

Chapter 3: Global Climate Change



What is global warming?

Can anything be done about it?

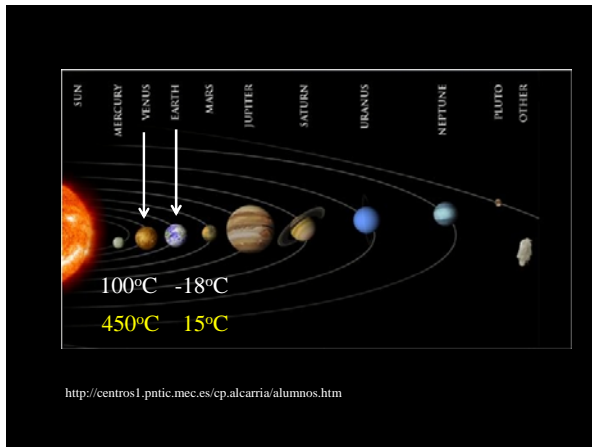
Is there really cause for alarm?

How can we assess the information from the popular press?

Earth gets its energy from the sun, *directly or indirectly*.

The distance of earth to the sun is important – just considering the distance should yield a temperature of -18°C or 0°F on earth.

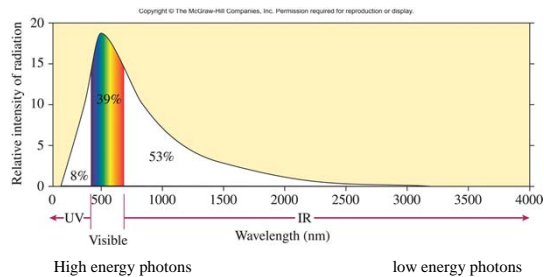
Some atmospheric gases act as a green house raising the temperature to an average livable 15°C . *It is a natural, necessary process. It is a beneficial effect.*



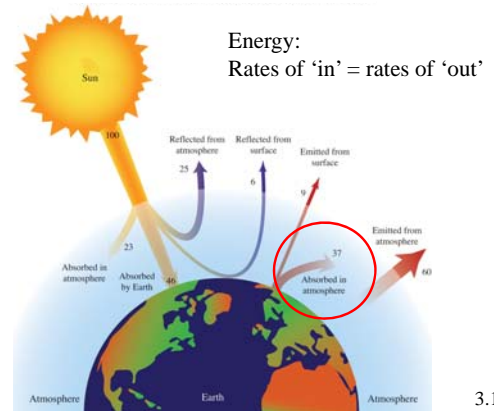
Greenhouse effect:

Energy absorbed as radiation is reemitted.

Energy radiated from the earth is in the infra-red (heat) region. Some atmospheric gases trap a major portion of the heat radiating from the Earth.



The Earth's Energy Balance



There is a dynamic balance of energy between the earth, Atmosphere and the outer space. Maintains a constant temperature of the planet.

Green House gases: Atmospheric gases that absorb and trap infra red radiation and thereby keep the atmosphere warm. E.g. water vapor, CO₂, CH₄, N₂O, O₃, CFCs.....

Past and present constitution of green house gases are very different.

“*Global warming* is a misnomer, because it implies something that is *gradual*, something that is *uniform*, something that is quite possibly *benign*. What we are experiencing with *climate change* is none of those things”

-John Holdren

Examine (experimental) data to understand the:

- changes in global temperatures over time.
- the natural and human contributions to the global climatic changes.

Over billions of years the earth's climate has changed due to natural changes such as astronomical, chemical, geological, orbital path, sun's radiation levels etc.

Such natural effects has enormously changed the climate and dragged the earth into unlivable conditions..

Disturbance of the energy balance by the rise of the greenhouse gases enhances the greenhouse effect – increases the average terrestrial temperature (global warming).

Reason – Natural phenomena. Human activities: industry, transportation, mining, agriculture ?

Natural phenomena – For the last million years, 10 major And 40 minor glacier activity changes. Over billions of years the earth's climate has changed due to changes such as astronomical, chemical, geological, orbital path, sun's radiation levels, airborne, CO₂, CH₄, dust cover etc.

