SOLAS Summer School 2007

Atmospheric Gas Phase Reactions (Oct. 25)

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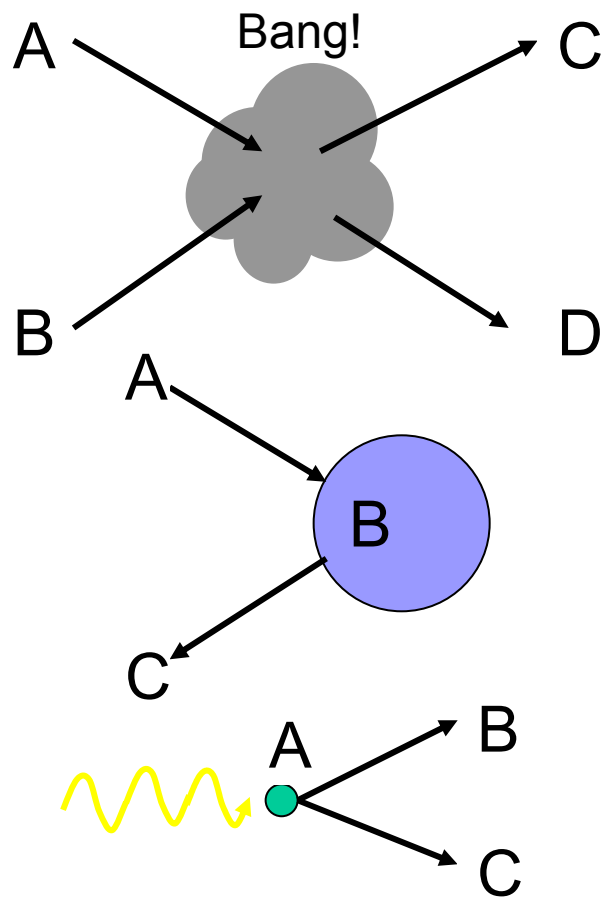
Reaction Kinetics

Chemical reactions in the atmosphere are relevant for:

- Ozone formation
- Degradation of air pollutants (self cleaning of the atmosphere)
- Degradation of climate gases

We categorise chemical reactions in:

- Homogeneous Reactions: The reactands are all in the same phase (in the atmosphere usually in the gas phase).
- Heterogeneous Reactions: The reactands are in different phases (e.g. reactions of gas molecules at aerosol surfaces, cloud droplets or ice crystals).
- Photochemical Reactions, i.e. the chemical transformation of gas molecules by solar radiation.



Outline

- Evolution of reactant concentrations as a function of time (reaction velocity)
- Elementary reactions vs. complex reactions
- Reaction order
- Chemical equilibria
- How can the thousands of chemical reactions occuring in the atmosphere simultaneously be captured in a numerical model?
- Some examples (HO_X – Radicals, NO_X-Reactions, Bromine Explosion)
- Summary

Reaction Velocity and Reaktion Order (1)

Reactions of ‚zeroth' Order:

$$A \quad \rightarrow \quad Products$$

Educt A decays with constant reaction velocity.

Def: **reaction velocity**:

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

With the reaction rate constant k
in units of Molek./(cm^3·s).

Reactions of 1st Order (unimolekular Reactions)

$$A \quad \rightarrow \quad Products$$

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

reaction rate constant k in 1/s

Def: [A] denotes the concentration i.e. amount of matter per unit volume of the atom or molecular species A.

Units: **Molecules per cm^3** or Mol per liter

Temporal Evolution of the Concentration (2)
→ Reaction Velocity

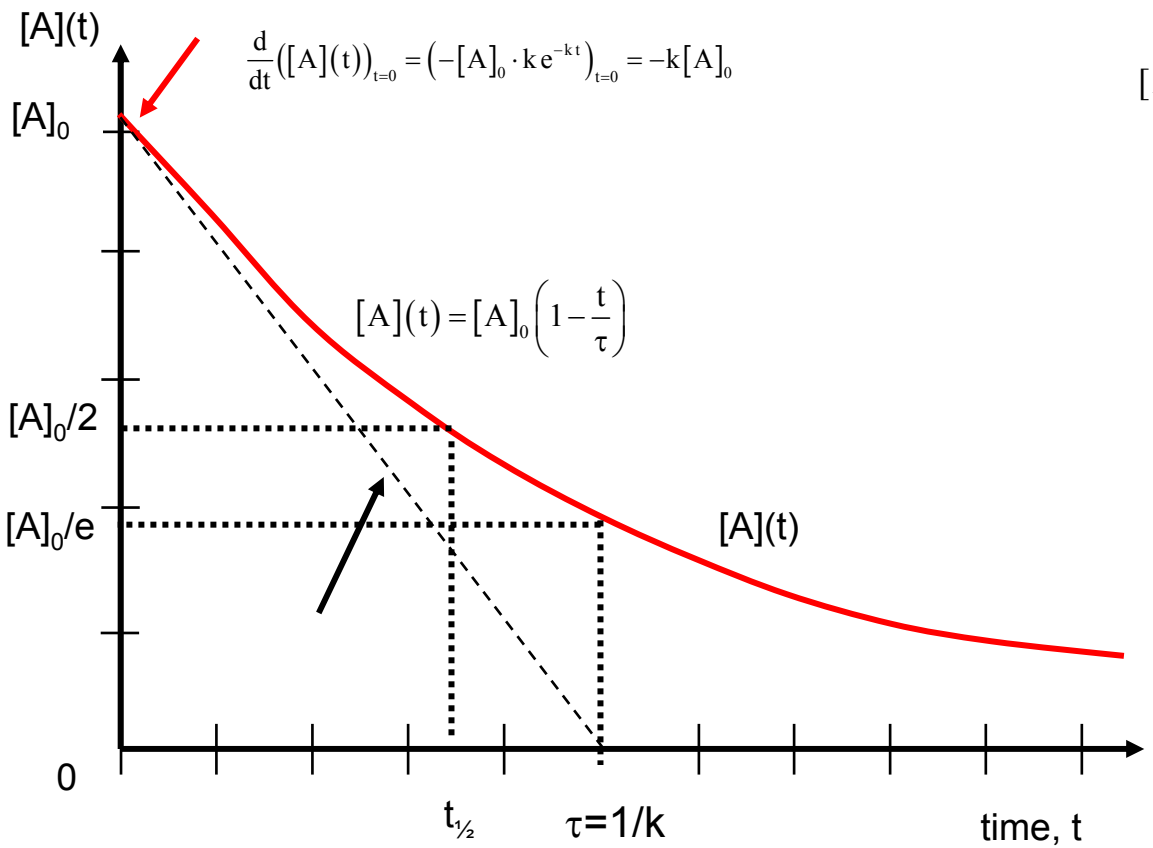
Reaction of 1st Order: $$\frac{d[A]}{dt} = -k \cdot [A]$$

Integration:

$$\int_{[A]_0}^{[A]} \frac{1}{[A]} \cdot d[A] = -k \cdot \int_0^t dt$$

$$\ln\left(\frac{[A]}{[A]_0}\right) = -k \cdot t$$

$$[A] = [A]_0 \cdot e^{-k \cdot t}$$



Reactions Velocity and Reaktion Order (3)

Reactions of 2nd order:

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

A collides with B:

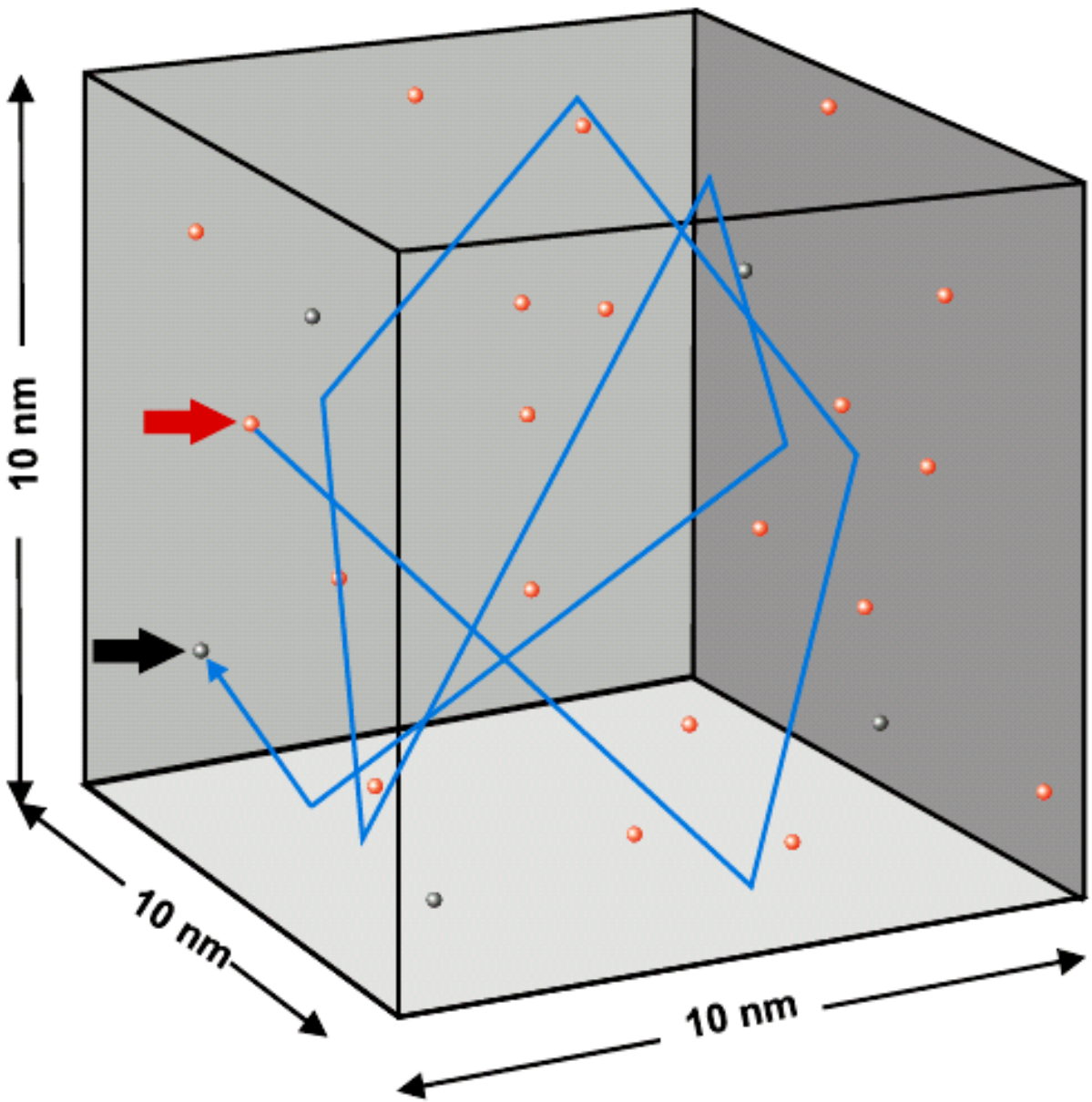
1) Reactions can only occur during collisions
2) Usually only a small fraction of the collisions leads to reactions

Reaction velocity:

$$-\frac{d[A]}{dt} = -\frac{d[B]}{dt} = \frac{d[C]}{dt} = \frac{d[D]}{dt} = k_2[A]\cdot[B]$$

Reaction rate constant of 2nd order: k_2 in $s^{-1}(konz.)^{-1}$, e.g. $cm^3 molec.^{-1} s^{-1}$

Snapshot of a Volume of Air (10^{-18} cm^3)



Volume: 10 x 10 x 10 nm

At 1000hPa and 17°C
It contains on average:

5 O_2 molecules

20 N_2 molecules

Blue trajectory:
mean free path (60 nm) of an air molecule (red arrow) until it hits another molecule (black arrow).

In reality the mean free path is a straight line!

oxygen, diameter 0.295 nm

nitrogen, diameter 0.315 nm

Reactions of 2nd Order

$$A + B \rightarrow Products$$

(Example: $O_3 + NO \rightarrow O_2 + NO_2$)

In this case A and B are consumed in equal amounts, and the velocity of the reaction is proportional to the product of the concentrations of A and B:

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

with the Reaction rate constant k in units of:
$1/((Molek/cm^3) \cdot sec) = cm^3/(Molek.\ s)$

Solution for special case [A]=[B]:

$$\frac{d[A]}{dt} = -2k \cdot [A]^2 \Rightarrow \frac{d[A]}{[A]^2} = -2k \cdot dt$$

$$\int_{[A]_0}^{[A]} \frac{d[A]'}{[A]'^2} = \int_0^t -2k \cdot dt' \Rightarrow -\frac{1}{2}\left(\frac{1}{[A]} - \frac{1}{[A]_0}\right) = -2k \cdot t \Rightarrow \frac{1}{[A]} = 4k \cdot t + \frac{1}{[A]_0} \Rightarrow [A] = \frac{[A]_0}{4k \cdot t \cdot [A]_0 + 1} \underbrace{\propto \frac{[A]_0}{t}}_{t \gg}$$

Reactions Velocity and Reaction Order (4)

1) A → Products $\frac{d[A]}{dt} = -k[A]$ $\{k\} = \frac{1}{s}$

2) A + B → Products $\frac{d[A]}{dt} = \frac{d[B]}{dt} = -k[A][B]$ $\{k\} = \frac{cm^3}{molec. \cdot s}$

3) A + B + C → Products $\frac{d[A]}{dt} = \frac{d[B]}{dt} = \frac{d[C]}{dt} = -k[A][B][C]$

$\{k\} = \frac{cm^6}{molec.^2 \cdot s}$

pseudo 1. Order:

A + B → Products, but [B] >> [A] → [B] ≈ const. (e.g. O_2)

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

$$\frac{1}{[B]} \cdot \frac{d[B]}{dt} \approx 0$$

Elementary vs. Complex Reactions

Thesis:

Only Reactions of 2nd Order of the type:

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

Are **Elementary reactions**

Any other type of reaction (in particular the unimolecular decay and reactions of the type $A+B \rightarrow C$) are

Complex Reactions, i.e. reactions, which are not occurring within a single collision, but rather proceed in a series of steps.

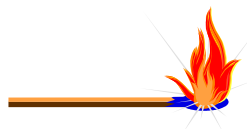
Example for a Complex Reaction: Oxyhydrogen Gas Explosion

Atmospheric mixing ratios of radicals are exceedingly low
e.g. about 1 OH-radical for every 10^{13} air molecules

But:
In chemical reactions with molecules the radical status is „hereditary“ e.g.:

$OH^{\bullet} + CO \rightarrow CO_2 + H^{\bullet}$

Example (oxyhydrogen gas):

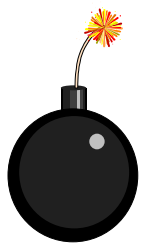


$H_2 + O_2 \rightarrow HO_2^{\bullet} + H^{\bullet}$ „Start“

$H_2 + HO_2^{\bullet} \rightarrow OH^{\bullet} + H_2O$
$H_2 + OH^{\bullet} \rightarrow H^{\bullet} + H_2O$
Propagation
(inherit radical status)

$H^{\bullet} + O_2 \rightarrow OH^{\bullet} + O^{\bullet}$
$O^{\bullet} + H_2 \rightarrow OH^{\bullet} + H^{\bullet}$
Branching
(from one radical we get two)

$OH^{\bullet} + HO_2^{\bullet} \rightarrow H_2O + O_2$
Termination



Net: $2H_2 + O_2 \rightarrow 2\,H_2O$

Consequence: The radikal concentration and thus the speed of reaction can increase exponentially.
→ **„Oxyhydrogen gas“**

Does that also happen in the atmosphere?

