# An introduction to atmospheric chemistry 

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## An introduction to atmospheric chemistry

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## Lecture outline

- Why does chemical composition matter?
- Air quality
- Climate
- Getting to know the atmosphere
- Physical attributes (structure, temperature, pressure)
- Chemical composition
- Chemical reactions in the troposphere
- Chemical reactions in the stratosphere
- Approaches to studying the atmosphere

Part 1 - Why does chemical composition matter?
"the simple act of breathing is killing 7 million people a year and harming billions more"

Dr. T.A. Ghebreyesus, head of the World Health Organization

## Air pollution: an invisible pandemic? $\alpha^{2}$



- Impact of our emissions is defined by atmospheric chemistry
- Air pollution is atmospheric chemistry
- Air pollution is an urgent problem
- And it will get worse in the future ${ }^{2}$
- The only vaccine is to understand it and legislate against it
- But there is still so much that we don't yet understand


## Air pollutions an old problem

| Air pollution episode | Date | Cause | Consequences |
| :---: | :---: | :---: | :---: |
| Meuse River Valley, Belgium | 1930 | High concentrations of $\mathrm{SO}_{2}$ in the atmosphere during a temperature inversion | 63 people died and thousand sick |
| Donora, Pennsylvania, USA | 1948 | High concentrations of $\mathrm{SO}_{2}$ coupled with temperature inversion and foggy weather | 20 people died due to cardiac respiratory disease and about half of town's 12,000 residents complained of cough, respiratory tract irritation, chest pain, headaches, nausea, and vomiting |
| Poza Rica, Mexico | 1950 | Natural gas plant inadvertently released hydrogen sulphide coupled with temperature inversion and foggy weather | 22 people died and 320 were hospitalized |
| London, England | 1952 | A five day temperature inversion trapped deadly acid aerosols in the atmosphere | 8000 deaths. Over 4000 succumbed to bronchitis, pneumonia, and respiratory and cardiac disease |

## $\boxed{\Delta}$

 Air pollutiont a brief history

SMOC/Aerosols

What we know today:
$\mathrm{S}^{\mathrm{Dos}} \mathrm{or}_{0}$

$+\mathrm{H}_{2} \mathrm{SO}_{4},+\mathrm{HNO}_{3}+\ldots=$ Aerosols
Gen. $n$

## Is air pollution a thing of history?



It depends on your perspective

## Is air pollution a thing of history?

China, 2014
India, 2018

Nigeria, 2018

Clearly not

## The export of pollution

It's an ill wind
Deaths caused by pollution, net exported/imported
Per million residents, 2007


- The Global North is transitioning away from industrialization
- But our appetite for consumer goods and resources has increased
- As a consequence, we are seeing an explosion of pollution in the developing world
- Note: this figure is from 2007, the geopolitical picture is changing fast
- What about Africa?


## The health effects of air pollution



- Fine particulate matter is considered be the most dangerous component of air pollution
- These are the most aerodynamic/ mobile particles and they can reach the alveoli
- It is suspected that chemical composition may play a role in toxicity of particulates
- Lung cancer and chronic obstructive pulmonary disease are very bad outcomes
- But many other conditions are correlated with air pollution: asthma, dementia, COVID deaths
- Even behavioural patterns and cognitive ability



## The ozone hole

- The use of ozone-depleting substances starting in the 1960s has had a profound effect on the upper atmosphere
- These chemicals were used in a large variety of applications (not only hairspray!)
- This can be viewed as stratospheric air pollution


## Climatic effects

- Many pollutants (such as $\mathrm{CO}_{2}$ ) absorb infrared radiation
- Some pollutants absorb strongly in the atmospheric "window" $\rightarrow$ radiative efficiency (RE)
- Some pollutants are highly persistent in the atmosphere, leading to a high global warming potential (GWP)
- Some of the worst greenhouse gases can have a GWP 1000s of times higher than $\mathrm{CO}_{2}$



