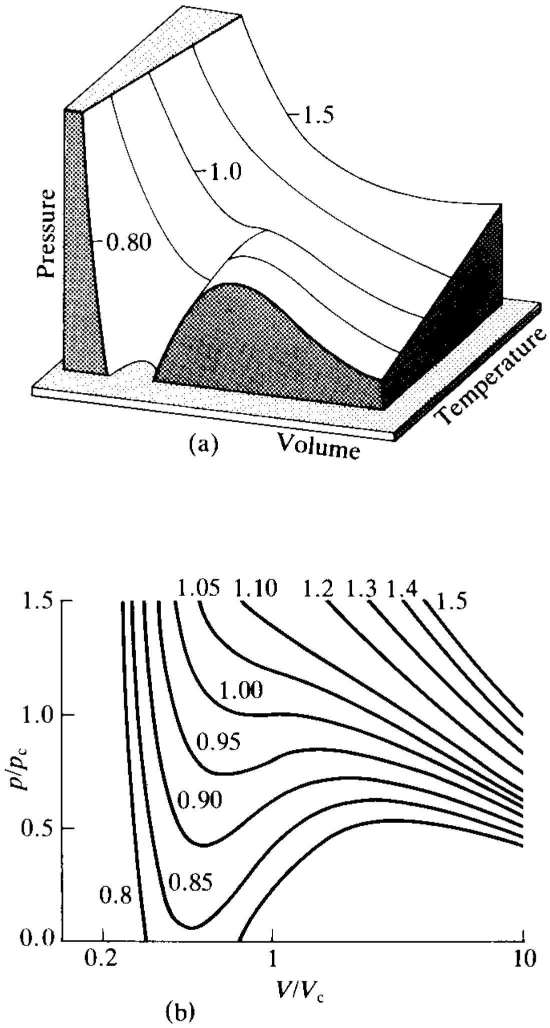


Fig. 1.10 The van der Waals isotherms at several values of T/T_c. (a) The shape of the surface (compare it with the perfect gas surface in Fig. 1.4). (b) A selection of individual isotherms. The van der Waals 'loops' are normally replaced by horizontal straight lines. The critical isotherm is the one at $T/T_c = 1$.

Work, Heat and Energy

A **system** is a part of the world in which we have a special interest, such as a reaction vessel or an air parcel.

The energy of a system can be changed by doing (mechanical) **work** on it like changing the volume by a piston or heating it by electrical current.

The energy of a system can also be changed by transferring **heat** as a result of a temperature difference between system and surroundings.

An change in state of the system that is performed without heat being transferred is called **adiabatic**.

A process that releases energy is **exothermic**, a process that absorbs energy is called **endothermic**.

By convention, energy supplied to a system is written positive, energy that has left the system is negative.

Energy and Enthalpy

The **Internal Energy U** is the total energy of a system.
A change in internal energy of a system is the sum of the changes of energy through work dw and heat dq:

$$dU = dq + dw = TdS - pdV$$

For a system with constant volume, no mechanical work is performed and the change in internal energy equals the transferred heat:

$$dU = dq\big|_V$$

The **Enthalpy** of a system is defined as

$$H = U + pV.$$

At constant pressure, a change in enthalpy equals the transferred heat:

$$dH = dq\big|_p$$

Entropy

The internal energy U is a state function that lets us assess if a process is permissible, the **Entropy** S is a state function that tells us, which processes proceed spontaneously.

The **statistical definition of Entropy** S is

$$S = k \ln W$$

where k is Boltzmann's constant and W the number of possible states of the system giving the same energy.

The **thermodynamic definition of an Entropy** change dS is

$$dS = \frac{dq}{T}$$

where dq is the transfer of heat taking place at temperature T.

Both definitions are identical.
In general, only processes can occur that lead to an overall increase in entropy in system and surroundings.

Gibbs Free Energy

The **Gibbs Free Energy** of a system is defined as

$$G = H - TS$$

Where S is the Entropy. At constant temperature and pressure, spontaneous changes of a system occur only if changes of G are <= 0.

$$\Delta G \leq 0$$

Most spontaneous reactions are exothermic, but a large increase in entropy can sometimes overcome a decrease in Enthalpy, in particular at high temperature.

In the atmosphere, most reactions take place at constant T and p as the surrounding atmosphere acts as an effective “bath”.

Enthalpy of Formation

The **standard reaction enthalpy** ΔH^0 is the change in enthalpy when the reactants in their standard states (p_0, T_0) change to products in their standard states. The standard pressure is 1 bar, the standard temperature usually 298.15K.

The **standard enthalpy of formation** ΔH_f^0 is the standard reaction enthalpy for the formation of a compound from its elements in their reference states. By convention, the standard enthalpy of elements in their reference states is 0. Standard enthalpies of formation are tabulated.

Example:

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

$$\Delta H_R^0 = \Delta H_f^0(C) + \Delta H_f^0(D) - \Delta H_f^0(A) - \Delta H_f^0(B)$$

Hess's law: The overall reaction enthalpy is the sum of the reaction enthalpies of the individual reactions into which a reaction might be divided.

Use of Reaction Enthalpy

From the reaction enthalpy, it can be decided if a reaction is exothermic or endothermic, and thereby if a reaction can proceed without external energy supply:

$\Delta H_R^0 > 0$ exothermic

$\Delta H_R^0 < 0$ endothermic

From the free energy of reaction, that is defined in analogy to the reaction enthalpy based on the free energy of formation $\Delta G^0 = \Delta H^0 - T\Delta S^0$, it can be decided if a reaction can occur spontaneously:

$\Delta G_R^0 < 0$ reaction can proceed spontaneously

In summary, the reaction enthalpy and free energy of reaction can be used to evaluate the feasibility of reactions and the heat budget from exothermic reactions in the atmosphere.

Heat Capacities

The **heat capacity** C of a system is the amount of heat q needed to change the temperature T of a system: $dq = CdT$.

The heat capacity of a system depends on the conditions:

The **heat capacity at constant volume** C_V is related to the change in internal energy U:

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

The **heat capacity at constant pressure** C_p is related to the change in enthalpy H:

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

At constant pressure, work is performed by the system during heating, and therefore

$$C_P > C_V$$

For an ideal gas, $C_p - C_v = R$

Temperature dependence of Reaction Enthalpy

In principle, reaction enthalpies depend on temperature, and therefore are tabulated as a function of temperature. As a first guess, the temperature dependence can be estimated as

$$\Delta H^0(T_2) = \Delta H^0(T_1) + \int_{T_1}^{T_2} \Delta C_p dT$$

However, under atmospheric conditions, the temperature dependence of the reaction enthalpy is small and can be neglected.

Laws of Thermodynamics:

0th law: If A is in thermal equilibrium with B, and B is in thermal equilibrium with C, then C is also in thermal equilibrium with A.

1st law: The internal energy U of a system is constant unless it is changed by doing work (*w)* or by heating (*q*):

$$\Delta U = q + w$$

2nd law: The entropy S of an isolated system increases in the course of a spontaneous change:

$$\Delta S_{tot} > 0$$

3rd law: The entropy change of a transformation approaches zero as the temperature approaches zero:

$$\Delta S \rightarrow 0 \text{ as } T \rightarrow 0$$

Kinetic Gas Theory

Basic assumptions:

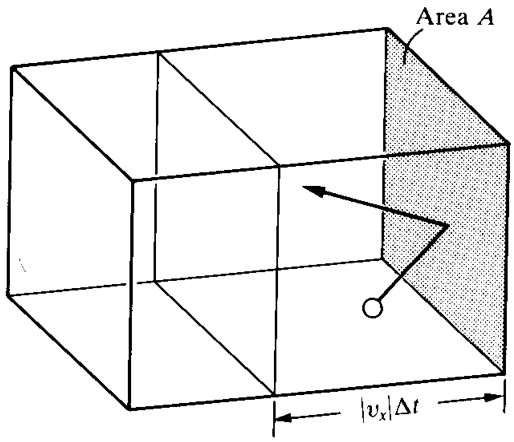
- a gas consists of molecules of mass m and diameter *d* in ceaseless random motion
- the size of the molecules is negligible
- the molecules do not interact except that they make perfect elastic collisions when the separation of their centres is equal to *d*

The total energy of such a gas is the sum of the kinetic energies of the molecules.

The **collision frequency** z is the average number of collisions per unit time made by a single molecule.

The **mean free path** λ is the average distance a molecule travels between two collisions.

Pressure from Kinetic Gas Theory



Change of momentum ΔP for collision with wall:

$$\Delta P = 2m|v_x|$$

The number of collisions in an interval Δt is the number of molecules contained in the distance that the molecules travel in Δt times the area of the wall

$$\frac{N}{V}A|v_x|\Delta t$$

On average, half of the molecules move to the left, half to the right

$$\frac{N}{2V}A|v_x|\Delta t$$

The total momentum change then is

$$\frac{N}{2V}A\Delta t 2mv_x^{\ 2}$$

the rate of change is

$$\frac{N}{V} A m v_x{}^2$$

and the pressure *p=F/A*

$$p = \frac{N}{V} m v_x{}^2$$

Not all particles travel at the same speed, so the average pressure is

$$p = \frac{N}{V} m \left\langle v_x{}^2 \right\rangle$$

If we consider that no direction is special

$$c = \left\langle v^2 \right\rangle^{1/2} = \left(\left\langle v_x{}^2 \right\rangle + \left\langle v_y{}^2 \right\rangle + \left\langle v_z{}^2 \right\rangle \right)^{1/2} = \left(3 \left\langle v_x{}^2 \right\rangle \right)^{1/2}$$

In summary, kinetic gas theory relates pressure to the average speed of the molecules in a gas:

$$\boxed{p = \frac{N}{3V} m c^2}$$

For a perfect gas it follows immediately that

$$c = \sqrt{3kT / m}$$

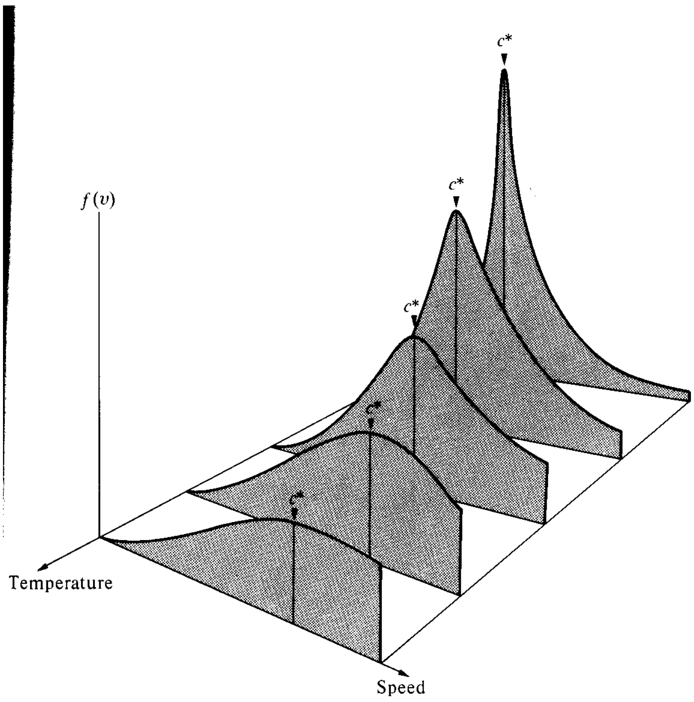
Distributions of Speed

The **Maxwell-Boltzmann distribution** of speed is

$$f(v_x) = \left(\frac{m}{2\pi kT}\right)^{1/2} e^{-mv_x^2/2kT}$$

The **Maxwell distribution** of speeds is

$$f(v) = 4\pi\left(\frac{m}{2\pi kT}\right)^{3/2} v^2 e^{-mv^2/2kT}$$



Gas Velocities

The **most probable speed** c* is the speed corresponding to the maximum of the distribution:

$$c^* = \left(\frac{2KT}{m}\right)^{1/2}$$

The **mean speed** in contrast is the weighted speed

$$\bar{c} = \left(\frac{8KT}{\pi m}\right)^{1/2}$$

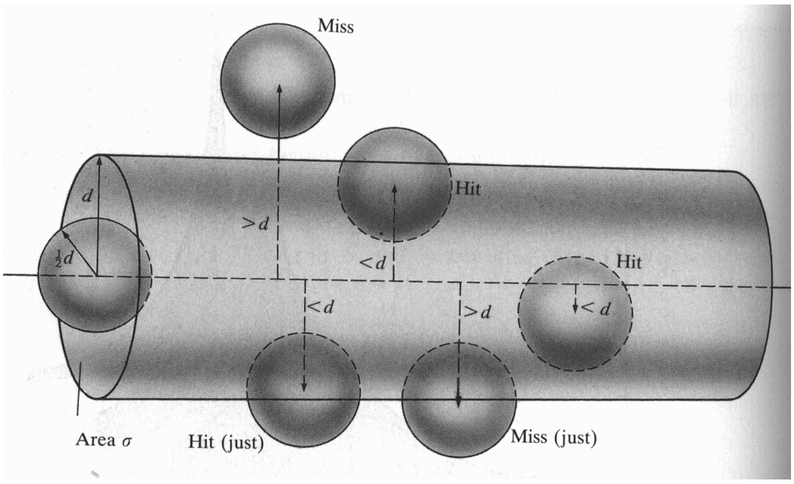
which again is slightly different from the **root mean square speed**

$$c = \left(\frac{3KT}{m}\right)^{1/2}$$

Speed depends on mass, typical values for mean speed at 25°C are

N_2 : 475 m/s
He : 1256 m/s

Collision Frequencies



Assumption: All molecules are frozen, with the exception of one that is moving. In moving, it hits all molecules within the tube with area $\sigma = \pi d^2$ and length $\bar{c}\Delta t$. σ is called **collision cross-section.**

The number of molecules inside the tube is

$$\frac{N}{V}\bar{c}\sigma\Delta t$$

and the collision frequency is

$$\frac{N}{V}\bar{c}\sigma$$

However, the molecules are not stationary, so we should use the relative speed using the **Reduced Mass** μ:

$$\bar{c}_{Rel} = \left(\frac{8KT}{\pi\mu}\right)^{1/2} \quad \text{with} \quad \mu = \frac{m_A m_B}{m_A + m_B}$$

For identical molecules, $\mu = 1/2\, m$, and therefore $\bar{c}_{Rel} = 2^{1/2}\bar{c}$ leading to the **collision frequency**

$$z = \frac{2^{1/2}\sigma\bar{c}N}{V} = \frac{2^{1/2}\sigma\bar{c}p}{kT}$$

The **collision density** Z_{AA} is the total number of collisions of molecules A per unit time and unit volume and is given by

$$Z_{AA} = \sigma\left(\frac{4kT}{\pi m}\right)^{1/2} N_A^2[A]^2$$

The collision density is a very large number, for N_2 at room temperature and pressure,

$Z = 5\text{x}10^{34}\,s^{-1}m^{-3}$

For collisions of different molecules, we have to take into account the different collision cross-section $\sigma^*=\pi d^{*2}$ with $d^* = (d_A + d_B) / 2$, the reduced mass μ, and the different molecule concentrations:

$$Z_{AB} = \sigma^* \left(\frac{8kT}{\pi\mu} \right)^{1/2} N_A^2 [A][B]$$

From the **collision frequencies**, the mean free path can be calculated:

$$\lambda = \frac{\bar{c}}{z}$$

or if *z* is inserted in the equation

$$\lambda = \frac{1}{2^{1/2} \sigma N_A [A]}$$

The mean free path does not depend on temperature!

Reaction Kinetics

Observation: The speed of chemical reactions depend on

- composition
- temperature

How is the rate of reaction defined?

$$A + B \rightarrow C$$

$[A]$ = concentration of A

Rate of Consumption: $v_A = \frac{-d[A]}{dt}$

Rate of Production: $v_C = \frac{d[C]}{dt}$

Both rates are positive! To simplify things:

Rate of Reaction: $v = \frac{1}{\nu_J}\frac{-d[J]}{dt}$

$\nu_J < 0$ for reactants, $\nu_J > 0$ for products

units: $Ms^{-1} = mol/dm^3s$

Rate Law

Observations:

- The rate of reaction can be expressed as function of the concentrations of all species present, including the products.
- It often has the simple form of

$$v = k[A]^a [B]^b [C]^c$$

The relation between rate of reaction and the concentrations is called **Rate Law**, the factor of proportionality k is called the **Rate Constant** or **Rate Coefficient**.

The rate constant is independent of the concentrations of the species, but does depend on temperature!

The rate law can be used to

- predict, how reactions proceed
- determine the mechanism of reaction

Reaction Order

The **Reaction Order** is the power to which the concentration of a species is raised in the rate law, the **Overall Reaction Order** is the sum of all orders.

In the simple case of $v = k[A]^a[B]^b[C]^c$,
the reaction order for species A is a and the total order is $a+b+c$

Important:

- The reaction order needs not to be integral
- Not all rate laws have the form of simple products of concentrations raised to a power, and therefore not all reactions do have an order, and some have an order for some but not for all species involved

The rate law not necessarily reflects the **Reaction Mechanism**, that may be much more complex. Only for **Elementary Reactions**, the rate law can be deduced immediately from the reaction equation.

How to Measure Rate Laws?

“Measure all reactants and all products as a function of time and to find the function describing the relations”

$\Rightarrow$ rapidly becomes very complex, in particular as (intermediate) products are not known a priori

Simplifications: Look at special cases

Isolation Method: Supply all reactants with the exception of one in large excess to reduce problem:

$$v = k[A]^a [B]^b [C]^c$$

If B and C are in large excess, so that [B] and [C] do not change significantly:

$$v = k'[A]^a \qquad k' = k[B]^b [C]^c$$

This is now a pseudofirst-order rate law.

$\Rightarrow$ repeat for all species

Method of Initial Rates: Measure rates at the beginning of reaction for different initial concentrations (used in combination with isolation method):

$$v = k'[A]^a$$

$$v_0 = k'[A]_0^a$$

$$\lg v_0 = \lg k' + a \lg[A]_0$$

If we plot $\lg v_0$ as a function of $\lg[A]_0$, we should get a straight line with slope a and offset $\lg k'$.

⇒ These methods might not give the full answer as products are neglected!

Integrated Rate Laws

- Rate laws are differential equations and need to be integrated if the change of concentrations with time is to be deduced.
- For realistic systems, this rapidly becomes very difficult, and eventually necessitates numerical models.
- For very simple systems, this can be done analytically

1st Order Reaction:

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

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

$$\ln\frac{[A]}{[A]_0} = -kt$$

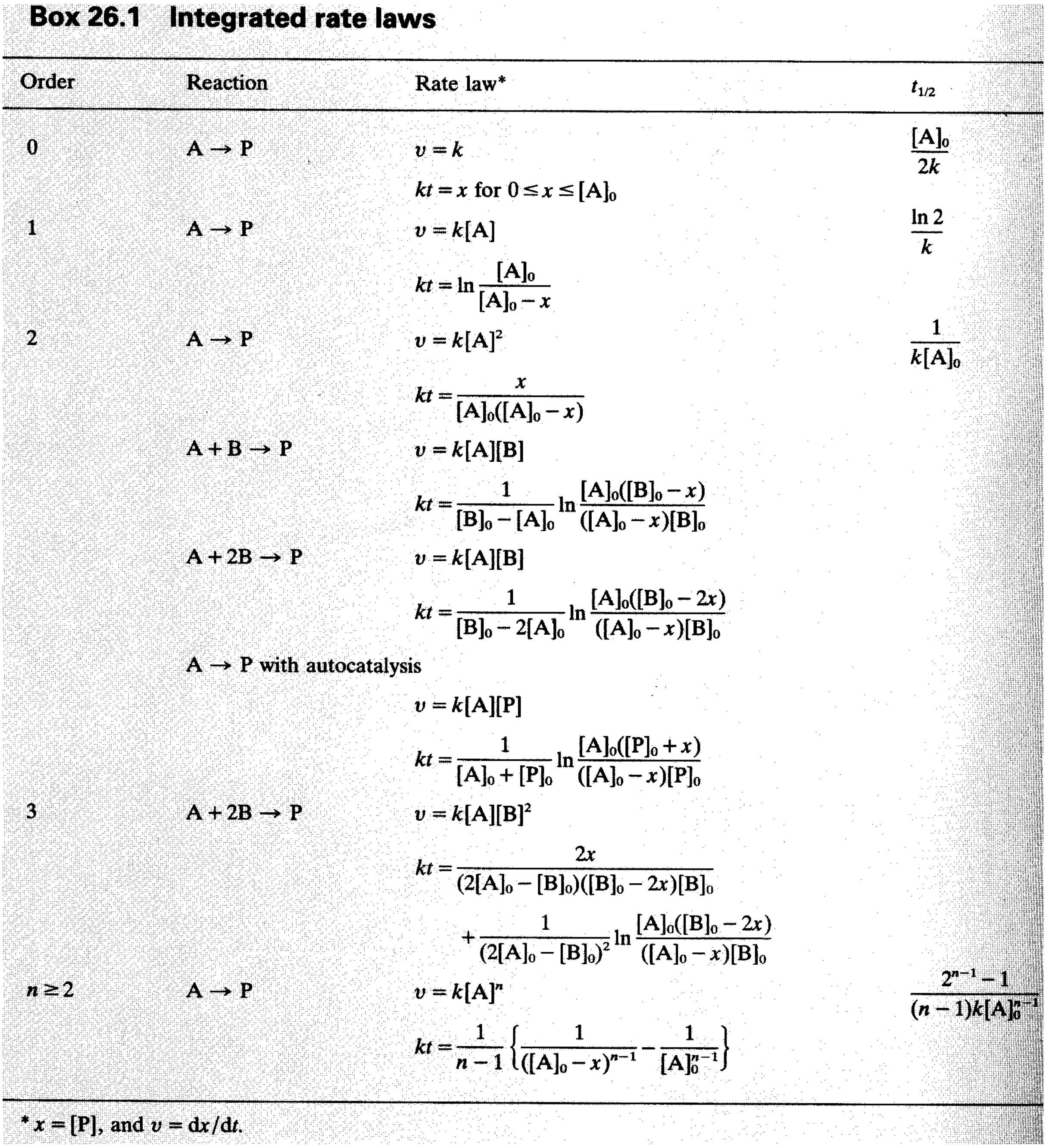
$$[A](t) = [A]_0 e^{-kt}$$

2nd Order Reaction:

$$\frac{d[A]}{dt} = -k[A]^2 \rightarrow .... \rightarrow [A](t) = \frac{[A]_0}{1 + kt[A]_0}$$

⇒ 2nd order reactions decay slower than 1st order

More Integrated Rate Laws:



Box 26.1 Integrated rate laws

Order	Reaction	Rate law*	$t_{1/2}$
0	$A \rightarrow P$	$v = k$ $kt = x$ for $0 \leq x \leq [A]_0$	$\frac{[A]_0}{2k}$
1	$A \rightarrow P$	$v = k[A]$ $kt = \ln \frac{[A]_0}{[A]_0 - x}$	$\frac{\ln 2}{k}$
2	$A \rightarrow P$	$v = k[A]^2$ $kt = \frac{x}{[A]_0([A]_0 - x)}$	$\frac{1}{k[A]_0}$
	$A + B \rightarrow P$	$v = k[A][B]$ $kt = \frac{1}{[B]_0 - [A]_0} \ln \frac{[A]_0([B]_0 - x)}{([A]_0 - x)[B]_0}$	
	$A + 2B \rightarrow P$	$v = k[A][B]$ $kt = \frac{1}{[B]_0 - 2[A]_0} \ln \frac{[A]_0([B]_0 - 2x)}{([A]_0 - x)[B]_0}$	
	$A \rightarrow P$ with autocatalysis	$v = k[A][P]$ $kt = \frac{1}{[A]_0 + [P]_0} \ln \frac{[A]_0([P]_0 + x)}{([A]_0 - x)[P]_0}$	
3	$A + 2B \rightarrow P$	$v = k[A][B]^2$ $kt = \frac{2x}{(2[A]_0 - [B]_0)([B]_0 - 2x)[B]_0} + \frac{1}{(2[A]_0 - [B]_0)^2} \ln \frac{[A]_0([B]_0 - 2x)}{([A]_0 - x)[B]_0}$	
$n \geq 2$	$A \rightarrow P$	$v = k[A]^n$ $kt = \frac{1}{n-1} \left\{ \frac{1}{([A]_0 - x)^{n-1}} - \frac{1}{[A]_0^{n-1}} \right\}$	$\frac{2^{n-1} - 1}{(n-1)k[A]_0^{n-1}}$

* $x = [P]$, and $v = dx/dt$.

Equilibrium Concentrations

Up to now, only one direction of reactions has been taken into account. However, in principle, all reactions are reversible. After some time, a **Steady State** is reached, where the concentrations do not change anymore because reaction and back reaction are proceeding at the same rate.

$$A \leftrightarrow B$$

$$A \rightarrow B \qquad v = k[A]$$

$$B \rightarrow A \qquad v = k'[B]$$

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

$$\text{in equilibrium}: \frac{d[A]}{dt} = 0$$

$$0 = -k[A] + k'[B]$$

$$k[A] = k'[B]$$

$$K = \frac{[B]}{[A]} = \frac{k}{k'}$$

The thermodynamic **Equilibrium Constant** *K* is directly related to ratio of rate constants!

This can readily be extended to complex systems.

Steady State Approximation

"In a reaction scheme going through several reaction steps, for the major part of the reaction, the rates of change of the concentrations of all intermediates can be set to zero."

This is possible

- after an introduction period
- before the reactants have become depleted

In the atmosphere, this is only useful if the introduction period is small compared to atmospheric processes (day / night, transport, rainout, ...)

Example: $2N_2O_5 \rightarrow 4NO_2 + O_2$

$$N_2O_5 \xrightarrow{k_a} NO_2 + NO_3$$

$$NO_2 + NO_3 \xrightarrow{k'_a} N_2O_5$$

$$NO_2 + NO_3 \xrightarrow{k_b} NO_2 + O_2 + NO$$

$$NO + N_2O_5 \xrightarrow{k_c} 3NO_2$$

$$\frac{d[N_2O_5]}{dt} = \frac{-2k_a k_b [N_2O_5]}{k'_a + k_b}$$

$$\rightarrow \ldots \rightarrow$$

$$v = k[N_2O_5] \qquad k = \frac{k_a k_b}{k'_a + k_b}$$

Pre-Equilibrium:

If a reaction proceeds in several steps, and the first step is fast compared to the following steps, we can assume equilibrium for the fast step:

$$A + B \xleftrightarrow{fast} C \xrightarrow{slow} P$$

$$K = \frac{[C]}{[A][B]}$$

$$\frac{d[P]}{dt} = k_d [C]$$

$$= k_b K [A][B]$$

$$= k_b \frac{k_a}{k'_a} [A][B]$$

Arrhenius Expression

When does a reaction actually take place?

- molecules have to meet → collision frequency Z_{AB}
- molecules need to have enough energy to overcome activation energy E_A → Boltzmann distribution of energy P_{Boltz}

$$\frac{d[A]}{dt} = Z_{AB} P_{Boltz} [A][B]$$

$$Z_{AB} = \sigma * \left(\frac{8kT}{\pi\mu}\right)^{1/2} [A][B]$$

$$P_{Boltz} = c e^{-\frac{E_a}{RT}}$$

$$k = A e^{-\frac{E_a}{RT}}$$

A is called the **Pre-Exponential Factor**, E_A is the **Activation Energy.**

An Arrhenius expression is often used to describe the temperature dependence of reactions.

However, Z_{AB} does also depend on temperature!

The pre-exponential factor *A* generally does not agree with the value derived from kinetic gas theory.

It usually is much smaller, as

- not all collisions lead to a reaction
- collision energy can be redistributed to internal energies (vibration, rotation, excitation)
- steric considerations can make reactions difficult

It sometimes is also larger, if attractive forces exist, such as in the case of

- induced dipole moments
- ion reactions

The temperature dependence of reactions can also differ from that of the Arrhenius equation as increasing internal and kinetic energy can also sometimes make reactions more difficult if the lifetime of intermediates is reduced.

3 body reactions

Reactions with two bodies can be understood from collision theory. However, collision of three bodies at exactly the same time is very improbable, so reactions of the type

$$A + B + M \rightarrow AB + M$$

are difficult to understand.

Idea: not an elementary step, but a reaction scheme is involved:

$$A + B \xrightarrow{k1} AB*$$

$$AB* \xrightarrow{k1'} A + B$$

$$AB* + M \xrightarrow{k2} AB + M*$$

$$M* \longrightarrow M + heat$$

Rate of reaction: $\dfrac{d[AB]}{dt} = k_2[AB*][M]$

Assumption: lifetime of AB* is very short, immediate reaction, AB* is in steady state:

$$\frac{d[AB^*]}{dt} = 0 = [A][B]k_1 - [AB^*]k_1' - [AB^*][M]k_2$$

$$\frac{-d[A]}{dt} = \frac{-d[B]}{dt} = \frac{d[AB]}{dt} = \frac{k_1 k_2 [A][B][M]}{k_1' + k_2[M]}$$

Two different limits of this rate law can be discussed:

Low Pressure Limit:

low pressure → low density → [M] << k_1'/k_2

$$\frac{d[AB]}{dt} = \frac{k_1 k_2}{k_1'}[A][B][M] \equiv k_0[A][B][M]$$

→first order in A, B and M →overall third order

High Pressure Limit:

high pressure → high density → [M] >> k_1'/k_2

$$\frac{d[AB]}{dt} = k_1[A][B] \equiv k_\infty[A][B]$$

→first order in A and B →overall second order

Inserting gives an alternative formulation:

$$\frac{d[AB]}{dt} = \frac{k_0[A][B][M]}{1 + k_0/k_\infty[M]}$$

Unimolecular Reactions

For reactions involving only one compound, the question is, how the activation energy is provided:

- internal energy conversion
- photolysis
- collisions in a reaction scheme

Idea: Similar to three body reaction:

$$AB + AB \xrightarrow{k1} AB^* + AB$$

$$AB^* + AB \xrightarrow{k1'} AB + AB$$

$$AB^* \xrightarrow{k2} A + B$$

If the deactivation dominates, AB* is in equilibrium and decomposition of AB* is the rate determining step, showing 1st order behaviour.

If [AB] is small (low pressure), activation will become the rate determining step, and overall behaviour is 2nd order.

Half Life

The **Half Life** is the time it takes to reduce the concentration of a compound to half its initial value.

- artificial quantity, as back reaction is not included
- half life is indicative of reaction order
- in the atmosphere, it is an important quantity for anthropogenic emissions

For 1st order reactions:

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

→ independent of $[A]_0$!

For 2nd order reactions:

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

→ changes with $[A]_0$, increases with decreasing concentration (time)

Solar Radiation

Solar Radiation in the earth's atmosphere has two main effects:

- heating
- energy input for deviations from equilibrium

Most chemical processes in the atmosphere are started by energy input from the sun; the consequences are determined by kinetics.

Energy of photons:

$$E = h\nu = hc/\lambda$$

h = Planck's constant, *c* = velocity of light

L=Lohschmidt's number

Convenient units:

$$\begin{aligned} E(\text{per mole}) &= Lh\nu \\ &= Lhc/\lambda \\ &= \frac{119625}{\lambda}\,\frac{\text{KJ}}{\text{mol}} \end{aligned}$$

$\Rightarrow$ extreme red (800nm) $\approx$ 150KJ/mol

extreme blue (400nm) $\approx$ 300 KJ/mol

$\Rightarrow$ visible light can produce electronic transitions up to photolysis of loosely bound chemical species

Radiation in the Atmosphere

Source: sun, black body radiation of approx. 6000 K, cooler in the UV, warmer in the IR, strong absorptions in the solar atmosphere (Fraunhofer lines)

In the earth’s atmosphere, there is

- strong absorption by O_2, O, N_2, and O_3 in the UV and many other absorbers in the IR (H_2O, CO_2, CH_4, ...)

