2 Stratospheric ozone chemistry
2.1 Chapman’s reactions

1 source, photolysis of $\text{O}_2$, +
1 sink, recombination to $\text{O}_2$:
$\text{O}_2 + \text{hv} (\lambda < 242 \text{ nm}) \rightarrow 2 \text{ O}$
$\text{O} + \text{O}_2 + \text{M} \rightarrow \text{O}_3 + \text{M}$
$\text{O} + \text{O}_3 \rightarrow 2 \text{ O}_2$
Net sum:

Second sink: Photolysis
$\text{O}_3 + \text{hv} \rightarrow \text{O} + \text{O}_2$

Chapman 1930

• Localized ozone layer too high in agreement with wrong measurements based, in turn, on wrong optical properties: ozone formation $< 200 \text{ nm}$ ignored
• Failed to recognize all sinks
2.2 Homogeneous catalysis of the ozone sink reaction

The sink reaction
\[ O + O_3 \rightarrow 2 \ O_2 \] can be catalyzed:

\[ X + O_3 \rightarrow XO + O_2 \]
\[ XO + O \rightarrow X + O_2 \]

Sum:
\[ O_3 + O \rightarrow 2 \ O_2 \]

\[ X = \text{Cl, Br (anthropogenic),} \]
\[ X = \text{OH, NO (natural)} \]

- This results in another steady-state concentration and vertical profile
- Vertical distribution of sinks (1D model results):

*NO, like NO₂, because not really short-lived is usually not called a radical, although the electron shell contains an unpaired electron*
2.2.1 Homogeneous catalysis of the ozone sink reaction: OH

Catalyzed sink reaction
\[ \text{O} + \text{O}_3 \rightarrow 2 \text{ O}_2 \]

Example \( X=\text{OH} \)

\[ \text{OH} + \text{O}_3 \rightarrow \text{HO}_2 + \text{O}_2 \]
\[ \text{HO}_2 + \text{O} \rightarrow \text{OH} + \text{O}_2 \]

Sum:
\[ \text{O}_3 + \text{O} \rightarrow 2 \text{ O}_2 \]

OH source reactions:

(3a) \[ \text{N}_2\text{O} + \text{hv} \rightarrow \text{N}_2 + \text{O}^{(1}\text{D}) \]
\[ \text{O}^{(1}\text{D}) + \text{H}_2\text{O} \rightarrow 2 \text{ OH} \]

(5) \[ \text{H}_2\text{O}_2 + \text{hv} \rightarrow 2 \text{ OH} \]
2.2.2 Homogeneous catalysis of the ozone sink reaction: Cl, Br

_Catalyzed sink reaction_

\[ O + O_3 \rightarrow 2 \text{O}_2 \]

*example X=Cl:*

\[ \text{Cl} + O_3 \rightarrow \text{ClO} + \text{O}_2 \]
\[ \text{ClO} + O \rightarrow \text{Cl} + \text{O}_2 \]

*example X=Br:*

\[ \text{Br} + O_3 \rightarrow \text{BrO} + \text{O}_2 \]
\[ \text{BrO} + O \rightarrow \text{Br} + \text{O}_2 \]
**Deactivation reactions (sinks of effective radicals)**

**Formation of temporary reservoir substances**

\[ \text{X}=\text{Cl}: \]
\[ \text{Cl} + \text{CH}_4 \rightarrow \text{HCl} + \text{CH}_3 \quad (\text{fast}) \]
\[ \text{CH}_3 + \text{O}_2 \rightarrow \text{CH}_3\text{OO} \]

\[ \text{ClO} + \text{NO}_2 + \text{M} \rightarrow \text{ClONO}_2 + \text{M} \quad (\text{major}) \quad c_{\text{ClO}} \sim c_{\text{NO}_2}^{-1} \]

\[ \text{ClONO}_2 + \text{hv} \rightarrow \text{ClO} + \text{NO}_2 \]

**Fate of X reservoirs**

\[ \text{HCl} + \text{OH} \rightarrow \text{Cl} + \text{H}_2\text{O} \quad (\text{slow}) \]

\[ \text{Br} + \text{CH}_4 \rightarrow \text{HBr} + \text{CH}_3 \quad (\text{slow}) \]

\[ \text{Br} + \text{HO}_2 \rightarrow \text{HBr} + \text{O}_2 \]

\[ \text{BrO} + \text{NO}_2 + \text{M} \rightarrow \text{BrONO}_2 + \text{M} \quad (\text{major}) \quad c_{\text{Br}}/c_{\text{Br-Res}} > c_{\text{Cl}}/c_{\text{Cl-Res}} \]

\[ \tau_{\text{Br}} > \tau_{\text{Cl}} \]

\[ \text{HBr} + \text{hv} \rightarrow \text{Br} + \text{H} \quad (\text{faster}) \]

\[ \text{BrONO}_2 + \text{hv} \rightarrow \text{BrO} + \text{NO}_2 \quad (\text{faster}) \]
Further deactivation reaction?
Formation of temporary reservoir substances

