## 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.

# Global Cycles

- Your package includes diagrams from:
  - Brasseur
  - Manahan
  - Safe (unpublished)
- Will consider global cycles for:
  - Energy
  - Water (Hydrologic cycle)
  - Carbon
  - Nitrogen
  - Oxygen
  - Phosphorous
  - Sulphur
- All these cycles are coupled:
  - To each other
  - To anthropogenic impacts
  - To climatic impacts

# Energy Cycle

- The two main sources of energy are:
  - The Sun
  - The Earth
- Each of these may be treated as a blackbody radiator:

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

  - This integrates to:

$$\int_0^\infty \rho(\lambda;T)d\lambda = \frac{8\pi^5}{15}\frac{(kT^4)}{(hc)^3} = \eta T^4$$

- Radiation from the sun that reaches the earth is insolation and is expressed as radiative flux in units of W m$^{-2}$ where 1 W = 1 J s$^{-1}$
  - Energy flux intercepted by the earth is 1370 W m$^{-2}$
  - Energy flux captured by the earth is 342 W m$^{-2}$

- The energy cycle is coupled to the hydrologic cycle by the thermal properties of water.
    - Water requires energy to undergo phase transitions.

$$\Delta H_{fus} = 6.008 \text{ kJ mol}^{-1}$$

$$\frac{C_p(l)}{R} = 12.16 - 1.943 \times 10^{-2} T + 3.042 \times 10^{-5} T^2$$

$$\Delta H_{vap} = 40.66 \text{ kJ mol}^{-1}$$

$$C_p(g) = 33.59 \text{ J mol}^{-1} \text{ K}^{-1}$$

- The energy cycle is coupled to the carbon cycle by:
    - Photosynthesis (which is also essential for nitrogen and phosphorous fixation.
    - Burning of fossil fuels.
- Sources of energy are well-defined
    - Sun and earth
- Sinks of energy include:
    - Photosynthesis
    - Thermal absorption
    - Chemical

  - Mechanical
  - Reflection
  - Scattering
- The atmosphere has a significant role in the energy cycle because it is where absorption and scattering occur.

## Water Cycle
## (or Hydrologic cycle)

- In the energy cycle we have already discussed the thermodynamic properties of water.
  - Because of these thermodynamic properties, water acts as a thermal buffer, especially at temperatures near the freezing point.
- Examination of a phase diagram for water indicates the temperature and pressure for coexistence of phases.
  - It is from this diagram that relative humidity, dew point and frost point may be determined.

  - For a given $T$, the relative humidity is:

$$\frac{P_{actual}(H_2O)}{P_{equilibirum}(H_2O)}$$

  - The dew point or the frost point is the temperature at which the ambient $P(H_2O)$ becomes the $P_{equilibirum}(H_2O)$
  - As a saturated air mass cools it must lose water by precipitation.
- Reservoirs and fluxes for the hydrologic cycle include:

| Reservoir | $10^6$ km$^{+3}$ | Fluxes |
|---|---|---|
| Ground water | 8 | precipitation |
| Surface water | 0.1 (Lakes)<br>0.1 (Salt lakes)<br>0.001 (Rivers) | evaporation |
| Snow & Ice | | transpiration. |
| Clouds & Vapour | 0.013 | cloud momentum |

| | | |
|---|---|---|
| Oceans | 1350 | run off |
| Glaciers & icecaps | 29 | movement of moist air |
| Soil Moisture | 0.07 | |

- The hydrosphere is defined as where water is found.
- The lithosphere is defined as the portion of the geosphere that is accessible to water.
- Water is a significant factor in human history.
    - Denial of access to water is a tool of war, siege,and oppression.
    - Movement of nomadic peoples often correlated with the availability of water.
    - Presence of water is a significant factor in human settlement patterns.
    - Increasing important issue in international trade.
- Water is an economic factor for:
    - Transport

  - Coolant
  - Raw Material
- Anthropogenic impacts on water include:
  - Contamination
  - Warming
  - Salinization

## Impact of Water Usage

- For the United States of America
  - Precipitation is $1.48 \times 10^{13}$ L day$^{-1}$
  - Evaporation is $1.02 \times 10^{13}$ L day$^{-1}$
  - which leaves $4.6 \times 10^{12}$ L day$^{-1}$
- Daily usage in the USA has evolved with time:

| Usage | L day$^{-1}$ | L day$^{-1}$ capita$^{-1}$ (Domestic Use) |
|---|---|---|
| 2002 | | 1200 |
| 1990 | $1.6 \times 10^{12}$ | 600 |
| 1900 | $1.7 \times 10^{11}$ | 40 |