## Conclusions:

## Part 1 - Why does air pollution matter?

- Air pollution is estimated to kill millions of people each year
- It impacts the lives of billions
- It's less problematic now than it was (in the developed world)
- But it's becoming worse (in the developing world)
- Air pollution now kills more people than tobacco (a lifestyle choice)
- Breathing is not a lifestyle choice, it is a necessity!
-     + we should not forget the climatic effects that will impact the whole world


Part 2 - Getting to know the atmosphere

## Physical attributes (structure)



[^0]- The atmosphere is categorized as a set of layers
- We spend almost all of our time in the planetary boundary layer


Fig. 1.1 The troposphere can be divided into two parts: a boundary layer (shaded) near the surface and the free atmosphere

## Physical attributes (atmospheric pressure)



## Physical attributes (in context)



- In terms of spatial extent: the atmosphere is to the solid Earth, what an apple's skin is to its diameter
- In terms of mass: it is a single eyelash lying next to the apple...
- From a physical point of view, the atmosphere is therefore a thin, insubstantial layer


## Chemical composition (major components)



$$
\begin{gathered}
N_{2}=78.08 \% \\
O_{2}=20.95 \% \\
\mathrm{Ar}^{2}=0.93 \% \\
99.96 \%
\end{gathered}
$$

Most of the
atmosphere is very boring!

## Chemical composition (trace components)

| Gas | Mixing ratio | Source(s) |
| :--- | :--- | :--- |
| Carbon dioxide | $420(\mathrm{ppm})$ | Combustion, ocean, biosphere |
| Methane | $1.7(\mathrm{ppm})$ | Biogenic, anthropogenic |
| Helium | $5.2(\mathrm{ppm})$ | Radioactive decay, anthropogenic |
| Nitrous oxide | $0.31(\mathrm{ppm})$ | Biogenic, anthropogenic |
| Ozone (stratosphere) | $0.5-10(\mathrm{ppm})$ | Photochemical |
| Ozone (troposphere) | $10-500(\mathrm{ppb})$ | Photochemical |
| Carbon monoxide | $50-200(\mathrm{ppb})$ | Photochemical, combustion |
| Formaldehyde | $0.1-1(\mathrm{ppb})$ | Photochemical, anthropogenic |
| NMHCs | $\mathrm{ppqs}-\mathrm{ppbs}$ | Photochemical, anthropogenic, bioger |
| Hydroxyl radical <br> (daytime) | $\sim 40(\mathrm{ppq})$ | Photochemical |
| Tofal $=0.0438 \%$ |  |  |

## How has Earth's atmosphere changed?

- Earth's atmosphere was very different millions/ billions of years ago
- The evolution of photosynthetic organisms transformed much of the $\mathrm{CO}_{2}$ into $\mathrm{O}_{2}$
- Further back in time, Earth's atmosphere would have contained much more of the most abundant components of the solar system: hydrogen and helium
- Because of atmospheric escape, most has been lost to space



## Atmospheric emissions

## https://www.nps.gov/subjects/air/sources.htm

Pollutant Emissions

Wildfires


- 55,000 different terpenoid species known to science
- Wildfires, >10,000 species identified in the tar-ball component of a single burning plume
- Hydrocarbon fuels are complex mixtures, containing $10^{3}-10^{4}$ species (maybe more)
- >75,000 industrial chemicals registered in environmental monitoring networks (US EPA CPDAT)

A paradox: low concentration, big effect

- How can things at such low concentrations be so important?
- Possibility 1: the mass flux is high

Field concentration: pots
sources $\rightarrow$ [isoprene] $\rightarrow$ sinks
Atmospheric emission.
$5-7.5 \times 10^{6}$ tons $y^{-1}$

- Possibility 2: a molecule has a catalytic effect
e.g. stratospheric chlorine sources (see later)
- Possibility 3: high toxicity
high specific toxicity / high collective toxicity
- Possibility 4: extremely sensitive effect
aerosol nucleation / infrared absorption / catalytic behaviour / biological role