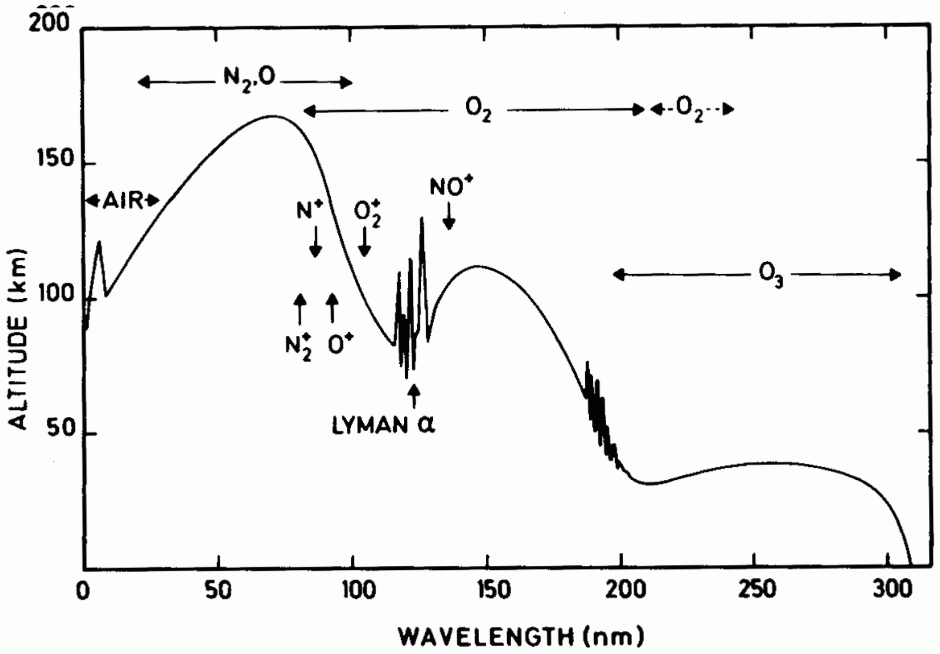


Fig. 4.3. Depth of penetration of solar radiation as a function of wavelength. Altitudes correspond to an attenuation of 1/e. The principle absorbers and ionization limits are indicated.

- scattering by air molecules (Rayleigh scattering)
- scattering by aerosols and clouds (Mie scattering)

⇒ The photon flux in the atmosphere is a strong function of wavelength, height, solar elevation and atmospheric constitution

Absorption of Light

When photons are absorbed by a molecule, they change the energy states of

- the electrons
- the vibration
- the rotation

In general, energy levels of atoms or molecules are discrete, and the energy of the absorbed photon must fit the difference in energy

$$\nu = \Delta E / h$$

(**Resonance Condition**).

The **Intensity of a Transition** is determined by

- electronic transition moment, computed from the wavefunctions and transition dipole
- population of the upper and lower states

To avoid computation of the transition moment, often **Selection Rules** are given ($\Delta S=0$ or $\Delta L=\pm1$ in atoms) to decide which transitions are allowed, and which forbidden.

In the atmosphere, many **Forbidden Transitions** can be observed as a result of the long optical paths involved.

Absorption at a certain frequency always comes with the possibility of **Emission** at the same frequency!

Notation:

Interaction with radiation is usually noted as

$$O_3 + h\nu \rightarrow O_2 + O$$

Absorption that leads to an excited state is noted as

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

Photochemical Primary Processes

Absorption leads to electronic excitation that can lead to different processes:

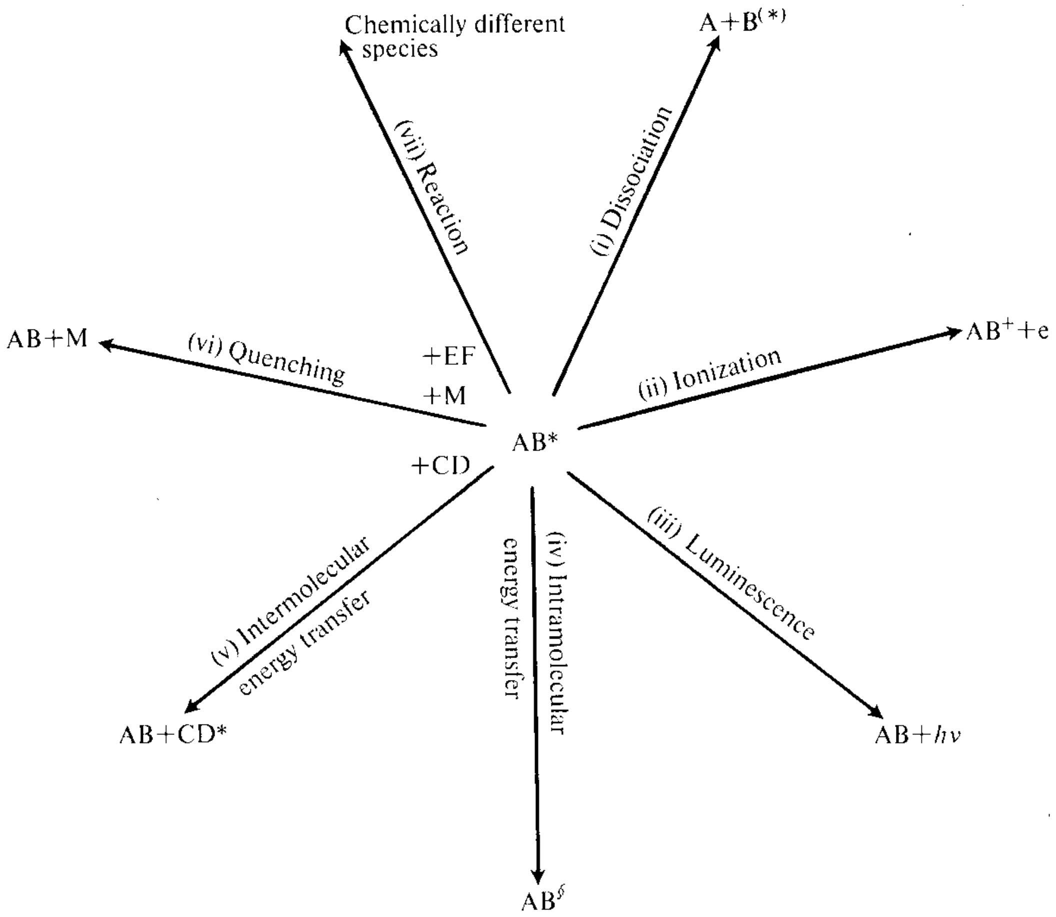
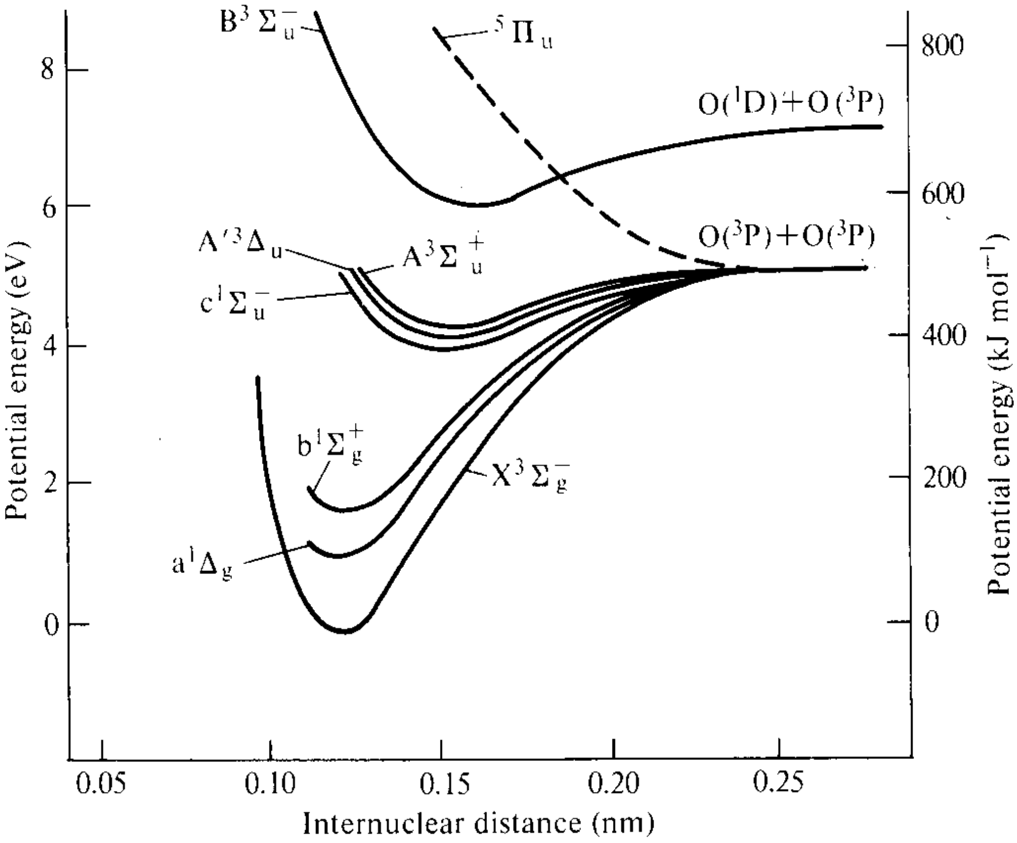


Fig. 3.1. Pathways for loss of electronic excitation that are of importance in atmospheric chemistry. The use of the symbols * and § illustrates the presence of electronic excitation: the products of any of the processes *may* be excited. With the exception of pathways (i) and (iv), excited atoms can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

Quantum Yield: Number of reactant molecules decomposed for each quantum of radiation absorbed. The sum of the quantum yields for all possible processes equals one.

Photodissociation

Dissociation is possible, if AB* lies energetically above the dissociation threshold.



Optical Dissociation: Dissociation from the electronic state to which absorption first occurred.

- continuum spectrum
- at larger wavelengths, bound bands exist that approach each other and converge at the dissociation energy

- usually, in diatomic molecules allowed transitions produce excited fragments
- all excess photon energy is converted to kinetic energy

Pre-Dissociation: Dissociation that involves an electronic state different from that initially populated.

- blurred spectrum
- fragmentation occurs before the dissociation limit is reached
- internal radiationless energy transfer leads to population of repulsive state
- pathway to allowed transitions producing non excited products

Photodissociation of Large Molecules

Many different products can be formed, for example from the photodissociation of ozone:

$$O_3 + h\nu \rightarrow O_2 + O$$

1. What is the absorption spectrum of ozone?

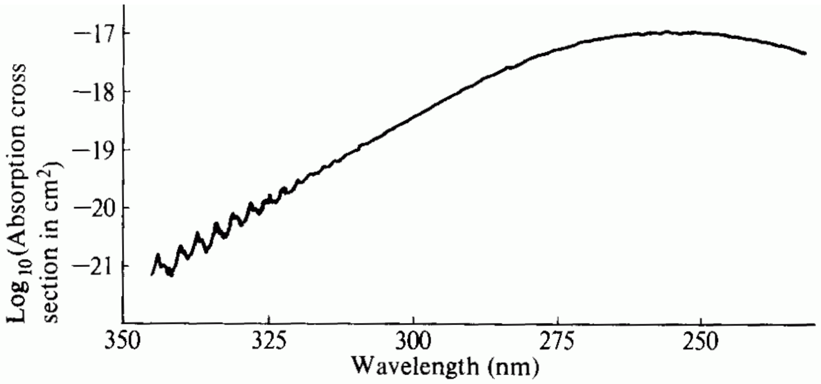


Fig. 3.4. Absorption spectrum of ozone in the ultraviolet region at 300 K. (Data of Bass, A. M. and Paur, R. J., represented at the International Workshop on Atmospheric Spectroscopy, Rutherford Appleton Laboratory, Chilton, July 1983.)

2. What energies are needed to create the different products?

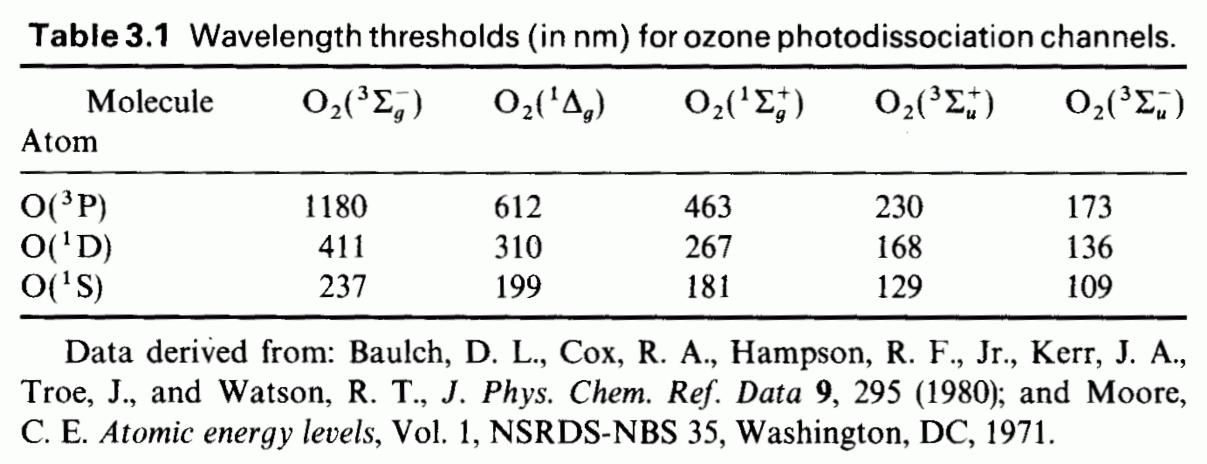


Table 3.1 Wavelength thresholds (in nm) for ozone photodissociation channels.

Molecule Atom	$O_2(^3\Sigma_g^-)$	$O_2(^1\Delta_g)$	$O_2(^1\Sigma_g^+)$	$O_2(^3\Sigma_u^+)$	$O_2(^3\Sigma_u^-)$
$O(^3P)$	1180	612	463	230	173
$O(^1D)$	411	310	267	168	136
$O(^1S)$	237	199	181	129	109

Data derived from: Baulch, D. L., Cox, R. A., Hampson, R. F., Jr., Kerr, J. A., Troe, J., and Watson, R. T., *J. Phys. Chem. Ref. Data* **9**, 295 (1980); and Moore, C. E. *Atomic energy levels*, Vol. 1, NSRDS-NBS 35, Washington, DC, 1971.

3. What selection rules apply?

Spin conservation: Products should be both singlets or both triplets.

$\Rightarrow$ O(^{1}D) productino at $\lambda < 310$ nm

$\Rightarrow$ confirmed by experiment

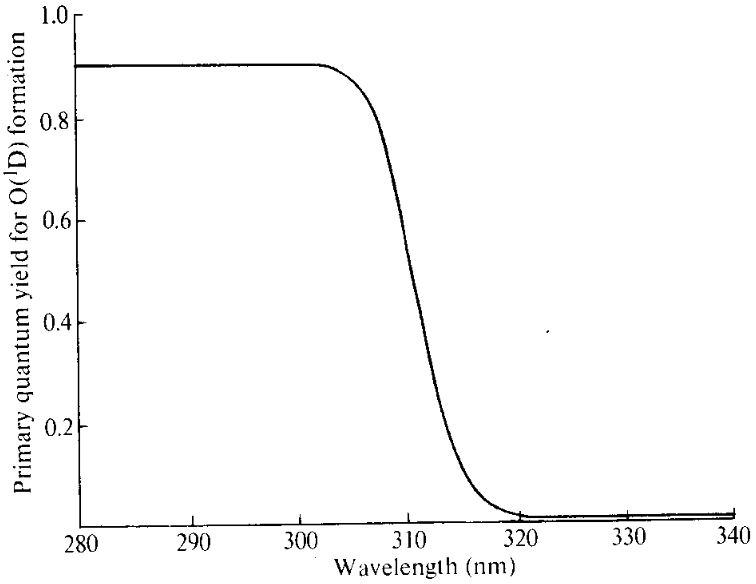


Fig. 3.5. Primary quantum yield for O(^{1}D) formation in the photolysis of ozone displayed as a function of photolysis wavelength. (Curve drawn from data presented in Hudson R. (ed.-in-chief) *The stratosphere*, 1981, World Meteorological Organization, Geneva, 1981.)

Reactions of Excited Species

If a reactant is excited, this has two impacts on the reaction:

- higher energy ⇒ activation barrier can be overcome more readily ⇒ faster
- electronic structure is altered ⇒ increased or decreased speed of reaction depending on details

<u>Examples:</u>

$O(^3P) + H_2O \rightarrow OH + OH \quad \Delta H = 70$ KJ/mol

$O(^1D) + H_2O \rightarrow OH + OH \quad \Delta H = -120$ KJ/mol

⇒ Reaction with $O(^1D)$ is exothermic!

$O(^3P) + O_3 \rightarrow 2O_2$

$O(^1D) + O_3 \rightarrow 2O_2$ and $2O + O_2$

⇒ At 220 K, reaction with $O(^1D)$ is about 3.10^5 times faster!

⇒ Effect of both increased energy and changed structure

Photolysis Rate

The **Photolysis Rate** *J* is defined as the unimolecular rate constant for photolytic loss of a substance:

$$NO_2 + h\nu \rightarrow NO + O(^3P)$$

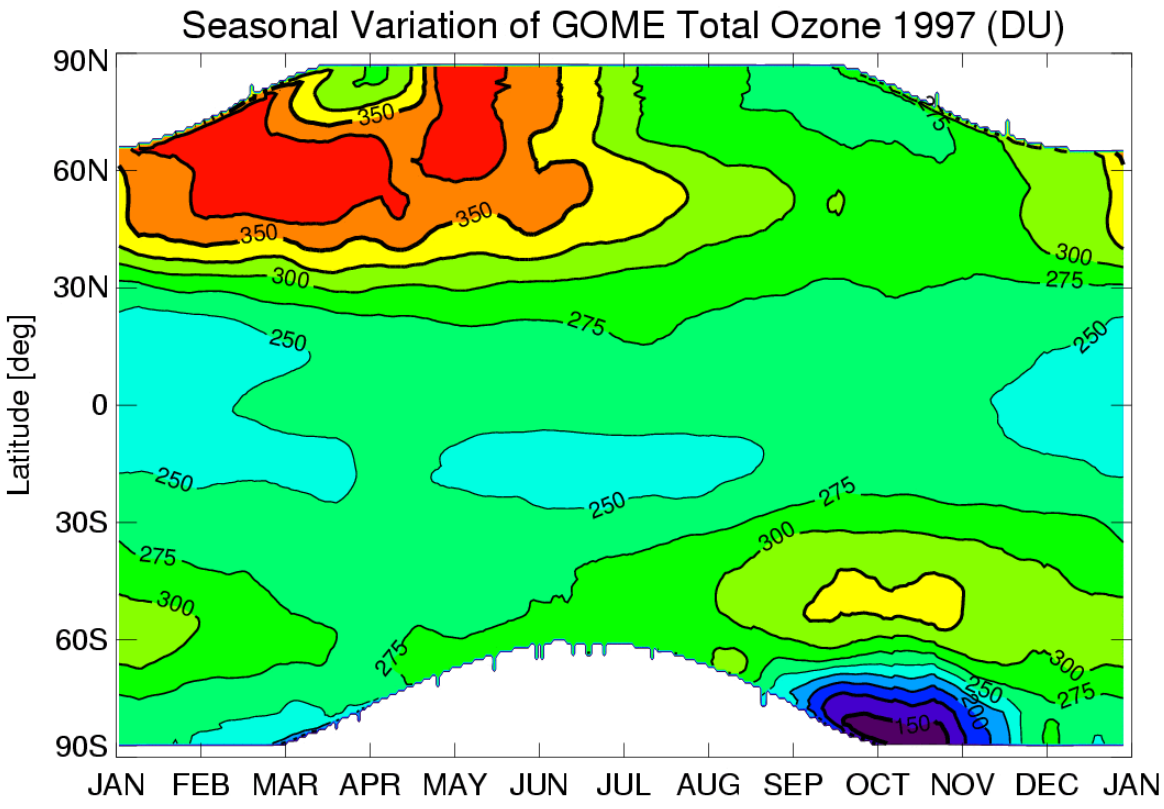
$$-\frac{d[NO_2]}{dt} = J[NO_2]$$

The photolysis rate is computed as integral over the absorption cross-section σ, the quantum efficiency Φ, and the flux *I*:

$$\int \sigma(\lambda)\Phi(\lambda)I(\lambda)d\lambda$$

It depends on wavelength, temperature, pressure, height, solar elevation and ozone column.

Stratospheric Ozone



Global distribution:

- low columns and small variability in equatorial regions
- larger columns and large variability in mid-latitudes
- historically: largest columns in spring in polar regions
- recently: very low ozone in spring in polar regions, in particular above Antarctica (“ozone hole”)

Vertical distribution:

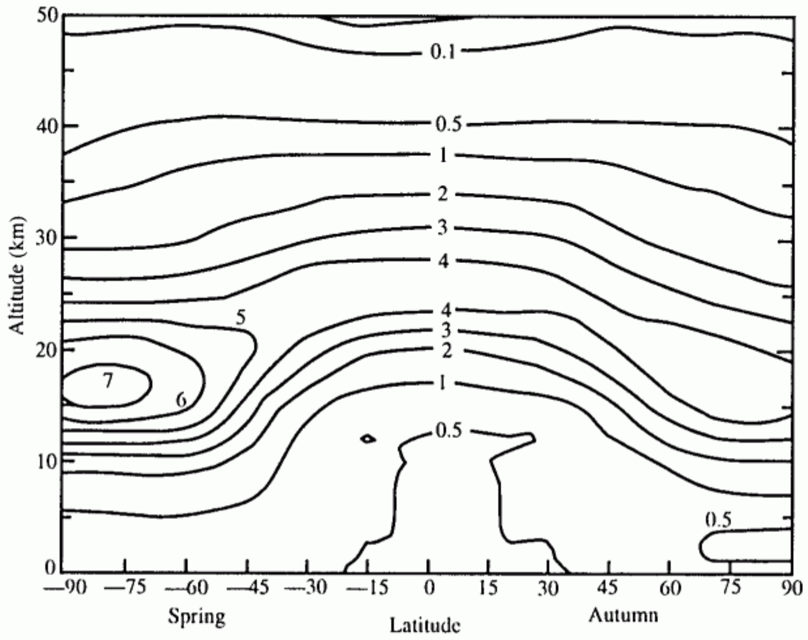


Figure 10-1 The natural ozone layer: vertical and latitudinal distribution of the ozone number density (10^{12} molecules cm^{-3}) at the equinox, based on measurements taken in the 1960s. From Wayne, R.P., *Chemistry of Atmospheres*, Oxford, 1991.

- ozone mixing ratio highest in the tropics
- ozone maximum decreasing with latitude
- production at the equator
- transport to mid-latitudes
- subsidence in polar regions

Measurement methods:

- in-situ (ozone sondes)
- UV/visible absorption spectroscopy (Dobson, DOAS, TOMS, SBUV, GOME, SCIAMACHY)

- IR absorption spectroscopy (FTIR, TOVS, MIPAS)
- microwave radiometry (RAM, MLS)

Importance of Stratospheric Ozone

Ozone is

- responsible for the vertical structure of the atmosphere
- an effective natural greenhouse gas
- the natural filter for harmful UV radiation from the sun

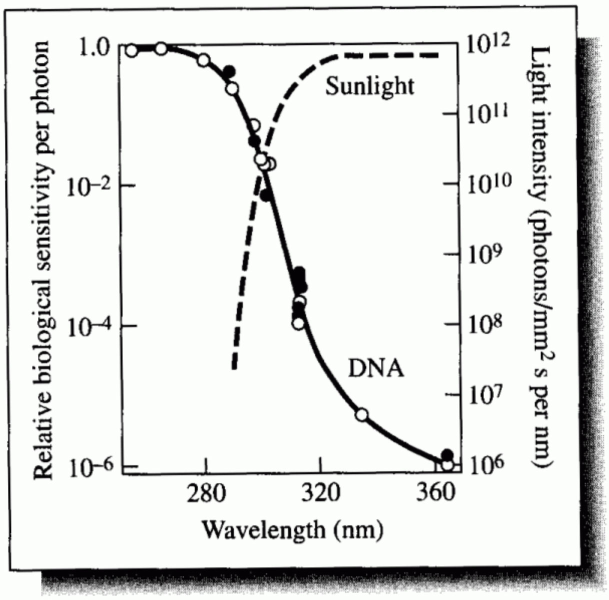


FIGURE 2-8
The absorption spectrum for DNA and the intensity of sunlight at ground level versus wavelength. The degree of absorption of light energy by DNA reflects its biological sensitivity to a given wavelength. (Source: Adapted from R. B. Setlow, *Proceedings of the National Academy of Sciences USA* 71 (1974): 3363–3366.)

Chapman Mechanism

Idea: Oxygen only chemistry, photolysis of O_2 as starting point (Chapman 1930)

$$\text{R1} \quad O_2 + h\nu \xrightarrow{J_1} O(^3P) + O(^3P) \quad (\lambda < 240\,\text{nm})$$

$$\text{R2} \quad O + O_2 + M \xrightarrow{k_2} O_3 + M$$

$$\text{R3} \quad O_3 + h\nu \xrightarrow{J_3} O_2 + O(^1D) \quad (\lambda < 320\,\text{nm})$$

$$\text{R2} \quad O + O_3 \xrightarrow{k_4} 2O_2$$

measurements in the lab show, that R1 and R4 are much slower than R2 and R3, leading to rapid cycling between O and O_3.

Odd Oxygen (Ox) Family: O + O_3

The idea of chemical families is to treat species together that can transform into each other. This saves computational time in chemical modelling both for chemistry and transport. Often, transformation within a family is fast, and steady state can be assumed.

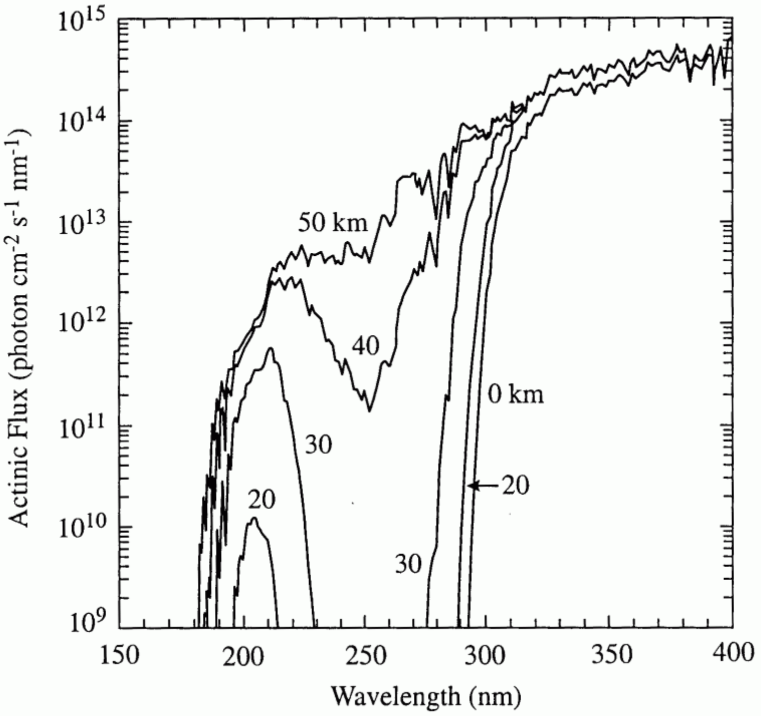


Figure 10-2 Solar actinic flux at different altitudes, for typical atmospheric conditions and a 30° solar zenith angle. From DeMore, W.B., et al., *Chemical Kinetics and Photochemical Data for Use in Stratospheric Modeling,* JPL Publication 97-4, Jet Propulsion Lab, Pasadena, CA, 1997.

What is the lifetime of O against O_3 formation? Assuming the low pressure limit, R4 is first order in [O] and the lifetime can be computed from R4:

$$\tau_{\mathrm{O}} = \frac{1}{k_2[\mathrm{O}_2][\mathrm{M}]}$$

For stratospheric conditions, the lifetime of O is of the order of seconds → steady state assumption is OK.

Assuming steady state for [O] it follows that

$$k_2[O][O_2][M] = J_3[O_3] \text{ and}$$

$$\frac{[O]}{[O_3]} = \frac{J_3}{k_2[O_2][M]}$$

- for stratospheric conditions, $[O]/[O_3] << 1$
- $[O_3]$ is controlled by slow production and loss through R1 and R4
- the lifetime of ozone is similar to the lifetime of Ox

From R2, the lifetime of Ox can be determined to

$$\tau_{\mathrm{Ox}} = \frac{1}{2k_4[\mathrm{O}]}$$

As a result of the [o] vertical distribution, the lifetime of Ox is hours in the upper stratosphere but years in the lower stratosphere. This implies, that transport is very important for ozone concentrations, and that we should expect no diurnal cycle!

If we assume steady state for Ox (not necessarily reasonable in the lower stratosphere), the ozone concentration can be determined:

$$[O_3] = \sqrt{\frac{J_1 k_2 [M]}{K_4 J_3}} [O_2]$$

The Chapman mechanism explains the observed stratospheric ozone qualitatively, but

- the concentrations are too large (factor of 2)
- the maximum is to high

Uncertainties in the ozone measurements and the reaction data can not explain the discrepancies!

→ there must be an additional loss mechanism!

Catalytic Ozone Loss Cycles

Idea: even very small amounts of a trace species can influence the ozone concentration if it acts as a catalyst.

<u>HOx cycle:</u>

Initiation step :

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

Chain reaction :

$$\begin{array}{l} OH + O_3 \rightarrow HO_2 + O_2 \\ HO_2 + O_3 \rightarrow OH + 2O_2 \\ \hline \text{net}: 2O_3 \rightarrow 3O_2 \end{array}$$

Termination step :

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

HOx Family = OH + HO_2

HOx is not consumed in the process and acts as a catalyst.

The sources of H_2O in the stratosphere are transport from the troposphere and oxidation of CH_4.

- in the lowermost stratosphere, the HOx cycle is the dominating ozone loss
- however, it can not explain all differences to the Chapman cycle

→ more catalysts are needed!

NOx cycle:

Discussion of the implementation of a large fleet of supersonic aircrafts lead to the discovery, that NO can effectively destroy ozone:

$$
\begin{array}{ll}
NO + O_3 & \rightarrow NO_2 + O_2 \\
NO_2 + O & \rightarrow NO + O_2 \\
\hline
\text{net}: O_3 + O & \rightarrow 2O_2
\end{array}
$$

Alternatively (null cycle):

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

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

Termination (formation of reservoirs):

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

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

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

Both HNO_3 and N_2O_5 are no permanent losses of NOx, but have lifetimes of weeks (HNO_3) or hours - days (N_2O_5) and therefore are called **Reservoirs**:

$$\begin{aligned} HNO_3 + h\nu &\rightarrow NO_2 + OH \\ HNO_3 + OH &\rightarrow NO_3 + H_2O \\ NO_3 + h\nu &\rightarrow NO_2 + O \\ N_2O_5 + h\nu &\rightarrow NO_2 + NO_3 \end{aligned}$$

NOy Family: NOx + all reservoirs
Sources of NOy in the stratosphere are transport of N_2O from the troposphere and subsequent reaction with $O(^1D)$ or aircraft emissions. The only sink for NOy is sedimentation to the troposphere and subsequent deposition.

Using the HOx and NOx cycles together with the Chapman mechanism, models can accurately simulate stratospheric ozone.
→ Nobel prize 1995 for Paul Crutzen

However: Human emissions change the concentrations of atmospheric trace species, and additional catalysts threaten to change stratospheric ozone concentrations:

- N_2O concentrations are increasing as a result of usage of fertilizers
- Cl and Br are release in the stratosphere as result of usage of CFCs
- Br is released in the stratosphere as a result of CH_3Br use in agriculture

ClOx-cycle:

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

Termination (formation of reservoirs):

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

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

Re-release of Cl:

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

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

The lifetime of $ClONO_2$ is about a day, that of HCl much longer (weeks). Therefore, most of the ClOx usually is in its reservoirs. Through the $ClONO_2$, the ClOx and NOx cycles are connected. NOx is both an effective ozone destroyer and provides a reservoir for ClOx.

Cly Family: Cl + ClO + all reservoirs

The source of Cly in the stratosphere is photolysis of CFCs that are stable in the troposphere and are transported in the stratosphere:

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

In the long run, continued used of CFCs would lead to decreasing ozone in the upper stratosphere, threatening to weaken the UV filtering effect of ozone.

