## Structure of the Atmosphere

- The structure of the atmosphere is a function of
  - Gravity
  - Composition
  - Radiation
- The density of the atmosphere decreases approximately exponentially.
- The composition of the atmosphere is influenced by gravitational fractionation.
  - The heavier gases sink.
  - The lighter gases can be lost to outer space.
- If there are no sources or sinks of chemical species (i.e. no reactions or emissions), the composition of the atmosphere is controlled by diffusion and mixing due to fluid motions (i.e. meteorology).
- If equilibrium were to be attained, the atmosphere would become stratified by composition.

**THE ATMOSPHERE IS NOT AT EQUILIBRIUM!**

- The atmosphere is not at equilibrium from a thermodynamic perspective because
  - It is an open system and mass and energy are transferred.
- Mass transfer takes the form of:
  - Terrestial emissions.
  - Loss to the interplanetary medium.
  - Chemical reactions in the atmosphere.
  - Deposition
- Sources of energy:
  - The Sun (approximately a blackbody at 5780 K).
  - Geothermal (approximately a blackbody at 255 K).
- Sinks of energy:
  - Radiative loss to the interplanetary medium.
- The stratification of the atmosphere is the result of the interaction between radiative energy and composition.

## Radiation

- Light is quantized.
    - A quantum of light is a photon.
- The energy of a photon may be related to
    - $\nu$, the frequency of light:

$$E = h\nu$$

    - $\lambda$, the wavelength of light:

$$E = \frac{hc}{\lambda}$$

- Many natural sources of radiation may be characterized as blackbody radiators which emit photons that have a distribution over wavelength (or frequency) that is characteristic of the temperature of the blackbody.
- In terms of wavelength the distribution function, $\rho$, the energy density per wavelength is:

$$\rho(\lambda, T) = \frac{8\pi hc}{\lambda^5} \frac{1}{e^{hc/\lambda kT} - 1}$$

- In terms of frequency the distribution function, $\rho$, the energy density per frequency is:

$$\rho(\nu, T) = \frac{8\pi h\nu^3}{c^3} \frac{1}{e^{h\nu/kT} - 1}$$

- For chemical reactions, the number density of the photons is more important than the energy density.
  - To transform the energy density distribution function into a photon density distribution function, divide the energy density function by the energy of a photon.

$$\rho_\phi(\lambda, T) = \frac{\rho(\lambda, T)}{hc/\lambda} = \frac{8\pi}{\lambda^4}\frac{1}{e^{hc/\lambda kT} - 1}$$

$$\rho_\phi(\nu, T) = \frac{\rho(\nu, T)}{h\nu} = \frac{8\pi\nu^2}{c^3}\frac{1}{e^{h\nu/kT} - 1}$$

- From the number density distribution function for photons, the number of photons with energy in a particular energy range may be determined.
  - This is essential to the determination of rates of photochemical reactions.
- How photons can interact with a chemical entity such as an atom, a molecule, an ion or a radical is determined by the quantization of the energy levels for
  - Electronic energy
  - Vibrational energy
  - Rotational energy

- If a photon's energy matches an energy gap between quantized energy levels (and certain symmetry conditions required by quantum mechanics) then there is a probability that the photon will be able to be absorbed by that molecule.
    - The result is an excited chemical species that must do something with the extra energy.
- The fate of a photon's energy can:
    - cause a molecule to fall apart or photodissociate.
    - cause a chemical species to eject an electron or photoionize.
    - cause a molecule to rearrange or photoisomerize.
    - cause a chemical species to redistribute the energy internally. (Sunscreens do this).
    - cause a chemical species to transfer energy to other molecules. (This is how microwave ovens work. In the atmosphere, this is part of the greenhouse effect.)
    - cause a chemical species to emit a photon of the same or lower energy (fluorescence

and phosphorescence). This is also part of the greenhouse effect.

