

The Atmosphere - Origins of the Earth's Atmosphere

- *Early Earth would have been very hot.*

Why? - Primordial heat, collisions and compression during accretion, decay of short-lived radioactive elements

Consequences - Constant volcanism, surface temperature too high for liquid water or life as we know it, molten surface or thin, unstable basaltic crust.

Atmosphere - early atmosphere probably completely different in composition (H₂, He)

Composition - Probably H₂, He

These gases are relatively rare on Earth compared to other places in the universe and were probably lost to space early in Earth's history because

1. Earth's gravity is not strong enough to hold lighter gases
2. Earth still did not have a differentiated core (solid inner/liquid outer core) which creates Earth's magnetic field (magnetosphere = Van Allen Belt) which deflects solar winds.
3. Once the core differentiated the heavier gases could be retained

The Atmosphere - Origins of the Earth's Atmosphere 2

During cooling

Primordial heat dissipated to space

Condensation of water (rain), accumulation of surface water.

Accumulation of new atmosphere due to volcanic out gassing

Gases produced were probably similar to those created by modern volcanoes (H_2O , CO_2 , SO_2 , CO , HS_2 , Cl_2 , N_2 , H_2) and NH_3 (ammonia) and CH_4 (methane)

No free O_2 at this time (not found in volcanic gases).

Ocean Formation - As the Earth cooled, H_2O produced by out gassing could exist as liquid in the Early Archean, allowing oceans to form.

Evidence - pillow basalts, deep marine sediments in greenstone belts.

Conditions appropriate for evolution of life

The Atmosphere - Origins of the Earth's Atmosphere 3

Evidence from the Rock Record

Iron (Fe) is extremely reactive with oxygen. If we look at the oxidation state of Fe in the rock record, we can infer a great deal about atmospheric evolution.

Archean - Find occurrence of minerals that only form in non-oxidizing environments in Archean sediments: Pyrite (Fools gold; FeS_2), Uraninite (UO_2). These minerals are easily dissolved out of rocks under present atmospheric conditions.

Banded Iron Formation (BIF) - Deep water deposits in which layers of iron-rich minerals alternate with iron-poor layers, primarily chert. Iron minerals include iron oxide, iron carbonate, iron silicate, iron sulfide. BIF's are a major source of iron ore, b/c they contain magnetite (Fe_3O_4) which has a higher iron-to-oxygen ratio than hematite. These are common in rocks 2.0 - 2.8 B.y. old, but do not form today.

Red beds (continental siliciclastic deposits) are never found in rocks older than 2.3 B. y., but are common during Phanerozoic time. Red beds are red because of the highly oxidized mineral hematite (Fe_2O_3), that probably forms secondarily by oxidation of other Fe minerals that have accumulated in the sediment.

Conclusion - amount of O_2 in the atmosphere has increased with time. **Biological Evidence**

Chemical building blocks of life could not have formed in the presence of atmospheric oxygen. Chemical reactions that yield amino acids are inhibited by presence of very small amounts of oxygen.

The Atmosphere - Origins of the Earth's Atmosphere 4

Addition of O₂ to the Atmosphere

How did oxygen reach 21% fractional abundance in the atmosphere?

Oxygen Production

Photochemical dissociation - breakup of water molecules by ultraviolet radiation

Produced O₂ levels approx. 1-2% current levels

At these levels O₃ (Ozone) can form to shield Earth surface from UV

Photosynthesis - CO₂ + H₂O + sunlight = organic compounds + O₂ - produced by cyanobacteria, and eventually higher plants - supplied the rest of O₂ to atmosphere. Thus plant populations

Oxygen Consumers

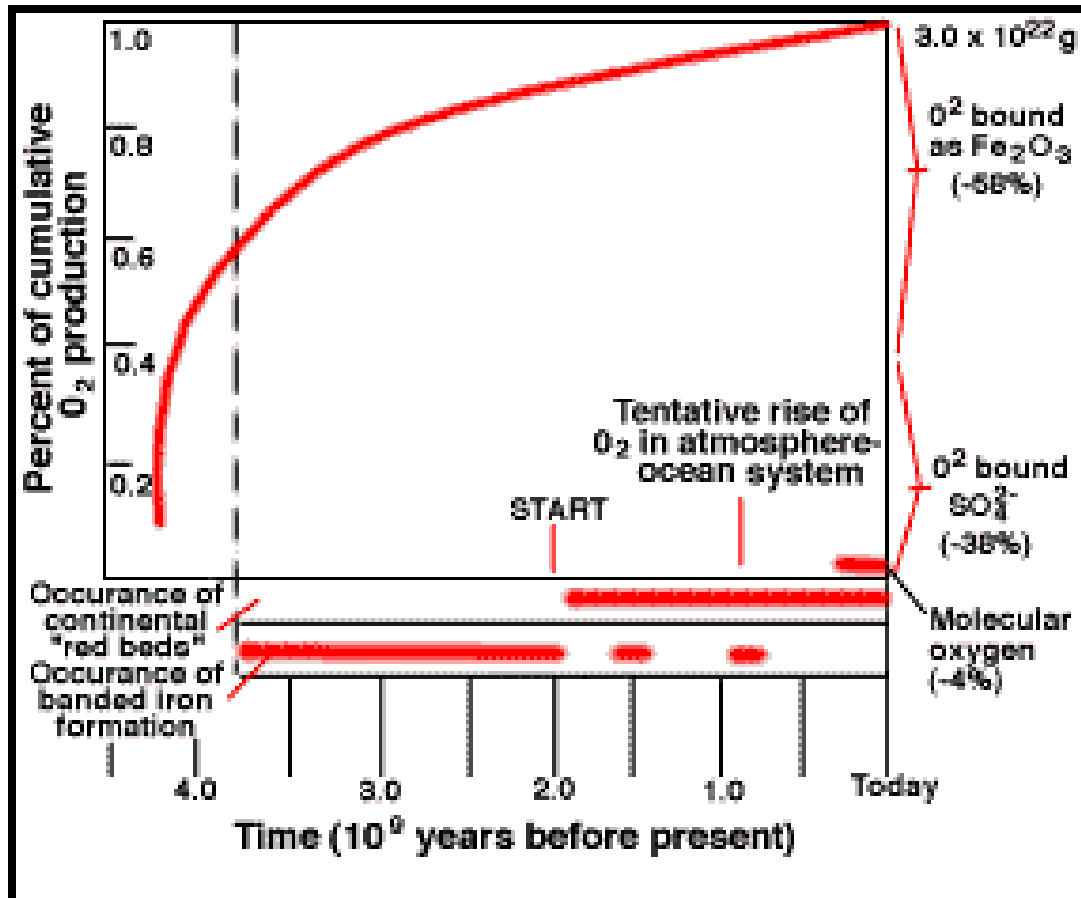
Chemical Weathering - through oxidation of surface materials (early consumer)

Animal Respiration (much later)

Burning of Fossil Fuels (much, much later)

Throughout the Archean there was little to no free oxygen in the atmosphere (<1% of present levels). What little was produced by cyanobacteria, was probably consumed by the weathering process. Once rocks at the surface were sufficiently oxidized, more oxygen could remain free in the atmosphere. During the Proterozoic the amount of free O₂ in the atmosphere rose from 1 - 10 %. Most of this was released by cyanobacteria, which increase in abundance in the fossil record 2.3 Ga. Present levels of O₂ were probably not achieved until ~400 Ma.

The Atmosphere - Origins of the Earth's Atmosphere 5



Atmospheric oxygen built up in the early history of the Earth as the waste product of photosynthetic organisms and by burial of organic matter away from surficial decay. This history is documented by the geologic preservation of oxygen-sensitive minerals, deposition banded iron formations, and development of continental "red beds" or BIFs.

The Atmosphere - Origins of the Earth's Atmosphere 6

Conclusion - amount of O₂ in the atmosphere has increased with time. **Biological Evidence**

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Oxygen prevents growth of the most primitive living bacteria such as photosynthetic bacteria, methane-producing bacteria and bacteria that derive energy from fermentation.

Conclusion - Since today's most primitive life forms are anaerobic, the first forms of cellular life probably had similar metabolisms.

Today these *anaerobic* life forms are restricted to anoxic (low oxygen) habitats such as swamps, ponds, and lagoons.