“*Global warming* is a misnomer, because it implies something that is *gradual*, something that is *uniform*, something that is quite possibly *benign*. What we are experiencing with *climate change* is none of those things”

-John Holdren

Very rapid – geologic times; millennia not decades

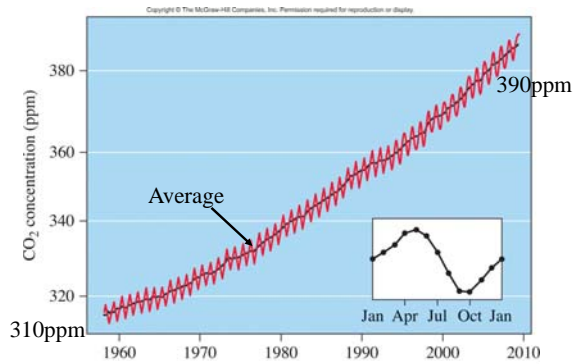
Non uniform – today – poles are mostly affected,

Not benign – assessment difficult due to complexity, unpredictability w. r. t. which aspects and extent.

The issue at hand today with regard to climate change associated with 'global warming is the energy imbalance.

Human activity has increased the concentrations of greenhouse gases in the atmosphere.

Examine the CO₂ concentrations directly measured since late 1950's.



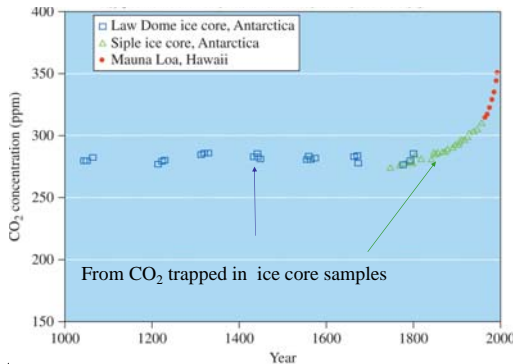
According to data taken at Mauna Loa, Hawaii since 1958, CO₂ levels are on the rise.

3.2

Microscopic air bubbles in ice core samples from glaciers can be used to determine changes in greenhouse gas concentrations over time.

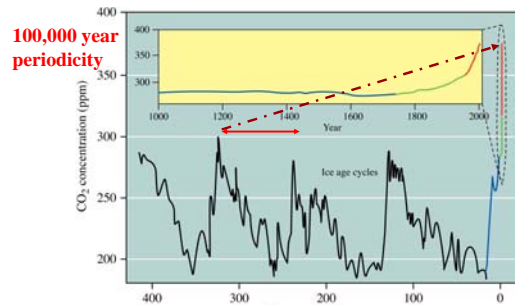


3.2



Comparing ice core data from Antarctica and Mauna Loa observations, the concentration of carbon dioxide appears to be increasing over time.

3.2



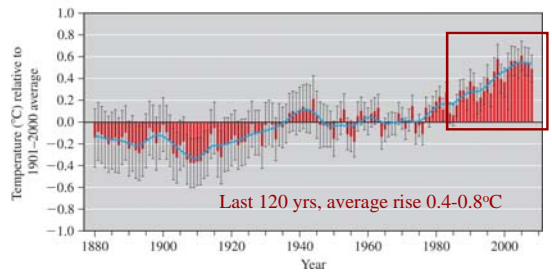
Vostok ice core shows data going back 400,000 years, other ice cores go back even further. Current atmospheric CO₂ is 100 ppm higher than any time in the last million years.

3.2

Human activity has moves terrestrial carbon into the atmosphere.

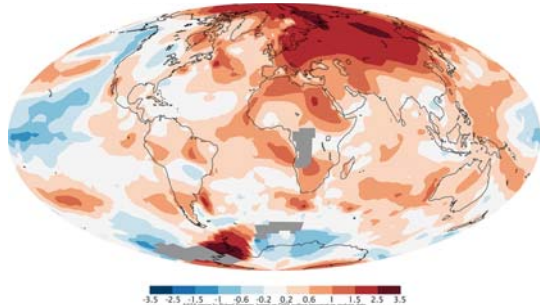
Fossil fuels – coal, petroleum and natural gas.

Average **global surface temperatures** have increased since 1880.



The red bars indicate average temperatures for the year while the black error bars show the range for each year. The blue line is the 5-year moving average.

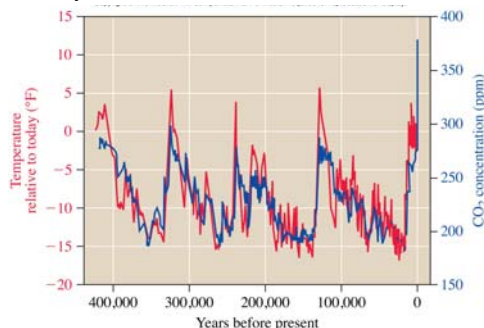
3.2

Last 120 yrs, temperature rise - uneven.