- This usage breaks down as:
  - 46 % agricultural
  - 46% industrial
  - 8% municipal
- The impact of this usage has caused:
  - The depletion of the Ogallala aquifer
  - Salinization of irrigated soils
  - Desertification
  - Deterioration of water quality
- Precipitation is irregularly distributed.
  - Linked to terrain and energy transfer.
- The likelihood of precipitation is linked to the thermal lapse rate.

  $$\text{Lapse Rate} = \frac{\Delta T}{\Delta h}$$

  where $h$ is altitude.
  - Warm air rises and cools.
  - For dry air undergoing an adiabatic expansion, the lapse rate is $10^\circ$ C/km.
  - For moist air undergoing an adiabatic expansion, the lapse rate is $6^\circ$ C/km.

  - The difference is due to the heat capacity of water.
  - The difference in lapse rates can contribute to the forming of thermal inversion as wet air moves over dry air.
- Inversions occur when warm air rest on top of cooler air.
  - Traps vertical circulation patterns.
  - Decreases mixing volumes for ground level emissions.
- Inversions can also be caused by the difference in the heat capacity of air and ground.
  - These are radiation inversions.
- Another type of inversion is a subsidence inversion when high air drops, compresses, and warms.
- Marine inversions are due to the difference in heat capacity of the ocean and land.
  - Land warms more rapidly than ocean.
  - Cool air from the ocean moves under the warmer air originally over the land mass.

# The Carbon Cycle

- Consider the oxidation states of carbon.
  - The range of oxidation states is determined by the ground state electronic configuration of the C atom, $1s^2 2s^2 2p^2$.
  - Carbon must either gain four electrons or lose four electrons to have a closed shell configuration.
  - Range of oxidation states is therefore +4 to -4.
- Some examples of oxidation state of carbon:
  - $CO_2$ is in oxidation state +4.
  - CO is in oxidation state +2.
  - HCO is in oxidation state +1.
  - $H_2CO$, C(graphite), C(diamond) are in oxidation state 0.
  - $C_2H_2$ is in oxidation state -1.
  - $C_2H_4$ is oxidation state -2.
  - $CH_3$ is in oxidation state -3.
  - $CH_4$ is in oxidation state -4.

- Carbon fixation puts carbon into biologically available forms.
  - Photosynthesis uses 8 photons to drive the reaction:

    $$8CO_2 \ + \ 6H_2O \rightarrow \ C_6H_{12}O_6 \ + \ 6O_2$$

    which requires 2801.3 kJ per mole of glucose (467 kJ per mole of carbon).
- Photosynthesis is coupled to the energy cycle by the phosphorous cycle.
- The $\mathrm{CO_2}$ cycle is coupled to the hydrologic and energy cycle.
  - Before 1800, the level of atmospheric $\mathrm{CO_2}$ was about 280 ppm.
  - The 1800's saw the beginning of the industrial revolution and increased use of fossil fuel.
  - In 1994, atmospheric $\mathrm{CO_2}$ was observed to be 358 ppm.
- The global budget of $\mathrm{CO_2}$ has not been fully determined.

$$\mathrm{CO_2(atmospheric) + H_2O \rightarrow solubilized\ speciated\ C(IV)}$$

$$\mathrm{CO_2(g)} \rightleftharpoons \mathrm{CO_2(aq)}$$

$$\mathrm{CO_2(aq)} + \mathrm{H_2O} \rightleftharpoons \mathrm{H_2CO_3(aq)}$$

$$\mathrm{H_2CO_3(aq)} \rightleftharpoons \mathrm{HCO_3^-(aq)} + \mathrm{H^+(aq)}$$

$$\mathrm{HCO_3^-} \rightleftharpoons \mathrm{CO_3^{2-}} + \mathrm{H^+}$$

  - $CO_3^{2-}$ precipitates and is incorporated into shells of aquatic animals such as coral.
- Organic carbon comprises oxidation states 0 to -4.
  - Living organic carbon may be represented as $\{CH_2O\}$
  - Fossil organic carbon is reduced and may be represented as $(CH_2)_nH_2$ and is produced by biogeochemical processes.
- Reservoirs of organic carbon include:
  - Oceans with $5.8 \times 10^{14}$ moles of carbon in biomass, $5 \times 10^{15}$ moles C as suspended $\{CH_2O\}$ particles, $5.8 \times 10^{16}$ moles C as dissolved organic carbon.
  - By comparison, oceans contain $3.2 \times 10^{18}$ moles of C as C(IV).
  - On land, $4 \times 10^{16}$ moles C is found in living biomass with a residence time of 16 years.