Reactions of 3rd Order (Termolecular Reactions)

- In general: A + B + C → Products
- In the atmosphere: C usually N_2 or O_2 → M ("Molecule")
- Popular special case: Rekombination reactions

  A + B + M → AB + M
- M absorbs the reaction energy (+momentum)
- In detail:

A + B → (AB)*	(a)
(AB)* → A + B	(b)
(AB)* + M → AB + M	(c)

Thus: Not a elementary reaction

- High pressure limit: $k_\infty = k_a$ – reaction (b) can be neglected
- Low pressure limit: $k_0 = k_a k_c / k_b$ – reaction (a)+(c) slower than (b)
- Overall – Reaction rate constant (Lindemann – Hinshelwood Formula):

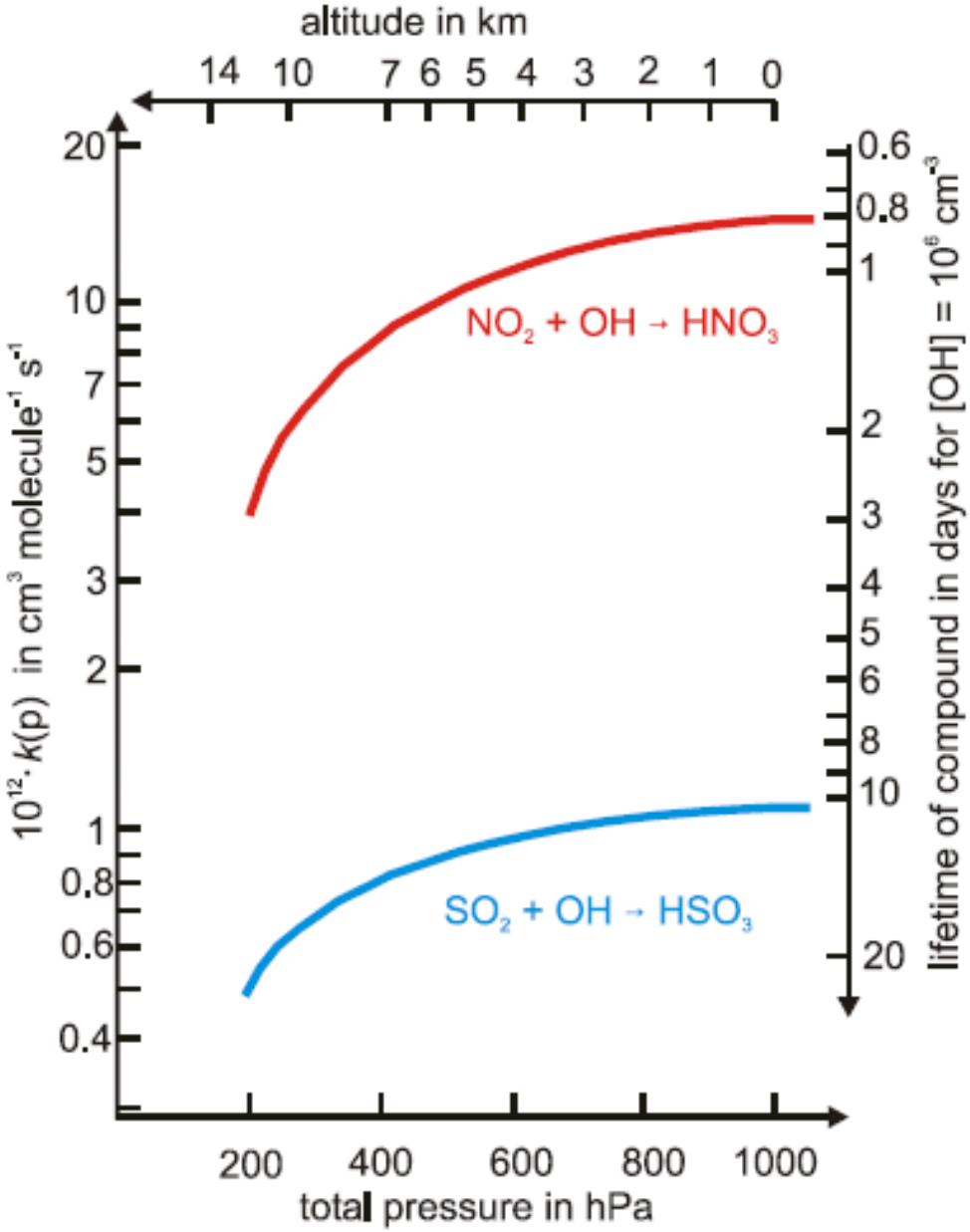
$$k([M]) = k(p) = \frac{k_a k_c [M]}{k_b + k_c [M]} = \frac{k_0 k_\infty [M]}{k_0 [M] + k_\infty}$$

Pressure: $p \propto [M]$ Hence the name: pressure dependent reaction

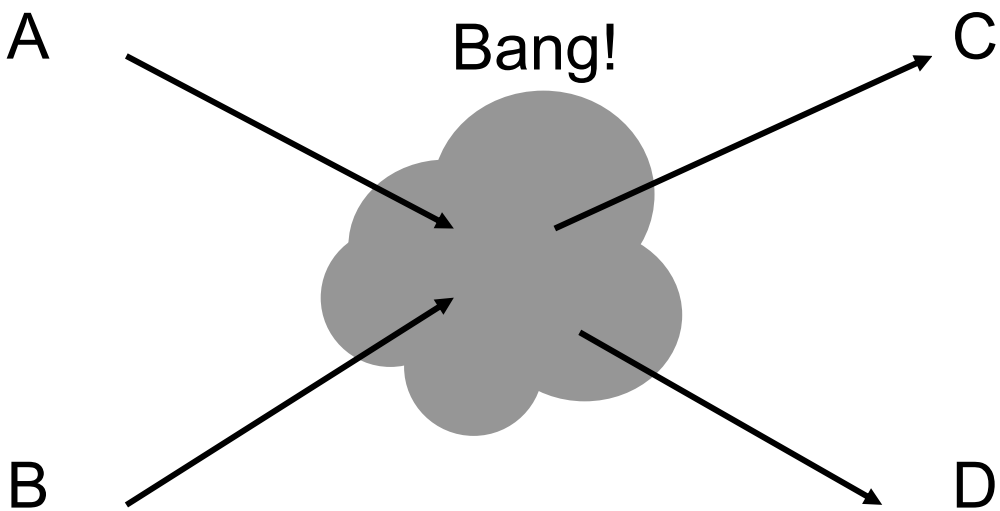
Pressure dependent Reactions (Termolekular Reactions 2)

Pressure and altitude dependence of two pseudo-bimolecular reactions.
The scale on the right-hand side denotes the lifetimes of NO_2 and SO_2, respectively, which would result if these compounds were only removed by reaction with 10^6 OH cm^{-3} at all altitudes.

From: U. Schurath

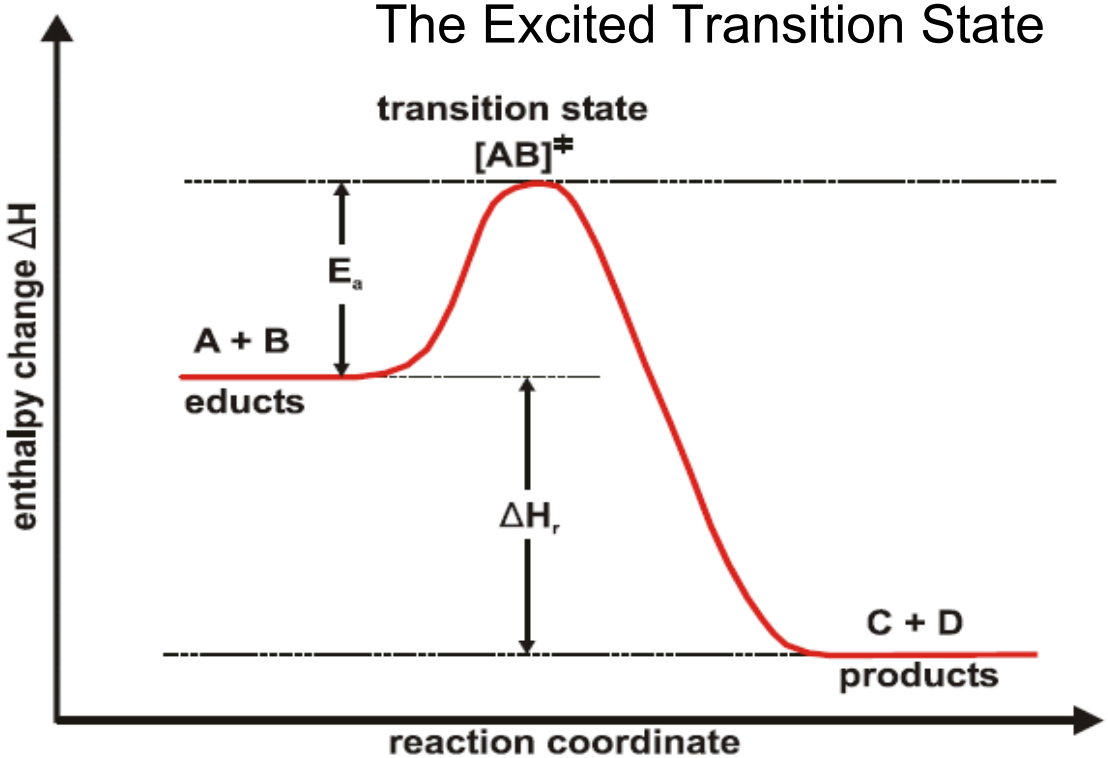


What Happens During a Chemical Reaction?



Activation energy E_a

The Excited Transition State



The Maxwell-Boltzmann-Distribution

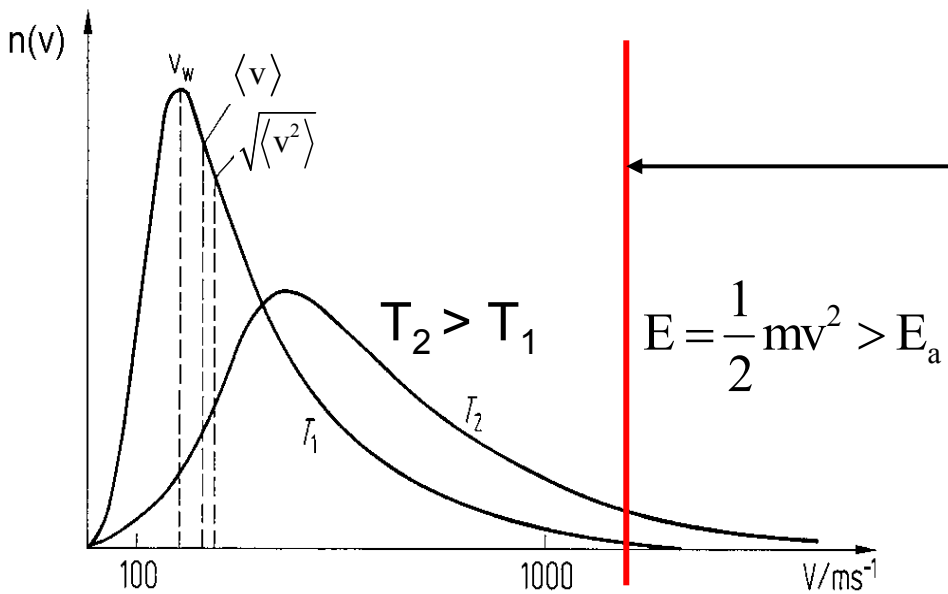
The velocity distribution function, i.e. the number of gas molecules in the velocity interval [*v, v+dv*] given by the Maxwell-Boltzmann - distribution:

$$f(v)dv = \sqrt{\frac{2}{\pi}}\left(\frac{m}{kT}\right)^{3/2} \cdot v^2 \cdot \exp\left(-\frac{mv^2}{2 \cdot kT}\right)dv \text{ with } v = \sqrt{2\frac{E}{m}}$$

We obtain:

$$dv = \frac{dv}{dE} \cdot dE = \frac{dE}{\sqrt{2 \times E \times m}}$$

$$f(E) \cdot dE = \frac{2}{\sqrt{\pi}} \cdot \frac{1}{(k \cdot T)^{3/2}} \cdot \sqrt{E} \cdot \exp\left(-\frac{E}{k \cdot T}\right) \cdot dE$$



→Fraction of molecules with $E>E_a$:

$$n(E > E_a) = \int_{E_0}^{\infty} f(E) \cdot dE = \frac{2}{\sqrt{\pi}} \cdot \frac{1}{(k \cdot T)^{3/2}} \cdot \int_{E_0}^{\infty} \sqrt{E} \cdot \exp\left(-\frac{E}{k \cdot T}\right) \cdot dE$$

Fraction of Molecules with $E>E_a$

The integration becomes simple, if the term $E^{1/2}$ in the integrand is assumed to be constant in comparison to the exponential:

$$n(E > E_a) = \frac{2}{\sqrt{\pi}} \cdot \sqrt{\frac{E_a}{k \cdot T}} \cdot \exp\left(-\frac{E_a}{k \cdot T}\right)$$

Thus the reaction rate constant k should be ist proportional to $n(E>E_a)$.