The Atmosphere – Current Composition

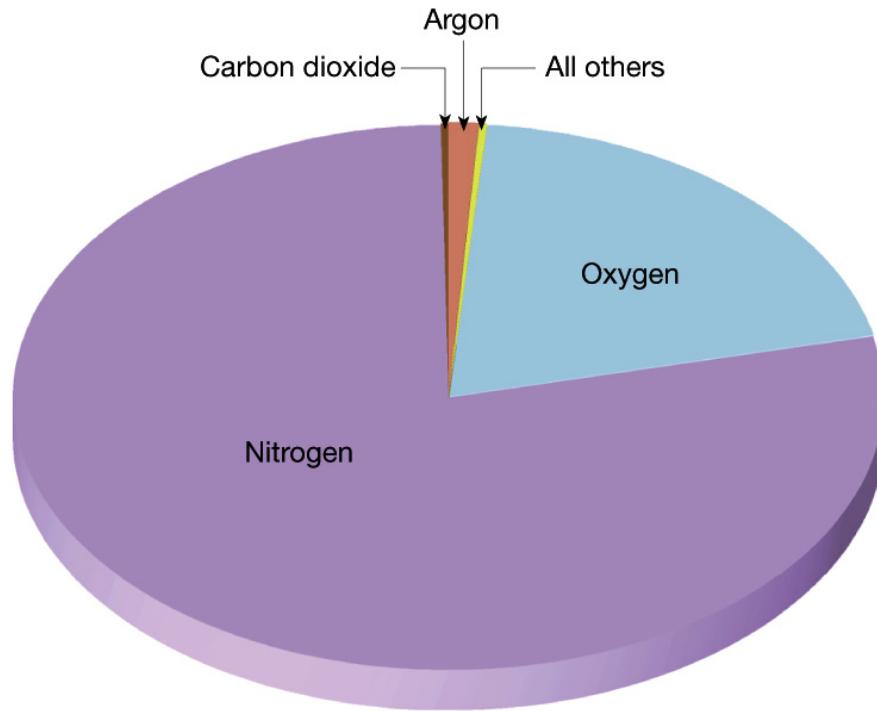
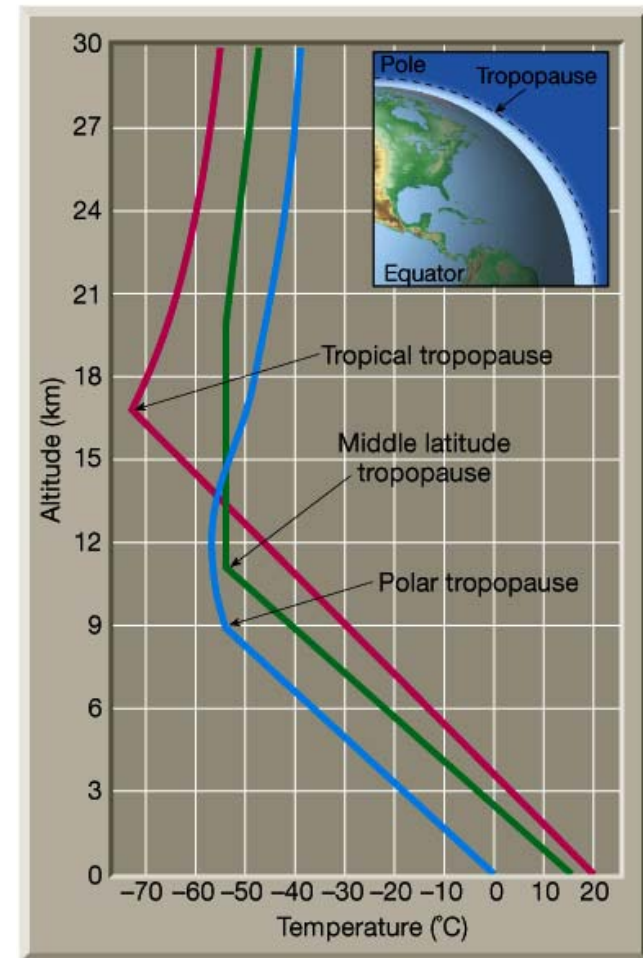
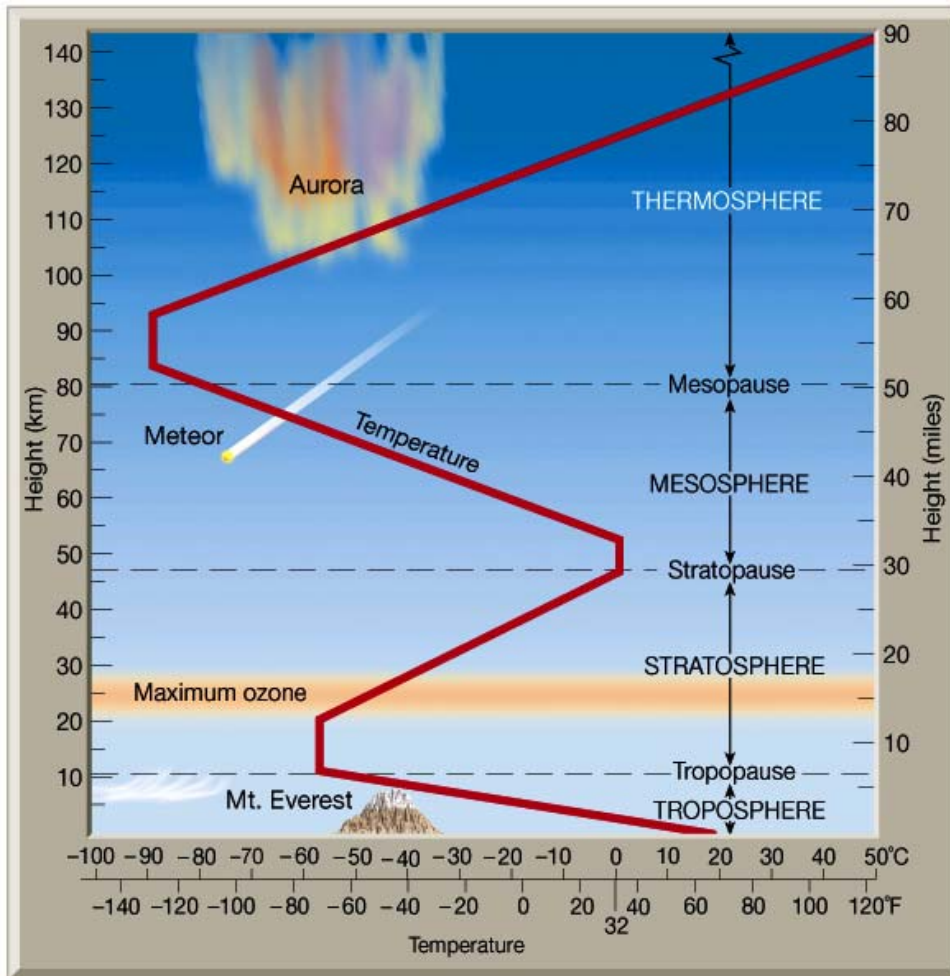


Table 1-2 Principal gases of dry air

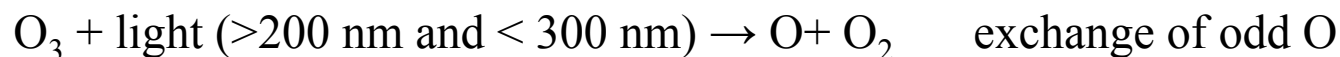
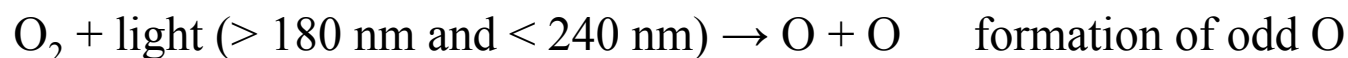
Constituent	Percent by Volume	Concentration in Parts Per Million (PPM)
Nitrogen (N ₂)	78.084	780,840.0
Oxygen (O ₂)	20.946	209,460.0
Argon (Ar)	0.934	9,340.0
Carbon dioxide (CO ₂)	0.036	360.0
Neon (Ne)	0.00182	18.2
Helium (He)	0.000524	5.24
Methane (CH ₄)	0.00015	1.5
Krypton (Kr)	0.000114	1.14
Hydrogen (H ₂)	0.00005	0.5

The Atmosphere – Vertical Structure



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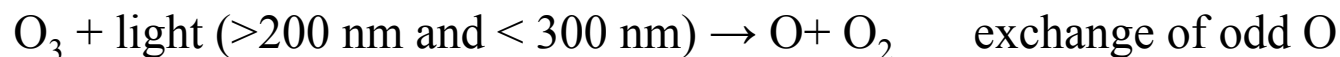
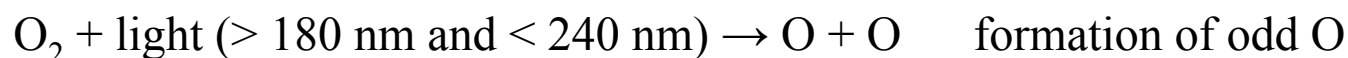
- The temperature in the troposphere falls by between 3 and 10 K/km⁻¹. This is as a result of convection, as rising air rises it expands and cools, condensation of water and freezing of ice also free energy for lift
- The troposphere is turbulently mixed – a rapid process
- At the tropopause there is insufficient energy in the rising air for further lift, heat is transferred by radiation – in the stratosphere the temperature does not fall and the air is stable and laminar. Mixing is achieved by slow diffusion and is much slower
- Temperature rise occurs through the stratosphere – a result of photolysis of O₂ and O₃ by UV radiation – the Chapman cycle



- Above the ozone layer, the temperature falls and is also stable
- In the thermosphere the temperature increases but this is because the atmosphere absorbs intense solar radiation and cannot exchange it with other molecules.