  - On land, living and dead biomass combined account for $1 \times 10^{17}$ moles of C with a residence time of 40 years.

- The atmosphere provides a reservoir for a number of carbon containing species.

| ppm | Species | mol C | $\tau$ |
|---|---|---|---|
| 1.7 | $CH_4$ | $5.2 \times 10^{14}$ | 3.6 yrs |
| 0.1 | CO | $1.9 \times 10^{13}$ | 0.1 yr |
| 360 | $CO_2$ | $5 \times 10^{16}$ | 4 yr |

  - In addition the atmosphere contains smog (smoky fog) and carbon containing particulates (such as soot) which account for 2.9 $\times$ $10^{14}$ mol of C.
  - The atmospheric reservoirs are coupled to the biomass cycle.

- Recent sediments under the ocean are also significant reservoirs for carbon.
  - $50.8 \times 10^{20}$ mol of C as $CO_3^{2-}$
  - $10.4 \times 10^{20}$ mol of C as $\{CH_2O\}$

  - Both of these have a lifetime 342 years.
- Sources for recent sediments are in the form of:
  - $6.1 \times 10^{12}$ mol C yr$^{-1}$ as $\{CH_2O\}$
  - $11.8 \times 10^{12}$ mol C yr$^{-1}$ as $CO_3^{2-}$
- Sinks for recent sediments consist of transfer to old sediments (burial):
  - $2.5 \times 10^{12}$ mol C yr$^{-1}$ as $\{CH_2O\}$
  - $15.4 \times 10^{12}$ mol C yr$^{-1}$ as $CO_3^{2-}$ in the form of $CaCO_3$ and $MgCO_3$
  - These sinks are balanced by transfer from old to recent sediments.
- Anthropogenic activity extracts $3.88 \times 10^{12}$ mol C yr$^{-1}$ as fossil fuel.
  - This is a net loss.

## Nitrogen Cycle

- Consider the oxidation states of nitrogen.
  - The range of oxidation states is determined by the ground state electronic configuration of the N atom, $1s^2 2s^2 2p^3$.

  - Nitrogen must either gain three electrons or lose five electrons to have a closed shell configuration.
  - Range of oxidation states is therefore +5 to -3.
- Some examples of oxidation state of nitrogen:
  - $NO_3^-$ and $N_2O_5$ are in oxidation state +5.
  - $NO_2$ is in oxidation state +4.
  - $N_2$ is in oxidation state 0.
  - $NH_3$ and $NH_4^+$ are in oxidation state -3.
- Nitrogen is essential to amino acids.
- The atmosphere is the main reservoir of nitrogen:
  - Contains $3.9 \times 10^{18}$ N
  - 78% of the atmosphere
  - $\tau \sim 10^7$ years
- In order to be biologically available, N must be fixed.
  - $2 \times 10^{11}$ kg N fixed a year.
  - Anthropogenic fixation accounts for $5 \times 10^{10}$ kg N $y^{-1}$.

- Biological fixation of nitrogen is coupled to the carbon cycle.

$$3\ \{CH_2O\} + 2\ N_2 + 3\ H_2O + 4\ H^+ \rightarrow 3\ CO_2 + 4\ NH_4^+$$

  - If the pH is sufficiently high, $NH_3$ is released.

- Fixation of nitrogen may be considered from a redox perspective:

$$N_2 + 8H^+ + 6e^- \rightarrow 2NH_4^+$$
$$\{CH_2O\} + H_2O \rightarrow CO_2 + 4e^-$$