In 1889 **Svante Arrhenius** derived the following expression for the reaction rate constant:

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

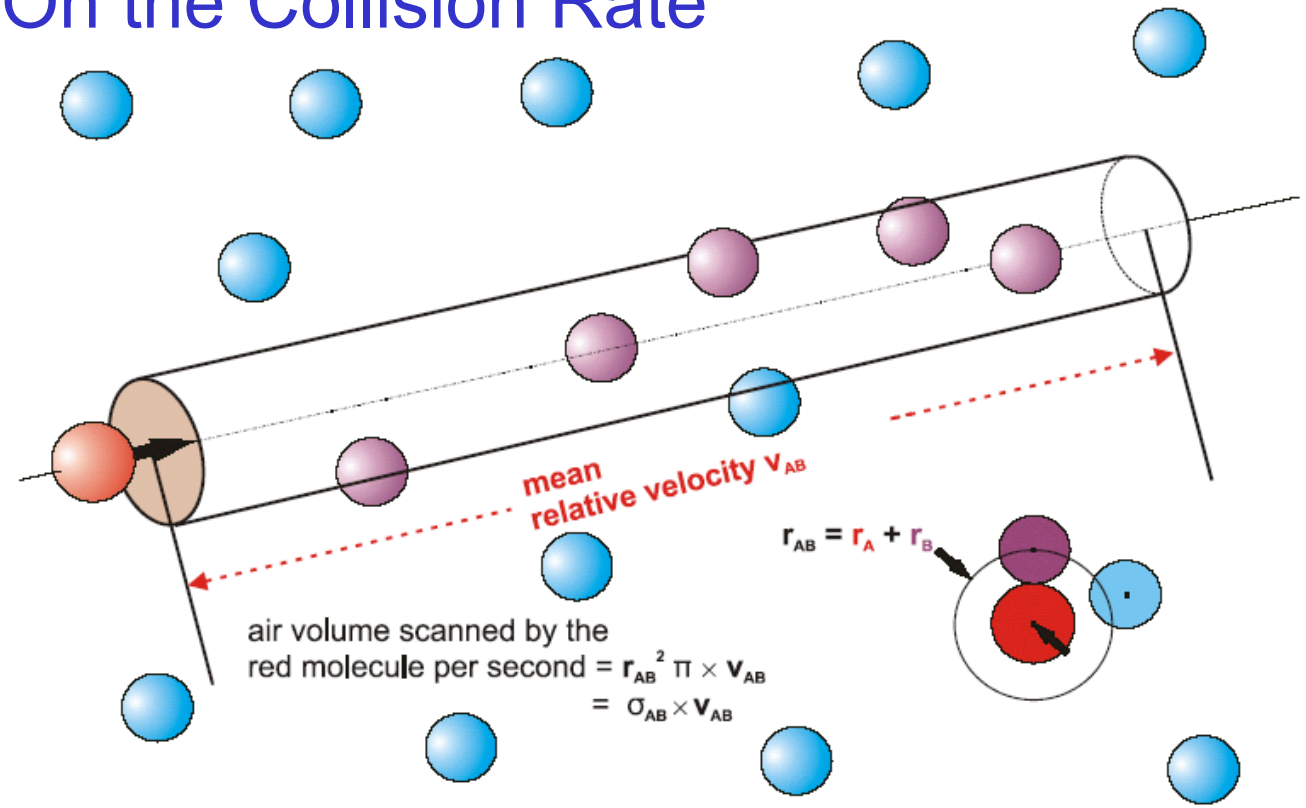
The constant *A* depends on the collision rate of the molecules (as well as of further conditions, e.g. the orientation of the molecules during the collision). The maximum value of *A* thus is the collision rate.

Svante Arrhenius

On the Collision Rate

A molecule can be though to traverse a „collision cylinder“ with radius r = diameter of the molecule d.

Number of collisions per time interval t is given by the number of moleculs in the volume $V=\pi d^2 tv$



Molec.	Collision Cross Section [10^{-15}cm²]
H_2	2.7
N_2	4.3
O_2	4.0
CO_2	5.2

If each collision would lead to a chemical reaction (A+B → C+D) it would proceed with a reaction rate of:

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

$$= \underbrace{\sqrt{2} \cdot \sigma \cdot \bar{v}}_{k_{AB}} \cdot [A][B]$$

Estimating Reaction Rate Constants

Mean kinetic energy E_{kin} of air molecules at temperature T:

$$\langle E_{kin} \rangle = \frac{3}{2} \cdot k \cdot T$$

corresponding mean velocity:

$$|\bar{v}| \approx \sqrt{\langle v^2 \rangle} = \sqrt{\frac{3 \cdot k \cdot T}{m}} \approx 500 \frac{m}{s} \text{ (air at } T = 293K)$$

Collision frequency (T = 293K, m = $4.81 \cdot 10^{-26}$ kg):

$$z = \frac{N}{\Delta t} = \sqrt{2} \cdot \rho \cdot \sigma \cdot \bar{v} \approx 8.0 \cdot 10^9 \; Hz$$

With these numbers we obtain a maximum reaktion rate constant (for P_{AB} = 1, i.e. a reaction ocurring at each collision):

$$k_{AB} = \sqrt{2} \cdot \sigma \cdot \bar{v} \approx 1.41 \bullet 4.3 \cdot 10^{-15} \bullet 5 \cdot 10^4 \approx 3 \cdot 10^{-10} \frac{cm^3}{Molec. \cdot s}$$

However, in reality usually $P_{AB} << 1$, e.g. because of the energy barrier, thus the Arrhenius Eq. Becomes:

$$k(T) = k_{AB} \cdot \exp\left(-\frac{E_a}{k \cdot T}\right)$$

Some Important Reaction Rate Constants

Reaction			k in cm^3 $molecule^{-1}$ s^{-1} at 298K
$OH + CO$	→	$H + CO_2$	$2.1 \cdot 10^{-13}$ (1 atm)
$OH + CH_4$	→	$H_2O + CH_3$	$6.2 \cdot 10^{-15}$
$OH + C_2H_6$	→	$H_2O + C_2H_5$	$2.5 \cdot 10^{-13}$
$CH_3 + O_2 + M$	→	$CH_3O_2 + M$	$1.0 \cdot 10^{-30}$ (k_0, $Molek^{-2}$ $cm^6 s^{-1}$) $1.8 \cdot 10^{-12}$ (k_∞)
$OH + NO_2 + M$	→	$HNO_3 + M$	$2.6 \cdot 10^{-30}$ (k_0, $Molek^{-2}$ $cm^6 s^{-1}$) $6.7 \cdot 10^{-11}$ (k_∞)
$HO_2 + O_3$	→	$OH + 2\ O_2$	$2.0 \cdot 10^{-15}$
$NO + O_3$	→	$NO_2 + O_2$	$1.8 \cdot 10^{-14}$
$NO_2 + O_3$	→	$NO_3 + O_2$	$3.2 \cdot 10^{-17}$
$O + O_3$	→	$O_2 + O_2$	$8.0 \cdot 10^{-15}$

Atkinson et al. 1997, J. Phys. Chem. Ref. Data, 26, 521-1029
JPL compilations: http://jpldataeval.jpl.nasa.gov/index.html
IUPAC compilations: http://www.iupac-kinetic.ch.cam.ac.uk/

Photo Chemistry

Absorption of a photon with frequency ν by a molecule can lead to a chemical reaction, e.g. break-up of the molecule (Photolysis).

$$A + h\nu \rightarrow \text{Products}$$

Analogous to first order reactions we can describe the reaction velocity of photolysis as:

$$\frac{d[A]}{dt} = -J \cdot [A] \quad \text{units of } J: \ s^{-1}$$

The reaction rate constant *J* is called Photolysis Frequency. (Not to be confused with the photolysis rate which is defined as:

$$R_J = -\frac{d[A]}{dt} = J \cdot [A] \quad \text{units of } R: \ molec.cm^{-3}s^{-1}$$

The Photolysis Frequency (1)

The absolute value of the photolysis frequency J depends on three factors:

1) The property of the molecule, to absorb radiation of a given frequency ν (or wavelength λ).
   Quantitatively:
   - I(ν) = Intensity of the radiation field
   - $\sigma(\nu)$= Absorption cross section of A at the frequency ν
   - ds = Thickness of the absorbing layer

$$dI(\nu) = -I(\nu)\cdot\sigma(\nu)\cdot[A]\cdot ds \quad \text{bzw.} \quad dI(\lambda) = -I(\lambda)\cdot\sigma(\lambda)\cdot[A]\cdot ds$$

2) The probability, that the absorption of a photon will lead to a reaction (e.g. to the dissoziation) of the molecule.
   Prerequisit: Photon energy > Binding energy of the molecule (or the activiation energy E_a. This probability is called Quantum Efficiency (quantum yield) ϕ.
   Frequently ϕ can be approximated by a step funktion, i.e.

$$\phi(\nu) \approx \begin{cases} 0; & h\nu < E_a \\ 1; & h\nu \geq E_a \end{cases}$$

The Photolysis Frequency (2)

Example:

UV – Photolysis of O_3:

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

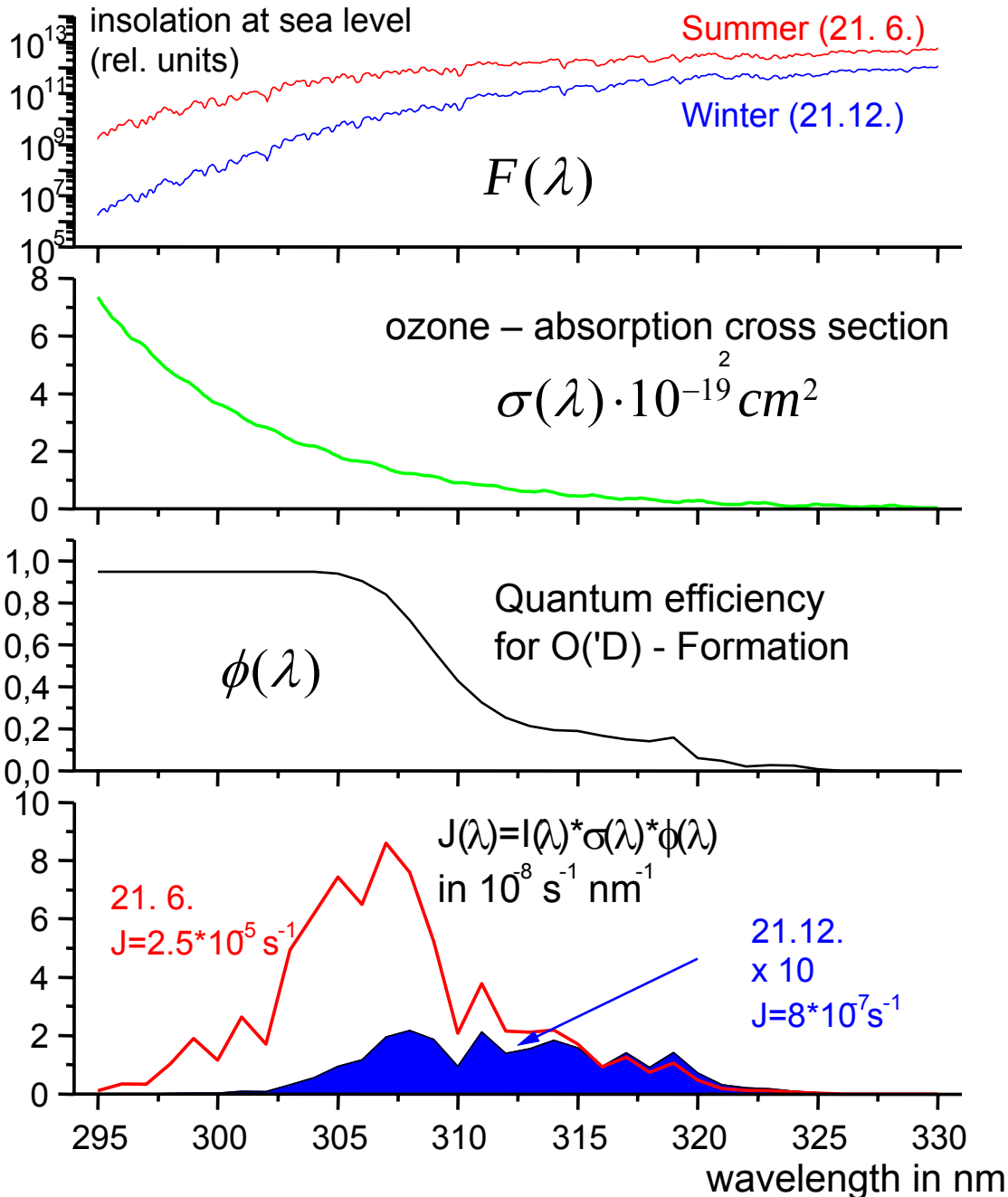
$$J(\lambda) = \phi(\lambda) \cdot \sigma(\lambda) \cdot F(\lambda)$$

$$J = \int_0^\infty J(\lambda) \cdot d\lambda$$

$$= \int_0^\infty \phi(\lambda) \cdot \sigma(\lambda) \cdot F(\lambda) \cdot d\lambda$$

Typical daily mean:

OH-Production: $3 \cdot 10^5$ $cm^{-3}s^{-1}$
Daily integral: $3 \cdot 10^{10}$ cm^{-3}



The Photo - Stationary State

- NO_x – O_3 Reactions:

$NO_2 + hv \rightarrow NO + O(^3P)$	J
$O(^3P) + O_2 \rightarrow O_3$	“very fast”
$O_3 + NO \rightarrow NO_2 + O_2$	$k = 1.8 \cdot 10^{-14}$

- No net reaction
- The stationary state NO - concentration is a function of the UV-flux

$$\frac{d[NO]}{dt} = J[NO_2] - k[NO][O_3]$$

- Stationary state:

$$\frac{d[NO]}{dt} = 0$$

$$\frac{[NO_2]}{[NO]} = -\frac{k}{J}[O_3] \approx \frac{1.8 \cdot 10^{-14}}{8 \cdot 10^{-3}} 10^{12} \approx 2.25$$

Also known as “Leighton-ratio”

(thermodynamic) Equilibrium ≠ Stationary State

The Thermodynamic Equilibrium

Equilibrium reaction: $A + B \leftrightarrow C + D$

Law of Mass Action (Massenwirkungsgesetz):

Equilibrium constant:

$$K = \frac{[C][D]}{[A][B]} = e^{-\frac{\Delta G}{RT}} = \frac{[A][B] \cdot k_{\rightarrow}}{[C][D] \cdot k_{\leftarrow}}$$

$$\Delta G = \Delta H - T \cdot \Delta S = G_{fC} + G_{fD} - \left[G_{fA} + G_{fB}\right]$$

$$= \left(H_c - TS_c\right) + \left(H_D - TS_D\right) - \left[\left(H_A - TS_A\right) + \left(H_B - TS_B\right)\right]$$

The equilibrium constant is only determined by the difference in the Gibbs free energy (i.e. the heat of formation and the entropy) of the involved species and the temperature.

However: The time it takes to reach the equilibrium depends on the magnitude of the reaction rate konstants!

