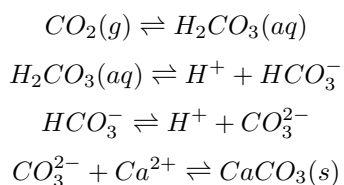


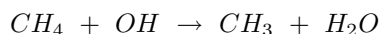
## The Greenhouse Effect

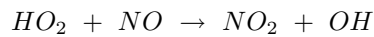
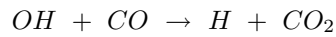
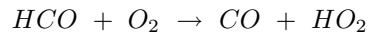
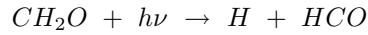
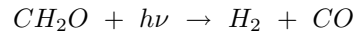
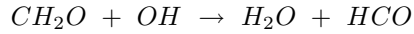
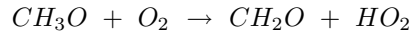
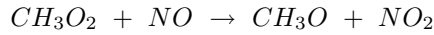
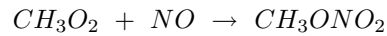
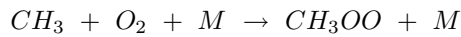
- The greenhouse effect results in the trapping of energy in the troposphere.
  - Infrared radiation is efficiently converted to thermal energy.
- In order to be able to absorb infrared radiation the molecule must have either
  - a transient dipole.
  - or a permanent dipole.
- A heteronuclear diatomic has a permanent dipole:
  - CO
  - NO
- Many nonlinear molecules also have permanent dipoles:
  - CH<sub>2</sub>F<sub>2</sub>
  - H<sub>2</sub>O
  - O<sub>3</sub>
- Non-symmetric linear molecules often have permanent dipoles:
  - NNO
- Symmetric molecules can have transient dipoles as the result of asymmetric stretching vibrations.
  - CO<sub>2</sub>
  - CH<sub>4</sub>
- Greenhouse gas levels are increasing.
- Methane (CH<sub>4</sub>) 1.7 ppmv and increasing by 1 to 2% annually.
- Methane is a product of anaerobic decay.
  - 150 × 10<sup>6</sup> tonnes from natural sources such as marsh gas, wetlands, and ruminants.
  - 25 × 10<sup>6</sup> tonnes from oceans
  - 150 × 10<sup>6</sup> tonnes from natural gas
  - Anthropogenic sources include 95 × 10<sup>6</sup> tonnes from rice paddies and 120 × 10<sup>6</sup> tonnes from cattle.
- Carbon dioxide (CO<sub>2</sub>) 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:



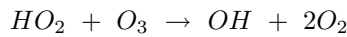
with about 60 times as much in the aqueous phase as in the gas phase.

- CO<sub>2</sub> is also the product of atmospheric decomposition of CH<sub>4</sub> and other hydrocarbons.
- The atmospheric decomposition of methane occurs as a sequence of reactions:

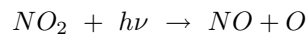




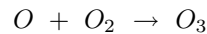
- Other fates for  $HO_2$ :



- Other fates for  $NO_2$ :



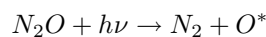
- Atomic oxygen contributes to the formation of ground level ozone.



- 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  $\cong 300$  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:



### 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  $\text{CFCl}_3$ .
- 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  $\text{CO}_2$ .
- Radiative forcing is represented by  $F_R$  and has units of  $\text{watts m}^{-2}$ .
  - It may be thought of as the amount of photon energy converted to thermal energy per unit area.
- Global warming potential is defined as:

$$GWP = \frac{\int_0^T \Delta F_{R,i}(t) dt}{\int_0^T \Delta F_{R,\text{CO}_2}(t) dt}$$