- This provides a context from which the thermal structure of the atmosphere may be examined.
- Each layer of the atmosphere is separated by a thermal inversion.
- The thermosphere is regarded as that above 85 km with a pressure of less than 10–8 atm.
    - Exposed to the sun's full radiative flux of 1370 W $m^{-2}$, including wavelengths less than 200 nm.
    - A photon of 200 nm wavelength has an energy of:

$$E(\lambda = 200 \;\; \text{nm}) = \frac{hc}{\lambda} =$$

$$\frac{6.626 \times 10^{-34} \text{ J s} \cdot 2.998 \times 10^{8} \text{ m s}^{-1}}{200 \times 10^{-9} \text{ m}} =$$

$$9.9324 \times 10^{-19} \text{ J photon}^{-1}$$

    - This could dissociate a molecule with a bond energy of:

$$9.9324 \times 10^{-19} \text{ J molec}^{-1} \cdot 6.022 \times 10^{23} \text{ molec mol}^{-1}$$
$$= 5.98 \times 10^{5} \text{ J mol}^{-1} = 598 \text{ kJ mol}^{-1}$$

which includes most chemical bonds.

- Shorter wavelengths can dissociate or ionize chemical species:

$$N_2 \; + \; h\nu \; \rightarrow 2N \quad \Delta H = 946 \text{ kJ mol}^{-1}$$
$$N \; \rightarrow \; N^{+} \; + \; e^{-} \quad \Delta H = 1400 \text{ kJ mol}^{-1}$$
$$O_2 \; \rightarrow \; O_2^{+} \; e^{-} \quad \Delta H = 1160 \text{ kJ mol}^{-1}$$

  - Therefore the thermosphere is mostly atoms and ions.

- The top of the thermosphere is hot, because collisions are rare and energy transfer for excited chemical species is inefficient.

- As the altitude decreases, the thermosphere gets colder because fewer high energy photons are able to penetrate this far.

- At the mesopause (85 km altitude), the density of gas has increased to the point that collisional energy transfer can be effective in the redistribution energy of absorbed photons.

- In the mesosphere (50-85 km altitude), the density continues to increase as altitude decreases.
  - Collisional energy transfer increases in efficiency as density increases.
  - Less energy is lost as photons.
  - More of the sun's energy is transferred to kinetic energy of the chemical species.
  - Ozone can play an important role in this.

| | $\Delta$ H (kJ mol$^{-1}$) |
|---|---|
| $O_2 + h\nu(\lambda < 240nm) \rightarrow 2O$ | 495 -$E_{photon_1}$ |
| $O + O_2 + M \rightarrow O_3 + M$ | -105 |
| $O + O_3 \rightarrow O_2 + O_2$ | -389 |
| $O_3 + h\nu(\lambda < 325nm) \rightarrow O_2 + O$ | 105 - $E_{photon_2}$ |

- This is the Chapman cycle and gives the net reaction:

$$2O_3 + 3O + 3O_2 \rightarrow 2O_3 + 3O + 3O_2 \quad -E_{photon_1}-E_{photon_2}$$

which has the net effect of converting photon energy to thermal energy.

- The mass of the mesophere is about two orders of magnitude greater than the mass of the thermosphere.
  - With sufficient density for efficient energy transfer, warm air will rise, cold air will sink and there will be efficient mixing.
- At the stratopause ($\sim$ 50 km) there is a temperature inversion.
  - Absorbable photons have been depleted by the stratoshere and energy transfer stops being efficient.
- The stratosphere is very stratified.
  - Not well mixed.
  - Temperature at the top of the stratosphere is $\sim$ 273 K.
  - Temperature at the bottom of the stratosphere is $\sim$ 213 K and the density is $\sim$ 0.4 atm, which is sufficient for three body collisions to become significant.
- Chapman cycle is important.
  - With significant $O_3$ formation, absorption between 200 and 290 nm is efficient as is

transfer of radiative energy to collisional energy.