Example: **CH_4 + OH → CH_3 + H_2O,** see listings of ΔG_f in JPL:

$\Delta G(CH_4)$=-17.9 kcal mol^{-1}, $\Delta G(OH)$=9.3 kcal mol^{-1}, $\Delta G(CH_3)$=35.0 kcal mol^{-1}, $\Delta G(H2O)$=-57.8 kcal mol^{-1}

→ ΔG_{react} $=\Delta G(CH_4)+\Delta G(OH)-\Delta G(CH_3)-\Delta G(H_2O)$
$=$-17.9 kcal mol^{-1} + 9.3 kcal mol^{-1} - 35 kcal mol^{-1}+ 57.8 kcal mol^{-1} = 14.2 kcal mol^{-1}

Reaction Systems (very simple example)

NO_x – O_3 Reactions:

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

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

$O_3 + NO \rightarrow NO_2 + O_2$

$$\frac{d[NO_2]}{dt} = -J[NO_2] + k[NO][O_3]$$

$$\frac{d[NO]}{dt} = J[NO_2] - k[NO][O_3]$$

$$\frac{d[O]}{dt} = J[NO_2] - k_2[O][O_2]$$

$$\frac{d[O_3]}{dt} = k_2[O][O_2] - k[NO][O_3]$$

System of coupled differential equations

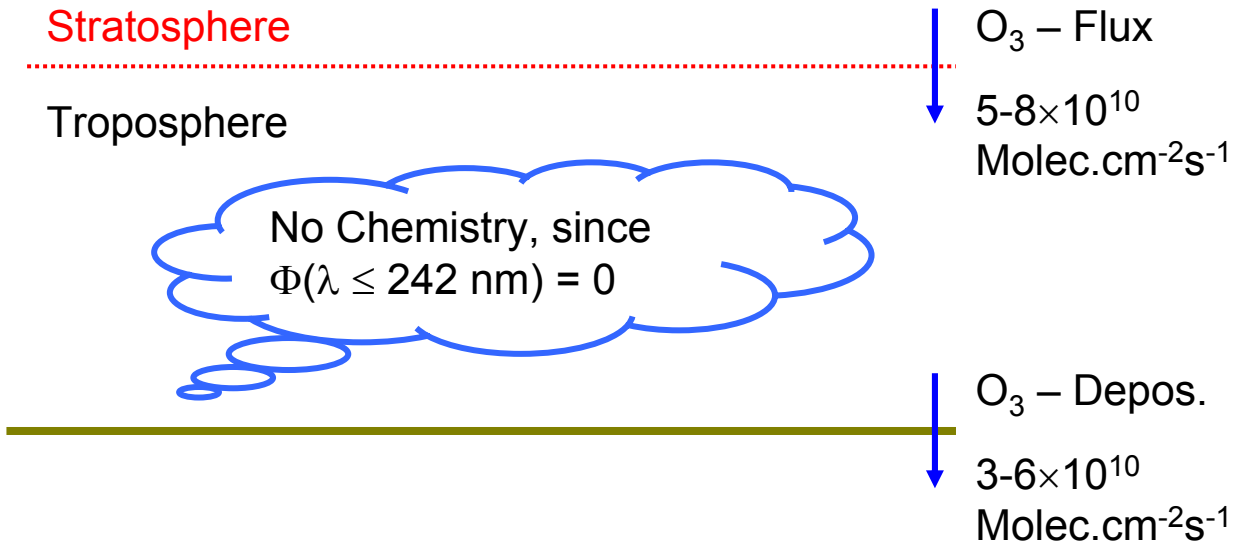
→ Numerical generation by „reaction compilers“ + Numerical integration

e.g. CHEMC (http://lpas.epfl.ch/MOD/software.html)

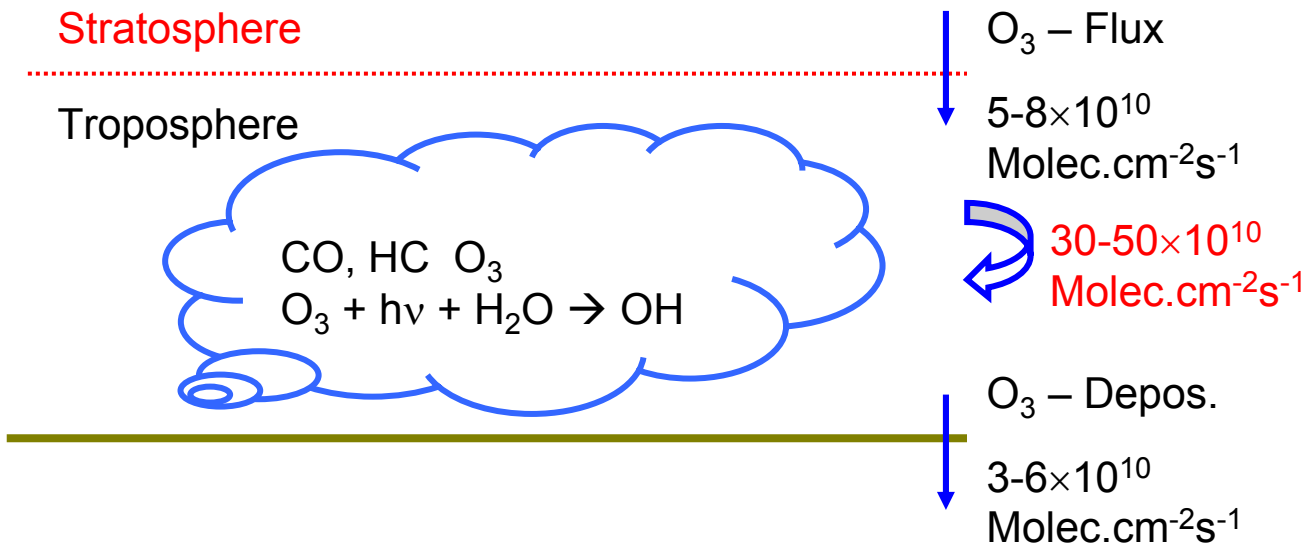
Reaction Kinetics at Work - Some Examples from the Atmosphere

The Origin of Tropospheric Ozone

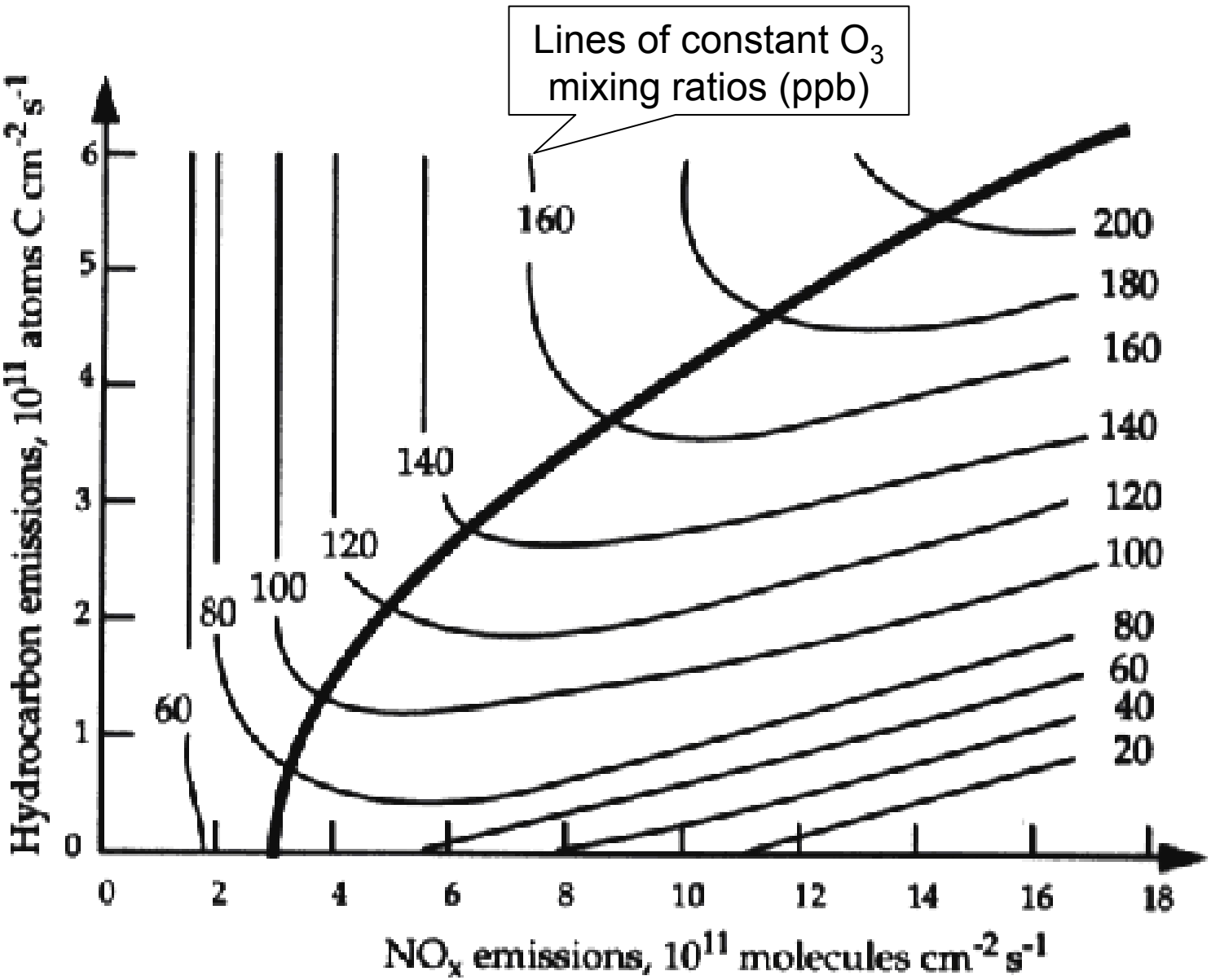
Initial Idea:



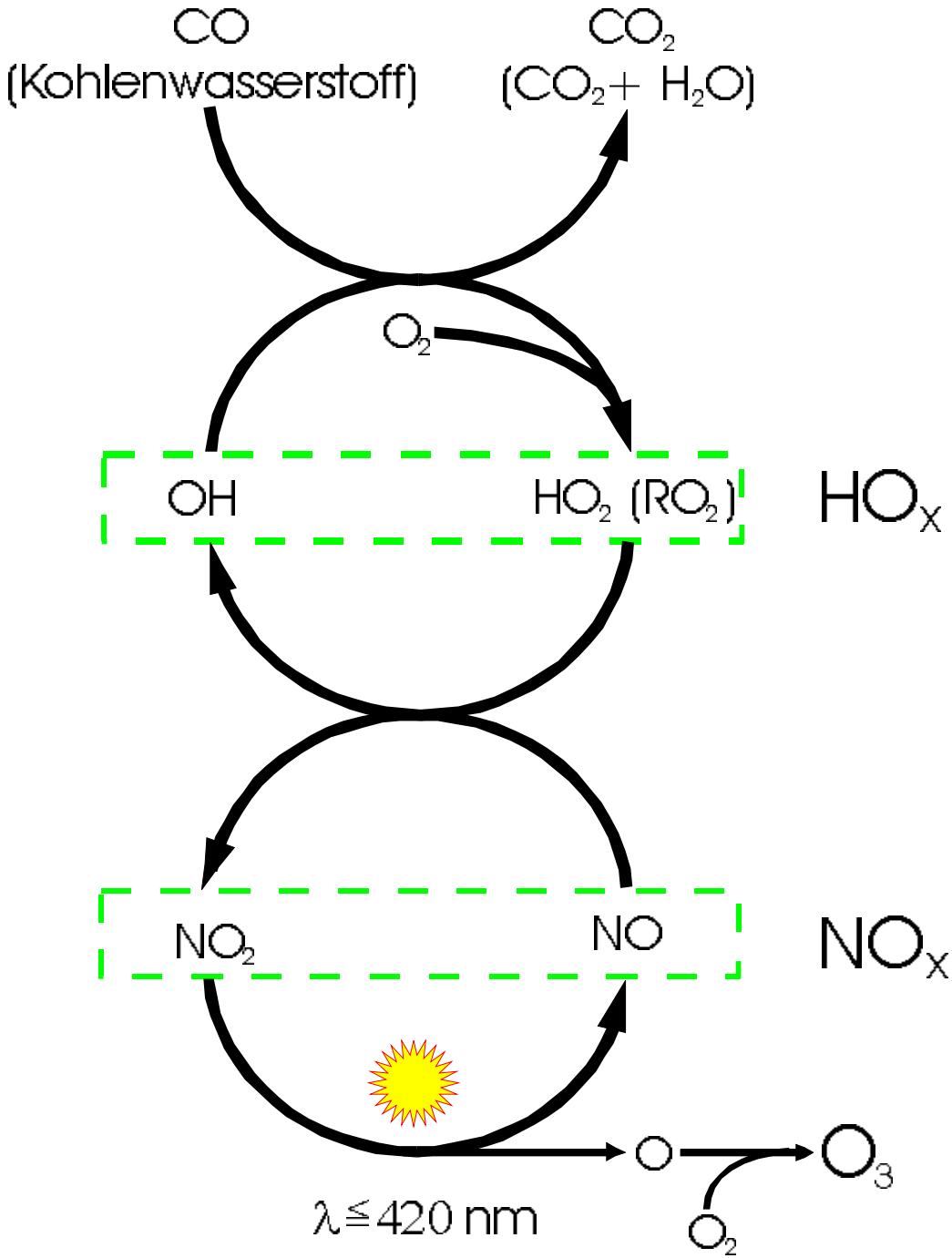
Today:



Smog Chamber Experiments --> Ozon 'Isoplets'



NO_X- and HO_X - Katalysis of the photochemical Ozone Production in the Troposphere



Disturbance of the Leighton Ratio and the rate of O_3 Formation

There is no net ozone production. However, if other reactions, in particular by Peroxy radicals oxidise NO to NO_2:

$$RO_2 + NO \rightarrow NO_2 + RO \qquad (R4)$$

Ozone will be formed at the rate P_{O3}. Also the **Leighton Ratio** will be reduced:

$$L_1 = \frac{[NO]}{[NO_2]} = \frac{J}{k \cdot [O_3] + k_R \cdot [RO_2]}$$

The rate of ozone formation, P_{O3} in a given airmass can be calculated from measurements of the **Leighton Ratio** $[NO]/[NO_2]=L_1$ together with $[O_3]$, and J:

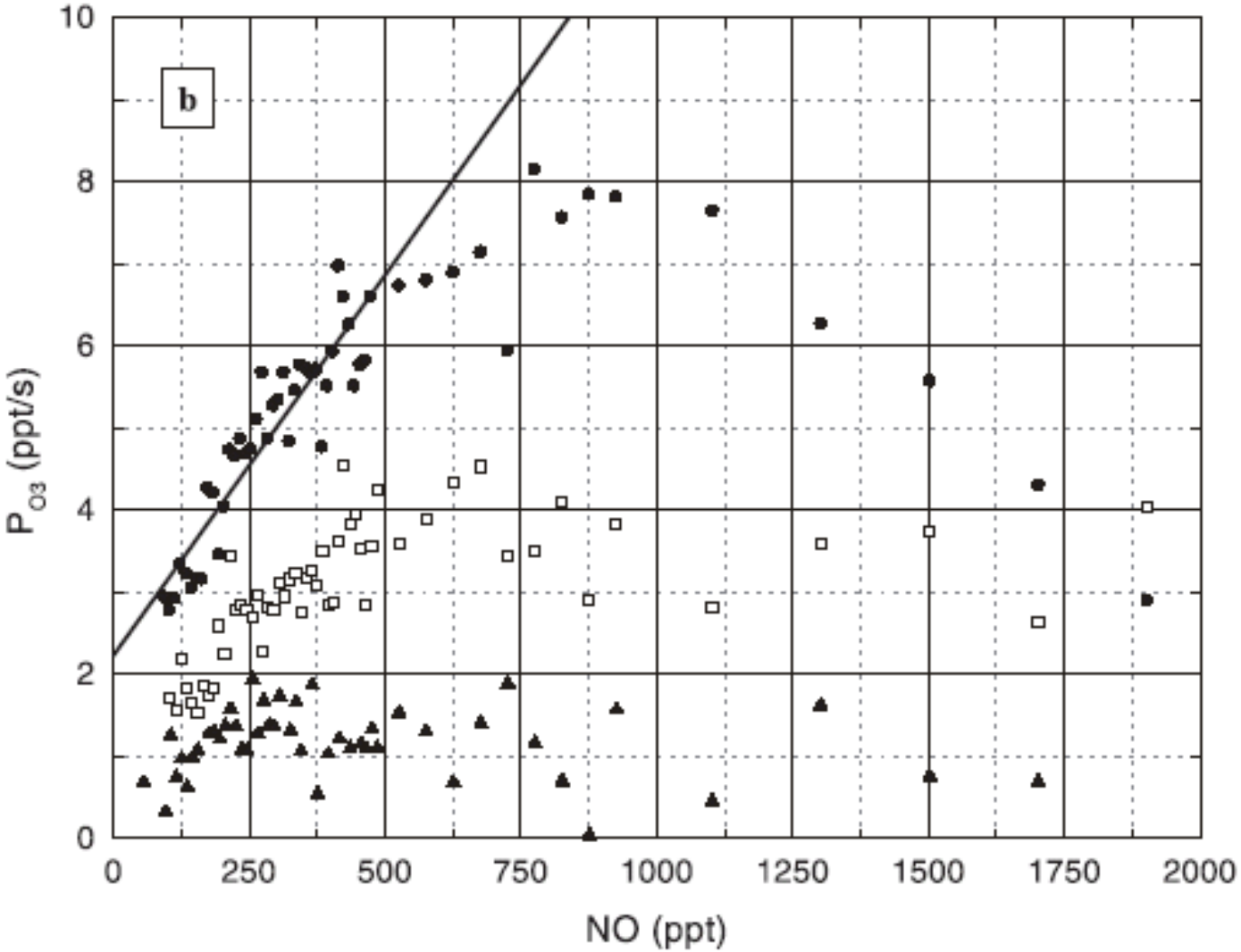
$$P_{O3} = \left(\frac{1}{L_1} - \frac{1}{L_0} \right) \cdot j_1 \cdot [NO]$$