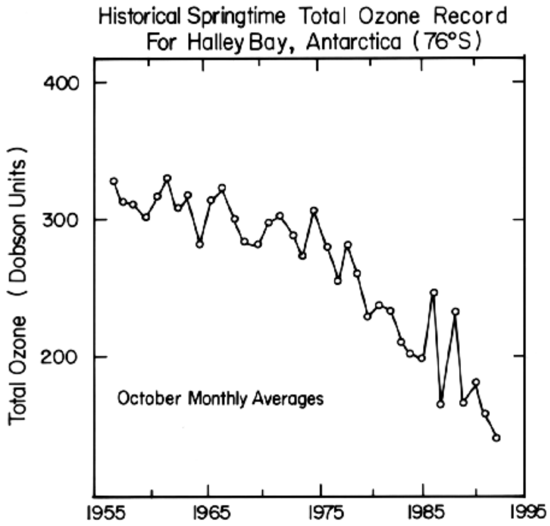
→ Nobel prize for Rowland and Molina in 1996

→ Montreal protocol and following international agreements banned use of CFCs by 1996

In principle, bromine and iodine could also act as catalytic ozone destructors, and even more efficiently as the reservoir species are much less stable and at lower altitudes as the source gases photolyse more rapidly. However, the atmospheric concentrations are much lower than those of Cly

Polar Ozone Loss

In1985, scientists from the British Antarctic Survey realised, that their ozone measurements at Halley Bay Antarctica were decreasing systematically



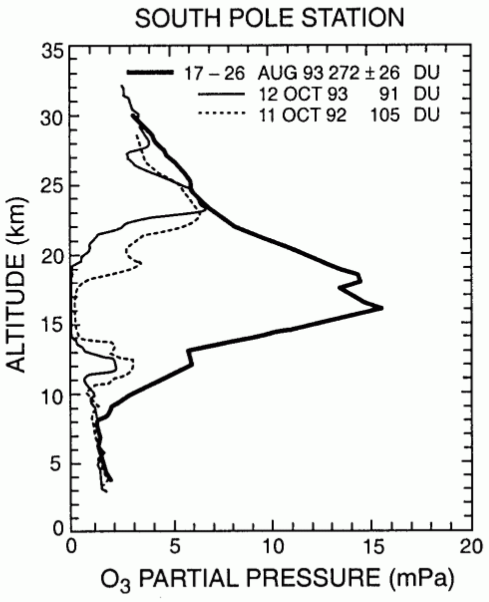


Figure 10-10 Vertical profiles of ozone over Antarctica measured by chemical sondes. In August the ozone hole has not developed yet, while in October it is fully developed. From Harris, N.R.P., et al., Ozone measurements, in WMO, op. cit..

- large ozone loss in polar spring
- other seasons not affected
- increasing from year to year
- confirmed by satellite measurements
- ozone destruction in the maximum of the profile

→ today, the Antarctic ozone hole is covering the complete Polar Vortex every year in spring!

→ this ozone destruction can not be explained by the above catalytic cycles, as the concentration of [O] is too low in these altitudes at this time of the year!

→ why only in Antarctica in spring?

Airborne and satellite observations showed, that the low ozone is correlated with unusually high ClO at rather low altitude:

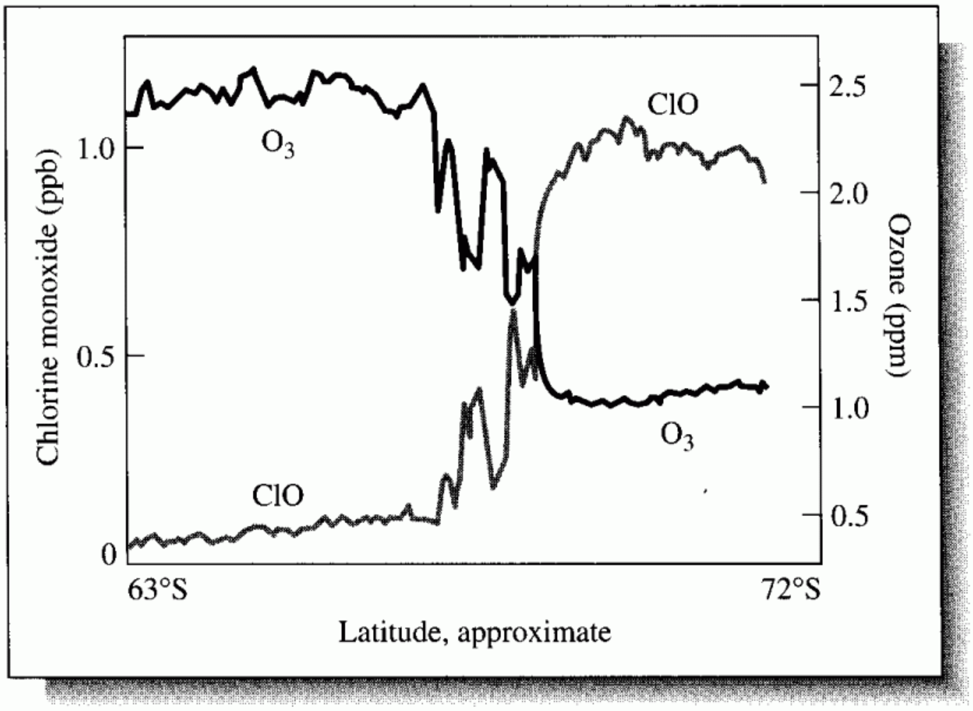


FIGURE 2-14

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.

A new catalytic cycle is possible:

$$\begin{array}{lll} ClO + ClO + M & \rightarrow & ClOOCl + M \\ ClOOCl + h\nu & \rightarrow & ClOO + Cl \\ ClOO + M & \rightarrow & Cl + O_2 \\ Cl + O_3 & \rightarrow & ClO + O_2 \\ \hline \end{array}$$

$$\text{net}: 2O_3 \rightarrow 3O_2$$

This **ClO-dimer-cycle** does not depend on [O], but is second order in [ClO]. Rate determining step is the dimer reaction. A similar cycle is possible with BrO:

$$\begin{array}{ll} Cl + O_3 & \rightarrow ClO + O_2 \\ Br + O_3 & \rightarrow BrO + O_2 \\ BrO + ClO & \rightarrow Cl + Br + O_2 \\ \hline \text{net}: 2O_3 \rightarrow 3O_2 & \end{array}$$

The BrO cycle is responsible for about 30% of the ozone destruction in the “ozone hole”.

Why is ClO so high in polar spring?

Measurements show, that the enhanced ClO concentrations are related to the occurrence of **Polar Stratospheric Clouds (PSC)**, on which certain heterogeneous reactions can take place, such as:

$$\begin{array}{ll} ClONO_2 + HCl & \xrightarrow{PSC} Cl_2 + HNO_3 \\ ClONO_2 + H_2O & \xrightarrow{PSC} HOCl + HNO_3 \\ HOCl + HCl & \xrightarrow{PSC} Cl_2 + H_2O \\ N_2O_5 + HCl & \xrightarrow{PSC} ClNO_2 + HNO_3 \\ N_2O_5 + H_2O & \xrightarrow{PSC} 2HNO_3 \end{array}$$

As a result, ClOx is released from its reservoirs, and NOx is converted to HNO_3 (**Denoxification**). Over the polar night, these reactions proceed almost to 100%.

All reactions are significant only at very low temperatures.

PSC Formation

- stratosphere is very dry → very low temperatures need for condensation (185K - 190K)
- PSCs are observed at these low temperatures on a regular basis in Antarctica
- Some PSCs form at higher temperatures (up to 197 K), and therefore are very common in Austral winter

PSCs can consist of

- NAT (nitric acid trihydrate $HNO_3.3H_2O$
- ICE (at very low temperature)
- ternary solutions of HNO_3, H_2SO_4 and H_2O

Differences between the two hemispheres:

- Antarctica: very low temperatures in polar vortex, many PSCs every year, long and stable vortex
- Antarctica: HNO_3 and ice sediment and are removed from the stratosphere
- Arctic: very variable temperatures, few PSCs, early break-up of vortex, no or very little **Denitrification** and **Dehydration**

Phases of Antarctic Ozone Loss:

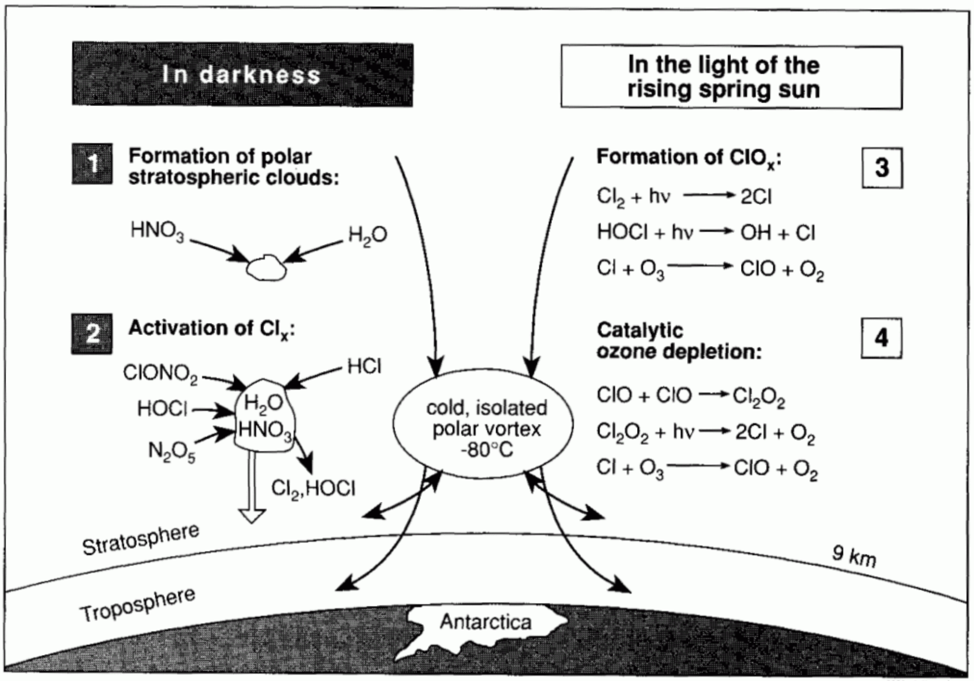
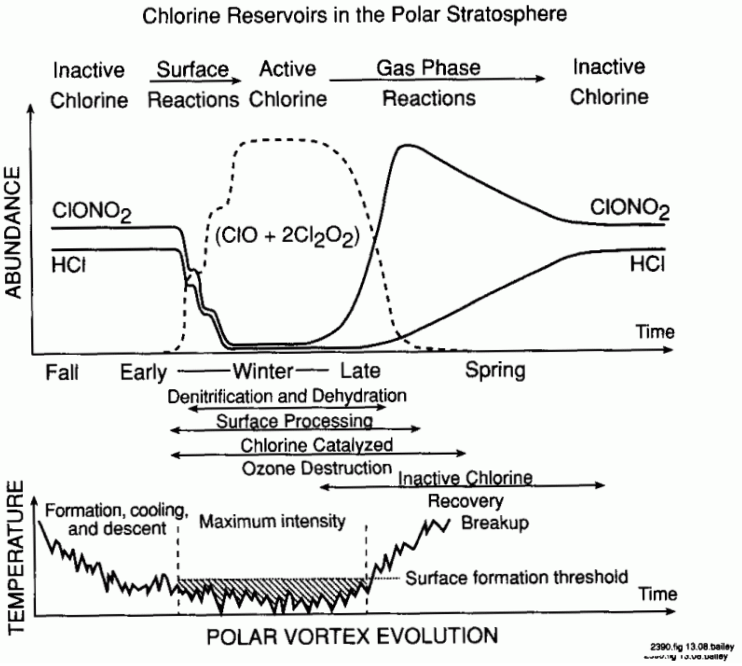


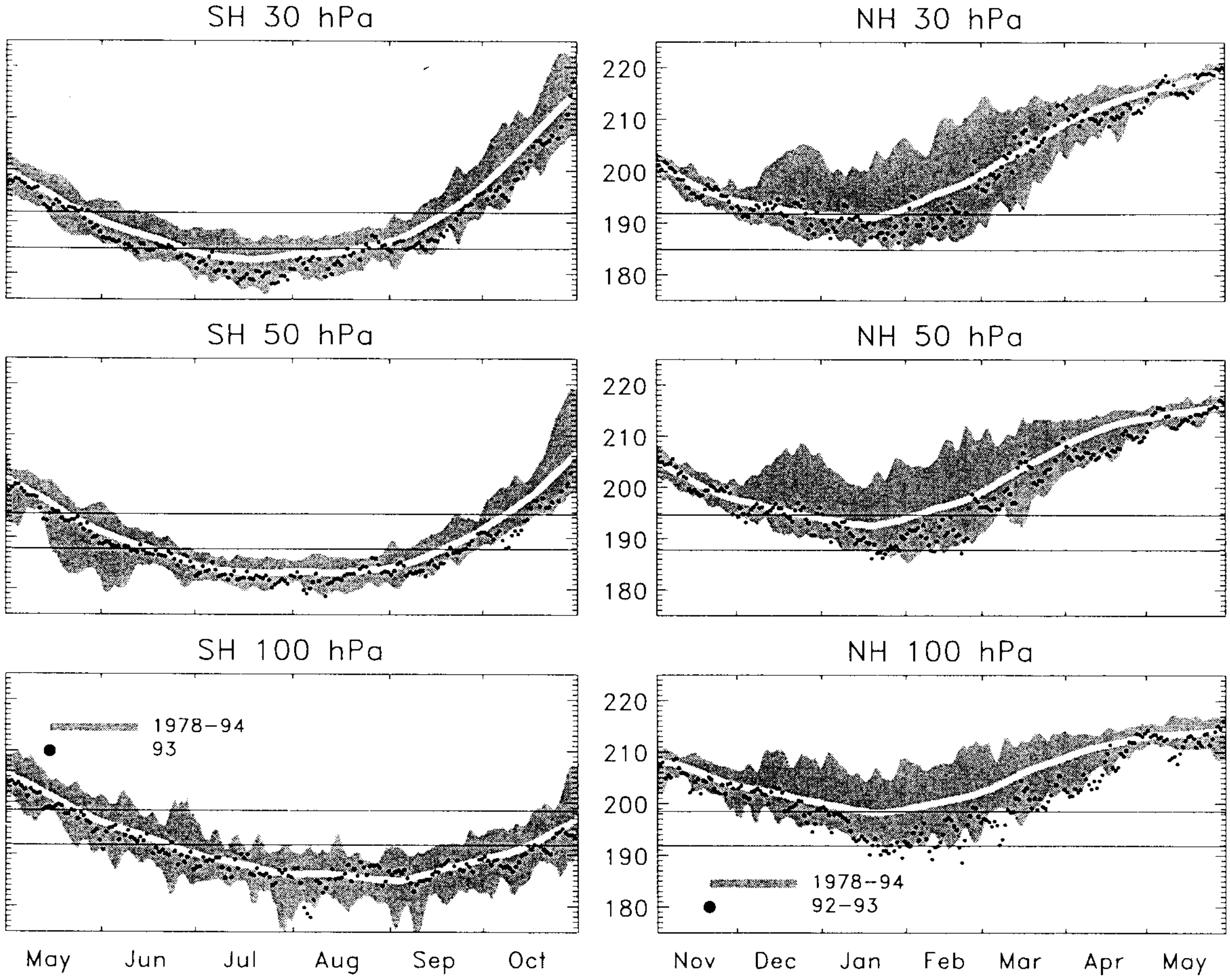
Figure 14.12. *Schematic of the dynamical and chemical processes leading to ozone depletion within the Antarctic vortex. Processes (1) and (2) occur during the polar night, while processes (3) and (4) require the presence of sunlight.*

Figure 14.14. *Schematic of chlorine photochemical and dynamical evolution of polar regions (WMO, 1995). Note the rapid conversion of $ClONO_2$ and HCl reservoirs into active chlorine as soon as polar stratospheric clouds are formed (air temperature reaching the PSC formation threshhold). The recovery of $ClONO_2$ in late spring is much faster than that of HCl.*



1. vortex formation
2. PSC formation
3. conversion of chlorine reservoirs to active species and NOx to HNO_3
4. sedimentation of PSCs (denitrification)
5. sunrise → ozone loss
6. vortex break-up
7. reformation of reservoirs

PSC Probabilities in Both Hemispheres



3-3. A summary of the minimum polar vortex temperatures in the period 1978 to 1994 at 30 hPa, 50
d 100 hPa (1 hPa = 1 mb) in the lower stratosphere in the Northern (NH) and Southern (SH) hemi-
s (National Meteorological Center analysis). The range of observations between 1978 and 1992 is
y the shaded region. The narrow white band is the average of the data set. The black dots represent
r 1993 in the Antarctic and 1992-93 in the Arctic winter. Lines indicate approximate temperature
lds for Type I (upper) and Type II (lower) PSC formation (adapted from Nagatani *et al.*, 1990).

Heterogeneous Reactions

In atmospheric chemistry, the term **Heterogeneous Reactions** is used to describe reactions occurring inside or at the surface of a droplet or uptake into a droplet.

The physical uptake on the particle is described by the **Accommodation Coefficient** α that tends towards 0 as the surface becomes saturated.

The reaction rate is derived from the rate of collisions with the particle and the **Reaction Probability** γ that combines physical uptake and chemical reaction.

At low pressures, heterogeneous reactions are assumed to be of first order and the reaction rate is proportional to the aerosol surface A, the reaction probability γ, and the mean speed c:

$$k = \frac{\gamma \bar{c} A}{4}$$

Heterogeneous reactions are often very temperature dependent:

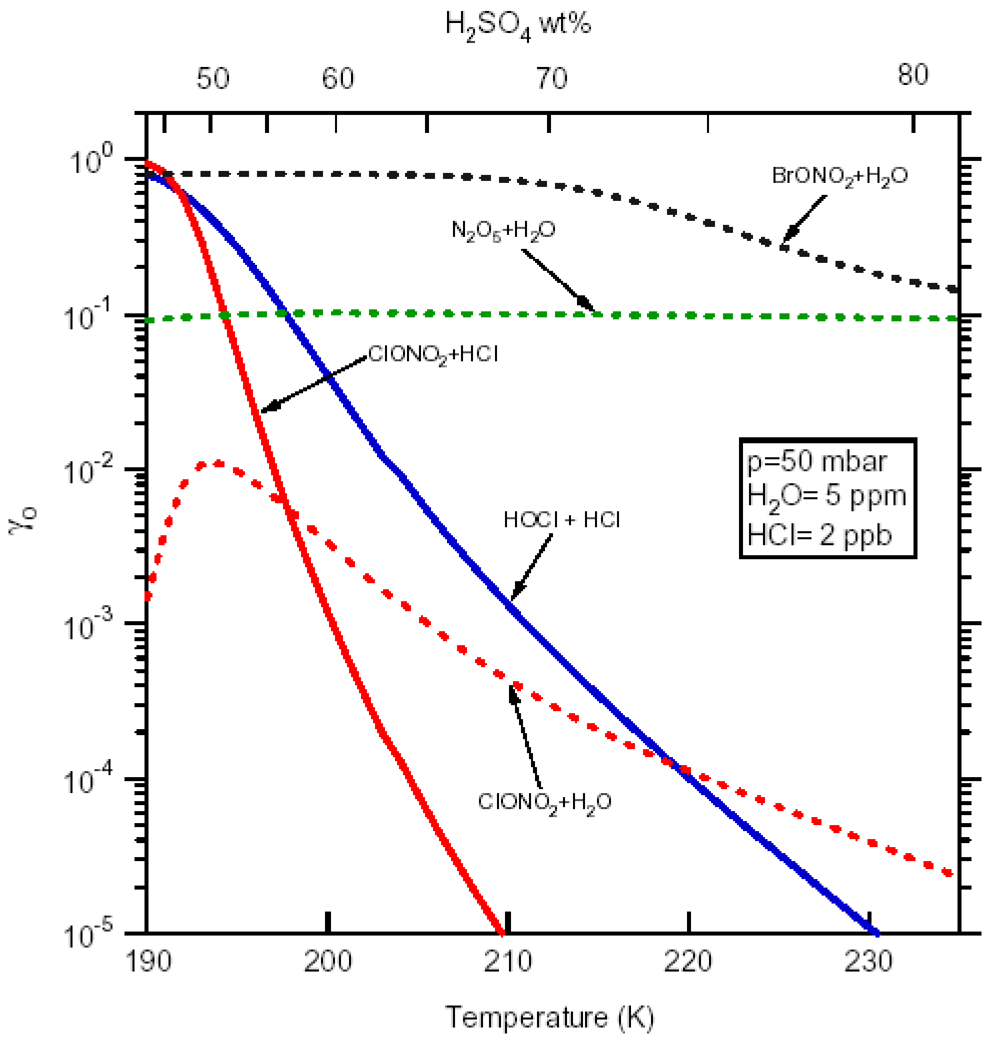


Figure 3: Recommended Reactive Uptake Coefficients as a Function of Temperature for Key Stratospheric Heterogeneous Processes on Sulfuric Acid Aerosols.

Ozone Loss at Mid-Latitudes

Measurements show, that ozone at mid-latitudes is decreasing by about 4% per decade.

Ozone loss at mid-latitudes can have different origins:

- in situ depletion from HOx, NOx, ClOx, or BrOx chemistry
- transport of low ozone air from the polar vortex
- dilution of low ozone air masses after the break-up of the polar vortex

On top of a possible chemical ozone destruction, other effects have to be considered:

- natural dynamic variability
- solar cycle (1-2%)
- Quasi-Biennial Oscillation (QBO) (1-5%)
- changes in transport patterns

Effect of Volcanic Eruptions

Eruption of Mt. Pinatubo in 1991:

- 15-20 Mt of SO_2 deposited in the stratosphere
- rapid conversion to H_2SO_4
- transport to all latitudes

Effects of aerosols in the stratosphere:

- shading of atmosphere below aerosol layer
- increased flux above aerosol layer
- reduced temperature below layer
- strongly increased surface area available for heterogeneous reactions
- light absorption by SO_2 → less ozone production
- ozone production by SO_2 photolysis
- circulation changes resulting from temperature changes

Observations after Mt. Pinatubo eruption:

- in first phase: low ozone in the tropics
- later: low ozone in mid-latitudes

- low NO_2 (-25-50%), high HNO_3 in mid and high latitudes
- enhanced ClO/Cly
- reduced $ClONO_2$, HCl, and HNO_3 at very low temperatures
- enhanced OClO at high latitudes without PSC

Chemical mechanism:

- hydrolosis of N_2O_5 on aerosols

  $$N_2O_5 + H_2O \xrightarrow{\text{aerosol}} 2HNO_3$$

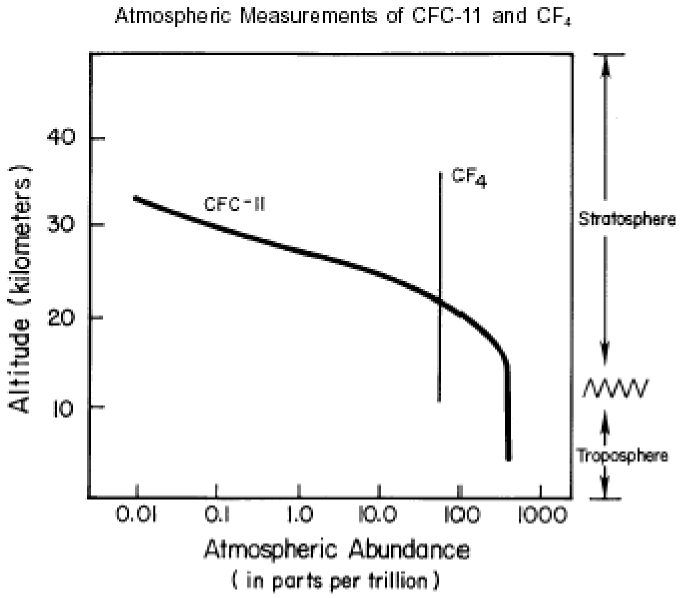
  leads to reduction in NO_x
- reduction in NO_x leads to increase in ClO/Cly
- at low temperatures or very large surface areas, hydrolosis of $ClONO_2$ can also become important

  $$ClONO_2 + H_2O \xrightarrow{\text{aerosol}} HOCl + HNO_3$$

  leading to further increase in ClO/Cly
- increased ClO leads to reduced ozone
- increased flux above aerosol layer increases photolysis rates and thereby reduces ozone and NO_2 concentrations

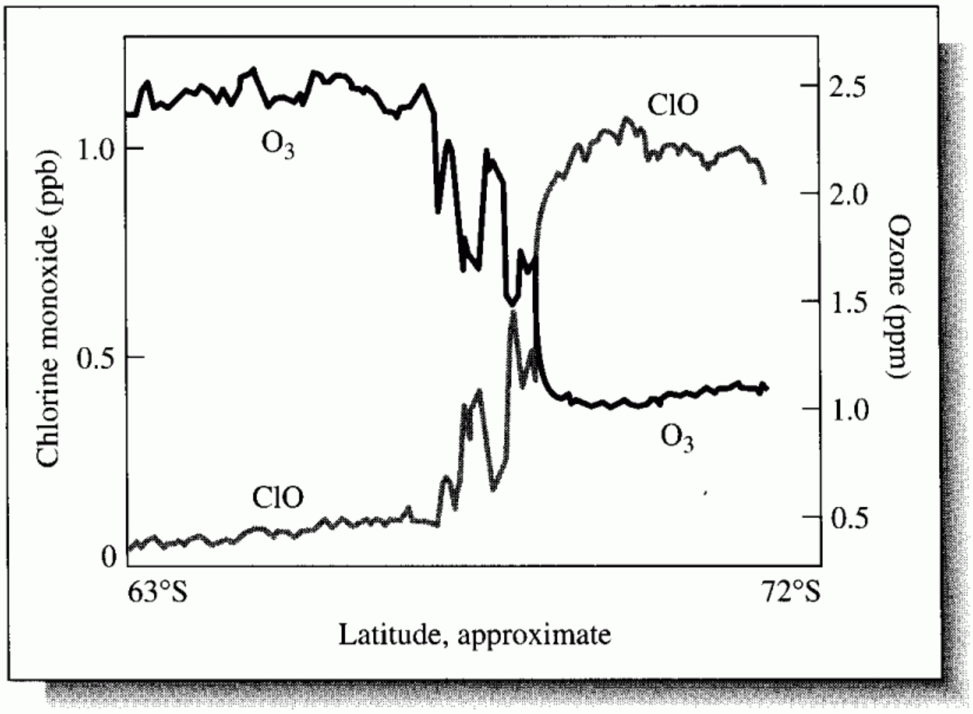
How Can CFCs Get to the Stratosphere?

- CFCs are much heavier than air
- CFCs are stable in the troposphere and therefore well mixed
- mixing and transport are much more effective than sedimentation in the **Homosphere**
- measurements show that all stable species are well mixed in the atmosphere, both if they are lighter than air (Neon) or heavier (Argon)
- measurements show, that CFCs reach the stratosphere, but decrease with height (photolysis)



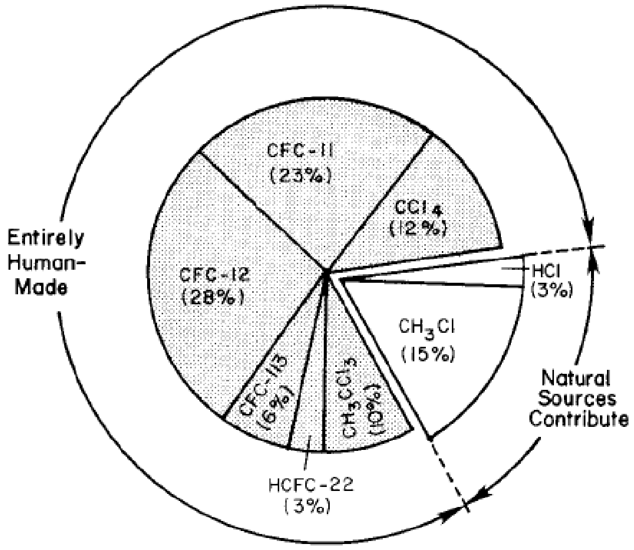
What is the Evidence that Cl and Br Destroy Ozone in the Stratosphere?

- measurements in the lab have established the catalytic ozone destruction schemes
- as the measurements have been performed under “stratospheric” conditions (p, T, []), the same mechanisms will also act in the atmosphere
- however: the atmosphere is much more complex
- some special measurements have shown direct anti-correlation of ClO and BrO



What are the Sources of Cl in the Stratosphere?

- NaCl from sea salt → dissolves
- Cl from swimming pools → converted + dissolves
- HCl from volcanoes → solved + rained out
- Cl from Space Shuttle and other rockets → partly emitted in the stratosphere, but small amounts
- CFCs, CCl_4, methyl chloroform → stable in the troposphere, reach stratosphere



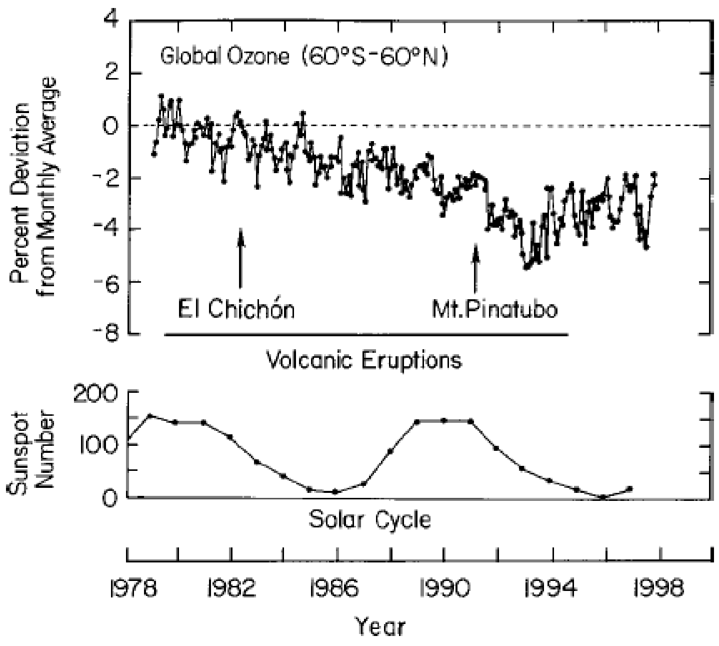
Experimental evidence:

- measurements of chlorinated species
- measurements of Cly
- increase in Cly

Can Changes in the Suns Output Explain Ozone Depletion?

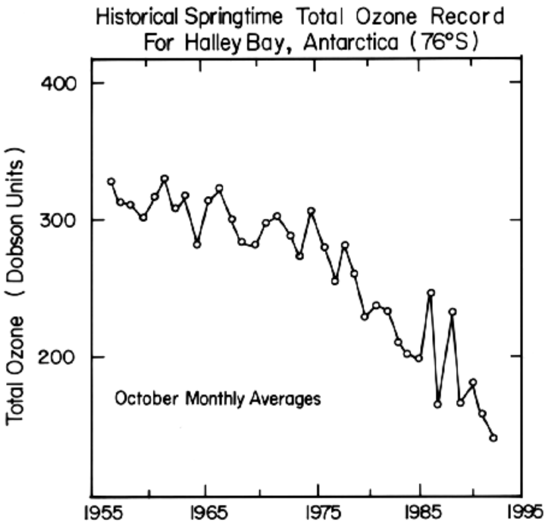
- UV for ozone destruction comes from the sun
- UV intensity of the sun varies (11 year cycle)
- stratospheric ozone varies in phase with solar variation (more ozone during solar maximum) by 1-2%
- the observed ozone trends are larger
- observations show trend, not 11 year cycle
- impact of solar variation is corrected in trend analysis

Global Ozone Trend, Major Volcanic Eruptions, and Solar Cycles



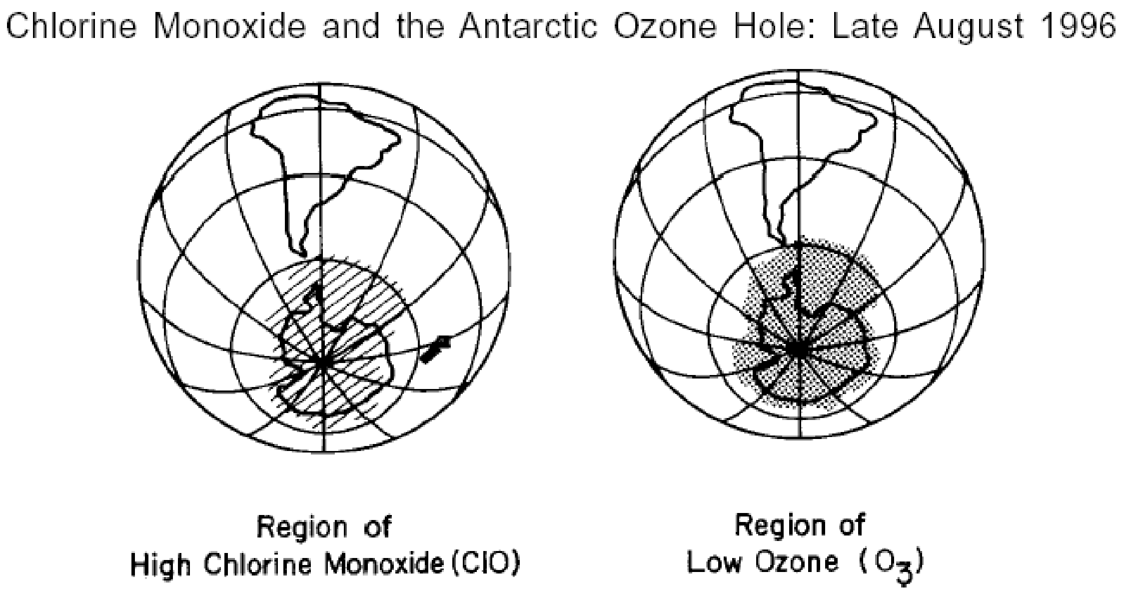
When did the Ozone Hole First Appear?