- Other molecules are present since there are not enough high energy photons to destroy them, such as NO, $NO_2$, CFC's, $Cl_2$, and $H_2O$.
- At the tropospause ($\sim$ 18 km), virtually all radiation with wavelength shorter than 290 nm is screened out.
- The troposphere has two energy sources.
  - Solar radiation ($\lambda > 290$ nm).
  - Geothermal radiation (infrared).
- The troposphere absorbs geothermal radiation more efficiently near the earth's surface.
- The troposphere cools as altitude increases.
  - Because of its thermal structure, the troposphere is well mixed.
  - Fewer molecules are available to absorb radiation and fewer infrared photons are available to be absorbed.
  - The absorption of long wavelength radiation by the troposphere is known as the greenhouse effect.

## The Greenhouse Effect

- The greenhouse effect results in the trapping of energy in the troposphere.
    - Infrared radiation is efficiently converted to thermal energy.
- In order to be able to absorb infrared radiation the molecule must have either
    - a transient dipole.
    - or a permanent dipole.
- A heteronuclear diatomic has a permanent dipole:
    - CO
    - NO
- Many nonlinear molecules also have permanent dipoles:
    - $CH_2F_2$
    - $H_2O$
    - $O_3$
- Non-symmetric linear molecules often have permanent dipoles:
    - NNO

- Symmetric molecules can have transient dipoles as the result of asymmetric stretching vibrations.
    - $CO_2$
    - $CH_4$
- Greenhouse gas levels are increasing.
- Methane ($CH_4$) 1.7 ppmv and increasing by 1 to 2% annually.
- Methane is a product of anaerobic decay.
    - $150 \times 10^6$ tonnes from natural sources such as marsh gas, wetlands, and ruminants.
    - $25 \times 10^6$ tonnes from oceans
    - $150 \times 10^6$ tonnes from natural gas
    - Anthropogenic sources include $95 \times 10^6$ tonnes from rice paddies and $120 \times 10^6$ tonnes from cattle.
- Carbon dioxide ($CO_2$) is at a level of about 350 ppm and is rising by about 0.5% per year.
    - Carbon dioxide is the result of fossil fuel combustion.

- Speciates in water:

$$CO_2(g) \rightleftharpoons H_2CO_3(aq)$$

$$H_2CO_3(aq) \rightleftharpoons H^+ + HCO_3^-$$
$$HCO_3^- \rightleftharpoons H^+ + CO_3^{2-}$$
$$CO_3^{2-} + Ca^{2+} \rightleftharpoons CaCO_3(s)$$

  with about 60 times as much in the aqueous phase as in the gas phase.

- $CO_2$ is also the product of atmospheric decomposition of $CH_4$ and other hydrocarbons.

- The atmospheric decomposition of methane occurs as a sequence of reactions:

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

$$CH_3 \ + \ O_2 \ + \ M \ \rightarrow \ CH_3OO \ + \ M$$
$$CH_3O_2 \ + \ NO \ \rightarrow \ CH_3ONO_2$$
$$CH_3O_2 \ + \ NO \ \rightarrow \ CH_3O \ + \ NO_2$$
$$CH_3O \ + \ O_2 \ \rightarrow \ CH_2O \ + \ HO_2$$
$$CH_2O \ + \ OH \ \rightarrow \ H_2O \ + \ HCO$$

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

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

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

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

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

  - Other fates for $HO_2$:

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

  - Other fates for $NO_2$:

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

  - Atomic oxygen contributes to the formation of ground level ozone.

$$O + O_2 \rightarrow O_3$$

- Decomposition of other hydrocarbons is initiated by the abstraction of an H atom by OH.

