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
 - H₂O
 - O₃
- 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 (CH₄) 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:

$$CO_{2}(g) \rightleftharpoons H_{2}CO_{3}(aq)$$
$$H_{2}CO_{3}(aq) \rightleftharpoons H^{+} + HCO_{3}^{-}$$
$$HCO_{3}^{-} \rightleftharpoons H^{+} + CO_{3}^{2-}$$
$$CO_{3}^{2-} + Ca^{2+} \rightleftharpoons CaCO_{3}(s)$$

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

- CO₂ is also the product of atmospheric decomposition of CH₄ 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 N₂O becomes globally distributed.
 - Transported to the stratosphere resulting in a tropospheric lifetime of about two years.
 - Stratospheric sink reactions include:

$$N_2 O + h\nu \to N_2 + O^*$$
$$N_2 O + O^* \to 2NO$$

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 CFCl₃.
 - 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 CO₂.
- 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 $\sim 100 \ {\rm years}$
- Maximum rate of change in temperature or sea level \sim 50 years.
- Values for a_i and $\Delta F_{R,i}$ are determined from general circulation models (GCM).

Stratospheric Ozone

- O_3 absorbs photons with 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:

 $\Delta \text{ H} (\text{kJ mol}^{-1})$

$$O_2 + h\nu(\lambda < 240nm) \rightarrow 2O$$
 495 - E_{photon_1}

$$O + O_2 + M \to O_3 + M$$
 -105
 $O_3 + h\nu(\lambda < 325 \ nm) \to O_2^* + O^*$
383 -E_{photon2}

or

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

 $O + O_3 \to O_2 + O_2$ -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:

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

- 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, O₂ and O₃ may be predicted.
- Observed O, O₂ and O₃ 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 .
- O₃ can be depleted catalytically by a species "X":

 $X + O_3 \to XO + O_2$ $XO + O \to X + O_2$

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/NO₂

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

 $NO_2 + O \rightarrow NO + O_2$

• 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:

Rate₁ =
$$k_1[X][O_3]$$

 $k_1 = A_1 e^{-E_1/RT}$
Rate₂ = $k_2[XO][O]$
 $k_2 = A_2 e^{-E_2/RT}$

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:

Х	$X+O_3$	XO+O
Cl	2.1	1.1
NO	13.1	0
Н	3.9	0
ОН	7.8	0

- Exact rate of O₃ 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:

$$NO_2 + OH + M \to HNO_3 + M$$

- An active ozone depleting species NO_2 is converted to the inactive (from an ozone depleting perspective) HNO_3 .
- Photolysis can regenerate NO₂:

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

• Consider the reactions:

 $Cl + CH_4 \rightarrow HCl + CH_3$

 $HCl + OH \rightarrow Cl + H_2O$

- Again an ozone depleting species (Cl) is converted to a reservoir species (HCl), which in turn (this time by reaction with OH) can be converted back to an active ozone depleter.
- There are also null cycles which have the effect of converting photons to thermal energy.

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

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

which may be rewritten as a pseudoequilibrium:

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

with the forward reaction driven by availability of photons.

- This cycle can affect ratios of NO/NO_2 and HO/HO_2 .
- Termination reactions permanently remove free radical species.

$$2ClO + M \rightarrow ClOOCl + M$$
$$2HO_2 \rightarrow H_2O_2 + O_2$$
$$NO_2 + Cl \rightarrow NO_2Cl$$

• Initiation reactions produce free radicals:

$$HNO_3 + h\nu \rightarrow HO + NO_2$$
$$NO_2 + h\nu \rightarrow NO + O$$
$$O_3 + h\nu \rightarrow O_2 + O$$
$$CH_3Cl + h\nu \rightarrow CH_3 + Cl$$
$$O + H_2O \rightarrow 2OH$$
$$N_2O + O \rightarrow 2NO$$

- Ozone depleting potential (ODP) is the propensity of a substance (i.e. a source of X) to destroy O₃ over the life of the compound relative to the propensity of CFC-11 to lead to the destruction of O₃ 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 $-70^{\circ}C$ and water crystals form at $-85^{\circ}C$.
- 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, ClONO₂ and HCl are broken down on crystals in the polar stratospheric clouds to form Cl₂ 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, HNO₃ stays in the gas phase.
 - It can photolyze generating NO₂:

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

• NO₂ 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 O₃ 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 $1.48 \times 10^{13} \text{ L day}^{-1}$
 - Evaporation is $1.02 \times 10^{13} \text{ L day}^{-1}$
 - which leaves $4.6 \times 10^{12} \text{ L day}^{-1}$
- 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.

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.