This material is for reference only. Points present in the slides are only for assistance and their elaboration are present in book. Examination questions will be in depth and can be solved by following text book only.

Earth's Energy Balance and Green House Effect

The Earth’s Energy Source

Wien’s Displacement Law

Wavelength at which maximum emission of radiation occurs

Wavelength of maximum emission is inversely proportional to temperature

Sun behaves as blackbody

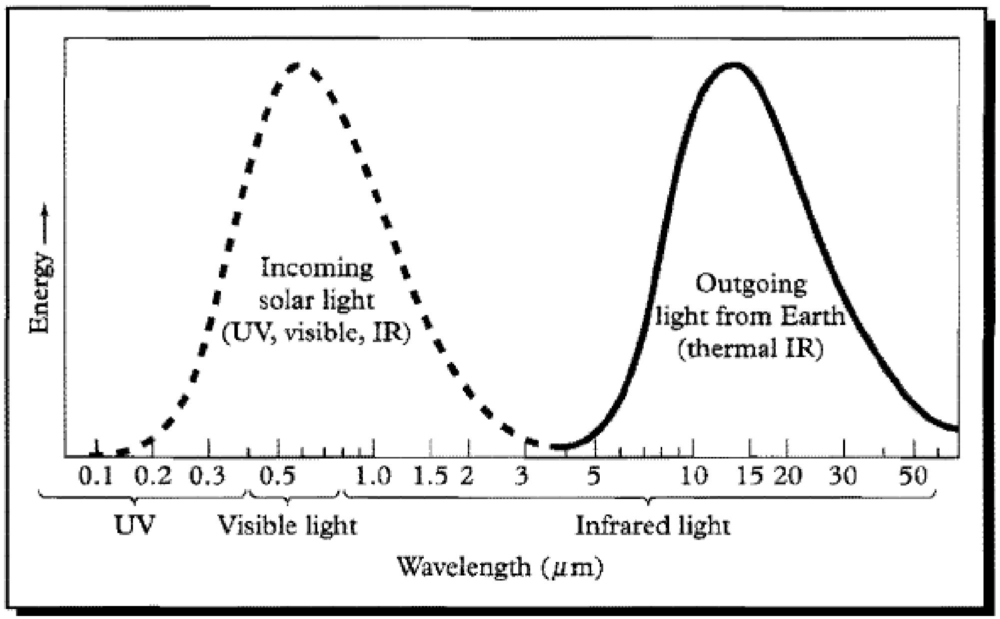
$$\lambda_{peak} = 2897/T$$

T for sun ≈ 5800 or 6000

Therefore λ_{peak} is about 0.50 μm

Earth = 2897/288 or 300

= 10 microns



100%

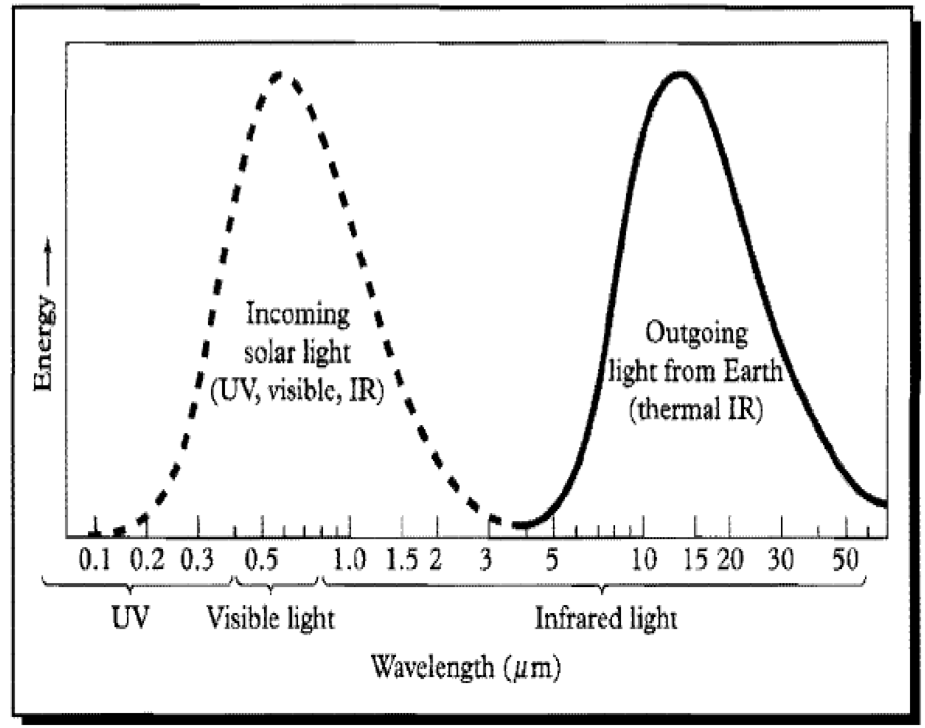
- 50% is absorbed at the surface by water bodies, soil, vegetation, buildings etc.
- 20% is absorbed by water droplets in air (mainly clouds) and by molecular gases e.g. UV by ozone and diatomic oxygen and IR by carbon dioxide.
- The remaining 30 % of incoming sunlight is reflected back into the space by clouds, suspended particles, ice , snow, sand and other reflecting bodies.

The fraction of sunlight reflected back to the space by an object is called its **albedo**.

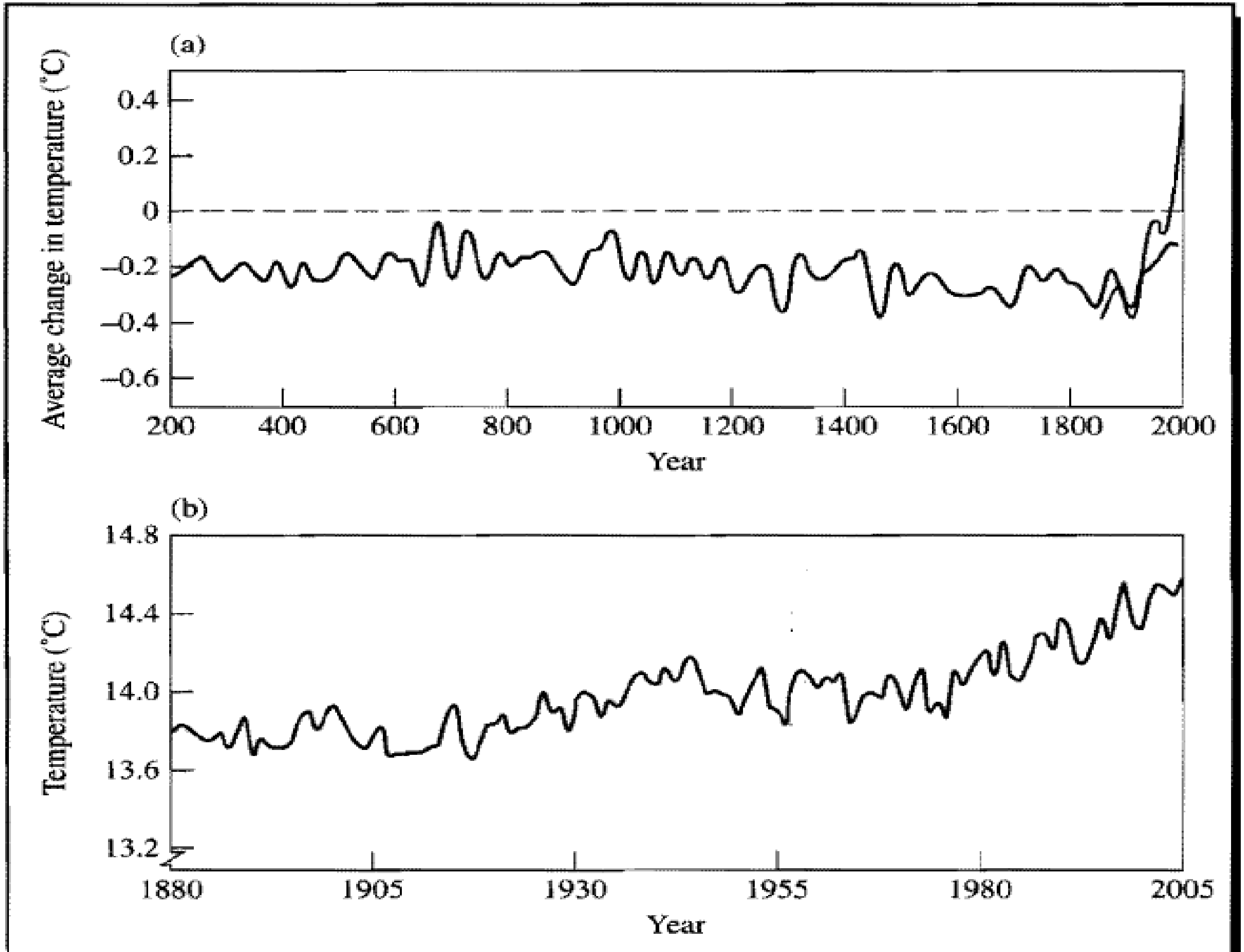
Earth's Energy Emissions and Green House effect

- T for earth ≈ 300
- Therefore λ_{peak} is about 10 μm
- 5-100 μm is called *thermal infrared region*.