## Nitrous Oxide

- $N_2O$ (N=N=O) is present in the troposphere at $\cong$ 300 ppbv.
    - Asymmetric with a permanent dipole. Therefore it is a greenhouse gas.
- Sources include:
    - natural biological denitrification
    - anthropogenic biological denitrification as the result of the use of fertilizers.
    - industrial sources such as nylon manufacture.
    - combustion of fossil fuels.
- No tropospheric sinks.
    - This means that $N_2O$ becomes globally distributed.
    - Transported to the stratosphere resulting in a tropospheric lifetime of about two years.
    - Stratospheric sink reactions include:

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

$$N_2O + O^* \rightarrow 2NO$$

## Chlorofluorocarbons and Halons

- Chlorofluorocarbons or CFC's follow a nomenclature based on the rule of 90.
  - Consider CFC-11.
  - Add 90 to 11 to get 101.
  - The first digit indicates the number of carbon atoms present in the molecule.
  - The second digit indicates the number of hydrogen atoms present in the molecule.
  - The third digit indicates the number of fluorine atoms present in the molecule.
  - The remaining valence sites are occupied by chlorine.
  - Thus CFC-11 is $CFCl_3$.
  - HCFCs (hydrochlorofluorocarbons) also follow the rule of 90 (see page 19 of Bunce.)
- Halons are brominated analogs of CFC's with one or more bromine atoms in the structure.
- Halons are designated by a four digit number.
  - Consider Halon-1211

  - The first digit indicates the number of carbon atoms.
  - The second digit indicates the number of fluorine atoms.
  - The third digit indicates the number of chlorine atoms.
  - The fourth digit indicates the number of bromine atoms.
  - All remaining valence sites are occupied by hydrogen.
- CFCs, HCFCs and Halons are substituted hydrocarbons.
  - Therefore they are greenhouse gases.
  - Whether or not they have a tropospheric sink depends on whether an H atom is present in the structure.
  - In the absence of an H atom, they are sufficiently longlived to be transported to the stratosphere, where photodissociation can occur.

## Greenhouse Gases and Climate Change

- Increases in levels of greenhouse gases has been correlated with increases in tropospheric temperatures.
- The impact of a greenhouse gas may be considered in terms of its global warming potential.
    - Usually defined relative to the global warming potential of $CO_2$.
- Radiative forcing is represented by $F_R$ and has units of watts $m^{-2}$.
    - It may be thought of as the amount of photon energy converted to thermal energy per unit area.
- Global warming potential is defined as:

$$GWP = \frac{\int_0^T \Delta F_{R,i}(t)dt}{\int_0^T \Delta F_{R,CO_2}(t)dt}$$

- 
    - $\Delta F_{R,i}$ is the change in radiative forcing due to an instaneous release at $t = 0$ of 1 kg of gas $i$.
    - $T$ is the time horizon of interest.

- This may be approximated by:

$$GWP = \frac{\int_0^T a_i n_i(t)dt}{\int_0^T a_{CO_2} n_{CO_2}(t)dt}$$

where

  - $a_i$ in W m$^{-2}$ kg$^{-1}$ is the radiative forcing due to the presence of trace gas $i$
  - $n_i(t)$ is the amount of gas $i$ present at time $t$ after release.

- If $\tau_i$ is the atmospheric lifetime of molecule $i$ then

$$n_i(t) = n_i(0)e^{-t/\tau_i}$$

  - Since $n_i(0)$ is 1 kg, the global warming potential becomes:

$$GWP = \frac{a_i \int_0^T e^{-t/\tau_i} dt}{a_{CO_2} \int_0^T e^{-t/\tau_{CO_2}} dt}$$

$$\frac{a_i \tau_i \left(1 - e^{-T/\tau_i}\right)}{a_{CO_2} \tau_{CO_2} \left(1 - e^{-T/\tau_{CO_2}}\right)}$$

- The integration time $T$ depends on the timescale for the phenomena of interest.

- Maximum change in temperature or sea level $\sim$ 100 years
- Maximum rate of change in temperature or sea level $\sim$ 50 years.

- Values for $a_i$ and $\Delta F_{R,i}$ are determined from general circulation models (GCM).