Since P_{O3} relates to the concentration of peroxy radicals (RO_2), there concentration can also be inferred from these measurements.

$$P_{O3} = k_R \cdot [RO_2]$$

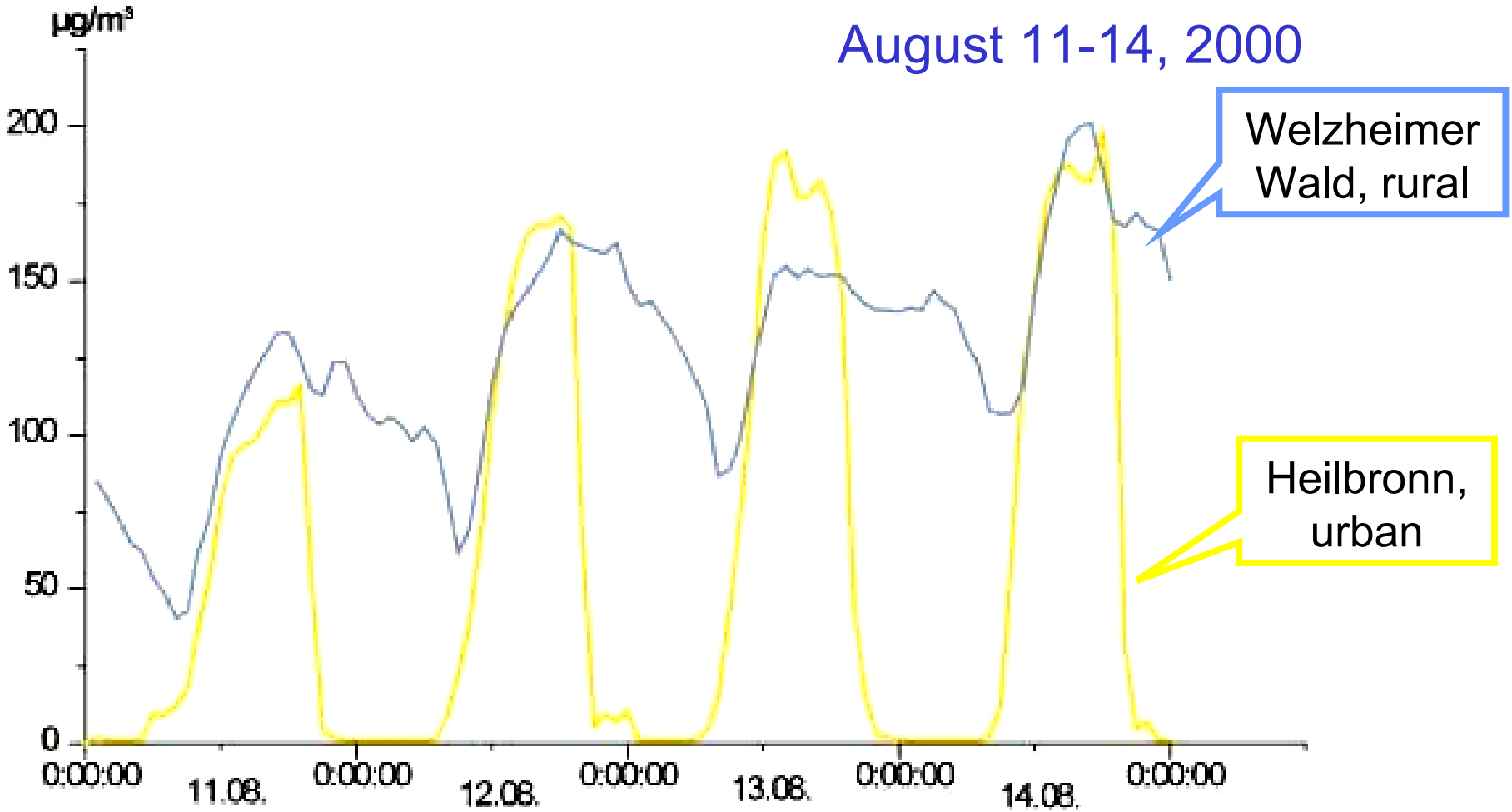
Observed O_3 Production Rates

'Southern Oxidant Study'
June 15 to July 15, 1999
at Cornelia Fort Airpark,
Nashville, Tennessee
[Thornton et al. 2002]



Averaged O_3 production rates P_{O3} calculated from simultaneous observations of NO, NO_2, O_3, OH, HO_2, H_2CO, actinic flux, and T. Data were placed into three P_{HOx} bins: high ($0.5 < P_{HOx} < 0.7$ ppt/s, circles), moderate ($0.2 < P_{HOx} < 0.3$ ppt/s, squares), and low ($0.03 < P_{HOx} < 0.07$ ppt/s, triangles), and then averaged as a function of NO. All three P_{HOx} regimes demonstrate the expected dependence on NO: P_{O3} increases linearly with NO for low NO (<600 ppt NO), P_{O3} becomes independent of NO for high NO (>600 ppt NO). Crossover between NO_X - limited and NO_X - saturated P_{O3} occurs at different levels of NO in the three P_{HOx} regimes.

Diurnal Variation of O_3 Levels in Different Air Masses: Forest (Weltzheimer Wald) and City of Heilbronn (southern Germany).



Landesanstalt für Umweltschutz Baden-Württemberg and UMEG)

Removal of CH_4

$CH_4 + OH \rightarrow CH_3 + H_2O$

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

$CH_3O_2 + NO \rightarrow CH_3O + NO_2$

$CH_3O + O_2 \rightarrow CH_2O + HO_2$

Formaldehyde

Another Radical

$CH_2O + h\nu \rightarrow CO + H_2$

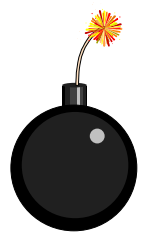
$\rightarrow CHO + H$

$CHO + O_2 \rightarrow CO + HO_2$

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

$HO_2 + NO \rightarrow OH + NO_2$

$CH_4 + OH + 2\ NO + h\nu \rightarrow CO + 2\ OH$



Free Radicals - Which are Important in Atmospheric Chemistry

First suggestion of OH reactions in the atmosphere by B. Weinstock 1969.
Formation of OH by:

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

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

Role of OH in the formation of CO and formaldehyde suggested [H. Levy 1971].
Role of OH in tropospheric ozone formation (P. Crutzen 1974)

Other Radicals (by either definition)? $O_2(^1\Delta)$, Cl-atoms, NO_3 ...

HO_X - Cycle

OH

- Degradation of most VOC
- Key intermediate in O_3 formation
- $NO_X \Rightarrow NO_Y$ conversion

HO_2

- Intermediate in O_3 formation
- Intermediate in H_2O_2 formation

RO_2

- Intermediate in ROOR´ formation
- Aldehyd – precursor
- PAN – precursor
- Intermediate in O_3 formation

NO_3

- Degradation of certain VOC
- $NO_X \Rightarrow NO_Y$ conversion (via N_2O_5)
- RO_2 – precursor

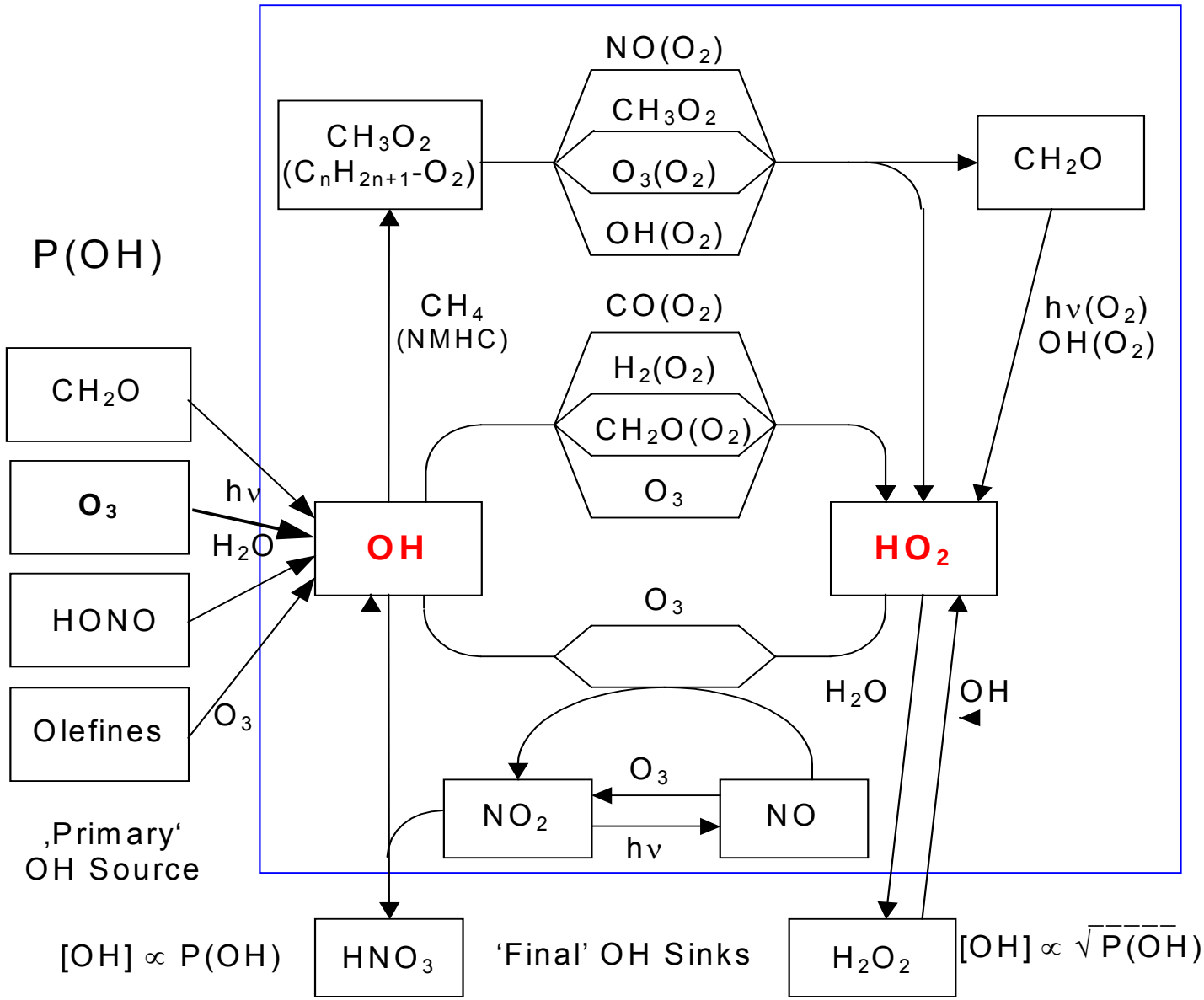
XO

- Catalytic O_3 destruction **(X = Cl, Br, I)**
- Degradation of DMS (BrO)
- Particle formation (IO)
- Change of the Leighton – Ratio

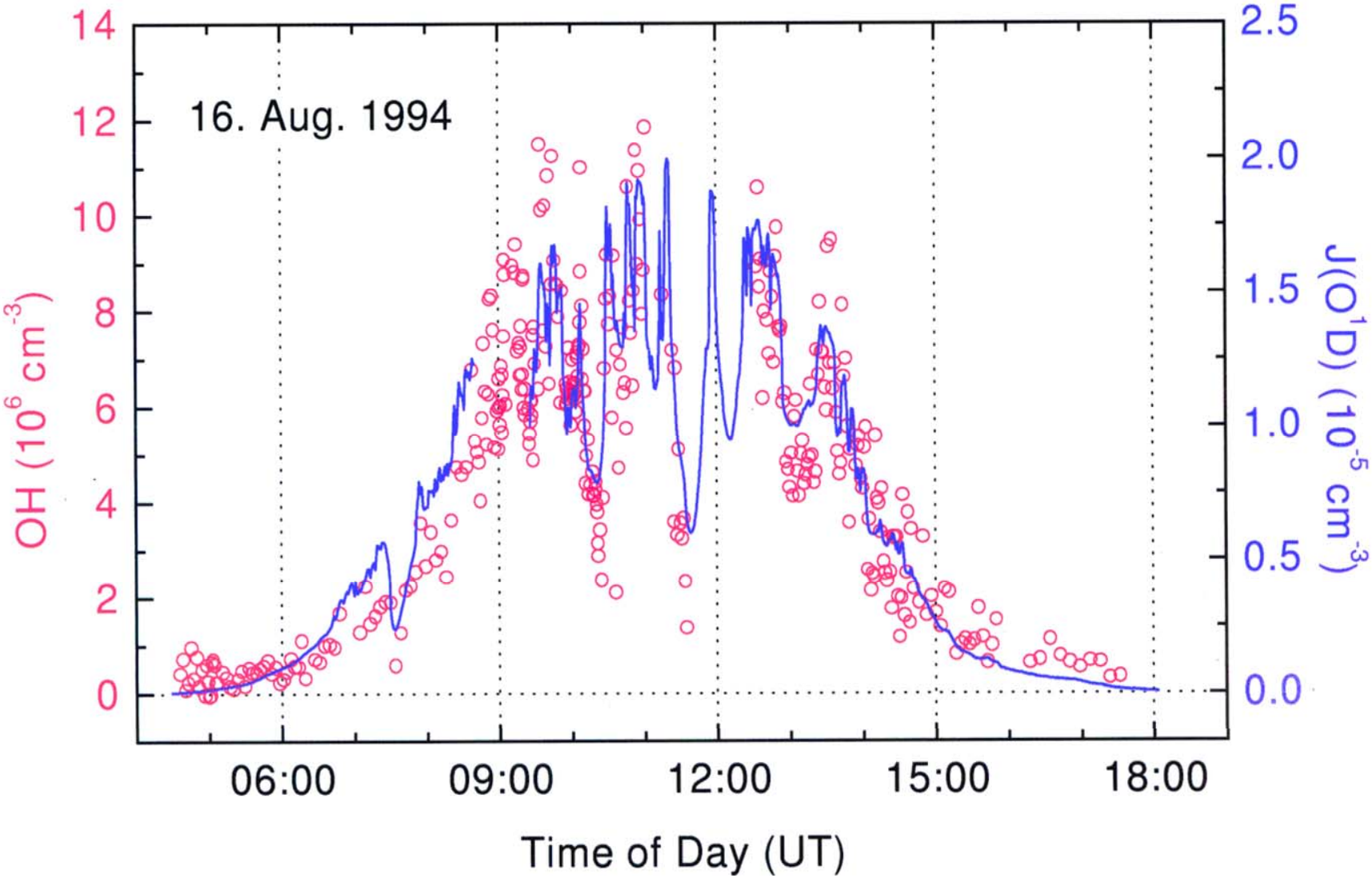
X

- Degradation of most (some) VOC: Cl (Br)
- Initiates O_3 formation
- RO_2 – precursor