The Atmosphere – Vertical Structure

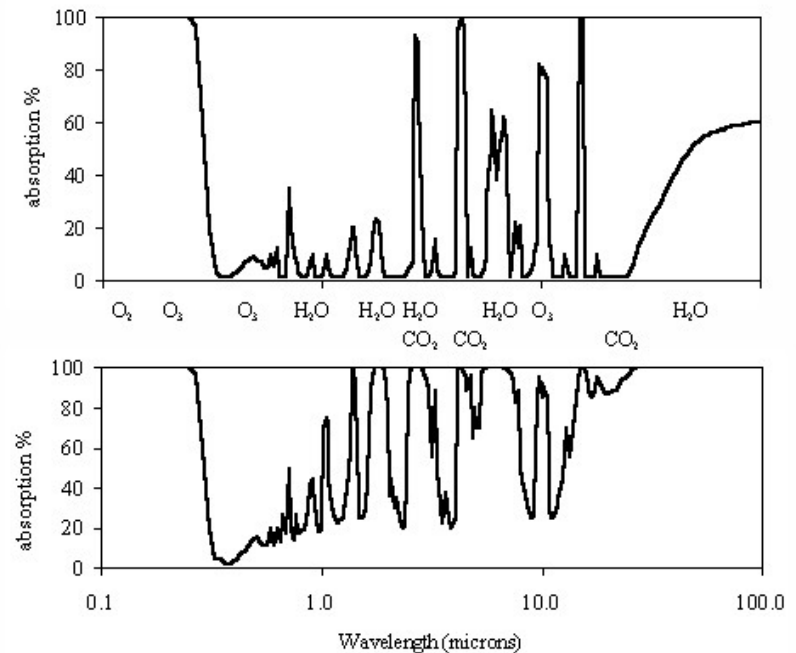
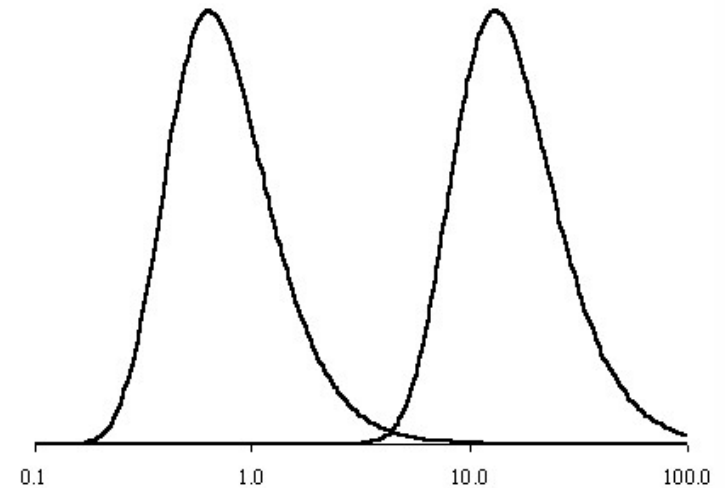
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The Atmosphere – Absorption of IR radiation

- Solar radiation is mainly at visible wavelengths and the atmosphere is essentially transparent
- Most of the energy is absorbed at the surface but a significant fraction is reflected to space by the surface and clouds – the *albedo* or reflectivity
- The fraction absorbed heats the surface. Warm bodies like fires and us radiate at infra red wavelengths but the atmosphere is highly absorbing at these wavelengths
- The main absorbers are H₂O, CO₂, CH₄, N₂O, O₃
- These gases absorb radiation, become excited and then re-radiate it once more but this time in every direction, some of which is down again, warming the surface
- The absorption of IR gives rise to heating of the lower atmosphere