- in the “natural” state, Antarctic ozone columns in spring were lower than those in the Arctic by 30-40% (lower T, stronger winds)
- the ozone hole developed slowly after 1957
- measurements at all 4 stations in the Antarctic and satellite measurements give the same picture
- one single report from 1958 on very low ozone is not consistent with the other measurements and was obtained using an unproven technique
- stratospheric dynamics and temperatures have not changed before the ozone hole



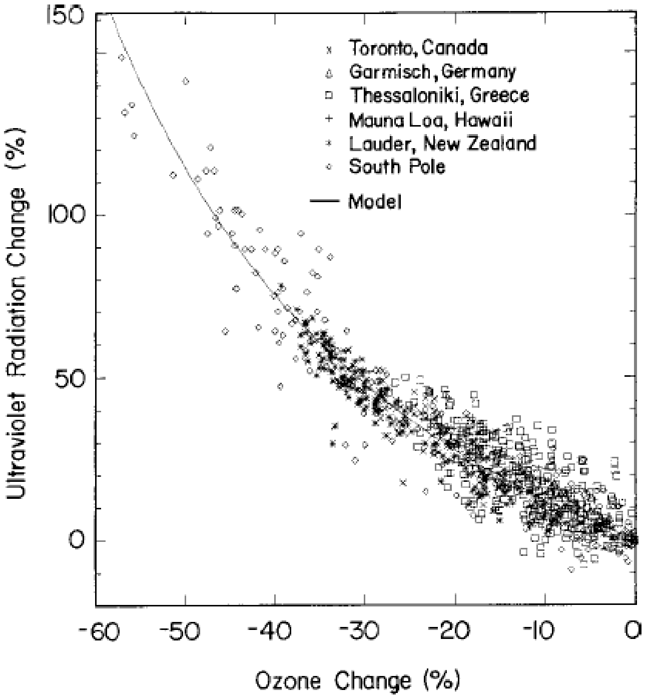
Why is the Ozone Hole Observed Only above Antarctica?

- CFCs have mostly been emitted in the Northern Hemisphere
- long lifetime → well mixed in the troposphere within 2 years
- uplifting in the tropics
- stratospheric transport to high latitudes
- special conditions in polar vortex
    - darkness
    - very low temperatures
    - isolated airmass
- asymmetry between the hemispheres



Is Surface UV Increasing with Ozone Depletion?

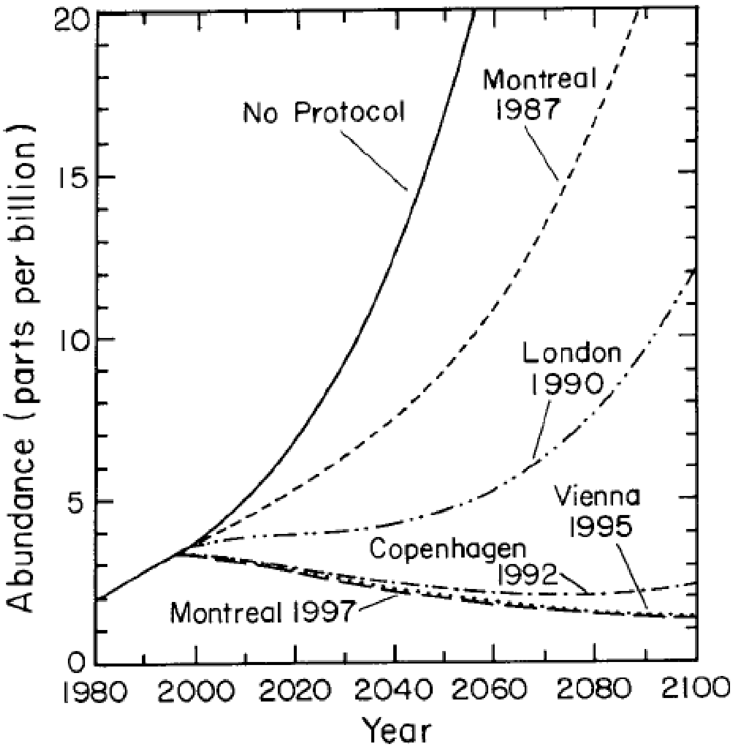
- measurements in Antarctica show clear correlation
- measurements at other latitudes are not so clear
- problem: UV also influenced by
  - clouds
  - aerosols
  - ozone smog
- problem: measurements are very difficult and old measurements lack the necessary accuracy and stability



What is the Current Status and Expected Future of Ozone Depletion?

- global reduction -5% since 1965
- 10% reduction in mid-latitudes winter/spring
- 60% reduction in Antarctic spring
- 5-30% reduction in Arctic spring
- up to 20% reductions after eruption of Pinatubo
- maximum of stratospheric Cl levels reached ?
- back to normal in 2100 ?

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



How are Ozone Levels and Global Warming Related?

- ozone is absorbing UV radiation, heating the stratosphere → less ozone means a colder stratosphere
- green house gases absorb IR radiation from the earth surface, heating the lower atmosphere but cooling down the upper atmosphere → global warming leads to a colder stratosphere
- models predict, that global warming will lead to less planetary waves and therefore a more stable polar vortex → lower temperatures, longer ozone destruction

All changes reduce stratospheric temperature, and thereby increase PSC probability and springtime ozone depletion. Some increase in heterogeneous processes at mid-latitudes is also possible

Tropospheric Chemistry

The main differences between troposphere and stratosphere relevant to atmospheric chemistry are

Stratosphere	Troposphere
low pressure	high pressure
high UV radiation	low UV radiation
low T	high T
few sinks	many sinks
few sources	many sources
“no biology”	biological emissions
little anthropogenic impact	many anthropogenic emissions
low vertical mixing	strong vertical mixing
low humidity	high humidity

As a result, a multitude of species is present in the troposphere, and different sources and sinks as well as reaction pathways compete in a complex way.

Lifetimes in the troposphere range from seconds to years, and often transport is important between sources and sinks.

Table 5.1 Natural and man-made sources of the minor trace gases of the troposphere

Compound	Natural sources	Man-made sources
Carbon-containing trace gases		
Carbon monoxide (CO)	Oxidation of natural methane, natural C_5, C_{10} hydrocarbons; oceans, forest fires	Oxidation of man-made hydrocarbons; incomplete combustion of wood, oil, gas, and coal, in particular motor vehicles, industrial processes; blast furnaces
Carbon dioxide (CO_2)	Oxidation of natural CO; destruction of forests; respiration by plants	Combustion of oil, gas, coal, and wood; limestone burning
Methane (CH_4)	Enteric fermentation in wild animals; emissions from swamps, bogs, *etc.*, natural wet land areas; oceans	Enteric fermentation in domesticated ruminants; emissions from paddies; natural gas leakage; sewerage gas; colliery gas; combustion sources
Light paraffins, C_2—C_6	Aerobic biological source	Natural gas leakage; motor vehicle evaporative emissions; refinery emissions
Olefins, C_2—C_6		Motor vehicle exhaust; diesel engine exhaust
Aromatic hydrocarbons		Motor vehicle exhaust; evaporative emissions; paints, petrol, solvents
Hemiterpenes, C_5H_8	Trees, broadleaves, and conifers; plants	
Terpenes, $C_{10}H_{16}$		
Diterpenes, $C_{20}H_{32}$		
Nitrogen-containing trace gases		
Nitric oxide (NO)	Forest fires; anaerobic processes in soil; electric storms	Combustion of oil, gas, and coal
Nitrogen dioxide (NO_2)	Forest fires; electric storms	Combustion of oil, gas and coal; atmospheric transformation of NO
Nitrous oxide (N_2O)	Emissions from denitrifying bacteria in soil; oceans	Combustion of oil and coal

Table 5.1 (*continued*)

Compound	Natural sources	Man-made sources
Peroxyacetyl nitrate (PAN)	Degradation of isoprene	Degradation of hydrocarbons
Ammonia (NH_3)	Aerobic biological source in soil Breakdown of amino acids in organic waste material	Coal and fuel oil combustion; waste treatment
Sulphur-containing trace gases		
Sulphur dioxide (SO_2)	Oxidation of H_2S; volcanic activity	Combustion of oil and coal; roasting sulphide ores
Hydrogen sulphide (H_2S)	Anaerobic fermentation; volcanoes and fumaroles	Oil refining; animal manure; Kraft paper mills; rayon production; coke oven gas
Carbon disulphide (CS_2)	Anaerobic fermentation	Viscose rayon plants; brick making; fish meal processing
Carbonyl sulphide (COS)	Oxidation of CS_2; slash and burn agriculture; volcanoes and fumaroles	Oxidation of CS_2; brick making; effluent from Kraft mills; blast furnace gas; coke oven gas; shale and natural gas
Sulphur trioxide (SO_3)		Combustion of S-fuel
Methyl mercaptan (CH_3SH)	Anaerobic biological sources	Animal rendering; animal manure; pulp and paper mills; brick manufacture; oil refining
Dimethyl sulphide (CH_3SCH_3)	Aerobic biological sources	Animal rendering; animal manure; pulp and paper mills
Dimethyl disulphide (CH_3SSCH_3)		Animal rendering; fishmeal processing
Other organic sulphur compounds: C_2—C_4 mercaptans, dialkyl disulphides, dimethyl trisulphide, alkyl thiophenes, benzothiophenes	Anaerobic biological sources	Animal rendering; fishmeal processing; brick making

Chlorine-containing trace gases		
Hydrogen chloride (HCl)	Volcanoes and fumaroles; degradation of CH_3Cl	Coal combustion; degradation of chlorocarbons
Methyl chloride (CH_3Cl)	Slow combustion of organic matter; marine environment; algae	PVC and tobacco combustion
Methylene dichloride (CH_2Cl_2)		Solvent
Chloroform ($CHCl_3$)		Pharmaceuticals; solvent; combustion of petrol; bleaching of wood pulp; degradation of C_2HCl_3
Carbon tetrachloride (CCl_4)		Solvent; fire extinguishers; degradation of C_2Cl_4
Methyl chloroform (CH_3CCl_3)		Solvent; degreasing agent
Trichloroethylene (C_2HCl_3)		Solvent; dry cleaning agent; degreasing agent
Tetrachloroethylene (C_2Cl_4)		Solvent; dry cleaning agent; degreasing agent
Other chlorofluorocarbons: CCl_3F, CCl_2F_2, $C_2Cl_3F_3$, $C_2Cl_2F_4$, C_2ClF_5		Aerosol propellants; refrigerants; foam blowing agents; solvents
Other minor trace gases		
Hydrogen	Oceans: soils; oxidation of methane, isoprene and terpenes via formaldehyde	Motor vehicle exhaust; oxidation of methane via formaldehyde
HF	Volcanoes and fumaroles	
Ozone	Stratosphere: natural NO–NO_2 conversion	Man-made NO–NO_2 conversion
H_2O	Evaporation from oceans	Insignificant
SF_6		Electrical insulator
CF_4		Aluminium industry
CH_3Br	Aerobic biological source	Fumigation of soil and grain
CH_3I	Aerobic biological source	Insignificant

Reproduced from Cox, R. A. and Derwent, R. G. *Gas kinetics and energy transfer*, *Specialist Periodical Reports Chem. Soc.* **4**, 189 (1981).

Oxidation in the Troposphere

- many source gases are partially oxidized (CO, SO_2) or highly reduced (H_2S, NH_3)
- in the troposphere, they are oxidized, but not by direct reaction with O_2
- first step to the oxidation usually is attack by the **Hydroxyl Radical OH**
- therefore, OH is often called the “Detergent of the Atmosphere”

Standard example:

$$CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O$$

where CO_2 is taken up by the oceans and is eventually deposited on the ocean floor as carbonate.

Oxidation is achieved through a series of reaction steps that produces radicals and depends on photolysis, the concentration of OH and other radicals and also of NOx.

What is Oxidation?

Original meaning: oxidation is a reaction where oxygen is added to a substance, reduction a reaction where oxygen is removed.

Extended meaning: oxidation is a process where an atom is loosing electrons (even partially), a reduction is a reaction where an atom is gaining electrons (even partially).

An identical definition is that oxidation is an increase in oxidation number.

Each oxidation is accompanied by a reduction!

Rules for **Oxidation Numbers**:

1. The oxidation number of an atom in the elemental state is zero.
2. The oxidation number of a monatomic ion is equal to its charge.
3. The algebraic sum of the oxidation numbers in the formula of a compound is zero.

4. The oxidation number of hydrogen in a compound is 1+, except when hydrogen forms compounds called hydrides with active metals, and then it is 1-.
5. The oxidation number of oxygen in a compound is 2-, except in peroxides when it is 1-, and when combined with fluorine. Then it is 2+.
6. The algebraic sum of the oxidation numbers in the formula for a polyatomic ion is equal to the charge on that ion.

Examples:

$$\overset{0}{S} + \overset{0}{O_2} \rightarrow \overset{+IV}{S}\,\overset{-II}{O_2}$$

$$\overset{+IV}{S}\,\overset{-II}{O_2} + \overset{+I}{H_2}\,\overset{-II}{O} \rightarrow \overset{+I}{H_2}\,\overset{+IV}{S}\,\overset{-II}{O_3}$$

What is a Free Radical?

- **Free Radicals** have an unpaired outer electron
- they often are identified by a dot:
  $NO_2^\bullet$ or $OH^\bullet$
- they are very reactive
- they are often formed by photolysis
- reaction between a radical and a non radical leads to formation of another radical
- reaction between two radicals leads to formation of a non radical

The Hydroxyl Radical in the Troposphere

- OH is the most important radical in the troposphere
- most decomposition processes in the troposphere start with OH attack
- lifetime of OH is about 1 s
- concentrations are very small (10^6 molec/cm^3)
- concentrations are varying very much, depending on photolysis and the concentrations of ozone and other radicals

<u>Sources of OH:</u>

1. reaction of excited oxygen atoms with water vapour:

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

   The main source of $O(^1D)$ is ozone photolysis:

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

   As a result, ozone and water vapour concentrations very much determine OH concentrations.

2. photolysis of formaldehyde:

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

$$\rightarrow H_2 + CO$$

   followed by reaction of HCO and H with O_2

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

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

   and conversion of HO_2 to OH by reaction with ozone (clean air) or NO:

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

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

3. reaction of O_3 with alkenes
4. reaction of NO_3 with aldehydes or alkenes at night

<u>Sinks of OH:</u>

1. Direct determination reactions:

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

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

2. formation of stable peroxides

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

3. reaction with NO_2 & HNO_3 in polluted regions:

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

$$OH + HNO_3 \rightarrow H_2O + NO_3$$

Determining global OH concentrations

OH concentrations vary strongly in space and time, and measurements are very difficult. Therefore, no good representation of the global OH concentrations is available from measurements. However, an estimate of these values is needed to estimate lifetimes of many species!

Idea: Take measurements of a species

- with reasonable long lifetime (→ well mixed)
- good concentration values from measurements
- with well known sources and source strengths
- with the main loss via reaction with OH

For such a species, the concentration in the troposphere can be computed as a function of the average OH concentration which then can be varied to fit the observations!

Such a species is methylchloroform CH_3CCl_3 which has only anthropogenic sources.

Principles of Reactivity in the Troposphere

Some generalized principles can be formulated that help to determine the fate of trace species in the troposphere:

A: Reaction with OH

The first step in many processes is reaction with OH:

- if reactive multiple bonds exist, than OH adds to the multiple bond if this leads to a stronger bond than before:

  $SO_2 + OH \rightarrow OSOOH$

  $CO + OH \rightarrow HOCO$

  OH does not add to multiple bonds in any fully oxidized species

- if no reactive multiple bonds exist but an H, then OH abstracts a hydrogen to form H_2O and a new radical:

  $CH_4 + OH \rightarrow CH_3 + H_2O$

  $NH_3 + OH \rightarrow NH_2 + H_2O$

  $H_2S + OH \rightarrow SH + H_2O$

  $CH_3Cl + OH \rightarrow CH_2Cl + H_2O$

B: Photolysis

Some species are photolysed in the troposphere:

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

C: Reaction of simple radicals with O_2

Simple radicals can react with O_2 to form a peroxy radical:

$CH_3 + O_2 \rightarrow CH_3OO$

D: Reaction of peroxy radicals with NO

Peroxy radicals are not as reactive as other radicals, and mostly react with NO (if present)

$HOO + NO \rightarrow OH + NO_2$

$CH_3OO + NO \rightarrow CH_3O + NO_2$

E: Abstraction of H by O_2:

Non peroxy radicals often react with O_2 forming HO_2 and a nonradical:

$CH_3O + O_2 \rightarrow CH_2O + HO_2$

$HOCO + O_2 \rightarrow OCO + HO_2$

$HCO + O_2 \rightarrow CO + HO_2$

F: Addition of O_2:

If no H can be abstracted, O_2 just adds to the radical, forming a peroxy radical:

$$RCO + O_2 \rightarrow ROCOO$$

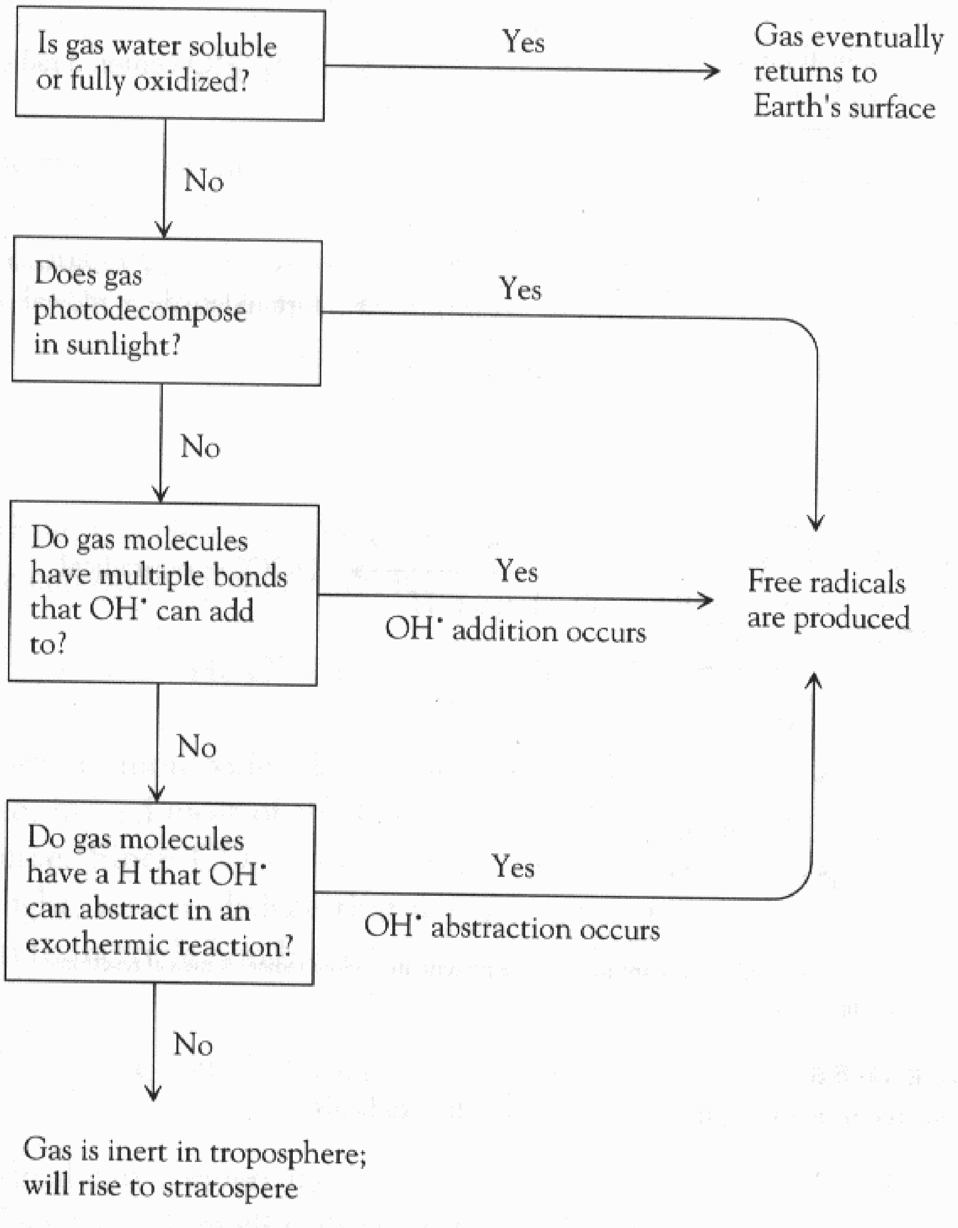
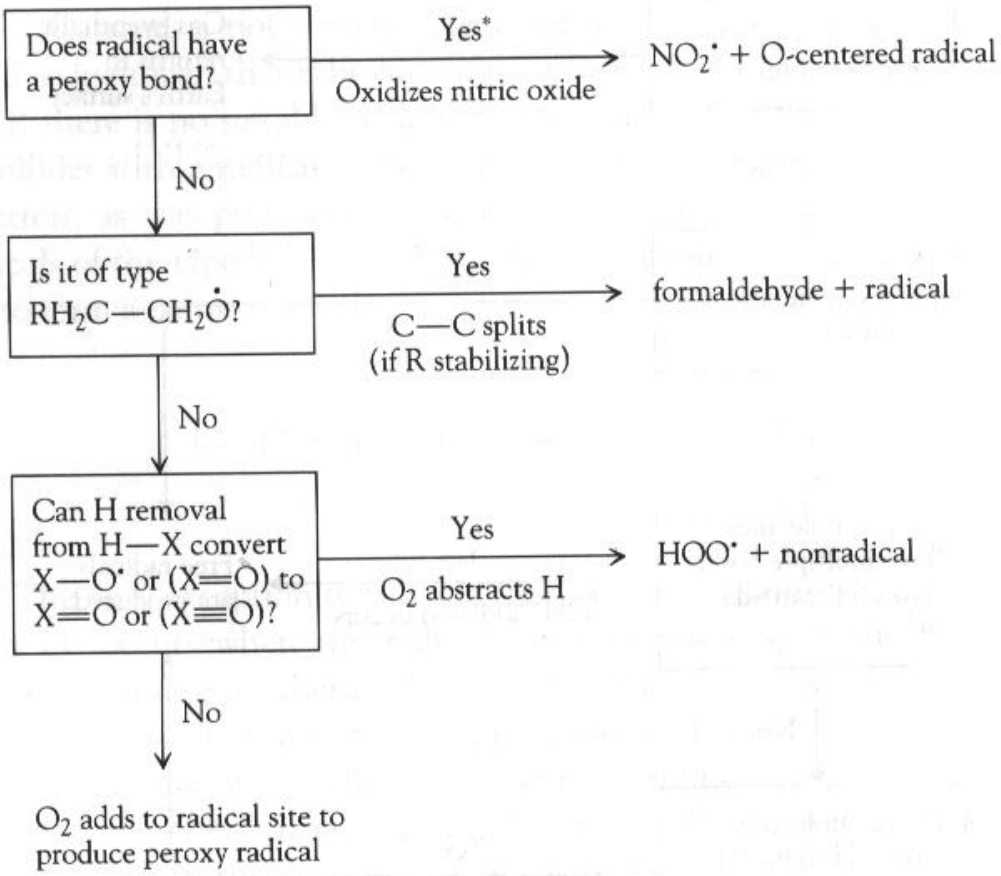


FIGURE 3-6A
Decision tree illustrating the fate of gases emitted into air.



*Under conditions with significant nitric oxide present and before radical + radical reactions become important.

FIGURE 3-6B
Decision tree illustrating the fate of airborne free radicals.

Tropospheric Oxidation of Methane

Sources of CH_4:

- anerobic biological decay
- combustion sources
- natural gas leaks

$$\begin{array}{ll}
CH_4 + OH & \rightarrow CH_3 + H_2O \\
CH_3 + O_2 + M & \rightarrow CH_3OO + M \\
CH_3OO + NO & \rightarrow NO_2 + CH_3O \\
CH_3O + O_2 & \rightarrow CH_2O + HO_2 \\
HCHO + h\nu & \rightarrow H + HCO \\
H + O_2 + M & \rightarrow HO_2 + M \\
HCO + O_2 & \rightarrow CO + HO_2 \\
CO + OH + M & \rightarrow HOCO + M \\
HOCO + O_2 & \rightarrow CO_2 + HO_2
\end{array}$$

$$CH_4 + 5O_2 + NO + 2OH \rightarrow$$
$$CO_2 + H_2O + NO_2 + 4HO_2$$

or with conversion of HO_2 to OH via NO:

$$CH_4 + 5O_2 + 5NO \rightarrow$$
$$CO_2 + H_2O + 5NO_2 + 2OH$$

Summarizing the methane oxidation, it turns out that

- CH_4 and NO are oxidized in parallel
- OH is being produced in this oxidation
- formaldehyde and CO are intermediate products
- the first reaction step (reaction of OH with methane) is slow, but the rest of the oxidation is fast
- lifetime of CH_4 is large due to the slow first step → CH_4 accumulates in the atmosphere as a result of anthropogenic emissions

Methane oxidation is taken as a model for the oxidation of more complex hydrocarbons that are oxidized in similar but more complex chain reactions.

Ozone in the Troposphere

Some ozone is transported from the stratosphere down to the troposphere, and this accounts for roughly half the observed tropospheric O_3.

The only known way of producing ozone in the troposphere is photolysis of NO_2.This NO_2 is produced by the oxidation of NO by the peroxy radicals, linking hydrocarbon oxidation with ozone production:

Ozone production:

$$NO_2 + h\nu \rightarrow O + NO$$
$$O + O_2 + M \rightarrow O_3 + M$$
$$OH + CO \rightarrow H + CO_2$$
$$H + O_2 + M \rightarrow HO_2 + M$$
$$HO_2 + NO \rightarrow OH + NO_2$$

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

Similar schemes can be written using other peroxy radicals RO_2. Each molecule of CO can create one ozone molecule while each molecule of CH_4 creates 3.5 ozone molecules.

Ozone loss:

$HO_2 + O_3 \rightarrow OH + O_2$
$CO + OH \rightarrow H + CO_2$
$H + O_2 + M \rightarrow HO_2 + M$

$CO + O_3 \rightarrow CO_2 + O_2$

At low [NO] / [O3], ozone loss can dominate ozone production! Therefore, NOx concentrations determine, if ozone builds up or is destroyed at a certain level of hydrocarbons!

Today, only very remote regions have low enough NOx concentrations to serve as ozone sinks!

Importance of NOx

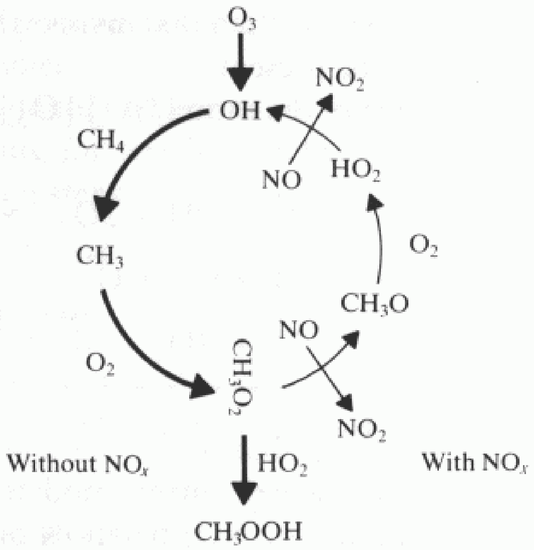


Fig. 5.2. Essential steps in tropospheric methane oxidation. The heavier arrows on the left-hand side of the diagram indicate the steps that can occur in the absence of NO_x. With NO_x present, the processes on the right-hand side can close a loop, with regeneration of OH and oxidation of NO to NO_2 (from a diagram devised by M. E. Jenkin.)

The presence of NOx in the troposphere closes the loop and enables recycling of OH and production of NO_2 which in turn can start ozone formation.

Sources of NOx:

- microbial actions in soil
- oxidation of biogenic NH_3
- lightning
- biomass burning
- combustion

Air Pollution

There is no such thing as “clean air” - trace species have always been present in the atmosphere from “**Natural Pollution**”:

- volcanic eruptions
- plant emissions
- fires
- sea spray
- dust

Human activities always added to pollution by

- agriculture (erosion, fires, changes in plant and animal population)
- industrial activities
- burning processes (heating, energy production, transport, biomass burning)

In general, one distinguish **Primary Pollutants** that are emitted directly such as SO_2 or NO and **Secondary Pollutants** (O_3, H_2SO_4) that are formed from primary pollutants. often, secondary pollutants have a larger impact on environment and health than primary pollutants!

Photochemical Smog

Observations (LA, mid 40s):

- haze in summer on sunny days
- damage on rubber and plastics
- visible damage to plants
- eye and nose irritation, respiratory problems, short breath, headache in humans

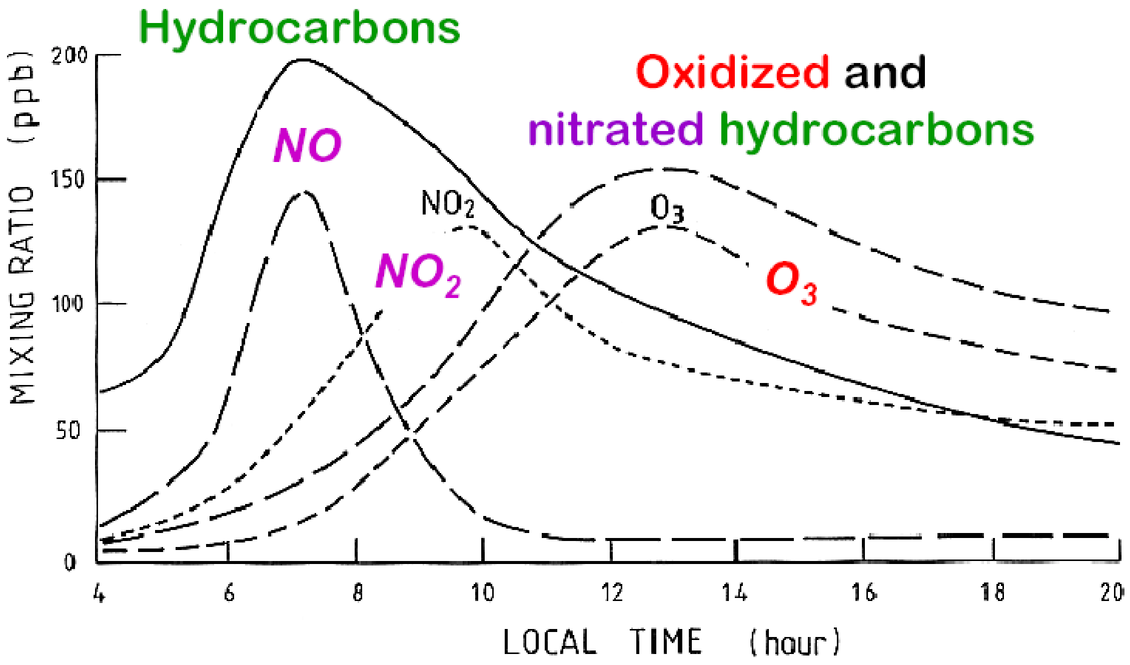
Ingredients:

- high temperature
- intense sun
- stable inversion
- high density of cars

Conclusions:

- pollutants at least partly emitted by cars can lead to formation of oxidizing species such as O_3
- pollutants accumulating in inversion layers augment the problem
- formation of pollutants seems to be a photochemical process

For a typical ozone smog day, the diurnal variation of pollutants follow a certain pattern:



- peaks of NO and hydrocarbons in the morning
- formation of NO2 at the expense of NO
- formation of aldehydes at the expense of hydrocarbons
- formation of ozone
- reduction of concentrations in the evening

What are the mechanisms explaining these observations?