## Stratospheric Ozone

- $O_3$ absorbs photons with $\lambda$ between 240 and 320 nm.
- The term "ozone layer" refers not to a physical layer, but rather the ozone distributed throughout the stratosphere at $\sim$ 10 ppmv.
    - If all the stratospheric $O_3$ were compressed to into a layer at standard temperatue and pressure, the layer would be 3 mm thick.
    - The stratosphere is not well mixed and concentration of $O_3$ varies with altitude.
- Recall the Chapman cycle:

| | $\Delta$ H (kJ mol$^{-1}$) |
|---|---|
| $O_2$ + h$\nu(\lambda < 240nm) \rightarrow$ 2O | 495 -E$_{photon_1}$ |

$O + O_2 + M \rightarrow O_3 + M$ -105

$O_3 + h\nu(\lambda < 325\ nm) \rightarrow O_2^* + O^*$
383 -$E_{photon_2}$

or

$O_3 + h\nu(\lambda < 325\ nm) \rightarrow O_2 + O$ 105 - $E_{photon_2}$

$O + O_3 \rightarrow O_2 + O_2$ -389

- The associated rate coefficients are $k_1$, $k_2$, $k_3$, $k_{3'}$, and $k_4$

- The Chapman cycle can reach a steady state:

$$\frac{d[O_2]}{dt} = 0 = -k_1[O_2] - k_2[O][O_2][M]$$
$$+(k_3 + k_{3'})[O_3] + 2k_4[O][O_3]$$
$$\frac{d[O]}{dt} = 0 = 2k_1[O_2] - k_2[O][O_2][M]$$
$$+(k_3 + k_{3'})[O_3] - k_4[O][O_3]$$
$$\frac{d[O_3]}{dt} = 0 = k_2[O][O_2][M] - (k_3 + k_{3'})[O_3]$$
$$-k_4[O][O_3]$$

- But this steady state is NOT an equilibrium because energy is processed from photons into kinetic energy.
  - $k_1$, $k_3$, and $k_{3'}$ depend on the photon supply.
- From the steady state equations, relative amounts of O, $O_2$ and $O_3$ may be predicted.
- Observed O, $O_2$ and $O_3$ levels do not match that predicted from steady state equations.
  - Observed $O_3$ levels are low.
  - Therefore there must be additional sinks for $O_3$.
- $O_3$ can be depleted catalytically by a species "X":

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

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

  with the net reaction:

$$O_3 + O \rightarrow 2O_2$$

- "X" is usually an odd electron species.
- Some X/XO pairs are:

- Cl/ClO

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

$$ClO + O \rightarrow Cl + O_2$$

- Br/BrO

$$Br + O_3 \rightarrow BrO + O_2$$

$$BrO + O \rightarrow Br + O_2$$

- NO/$NO_2$

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

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

- OH/$HO_2$

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

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

- H/OH

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

$$OH + O \rightarrow H + O_2$$

- Cl and Br in the stratosphere are mostly anthropogenic and come from CFC's and Halons.
- NO, H and OH occur naturally.
- These act as catalysts, increasing the rate of reaction by decreasing the activation energy. (See Table 1 page 37.)
- Consider:

$$\text{Rate}_1 = k_1[X][O_3]$$

$$k_1 = A_1 e^{-E_1/RT}$$

$$\text{Rate}_2 = k_2[XO][O]$$

$$k_2 = A_2 e^{-E_2/RT}$$

  where

  - $k$'s are the rate coefficients
  - $A$ is the Arrhenius pre-exponential factor which represents the chance of two molecules hitting each other in an orientation favourable for reaction.
  - $E$ is the Arrhenius activation energy and $e^{-E/RT}$ is the fraction of molecular collisions with at least this energy.

