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.
  - 150×10^6 tonnes from natural sources such as marsh gas, wetlands, and ruminants.
  - 25×10^6 tonnes from oceans
  - 150×10^6 tonnes from natural gas
  - Anthropogenic sources include 95×10^6 tonnes from rice paddies and 120×10^6 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 ≅ 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 τ_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 ~ 100 years
  - Maximum rate of change in temperature or sea level ~ 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 λ between 240 and 320 nm.
- The term "ozone layer" refers not to a physical layer, but rather the ozone distributed throughout the stratosphere at ~ 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:

	Δ H (kJ mol^{-1})
O_2 + h$\nu(\lambda < 240 nm) \rightarrow$ 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 $\mathrm{NO_2}$:

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

- 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 $\mathrm{NO/NO_2}$ and $\mathrm{HO/HO_2}$.

- 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 $\mathrm{O_3}$ over the life of the compound relative to the propensity of CFC-11 to lead to the destruction of $\mathrm{O_3}$ 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 ΔH_{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.

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.

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

$$\frac{C_p(l)}{R} = 12.16 - 1.943\times10^{-2}T + 3.042\times10^{-5}T^2$$

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

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

- 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.