## VOCs and ecosystems

- The most sensitive VOC detectors on Earth are not in our laboratories
- Certain species of insect are hypothesized to be able to detect single molecules

- We are capable of measuring 10 s of ppq levels with certain mass spectrometric and fluorescence techniques (if we are lucky)
- For a sample volume of $1 \mathrm{~cm}^{3}$ at atmospheric pressure and room temperature, this is $>2.5 \times 10^{5}$ molecules


## Conclusions Part 2 - Getting to know the atmosphere

- We live in a thin, fragile and insubstantial part of the Earth system
- Most of the atmosphere is relatively inert
- Earth's atmosphere has changed a lot since it was formed
- Trace components affect air quality, climate, ecosystems
- These are the things that react...

Part 3 - Chemical reactions in the troposphere

## The atmosphere as a combustion engine

- Much like an engine, the atmosphere is an oxidizing environment
- The volatile organic compounds (VOCs) emitted to the atmosphere represent the fuel
- What we learned at school:

$$
\text { Fuel }+\mathrm{O}_{2} \rightarrow \rightarrow \mathrm{CO}_{2}+\mathrm{H}_{2} \mathrm{O}
$$

- However, under ambient (and most other) conditions, these things don't react together...


## Getting things started...

- Atmospheric chemistry is a complex set of cycles, and it's difficult to choose a starting point!
- Remember, the atmosphere is mostly $\mathrm{N}_{2}, \mathrm{O}_{2}$ and Ar with trace VOCs
- But none of these things react together...
- We need some extra ingredients: $\mathrm{NO}_{x^{\prime}}$, sunlight, $\mathrm{O}_{3}$, organic molecules

- These create the conditions for the autocatalytic oxidizing environment of the troposphere

- Nitrogen yfixationt may be biotic or abiotic
- Biotic: biocnemical reaction's involving the nitrogentase enzyme
- Abiotic: generally involves extreme heat (the core of lightning bolti) a 'hightemperature conobustion engine)



## Ingredient 2: sunlight

- The sun is the energy source
- Top of the atmosphere: solar irradiance resembles 5778 K black body
- Ground-level: the layers above act as a filter
- If a molecule absorbs enough energy it can transform...



## Photodissociation

- Reaction $\mathrm{AB}+h v \rightarrow \mathrm{~A}+\mathrm{B}$
- Rate of reaction is given by:

$$
-\frac{d[A B]}{d t}=J \times[A B]
$$

- $J$, the photolysis frequency, is described as follows:

$$
J=\int_{\lambda_{1}}^{\lambda_{2}} F(\lambda) \times \Phi(\lambda) \times \sigma(\lambda)
$$

Where: $\quad F(\lambda)=$ actinic flux
$\sigma(\lambda)=$ absorption cross section
$\Phi(\lambda)=$ quantum yield

$$
\Phi(\lambda)=\frac{\# p h o t o n s ~ l e a d i n g ~ t o ~ r e a c t i o n ~}{\# p h o t o n s ~ a b s o r b e d ~}
$$

- Example:

$$
\mathrm{NO}_{2}+h v \rightarrow \mathrm{NO}+\mathrm{O}\left({ }^{3} \mathrm{P}\right) \quad J\left(\mathrm{NO}_{2}\right)
$$

However, there are other processes besides dissociation...


## Ingredient 3: ozone

- Now we have some fixed nitrogen and some sunlight:
$\mathrm{NO}_{2}+h \nu \longrightarrow \mathrm{NO}+\mathrm{O}\left({ }^{3} \mathrm{P}\right)$
$\mathrm{O}\left({ }^{3} \mathrm{P}\right)+\mathrm{O}_{2} \rightarrow \mathrm{O}_{3}$
$\mathrm{O}_{3}+h v \rightarrow \mathrm{O}\left({ }^{1} \mathrm{D}\right)+\mathrm{O}_{2}$
$\mathrm{O}_{3}+h v \rightarrow \mathrm{O}\left({ }^{3} \mathrm{P}\right)+\mathrm{O}_{2}$
$\mathrm{O}\left({ }^{1} \mathrm{D}\right)+\mathrm{H}_{2} \mathrm{O} \longrightarrow 2 \mathrm{OH}$
$\mathrm{RCHO}+\mathrm{hV} \rightarrow \mathrm{R}+\mathrm{CHO}_{\text {, }}$
$\mathrm{CHO}+\mathrm{O}_{2} \rightarrow \mathrm{HO}_{2}$
$\mathrm{HO}_{2}+\mathrm{NO} \longrightarrow \mathrm{OH}+\mathrm{NO}_{2}$