Global temperatures for 2006 (in °C) relative to the 1951–1980 average. The most dramatic changes have been observed in the higher latitudes (dark red areas).

3.2

The concentration of CO₂ (blue) and the global temperature (red) are well correlated over the past 400,000 years as derived from ice core data.

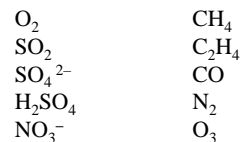


3.2

Review: Lewis structures

1. Determine the sum of valence electrons.
2. Use a pair of electrons to form a bond between each pair of bonded atoms.
3. Arrange the remaining electrons to satisfy octet rule (duet rule for H).
4. Assign **formal charges**.

Draw Lewis Structures for:



Formal charge = # v. e. - [# nonbonding e⁻ + ½ bonding e⁻]

Remember: Resonance, relative lengths, and bond order!

3.3

Why do 'green house' gases absorb heat?

Absorption of 'heat' is depends on the molecular shape and molecular vibrations.

Molecular shape: Location of atoms in space.



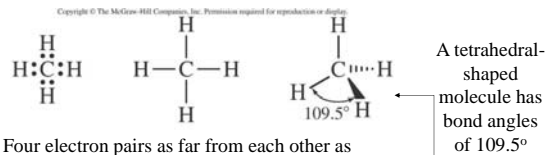
linear

Determination of Molecular shape.

1. Draw the Lewis structure; show connectivity.
2. Draw the Lewis structure is drawn in 3-D. Consider the fact the electron 'pairs' repel each other and the most stable molecule will arrange the electron pair in 3D to give the minimum repulsion.
3. The atom arrangement at minimum repulsion determines the 'molecular shape'.

Valence Shell Electron Pair Repulsion Theory

Consider methane (CH_4), where the central carbon atom has 4 electron pairs around it:



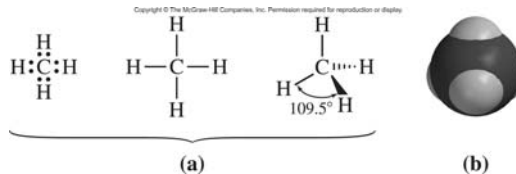
Four electron pairs as far from each other as possible indicates a tetrahedral arrangement.

3.3

Representations of methane

CH_4 = molecular formula; does not express connectivity

Structural formulas show how atoms are connected:



Lewis structures show connectivity.

This Lewis structure is drawn in 3-D.

Space-filling

3.3

Valence Shell Electron Pair Repulsion Theory

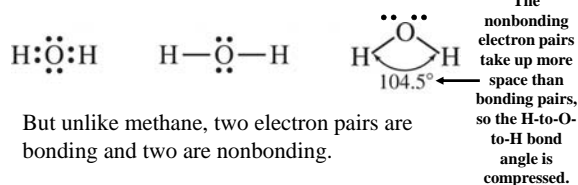
Assumes that the most stable molecular shape has the electron pairs surrounding a central atom as far away from one another as possible.

The **3-D shape** of a molecule affects its ability to absorb IR radiation.

3.3

3.3

The central atom (O) in H_2O also has four electron pairs around it.



But unlike methane, two electron pairs are bonding and two are nonbonding.

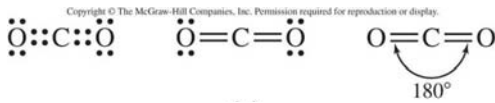
The electron pairs are tetrahedrally arranged, but the shape is described only in terms of the atoms present: water is said to be bent shaped.

3.3

Number of electron pairs around central atom	Shape of molecule	Bond angle
4 electron pairs, all bonding: CH_4 , CF_4 , CF_3Cl , CF_2Cl_2	tetrahedral	109.5°
4 electron pairs, three bonding, one nonbonding: NH_3 , PCl_3	Triangular pyramid	about 107°
4 electron pairs, two bonding, two nonbonding: H_2O , H_2S	bent	about 105°

3.3

CO₂:



Two groups of four electrons each are associated with the central atom.

The two groups of electrons will be 180° from each other: the CO₂ molecule is linear.

3.3

Molecules vibrate in definite patterns - *vibrational modes*.

Molecules can interact (absorb) with electromagnetic radiation. (UV to IR) from the sun.

UV photons absorption often result in breaking bonds.