$$\text{rate of energy release} = kT^4$$

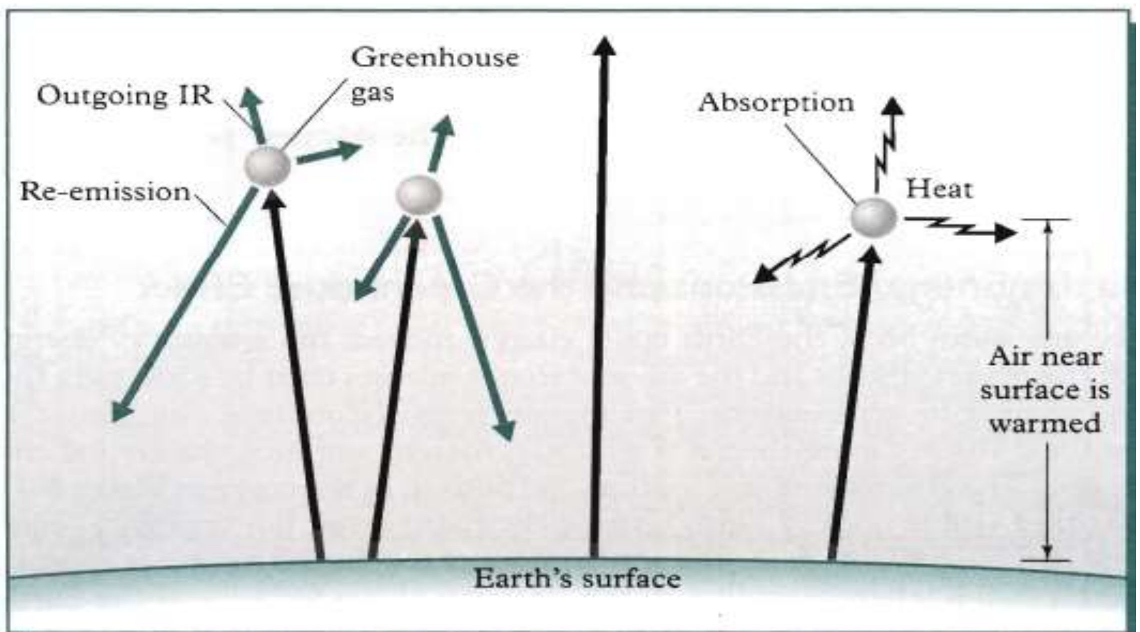


Historical Temperature Trend



Green House Effect

- Cloud do not radiate much energy as they absorb. Why?
- What would be the temperature without this effect?
- Enhanced green house effect: piling on more blanket.
- Principle constituents of atmosphere and absorption of IR light.
- Water and Carbon dioxide.
- Desert night temperature and cloudy nights temperature.



which the Earth loses energy to space as IR is not simply kT^4, but rather $0.6\,kT^4$. Since we know that

rate of loss of energy from Earth = rate of energy input from Sun

it follows for the real Earth that

$$0.6\,kT^4 = k\,(255)^4$$

Taking the fourth root of both sides, we obtain an expression for the temperature:

$$T = (255)/0.6^{0.25}$$

so

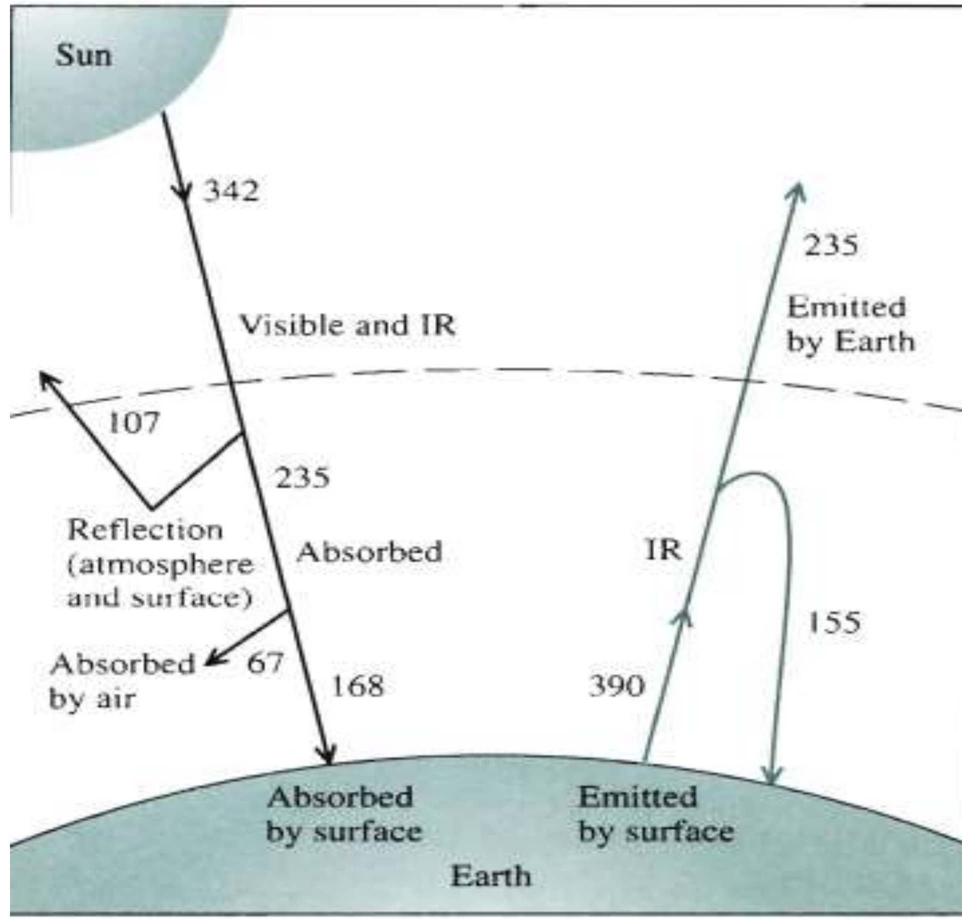
$$T = 290\ \text{K}$$

From this model, the Earth's calculated surface temperature is 290 K, i.e., +17°C, an increase of 35 degrees by the operation of the natural greenhouse effect.

Temperature decrease in troposphere with height.
What at the top of the troposphre?

Earth's Energy Balance

FIGURE 6-4 Globally and seasonally averaged energy fluxes to and from the Earth, in watts per square meter of surface.



Reasons of stratosphere cooling due to increased concentration of CO_2.:

- More absorption at lower level than stratosphere.
- CO2 emits more thermal IR upward and downward than it absorb at stratospheric temperature.

Infrared Spectroscopy (IR)

Molecular Vibrations

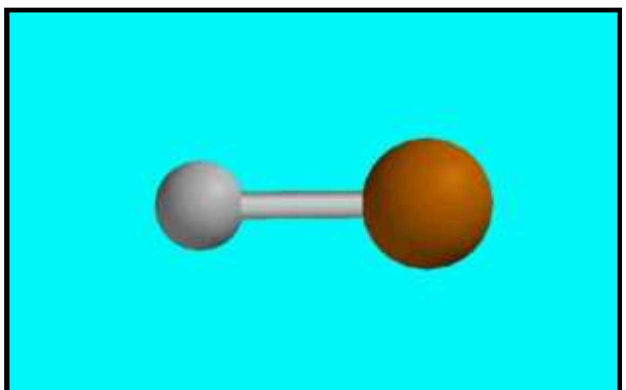
Fundamental principle

Absorption of photons causes changes in molecular vibrations

Molecular Vibrations

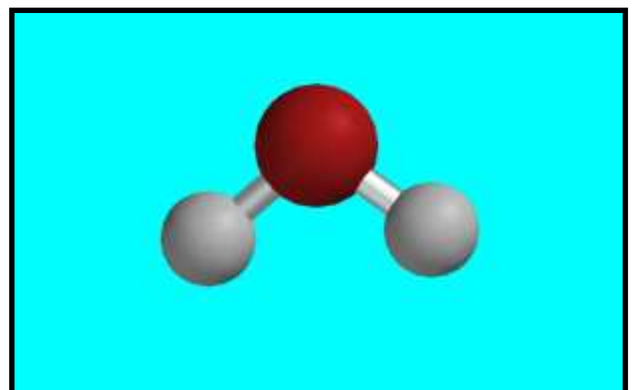
•Bonded atoms move around in space

•Very fast: one vibration cycle ~10^{-15} seconds



Stretching (H-Cl)

•Atoms move along bond axis



Bending (H-O-H)