Simplified Outline of the HO_X (=OH + HO_2 + RO_2) Cycles

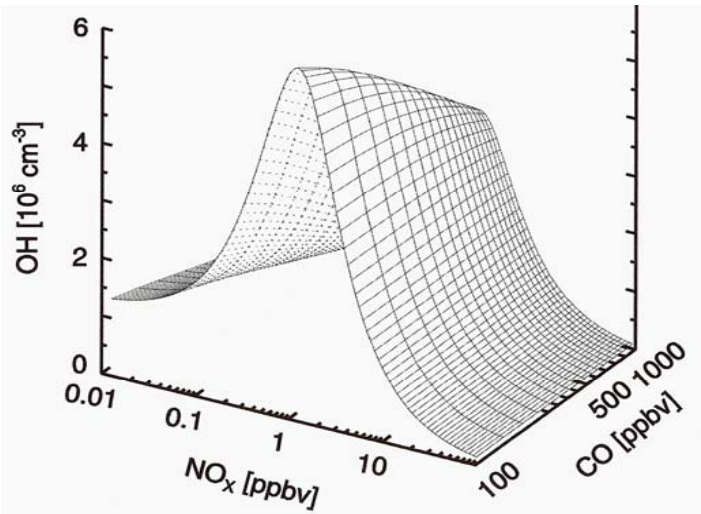


DiurnalVariation of OH - Concentration

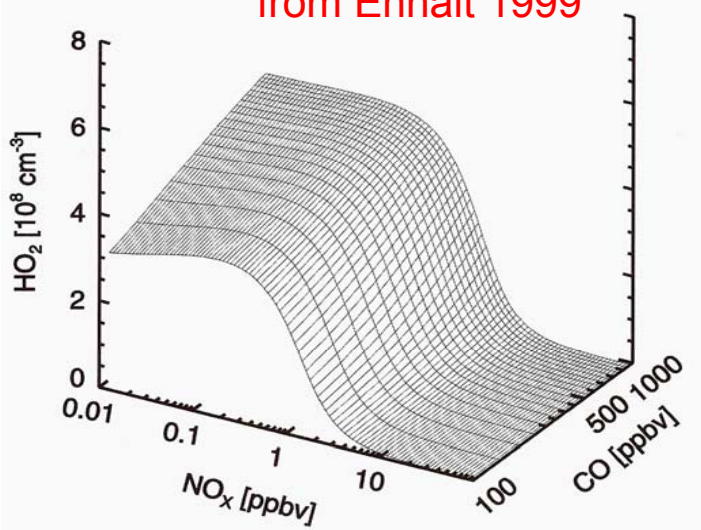


Hofzumahaus et al. – FZ Jülich

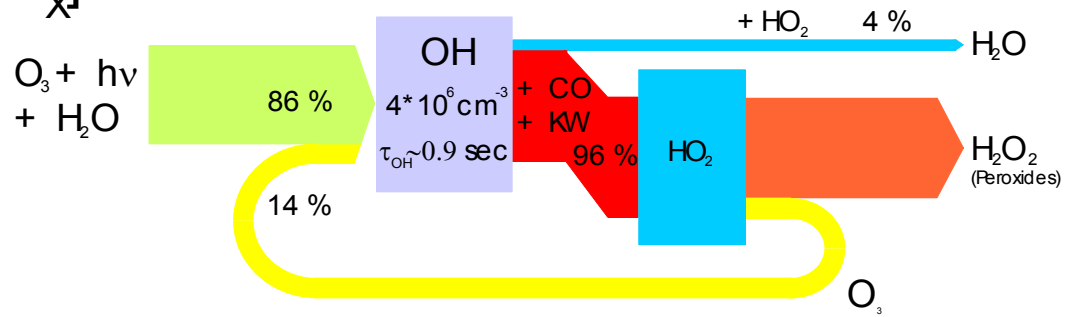
NO_X Dependence of OH - **Model**



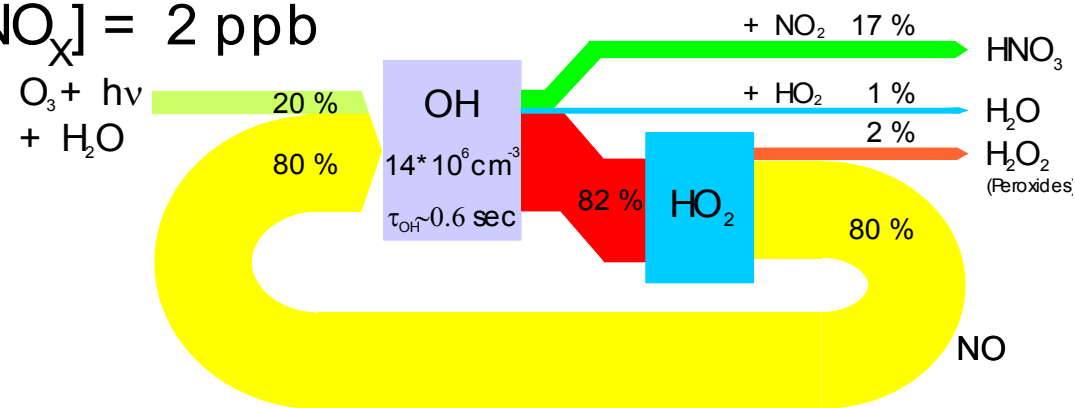
from Ehhalt 1999



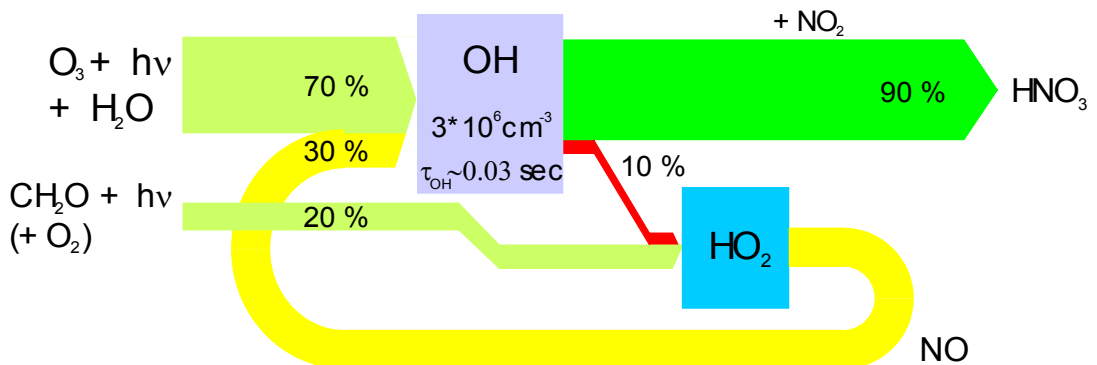
$[NO_X]$ = 0



$[NO_X]$ = 2 ppb



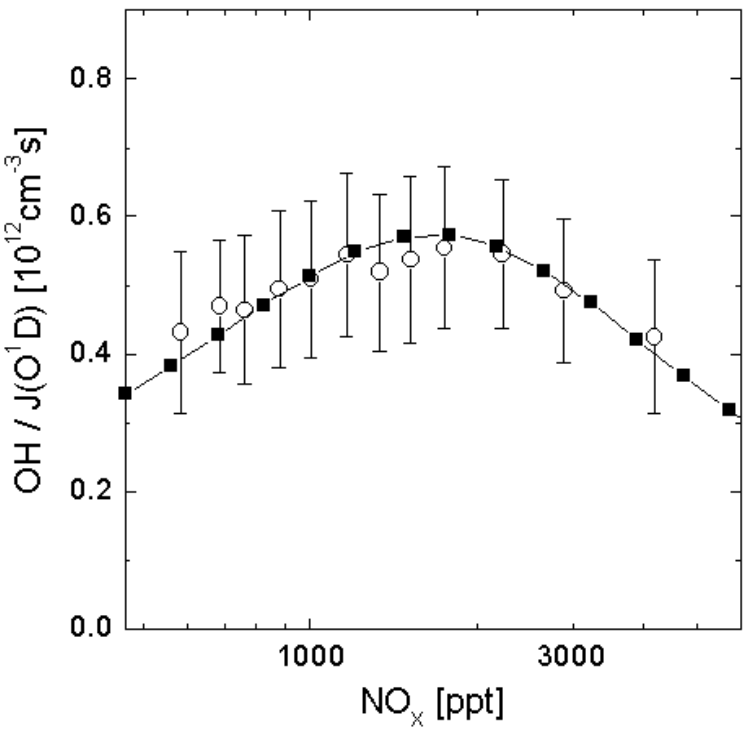
$[NO_X]$ = 100 ppb

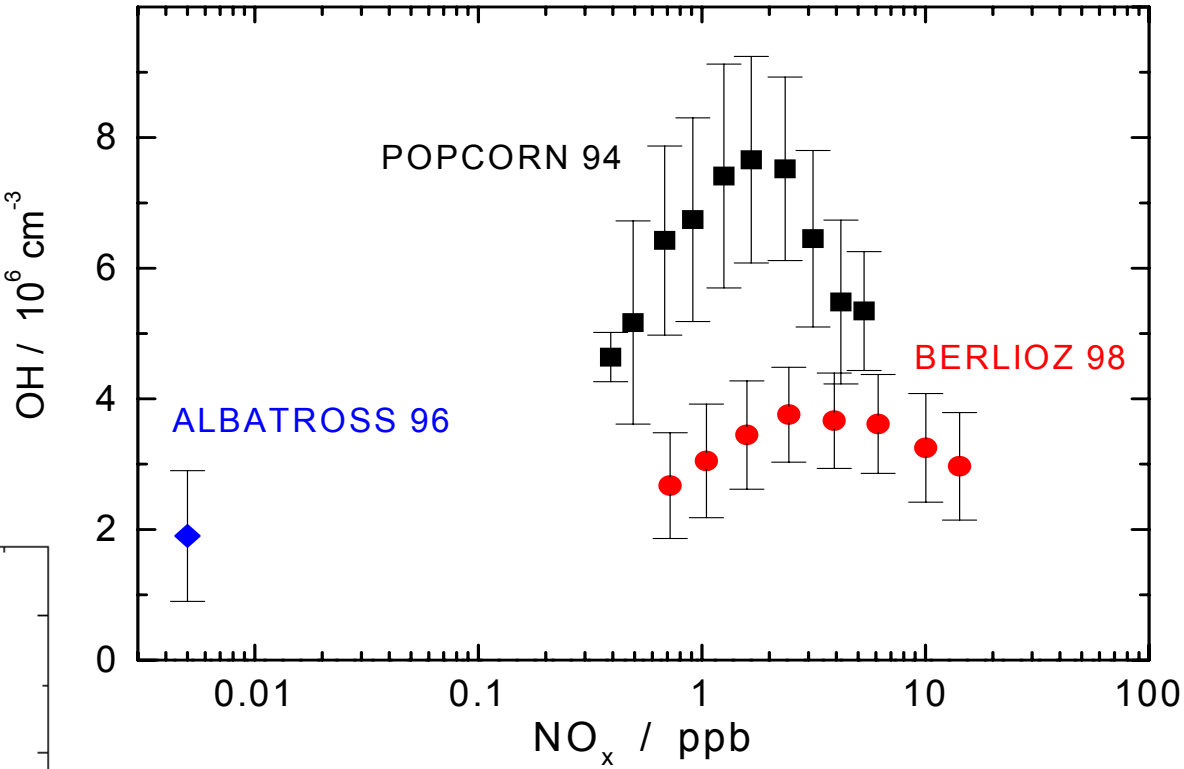


NO_X Dependence of OH -**Observation**

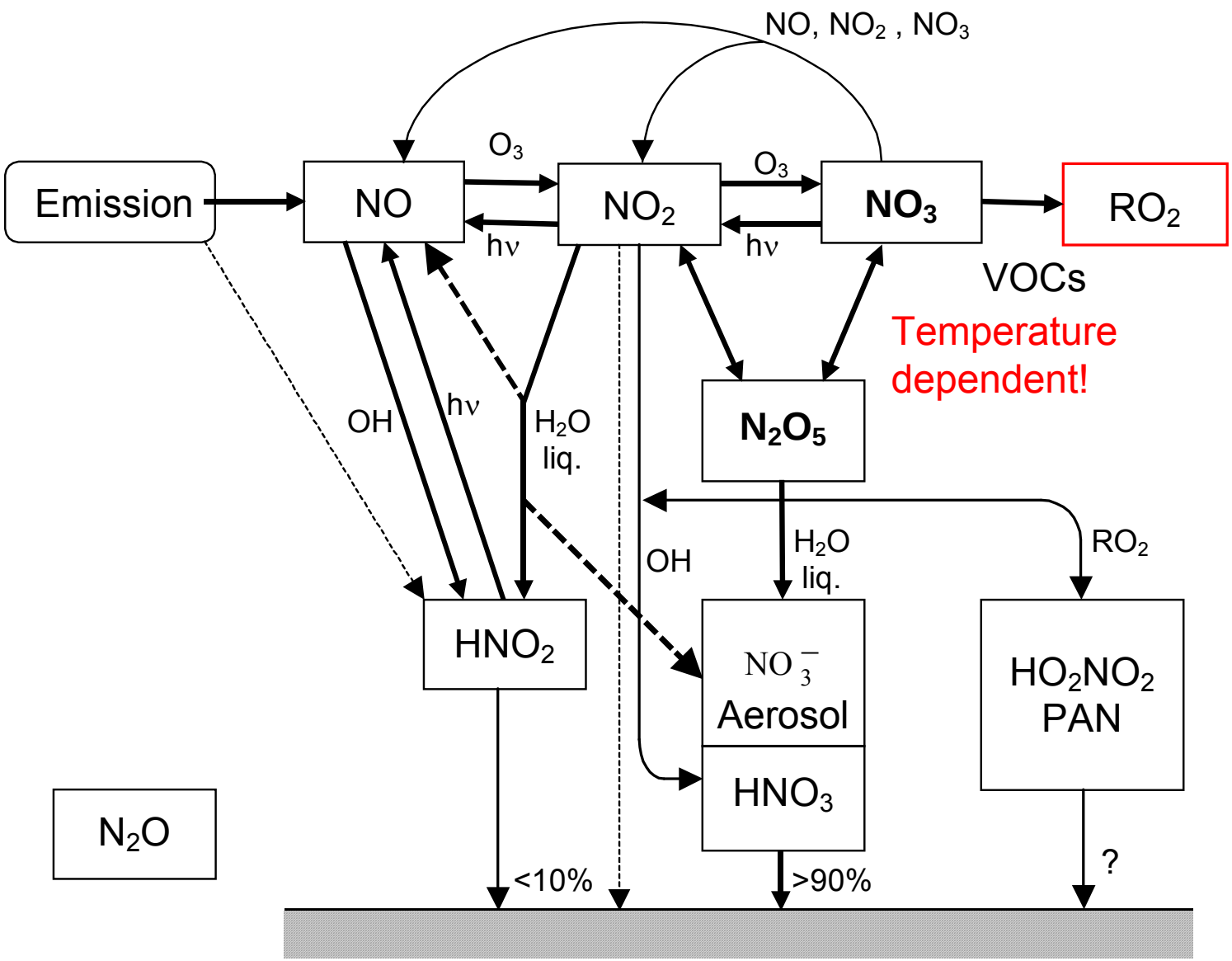
Forschungs
zentrum

Jülich

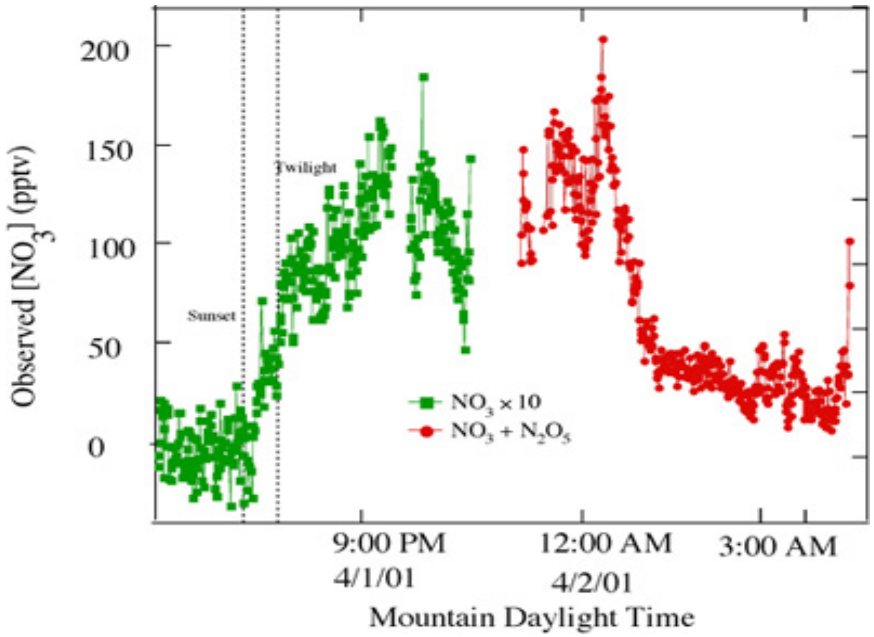




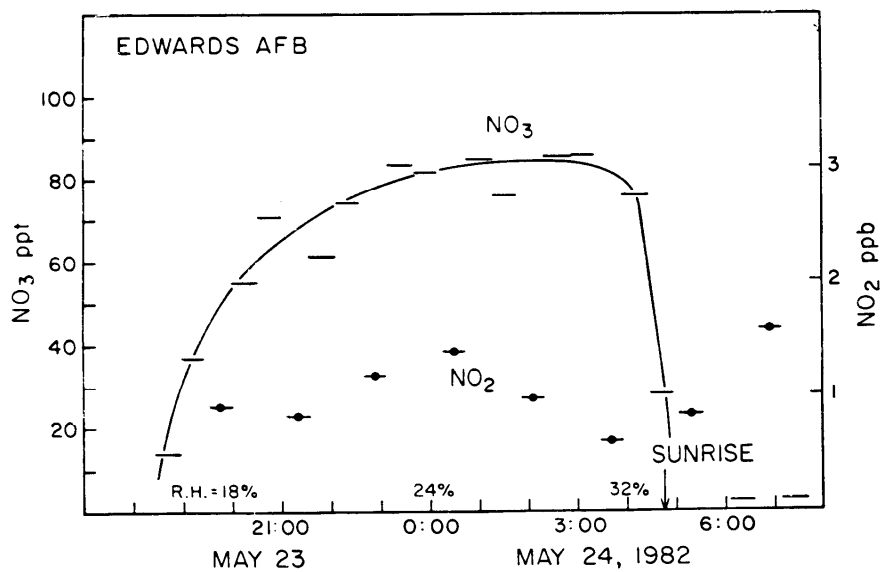
Simplified Outline of the NO_X- (=NO + NO_2) and NO_Y- Cycles



NO_3 Field Measurements



Cavity Ringdown
(Boulder, CO)
Brown et al. 2001



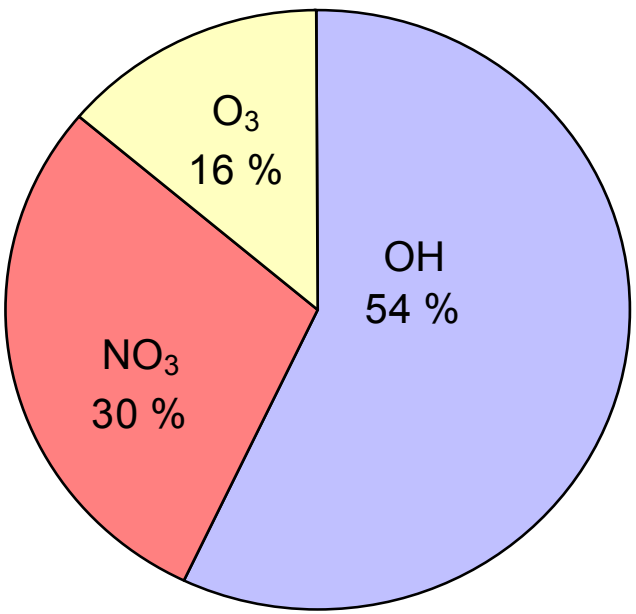
DOAS
(Edwards AFB)
Platt et al. 1984

