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) 0.1 (Salt lakes) 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 1.48×10^{13} L day^{-1}
  - Evaporation is 1.02×10^{13} L day^{-1}
  - which leaves 4.6×10^{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	1.6×10^{12}	600
1900	1.7×10^{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° C/km.
  - For moist air undergoing an adiabatic expansion, the lapse rate is 6° 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 CO_2 cycle is coupled to the hydrologic and energy cycle.
  - Before 1800, the level of atmospheric 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 CO_2 was observed to be 358 ppm.
- The global budget of CO_2 has not been fully determined.

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

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

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

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

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

  - 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 5.8×10^{14} moles of carbon in biomass, 5×10^{15} moles C as suspended $\{CH_2O\}$ particles, 5.8×10^{16} moles C as dissolved organic carbon.
  - By comparison, oceans contain 3.2×10^{18} moles of C as C(IV).
  - On land, 4×10^{16} moles C is found in living biomass with a residence time of 16 years.

  - On land, living and dead biomass combined account for 1×10^{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	τ
1.7	CH_4	5.2×10^{14}	3.6 yrs
0.1	CO	1.9×10^{13}	0.1 yr
360	CO_2	5×10^{16}	4 yr

  - In addition the atmosphere contains smog (smoky fog) and carbon containing particulates (such as soot) which account for 2.9×10^{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:

$$NH_4^+ + 3\ H_2O \rightarrow NO_3^- + 10\ H^+ + 8\ e^-$$
$$4\ H^+ + 4\ e^- + O_2 \rightarrow 2\ H_2O$$
$$NH_4^+ + 2\ O_2 \rightarrow NO_3^- + H_2O + 2\ H^+$$

  - 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:
$$\mathrm{O_3 + h\nu \rightarrow O(^1D) + O_2(^1\Delta)}$$
  - Ozone also photolyzes to the ground states:
$$\mathrm{O_3 + h\nu \rightarrow O(^3P) + O_2(^3\Pi)}$$
  - 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:

$$H_2S + OH \rightarrow HS + H_2O$$
$$HS + O_2 \rightarrow OH + SO$$
$$SO + O_2 \rightarrow SO_2 + O$$

- 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:

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