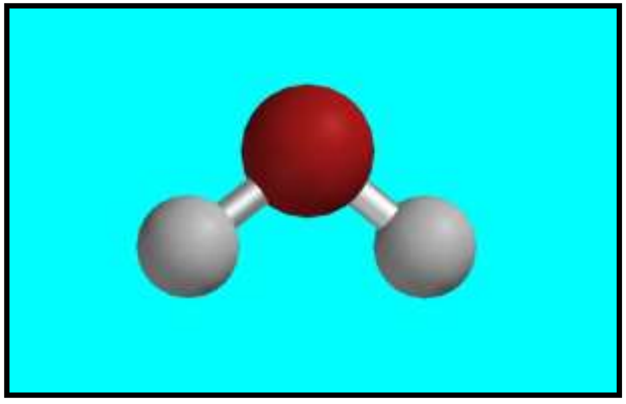
•Motion not along bond axis

•Less important than stretching

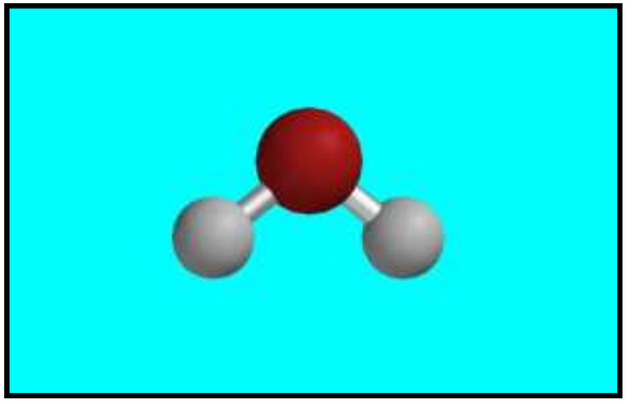
Molecular Vibrations

Vibration energy

• ↑ vibration energy ↑ average bond length



add energy



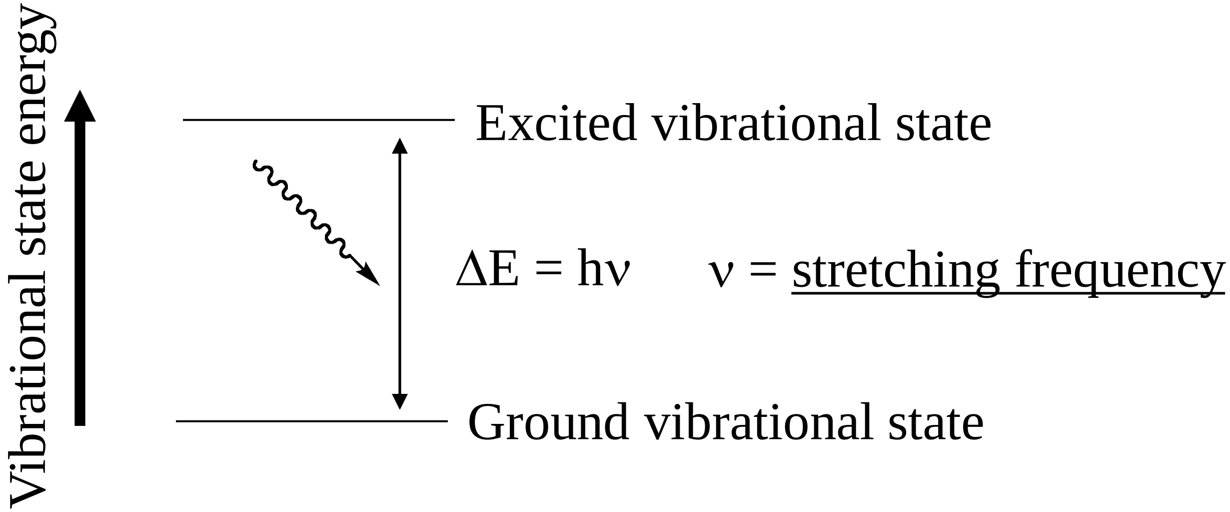
Ground state
lower energy

Excited state
higher energy

Molecular Vibrations

Vibration energy

• Vibrational energy is *quantized* (only certain energy values are possible)



For bond vibrations:

ΔE = dependent on bond

= ~5 kcal mol^{-1}

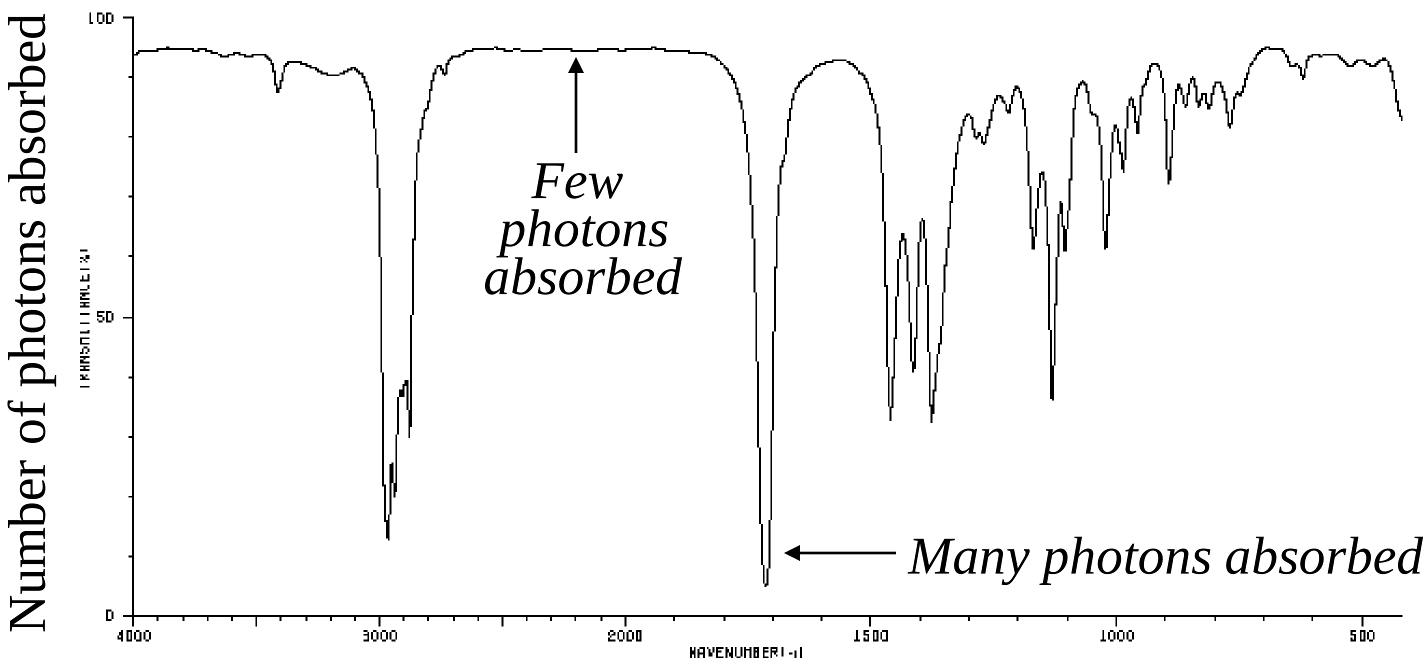
= lower energy than red light photons

= *infrared photons*

The Infrared Spectrum

<u>Spectrum</u> = plot of photon energy versus photon quantity

Typical infrared spectrum:



Stretching frequency

Proportional to photon energy

- Dipole moment and IR absorption
- Oxygen, nitrogen, Ar and all homonuclear diatomic molecules

symmetric stretch

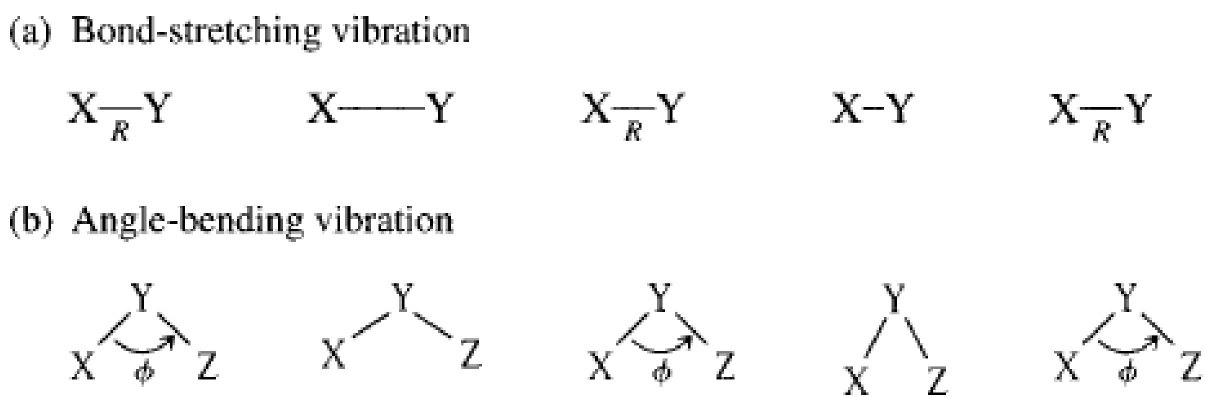
antisymmetric stretch

- CH_4.

Deduce whether the following molecules will absorb infrared light due to internal vibrational motions:

(a) H_2 (b) CO (c) Cl_2 (d) O_3 (e) CCl_4 (f) NO

Molecular Vibrations: Energy Absorption by Greenhouse Gases

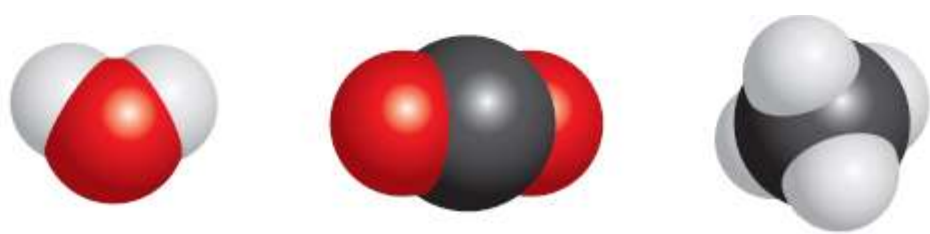


Do Greenhouse Gases Trap Infrared Radiation?