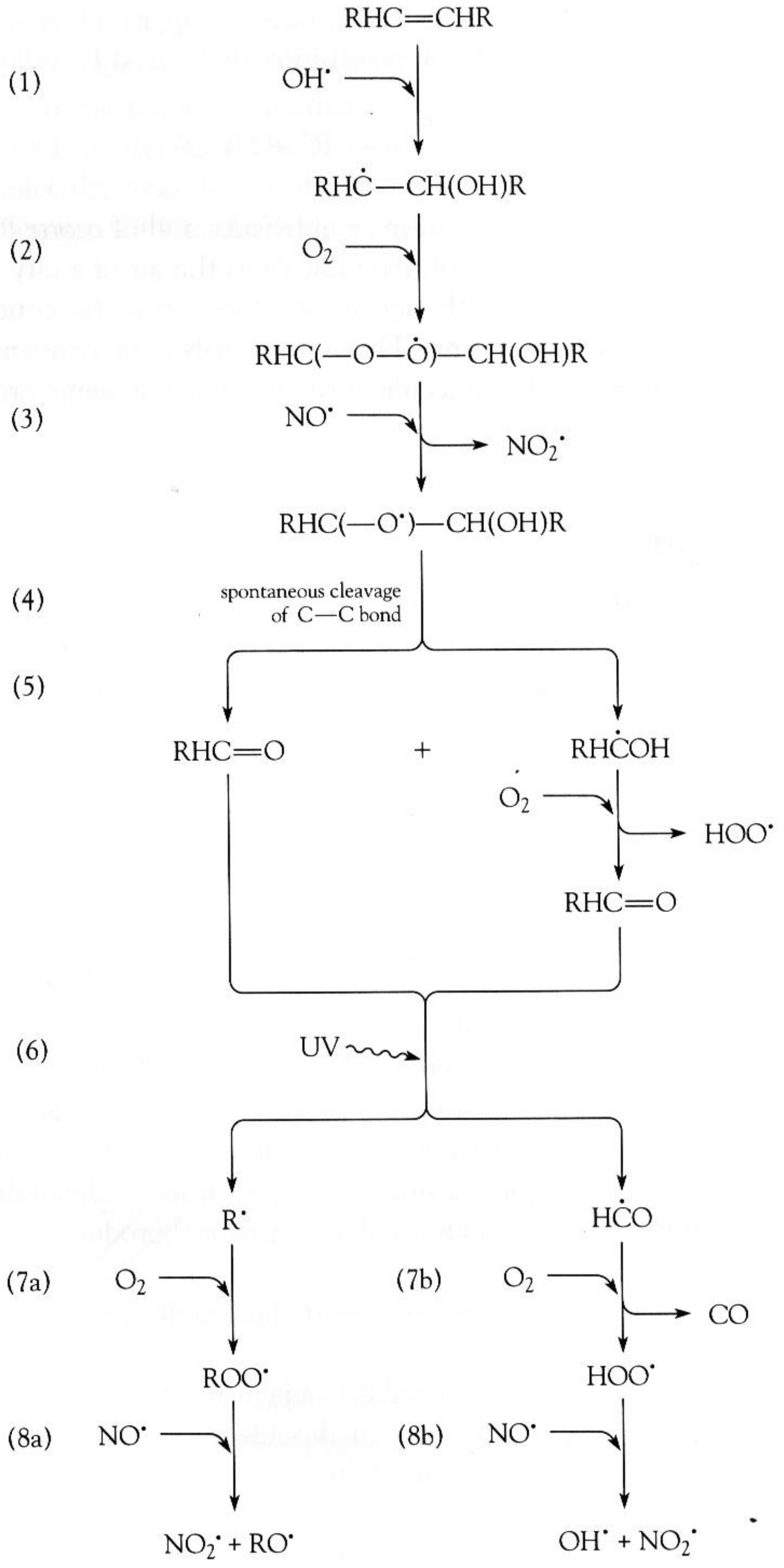
In the sunlit atmosphere with NOx but without hydrocarbons, ozone concentrations are in photostationary state:

$$
\begin{aligned}
NO_2 + h\nu &\rightarrow O + NO \\
O + O_2 + M &\rightarrow O_3 + M \\
NO + O_3 &\rightarrow NO_2 + O_2 \\
\hline
NO_2 + O_2 + h\nu &\leftrightarrow NO + O_3
\end{aligned}
$$

Ozone concentrations are larger if there is more sun, and smaller in the presence of NO (ozone titration).

Ozone concentrations can be enhanced if NO is reacting with other species such as peroxyradicals to reform NO_2 without destroying O_3.

Large amounts of radicals are formed in the oxidation of hydrocarbons, an exaggerated form of the methane oxidation in the clean atmosphere. As an example, hydrocarbons containing a double bond such as ethylene ($H_2C=CH_2$) are treated:


RHC═CHR
(1)
OH˙
RHĊ—CH(OH)R
(2)
O2
RHC(—O—Ȯ)—CH(OH)R
(3)
NO˙
NO2˙
RHC(—O˙)—CH(OH)R
(4)
spontaneous cleavage of C—C bond
(5)
RHC═O
+
RHĊOH
O2
HOO˙
RHC═O
(6)
UV
R˙
HĊO
(7a)
O2
(7b)
O2
CO
ROO˙
HOO˙
(8a)
NO˙
(8b)
NO˙
NO2˙ + RO˙
OH˙ + NO2˙

Thus, in the presence of NOx, hydro carbons such as RHC=CHR are converted into two aldehydes while NO_2 and HO_2 is formed.

Later, the aldehydes are photolysed, forming RO radicals and more NO_2 and OH.

As a result, radical concentrations are hugely increased by mid-afternoon, and radical-radical reactions can no longer be neglected.

1) HONO

$OH + NO \rightarrow HONO$

$NO + NO_2 + H_2O \rightarrow 2HONO$

at night, HONO is stable

at dawn, HONO is photolysed ($\lambda < 400$ nm) to release OH + NO

2) H_2O_2

$2OH \rightarrow H_2O_2$

$2O_2 \rightarrow H_2O_2 + O_2$

H_2O_2 is soluble in water and can be a sink for OH.

3) PAN

$RHCO + OH \rightarrow RCO + H_2O$

$RCO + O_2 \rightarrow RCOO_2$

$RCOO_2$ can either react with NO or add NO_2:

$RCOO_2 + NO_2 \rightarrow RCOO_2NO_2$

with R = CH_3:

CH_3COO_2NO = PAN (Peroxy Acetyl Nitrate)

PAN is a very strong lachrymator and irritates eyes and nose. It is stable at low temperatures and decomposes at higher temperatures. It therefore can transport NOx over long distances in the cold free troposphere!

4) HNO_3

$NO_2 + O_3 \rightarrow NO_3 + O_2$

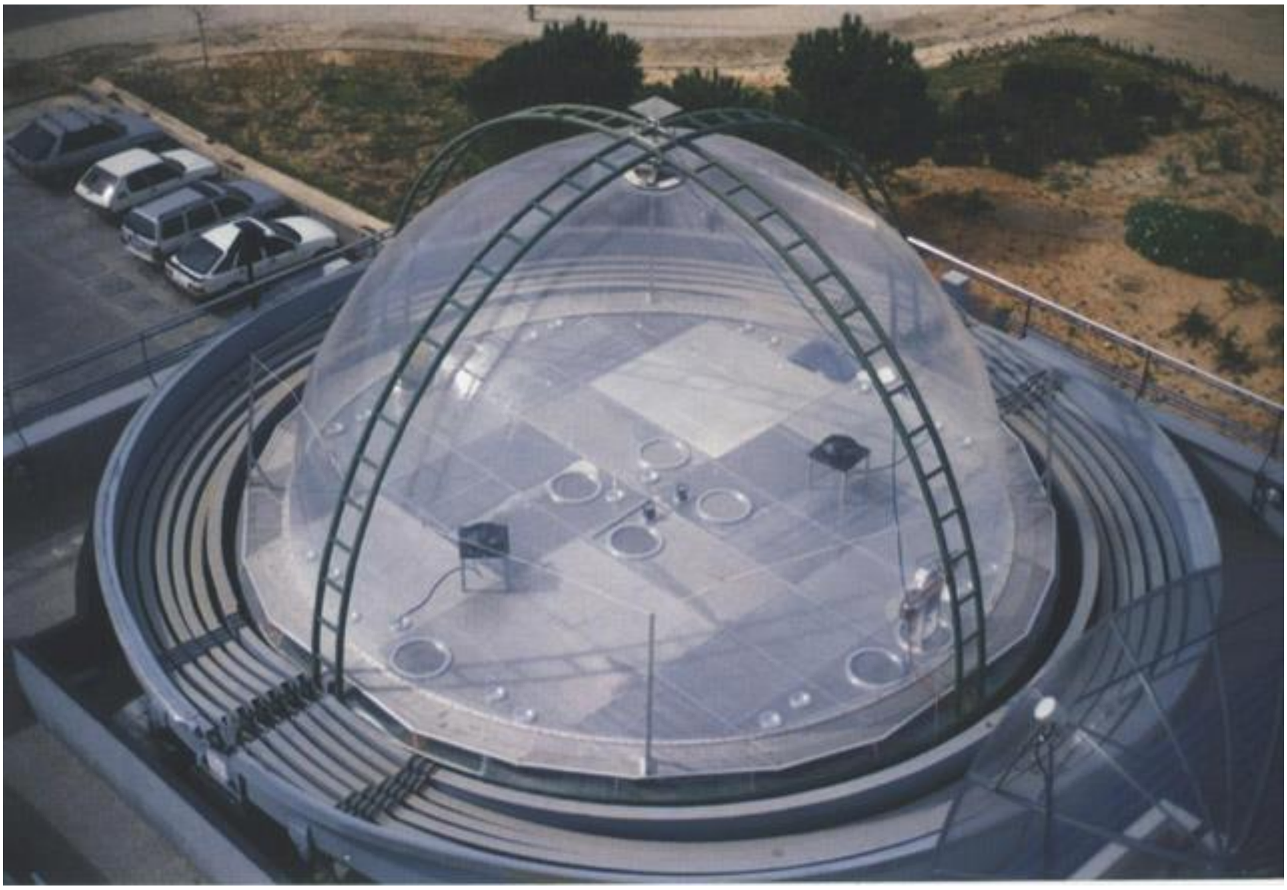
$NO_2 + NO_3 \rightarrow N_2O_5$

$N_2O_5 + H_2O \rightarrow 2HNO_3$

Nitric acid is removed from the atmosphere by rain out.

Smog Chamber Measurements

Some confidence in the proposed mechanisms can be gained by experiments in controlled environments (smog chambers) packed with instrumentation to measure different species as they are formed in photochemical smog such as EUPHORE:



Example 1: Irradiation of an olefin-NOx-air mixture:

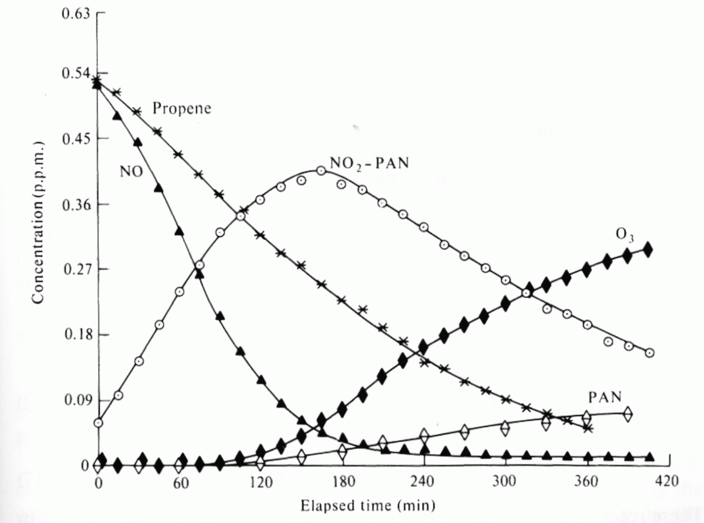


Fig. 5.10. Concentration–time profiles of the major primary and secondary pollutants during irradiation of 0.53 p.p.m. propene and 0.59 p.p.m. NO_x in 1 atm of purified air in an evacuable smog chamber (Source as for Fig. 5.8).

Example 2: Impact of HCHO on hydrocarbon-Nox-air mixtures:

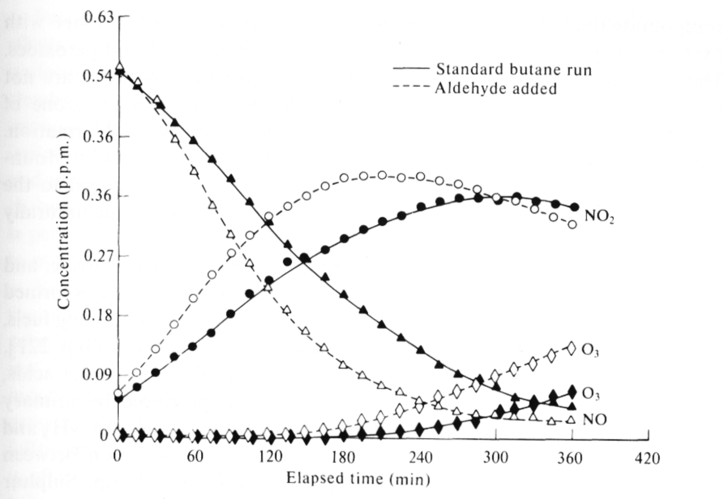


Fig. 5.11. Concentration–time profiles for some primary and secondary pollutants during irradiation of 2.2 p.p.m. *n*-butane and 0.61 p.p.m. NO_x in an evacuable smog chamber without added aldehyde (——) and with 0.13 p.p.m. HCHO added (---). (Source as for Fig. 5.8).

Tropospheric Ozone: Trends

Measurements from the 19 century show, that at least in Europe ozone values were lower by a factor of three to four at that time:

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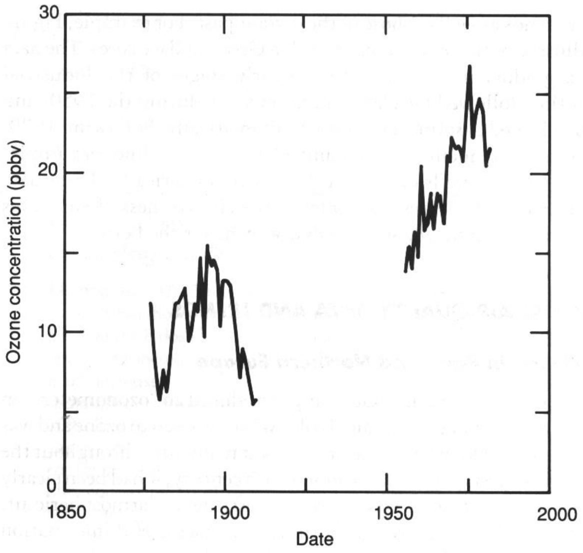


Figure 13.10 A comparison of 1876–1907 surface ozone volume mixing ratios at Montsouris (near Paris) with those at Arkona, Germany, 1956–1982. (Reproduced with permission from A. Volz and D. Kley, Evaluation of the Montsouris series of ozone measurements made in the nineteenth century, *Nature, 332*, 240–242. Copyright 1988 by Macmillan Magazines Limited.)

In most places on earth, a continues increase in surface ozone was observed in the last decades:

Regional Air Quality Data and Trends **265**

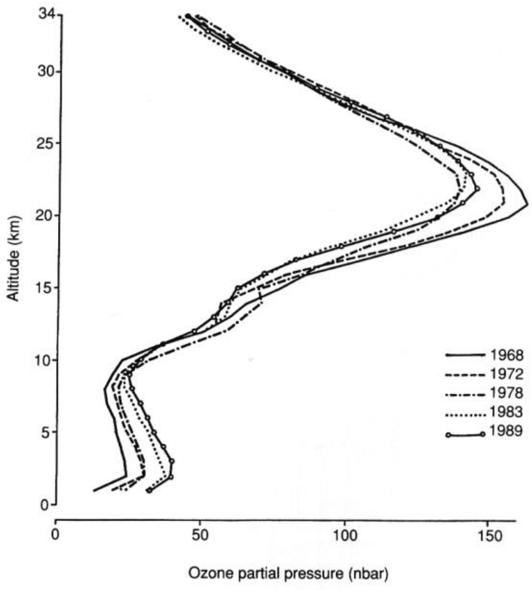


Figure 13.11 Tropospheric and stratospheric ozone annual average concentrations (expressed as partial pressure in nbar = 10^{-9} bar) measured at Hohenpeissenberg, Germany, during the period 1967–1988. (W. Attmannspacher, private communication, 1989.)

Ozone Smog outside of cities

Measurements show, that large ozone concentrations are observed not only in polluted cities, but also in rural areas downwind of cities. In fact, in Europe and the US, the largest ozone concentrations are often found outside the cities!

Reasons:

- transport of pollutants from the cities
- O3 has a long lifetime, but NO a short lifetime
- in the cities, NO from the evening rush hour titrates ozone to lower values in the evening
- ozone formation continues in rural areas, building concentrations up over several days
- ozone loss is largest close to the ground, but transport often coincides with uplifting
- natural hydrocarbons (isoprenes, terpenes, pinenes) can compete with anthropogenic hydrocarbons in some regions and lead to ozone formation if NOx is present

Health Effects

Many pollutants have a direct impact on humans:

- O_3: irritation of eyes, lungs and nose, short breath, coughing, in particular when exercising. Largest impact on children and asthmatics, but also on young, healthy people
- HCHO: irritation, infects, allergies, possibly also carcinogenic
- NO_2: impact on respiratory system, in particular for children
- CO: binds to haemoglobin in blood and impairs ability for O_2 transport. headache, fatigue, ... at high concentrations: death
- particles: impact on health system, largest correlation of all pollutants with premature deaths

Only ozone concentrations are large enough outdoors to have an impact, all other pollutants have higher concentrations indoors in certain situations.

Smoking is the most important indoor pollution source!

Control Strategies

Two strategies can be taken:

1. reduction in NOx emissions (catalytic converters, reduction in flame temperature, speed limits for cars, ...)
2. reduction in VOC emissions (catalytic converters, changes in fuel formulation, emission reduction at fuel stations, reductions in solvent use, ...)

Depending on the relative concentrations, O_3 formation is NOx or VOC limited, and reductions of one or the other source seem more appropriate. However, in some cases, a reduction in NOx can actually increase ozone concentrations:

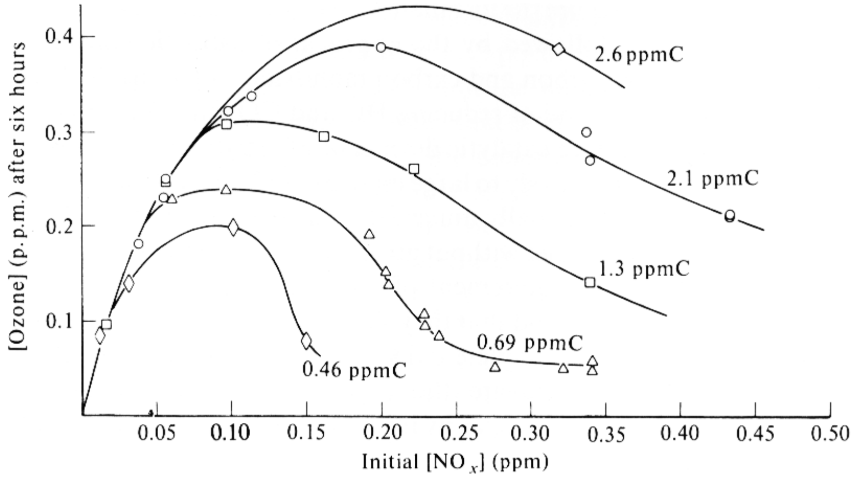
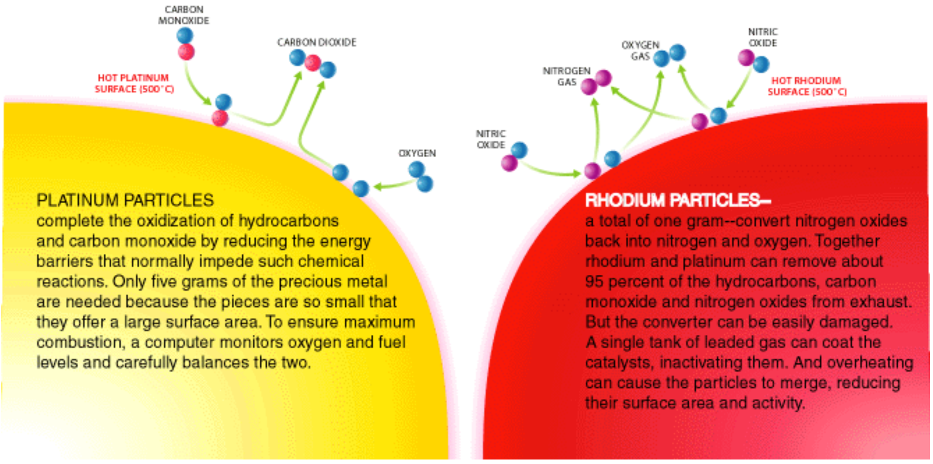


Fig. 5.12. Ozone concentration reached after a 6 h irradiation of NO_x with a surrogate mixture of hydrocarbons simulating ambient air, with varying initial concentrations and ratios of HC/NO_x. (Source as for Fig. 5.8).

Catalytic Converter

In principle, if fuel would be fully oxidized, cars should only emit H_2O and CO_2. However, in practice not all hydrocarbons are oxidized and NO is formed from N_2 and O_2. Catalytic converters strongly reduce car emissions by

- oxidizing hydrocarbons and CO on platinum
  $2CO + O_2 \rightarrow 2\ CO_2$
- converting NO to N_2 and O_2 using H_2 and CO from the exhausts on rhodium:
  $2NO \rightarrow N_2 + O_2$



PLATINUM PARTICLES
complete the oxidization of hydrocarbons and carbon monoxide by reducing the energy barriers that normally impede such chemical reactions. Only five grams of the precious metal are needed because the pieces are so small that they offer a large surface area. To ensure maximum combustion, a computer monitors oxygen and fuel levels and carefully balances the two.

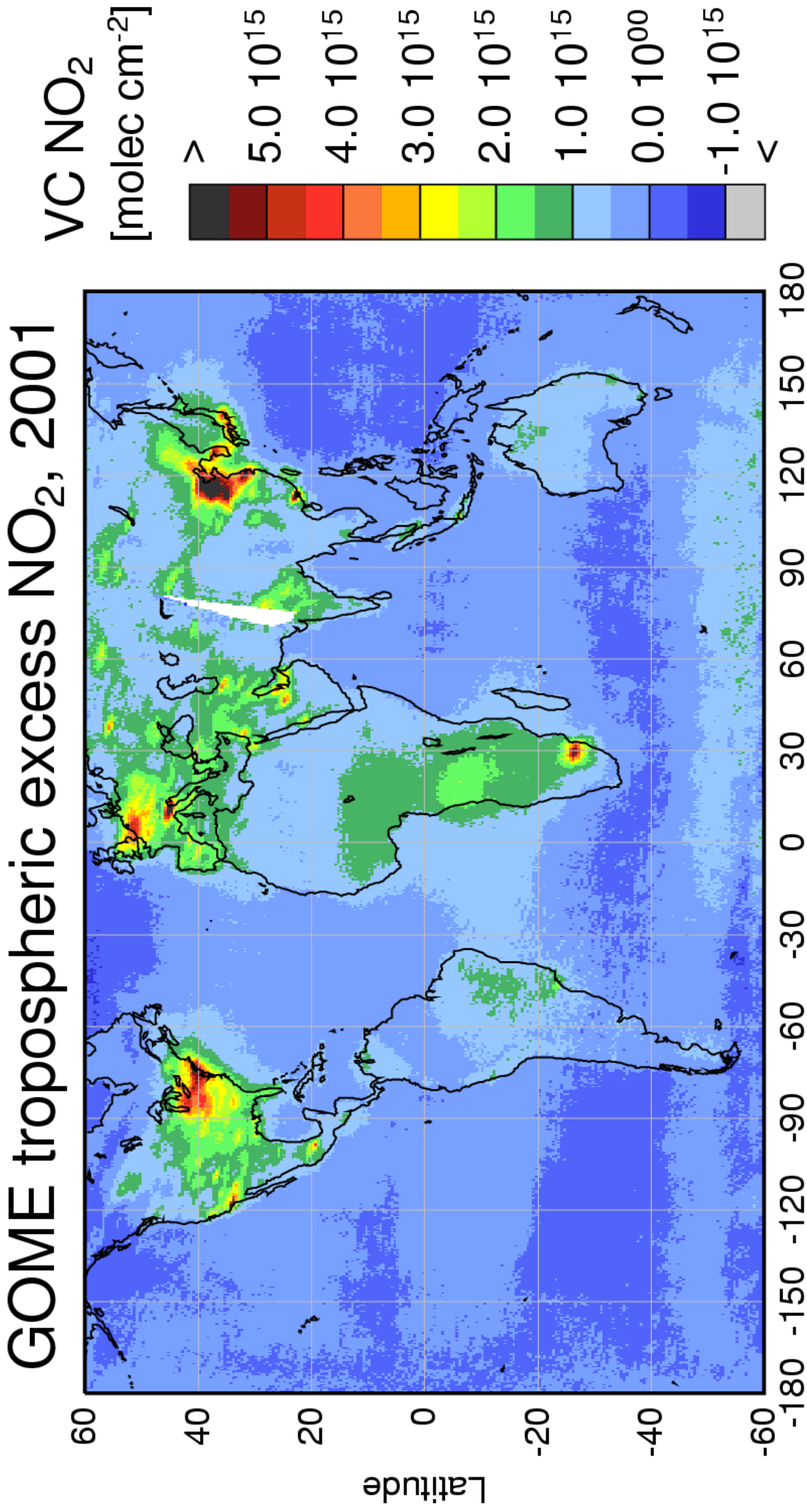
RHODIUM PARTICLES–
a total of one gram--convert nitrogen oxides back into nitrogen and oxygen. Together rhodium and platinum can remove about 95 percent of the hydrocarbons, carbon monoxide and nitrogen oxides from exhaust. But the converter can be easily damaged. A single tank of leaded gas can coat the catalysts, inactivating them. And overheating can cause the particles to merge, reducing their surface area and activity.

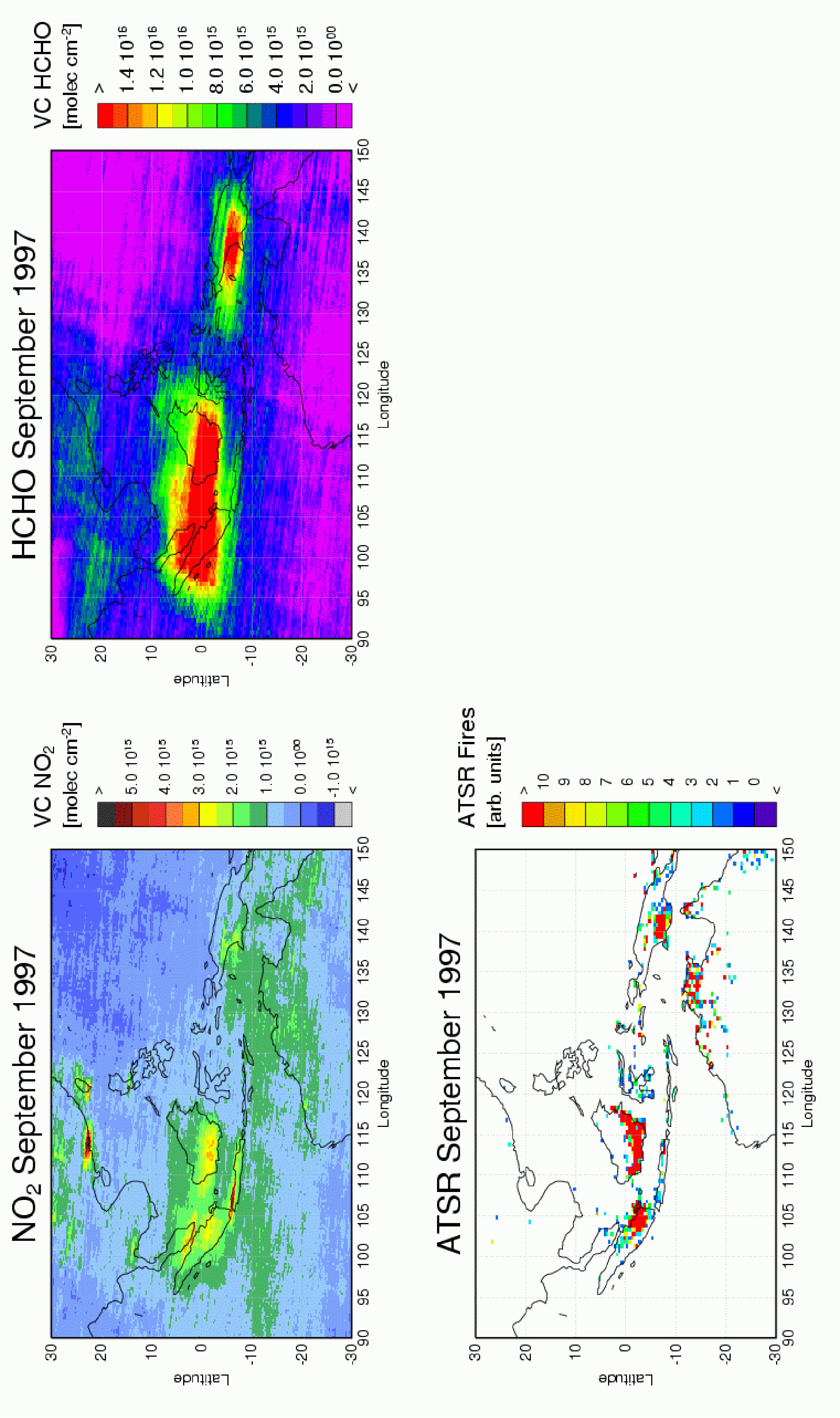
Catalytic converters are very effective (95%), so that today, 50% of all car emissions are from 10% of the cars (those having no or not working converters).