- Biological fixation occurs with
  - Aquatic organism such as Azobacter, Clostridium, and Cyanobacter (formerly known as bluegreen algae).
  - Terrestial organism Rhizobium in symbiosis with legumes (peas, beans, peanuts). The Rhizobium infect root hairs to draw on the legumes organic carbon from photosynthesis.
- Not enough nitrogen is fixed annually to satisfy the current biomass requirements.
- Anthropogenic fixation occurs by the Haber Process:

$$N_2 + 3H_2 \rightarrow 2NH_3$$

  - The process is catalyzed by Fe, $K_2O$, and $Al_2O_3$
  - The process is endothermic with $\Delta H = 92.6$ kJ mol$^{-1}$ $N_2$.
  - Used to form $NH_4NO_3$ for fertilizer and explosives.
- Organically bound N occurs in humus (N/C $\approx$ 1/10) and can be released on a time scale similar to that of plant growth.
- Nitrification is the process of transforming N(-3) to N(+5):
  - From a redox perspective:

$$\mathrm{NH_4^+ + 3\ H_2O \rightarrow NO_3^- + 10\ H^+ + 8\ e^-}$$

$$\mathrm{4\ H^+ + 4\ e^- + O_2 \rightarrow 2\ H_2O}$$

$$\mathrm{NH_4^+ + 2\ O_2 \rightarrow NO_3^- + H_2O + 2\ H^+}$$

  - Nitrification is a thermodynamically favoured process with $K = 10^{60.72} = 5.25 \times 10^{60}$.
- $NO_3^-$ may be absorbed by plants.
- Nitrification can occurs naturally as a two step process mediated by bacteria:

  - $NH_4^+ \rightarrow NO_2^-$ is mediated by nitrosomonas.
  - $NO_2^- \rightarrow NO_3^-$ is mediated by nitrobacter.
  - Both are obligate aerobes that require $O_2$ for the oxidation process.
  - This is why aeration of soil is important.
- $NO_3^-$ may act as an oxygen source for anaerobes.
  - Do not want nitrification to occur during sewage treatment because of subsequent denitrification.
- Thunderstorms may contribute to the production of $NO_3^-$.

$$N_2 + O_2 \rightarrow 2NO$$
$$NO \rightarrow \cdots \rightarrow HNO_3$$

  - $HNO_3$ is scavenged efficiently by cloud droplets.
- Decay of biomass leads to the mineralization of nitrogen in the form of $NO_2^-$ and $NO_3^-$.
- Denitrification is the removal of nitrogen from the biologically available forms.
  - Returns $N_2$ to the atmosphere.
  - Involves the reduction of $NO_3^-$ and the oxidation of $NH_3$.

- Reduction of $NO_3^-$ produces $N_2O$ and NO, both of which are greenhouse gases.
- If reduction of $NO_3^-$ occurs during sewage treatment, it is undesirable.
- Denitrification can also occur during sewage treatment:

$$4\ NO_3^- + 24\ H^+ + 20\ e^- \rightarrow 2\ N_2 + 12\ H_2O$$

$$5\ \{CH_2O\} + 5\ H_2O \rightarrow 5\ CO_2 + 20\ H^+ + 20\ e^-$$

$$4\ NO_3^- + 5\ \{CH_2O\} + 4\ H^+ \rightarrow 2\ N_2 + 5\ CO_2 + 2\ H_2O$$

  - $N_2$ and $CO_2$ bubbles are formed and prevent settling.

## Phosphorous Cycle

- Consider the oxidation states of phosphorous.
  - The range of oxidation states is determined by the ground state electronic configuration of the P atom, $1s^2 2s^2 2p^6 3s^2 3p^3$.
  - Phosphorous must either gain three electrons or lose five electrons to have a closed shell configuration.
  - $3d$ orbitals available for contribution expanded octet configurations.

  - Range of oxidation states is therefore +5 to -3.

- Some examples of oxidation state of phosphorous:
  - $PH_3$ is in oxidation state +3
  - $PO_4^{3-}$, $HPO_4^{2-}$, $H_2PO_4^-$, $H_3PO_4$ and associated polyphosphates are in oxidation state +5.

- In many cases, P is the limiting element in biological uptake.
  - C:N:P are taken up in the ratio 100:15:1
  - P is essential to ADP and ATP in organisms.

- The primary reservoir is the geosphere as various forms of phosphate.
  - There is no gas phase reservoir for P.
  - The solubilty of phosphates is strongly pH dependent.

- Phosphates in the geosphere include insoluble mineral forms of phosphate:

  - Hydroxyapatite is very insoluble ($K_{sp} = 10^{-59}$ $M^9$)

$$Ca_5(PO_4)_3OH \rightleftharpoons 5\ Ca^{2+} + 3\ PO_4^{-3} + OH^-$$

  - Hydroxyapatite is also found in tooth enamel.