- Molecules with two identical atoms can only vibrate back and forth. This limits the type of energy these molecules can absorb.
- Nitrogen and oxygen gases both consist of two identical atoms. They are poor absorbers of infrared radiation.

nitrogen, N_2 oxygen, O_2

- Molecules with three or more atoms, and different types of atoms, can vibrate and wiggle in many ways, and absorb different types of energy.
- Water, carbon dioxide, and methane all have three or more atoms, and different types of atoms. They can absorb infrared radiation, along with other kinds of energy

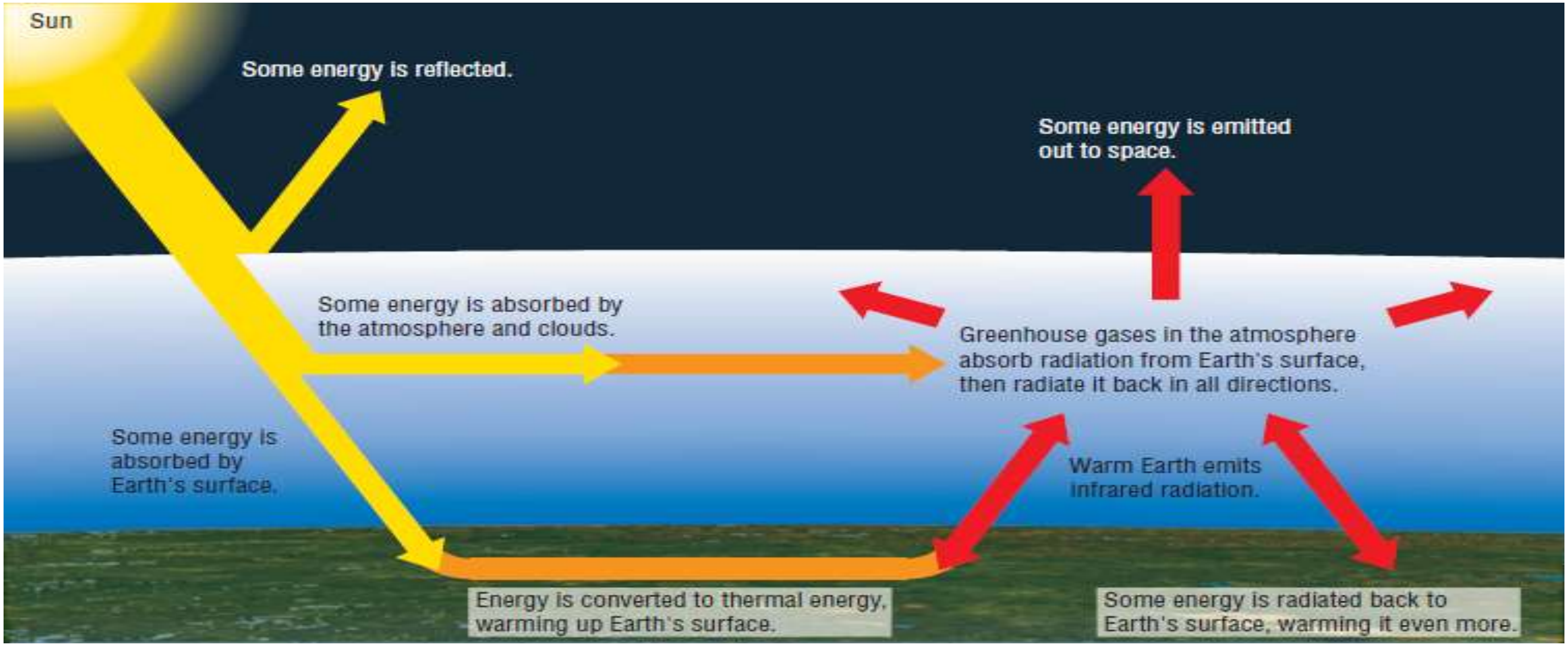


water, H_2O carbon dioxide, CO_2 methane, CH_4

The Greenhouse Effect

- The **greenhouse effect** is a natural process whereby gases and clouds absorb infrared radiation emitted by Earth's surface and radiate it, heating the atmosphere and Earth's surface.

- Earth's average global temperature is 15 ^{o}C. Without the natural greenhouse effect and the rest of the climate system, it would be about –18 ^{o}C, which is too cold for life.



Summary of the Greenhouse Effect

(1) Energy from the Sun passes through the atmosphere to reach Earth.

(2) Earth's surface warms up and radiates out lower-energy infrared (IR) radiation.

(3) Gases in the atmosphere absorb the IR radiation and radiate the energy back again in all directions.

(4) Some radiation goes back to Earth's surface and warms it up even more.

(5) As a result, much of the radiation from the Sun is trapped in a cycle between Earth's surface and the atmosphere.

Greenhouse Gases

- **Greenhouse gases** absorb lower-energy infrared radiation emitted by Earth's surface.

- Most of the air in the atmosphere is nitrogen and oxygen gases. Greenhouse gases exist in very low concentrations in the atmosphere.

- The main greenhouse gases are
  - water vapour, H_2O
  - carbon dioxide, CO_2
  - methane, CH_4
  - tropospheric ozone, O_3
  - nitrous oxide, N_2O

Note:-

They estimated that water vapor accounts for about 50% of Earth's *greenhouse effect*, with clouds contributing 25%, carbon dioxide 20%, and the minor *greenhouse gases* and aerosols accounting for the remaining 5%.

Greenhouse Gases

Water Vapour

•Water vapour in the atmosphere causes about two-thirds of the natural greenhouse effect.

•The quantity of water vapour depends on the temperature of the atmosphere.

•Water vapour and temperature are related by a **feedback loop**.

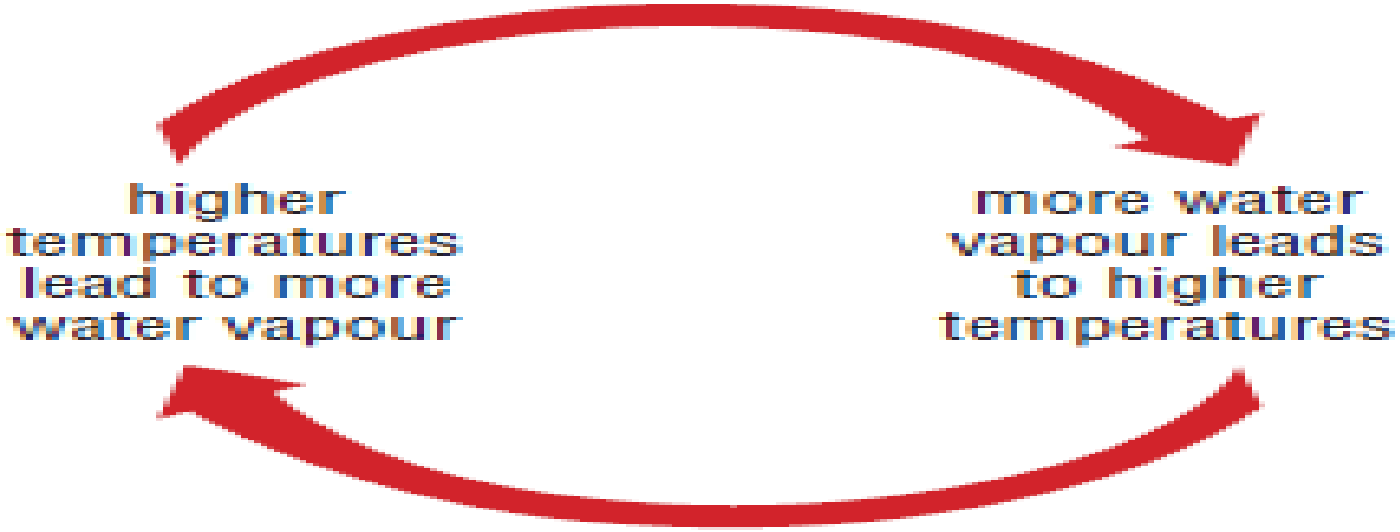


Figure Higher temperatures cause more water to evaporate and form water vapour. Since water vapour traps heat in the atmosphere, more water vapour increases the temperature further.

Greenhouse Gases

Carbon Dioxide

•Carbon dioxide causes up to a quarter of the natural greenhouse effect on Earth.

•Carbon dioxide comes from both natural and human sources.

•Natural sources of atmospheric carbon dioxide include volcanic eruptions, burning organic matter, and cellular respiration of plants and animals.

•Living things and oceans are important **carbon sinks**.