Heat budget of the Earth

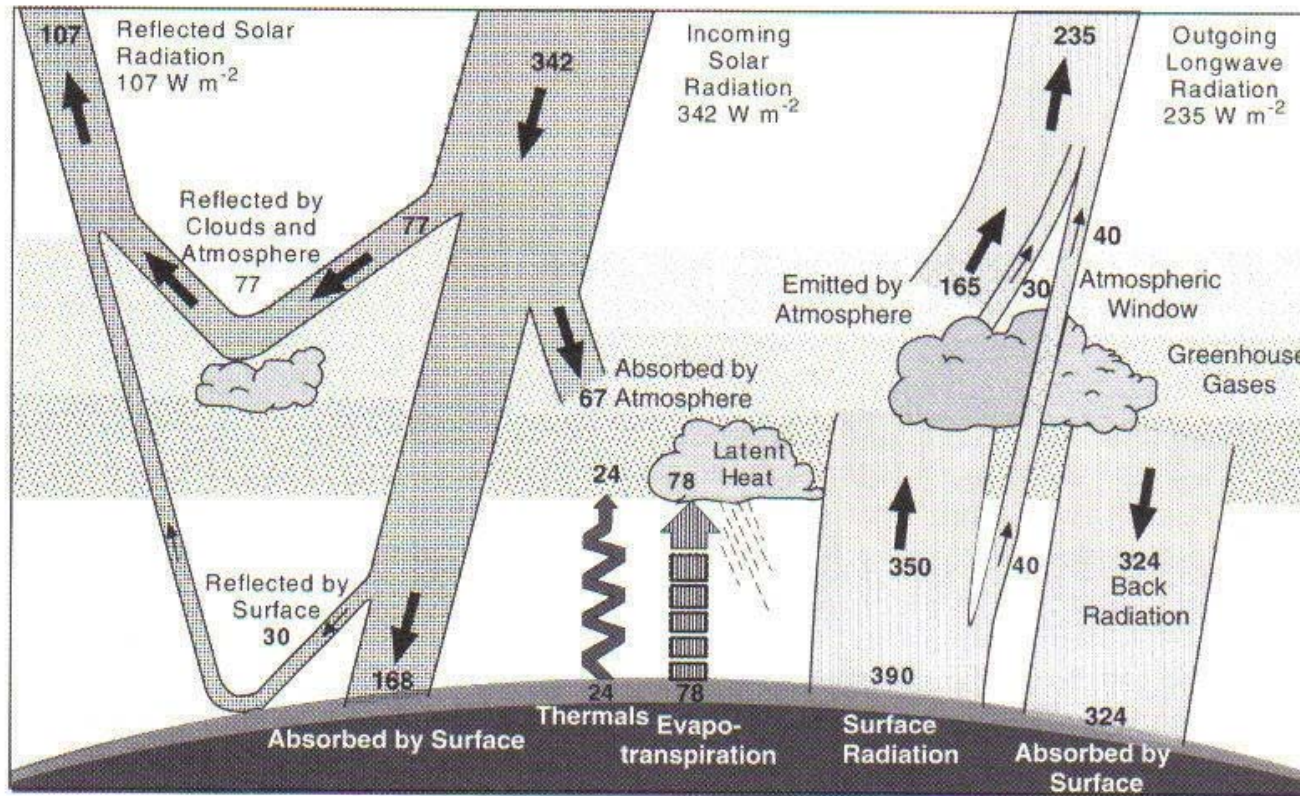


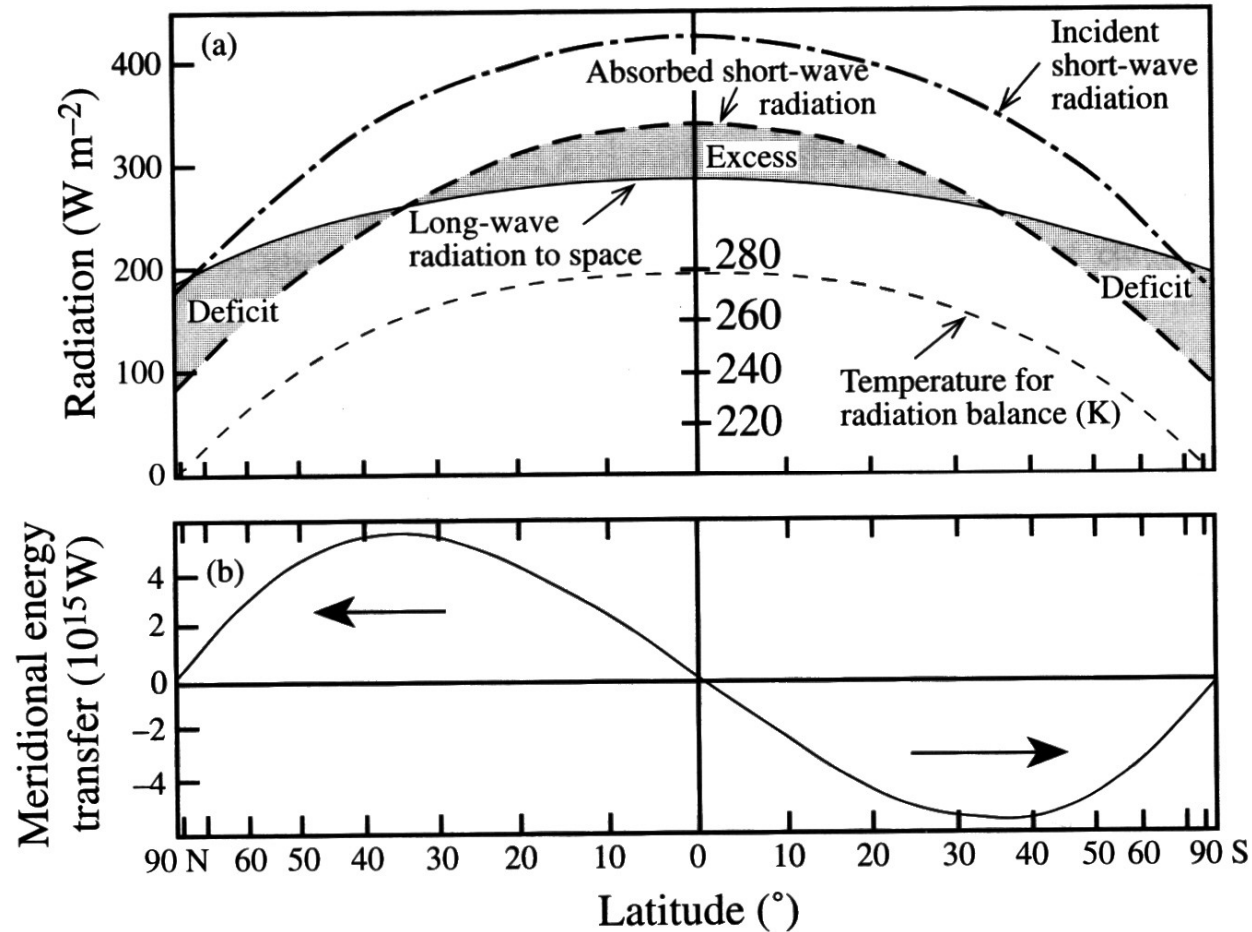
Figure 1. The earth's radiation balance. The net incoming solar radiation of 342 W m^{-2} is partially reflected by clouds and the atmosphere or at the surface, but 49% is absorbed by the surface. Some of that heat is returned to the atmosphere as sensible heating and most as evapotranspiration that is realized as latent heat in precipitation. The rest is radiated as thermal infrared radiation and most of that is absorbed by the atmosphere and re-emitted both upwards and downwards, producing a greenhouse effect, as the radiation lost to space comes from cloud tops and parts of the atmosphere much colder than the surface. From Kiehl and Trenberth (1997).

The Global Energy Budget

- Comments on previous overhead:
- 31% of the incoming solar radiation is reflected or scattered back to space – the ALBEDO
- 235 Wm^{-2} warms the Earth and atmosphere, 168 Wm^{-2} of which warms the surface.
- 235 Wm^{-2} corresponds to a black body temperature of -19 C , thermal emission at 10 um .
- This is colder than Earth's surface and is reached at around 5 km .
- Thus the peak terrestrial emission is in the atmospheric window in the IR.
- This fraction is transmitted directly to space, but majority is intercepted and interacts.
- Clouds can absorb and emit thermal radiation but are also reflectors of solar radiation and so act to cool the surface. **Clouds are important and will be covered in the water cycle**
- Strong cancellation between these effects the global net effect appears to be a slight cooling at the surface.
- 235 Wm^{-2} equates to 120 PW ($120 \times 10^{15} \text{ W}$) globally. A 1 % in this value (around 2.5 Wm^{-2}) will dominate over other present man-made energy inputs.

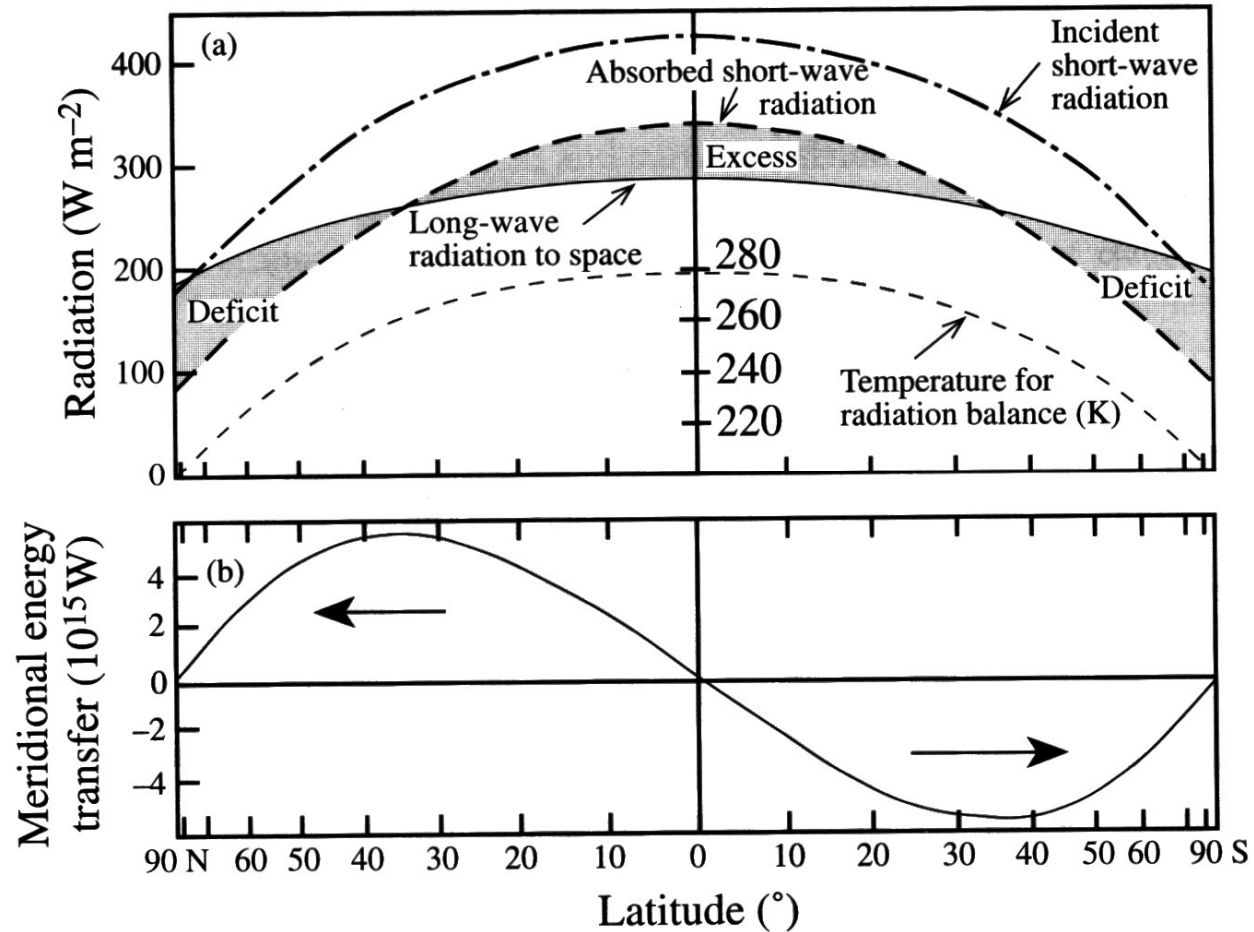
Variations in the Heat Budget Across the Globe

The calculated short and longwave energy budgets of the Earth-atmosphere system averaged over time as a function of latitude.



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Heat Transfer in the Ocean and Atmosphere