## Ingredient 4: fuel

- Finally, we need the fued
- In principle, this can be any VOC

- Some fuels are more reactive than others
- This leads to dirfferences in local and regional effects.
- Some fuels are "cleaner" than others
-i.e. contain more carbon $\Rightarrow$ longer chemical chain length
$\Rightarrow$ more efficient aerosol precursors


## Oxidation in the troposphere



- VOCs are emitted from many sources: trees, vehicles, industries, etc.
- They are consumed by OH , but other oxidants are important $\left(\mathrm{NO}_{3}, \mathrm{O}_{3}, \mathrm{Cl}\right)$
- Oxidants are produced in a collectively autocatalytic set
- Here, VOCs are transformed into a sequence of carbonyls of diminishing size $\rightarrow \mathrm{CO}_{2}$ However...


## But life is never that easy...



- There are many branching channels to consider
- $\mathrm{RO}_{2}$ and RO have a high capacity for isomerization and fragmentation
- Separate chemical cycles involving nitrogen and sulphur are important
- What if $R$ contains a heteroatom?


## Meandering through oxidation space



- Atmospheric chemistry is a very cold, very slow combustion
- Eventually, a "fuel" may be converted to $\mathrm{CO}_{2}$ and $\mathrm{H}_{2} \mathrm{O}$
- But the path through this space is not simple or direct
- At what point is atmospheric chemistry unknowable/ unpredictable?


## The hydroxyl radical

- Also known as the "detergent of the atmosphere"
- Daytime sources: $\mathrm{O}_{3}+h v$, HONO $+h v, \mathrm{RCHO}+h v$
- Nighttime source (minor): alkene ozonolysis
- Sinks: reactions with VOCs, reaction with $\mathrm{NO}_{2}$
- Ambient concentration: $\sim 1 \times 10^{6}$ molecule $\mathrm{cm}^{-3}$
- OH has the balance between high reactivity and high enough concentration to be an effective cleaner of the atmopshere


## Hydroxyl radical reactions

- Hydrogen abstraction

- Comparatively high reactivity with alkanes and other unsaturated species


## Hydroxyl radical reactions

- Hydroxyl addition

- High reactivity towards alkenes and aromatics
- Add alcohol functionality to alkenes


## The nitrate radical

- The nitrate radical can be the most effective oxidant at night
- Nitrate is part of the following equilibrium: $\mathrm{NO}_{2}+\mathrm{NO}_{3} \rightleftharpoons \mathrm{~N}_{2} \mathrm{O}_{5}$
- $\mathrm{NO}_{3}$ is most important in areas that are affected by anthropogenic $\mathrm{NO}_{x}$ and ozone
- Sinks: photolysis, reactions with alkenes and NO
- Ambient concentration: $\sim 5 \times 10^{8}$ molecule $\mathrm{cm}^{-3}$
- $\mathrm{NO}_{3}$ has a very high photolysis cross section in the actinic region, so it is effectively lost during the day


## Nitrate radical reactions

- Hydrogen abstraction

- Generally very low reactivity towards hydrogen abstraction
- Aldehydic C-H bonds are an exception to this rule



## Nitrate radical reactions

- Nitrate addition

- High reactivity towards activated alkenes
- Adds nitrate and epoxy functionality to alkenes