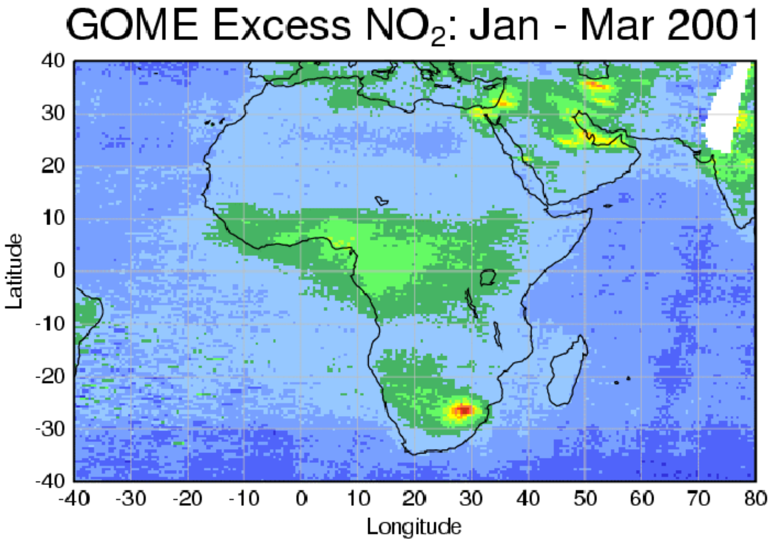
Air pollution: The Global View

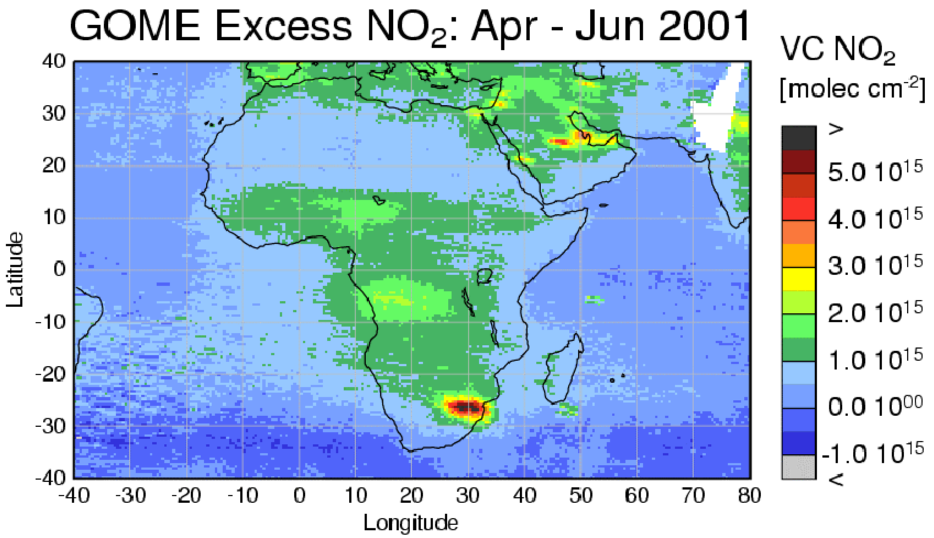
From satellite measurements (GOME, TOMS, MOPPIT), a global picture of air pollution is emerging, showing that

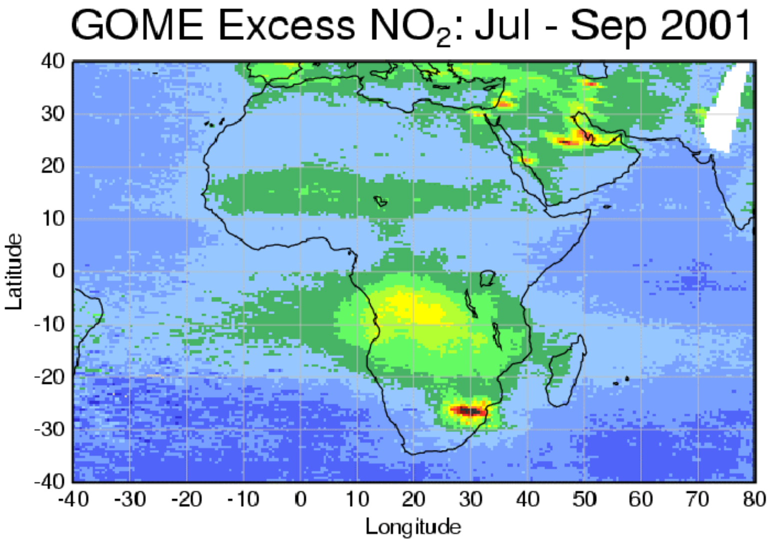
- NOx concentrations are largest in the industrialized ergions
- NOx concentrations are also large in regions of biomass burning
- HCHO concentrations are large over rain forests (isoprene emissions) but also in regions of intense biomass burning
- CO concentrations are larger in the Northern hemisphere than in the the Southern Hemisphere, China being a strong source. However, in the biomass burning season, CO concentrations are much larger than in all other places
- tropospheric ozone is high in NH summer, but very large concentrations are also observed in regions of biomass burning

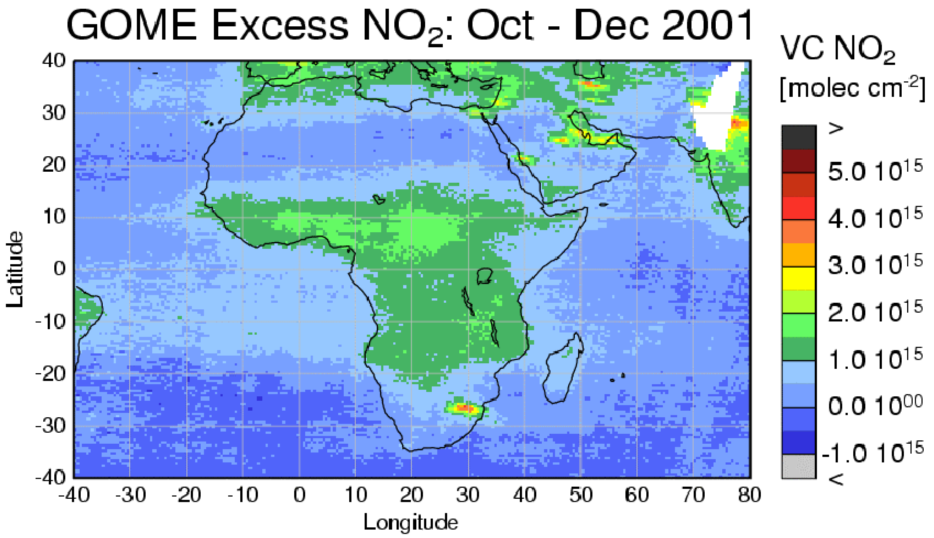

GOME tropospheric excess NO2, 2001
VC NO2
[molec cm-2]
>
5.0 10^15
4.0 10^15
3.0 10^15
2.0 10^15
1.0 10^15
0.0 10^00
-1.0 10^15
<
Latitude
60
40
20
0
-20
-40
-60
Longitude
-180
-150
-120
-90
-60
-30
0
30
60
90
120
150
180


NO$_2$ September 1997
VC NO$_2$
[molec cm^{-2}]
>
5.0 10^{15}
4.0 10^{15}
3.0 10^{15}
2.0 10^{15}
1.0 10^{15}
0.0 10^{00}
-1.0 10^{15}
<
HCHO September 1997
VC HCHO
[molec cm^{-2}]
>
1.4 10^{16}
1.2 10^{16}
1.0 10^{16}
8.0 10^{15}
6.0 10^{15}
4.0 10^{15}
2.0 10^{15}
0.0 10^{00}
<
ATSR September 1997
ATSR Fires
[arb. units]
>
10
9
8
7
6
5
4
3
2
1
0
<
Latitude
30
20
10
0
-10
-20
-30
Longitude
90
95
100
105
110
115
120
125
130
135
140
145
150


GOME Excess NO_2: Jan - Mar 2001


GOME Excess NO_2: Apr - Jun 2001


GOME Excess NO_2: Jul - Sep 2001


GOME Excess NO_2: Oct - Dec 2001

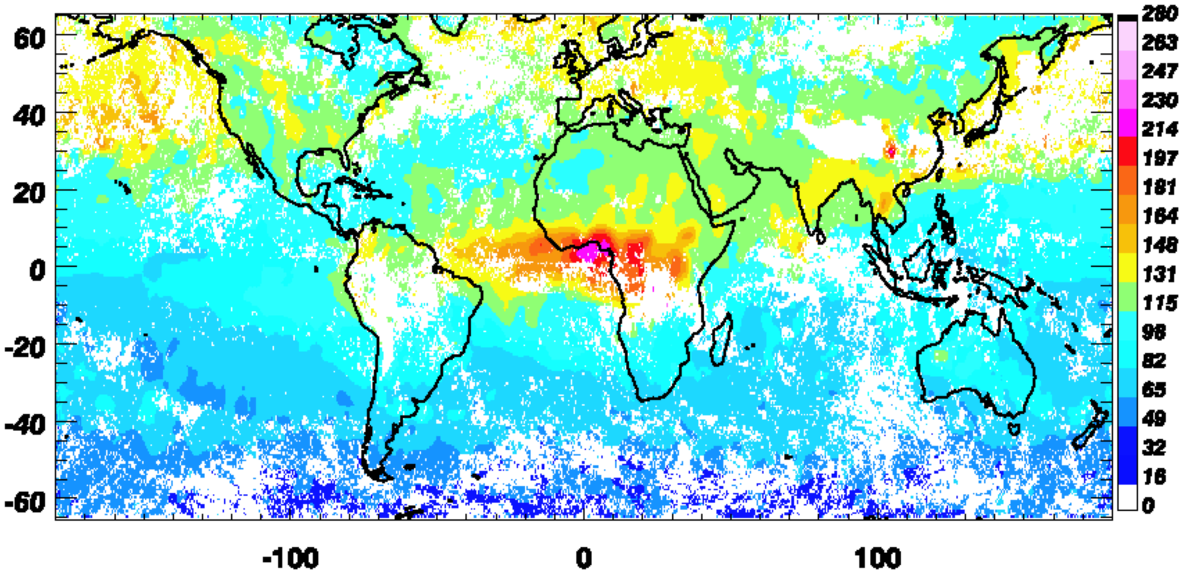
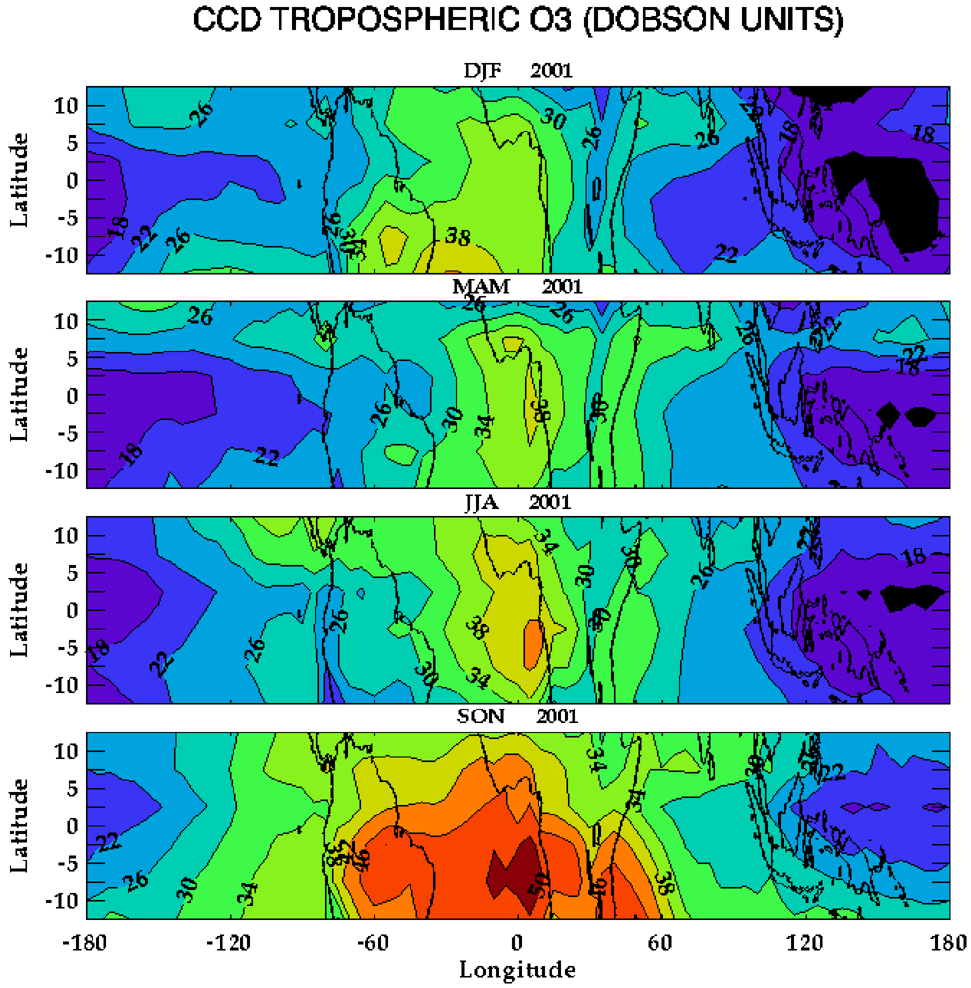


Figure 4.
MOPITT CO (ppbv) global mean distribution at 700 hPa for January 20 - 27, 2001.
Data resolution is 0.5∞longitude x 0.5∞latitude.


CCD TROPOSPHERIC O3 (DOBSON UNITS)

Acids and Bases

An **Acid** is a proton donor: $HA \rightarrow H^+ + A^-$ (HCl)

A **Base** is a proton acceptor: $B + H^+ \rightarrow BH^+$ (NH_3)

This is independent of solvent, but usually that is H_2O.

An acid solved in H_2O leads to the following equilibrium:

$HA(aq) + H_2O(l) \leftrightarrow A^-(aq) + H_3O^+(aq)$

$$K = \frac{[H_3O^+][A^-]}{[HA][H_2O]}$$

(more accurate: activities instead of concentrations, but for small ion concentrations the difference is small)

A **Conjugate Base** is A^- if HA is the acid

A base solved in H_2O leads to the following equilibrium:

$B(aq) + H_2O(l) \leftrightarrow BH^+(aq) + OH^-(aq)$

$$K = \frac{[BH^+][OH^-]}{[B][H_2O]}$$

A **Conjugate Acid** is BH^+ if B is the base

The conjugate acid in H_2O is also in equilibrium:

$BH^+(aq) + H_2O(l) \leftrightarrow B(aq) + H_3O^+(aq)$

$$K = \frac{[H_3O^+][B]}{[BH^+][H_2O]}$$

We therefore can unify treatment by looking only at acids and conjugate acids:

$Acid(aq) + H_2O(l) \leftrightarrow Base(aq) + H_3O^+(aq)$

$$K = \frac{[H_3O^+][\text{Base}]}{[\text{Acid}][H_2O]}$$

The concentration of water can be set to unity and the **Acidity Constant** K_a be defined:

$$K_a = \frac{[H_3O^+][\text{Base}]}{[\text{Acid}]}$$

K_a varies strongly, therefore the **pK** is defined, based the log base 10 of the acidity constant:

$\mathrm{pK_a} = -\lg K_a$

Water is **Amphoteric** meaning that it can act both as an acid and as a base:

$HF(aq) + H_2O(l) \rightarrow H_3O^+(aq) + F^-(aq)$

$H_2O(l)\ \ NH_3(aq) \rightarrow NH_4^+(aq) + OH^-(aq)$

Autoprotolysis of water: H_2O acts both as acid and as base:

$H_2O(l) + H_2O(l) \leftrightarrow H_3O^+(aq) + OH^-(aq)$

$K_w = [H_3O^+][OH^-]$
$pK_w = -\lg K_w = 14$

$\rightarrow [H_3O^+] = [OH^-]$ in pure water

$[H_3O] = K_w^{1/2} = 1.004 \times 10^{-7}$ (at 298 K)

Definition:
$pH = -\lg [H_3O^+]$
$pOH = -\lg [OH^-]$

$pK_w = pH + pOH = 14$

The pH describes how acid a solution is:

$pH < 7$ acid solution
$pH = 7$ neutrality
$pH > 7$ basic solution

A **Strong Acid** is strong proton donor that is completely ionised and has an acidity constant of infinity in water (HCl, H_2SO_4).

A **Weak Acid** is not completely ionise in water and has an acidity constant $K < 1$.

A strong acid has a weak conjugate base and vice versa.

Vapour Pressure of Solutions

How does the vapour pressure of a species over a solution depend on its concentration in the solution?

A: Ideal Solutions:

In first approximation, the vapour pressure should be proportional to the mole fraction χ of the species and the vapour pressure over the pure substance p_A^*:

Raoult's Law: $p_A = \chi_A \, p_A^*$

- valid for some solutions, in particular of similar species
- valid if approaching pure substance

B: Ideal dilute Solutions:

For dilute solutions, the vapour pressure is proportional to the mole fraction, but the slope is different:

Henrys Law: $p_B = \chi_B K_B$

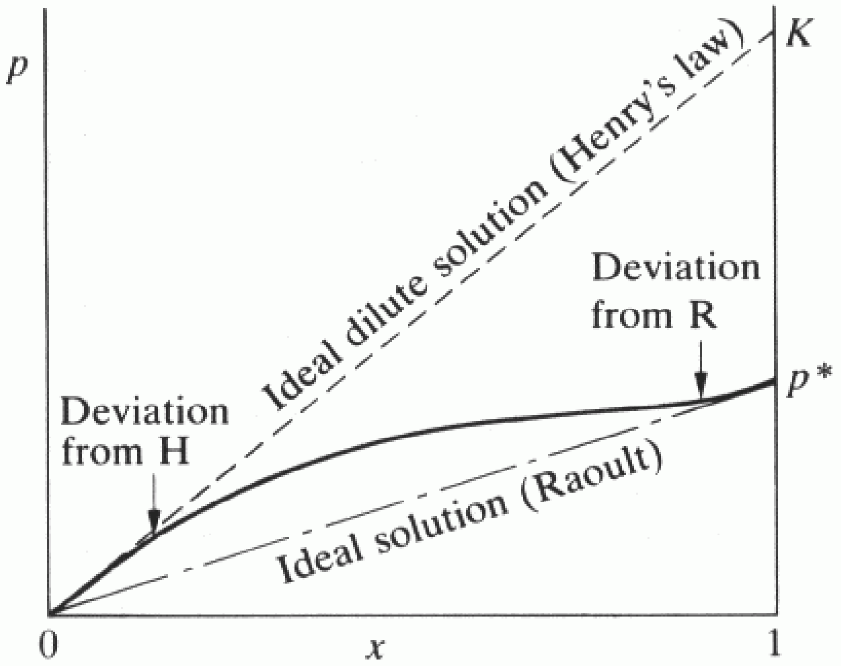


Fig. 7.3 When a component (the solvent) is nearly pure, it behaves according to Raoult's law and has a vapour pressure that is proportional to mole fraction with a slope p^*. When it is the minor component (the solute) its vapour pressure is still proportional to the mole fraction, but the constant of proportionality is now K. This is Henry's law.

Atmospheric Sulphur Cycle:

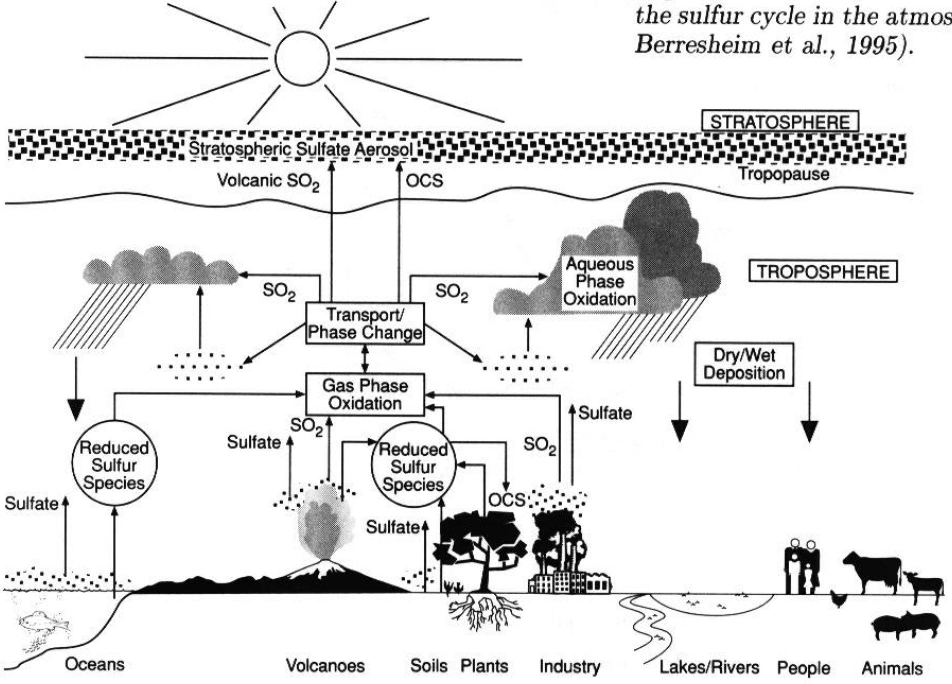


Figure 5.32. *Schematic diagram of the sulfur cycle in the atmosphere (from Berresheim et al., 1995).*

Sources

Volcanoes	SO2, H2S, OCS	7 - 10
Vegetation and soil	H2S, DMS, OCS, CS2, DMDS	0.4-1.2
Biomass burning	SO2, OCS, H2S	2-4
Ocean	DMS, OCS, CS2, H2S	10 - 40
Anthropogenic	SO2, sulphates	88 - 92

Sinks

Dry deposition	SO2, sulphates	50 - 75
Wet deposition	SO2, sulphates	50 - 75

(flux in TgS / yr)

SO_2 in the Atmosphere

Sources of SO_2

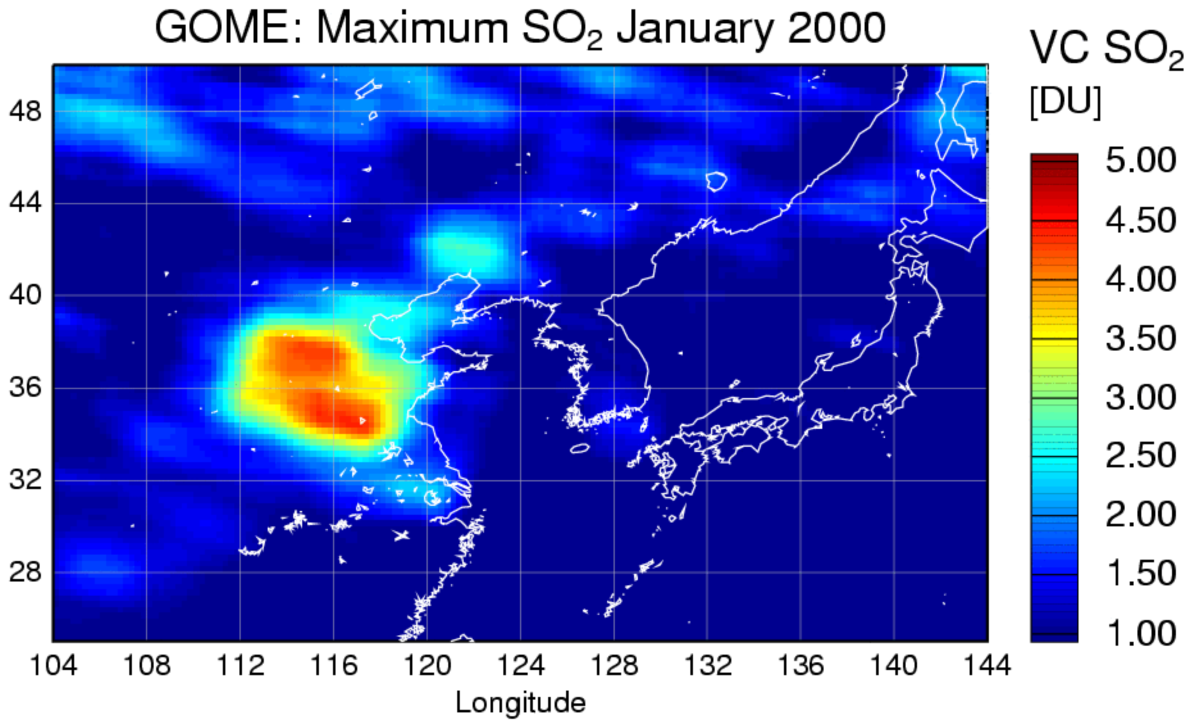
- volcanoes
- oxidation of sulphur gases produced by decomposition of plants
- combustion of coal (1 – 15% sulphur content)
  50% trapped in direct inclusion
  50% bonded to C
- emissions of refineries of oil and natural gas in the form of SO_2, H_2S, CH_3SH, $(CH_3)_2S$, CH_3SSCH_3
- nonferrous smelting industry such as
  $2NiS + 3O_2 \rightarrow 2NiO + 2SO_2$

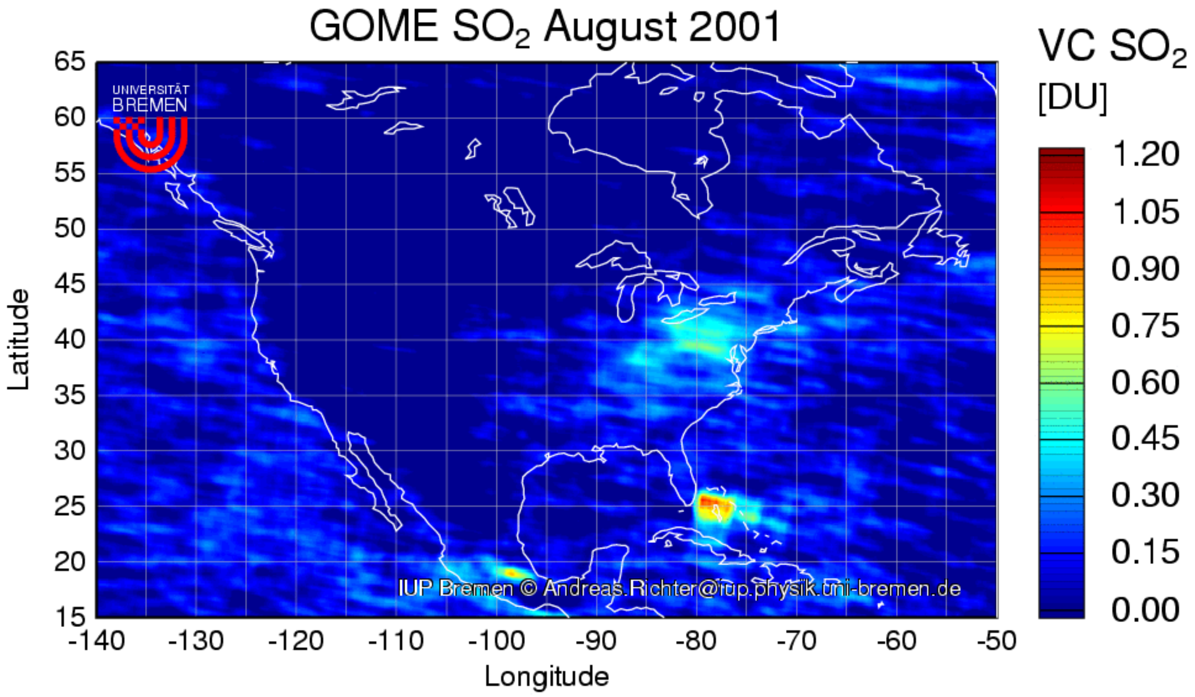
Today, anthropogenic emissions are larger than natural emissions!

Main anthropogenic source regions:

- China (increasing (?))
- Eastern Europe and Russia (reducing)
- US and Canada
- Europe

SO_2 as measured from space





Approaches to Reducing SO_2 Pollution

- high stacks (up to 400m!) => local improvements, but overall deterioration due to
    - reduction in dry deposition
    - long range transport
- change to other fuels such as gas (expensive, resources are limited)
- in refineries: Claus reaction

  $2H_2S + SO_2 \rightarrow 3S + H_2O$
- in smelting industry: conversion to H_2SO_4

  $2SO_2(g) + O_2(g) \rightarrow 2SOt(g)$

  $SO_3(g) + H_2O(a) \rightarrow \ldots \rightarrow H_2SO_4(aq)$
- if SO_2 is dilute, direct oxidation is not feasible, and Instead an acid-base reaction is used (**Scrubber**)

  $CaCO_3 + SO_2 \rightarrow CaSO_3 + CO_2$

  $CaSO_3 + ½\ O_2 \rightarrow CaSO_4$

  where $CaCO_3$ is supplied as wet limestone through which SO_2 is passed; calcium sulphate is buried or recycled

Oxidation of Atmospheric SO_2

Photolysis of SO_2 is not possible in the troposphere ($\lambda < 200$ nm). Once released to the atmosphere, SO_2 can be oxidised through two pathways: in the gas phase or in the liquid phase

Homogeneous gas phase oxidation of SO_2

$SO_2 + OH \rightarrow HSO_3$

$HSO_3 + O_2 \rightarrow SO_3 + HO_2$

$SO_3 + H_2O \rightarrow H_2SO_4(g)$

$H_2SO_4(s) \rightarrow H_2O \rightarrow H_2SO_4(aq)$

$HO_2 + NO \rightarrow NO_2 + OH$

$SO_2 + NO + O_2 \rightarrow H_2O \rightarrow NO_2 + H_2SO_4(aq)$

in effect, a co-oxidation of SO_2 and NO takes place

- in standard air, a few % of SO_2 are oxidized per hour
- much more is oxidized in polluted conditions
- deposition remains main sink for SO_2

Aqueous Phase Oxidation of SO_2

SO_2 has low solubility, but some SO_2 is still solved as soon as clouds, fog or mist are present

$$SO_2(g) + H_2O(aq) \leftrightarrow H_2SO_3\ (aq)$$

The ratio between H_2SO_3 concentration and SO_2 partial pressure is given by Henrys law:

$$K_H = \frac{\text{equilibrium molar fraction in liquid phase}}{\text{partial pressure in gas phase}}$$

$$K_H = \frac{[H_2SO_3(aq)]}{P_{SO_2}}$$

usual values:

- $[SO_2] = 0.1$ ppm
- at ground pressure 10^{-7} atm
- at 25°C $K_H = 1$ M / atm

$\rightarrow [H_2SO_3(aq)] = p_{SO2}\, K_H = 10^{-7}$ M

But: Most of he H_2SO_3 is ionised:

$2SO_3 \leftrightarrow HSO_3^- + H^+$

with $K_a = 1.7 \times 10^{-2}$ for H_2SO_4

→ equilibrium constant only fixes the concentration of the non ionised part!

The concentration of HSO_3^- can be determined for two limits using

$$K_a = \frac{[HSO_3^-][H^+]}{[H_2SO_3]}$$

A: No other acidity

$[HSO_3^-] = [H^+]$

$K_a = [HSO_3^-]^2 / [H_2SO_3]$

$[HSO_3^-] = 4\ 10^{-5}$ M

pH = 4.4

B: Strong acid present

pH ($[H^+]$) is controlled by strong acid

$K_a = [HSO_3^-]\ [H^+] / [H_2SO_3]$

$[HSO_3^-] = 4\ 10^{-9} / [H^+]$

→ the lower the pH, the lower $[HSO_3^-]$ (principle of le Chatelier)

- Dissolved SO_2 is oxidized to sulphate ions SO_4^{2-} by O_3 and H_2O_2 in the airborne droplets
- in most cases, this is thought to be the main oxidation pathway for atmospheric SO_2 with the exception of clear sky
- O_3 and H_2O_2 are formed in photochemical smog → oxidation of SO_2 is fastest under polluted conditions

Oxdation by H_2O_2:

What is the concentration of H_2O_2 in water?

$$K_H = \frac{[H_2O_2(aq)]}{P_{H_2O_2}}$$

$[H_2O_2] = 1\text{ppb} \rightarrow p_{H2O2} = 10^{-9}$ atm

$K_H = 7.4\text{x}10^4$ M / atm

$[H_2O_2(aq)] = K_H\, p_{H2O2} = 70\ \mu M$

→ very small, but enough to be effective!

Measurement show concentrations of 0.01 ... 200µM, depending on pollution and light

Dominant reaction path:

$H_2O_2 + HSO_3^- \rightarrow H_2O + HSO_4^-$ (overall)

acid catalysed, independent of pH

$H_2O_2 + H^+ \leftrightarrow HOOH_2^+$

$HOOH_2^+ \rightarrow H_2O + OH^+$

$OH^+ + HSO_3^- \rightarrow H_2SO_4$

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

Oxidation by O_3:

$HSO_3^- + O_3 \rightarrow HSO_4^- + O_2$ (overall)

depends on pH as increase in $[H^+]$ decreases $[HSO_3^-]$

→ oxidation by O_3 stops by itself

→ at low pH (<5), H_2O_2 oxidation is dominant

Oxidation by O_2:

Very slow, not important except when catalysts such as iron are available, then it might also contribute

Acid Rain

Natural rain: mildly acidic due to presence of dissolved CO_2 which forms carbonic acid:

$CO_2(g) + H_2O(aq) \leftrightarrow H_2CO_3\,(aq)$
$H_2CO_3(aq) \leftrightarrow H^+ + HCO_3^-$

the resulting pH is about 5.6
rain with a pH < 5 is called **Acid Rain**

Responsible acids:

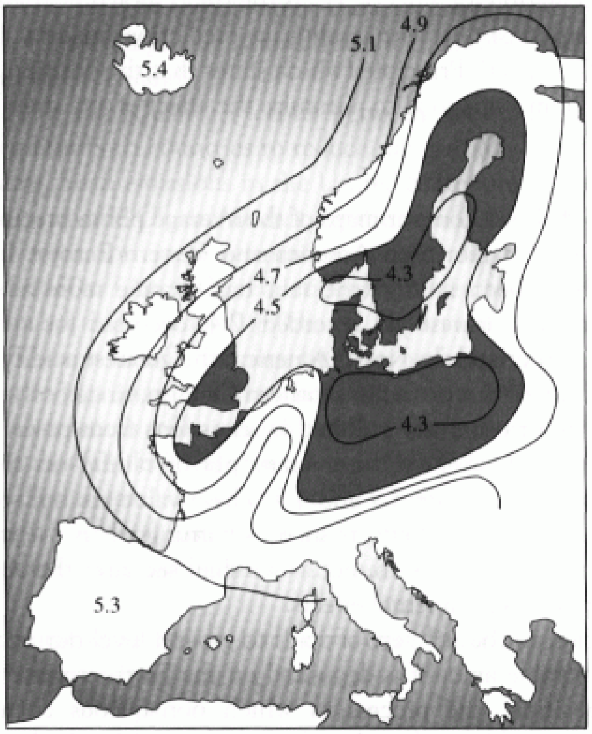
H_2SO_4 (sulphuric acid)	formed from SO_2
HNO_3 (nitric acid)	formed from NO_x

Source regions and affected regions differ, long range transport occurs - prominent examples are Norway (sources in Western Europe), Canada (sources in the US) and the US (sources in Mexico).

Acid Rain: Affected Regions

FIGURE 3-4
pH contours for rainfall (in 1985) for (a) central North America and (b) western Europe. Regions of very acidic rainfall are stippled. (Source: Redrawn from E. G. Nisbet, "Leaving Eden: To Protect and Manage the Earth." Cambridge, England, Cambridge University Press, 1991.)

Acid rain in central North America, 1985
(a)



Acid rain in Europe, 1985
(b)

Effects of Acid Rain

Humans:

pH 2.4 … 4.5 → no direct effect on humans

Soils:

effects depend strongly on ability of soil to neutralize acidity!