X=Cl: Fate of ClO (1)

\[ \text{CH}_3\text{OO} + \text{ClO} \rightarrow \text{CH}_3\text{O} + \text{ClOO} \]

chlorine peroxide radical

\[ \rightarrow \text{CH}_3\text{OCl} + \text{O}_2 \]

methylhypochlorite

\[ +\text{HCl (het)} \]

\[ \rightarrow \text{CH}_3\text{OH} + \text{Cl}_2 \]

Some rates and quantum yields involved are unknown → not totally clear

**Uncertainties remain**
Fate of ClO (2): Reaction with itself
The Cl catalyzed sink reaction in the absence of O atoms (i.e. efficient ozone destruction) is even accelerated:

1. \( \text{Cl} + \text{O}_3 \rightarrow \text{ClO} + \text{O}_2 \)
2. \( \text{ClO} + \text{O} \rightarrow \text{Cl} + \text{O}_2 \)
3. \( 2 \text{ClO} + \text{M} \rightarrow \text{ClOOCl} + \text{M} \)

chlorine peroxide (or 'ClO dimer')

4a. \( \text{ClOOCl} + h\nu \rightarrow \text{Cl} + \text{ClOO} \)
5. \( \text{ClOO} + \text{M} \rightarrow \text{Cl} + \text{O}_2 + \text{M} \)

2 \((1) \text{Cl} + \text{O}_3 \rightarrow \text{ClO} + \text{O}_2 \)

\text{Sum (4a+5+2*1)}:

\( 2 \text{O}_3 \rightarrow 3 \text{O}_2 \)
ClOOCl is key species for ozone depletion: \( \text{O}_3 \rightarrow \text{ClO} \rightarrow \text{ClOOCl} \rightarrow \rightarrow \text{Cl} \)

Uncertainties remain:

Availability of ozone depleting radi
(3) \( \text{ClO} + \text{ClO} \rightarrow \text{ClOOCl} \)
(-3) \( \text{ClOOCl} \rightarrow \text{ClO} + \text{ClO} \)
(4a) \( \text{ClOOCl} + h\nu \rightarrow 2 \text{ClO} \)

Sum:
(3+4a) –

(4b) \[ \rightarrow \text{Cl} + \text{ClOO} \]

\( \phi_{(4a)} \) yield: 100% ;

(5) \( \text{ClOO} \rightarrow \text{Cl} + \text{O}_2 \)

Sum:
(3+4b+5) \( 2 \text{ClO} \rightarrow 2 \text{Cl} + \text{O}_2 \) No te

Cross section measured < 410 nm (Burkholder et al., 1990) at 450 nm because of excitation.

Cross section \( \sigma_{(4)} > 310 \text{ nm} \) had been overestimated, ClOOCl is longer lived - and ozone sinks are incomplete (Pope et al., 2007)

Figure 10. Partial photolysis rates of ClOOCl in the atmosphere calculated for different cross sections. Conditions: altitude 20 km; solar zenith angle 86°; \( \text{O}_3 \) concentrations and temperature values measured in the polar vortex for March 2000.\(^{46}\) Cross sections: Burkholder et al. (red);\(^5\) JPL 2006 (black);\(^18\) Huder and DeMore (green);\(^7\) present values (blue).
Measurements of reactive chlorine from space
November 1994 (35° – 49°N)

- Chlorine nitrate (ClONO₂)
- Chlorine monoxide (ClO)
- Other gases

Altitude (kilometers) vs. Chlorine abundance (parts per trillion)

- Hydrogen chloride (HCl)
- Chlorine source gases (CFCs, HCFCs, carbon tetrachloride, etc.)
- Total available chlorine

Ozone Layer
Stratosphere
Troposphere
Ozone chemistry for X = Cl (catalyst, source, reservoir) including coupling reactions ClO_x/HO_x and ClO_x/NO_x:

Total flux between X and XO is proportional to \(-dc_{O_3}/dt\)