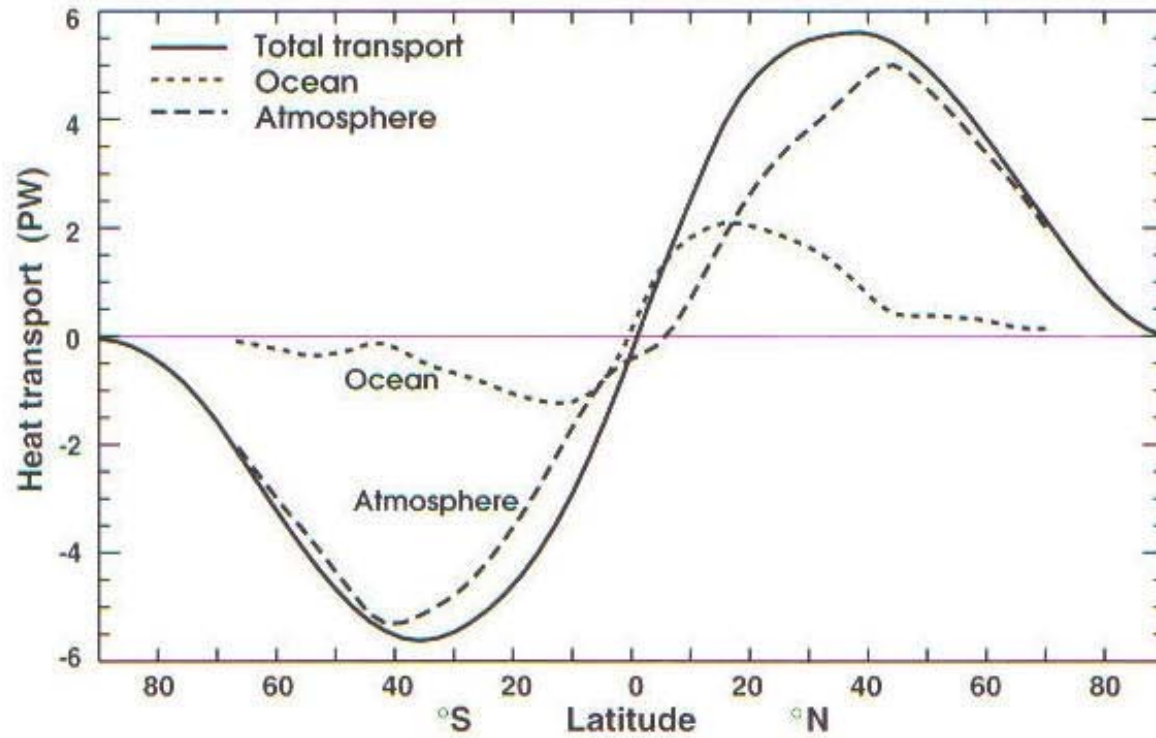


Figure 6. Poleward heat transports by the atmosphere (large-dashed line), ocean (small-dashed line) and the two combined (solid line) in petawatts (from Trenberth and Caron 2001).

Heat Transfer in the Ocean and Atmosphere

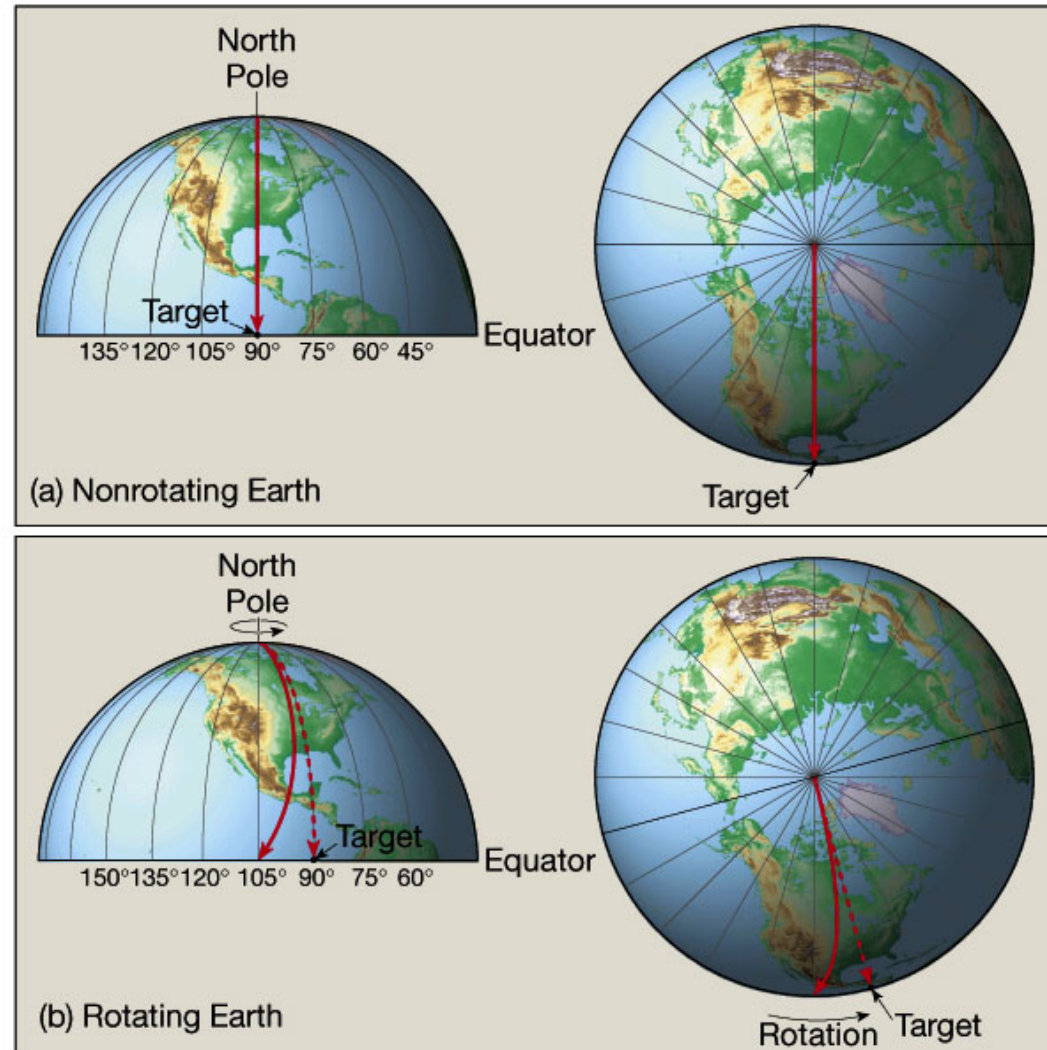
- Much of the heat transport polewards takes place by atmospheric circulation (see next lecture).
- However, a significant fraction, especially near the equator, where as we shall see the Hadley Cell only weakly transfers heat polewards, takes place through the surface waters of the ocean.
- The ocean surface heat transport is largely by wind blowing across the sea surface driving surface water currents
- The oceans are capable of storing heat for a wide range of time scales and subsequently transporting it to other locations.
- The thermohaline circulation (see Oceans) can store heat for several 100s of years.
- The strongest thermohaline circulation is in the Atlantic Ocean, whereas the Pacific Ocean is much fresher and features shallower circulations.
- This is largely due to differences in salinity. The atmosphere transports water vapour across the isthmus in central America from the Atlantic to the Pacific, leaving the former saltier than the latter.

The Circulation of the Atmosphere:

- Both symmetric and wavelike flows are observed in the atmosphere
- Near Equator the effects of rotation are small at higher latitudes wavelike motions with sloping convection are found.
- The Hadley Circulation:** The symmetrical flow regime. Air rises due heating near the Equator.
- The Coriolis Force turns the poleward moving air eastwards and increases with latitude. The CF also turns the low level returning low level flow westwards. These are the so called **Easterly Trade Winds**.
- Were the Earth to not be rotating the atmosphere would have one cell. However, the CF directs the poleward air westward and so prevents the Hadley circulation from transferring heat to the pole directly.
- NOTE:** Symmetric flow at all latitudes would imply an easterly surface flow at all latitudes. This would decelerate the rotation of the Earth due to frictional drag. Essentially altering the length of the day as the total angular momentum of the Earth-Atmosphere system must remain constant

The Coriolis Force

- A fictional force caused by the relative movement of an air parcel over the moving Earth.