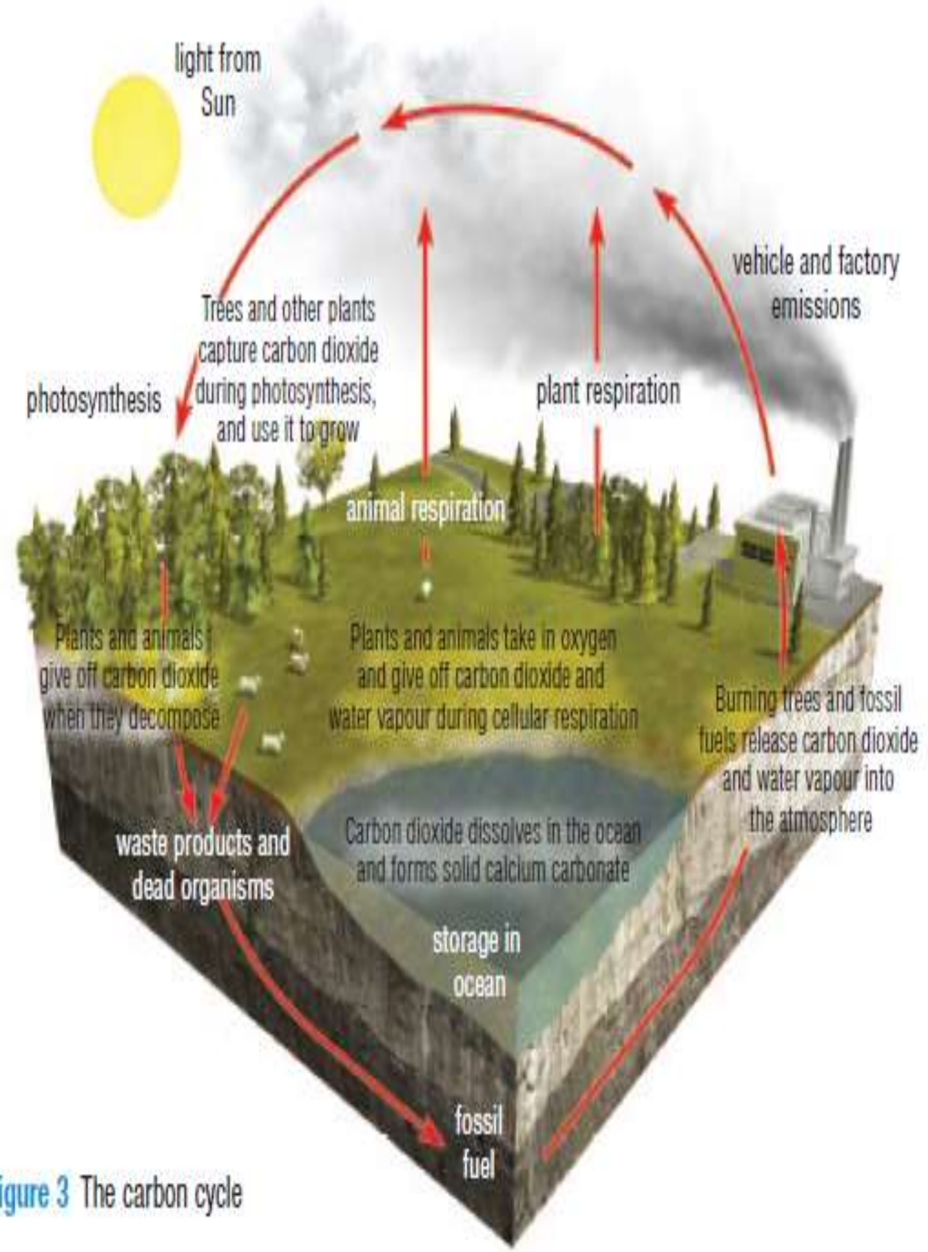


Figure 3 The carbon cycle

The Major Green House Gaes

Carbon Dioxide:

- Absorption of Infrared Light by a molecule occurs when the frequencies of the light and one of the molecule's vibrations match almost exactly.
- However, light of somewhat lower or higher frequency than that of the vibration is absorbed by a collection of molecules. (rotational energy)

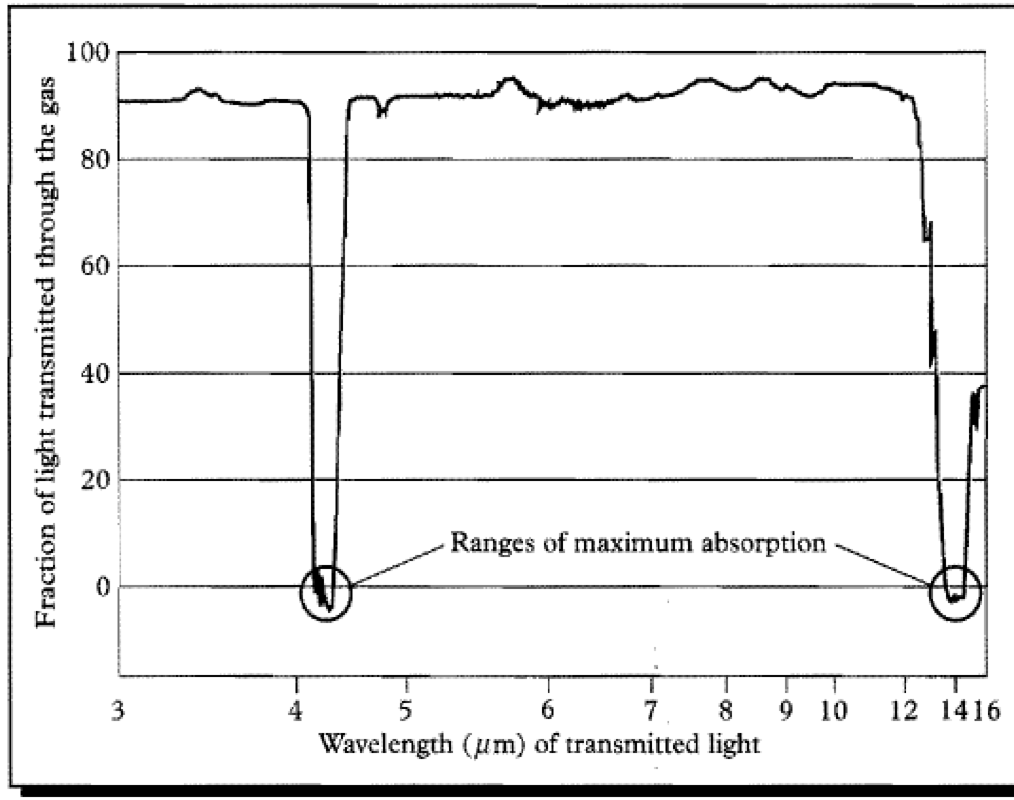


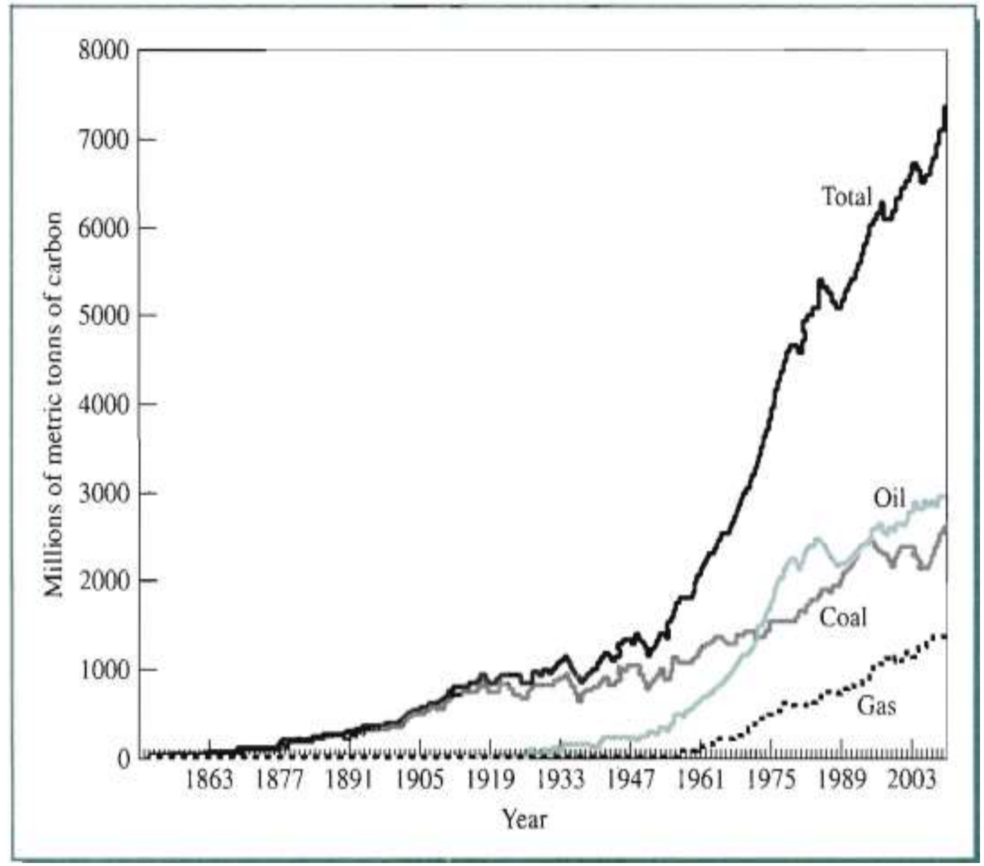
FIGURE 6-6 The infrared absorption spectrum for carbon dioxide. The scale for wavelength is linear when expressed in wavenumbers, which have units of cm^{-1}; wavenumber = 10,000/ wavelength in nm.

Sources of Carbon Dioxide

- Anthropogenic sources: Fossil Fuels i.e. coal, oil and natural gas, Deforestation and burning of wood for agricultural use.
- Manufacture of cement:

$$CaCO_3(s) \longrightarrow CaO(s) + CO_2(g)$$

- Note that as much carbon dioxide is released from the combustion of the fossil fuel needed to heat the limestone as is released from the limestone itself.



Greenhouse Gases

Methane

•There is much less methane in the atmosphere than carbon dioxide (1.785 ppm). This quantity has risen from 0.700 ppm before the industrial age.

•A molecule of methane is 23 times more powerful as a greenhouse gas than a molecule of carbon dioxide.

•Methane comes from both natural and human sources.