- Occluded phosphorous is not biologically available.
  - Soil contains $Fe_2O_3$ and $Al_2O_3$ and aluminosilicates.
  - The associated hydrates form an amorphous matrix, with orthophosphate (monophosphate) contained within the matrix.
- Non-occluded phosphorous is primarily in the form of orthophosphate bound to surface silicate ($SiO_2$) or $CaCO_3$.
  - Depending on pH, this is more soluble than occluded phosphorous
- Anthropogenic environmental impact of phosphorous compounds is of most concern in aquatic reservoirs.
  - Soluble forms of phosphate include orthophosphate, linear polyphosphate

($P_3O_{10}^{5-}$) and cyclic polyphosphates ($P_3O_9^{3-}$)

- Solubility of phosphates are closely connected to their speciation.
    - Consider rock phosphate, $Ca_3(PO_4)_2$, which has a $K_{sp} = 10^{-24}$ M$^5$

      $$Ca_3(PO_4)_2 \rightleftharpoons 3\ Ca^{2+} + 2\ PO_4^{2-}$$

    - This equilibrates with $HPO_4^{2-}$ and $H_2PO_4^-$ in according with pH, the above $K_{sp}$ and $K_{a1}$, $K_{a2}$, and $K_{a3}$.

$$H_3PO_4 \rightleftharpoons H_2PO_4^- + H^+;\ K_{a1} = 7.5 \times 10^{-3}\ \mathrm{M}$$

$$H_2PO_4^- \rightleftharpoons HPO_4^{2-} + H^+;\ K_{a2} = 6.2 \times 10^{-8}\ \mathrm{M}$$

$$HPO_4^- \rightleftharpoons PO_4^{3-} + H^+;\ K_{a3} = 4.8 \times 10^{-13}\ \mathrm{M}$$

    - Solubility of $CaHPO_4$ and $Ca(H_2PO_4)_2$ can be calculated from the above reactions.
    - It is the protonated forms that are effective for biological uptake.
    - Phosphate for fertilizer is prepared by mixing sulphuric acid with rock phosphate.
- Anthropogenic impact on P levels is due to:
    - Phosphate fertilizers

  - sewage
  - detergents

- Phosphate in detergents was primarily in the form of sodium tripolyphosphate or STP, $Na_3H_2P_3O_{10}$.
  - STP was added as a “builder”, or a source of hydroxide ion, but does not precipitate $Ca^{2+}$
  - This keeps the pH high enough that the detergent molecules are in their ionic form.
  - The ionic form of a detergent or soap is active as a surfactant.
  - In addition to detergent (or soap) and a builder, laundry detergent products may contain bleach, zeolites, non-ionic surfactants, and bluing or brightening agents.
  - Use of STP in detergents has been restricted since the late 1970’s. In Canada and Europe the sodium salt of nitrilotriacetic acid (NTA) is used as a builder instead of STP.

- Discharge of phosphates can lead to algal blooms in lakes and can promote eutrophication.
  - Treatment of sewage removes phosphates by precipitation with $Ca^{2+}$ at high pH.
- Biologically, phosphate is found in:
  - Nucleic acids
  - ADP/ATP
  - bones and teeth
- Phosphorothionate and phosophorodithionate pesticides do not bioaccumulate.

## Oxygen Cycle

- Electronic configuration of oxygen is $1s^2 2s^2 2p^4$.
  - Oxidation states are 0,-1, and -2.
- Some examples of oxidation states of oxygen are:
  - Oxidation state 0: $O_2$
  - Oxidation state -1: OH radical, peroxides HOOH, ROOH.

  - Oxidation state -2: $H_2O$, oxides, and organic compounds.
- Coupled to the energy cycle and the carbon cycle by photosynthesis.
  - All atmospheric $O_2$ comes from photosynthesis.
- Primary reservoir is the atmosphere.
  - O, $O_2$, and $O_3$ are involved in the Chapman Cycle and are found in the mesosphere, stratosphere, and troposphere.
- Many oxygen containing species in the atmosphere.
  - Nitrogen oxide species $NO_x$ and $NO_y$ include NO, $NO_2$, $NO_3$, and $N_2O$.
  - Sulphur containing species $SO_x$ refers to $SO_2$ which can be further oxidized.
  - Hydrogen containing species $HO_x$ refers to OH and $HO_2$, which are important free radicals in atmospheric chemistry.
  - Oxygen is also found in atmospheric organic compounds, known as VOCs or volatile organic carbon

- Sinks for oxygen include weathering and the formation of metal oxides.
  - These processes are exothermic and spontaneous.
  - In constrast, the smelting of metals (reducing the oxide to the pure metal) is endothermic.
- Properties and reactivity of atmospheric oxygen have their origins in the electronic structure with unpaired electrons in both the atom and diatom.
  - Two common electronic states of the atom are the ground state ($^3$P) and the excited state ($^1$D).
  - Two common electronic states of the molecule are the ground state ($^3\Pi$) and the excited state ($^1\Delta$).
  - The main source of atmospheric OH is:

    $$\mathrm{O(^1D) + H_2O \rightarrow 2OH}$$

  - The source of O($^1$D) is the photolysis of ozone:

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

  - Ozone also photolyzes to the ground states:

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

  - Photons of wavelength 310 nm or shorter required.