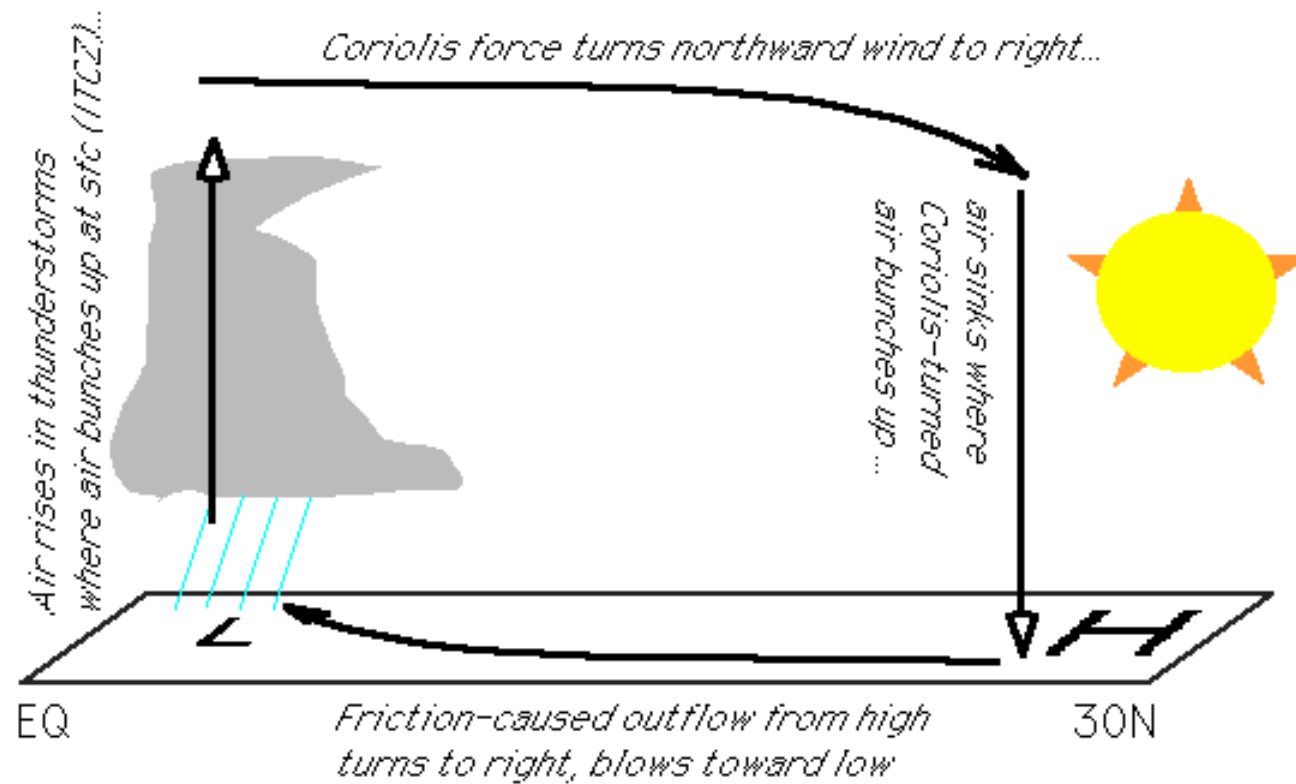


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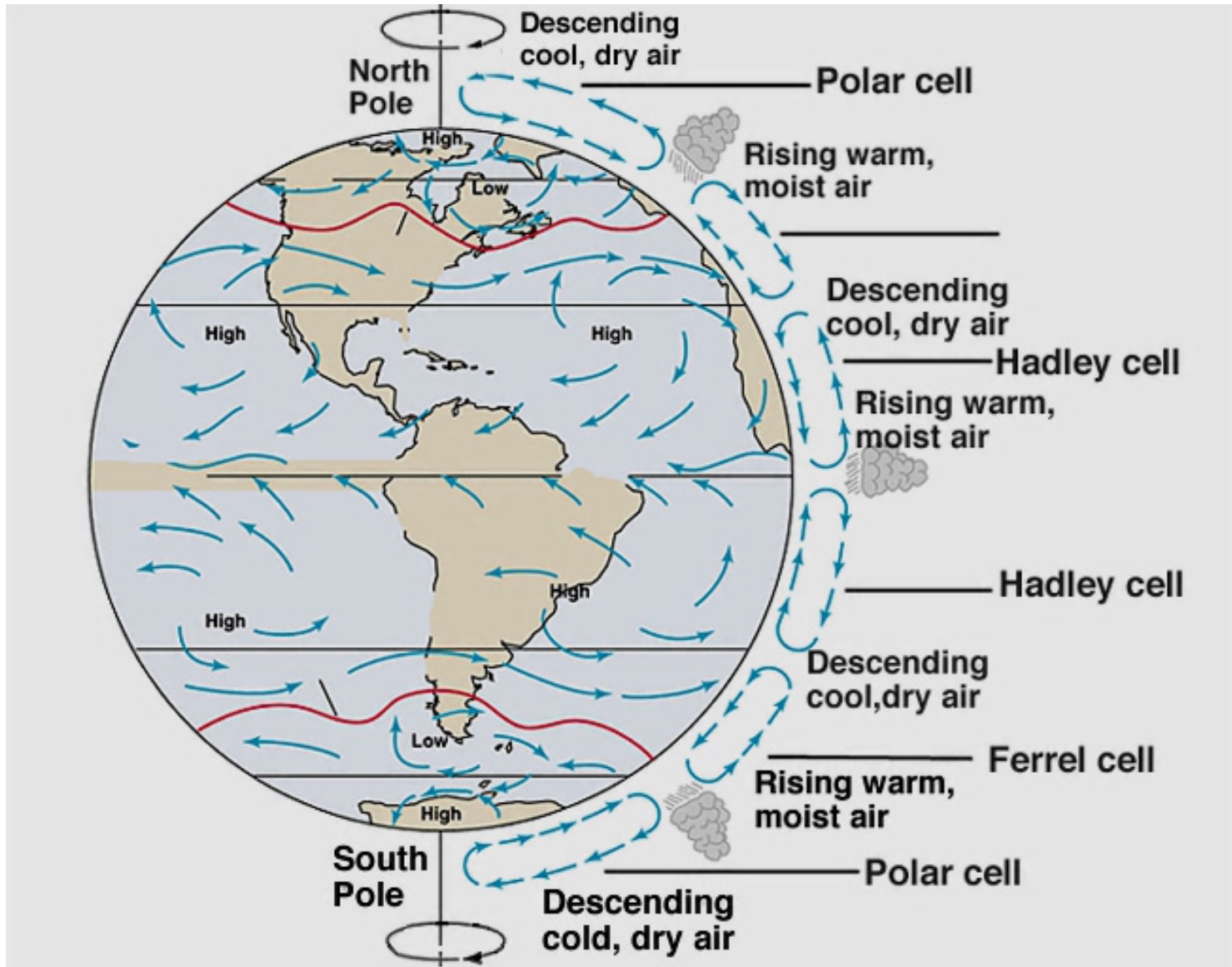
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THE HADLEY CELL

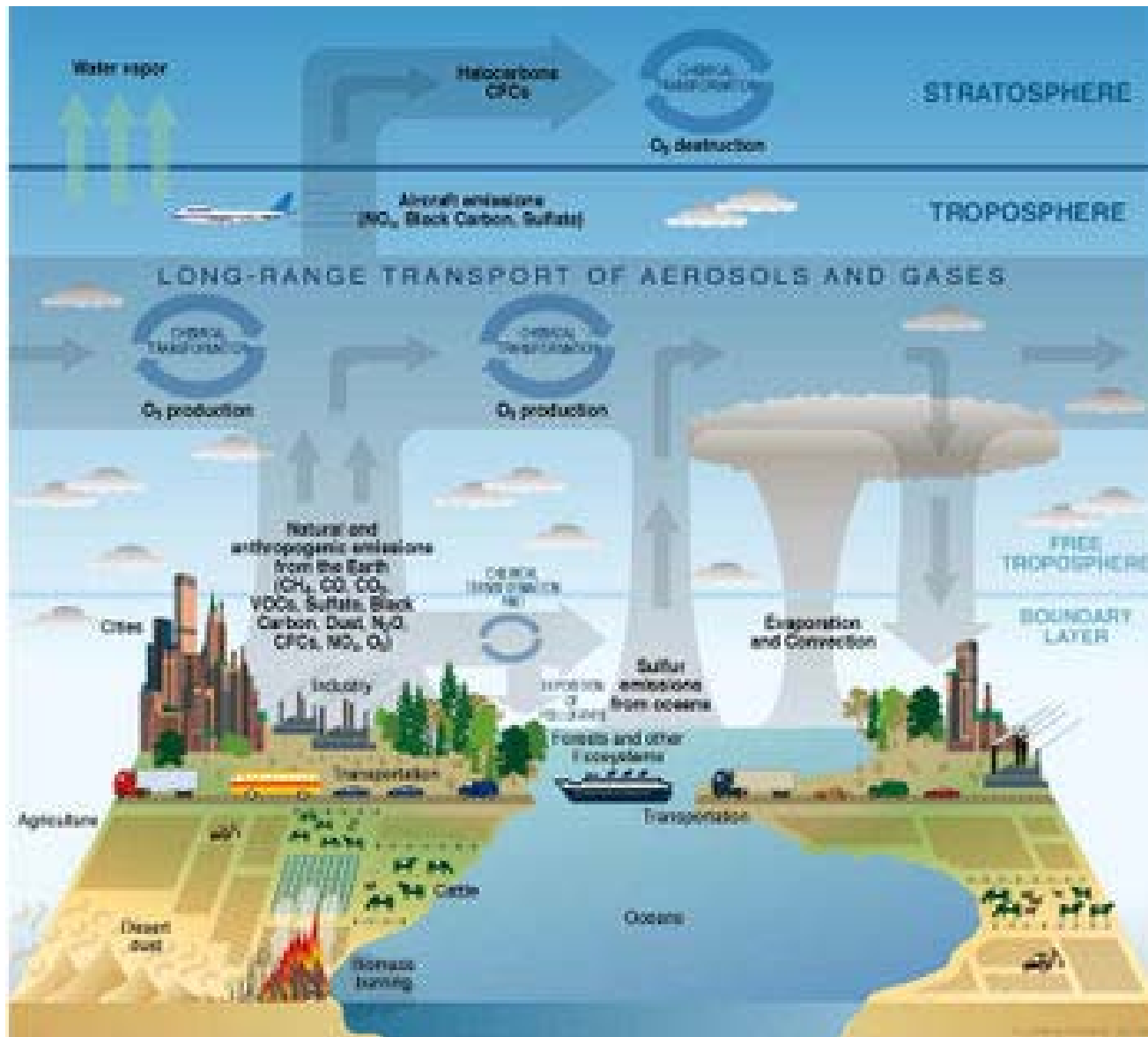
*Warmer stratosphere
forces air to move
horizontally...*



The Circulation of the Atmosphere:



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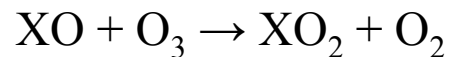
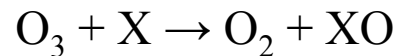


Chemistry in the Atmosphere:

- The chemistry of the atmosphere is driven by minor constituents and is largely oxidising, driven by ozone chemistry.