→ granite / quartz bedrock are strongly affected(Canada, Scandinavia)

→ limestone / chalk offer buffer

$$CaCO_3(s) + H^+(aq) \rightarrow Ca_2^+(aq) + HCO_3^-(aq)$$
$$HCO_3^-(aq) + H^+(aq) \rightarrow H_2CO_3(aq)$$
$$H_2CO_3(aq) \rightarrow CO_2(g) + H_2O(aq)$$

rock dissolves producing CO_2 and Ca ions to replace hydrogen

The same mechanism is responsible for acid rain damage on buildings and statues

Lakes:

- Lakes become strongly acidified from rain and snow (pH 7 is natural situation, at pH 5 most fish can not survive!)
- Al_3^+ is leached from rocks by H^+
- fish and plants die
- water is crystal clear but dead

Trees:

Trees are also affected

- nutrients are leached from soil
- Al is mobilised
- trees are stressed, together with O_3 pollution plants are weakened
- effects of droughts, storms and pests are exaggerated

→ Waldsterben

The Earth’s Energy Balance

- Input: energy from the sun, mainly in the visible wavelength region (400 - 700 nm)
- 20% absorbed in the atmosphere (O_2, O_3, H_2O, CO_2, ...)
- 50% absorbed on the ground
- 30% reflected back to space (**Planetary Albedo**)
- Output: thermal emission of surface and atmosphere (4 - 50 μm)

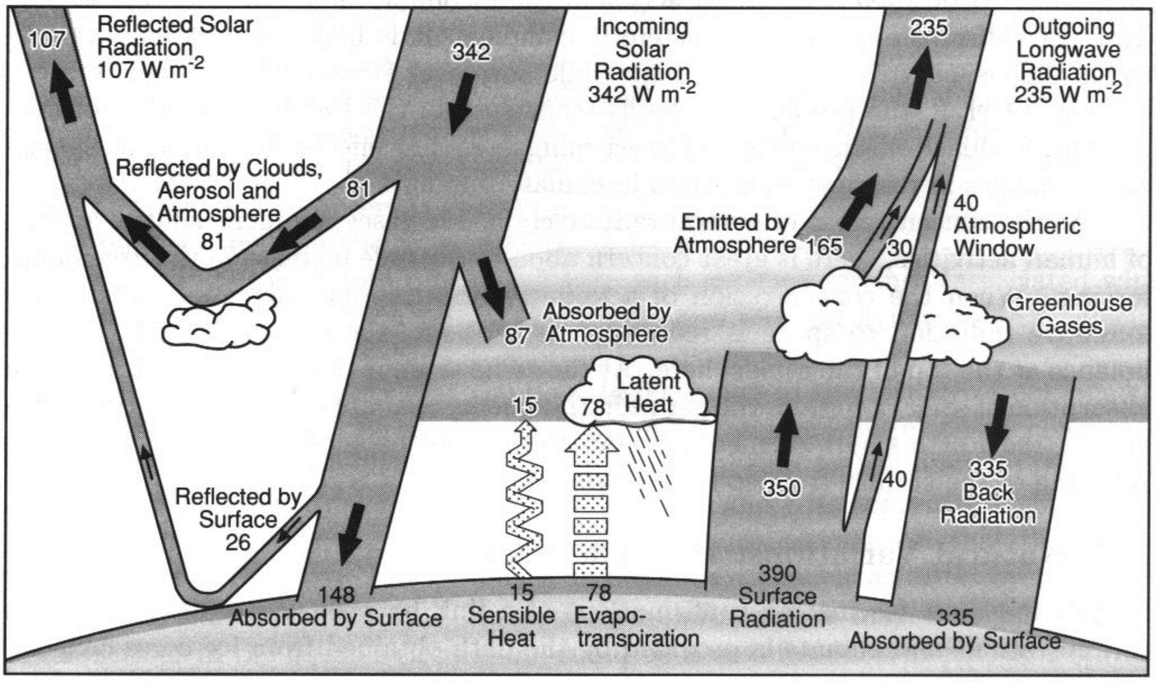


Figure 15.4. *Schematic diagram of the global energy budget. The values are expressed in* W m^{-2} *(IPCC, 1996).*

Greenhouse Effect

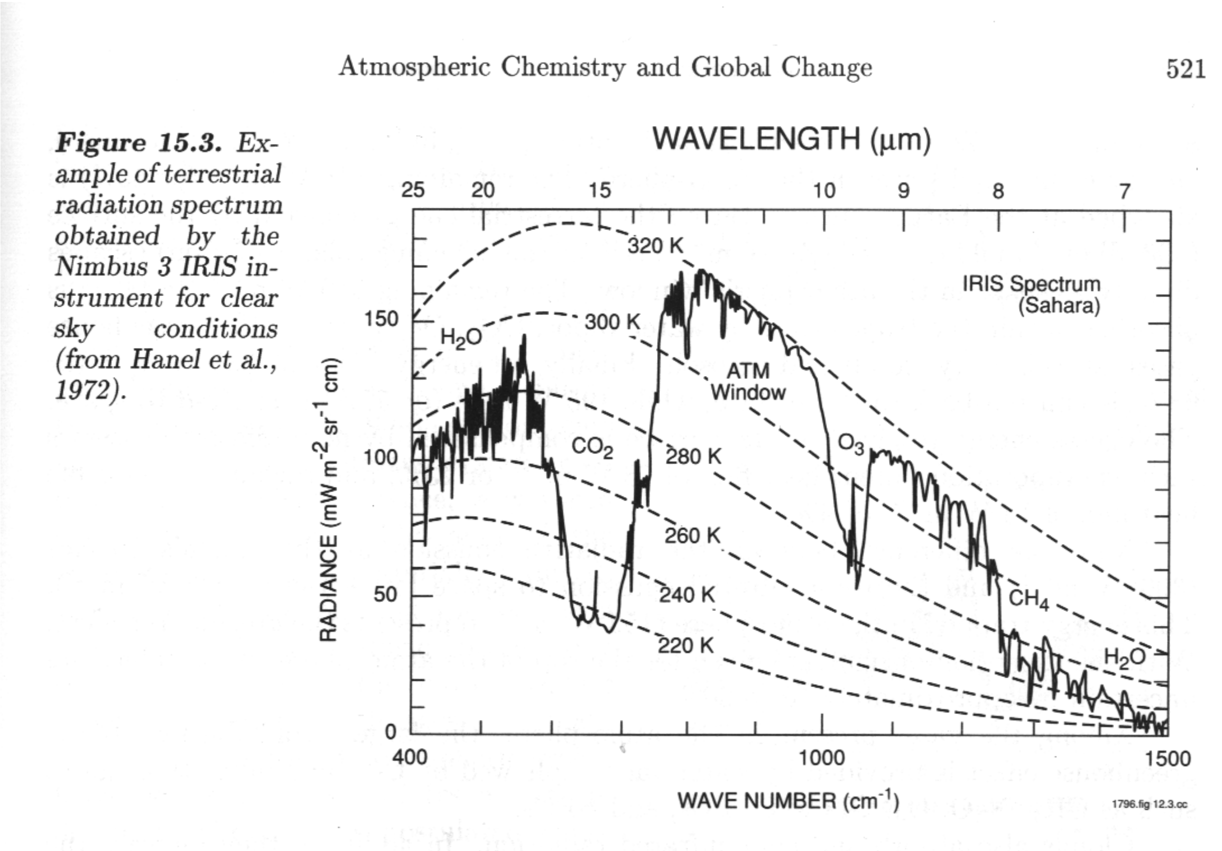


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Figure 15.3. *Example of terrestrial radiation spectrum obtained by the Nimbus 3 IRIS instrument for clear sky conditions (from Hanel et al., 1972).*

- Outgoing IR radiation is absorbed and re-emitted by CO_2, H_2O and CH_4
- emission is taking place at local temperature
- temperature is decreasing with height in the troposphere
- emission is proportional to T^4
- less energy is emitted than without atmosphere
- a higher surface temperature is established (15°C instead of -15°C without atmosphere)

IR Absorption by Molecules

Depending on wavelength (= energy), different physical processes are responsible for absorption:

UV	dissociation
VIS	electronic transitions
IR	vibrational transitions
MW	rotational transitions

In practice, combinations of the different processes occur leading to spectra with many lines (one vibration with several rotational transitions)

To absorb in the IR, a molecule must

- have more than one atom
- have the right oscillation frequency
- have a separation of charges (dipole moment) to couple to the electromagnetic waves

Molecules that <u>do not</u> absorb in the IR are

- Ar (one atom)
- N_2, O_2 (no dipole moment)
- CO (symmetric stretch)

Molecules that do absorb in the IR are

- CO_2, H_2O, CH_4, N_2O, CFCs

How efficient the IR absorption by a molecule is, depends on

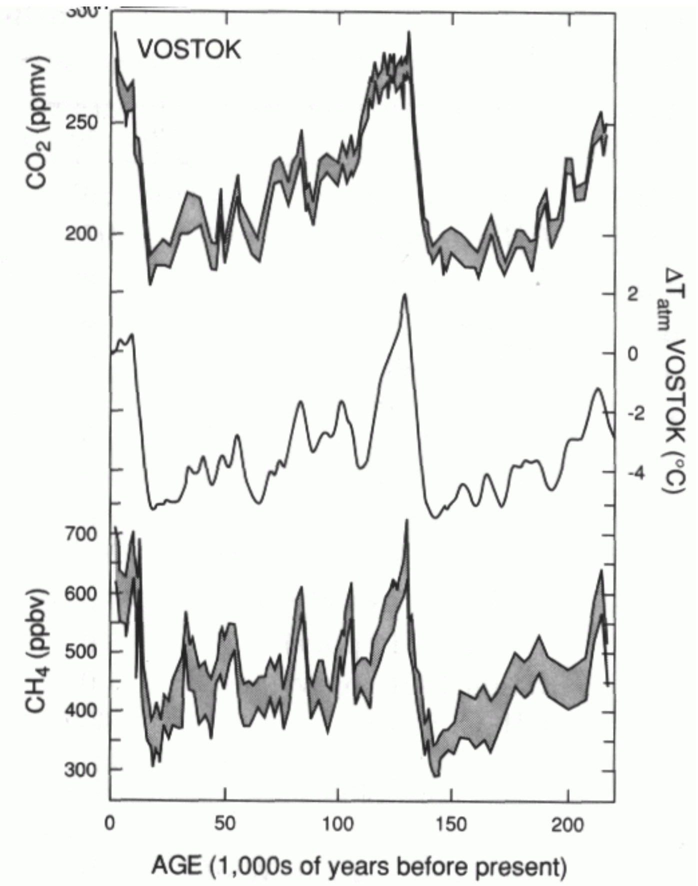
- concentration of the substance
- atmospheric lifetime of the substance
- absorption cross-section
- position of absorption bands relative to those of other absorbers

Non-linearity of absorption:

Absorption follows **Lambert Beer's law**, and only for very small absorptions it depends linearly on the amount of the absorber.

Therefore, absorbers are most effective in spectral regions, where no other absorbers are present (**Atmospheric Windows**) while in contrast adding more of an already strong absorber changes little in the radiative balance!

Past Climates



From ice cores, information can be deduced on the abundance of CO_2 and CH_4 as well as temperature in prehistoric times. They demonstrate

- high temperatures at high CO2 and CH4, low temperatures at low CO2 and CH4
- large variations in the past
- correlation with earth orbital parameters (**Milanchovich Forcing**)?

But: No proof of cause / effect !

Climate Relevance of CO_2

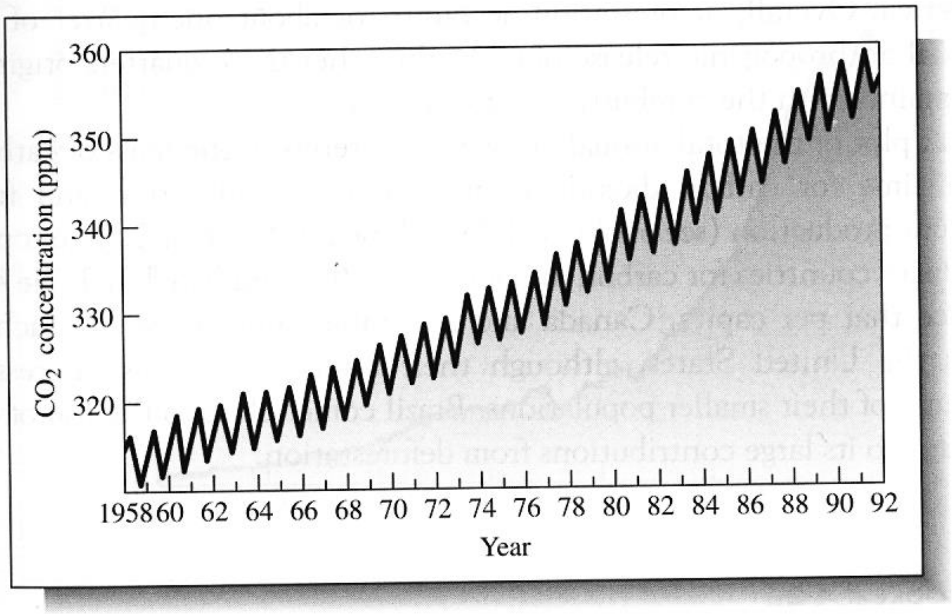


FIGURE 4-6
Yearly variation in atmospheric CO_2 concentrations. The sawtooth variations are due to seasonal effects (see text). (Source: Redrawn from B. Hileman. 1992. *Chemical & Engineering News* (April 27): 7–19.)

- CO_2 is the most important greenhouse gas
- concentrations increased from 280 ppm (pre-industrial) to 356 ppm
- seasonality as a result of photosynthesis, mainly in the northern hemispheric spring and summer and biological decay mainly in fall and winter
- atmospheric lifetime is approx. 100 years

Anthropogenic Sources:

- fossil fuel combustion and cement production (75%)
- biomass burning and deforestation (25%)

Sinks:

- oceans (solution, calcium carbonate formation and deposition)
- forests in the northern hemisphere (growing)

Feedbacks:

- photosynthesis is increased when more CO_2 is available (and often at higher temperature) → negative feedback
- solubility of CO_2 in water is reduced when temperature increases → positive feedback

Options for reductions in CO_2 emissions:

- more efficient energy use
- change to other energy sources
- change in fossil fuel:

  Coal: $C + O_2 \rightarrow CO_2$

  Oil: $CH_2 + 1.5O_2 \rightarrow CO_2 + H_2O$

  Gas: $CH_4 + 2O_2 \rightarrow CO_2 + H_2O$

  Energy gain is proportional to O_2, less CO_2 is emitted per energy when using gas instead of coal!
- active CO_2 extraction by
  - collection and deposition in sea
  - freezing at -79°C
  - chemical conversion:

    $$2CO_2 + H_2O + CaSiO_3 \rightarrow SiO_2 + Ca(HCO_3)_2\ (aq)$$

But: all active methods are expensive and only postpone the problem, the only long term solution being reduction in use of fossil fuels

Climate Relevance of H_2O

- second most important greenhouse gas
- often not explicitly named
- per molecule, H_2O is less effective than CO_2 but much more abundant
- concentrations vary strongly in space and time
- relatively small anthropogenic influence

Feedbacks:

- partial pressure of H_2O increases exponentially with temperature → positive feedback
- cloud formation depends on H_2O concentration
  - high cirrus clouds warm → positive feedback
  - low clouds cool → negative feedback
  - highly uncertain!

Climate Relevance of CH_4

- CH_4 concentrations doubled to 1.7 ppm today
- currently, concentrations are stable for unknown reasons
- highly uncertain emissions
- atmospheric lifetime is about 15 years

Sources:

- wetlands
- fossil fuel use (CH_4 losses in gas transport can offset advantage of using gas instead of coal!)
- landfills
- ruminants
- rice paddies
- forest clearing

Sinks:

- reaction with OH
- transport to stratosphere

Feedbacks:

- change in CH_4 could induce change in OH concentration → negative feedback (possible reason for observed reduction in trend)
- increase in stratospheric H_2O:
  $O^* + CH_4 \rightarrow OH + CH_3$
  $OH + CH_4 \rightarrow H_2O + CH_3$
  → positive feedback
- methane from permafrost regions might be released at higher temperatures → positive feedback
- methane (in methane hydrates $CH_4 \cdot 6H_2O$) from the ocean floors might be released at higher temperatures

→ **Runaway Greenhouse Effect** possible but rather speculative

Climate Relevance of N_2O

- concentration roughly 0.31 ppm
- growing 9% / year

Sources:

- ocean
- tropical soils
- nitrification / denitrification in soils have N_2O as by-product
- use of fertilizer
- burning of N-containing fuels (coal, biomass)
- older catalytic converters

Sinks:

- stratosphere, photolysis

Feedbacks:

- in the stratosphere, N_2O is a source of NOx which can lead to ozone destruction → negative feedback

Climate Relevance of CFCs

- completely anthropogenic sources
- long lifetime
- very strong absorption
- very effective greenhouse gases

Feedbacks:

- ozone destruction in the stratosphere → negative feedback, cancels warming effect (but not at the same altitude!)

CFC replacements (HCFC and HFC) are often also effective greenhouse gases, albeit with a shorter lifetime.

Climate relevance of O_3

- important natural greenhouse gas in the stratosphere
- in the troposphere less important due to overlap with CO_2 absorption
- in the troposphere variable in space due to short lifetime

Climate Relevance of Aerosols

- aerosols have a multitude of conflicting effects on climate
- sulphate aerosols mostly reflect solar light → net cooling
- soot mostly absorbs light → net warming
- aerosols provide condensation nuclei that affect
    - cloud formation
    - cloud droplet size → reflectivity (larger for smaller droplets)
- aerosols tend to cool in mid-latitudes and heat at low latitudes, leading to changes in temperature gradients
- many feedbacks exist for aerosol deposition, cloud formation and increased aerosol production in drier climates

<u>Sources:</u>

- sea-salt
- soils
- anthropogenic SO_2 emissions
- DMS emissions

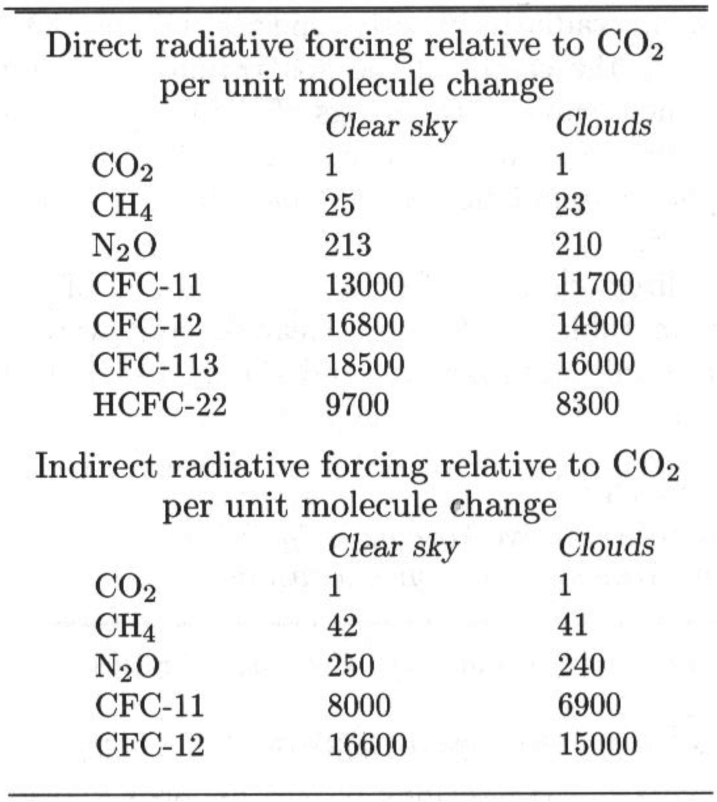
Quantification of Climate Relevance

The climate relevance of a species is often given as the **Radiative Forcing** = net change in radiative energy flux at the tropopause to changes in the concentration of a given trace gas

To simplify calculations, everything is given relative to the effect of CO_2:

Effective Carbon Dioxide Concentration = concentration of CO_2 that leads to same change in surface temperature

Often, **Indirect Effects** are also important and much more difficult to quantify:



Direct radiative forcing relative to CO_2
per unit molecule change

	Clear sky	*Clouds*
CO_2	1	1
CH_4	25	23
N_2O	213	210
CFC-11	13000	11700
CFC-12	16800	14900
CFC-113	18500	16000
HCFC-22	9700	8300

Indirect radiative forcing relative to CO_2
per unit molecule change

	Clear sky	*Clouds*
CO_2	1	1
CH_4	42	41
N_2O	250	240
CFC-11	8000	6900
CFC-12	16600	15000

Global Warming Potentials

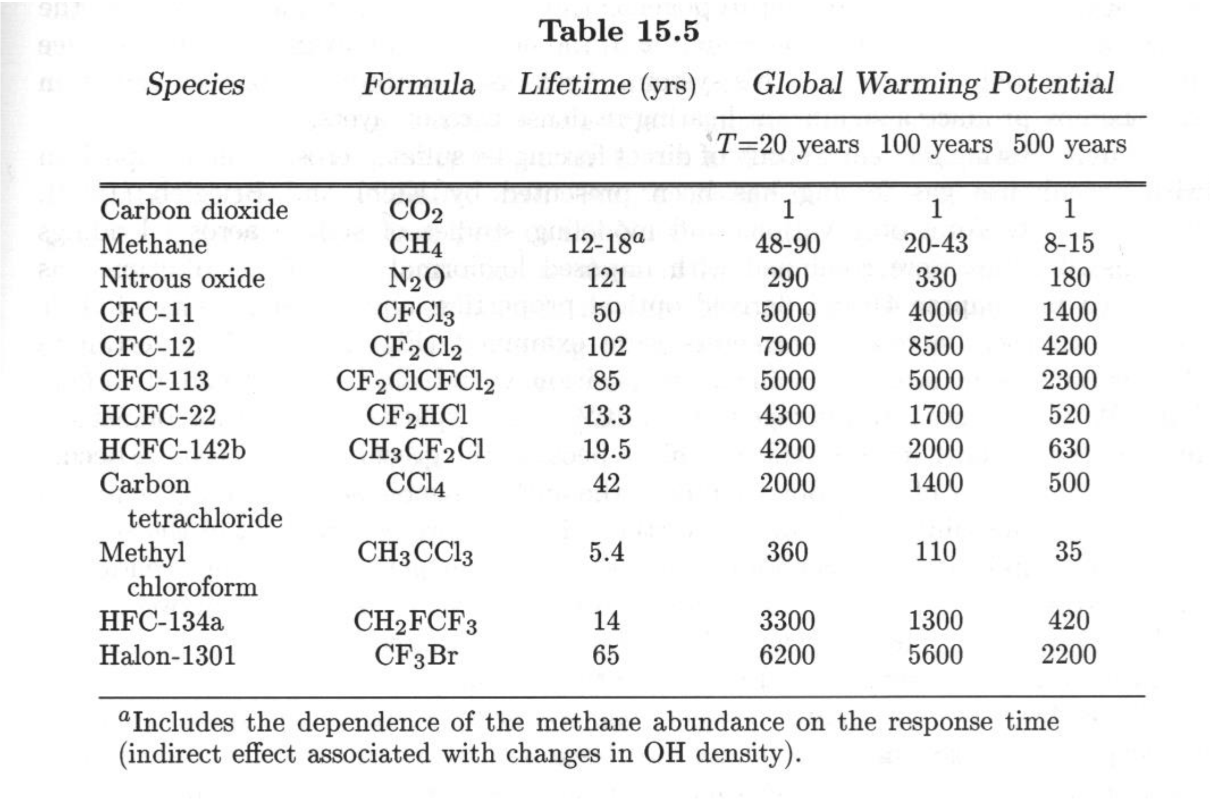


Table 15.5

Species	*Formula*	*Lifetime* (yrs)	*Global Warming Potential*		
			T=20 years	100 years	500 years
Carbon dioxide	CO_2		1	1	1
Methane	CH_4	12-18[a]	48-90	20-43	8-15
Nitrous oxide	N_2O	121	290	330	180
CFC-11	$CFCl_3$	50	5000	4000	1400
CFC-12	CF_2Cl_2	102	7900	8500	4200
CFC-113	$CF_2ClCFCl_2$	85	5000	5000	2300
HCFC-22	CF_2HCl	13.3	4300	1700	520
HCFC-142b	CH_3CF_2Cl	19.5	4200	2000	630
Carbon tetrachloride	CCl_4	42	2000	1400	500
Methyl chloroform	CH_3CCl_3	5.4	360	110	35
HFC-134a	CH_2FCF_3	14	3300	1300	420
Halon-1301	CF_3Br	65	6200	5600	2200

[a] Includes the dependence of the methane abundance on the response time (indirect effect associated with changes in OH density).

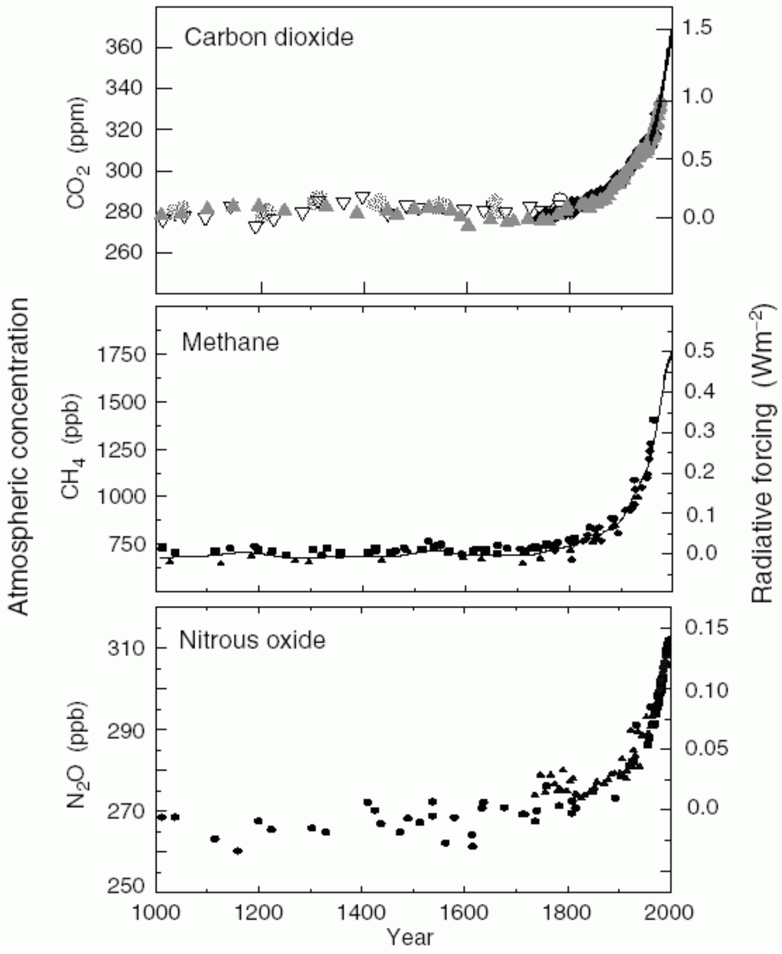
For each substance, a **Global Warming Potential** is computed, that gives the time integrated change of radiative forcing due to the instantaneous release of 1 kg of a trace gas relative to the effect of the release of 1 kg CO_2

The global warming potential depends on the time interval treated and also on many other assumptions!

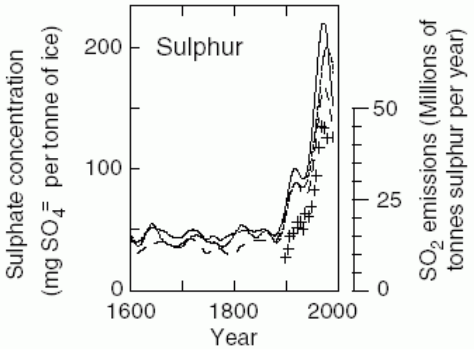
Is There a Man-Made Greenhouse Effect?

Indicators of the human influence on the atmosphere during the Industrial Era

(a) Global atmospheric concentrations of three well mixed greenhouse gases



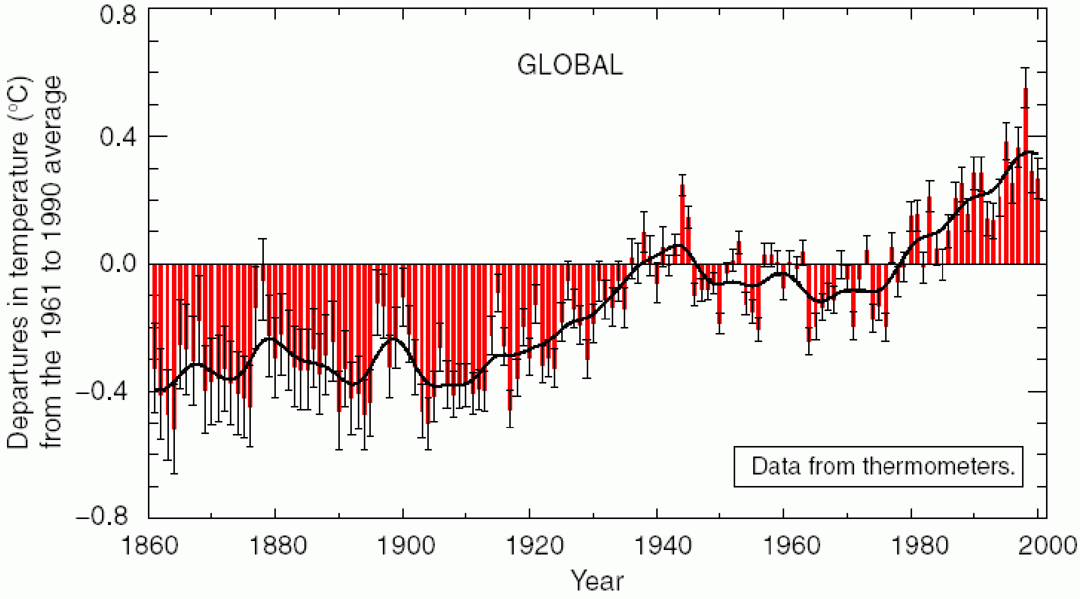
(b) Sulphate aerosols deposited in Greenland ice



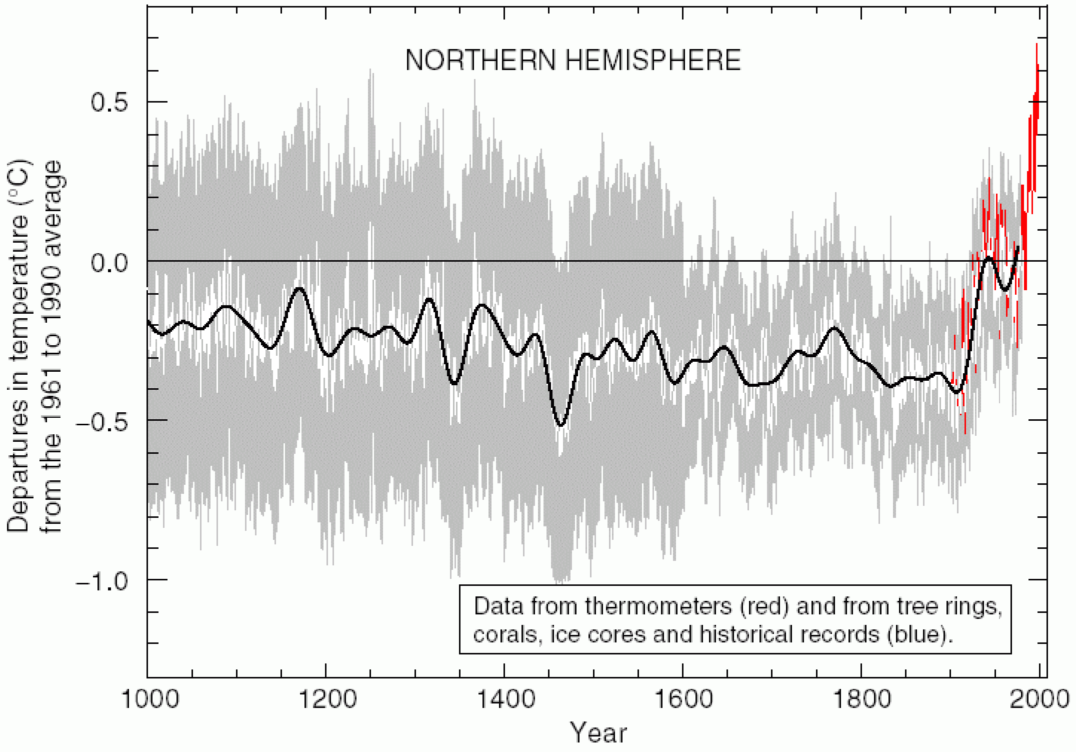
Is Temperature Changing on Earth?