Contribution of NO_3 to the Atmospheric Oxidation Capacity in Pabstthum (BERLIOZ 1998)

$$oc := \overline{\frac{d}{dt} VOCs} = [NO_3 / OH / O_3] \cdot f_{NO_3/OH/O_3-VOCs}$$

- average of all BERLIOZ-data
- 24h- mean values:

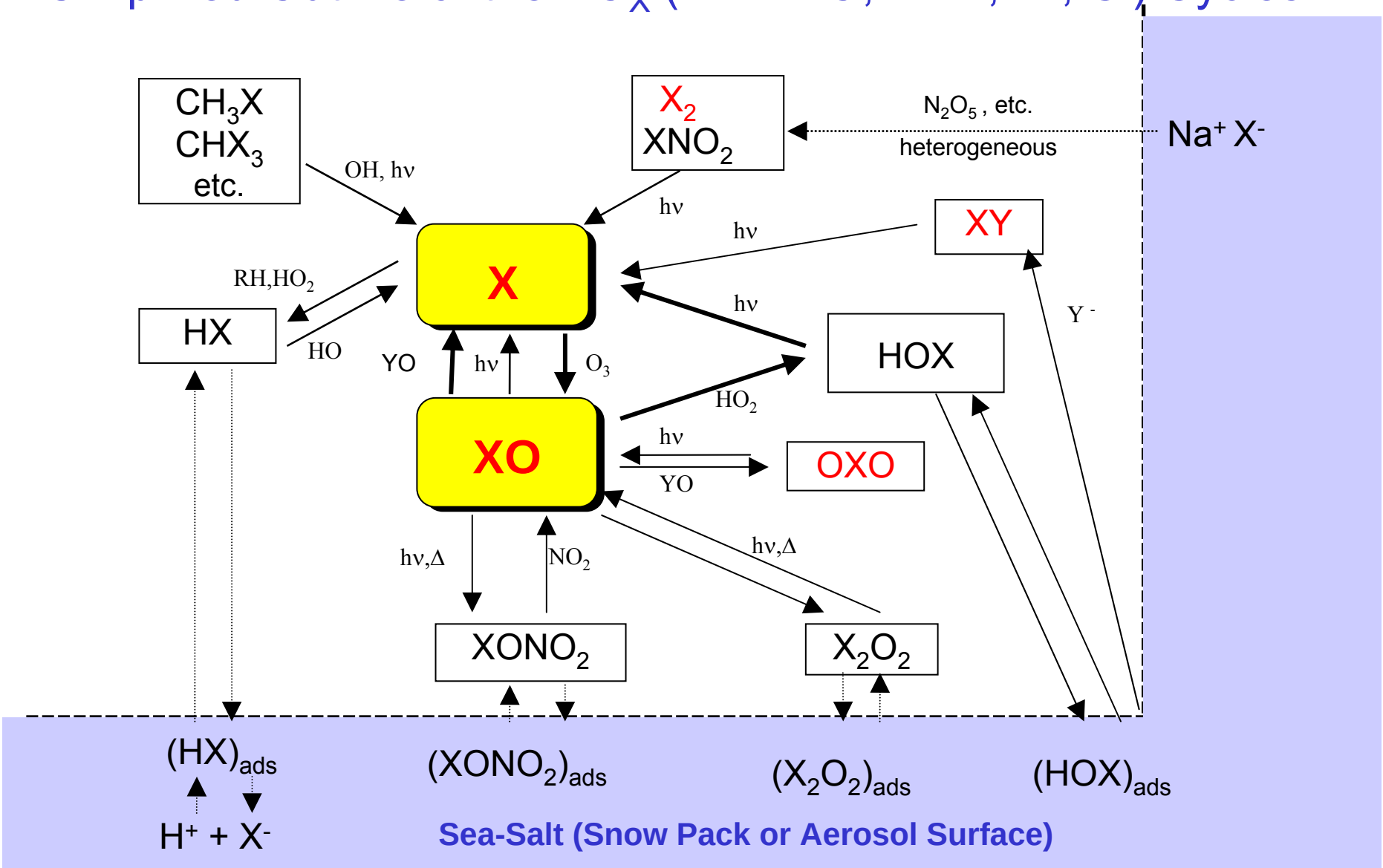
oc	$[cm^{-3}s^{-1}]$
NO_3	$4.5 \cdot 10^5$
OH	$8.1 \cdot 10^5$
O_3	$2.4 \cdot 10^5$



Geyer et al. 2001

$$\frac{oc(NO_3)}{oc(OH)} = \frac{1}{2}$$

Simplified Outline of the XO_X (=X + XO, X = I, Br, Cl) Cycles



$$\frac{[XO]}{[X]} \approx 1000(X = Cl),\ 100(X = Br),\ 10(X = I)$$

Daytime, rule of thumb

Observation of Reactive Halogens in the Troposphere

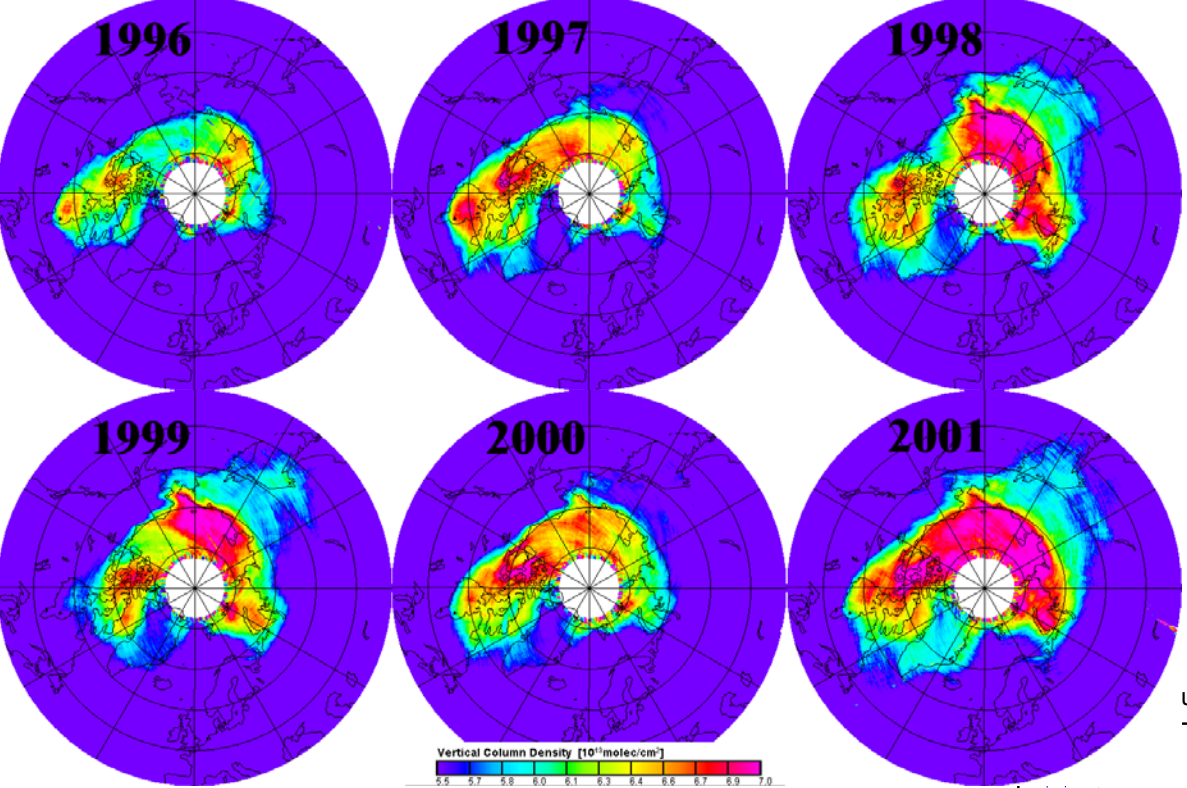
Reactive halogen species: Cl, Br, I, ClO, BrO, IO, OClO, OBrO, OIO, I_2O_2, ...

Domain	**ClO ppt**	**BrO ppt**	**IO ppt**
Free Troposphere	?	1-2	?
Coastal Regions	?	<2 ... 6	up to 10
Polar Regions (springtime)	several 10?	20 ... 40	?
Salt Lakes/Pans	up to 15	up to 200	up to 10
Volcanic Plumes	several 100 ppb	up to 1000	?