•Natural sources of methane include plant decomposition in swamps and in animal digestion.

•It is responsible for 1/3rd as much global warming as has carbon dioxide.

Ozone

•Ozone exists naturally in the stratosphere where it forms a protective layer blocking UV radiation from the Sun.

•Ozone also exists in the troposphere, mostly from human sources. In the troposphere, ozone acts as a greenhouse gas.

•It is difficult to calculate the quantity of ozone in the troposphere, as it changes rapidly.

Greenhouse Gases

Nitrous Oxide

•There is much less nitrous oxide in the atmosphere than carbon dioxide (0.321 ppm). This quantity has risen from 0.270 ppm before the industrial age.

•A molecule of nitrous oxide is almost 300 times more powerful as a greenhouse gas than a molecule of carbon dioxide.

•Nitrous oxide comes from both natural and human sources.

•Nitrous oxide is produced naturally by the reactions of bacteria in soil and water.

CFC’s

- Absorb strongly in the 8 – 13 μm atmospheric window region.
- Absorption due to C-F bond stretch is centered at 9 μm.
- Insulating freezers, refrigerators, and air conditioners.

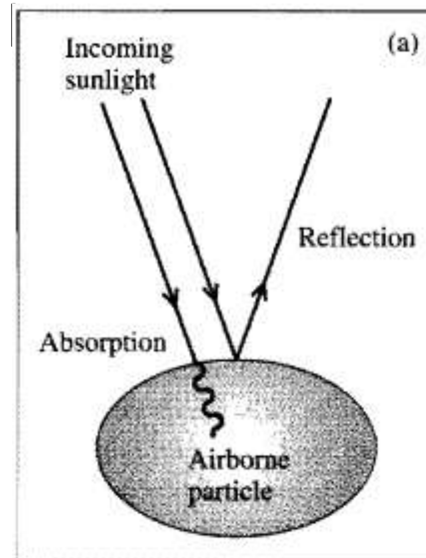
- Replacements are HCFC and HFC which have shorter life time and absorb less efficiently in the center of the atmospheric region.
- **Sink:** in stratosphere.

The Climate-Modifying Effects of Aerosols

Aerosols: An aerosol is a suspension of fine solid particles or liquid droplets, in air or another gas

Two types of aerosols:

- Powerful volcanic eruptions into the upper atmosphere
- Produced by industrial processes & expelled into troposphere



Types of Interactions

- Incoming Light can be reflected back
- Outgoing IR can be reflected towards earth.
- Redirection; scattering
- Absorption of light

- Certain types of particles have significant albedo which cools the air mass and surface below it.
- Some types of aerosol particles can absorb light and can heat surroundings; these are dark colored soot and ash particles released from volcanoes.

Sulfate Aerosol:

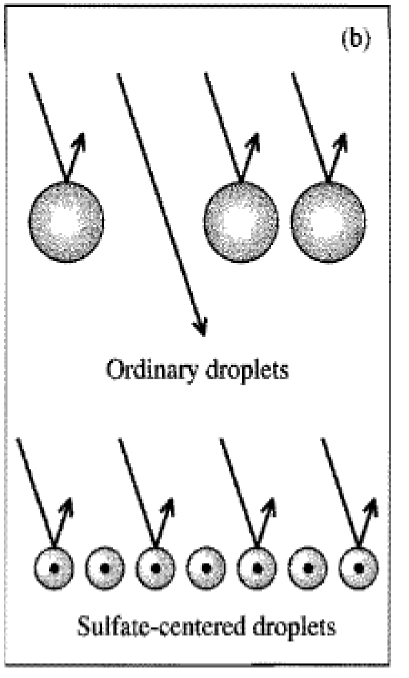
- Pure sulfate aerosol do not absorb sunlight or IR.

If soot particles are incorporated the absorption will be significant.

- Direct effects

Reflect sunlight back into the space more efficiently than they Absorb means increases albedo.

- **Net effect is cooling.**
- Indirect effects of sulfate aerosols:



Relative instantaneous radiative forcing (RIRF)

RIRF is a measure of the ability of an incremental addition of a gas in the present atmosphere, to increase the absorption of IR radiations.

Global warming potential (GWP):-

The term Global Warming Potential (GWP) is used to total up the contribution of all the individual GHGs in the atmosphere and is also used as a tool to compare the potency of different greenhouse gases with that of CO2.

The GWP is calculated using the integrated RF and lifetime of each gas relative to that of carbon dioxide. Carbon dioxide has an assigned GWP of 1 and is used as the baseline unit (i.e. the reference gas) to which all other greenhouse gases are compared

FOSSIL FUELS
85% of the world's commercial energy

COAL

NATURAL GAS

OIL

Fossil Fuels

Fossil fuels are fuels formed by natural resources such as anaerobic decomposition of buried dead organisms. The age of the organisms and their resulting fossil fuels is typically millions of years e.g. coal, petroleum and natural gas etc.

Coal

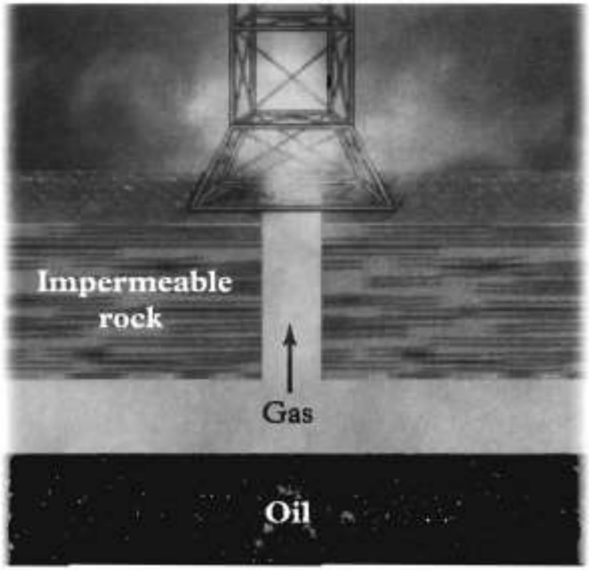
- Coal is a complex mixture of organic chemical substances containing carbon, Hydrogen and oxygen with smaller amounts of nitrogen and sulfur, minerals and moisture.
- It was formed from the tiny proportion of ancient plant matter that was covered over by water and could not be recycled back to CO_2.
- It is formed from Highly aromatic, polymeric component of land based woody plants called lignin over a long period of time subjected to high temperature and pressure.

- *Except from CO_2 Its burning also emits soot, sulfur dioxide, fluoride, uranium and other radioactive metals and heavy metals including mercury. "Dirty fuel".*

USES

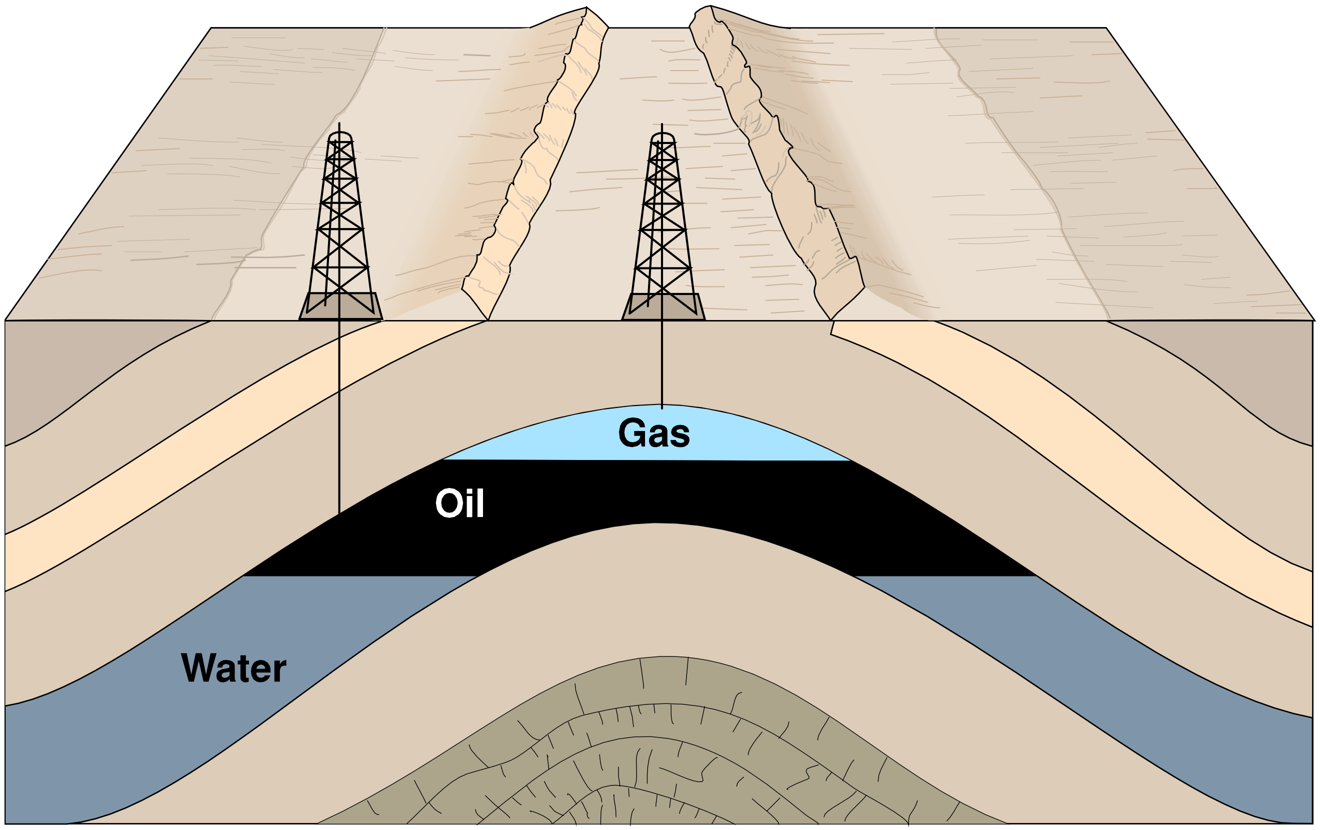
- Major use is electricity production
- Used to make steam for heating
- As coke in steel making
- Domestic use

NATURAL GAS/Compressed Natural Gas (CNG)



OIL and NATURAL GAS (Methane)

Made from the decayed remains of sea creatures which died millions of years ago



Mixture of hydrocarbons and originated as the small fraction of marine organisms and plant matter that were buried and cut off from the oxygen that was required for their complete oxidation.