Variations of the Earth's surface temperature for:

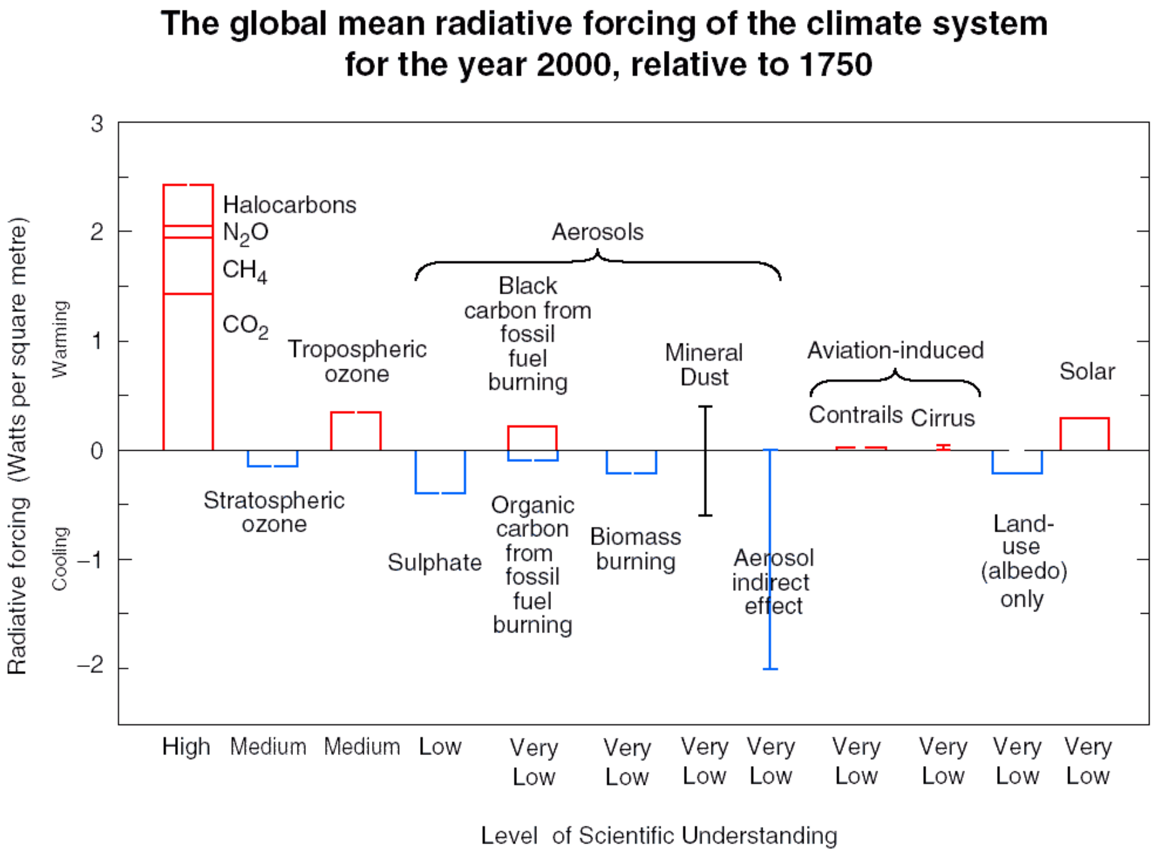
(a) the past 140 years



(b) the past 1,000 years

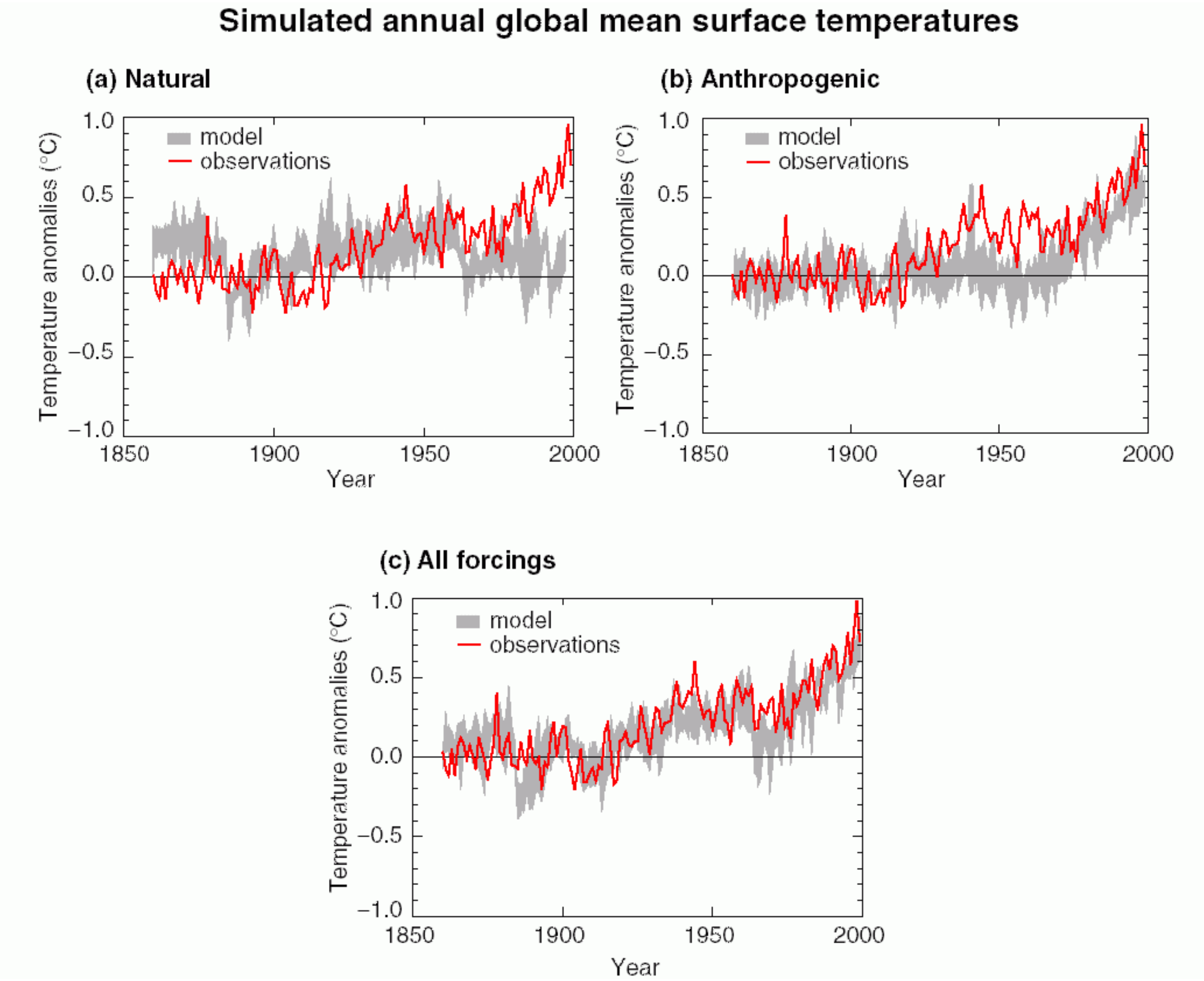


What are the Man Contributions to GW?



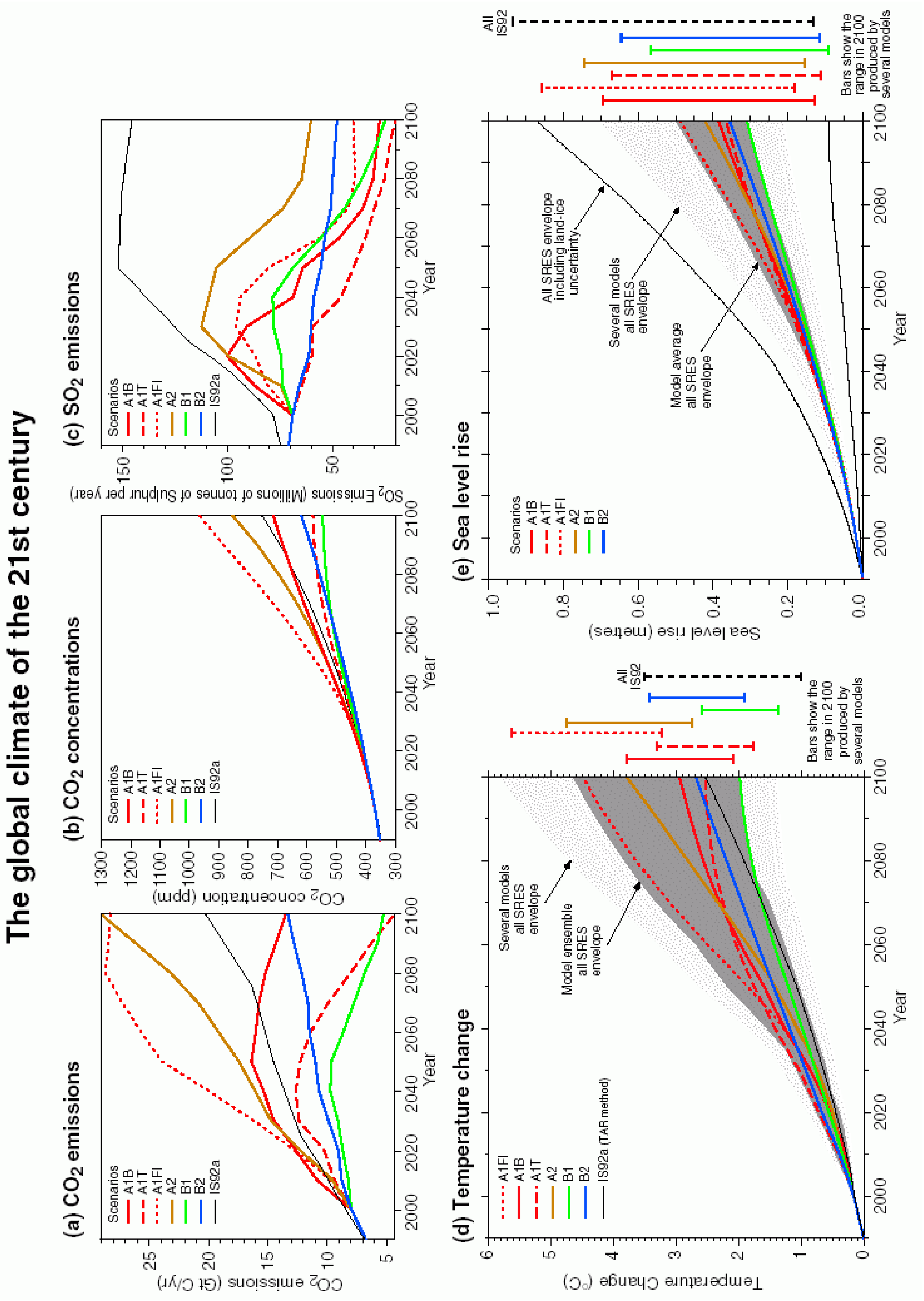
- many contributions are still not well quantified
- in particular aerosol effects are very uncertain
- the impact of CO_2 and CH_4 is well understood

How well do Models?



- models can qualitatively reproduce past temperature changes
- climate models still are rather simplistic
- chemistry is not well represented in climate models, which might have a big impact on the predictions
- input for models is still rather uncertain

What do Models Predict?



Halogens in the Troposphere

Ozone observations:

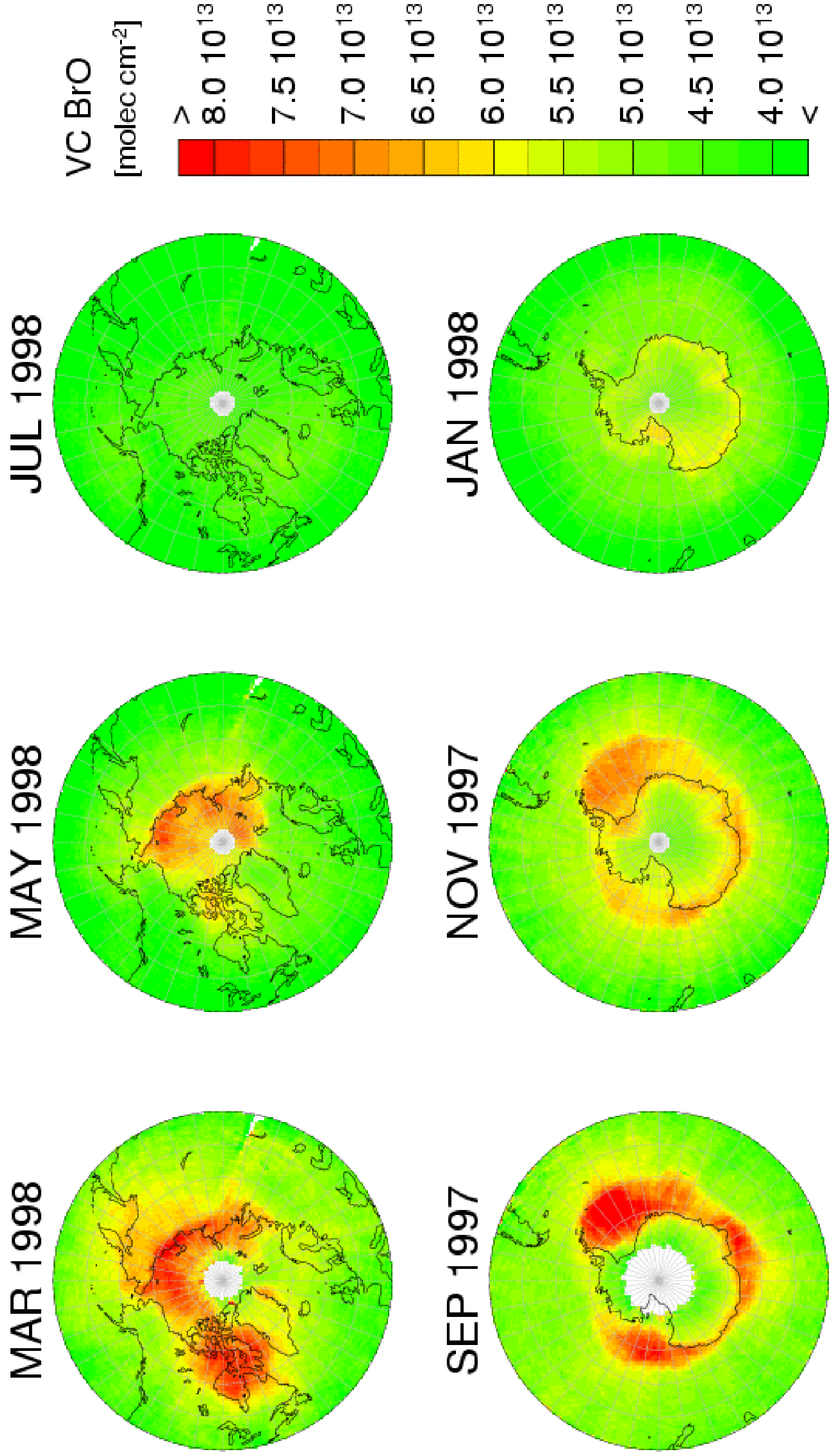
- episodic, rapid O_3 loss in the polar boundary layer is observed every spring
- affected regions are the polar ice caps and coastal regions close to sea ice
- ozone loss is observed only in spring, not in other seasons
- it starts only after polar sunrise
- it is observed in both hemispheres

Halogen Measurements:

- increased concentrations of “filterable bromine” correlate with ozone loss
- enhanced concentrations of Br_2, BrO (up to 30 ppt) , and BrCl are also observed during low ozone events
- GOME (Global Ozone Monitoring Experiment) satellite measurements reveal that enhanced BrO is present over large areas and extended time periods in both the Arctic and Antarctic

→ tropospheric ozone destruction by bromine?

Boundary Layer BrO measured by GOME



Are reactive halogens also present in the troposphere in other places?

- large BrO concentrations (up to 180 ppt) at the dead sea
- 1-2 ppt of BrO in marine boundary layer?
- 1-2 ppt in the free troposphere
    - mismatch between GOME satellite and ground-based measurements could be explained by this tropospheric background
    - profile measurements from balloons also give indication for such a background
- IO and OIO could be measured in coastal regions, in particular in high latitudes
- some evidence for Cl in polar and maritime regions

→ reactive halogens seem to be present in the troposphere in significant amounts

→ they potentially have a large impact on the tropospheric ozone budget

→ what are the sources and sinks?

Review: Stratospheric Halogens

Sources:

- transport of stable species from the troposphere + photolysis
- mainly anthropogenic sources

Sinks:

- temporary to reservoir substances such as HCl or $BrONO_2$
- eventually sedimentation to troposphere and deposition

Chemistry:

- fluorine inactive as HF
- Cl mainly in reservoir substances HCl and $ClONO_2$
- Br mainly in active forms Br and BrO
- reactive halogens act as catalysts in ozone destruction
- in polar spring, activation of reservoir species on and in cold surfaces of PSCs leads to large increase in concentrations of active chlorine and rapid ozone destruction

Tropospheric Halogen Chemistry

- F is unimportant as in the form of HF
- Cl, Br and I behave very similar
- life time very small, in the order of 0.08 s(Cl) to 0.8 s (Br, I)
- reactivity decreases strongly from F →I

(At least) two catalytic ozone destruction cycles involving reactive halogens are possible in the boundary layer:

1: Halogen-halogen cycle

$$\begin{aligned} X + O_3 &\rightarrow XO + O_2 \\ Y + O_3 &\rightarrow YO + O_2 \\ XO + YO &\rightarrow X + Y + O_2 \\ &\rightarrow XY + O_2 \\ &\rightarrow OXO + Y \\ \hline 2\,O_3 &\rightarrow 3\,O_2 \end{aligned}$$

where X and Y are Cl, Br or I

- XY will rapidly be photolysed to recycle X and Y
- rate determining step is generally the reaction of XO with YO
- in general, XO + YO is faster than XO + XO
- the third channel for the XO + YO reaction is a null cycle as OXO is usually rapidly photolysed:

  $OXO + h\nu \rightarrow XO + O$

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

  Exception : OIO, that can photodissociate to

  $OIO + h\nu \rightarrow I + O_2$

  which then leads to ozone destruction
- for the case where X = Y, the overall rate depends quadratically on the concentration of the reactive halogens

2: Halogen - HOx - cycle

$$X + O_3 \rightarrow XO + O_2$$
$$OH + O_3 \rightarrow HO_2 + O_2$$
$$XO + HO_2 \rightarrow HOX + O_2$$
$$HOX + h\nu \rightarrow OH + X$$

$$2O_3 + h\nu \rightarrow 3O_2$$

The second cycle depends linearly on reactive halogen concentrations, making it more important at low concentrations:

- $[BrO] = 15$ ppt, $[HO_2] = 1$ ppt → 1 : 1
- $[BrO] = 30$ ppt, $[HO_2] = 1$ ppt → 2 : 1

Alternative reactions for XO:

- $XO + h\nu \rightarrow X + O$ (null cycle)
- $XO + NO \rightarrow X + NO_2$
- $XO + NO_2 + M \rightarrow XONO_2 + M$
  $XONO_2 + h\nu \rightarrow XO + NO_2$ (null cycle)
  $\rightarrow X + NO_3$ (ozone loss)
- $XO + CH_3O_2 \rightarrow HOX + CH_2O_2$
  (very effective for Br)

The efficiency of the ozone loss depends on the chain length, and therefore on the probability of the reaction with other species:

- F: reaction with H_2O and $CH_4 \rightarrow HF$, stable
- Cl: reaction with CH4 → HCl, can react with OH
- Br: reaction with unsaturated hydrocarbons and fully oxidized compounds such as aldehydes
- I: reaction mainly with O_3 and other radicals

A rough estimate of the efficiency can be derived by comparing the rate of the reaction with ozone with the rate of the main competing reactions

$$X + RH \rightarrow XH + R$$

$$X + HO_2 \rightarrow HX + O_2$$

for typical concentrations:

$$\text{chain length} \approx \frac{R_{O3}}{\sum R_{RH} + R_{HO2}}$$

X	RH	k^*_{X+RH} (k_{X+O_3}) $[cm^3 s^{-1}]$	$typ[RH]$ $(typ[O_3])$ $[cm^{-3}]$	$R_{RH} = k_{X+RH}[RH]$ $(R_{O_3} = k_{X+0_3}[O_3])$ $[s^{-1}]$	$\frac{R_{O_3}}{R_{O_3}+\sum R_{RH}+R_{HO_2}}$	$\frac{R_{O_3}}{\sum R_{RH}+R_{HO_2}}$
F	H_2O	$1.4 \cdot 10^{-11}$	$7 \cdot 10^{16}$	$2.8 \cdot 10^6$	$3.5 \cdot 10^{-6}$	$3.5 \cdot 10^{-6}$
	CH_4	$6.4 \cdot 10^{-11}$	$4.0 \cdot 10^{13}$	$2.6 \cdot 10^3$		
				$\sum R_{RH} = 2.8 \cdot 10^6$		
	$(O_3$	$1.0 \cdot 10^{-11}$	$1.0 \cdot 10^{12}$	10.0)		
Cl	CH_4	$1.0 \cdot 10^{-13}$	$4.0 \cdot 10^{13}$	4.0	0.52	0.92
	C_2H_6	$5.7 \cdot 10^{-11}$	$3.0 \cdot 10^{10}$	1.7		
	C_3H_8	$1.4 \cdot 10^{-10}$	$1.0 \cdot 10^{10}$	1.4		
	CH_2O	$7.3 \cdot 10^{-11}$	$1.0 \cdot 10^{10}$	0.73		
	C_2H_2	$2.1 \cdot 10^{-10}$	$1.0 \cdot 10^{10}$	2.1		
	C_2H_4	$3.1 \cdot 10^{-10}$	$5.0 \cdot 10^9$	1.5		
				$\sum R_{RH} = 11$		
	$(O_3$	$1.2 \cdot 10^{-11}$	$1.0 \cdot 10^{12}$	12.0)		
Br	CH_2O	$1.1 \cdot 10^{-12}$	$1.0 \cdot 10^{10}$	0.01	0.984	60
	HO_2	$2.0 \cdot 10^{-12}$	$1.0 \cdot 10^8$	$2.0 \cdot 10^{-4}$		
				$\sum R_{RH} = 2.0 \cdot 10^{-2}$		
	$(O_3$	$1.2 \cdot 10^{-12}$	$1.0 \cdot 10^{12}$	1.2)		
I	HO_2	$3.8 \cdot 10^{-13}$	$1.0 \cdot 10^8$	$3.8 \cdot 10^{-5}$	0.99997	$3.1 \cdot 10^4$
	$(O_3$	$1.2 \cdot 10^{-12}$	$1.0 \cdot 10^{12}$	1.2)		

*rate constants taken from [DeMore et al. 1997]

→ Fluorine is unimportant, Cl, Br, and I are increasingly effective

→ concentrations have to be taken into account to determine relative importance!

- As a result of the different reactivity, the [XO] / [X] ratios vary strongly between the halogens:
  - [IO] / [I] = 1..10
  - [BrO] / [Br] = 100,
  - [ClO] / [Cl] = 1000

- Through reaction with HO_2, halogens can also change the [OH] / [HO_2] ratio significantly!

Sources of Reactive Halogens in the Troposphere

Sea salt is the basic natural source for all reactive halogens in the troposphere, either

1. directly from sea salt in sea water, deposited on snow or ice or in aerosols
2. or indirectly through photolysis of organohalogens released by algae

Sea salt composition by weight:

- 55.7 % Cl
- 0.19 % Br
- 2.10^{-5}% I

→ chlorine is dominant in sea salt but Br and I are enriched in organohalogens and are much enriched in aerosols and in the gas phase.

Direct release from sea salt is possible through a combination of gas phase and liquid phase reactions.

1. (Auto)catalytic liberation from sea salt

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

$$XO + HO_2 \rightarrow HOX + O_2$$

$$(HOX)_g \rightarrow (HOX)_{aq}$$

$$(HOX)_{aq} + (Y^-)_{aq} + (H^+)_{aq} \rightarrow (XY)_{aq} + H_2O$$

$$(XY)_{aq} \rightarrow (XY)_g$$

$$XY + h\nu \rightarrow X + Y$$

$$X + HO_2 + (Y^-)_{aq} + (H^+)_{aq} + O_3 \rightarrow X + Y + H_2O + 2O_2$$

In effect, one X catalytically releases one Y from the liquid phase while destroying one HO_2 and one O_3.

- If X = Y = Br, bromine concentrations in the gas phase can increase exponentially (**Bromine Explosion**).
- Some Chlorine is released in the bromine explosion, but HOCl formation in the gas phase is too slow for a “chlorine explosion”
- Iodine concentrations are too small for a “iodine explosion”

2. Halogen release through strong acids

Strong acids can react with halides in aerosols:

$$H_2SO_4 + 2\ (NaX)_{aero} \rightarrow 2HX + Na_2SO_4$$

HX is relatively stable in the gas phase, but can be activated on the surface of sea salt aerosols:

$$HOX + HX \rightarrow X_2 + H_2O$$

$$X_2 + h\nu \rightarrow 2X$$

On cold and acidified aerosol surfaces, additional reactions can take place such as

$$HONO + HBr \rightarrow BrNO + H_2O$$

$$BrNO + h\nu \rightarrow Br + NO$$

3. Halogen release from NOy species:

A slow activation that is effective also in polar night is possible through

$$(N_2O_5)_g + (NaX)_s \rightarrow (XNO_2)_g + (NaNO_3)_s$$

$$(XNO_2)_g + (NaX)_s \rightarrow (NaNO_2)_s + (X_2)_g$$

or after sunrise

$$XNO_2 + h\nu \rightarrow X + NO_2$$

4. Halogen released from organohalogens:

Natural sources:

- algae in oceans

Anthropogenic sources:

- biomass burning
- fungicides (CH_3Br)
- leaded gasoline ($C_2H_4Br_2$)

Compound	typ. mixing ratio [ppt]	approx. lifetime
CH_3Br	10^a	8 months^a
CH_2Br_2	$< 1.5^c$	4 months^b
CH_2BrCl	$< 0.5^c$	5 months^d
$CHBr_2Cl$	0.8^h	1.2 months^d
$CHBr_3$	6^h	1.2 months^e
$CHBrCl_2$	$< 0.5^c$	1.2 months^d
CH_3I	2.4^g	5 days^f
C_2H_5I	0.1^h	40 hours^f
CH_2ClI	0.11^h	5 hours^f
CH_2BrI	0.3^h	45 minutes^f
CH_2I_2	0.4^h	5 minutes^f

[a] [*Yvon and Butler* 1996]
[b] [*Mellouki et al.* 1992]
[c] [*Schall and Heumann* 1993]
[d] [*Bilde et al.* 1998]
[e] [*Moortgat et al.* 1993]
[f] [*Vogt et al.* 1999]
[g] [*Reifenhäuser and Heumann* 1992]
[h] [*Carpenter et al.* 1999]

→ concentrations too small to explain observed BrO concentrations (...30 ppt)

→ life times too long to explain “bromine explosion”

Tropospheric Bromine Chemistry

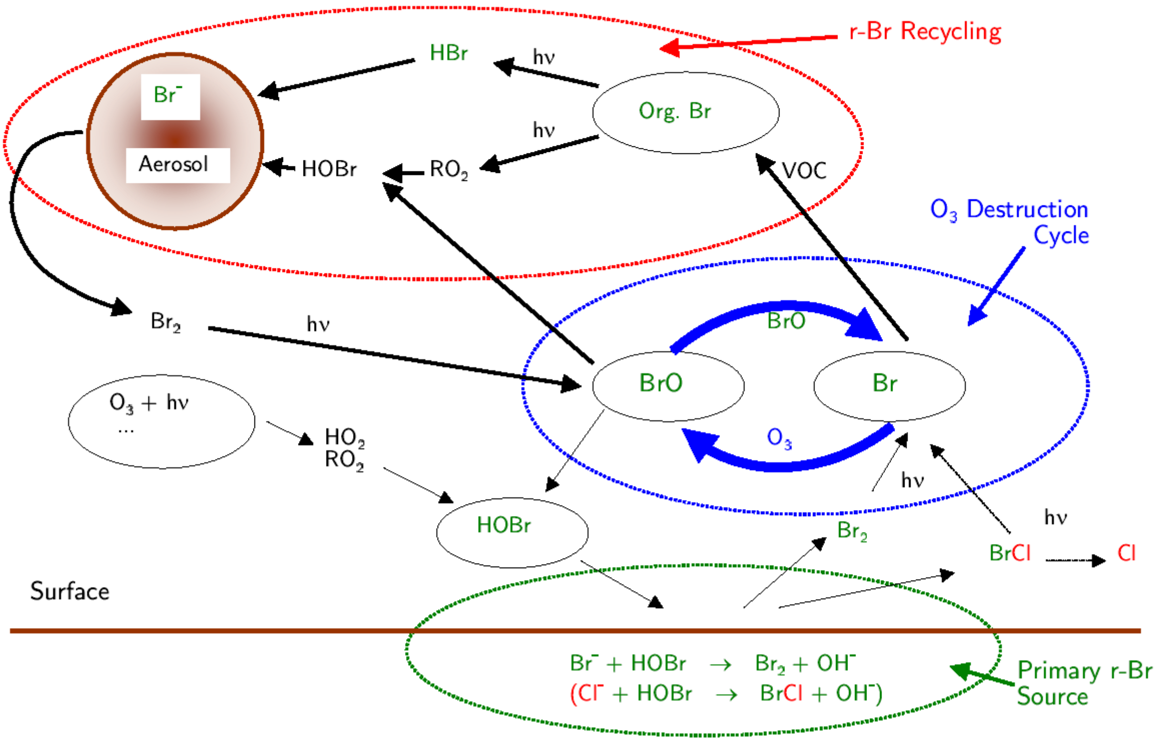
Main source: Autocatalytic liberation of Br from sea salt:

$$(HOBr)_g \rightarrow (HOBr)_{aq}$$
$$(HOBr)_{aq} + (Cl^-)_{aq} + (H^+)_{aq} \rightarrow (BrCl)_{aq} + H_2O$$
$$(BrCl)_{aq} + (Br^-)_{aq} \rightarrow (Br_2Cl)_{aq}$$
$$(Br_2)_{aq} \rightarrow (Br_2)_g$$
$$Br_2 + h\nu \rightarrow 2Br$$
$$2(Br + O_3) \rightarrow 2(BrO + O_2)$$
$$2(BrO + HO_2) \rightarrow 2(HOBr + O_2)$$

$$HOBr + 2HO_2 + (Br^-)_{aq} + (H^+)_{aq} + 2O_3 \rightarrow 2HOBr + H_2O + 4O_2$$

Sinks:

- reaction with HCHO
- reaction with HO_2
- dry or wet deposition of HBr



Prerequisites for a bromine explosion:

- pH < 6.5 for bromine release
- Br_2 release has to be faster than BrCl release
- stable BL inversion for high Br concentrations
- large, salt enriched surface (aerosols are not enough) → ice, frost flowers
- light
- some Br to start process
- O_3 or Br is “stored” in HBr

Tropospheric Iodine Chemistry

Main sources are iodo-hydrocarbons (CH_3I, CH_2I_2, ...)

- rapid photolysis
- heterogeneous paths for release not so important
- no “event character” but rather related to biologic activity
- potentially large impact on ozone
  - main cycle is with HOx
  - a few ppt of I would account for up to 75% of O_3 destruction in the marine boundary layer
- large impact on chemistry of other halogens through faster gas phase chemistry of “mixed” reactions

Sinks:

Iodine has other sinks than F, Cl, and Br:

- I does not react with hydrocarbons
- $I + HO_2 \rightarrow HI + O_2$

  but: $HI + OH \rightarrow I + H_2O$ (τ = 3 - 4 h)
- $IONO_2$, I_2O_2, INO_2 (τ < 1 h)

- uptake on aerosols seems to be major loss:

  $$IO + IO \rightarrow I_2O_2$$

  $$I_2O_2 + (H_2O)_{aq} \rightarrow (HOI)_{aq} + (IO_2^-)_{aq} + (H^+)_{aq}$$

  $$(IO_2^-)_{aq} + (H_2O_2)_{aq} \rightarrow (IO_3^-)_{aq} + H_2O$$
- formation of OIO is also a possible sink, depending on photolysis:

  $IO + IO \rightarrow OIO + I$

  $OIO + h\nu \rightarrow IO + O(^3P)$ (not possible!)

  $OIO + h\nu \rightarrow I + O_2$ (possible, τ = 1s)
- polymerisation of IO and OIO to I_xO_y as observed in lab

  → formation of new CCN?

Mercury Chemistry and Bromine

Through the chemistry of mercury, the natural bromine explosions in the polar regions are linked to pollution:

- Hg is a poisonous heavy metal that is emitted by both natural and anthropogenic (30%) sources.
- most atmospheric Hg is in the gas phase and due to its long lifetime is distributed globally
- probably through reaction with BrO:

  $$Hg + BrO \rightarrow HgO + Br$$

  Hg can be oxidized and transferred to particulate form
- particulate Hg is readily deposited on snow and ice and introduced in to the aquatic ecosystem at snow melt
- today, indigenous people in the Arctic have very high Hg levels although they live far from pollution!