## Atomic chlorine

- Atomic chlorine is one of the most reactive oxidants known
- Typically, higher concentrations are seen in coastal environments
- This is not always the case with longer-lived precursors such as $\mathrm{ClNO}_{2}$
- Sinks: rapid reactions with organic compounds
- Ambient concentration: $\sim 1 \times 10^{4}$ molecule $\mathrm{cm}^{-3}$


## Atomic chlorine reactions

- Hydrogen abstraction

- Generally very rapid reactions with most types of $\mathrm{C}-\mathrm{H}$ bonds


## Atomic chlorine reactions

- Chlorine addition

- Very rapid reactions with alkenes, less so with aromatics
- Adds chlorine functionality to alkenes structures
- Ozone is less reactive than other oxidants
- It is produced from the photochemical oxidation cycles in the atmosphere
- As a consequence, $\left[\mathrm{O}_{3}\right]$ can be much higher, especially in urban environments
- This means that reaction rates can be competitive with other oxidants
- Sinks: reactions with alkenes and NO
- Ambient concentration: $\sim 7 \times 10^{11}$ molecule $\mathrm{cm}^{-3}$


## Ozone reactions

- Ozonolysis



## Criegee intermediates



Above: A low-vapour pressure hydroperoxide
Right: A matrix of different Cl and acid combinations


Source: Chhantyal-Pun et al. (2018)

- There are potentially lots of different Criegee intermediates and $\mathrm{R}(\mathrm{O}) \mathrm{OH}$ in the atmosphere
- These rate constants are really big
- It's a way of adding carbon and oxygen in one step
- This could be a source of particles in the atmosphere


## Peroxy radicals $\left(\mathrm{RO}_{2}\right)$

- Peroxy radicals are produced from the reaction of carbon-centred radicals with $\mathrm{O}_{2}$

$$
\mathrm{R} \cdot+\mathrm{O}_{2} \rightarrow \mathrm{ROO} .
$$

- Carbon-centred radicals are produced during hydrogen abstraction and addition reaction mentioned earlier
- In urban environments, the sinks with $\mathrm{NO}_{x}$ are very important
- In more remote environments reactions with other peroxy radicals become important
- For certain $\mathrm{RO}_{2}$, hydrogen shifts are very important


## Peroxy radical reactions





## Alkoxy radicals

- Alkoxy radicals are short-lived intermediates that are produced from the reactions of $\mathrm{RO}_{2}$
- Because of their high reactivity towards $\mathrm{O}_{2}$, their propensity for decomposition and rearrangement, their concentrations in the atmosphere are low
- Because of their ubiquity and the branching pathways available to alkoxy radicals, they are a major source of atmospheric complexity


## Alkoxy radical reactions

## 安


$\cdots$

$$
\square \square \square \square \square \mathrm{CO}_{2}
$$



Parent
Hydrocarbon
$1^{\text {st }}$ generation
species


## The many unknowns of tropospheric chemistry

Area-proportional Venn diagram: number of products formed from two atmospheric


- Far more chemicals expected to form in the atmosphere ${ }^{1}$ than have been studied ${ }^{2}$
- Remember: these are just two primary emissions, what about the 1000s of others? ${ }^{3}$
- It is surprising how much we don't know yet (reactivity, products, multiphase)
- Why? Partly because of the huge numbers, partly because of the types of chemicals formed...


## Conclusions:

## Part 3 - Chemical reactions in the troposphere

- The troposphere contains the largest variety of chemical reactions in the atmosphere
- It is an auto-catalytic cycle involving sunlight, $\mathrm{NO}_{x}, \mathrm{O}_{3}$ and VOCs
- These reactions clean the atmosphere, but they also produce harmful degradation products along the way
- The level of complexity that is generated from tropospheric chemistry is an example of a combinatorial explosion

Part 4 - Chemical reactions in the stratosphere

## Stratospheric ozone

- The ozone layer is one of the most important features of the atmosphere
- It is what attenuates most of the UV wavelengths in the troposphere
- Going above the ozone layer opens up the Herzberg continuum...