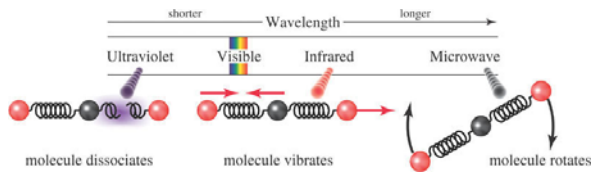
IR radiation is 'heat'.

IR photon absorption increases the vibrations of molecules.

Not all vibrational 'modes' can absorb IR radiation.

If a molecule has IR absorbing vibrational modes, the eventual absorption of IR radiation increases its energy and hence its temperature.

Molecular response to different types of radiation



3.4

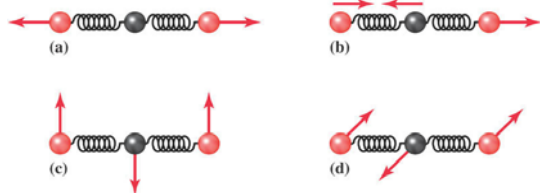
Greenhouse gases possess vibrational modes that absorb IR radiation absorption.

N₂ and O₂ IR inactive.

CO₂, H₂O, O₃, CH₄, CFCs etc IR active.

What is the difference?

Molecular geometry and absorption of IR radiation

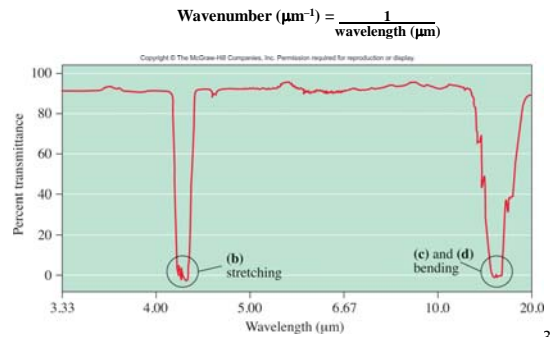


(a) = symmetrical movement; no net change in dipole - no IR absorption.

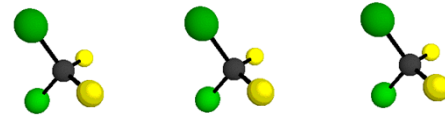
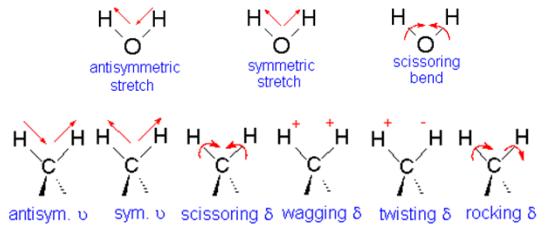
(b, c, d) = un-symmetrical movement; see a net change in dipole (charge distribution), so these account for IR absorption.

3.4

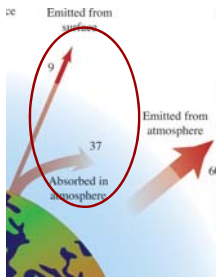
The infrared spectrum for CO₂



3.4



Characteristic Vibrations of CCl₂F₂

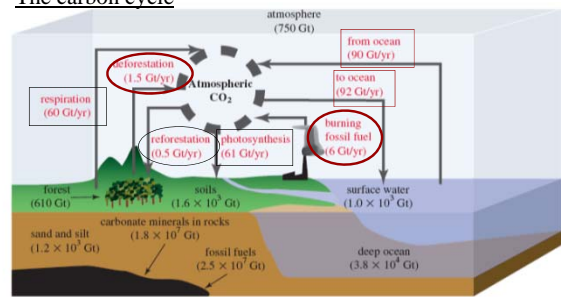


Once the greenhouse gases absorb heat emanating from the earth, they can either give up the energy as radiation or *transfer the absorbed energy to oxygen and nitrogen molecules by colliding with them.*

Green house gases acts as a heat transferring agent to the atmospheric gases; thereby trap radiation that would otherwise leave the earth.

3.4

The carbon cycle



Proper functioning (balance of ins and outs) of the carbon cycle is essential for sustaining life on earth.

3.5

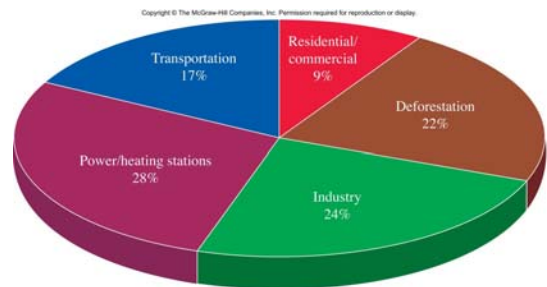
Human activities contributing to the imbalance:

Burning coal and natural gas (produce power, transportation).