Temporary reservoir HCl

Direct photolysis of RCl’s insignificant for \(-dc_{O_3}/dt\)
e.g.: 
CFCl_3 + hv \rightarrow CFCl_2 + Cl
Primary Sources of Chlorine and Bromine for the Stratosphere in 2004

**Chlorine source gases**
- Methyl chloroform (CH₃CCl₃)
- HCFCs (e.g. HCFC-22 = CHClF₂)
- CFC-113 (CCl₂FCClF₂)
- Carbon tetrachloride (CCl₄)
- CFC-11 (CCl₃F)
- CFC-12 (CCl₂F₂)
- Methyl chloride (CH₃Cl)

**Bromine source gases**
- Other gases
- halon-1301 (CBrF₃)
- halon-1211 (CBrClF₂)
- Methyl bromide (CH₃Br)
- Very short-lived gases (e.g. bromoform = CHBr₃)

Nomenclature for halogenated hydrocarbons:

Chlorofluorocarbons (CFCs)
Freons (F, trade name)

,F-xyz‘ or ,CFC-xyz‘ or ,HCFC-xyz‘ with:
x = number of C atoms –1
y = number of H atoms +1
z = number of F atoms
general: C_{x-1}H_{y+1}Cl_nF_z
dt.: Chlorfluorkohlenwasserstoffe

commonly:
FCKW for Fluorchlorkohlenwasserstoffe

Halogenated hydrocarbons in general:

Halons
,Halon-wxyz‘ for C_wH_nF_xCl_yBr_z
e.g.
CF_3Br = Halon-1301
CF_2ClBr = Halon-1211; CH_3Br would be Halon-1001
2.2.3 Homogeneous catalysis of the ozone sink reaction: NO

Catalyzed sink reaction

\[ \text{O} + \text{O}_3 \rightarrow 2 \text{O}_2 \]

*example X=NO* (Crutzen, 1970)

\begin{align*}
(1a) \quad \text{NO} + \text{O}_3 & \rightarrow \text{NO}_2 + \text{O}_2 \\
(2a) \quad \text{NO}_2 + \text{O} & \rightarrow \text{NO} + \text{O}_2 \\
\text{Sum:} & \\
(1a+2a) \quad \text{O}_3 + \text{O} & \rightarrow 2 \text{O}_2 \\
(2b) \quad \text{NO}_2 + \text{h} \nu & \rightarrow \text{NO} + \text{O} \\
(3) \quad \text{O} + \text{O}_2 & \rightarrow \text{O}_3
\end{align*}

NO source reactions:

\begin{align*}
(3a) \quad \text{N}_2\text{O} + \text{h} \nu & \rightarrow \text{N}_2 + \text{O}^{(1\text{D})} \\
(3b) & \rightarrow \text{NO} + \text{N}^{(4\text{S})} \\
(4a) \quad \text{N}_2\text{O} + \text{O}^{(1\text{D})} & \rightarrow \text{N}_2 + \text{O}_2 \\
(4b) & \rightarrow 2 \text{NO}
\end{align*}

(2a) vs. (2b) competition decides upon NO effect on O₃:
(2a) destroys O which otherwise would recycle O₃ and recycles O₃-destroying NO

Deactivation by formation of *reservoir compound*:

\[ \text{(1b) NO} + \text{HO}_2 \rightarrow \text{HNO}_3 \]

Yield \(\approx 15\%\) at 298 K but \(\approx 50\%\) at 223 K

(Butkovskaya et al., 2005).

→ additional HOₓ sink
→ lower NOₓ/HNO₃

\(1\%\) (1967: „\(\approx 20\%\)“)

\(60\%\) \(k=67\times10^{-12}\ \text{cm}^3/\text{molec/s}\) (1990)
Catalyzed sink reaction

\[ O + O_3 \rightarrow 2 \text{O}_2 \]

*example \( X = \text{NO} \)*) *(Crutzen, 1970)*

(1a) \[ \text{NO} + O_3 \rightarrow \text{NO}_2 + \text{O}_2 \]

(2a) \[ \text{NO}_2 + \text{O} \rightarrow \text{NO} + \text{O}_2 \]

Sum:

(1a+2a) \[ O_3 + \text{O} \rightarrow 2 \text{O}_2 \]

(2b) \[ \text{NO}_2 + h\nu \rightarrow \text{NO} + \text{O} \]

(3) \[ O + \text{O}_2 \rightarrow O_3 \]

Sum:

(1a+2b+3) -

The catalyzing radicals are coupled:

\[ \text{ClO} + \text{NO}_2 + M \rightarrow \text{ClONO}_2 + M \]

\[ \text{ClO} + \text{HO}_2 \rightarrow \text{HOCl} + \text{O}_2 \]

\[ \text{Cl} + \text{HO}_2 \rightarrow \text{HCl} + \text{O}_2 \]

\[ \text{NO} + \text{HO}_2 \rightarrow \text{OH} + \text{NO}_2 \]
Catalyzed sink reaction
\[ O + O_3 \rightarrow 2 O_2 \]
(example \( X=NO \))

\[ \text{(Crutzen, 1970)} \]

(1a) \[ NO + O_3 \rightarrow NO_2 + O_2 \]
(2a) \[ NO_2 + O \rightarrow NO + O_2 \]

Sum:
(1a+2a) \[ O_3 + O \rightarrow 2 O_2 \]

(2b) \[ NO_2 + h\nu \rightarrow NO + O \]
(3) \[ O + O_2 \rightarrow O_3 \]

Sum:
(1a+2b+3) -

Effect of emissions in the stratosphere?
500 supersonic airplanes would destroy
50 \% (Johnston, 1971), 12 \% (Johnston et al., 1974)

\[ k_{1a} (NO/O_3) \text{ was underestimated, } k_{2a}/k_{2b} \text{ was uncertain} \]

→ today: Ozone production from SSA because of Cl and OH deactivation!

The catalyzing radicals are coupled:
\[ \text{ClO} + \text{NO}_2 + \text{M} \rightarrow \text{ClONO}_2 + \text{M} \]
\[ \text{ClO} + \text{HO}_2 \rightarrow \text{HOCl} + \text{O}_2 \]
\[ \text{Cl} + \text{HO}_2 \rightarrow \text{HCl} + \text{O}_2 \]
\[ \text{NO} + \text{HO}_2 \rightarrow \text{OH} + \text{NO}_2 \]
History of the ozone hole over Antarctica:
Farman et al. 1985: (Dobson-Instrument) Halley Bay
Chubachi, 1985: Syowa 1984
Solomon et al.: PSC can activate Cl (1986)
Molina & Molina: ClO recycled via ClOOC1 (1987)

Figure 1 Satellite maps of total ozone over Antarctica on 24 September, when the ozone hole is near its annual peak, in 1980, 1981, 2000, 2001, 2002 and 2003. The colour scale shows the amount of ozone in Dobson units, indicating the depth of the hole. The images are based on multiple satellite records and analyses and are available from many sources, including the World Ozone and Ultraviolet Radiation Data Centre in Toronto, Canada, http://woudc.ec.gc.ca/cgi-bin/selectMap.

Seasonal ozone deviations from pre-ozone-hole (1957-1978) averages over Antarctica show a rapid decline during the austral spring and lesser decline during the summer.
Total ozone column density
N/A = 2.46 x 10^{19}
molec/cm^2 = 1000 DU

Temporal dynamics of ozone loss over Antarctica:

2006, 71°S

Losses mostly in 12-25 km altitude

1994/97 vs. 1979: -50% spring 60°S _90°S
2.3 Heterogeneous reactions in polar stratospheric clouds

Satellite (Calipso, NASA) based lidar data, 22.6.06: 1 = Antarctica, 2 = Antarctic Peninsula, 3 = cirrus, 4 = H$_2$O(l) PSCs, 5 = H$_2$SO$_4$-HNO$_3$-H$_2$O(l) or HNO$_3$ *3 H$_2$O(s) (NAT) PSCs, 6 = lee wave clouds, 7 = position of polar vortex
2.3 Heterogeneous reactions in polar stratospheric clouds

Overview

1. non-reactive Cl compound
2. reactive Cl compound
3. NO2, N2O5

1 = ClONO2, HCl
2 = Cl2, HOCl → Cl
3 = NO2, N2O5
**Deactivation by formation of reservoir compounds:**

Cl + CH₄ → HCl + CH₃  
Cl + HO₂ → HCl + O₂  
Cl + H₂ → HCl + H  
ClO + NO₂ → ClONO₂

**Deactivation by NOₓ compounds:**

HNO₃ + hv → NO + HO₂  
NO + O₃ → NO₂ + O₂  
NO₂ + ClO + M → ClONO₂ + M

As long as there is NO₂ available!