$$
\begin{aligned}
& \mathrm{O}_{2}+h v \rightarrow \mathrm{O}\left({ }^{3} \mathrm{P}\right)+\mathrm{O}\left({ }^{3} \mathrm{P}\right) \\
& 0 \rightarrow 249 \times 2 \mathrm{~kJ} \text { motrin } \\
& \text { From Hess's law: } \\
& \Delta H_{\mathrm{rxn}}=v(\mathrm{p}) \Delta H_{\mathrm{f}(\mathrm{p})}-v(\mathrm{r}) \Delta H_{\mathrm{f}(\mathrm{r})} \\
& =498 \mathrm{~kJ} \mathrm{mot}^{-1} \\
& =\frac{498,000 \mathrm{~J} \mathrm{mot}}{} \mathrm{~N}_{A} \\
& =\frac{8.27 \times 10^{-19}}{h \times c} \mathrm{~J} \text { photon } \\
& =240 \mathrm{~nm} \\
& \text { (the photolysis threshold) }
\end{aligned}
$$



## The Chapman Cycle

| $-\mathrm{O}_{2}+h v$ | $\rightarrow$ | $2 \mathrm{O}\left({ }^{3} \mathrm{P}\right)$ |
| :--- | :--- | :--- |
| $-\mathrm{O}_{2}+\mathrm{O}\left({ }^{3} \mathrm{P}\right)+\mathrm{M}$ | $\rightarrow$ | $\mathrm{O}_{3}+\mathrm{M}$ |
| $-\mathrm{O}_{3}+h v$ | $\rightarrow$ | $\mathrm{O}_{2}+\mathrm{O}\left({ }^{1} \mathrm{D}\right)$ |
| $-\mathrm{O}\left({ }^{1} \mathrm{D}\right)+\mathrm{M}$ | $\rightarrow$ | $\mathrm{O}\left({ }^{3} \mathrm{P}\right)+\mathrm{M}$ |
| $-\mathrm{O}\left({ }^{3} \mathrm{P}\right)+\mathrm{O}_{3}$ | $\rightarrow$ | $2 \mathrm{O}_{2}$ |



## The Chapman profile





Ozone production is a balance between number density, photon flus and absorption cross sections of $O_{2}$ and $O_{3}$

## - Quiz -

- Remember all those reactions that are available to oxidize chemicals in the troposphere?
- What happens to this molecule?
-No reaction


CFC-11 with any of the tropospheric oxidants
-No significant absorption in the actinic range



Iames Lovelock (1972)

## The Nobel Prize in Chemistry 1995



PaulJ.
Crutzen


Mario J.
Molina

F. Sherwood Rowland

- CFC-11 $\left(\mathrm{CFCl}_{3}\right)$ was observed in the air samples of James Lovelock in 1972
- Molina and Rowland determined that these molecules survive for decades/ centuries
- This indicates upward transport
- Together with Crutzen they anticipated the threat that this presents to the stratosphere...


## Catalytic ozone destruction

## Initiation:

## Ozone Destruction Cycle 1

e.g. $\mathrm{CFCl}_{3}+h v \rightarrow \mathrm{Cl}+\mathrm{CFCl}_{2}$

## Propagation:

$\mathrm{Cl}+\mathrm{O}_{3}$

$$
\rightarrow \mathrm{ClO}+\mathrm{O}_{2}
$$

$\mathrm{O}+\mathrm{ClO}$
$\rightarrow \mathrm{Cl}+\mathrm{O}_{2}$
Net: $\mathbf{O}_{\mathbf{3}} \mathbf{+ O} \rightarrow \mathbf{2 O}_{\mathbf{2}}$
$\mathrm{Cl}+\mathrm{O}_{3}$
$\rightarrow \mathrm{ClO}+\mathrm{O}_{2}$
$\mathrm{NO}+\mathrm{ClO}$
$\rightarrow \mathrm{Cl}+\mathrm{NO}_{2}$
$\mathrm{NO}_{2}+h v$
$\rightarrow \mathrm{NO}+\mathrm{O}$
$\mathrm{NO}_{2}+\mathrm{O}$
$\rightarrow \mathrm{NO}+\mathrm{O}_{2}$
$\mathrm{NO}+\mathrm{O}_{3}$
$\rightarrow \mathrm{NO}_{2}+\mathrm{O}_{2}$
Net: $\mathbf{2 O}_{\mathbf{3}}$
$\rightarrow \mathbf{3 O}_{\mathbf{2}}$