## Sulphur Cycle

- Electronic configuration of sulphur is $1s^2 2s^2 2p^6 3s^2 3p^4$.
  - Oxidation states range from +6 to -2.
- Some examples of the oxidation states of sulphur:
  - $SO_3$, $H_2SO_4$, $HSO_4^-$, and $SO_4^{2-}$ are in oxidation state +6.
  - $SO_2$, $H_2SO_3$, $HSO_3^-$, and $SO_3^{2-}$ are in oxidation state +4.
  - $S_8$ is in oxidation state 0.
  - $S_2^{2-}$ and $FeS_2$ (pyrite) are in oxidation state -1.
  - $H_2S$ and $Fe_2S_3$ contain S in oxidation state -2.

- The S cycle is coupled to the O cycle.
- The geosphere is an important reservoir with S found in:
    - Sulphate salts
    - Sulphite salts
    - metal disulfide ores
    - metal sulphide ores.
    - Since proteins contain S, fossil fuels will contain S.
- Anthropogenic impacts are most significant in the atmospheric reservoir.
- Atmospheric species include:
    - Sulphur dioxide, $SO_2$
    - Dimethyl sulphide or DMS, $CH_3SCH_3$
    - Dimethyl disulphide or DMDS, $CH_3SSCH_3$
    - Carbonyl sulphide or OCS, $O{=}C{=}S$
    - Carbon disulphide, $S{=}C{=}S$
    - Hydrogen sulphide or ($H_2S$)

- Anthropogenic emissions are three times natural emissions.
  - Most anthropogenic emissions are as $SO_2$ from smelting of metals and combustion of fossil fuels.
  - In contrast, most natural emissions are reduced forms of sulphur since anaerobic organisms use S(VI) as a source of oxygen.
  - Natural emissions include DMS, $CS_2$, and OCS from the reduction of amino acids.
  - With the exception of OCS, the reduced species can be oxidized in the troposphere.
  - OCS is transported to the stratosphere where it is photolyzed.
- Volcanic emissions include $SO_2$, $H_2S$, and OCS.
  - May be injected directly into the stratosphere.
- Atmospheric oxidation of $H_2S$ proceeds by the sequence:

$$\mathrm{H_2S + OH \rightarrow HS + H_2O}$$

$$\mathrm{HS + O_2 \rightarrow OH + SO}$$

$$\mathrm{SO + O_2 \rightarrow SO_2 + O}$$

- Atmospheric oxidation of $SO_2$ proceeds by several routes.
  - Direct gas phase oxidation is too slow to be significant.

    $$SO_2 + O_2 \rightarrow SO_3 + O$$

  - Gas phase oxidation can occur with photochemical oxidants formed in photochemical smog by nonmethane hydrocarbons (NMHC). These oxidants includes OH, $HO_2$, O, $O_3$, $NO_3$, $N_2O_5$, ROO, and RO.
- Aqueous phase oxidation inside cloud droplets is the dominant route.
  - $SO_2$ is effectively scavenged by cloud droplets as are oxidants such as $O_2$, $O_3$, HO, $H_2O_2$, ROOH, $CH_3OOH$, and $CH_3(CO)OOH$ (peroxyacetic acid or PAA).
  - Aqueous phase oxidation with $O_2$ is catalyzed by $Fe^{2+}$, $Mn^{2+}$ and C.
  - Aqueous phase oxidation with $O_3$, OH, and $H_2O_2$ is pH sensitive and is connected with the S(IV) speciation. $HSO_3^-$ is more easily oxidized than other species of S(IV).

- A major anthropogenic source of $SO_2$ is the roasting of metal ores. For example:

$$\mathrm{NiS} + \frac{3}{2}\mathrm{O_2} \rightarrow \mathrm{NiO} + \mathrm{SO_2}$$