- $\Delta F_{R,i}$  is the change in radiative forcing due to an instantaneous release at  $t = 0$  of 1 kg of gas  $i$ .
- $T$  is the time horizon of interest.
- This may be approximated by:

$$GWP = \frac{\int_0^T a_i n_i(t) dt}{\int_0^T a_{\text{CO}_2} n_{\text{CO}_2}(t) dt}$$

where

- $a_i$  in  $\text{W m}^{-2} \text{ kg}^{-1}$  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  $\tau_i$  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:

$$GWP = \frac{a_i \int_0^T e^{-t/\tau_i} dt}{a_{CO_2} \int_0^T e^{-t/\tau_{CO_2}} dt}$$

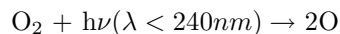
$$\frac{a_i \tau_i (1 - e^{-T/\tau_i})}{a_{CO_2} \tau_{CO_2} (1 - e^{-T/\tau_{CO_2}})}$$

- The integration time  $T$  depends on the timescale for the phenomena of interest.
  - Maximum change in temperature or sea level  $\sim 100$  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  $\lambda$  between 240 and 320 nm.
- The term “ozone layer” refers not to a physical layer, but rather the ozone distributed throughout the stratosphere at  $\sim 10$  ppmv.
  - If all the stratospheric  $O_3$  were compressed to into a layer at standard temperature 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:

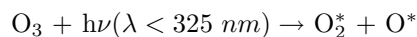
$$\Delta H \text{ (kJ mol}^{-1}\text{)}$$



$$495 - E_{\text{photon}_1}$$

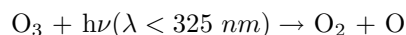


$$-105$$

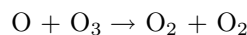


$$383 - E_{\text{photon}_2}$$

or



$$105 - E_{\text{photon}_2}$$



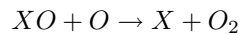
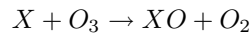
$$-389$$

- The associated rate coefficients are  $k_1$ ,  $k_2$ ,  $k_3$ ,  $k_{3'}$ , and  $k_4$
- The Chapman cycle can reach a steady state:

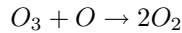
$$\frac{d[O_2]}{dt} = 0 = -k_1[O_2] - k_2[O][O_2][M]$$

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

- 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, O<sub>2</sub> and O<sub>3</sub> may be predicted.
- Observed O, O<sub>2</sub> and O<sub>3</sub> levels do not match that predicted from steady state equations.
  - Observed O<sub>3</sub> levels are low.
  - Therefore there must be additional sinks for O<sub>3</sub>.
- O<sub>3</sub> can be depleted catalytically by a species “X”:

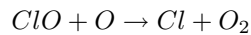
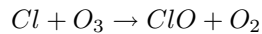


with the net reaction:

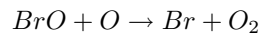
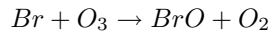


- “X” is usually an odd electron species.
- Some X/XO pairs are:

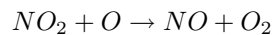
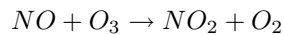
- Cl/ClO



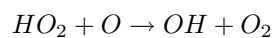
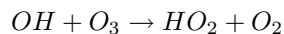
- Br/BrO



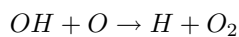
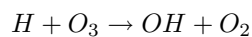
- NO/NO<sub>2</sub>



- OH/HO<sub>2</sub>



- H/OH



- 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:

$$\text{Rate}_1 = k_1[X][O_3]$$

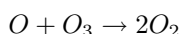
$$k_1 = A_1 e^{-E_1/RT}$$

$$\text{Rate}_2 = k_2[XO][O]$$

$$k_2 = A_2 e^{-E_2/RT}$$

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



has an activation energy of  $18.4 \text{ kJ mol}^{-1}$

- The X/XO pairs provide a lower energy two step pathway.
  - Some activation energies in  $\text{kJ mol}^{-1}$ :

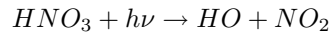
X	X+O <sub>3</sub>	XO+O
Cl	2.1	1.1
NO	13.1	0
H	3.9	0
OH	7.8	0

- 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 catalytic 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:

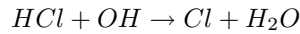
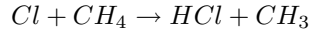


- An active ozone depleting species  $NO_2$  is converted to the inactive (from an ozone depleting perspective)  $HNO_3$ .