## Catalytic ozone destruction

## Termination:

Ozone Destruction Cycle 1

$$
\begin{array}{ll}
\mathrm{ClO}+\mathrm{NO}_{2}+\mathrm{M} & \rightarrow \mathrm{ClONO} \\
\mathrm{Cl}+\mathrm{HO}_{2} & \rightarrow \mathrm{MCl}+\mathrm{O}_{2} \\
\mathrm{Cl}+\mathrm{CH}_{4} & \rightarrow \mathrm{HCl}+\mathrm{CH}_{3} \\
\mathrm{ClO}+\mathrm{CH}_{3} \mathrm{OO} & \rightarrow \mathrm{CH}_{3} \mathrm{OCl}+\mathrm{O}_{2} \\
\mathrm{ClO}+\mathrm{HO}_{2} & \rightarrow \mathrm{HOCl}+\mathrm{O}_{2}
\end{array}
$$

Cl and ClO : active chlorine HCl and $\mathrm{ClONO}_{2}$ : important Cl reservoirs HOCl and $\mathrm{CH}_{3} \mathrm{OCl}$ : less important Cl reservoirs


## The ozone hole

Polar Ozone Depletion



- Observation of the ozone hole was very sudden and unexpected
- This led to a rapid international effort to understand this process further

In the polar night
1

Formation of polar stratospheric clouds: 2

Activation of $\mathrm{Cl}_{x}$ :


## $\mathrm{CIONO}_{2}$

## In the polar spring

3 Formation of $\mathrm{ClO}_{x}: \quad \mathrm{Cl}_{2}+h v \rightarrow 2 \mathrm{Cl}$

$$
\begin{array}{ll}
\mathrm{HOCl}+h v & \rightarrow \mathrm{OH}+\mathrm{Cl} \\
\mathrm{Cl}+\mathrm{O}_{3} \rightarrow \mathrm{ClO}+\mathrm{O}_{2}
\end{array}
$$

4 Catalytic $\mathrm{O}_{3}$ depletion: $\mathrm{ClO}+\mathrm{ClO} \rightarrow \mathrm{Cl}_{2} \mathrm{O}_{2}$ $\mathrm{Cl}_{2} \mathrm{O}_{2}+h v \rightarrow 2 \mathrm{Cl}+\mathrm{O}_{2}$ $\mathrm{Cl}+\mathrm{O}_{3} \rightarrow \mathrm{ClO}+\mathrm{O}_{2}$

## Conclusions:

## Part 3 - Chemical reactions in the stratosphere

- As you get higher into the atmosphere, shorter UV wavelengths become accessible
- This allows for the photolytic production of $\mathrm{O}_{3}$, and the destruction of very stable compounds such as CFCs
- This provides a source of chlorine into the stratosphere which has a catalytic effect on ozone depletion
- Society's rapid response to ozone depletion is often cited as a success story in atmospheric chemistry
- But there are other ways of looking at this...
- How will society respond to other future environmental threats?


## Approaches to studying the atmosphere

- Studying the atmosphere is a big job
- This requires many different activities
- This can be viewed metaphorically as a 3 -legged stool
- In the field, we can observe what the atmosphere is composed of
- In the lab, we can understand the individual processes to create and destroy species
- In models, we can couple our fundamental understanding from the lab with our field observations



A view of the HELIOS platform at sunrise


## 

HELIOS instrumentation
Wetumal sunlight



[^0]:    © The University of Waikato Te Whare Wananga o Waikato | www.sciencelearn.org.nz