**Activation through recycling reactions:**

\[ \text{HCl}_{\text{in Ice}} + n \text{H}_2\text{O} \rightarrow \text{H}_3\text{O}^+ (\text{H}_2\text{O})_{n-1} \text{Cl}^- \]

\[ \text{Cl}^- + \text{ClONO}_2 \rightarrow \text{Cl}_2 + \text{NO}_3^- \]

Sum:

\[ \text{HCl}_{\text{in Ice}} + \text{ClONO}_2 \rightarrow \text{Cl}_2 + \text{HNO}_3(s) \]

H₂O(s) + ClONO₂ → HOCl + HNO₃(s)  
HOCl + HCl → Cl₂ + H₂O

**Denitrification:** Sedimentation of HNO₃–containing ice particles of the PSCs

H₂O(s) + N₂O₅ → 2 HNO₃(s)  
HCl + N₂O₅ → ClNO₂ + HNO₃(s)

**Gas-phase activation reactions:**

CFCl₃ + hv → CFCl₂ + Cl  
N₂O + hv → N₂ + O(¹D)  
O(¹D) + N₂O → 2 NO  
O(¹D) + H₂O → 2 OH Slow
1.5 Heterogeneous reactions

\[- \frac{dc_{i(g)}}{dt} = k^{\text{het}}(1) c_{i(g)}\]

\[k^{\text{het}}(1) = \gamma_i \left(\frac{S}{V}\right) \beta_i \langle v_i \rangle / 4\]

\[\beta_i = \frac{(1 + Kn_i)}{(1 + 1.71 Kn_i + 1.33 Kn_i^2)}\]

\[\langle v_i \rangle = (8 RT / \pi M_i)^{0.5}\]

with:
- \(c_{i(g)}\) = concentration of trace gas \(i\) far from the interface,
- \(k^{\text{het}}\) = loss rate to condensed phase,
- \(\gamma_i\) = surface reaction probability, can be \(T\) dependent
- \(S/V\) = total (aerosol + ground) surface concentration
- \(\langle v_i \rangle\) = mean velocity of gas molecules,
- \(R\) = molar gas constant, \(T\) = absolute temperature, \(M_i\) = molar mass,
- \(\beta_i\) = correction for non-continuum effects (for \(r < 0.05\mu m\); Fuchs & Sutugin, 1971)

With:
- \(Kn_i = \frac{\lambda_i}{r}\) = Knudson number, \(r\) = particle radius
- \(\lambda_i = (\sqrt{2} \pi \sigma_i^2 N_i/V)^{-1}\) = mean free path of gas molecules,
- \(\pi \sigma_i^2\) = collision cross-section of gas molecules in air,
- \(N_i/V\) = molecule number concentration.
Kinetic description of heterogeneous reactions

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Ice</th>
<th>NAT</th>
<th>SAT</th>
</tr>
</thead>
<tbody>
<tr>
<td>ClONO$_2$ + HCl →</td>
<td>0.2</td>
<td>0.1</td>
<td>0.001-0.1</td>
</tr>
<tr>
<td>N$_2$O$_5$ + HCl →</td>
<td>0.3</td>
<td>0.003</td>
<td>-</td>
</tr>
<tr>
<td>HOCl + HCl →</td>
<td>0.3</td>
<td>0.1</td>
<td>-</td>
</tr>
<tr>
<td>ClONO$_2$ + H$_2$O →</td>
<td>&gt; 0.1</td>
<td>0.0001-0.01</td>
<td>0.001-0.01</td>
</tr>
<tr>
<td>N$_2$O$_5$ + H$_2$O →</td>
<td>0.02</td>
<td>0.0003</td>
<td>0.01</td>
</tr>
</tbody>
</table>

Example: Loss of N$_2$O$_5$ on particle surfaces: $\text{N}_2\text{O}_5 + 2 \text{H}_2\text{O} (l) \rightarrow 2 \text{NO}_3^- + 2 \text{H}_3\text{O}^+$

with:

- $\beta_i \approx 1$
- $<v_i> = (8 \text{ RT} / \pi M_i)^{0.5} \approx 5 \times 10^4 \text{ cm/s}$
- $\gamma_i = \text{reaction probability} \approx 0.0003-0.02$
- $S/V \approx (0.01-1) \times 10^{-6} \text{ cm}^{-1}$ for stratospheric aerosol
- $k^{\text{het}} = \text{loss rate to condensed phase} = \gamma_i (S/V) \beta_i <v_i>/4$:

$$k^{\text{het}} \approx (0.0003-0.02) \times (0.01-1) \times 10^{-6} \times 5 \times 10^4/4 \text{ s}^{-1} \approx (0.04-250) \times 10^{-6} \text{ s}^{-1},$$

$$\tau_{\text{het.loss}} \approx 1 \text{ h} - 300 \text{ d}.$$
Kinetic description of heterogeneous reactions

\( \gamma_i = \text{reaction probabilities} \)

**Concept: Resistance model**

The larger \( \gamma \) the lower the resistance, the higher the conductivity \( \Gamma \). In analogy to electrical circuits: serial and parallel processes dealt as resistances.