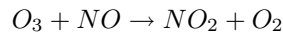
- Photolysis can regenerate NO<sub>2</sub>:



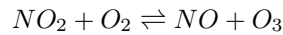
- Consider the reactions:



- 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.

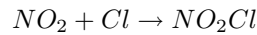
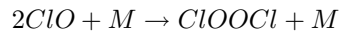


which may be rewritten as a pseudoequilibrium:

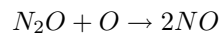
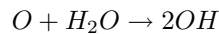
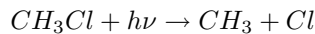
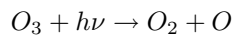
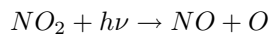
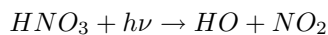


with the forward reaction driven by availability of photons.

- This cycle can affect ratios of NO/NO<sub>2</sub> and HO/HO<sub>2</sub>.
- Termination reactions permanently remove free radical species.



- Initiation reactions produce free radicals:



- Ozone depleting potential (ODP) is the propensity of a substance (i.e. a source of X) to destroy O<sub>3</sub> over the life of the compound relative to the propensity of CFC-11 to lead to the destruction of O<sub>3</sub> 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.

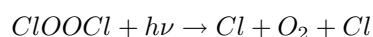
- $T_L$  is the temperature of the refrigeration chamber.
- For an ideal Carnot Cycle:
  - The system starts at  $T_H$  and  $P_1, V_1$ .
  - The first stroke is an adiabatic expansion to  $P_2, V_2$  accompanied by cooling to  $T_L$ .
  - The next stroke is isothermal at  $T_L$  and the fluid absorbs 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  $\Delta H_{vap}$  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.
  - Particularly 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<sub>3</sub>, H<sub>2</sub>SO<sub>4</sub> 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<sub>3</sub>·3H<sub>2</sub>O 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<sub>2</sub> and HCl are broken down on crystals in the polar stratospheric clouds to form Cl<sub>2</sub> 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.

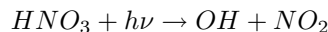


- In the early polar sunrise, the rate of ozone destruction increases, but photons with enough energy to run the Chapman cycle are not yet available.
- Later in the spring, more photons are available and the rate of ozone formation increases.

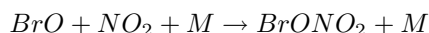
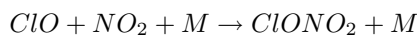
### Arctic Ozone Depletion

- 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,  $\text{HNO}_3$  stays in the gas phase.
  - It can photolyze generating  $\text{NO}_2$ :



- $\text{NO}_2$  can react with  $\text{ClO}$  and  $\text{BrO}$  to form the corresponding nitrates



In these forms they cannot contribute to  $\text{O}_3$  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  $\text{O}_3$  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  $\text{W m}^{-2}$  where  $1 \text{ W} = 1 \text{ J s}^{-1}$ 
  - Energy flux intercepted by the earth is  $1370 \text{ W m}^{-2}$
  - Energy flux captured by the earth is  $342 \text{ W m}^{-2}$
- 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:

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

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

Reservoir	10 <sup>6</sup> km <sup>+3</sup>	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	$\text{L day}^{-1}$	$\text{L day}^{-1} \text{ capita}^{-1}$ (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  $10^\circ \text{ C/km}$ .

- For moist air undergoing an adiabatic expansion, the lapse rate is  $6^{\circ} \text{ C/km}$ .
- 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.