- The uncatalyzed reaction

$$O + O_3 \rightarrow 2O_2$$

  has an activation energy of 18.4 kJ $mol^{-1}$

- The X/XO pairs provide a lower energy two step pathway.
  - Some activation energies in kJ $mol^{-1}$:

| X | X+$O_3$ | XO+O |
|---|---|---|
| Cl | 2.1 | 1.1 |
| NO | 13.1 | 0 |
| H | 3.9 | 0 |
| OH | 7.8 | 0 |

- Exact rate of $O_3$ decomposition depends on altitude, [X], and [XO].
- At 30 km altitude:
  - Decomposition by NO/$NO_2$ dominates over uncatalyzed rate.
  - Decomposition by Cl/ClO is comparable to the uncatalyzed rate.
  - The second step of each pair of catalytic reactions is the rate limiting step because

of the low concentration of XO, not the activation energy.

  - Both steps of the catalyic reaction are free radical propagation reactions.

- To complete a model of stratospheric ozone, it is necessary to consider other reactions involving ozone depleting species.

- These reactions can provide temporary reservoirs:

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

  - An active ozone depleting species $NO_2$ is converted to the inactive (from an ozone depleting perspective) $HNO_3$.

  - Photolysis can regenerate $NO_2$:

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

- Consider the reactions:

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

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

- Again an ozone depleting species (Cl) is converted to a reservoir species (HCl), which in turn (this time by reaction with OH) can be converted back to an active ozone depleter.

- There are also null cycles which have the effect of converting photons to thermal energy.

$$NO_2 + h\nu(\lambda < 400 \text{ nm}) \rightarrow NO + O$$

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

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

which may be rewritten as a pseudoequilibrium:

$$NO_2 + O_2 \rightleftharpoons NO + O_3$$

with the forward reaction driven by availability of photons.

  - This cycle can affect ratios of $NO/NO_2$ and $HO/HO_2$.

- Termination reactions permanently remove free radical species.

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

$$2HO_2 \rightarrow H_2O_2 + O_2$$

$$NO_2 + Cl \rightarrow NO_2Cl$$

- Initiation reactions produce free radicals:

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

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

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

$$CH_3Cl + h\nu \rightarrow CH_3 + Cl$$

$$O + H_2O \rightarrow 2OH$$

$$N_2O + O \rightarrow 2NO$$

- Ozone depleting potential (ODP) is the propensity of a substance (i.e. a source of X) to destroy $O_3$ over the life of the compound relative to the propensity of CFC-11 to lead to the destruction of $O_3$ over its lifetime.
    - Replacement compounds for CFC's need to have a lower ODP.
- CFC's were developed as working fluids for a heat engine working as a refrigerator.
- Heat engines are based on the Carnot Cycle with $T_H > T_L$.
    - $T_H$ is the temperature of the surroundings.
    - $T_L$ is the temperature of the refrigeration chamber.

- For an ideal Carnot Cycle:
  - The system starts at $T_H$ and $P_1, V_1$.
  - The first stroke is an adiabatic expansion to $P_2, V_2$ accompanied by cooling to $T_L$.
  - The next stroke is isothermal at $T_L$ and the fluid absorbs heat and expands to $P_3, V_3$.
  - The third stroke is an adiabatic compression that warms the fluid to $T_H$ at $P_4, V_4$.
  - The fourth stroke compresses the gas isothermally at $T_H$ to $P_1, V_1$, transferring heat to the surroundings.
- The choice of a working fluid, in this case a refrigerant, is selected on the basis of its ability to transfer heat.
  - Therefore a substance that can undergo a gas liquid phase transition between $T_L$ and $T_H$ with a large $\Delta H_{vap}$ is desirable.
- CFC's were chosen because:
  - Inexpensive
  - Easy to make
  - Nontoxic

    - Nonflammable
    - Odourless

- Candidate compounds for CFC's must have all these properties plus:
    - A short ($< 2$ years) tropospheric lifetime
    - Decomposition products that have short tropospheric lifetimes and do not get transported to the stratosphere.
    - Compatibility with existing technology.