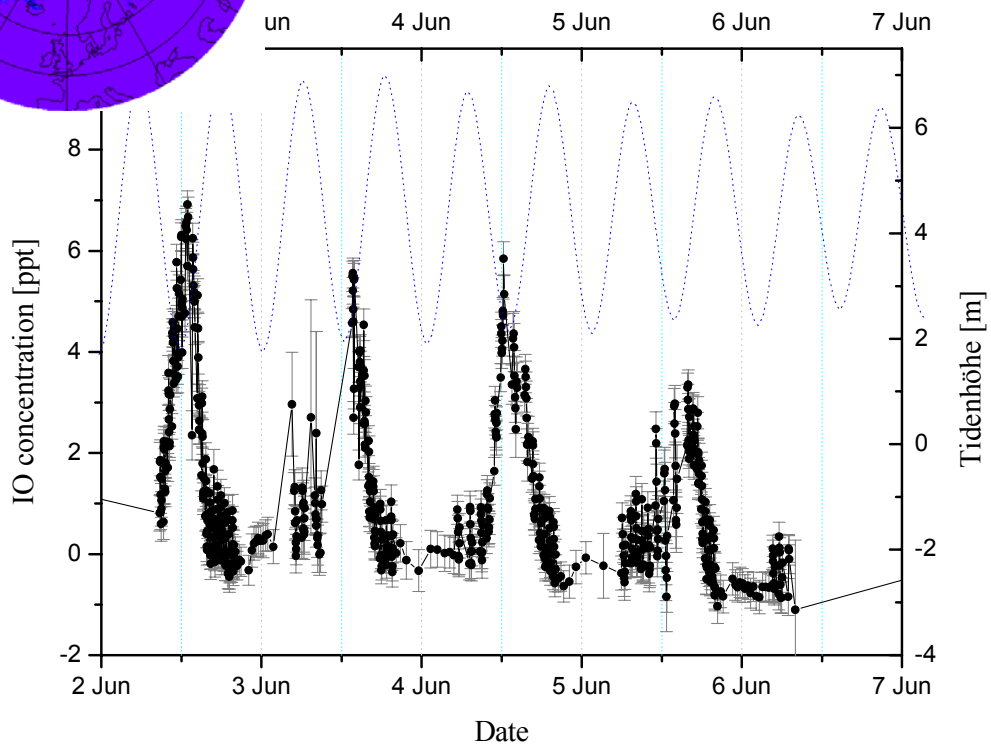
Halogen Catalysed Destruction of Tropospheric Ozone

1)	$BrO + BrO$	$\rightarrow$	$Br + Br + O_2$	(rate determining)
	$Br + O_3$	$\rightarrow$	$BrO + O_2$	
net:	$2\ O_3$	$\rightarrow$	$3\ O_2$	at high BrO levels
2)	$BrO + HO_2$	$\rightarrow$	$HOBr + O_2$	(rate determining)
	$HOBr + h\nu$	$\rightarrow$	$Br + OH$	
	$OH + AO$	$\rightarrow$	$HO_2 + A$	($AO = O_3$, CO, ...)
net:	$2\ O_3$	$\rightarrow$	$3\ O_2$	at low BrO levels
3)	$BrO + ClO$	$\rightarrow$	$Br + Cl + O_2$	(rate determining)
		$\rightarrow$	$BrCl + O_2$	
		$\rightarrow$	$Br + OClO + O_2$	
net:	$2\ O_3$	$\rightarrow$	$3\ O_2$	if ClO available
4)	$BrO + IO \rightarrow$		$Br + I + O_2$	(rate determining)
		$\rightarrow$	$BrI + O_2$	
		$\rightarrow$	$Br + OIO + O_2$	
				very fast, if IO available

Observation of Reactive Halogen Species in the Troposphere

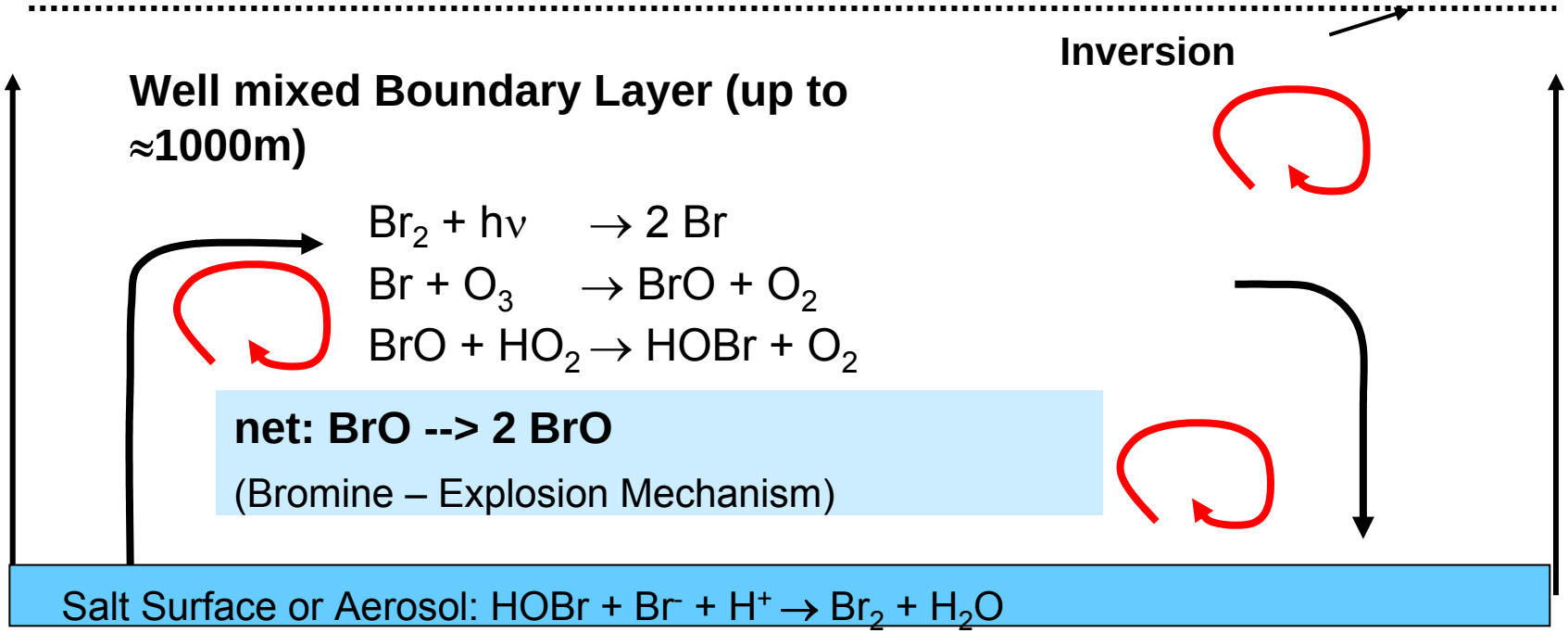


BrO-clouds in the Arctic,
Jens Hollwedel et al. 2004

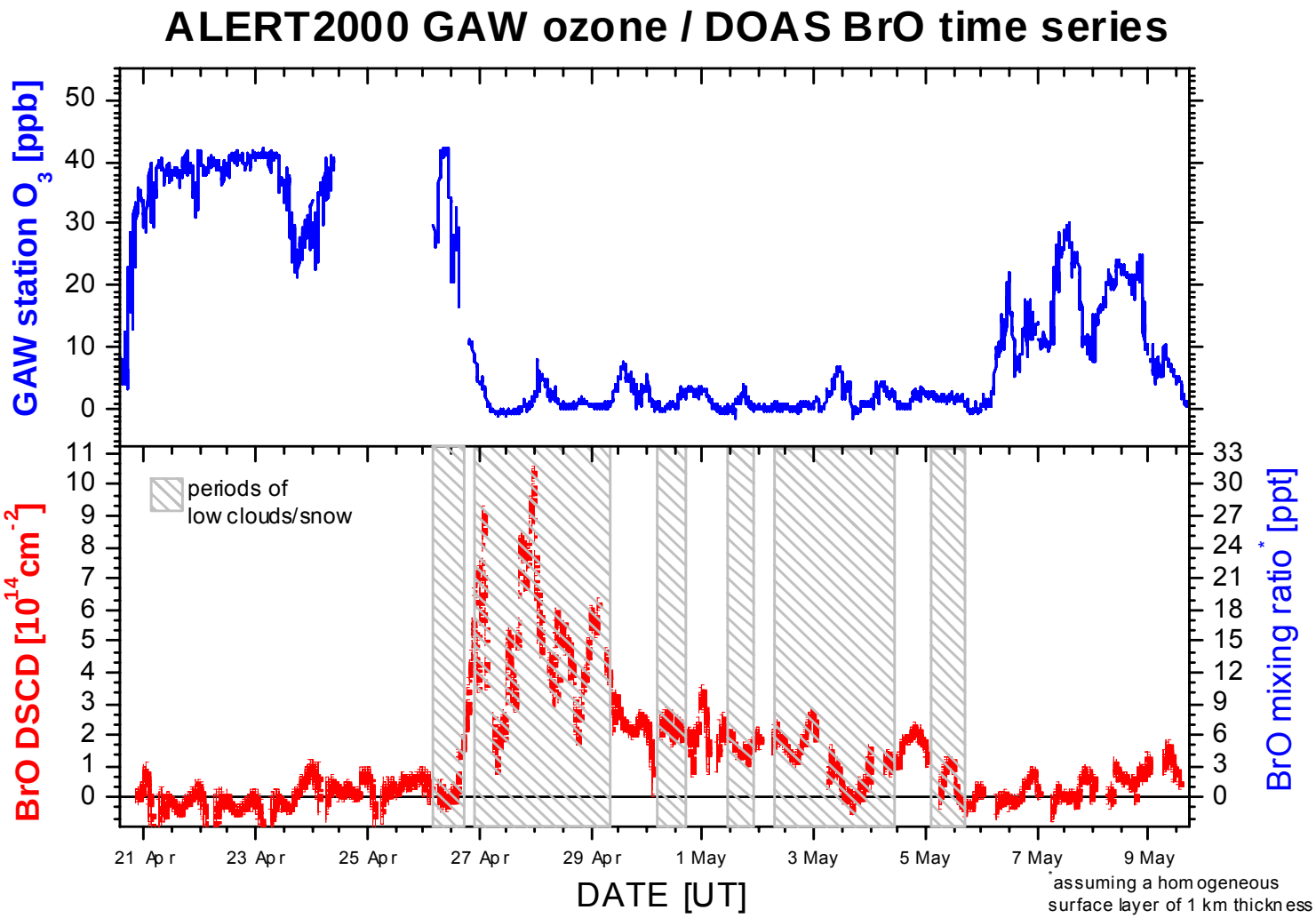


IO at a coastal site,
Christina Peters, 2005

A Chemical Instability: The "Bromine Explosion"

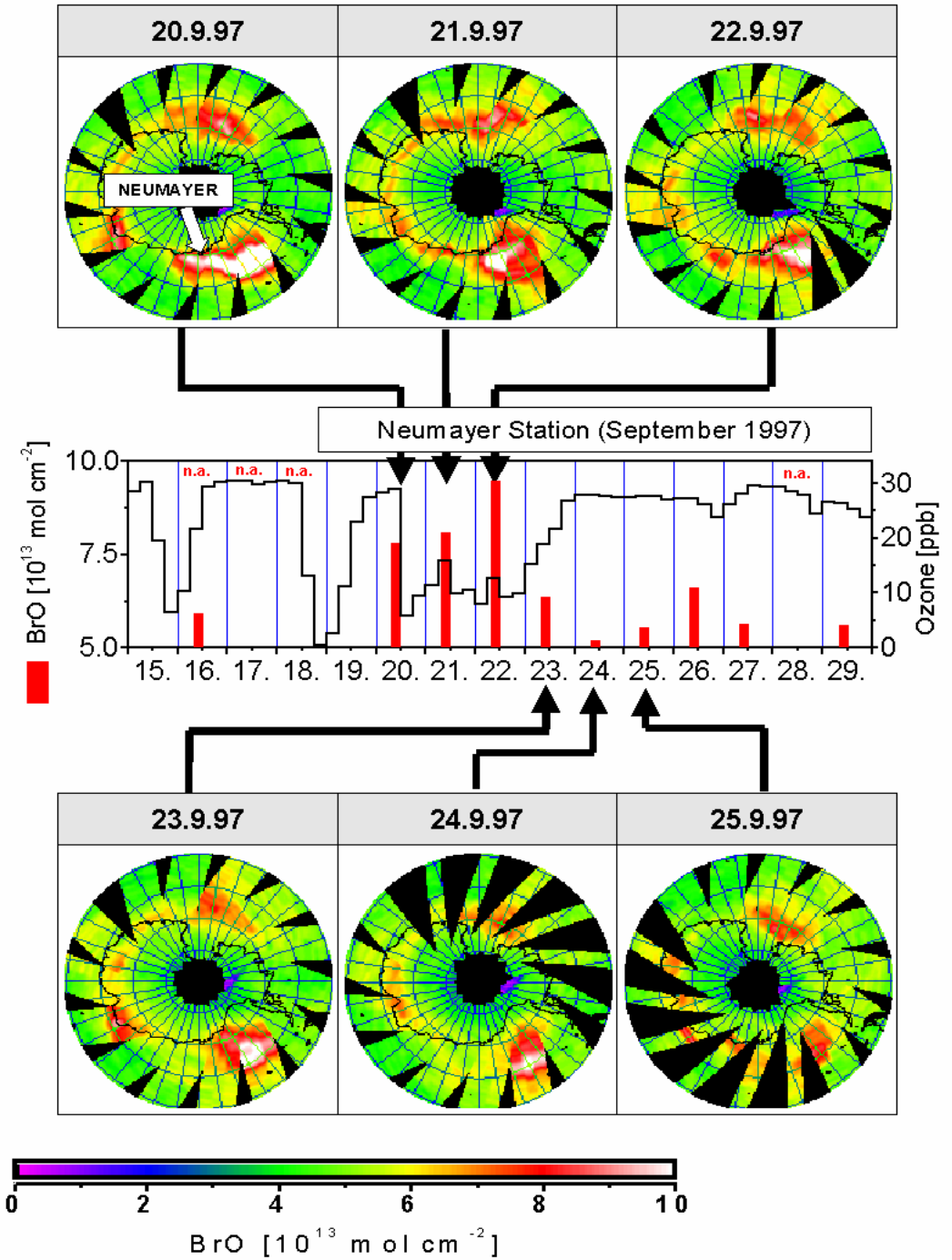


BrO and Ozone During the 'Polar Sunrise 2000' Experiment at Alert, Northern Canada



BrO by Multi-Axis DOAS (MAX-DOAS)
Hönninger et al. 2001

Satellite (GOME) Observations of BrO – ‚Plumes‘



Summary

Reactions of importance in the atmosphere are:

- Homogeneous Reactions
  They are always of the type A+B → B+C (elementary reactions). Each reaction can be treated independently from the others.
- Heterogeneous Reactions, they are difficult to quantify
- Photochemical Reactions

Elementary reactions interact to form complex schemes. Usually numerical models have to be used to integrate the very large systems (hundreds to thousands of equations) of differential equations.

Free radicals (OH, HO_2, NO_3, BrO, IO, ...) are the driving force of atmospheric chemistry