Individual processes in series:

\[
\Gamma = \gamma^{-1} = \sum_i \Gamma_i = \sum_i (\gamma^{-1})_i
\]

Parallel individual processes:

\[
\Gamma = \gamma^{-1} = (\sum_i \gamma_i)^{-1}
\]

\[
\gamma = \sum_i \gamma_i
\]
**Kinetic description of heterogeneous reactions: solid surface**

<table>
<thead>
<tr>
<th>Processes:</th>
<th>Condensed phase: Solid</th>
</tr>
</thead>
<tbody>
<tr>
<td>Transport in the gas phase</td>
<td>$\Gamma_g$</td>
</tr>
<tr>
<td>Initial interaction</td>
<td></td>
</tr>
<tr>
<td>Reversible sorption</td>
<td>Accommodation (‘sticking’) coefficient $\alpha$</td>
</tr>
<tr>
<td>Reaction on surface</td>
<td>Reactive uptake coefficient $\gamma_r$</td>
</tr>
<tr>
<td><strong>Overall</strong> process $\Gamma$</td>
<td>Total experimental uptake/reaction probability, coefficient $\gamma_{tot}$</td>
</tr>
</tbody>
</table>

Def.: $\alpha$:  = fraction of gas-surface collisions taken up by surface (reversible)

$\gamma_r$:  = fraction of gas-surface collisions leading to irreversible uptake, tabulated *

$\gamma_{tot}^{-1} \approx \gamma_r$ if surface and/or bulk reaction dominate the overall process kinetics =  

= reaction is slow while gas-phase diffusion and reversible sorption are fast
**Kinetic description of heterogeneous reactions: solid surface**

**Processes:**

<table>
<thead>
<tr>
<th>Condensed phase: Solid</th>
<th>Processes</th>
</tr>
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<tbody>
<tr>
<td></td>
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<td></td>
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**Def.:**

- $\alpha$: fraction of gas-surface collisions taken up by surface (reversible)
- $\gamma_r$: fraction of gas-surface collisions leading to irreversible uptake, tabulated
- $\gamma_{tot}^{-1} \approx \gamma_r$ if surface and/or bulk reaction dominate the overall process kinetics

**Table 64. Continued**

<table>
<thead>
<tr>
<th>Gaseous Species</th>
<th>Surface Type</th>
<th>Surface Composition</th>
<th>$T$ (K)</th>
<th>$\gamma$</th>
<th>Uncertainty Factor</th>
<th>Notes</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{N}_2\text{O}_5 + \text{H}_2\text{O} \rightarrow 2\text{HNO}_3$</td>
<td>Water Ice</td>
<td>$\text{H}_2\text{O}(s)$</td>
<td>195-200</td>
<td>0.01</td>
<td>3</td>
<td>14</td>
</tr>
<tr>
<td></td>
<td>Liquid Water</td>
<td>$\text{H}_2\text{O}(l)$</td>
<td>260-295</td>
<td>0.05*</td>
<td>2</td>
<td>15</td>
</tr>
<tr>
<td></td>
<td>Nitric Acid Ice</td>
<td>$\text{HNO}_3 \cdot 3\text{H}_2\text{O}(s)$</td>
<td>200</td>
<td>$3 \times 10^{-4}$</td>
<td>3</td>
<td>16</td>
</tr>
<tr>
<td></td>
<td>Sulfuric Acid Monohydrate</td>
<td>$\text{H}_2\text{SO}_4 \cdot \text{H}_2\text{O}(l)$</td>
<td>195-300</td>
<td>$\approx 0.1$</td>
<td>See Note</td>
<td>17</td>
</tr>
<tr>
<td></td>
<td>Sulfuric Acid Tetrahydrate</td>
<td>$\text{H}_2\text{SO}_4 \cdot 4\text{H}_2\text{O}(s)$</td>
<td>195-207</td>
<td>0.006</td>
<td>2</td>
<td>18</td>
</tr>
<tr>
<td></td>
<td>Ternary Acid</td>
<td>$\text{H}_2\text{SO}_4 \cdot \text{nHNO}_3 \cdot \text{nH}_2\text{O}(l)$</td>
<td>195-218</td>
<td>See Note</td>
<td>17</td>
<td></td>
</tr>
</tbody>
</table>
1.5.1 Heterogeneous reactions on solids

\[ \gamma_{tot} = \frac{1}{\alpha + \frac{1}{\gamma_r}} \approx \alpha \quad \text{if } \alpha \ll \gamma_r \]

\[ \approx \gamma_r \quad \text{if } \gamma_r \ll \alpha \]