In the Stratosphere:

The Chapman cycle is perturbed in the following way:



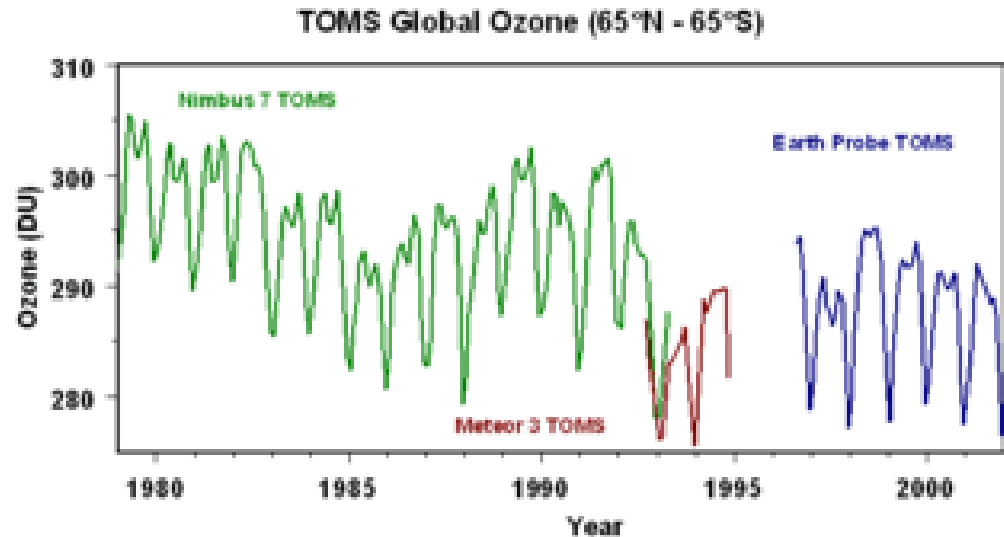
X can be OH, NO, or Cl or Br

This is a catalytic cycle, ozone is destroyed and the reactant is recycled.

OH is made from water vapour, formed from the destruction of methane in the stratosphere

NO comes from N_2O , part of the nitrogen cycle (see lecture 1 for inc in N_2O)

Cl and Br arise from some naturally occurring organic halogens but have also increased substantially from CFCs



Stratospheric Ozone Hole:

Unlike ozone in midlatitudes Antarctic and Arctic O_3 has been shown to catastrophically collapse during the polar springtime.

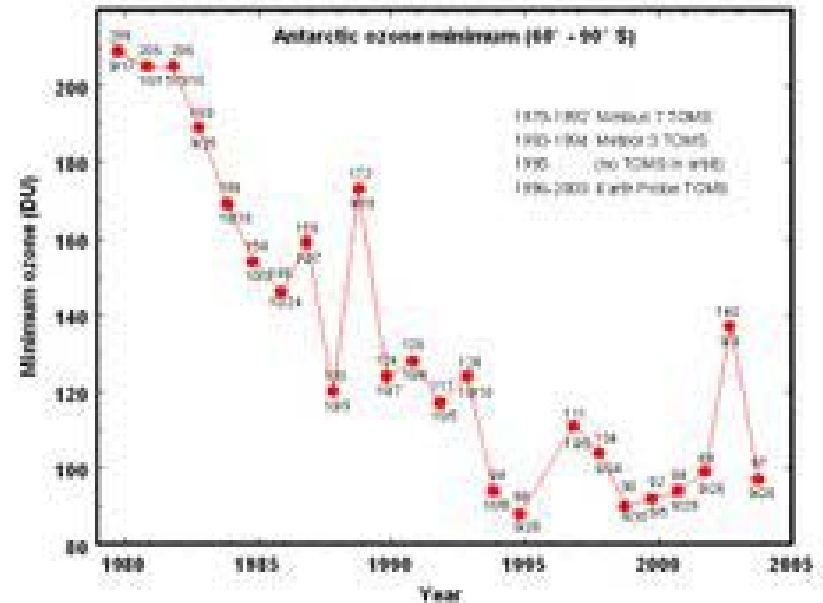
The reason is that in the cold polar winter night polar stratospheric clouds form and act as sites for reactive release of free Cl and Br which had been previously stored in inert reservoirs.

When the sun rises these species can begin to catalytically destroy O_3 .

Unlike at mid-latitudes their release is large and rapid and there are no reservoir species to limit their reaction

Furthermore, a vortex forms over the pole which limits mixing of air to restore the chemical reservoirs

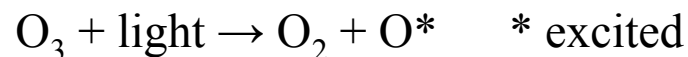
The lack of ozone, also removes the local heat source as ozone absorbs UV and so the situations persists for longer



Tropospheric Oxidation:

Oxidation processes in the troposphere control the lifecycle of many important components in the Earth System.

There is not much UV radiation but what does penetrate can photolyse ozone



Ozone comes from the stratosphere but as we will see, can also be made in situ

The excited oxygen can react with water vapour which is present in much larger quantities in the troposphere than the stratosphere

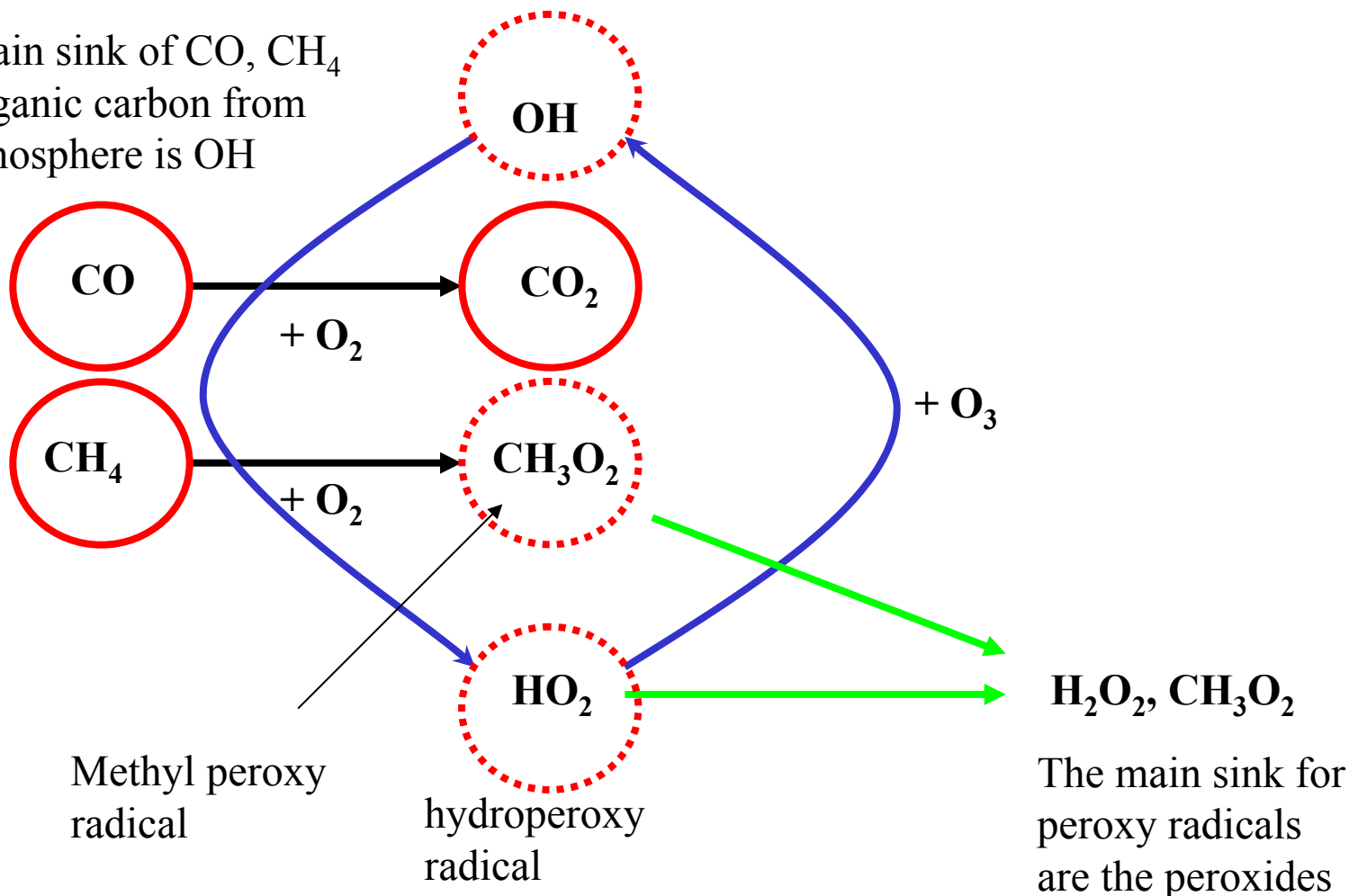


This makes 2 OH, the hydroxyl radical. This is central to much of the oxidation chemistry in the troposphere and is highly reactive.