- HFC's and HCFC's have shorter tropospheric lifetimes because an H atom can be abstracted leading to products that are scavenged in the troposphere.
    - More expensive than CFC's to produce.
    - Cost also affected by proprietary interests, which in turn can affect the availability in the developing world.
    - HCFC's have tropospheric lifetimes that are longer than two years, and thus they can produce stratospheric chlorine, so they are being phased out in favour of HFC's.

## Stratospheric Ozone Depletion

- An ozone hole is observed over Antarctica.
    - Particularily prominent at the polar sunrise.
- Ozone thinning is also observed over the Arctic.
- The Antarctic region can be characterized by:
    - Large land mass
    - Stable long-lived air circulation pattern
- The Arctic region can be characterized by:
    - Water and islands
    - Unstable air circulation.
- The mechanism of ozone depletion over Antarctica is currently understood to involve the following factors.
    - In the winter, a polar vortex develops.
    - This vortex is stable and the air in it is relatively isolated from the rest of the stratosphere.
    - Therefore photochemically active products build up over the winter.

- During the winter, in the absence of sunlight, the gases in the stratosphere cool radiatively. This means that they sink to below about 30 km altitude.
- This part of the stratosphere contains about 5 ppm water.
- The water freezes into polar stratospheric clouds (PSC) as the winter progresses.
- In addition, other species such as HCl, $HNO_3$, $H_2SO_4$ and other reservoir species also freeze out or stick to the surface of ice crystals.
- The stability of the PSC's is enhanced by the stability of the polar vortex over the land mass.
- In the late winter the clouds are at their coldest.
- Crystals of $HNO_3.3H_2O$ form at -70°C and water crystals form at -85°C.
- The crystals in the PSC's provide sites for heterogenous catalysis later.

- Recall that in the dark, the Chapman Cycle has halted because no photons are available.

  - No ozone is formed over the winter, but collisional depletion of ozone continues.
  - Depletion of ozone enhanced by the catalytic breakdown of ozone depleting reservoir species.
- In the late winter and early spring, $ClONO_2$ and HCl are broken down on crystals in the polar stratospheric clouds to form $Cl_2$ and HOCl, both of which can be photolyzed by visible and near-visible ultraviolet light.
  - This results in chlorine which can catalytic destroy ozone.
- As soon as the photons are available, ClOOCl photolyzes, producing two Cl atoms.

$$ClOOCl + h\nu \rightarrow Cl + O_2 + Cl$$

- In the early polar sunrise, the rate of ozone destruction increases, but photons with enough energy to run the Chapman cycle are not yet available.
- Later in the spring, more photons are available and the rate of ozone formation increases.

## Arctic Ozone Depletion

- In the Arctic, polar stratospheric clouds are not as long lived.
  - Average winter temperatures are not as cold.
  - When PSC's do form, unstable weather patterns break them up.
- The Arctic polar vortex is less isolated from external air, so there is more mixing of the air.
  - Photochemically active species do not accumulate.
  - Arctic depletion is not as extensive because there it is offset by tropospheric injection of ozone into the stratosphere over the winter.
- Because PSC's are not as common, $HNO_3$ stays in the gas phase.
  - It can photolyze generating $NO_2$:

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

  - $NO_2$ can react with ClO and BrO to form the corresponding nitrates

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

$$BrO + NO_2 + M \rightarrow BrONO_2 + M$$

In these forms they cannot contribute to $O_3$ depletion.

- Br from Halons is implicated in Arctic ozone depletion.
- Observed Arctic ozone depletion is of the order of 10-30%.

## Consequences of Ozone Depletion

- Greater penetration of UV into the troposphere.
  - UV-A (320-400 nm) increased over natural tropospheric levels.
  - UV-B (290-320) increased over natural tropospheric levels.
  - UV-C ($< 290$) does not naturally penetrate to the troposphere, but as a consequence of $O_3$ thinning is now getting through.
- UV-C can damage the DNA repair mechanism.
  - Can cause mutations.
  - Can lead to skin cancer.
  - Can cause death of microorganisms and plankton.