Reversible sorption and irreversible reaction can take place in parallel rather than in series, too. Then:

\[ \gamma = \gamma_r + \alpha \]

with \( \gamma_r \geq \alpha \), eventually \( \gamma_r \approx \alpha \).

Laboratory experiments often do not allow to unambiguously differentiate between \( \gamma \) and \( \alpha \). In these cases \( \gamma \) are tabulated* as ‘\( \alpha \)‘ – subject to change if more definitive data become available.

1.2.3 Heterogeneous reactions in polar stratospheric clouds

PSC properties

Solid or liquid, < 200 K growth of sulfuric acid particles, < 188 K partly solid wide range of particle/droplet sizes
S/V = (0.01-1)x10^{-6} cm^{-1}
V/V = (1-100)x10^{-12}

**Reaction rate** of ClONO₂/Cl⁻ : \( k_{\text{het}(1)} = -\frac{dc_{\text{ClONO}_2}}{dt} c_{\text{ClONO}_2} \) (s⁻¹)

- Type II PSC: \( D \approx 5-50 \mu m \)
- Type I PSC: \( D \approx 0.5 \mu m \)
Changing chemistry at sunrise:

• Advection: vortex opens and zonal transport of ozone rich air is possible again
• Temperature increase: ice crystals melt, release NO$_2$, ClONO$_2$ is formed again, binding Cl
• Photochemistry: O$_2$ photolysis supplies fresh O$_3$
2.4 Long-term trends

![Average Total Ozone in Polar Regions](chart.png)

- **Arctic Region in March**
- **Antarctic Region in October**

**Total ozone (Dobson units)**
- Chemical destruction and natural variation of ozone
- 1970 – 1982 Average
- (63° – 90° Average)

**Year**
- 1970
- 1975
- 1980
- 1985
- 1990
- 1995
- 2000
- 2005

*Src: WMO: Scientific Assessment of Ozone Depletion 2006, Geneva 2007*
Stratospheric ozone chemistry

$T < 190\;\text{K}$

Arctic stratosphere?

Arctic spring (March) and Antarctic Spring (September)

Frequency of PSCs, temperature trends:

(WMO, 1999)

(Labitzke & van Loon, 1999, updated 2004)
Emission reduction efficiency?
Basis for comparison of different substances = ?
→ Ozone depletion potentials
ODP: = (global ozone loss due to unit mass emission of i)/
(global ozone loss due to unit mass emission of CFC-11)

- assuming steady-state conditions (time dependent calculations are possible, but not common)
- assuming constant emissions (for compounds that are removed by linear processes, this is equivalent to assuming an emission pulse and integrating over the entire decay of the compound)
- not dependent on time

<table>
<thead>
<tr>
<th>Halogen Source Gas</th>
<th>Atmospheric Lifetime (years)</th>
<th>Global Emissions in 2003</th>
<th>Ozone Depletion Potential (ODP)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chlorine</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>CFC-12</td>
<td>100</td>
<td>101-144</td>
<td>1</td>
</tr>
<tr>
<td>CFC-113</td>
<td>85</td>
<td>1-15</td>
<td>1</td>
</tr>
<tr>
<td>CFC-11</td>
<td>45</td>
<td>60-126</td>
<td>1</td>
</tr>
<tr>
<td>Carbon tetrachloride (CCl₄)</td>
<td>26</td>
<td>58-131</td>
<td>0.73</td>
</tr>
<tr>
<td>HCFCs</td>
<td>1-26</td>
<td>312-403</td>
<td>0.02-0.12</td>
</tr>
<tr>
<td>Methyl chloroform (CH₃CCl₃)</td>
<td>5</td>
<td>~20</td>
<td>0.12</td>
</tr>
<tr>
<td>Methyl chloride</td>
<td>1.0</td>
<td>1700-13600</td>
<td>0.02</td>
</tr>
<tr>
<td>Bromine</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Halon-1301</td>
<td>65</td>
<td>~3</td>
<td>16</td>
</tr>
<tr>
<td>Halon-1211</td>
<td>16</td>
<td>7-10</td>
<td>7.1</td>
</tr>
<tr>
<td>Methyl bromide (CH₃Br)</td>
<td>0.7</td>
<td>160-200</td>
<td>0.51</td>
</tr>
<tr>
<td>Very short-lived gases (e.g., CHBr₃)</td>
<td>&lt; 0.5</td>
<td>c</td>
<td>c</td>
</tr>
</tbody>
</table>

a Includes both human activities and natural sources.
b Emission in gigagrams per year (1 gigagram = 10⁹ grams = 1000 metric tons).
c Estimates are uncertain for most species.
d Values are calculated for emissions of equal mass for each gas.