Tropospheric Oxidation in the Clean Atmosphere:

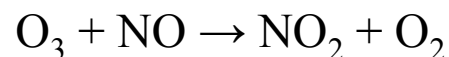
OH reacts with many atmospheric constituents and in the absence of the oxides of nitrogen:

The main sink of CO, CH₄ and organic carbon from the atmosphere is OH

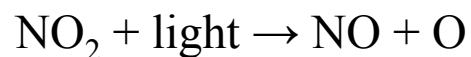


Ozone and nitrogen oxides:

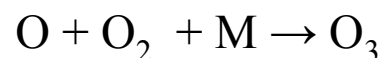
A very important reaction controlling ozone chemistry in the troposphere is its loss via NO:



But NO_2 is photolysed by sunlight to give:



The oxygen atom reacts with the nearest available oxygen to re-form ozone:

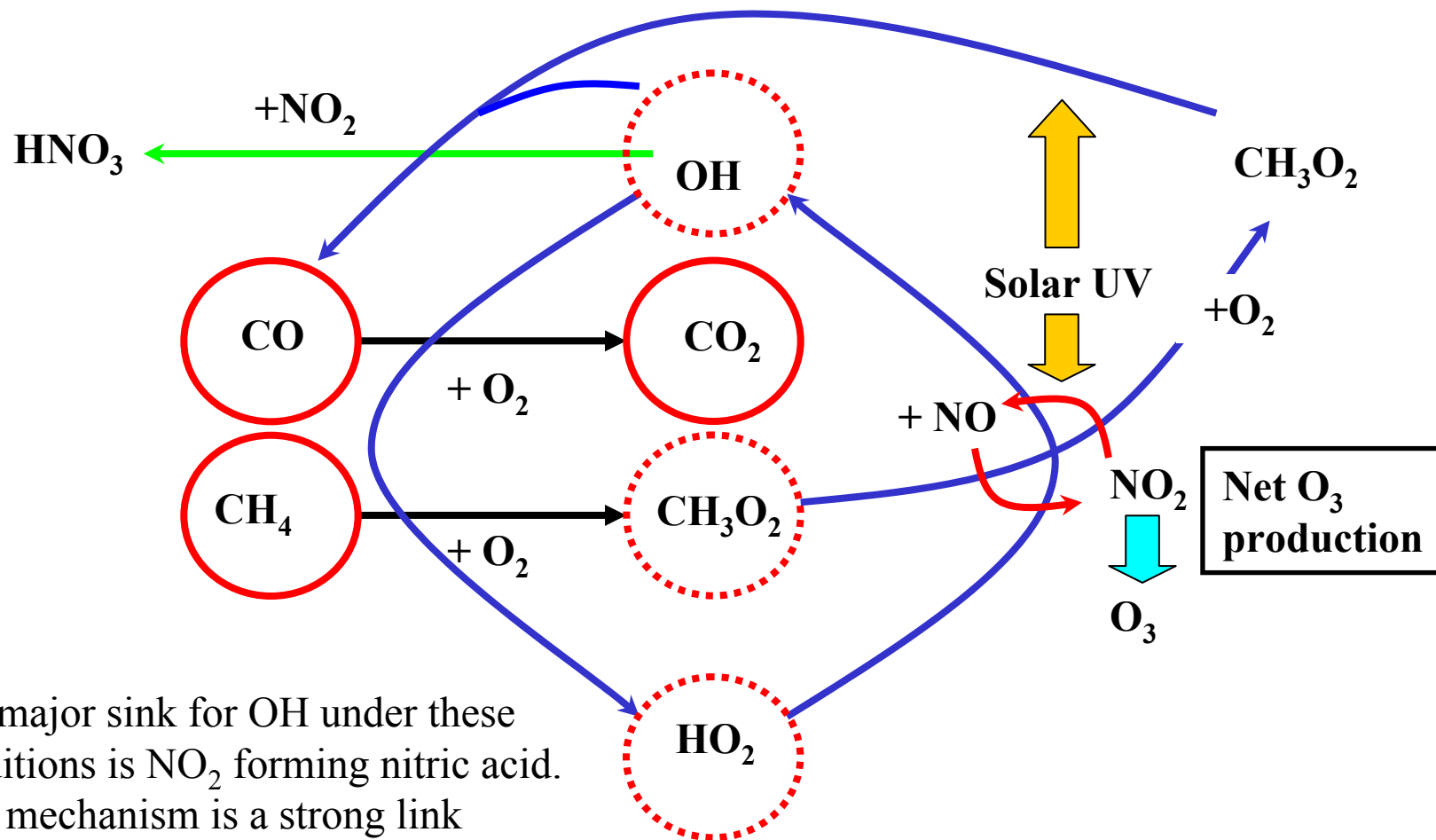


excess energy must be removed by another molecule M

This is a very rapidly reacting system and cycles round with a lifetime less than 1 minute.

Tropospheric Oxidation in the Polluted Atmosphere:

However, in polluted conditions peroxy radicals react far faster with NO and produce ozone. In the process CO and CH₄ are oxidised to CO₂.

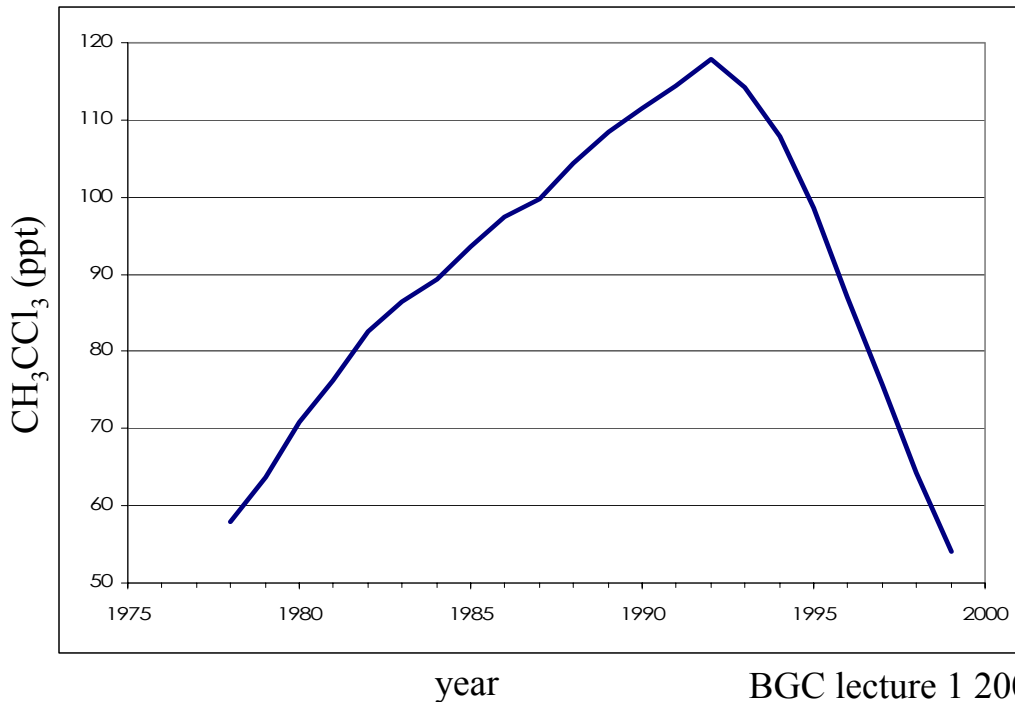


The major sink for OH under these conditions is NO₂ forming nitric acid. This mechanism is a strong link between the C and N cycles in the atmosphere

Problem 3.1

As we have seen OH is important in controlling atmospheric oxidation of N, C, and S. It is highly reactive and only exists at very low concentrations.

Methyl Chloroform has been used to calculate global concentration of OH as it is only lost via this reaction and its emission into the atmosphere has ceased due to the Montreal Protocol. The OH concentration can then be used to predict the lifetime of methane in the atmosphere. The loss rate of CH_3CCl_3 due to OH reaction is given by $k[\text{OH}]$ and k has been shown to be $0.73 \times 10^{-14} \text{ molecules}^{-1} \text{ cm}^3\text{s}^{-1}$. Use the figure below to calculate the lifetime of CH_3CCl_3 and so derive the OH concentration.



Methane is lost via reaction with OH in the same way but is being emitted into the atmosphere in large amounts. If its loss rate k_{CH_4} is known to be $3.6 \times 10^{-16} \text{ molecules}^{-1} \text{ cm}^3\text{s}^{-1}$,

What is the atmospheric lifetime of methane?