OIL (PETROLEUM)

Sequestration of CO_2

Methods of Disposal

- Deep oceans.
- Very deep aquifers under land or sea.
- In empty oil and natural gas wells or coal seams.
- CO_2 is first captured/concentrated and then deposited.

Problems associated with capturing:

- Energy input.
- Very large equipment for capture and concentrate.
- Capture/concentration accounts for 75% of the total cost.

Methods Capturing/concentrating CO_2

1. ***Chemical absorption***

a) By amine (95% recovery): 15-20% amine solution e.g. monoethanolamine and diethanolamine.

Gas is allowed to pass through this solution. After sometimes saturation occurs. This solution is then heated to produce concentrated steam of CO_2 and amine solution is again regenerated.

$$R_2NH + CO_2 \rightleftharpoons R_2N{-}CO_2^- + H^+$$
$$H_2O + CO_2 \rightleftharpoons HCO_3^- + H^+$$

b) Chemical absorption by Metal oxides e.g. CaO.

$$CaO(s) + CO_2(g) \rightleftharpoons CaCO_3(s)$$

After this solid is heated to 900 °C to reverse the reaction. CaO deactivate relatively quickly

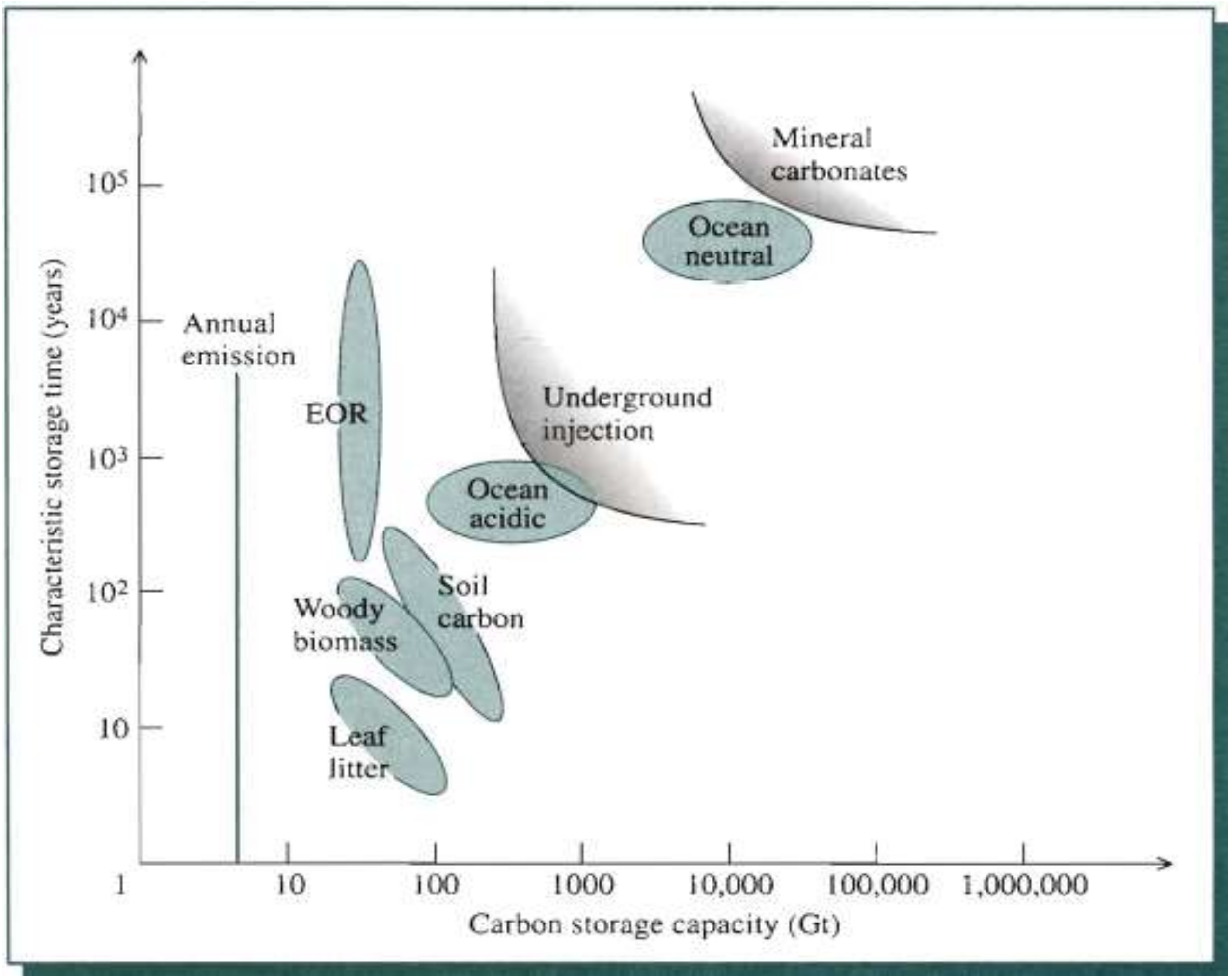
2. ***Membrane Separation*** (85% recovery): Polymeric membranes are used. More economical.
3. ***Physical Adsorption***: Zeolite, activated carbon, methanol and glycols.
4. ***Cryogenic separation***: CO_2 has higher condensation temperature than O_2 and N_2. High pressure and low temperature is applied. Energy requirement is more than chemical absorption.

Future technologies

5. ***Oxycombustion***: burning of fossil fuel in O_2.
6. ***Conversion to H_2 gas***: gassification. More economical gas separation.

$$\text{carbon-hydrogen fuel} + \text{water} \longrightarrow CO_2 + H_2$$

Disposal Methods of CO_2

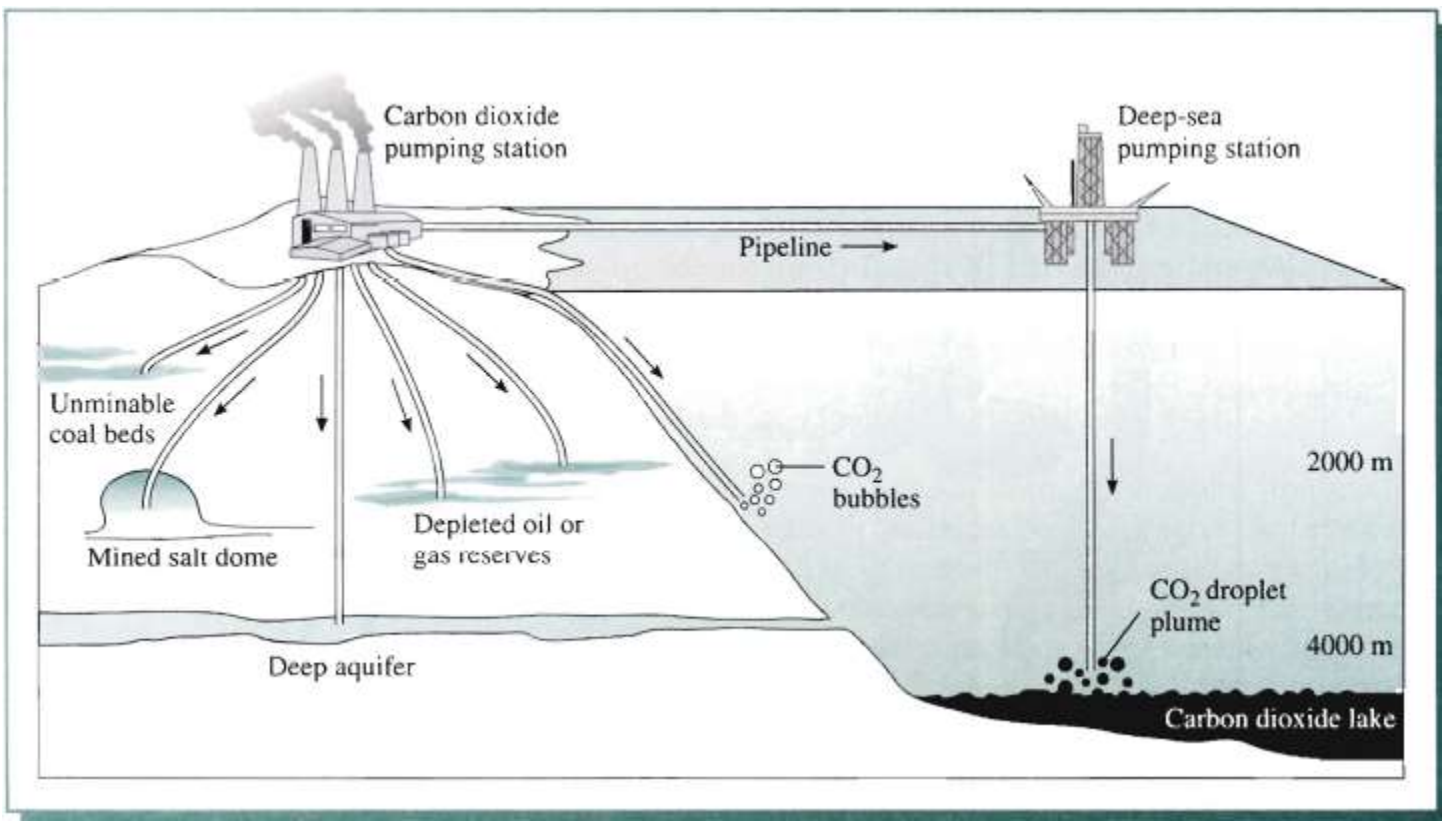


Deep Ocean Disposal of CO_2

- Ocean Acidic:

$$CO_2(g) + H_2O(aq) \rightleftharpoons H_2CO_3(aq)$$
$$H_2CO_3(aq) \rightleftharpoons H^+ + HCO_3^-$$

- Shallow Injection: provided that the seafloor there is slanted sufficiently to allow the dense, CO_2-rich water to be transported by gravity to greater depths !!!!



- ***Direct Disposal*: ** Require pipeline to penetrate a depth of 3000 to 5000 m producing a pool of liquified CO_2 denser than water and perhaps convert to solid clathrate hydrate.
- Near the Sea floor

$$CO_2(g) + H_2O(aq) + CaCO_3(s) \longrightarrow Ca(HCO_3)_2(aq)$$

- Drawbacks:

aquatic life

Earthquake or asteroid

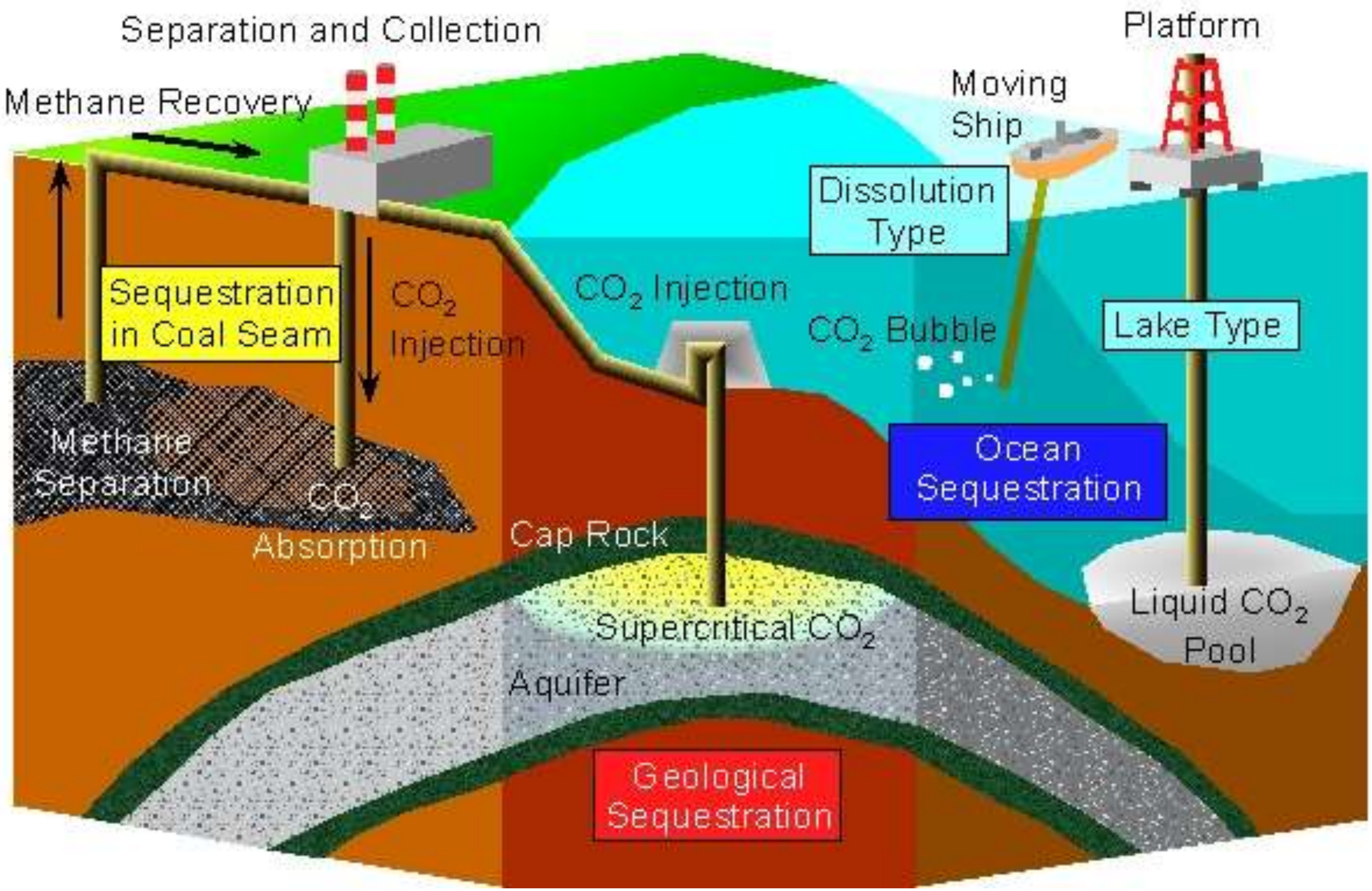
- Alternative Scheme is ***Ocean Neutral***:

$$2\,CO_2 + H_2O + CaSiO_3 \longrightarrow SiO_2\,(s) + Ca(HCO_3)_2(aq)$$

Deep Underground Storage

- Pumping deep underground into cracks and pores in common alkaline rocks such as calcium aluminosilicates and subsequent microorganism catalyzed process to produce calcium carbonate.
- **Enhanced oil Recovery (EOR):** to inject CO_2 into reservoirs containing crude oil or natural gas. Depleted oil and gas reservoirs could be used to store CO_2.
- CO_2 storage in coal seams that lie too far underground to be mined may also be feasible.
- Deposition in saline aquifers under ground well below the fresh water supplies.

Overview of CO_2 Sequestration Technology



Effects of Global warming

- Effect on human health
- Warming of water is killing much of the coral in ocean reefs and threatening sea life.
- Mosquito-borne disease have reached higher altitudes.
- Precipitation has increased in most areas.
- Extreme weather is becoming more common.

The 12 Principles of GREEN CHEMISTRY

Green chemistry is an approach to chemistry that aims to maximize efficiency and minimize hazardous effects on human health and the environment. While no reaction can be perfectly 'green', the overall negative impact of chemistry research and the chemical industry can be reduced by implementing the 12 Principles of Green Chemistry wherever possible.

1. WASTE PREVENTION

Prioritize the prevention of waste, rather than cleaning up and treating waste after it has been created. Plan ahead to minimize waste at every step.

2. ATOM ECONOMY

Reduce waste at the molecular level by maximizing the number of atoms from all reagents that are incorporated into the final product. Use atom economy to evaluate reaction efficiency.

3. LESS HAZARDOUS CHEMICAL SYNTHESIS

Design chemical reactions and synthetic routes to be as safe as possible. Consider the hazards of all substances handled during the reaction, including waste.

4. DESIGNING SAFER CHEMICALS

Minimize toxicity directly by molecular design. Predict and evaluate aspects such as physical properties, toxicity, and environmental fate throughout the design process.

5. SAFER SOLVENTS & AUXILIARIES

Choose the safest solvent available for any given step. Minimize the total amount of solvents and auxiliary substances used, as these make up a large percentage of the total waste created.

6. DESIGN FOR ENERGY EFFICIENCY

Choose the least energy-intensive chemical route. Avoid heating and cooling, as well as pressurized and vacuum conditions (i.e. ambient temperature & pressure are optimal).

7. USE OF RENEWABLE FEEDSTOCKS

Use chemicals which are made from renewable (i.e. plant-based) sources, rather than other, equivalent chemicals originating from petrochemical sources.

8. REDUCE DERIVATIVES

Minimize the use of temporary derivatives such as protecting groups. Avoid derivatives to reduce reaction steps, resources required, and waste created.

9. CATALYSIS

Use catalytic instead of stoichiometric reagents in reactions. Choose catalysts to help increase selectivity, minimize waste, and reduce reaction times and energy demands.

10. DESIGN FOR DEGRADATION

Design chemicals that degrade and can be discarded easily. Ensure that both chemicals and their degradation products are not toxic, bioaccumulative, or environmentally persistent.

11. REAL-TIME POLLUTION PREVENTION

Monitor chemical reactions in real-time as they occur to prevent the formation and release of any potentially hazardous and polluting substances.

12. SAFER CHEMISTRY FOR ACCIDENT PREVENTION

Choose and develop chemical procedures that are safer and inherently minimize the risk of accidents. Know the possible risks and assess them beforehand.