Total atmospheric lifetime (or residence time):

\[ \tau_i = \text{burden}/(\text{total loss rate}) = b_i / \tau_i^{-1} = b_i / [\Sigma_i (\tau_i^{-1})]^{-1} \]
\[ \tau_i^{-1} = \tau_{i \text{ strat}}^{-1} + \tau_{i \text{ trop}}^{-1} + \tau_{i \text{ dep}}^{-1} = \Sigma_j \tau_{ij}^{-1} \]

\( j: \) tropospheric reactions
stratospheric reactions
deposition

For CFCs:
\[ \tau_{\text{trop}} \approx \infty \]
\[ \sigma > 260 \text{ nm} < 10^{-21} \text{ cm}^2 \rightarrow \tau_{j \text{ strat}} \approx \infty \]
\[ \tau_{\text{CFC}} \approx \tau_{\text{strat}} \]

For most organic substances, however:
\[ \tau_{i \text{ trop}} \approx \tau_{i \text{ OH}} \]
\[ \tau_i \approx \tau_{i \text{ trop}} \]
For most organic substances:

\[-\frac{dc_i}{dt} = k_{OH}^{(2)} \cdot c_{OH} \cdot c_i; \ \tau_{OH} = (k_{OH}^{(2)} \cdot c_{OH})^{-1}\]

\[\tau = (\Sigma k \cdot c)^{-1}\]

\[\tau_{photochem} = (k_{OH} \cdot c_{OH})^{-1}\]

Diurnal means: differ by orders of magnitude according to averaging time

Annual mean 44°N: 740 h (2 weeks resolution) vs. 310 h
Annual mean 12°N: 173 h vs. 168 h
CFC trends

CFC lifetimes - uncertainties

CFC-11 in the atmosphere. The curves represent predicted abundance of CFC-11 for different atmospheric lifetimes. Actual data for Northern (circles) and Southern (triangles) Hemispheres show that CFC-11’s atmospheric lifetime is about 50 years.

Solomon, 2004
CFC trends

Stabilization, reduction: \( \frac{db}{dt} = F_e - \frac{b}{\tau} \leq 0! \)

\[
\frac{db}{dt}/b = \frac{F_e}{b} - \frac{1}{\tau}
\]

\[
F_e = \frac{db}{dt} + \frac{b}{\tau}
\]

<table>
<thead>
<tr>
<th>( \tau )</th>
<th>( \frac{db}{dt}/b )</th>
</tr>
</thead>
<tbody>
<tr>
<td>(2003-04)</td>
<td></td>
</tr>
<tr>
<td>CCl(_4) 26 a</td>
<td>-(1.1±0.1) %/a</td>
</tr>
<tr>
<td>CH(_3)CCl(_3) 5 a</td>
<td>-(18 ± 1) %/a</td>
</tr>
</tbody>
</table>

Even with \( F_e = 0 \) the CCl\(_4\) levels could not have been reduced < -4 %/a

Reported lifetimes assume uniform mixing in the global atmosphere – the more uncertain the shorter \( \tau \) is!

Stratospheric Cl trends

Past and Expected Future Abundances of Atmospheric Halogen Source Gases

Effective stratospheric chlorine
- CFCs
- Halons
- HCFCs
- CCl₄
- CH₃CCl₃

CH₃Br (natural + human sources)
CH₃Cl (natural sources)

Mid latitudes
1980 level

Atmospheric abundance (parts per trillion)
Year
1950 2000 2050 2100

Atmospheric abundance (parts per trillion)
Year
1950 2000 2050 2100
Cl trends

Total chlorine evolution in the midlatitude stratosphere

Cl trends

Protocols of the Vienna Convention (1985)
Atmospheric chemistry ← Climate

Feedbacks: Global warming causes stratospheric cooling, hence, more favourite conditions for ozone depletion!

(Lammel, 1997)