Deforestation by burning (removes efficient CO₂ absorbers), decaying forests (adds CO₂).

Net imbalance; 3.3Gt of C added per year into the atmosphere.

CO₂ emission sources by end use:



3.5

Expressing amounts in Chemistry:

The smallest amount of matter that we know to exist are atoms and molecules.

However dealing with single atoms and molecules in every day life is not practical because they are so small.

Lightest element = Hydrogen

Mass of *one* H atom $\sim 1.63 \times 10^{-24}$ g

We deal with large collections of atoms or molecules in real life.

A convenient unit to express collections of atoms is needed.

Amount' (in chemistry) is expressed in moles.

1 mole = 6.022×10^{23} units

6.02×10^{23} = Avogadro Number

Mole (mol) is the chemical counting unit.

Molar Masses

Direct measurement of the moles of substances of different elements in substances is impractical.

The mass of 6.02×10^{23} units of these entities (atoms/molecules) expressed in grams = 1 mol of the substance.

For pure elements; avg. atomic mass value (number) in grams = 1 mol of the substance. (non-molecular)

Unit: grams per mole; g/mol

Atomic Mass (weight):

Average mass of an atom of an element (**amu**).

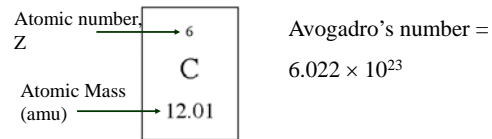
1 amu = $1.66053886 \times 10^{-27}$ kg

Calculated by considering the isotope composition of the element in nature.

E.g. ^{12}C 12.00000amu 98.892%
 ^{13}C 13.00335amu 1.108%

C 12.01 amu

Mole: the number equal to the number of carbon atoms in exactly 12 g of pure C-12 = 6.022×10^{23} .



A mole of atoms of any element has a mass (in grams) equal to the atomic mass of the element in amu.

3.7

Given the (average) atomic mass of O is 16.00amu, what is the mass of an atom of O (a) in grams (b) in amu?

$$(a) \frac{16.00 \text{ g O}}{6.02 \times 10^{23} \text{ O atoms}} = 2.66 \times 10^{-23} \text{ g}$$

(b) 16.00 amu

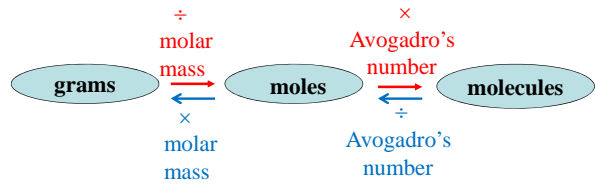
3.7

Q. If you have 36.0 g of carbon, how many moles of Carbon is that?

Fact: One mole of carbon has a mass of 12.01 grams.
 1 mol C = 12.01 g

$$36.0 \text{ g C} \times \frac{1 \text{ mol C}}{12.01 \text{ g C}} = 3.00 \text{ mol C}$$

Keep these relationships in mind:



Remember – the critical link between moles and grams of a substance is the **molar mass**.

IT'S SIMPLE – THINK IN TERMS OF PARTICLES!

3.7

Q. What mass of CO₂ contain 3.3 Gt of C?

1 Gt = 10⁹ metric tons.

What mass of CO₂ would contain 1 ton of C.

What is the mass of C:CO₂ in a molecule?

What is the mass of C:CO₂ in a mole?

$$\frac{\text{mass C}}{\text{mass CO}_2} = \frac{12.01 \text{ amu}}{12.01 \text{ amu} + 2 \times 16.01 \text{ amu}} = \frac{12.01 \text{ g}}{12.01 \text{ g} + 2 \times 16.01 \text{ g}}$$

$$= \frac{12.01}{44.01} = 0.2728$$

In any given sample of CO₂ *this ratio* is the same!!!

This characteristic is the same for all molecules.

$$\frac{\text{mass C}}{\text{mass CO}_2} = 0.2728$$

$$\text{mass CO}_2 = \frac{\text{mass C}}{0.2728} = \frac{3.3 \text{ Gt}}{0.2728}$$

$$= 12.09 \text{ Gt}$$

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Table 3.1 Ways to Interpret a Chemical Equation			
C	+	O ₂	→ CO ₂
1 atom		1 molecule	1 molecule
6.02 × 10 ²³ atoms		6.02 × 10 ²³ molecules	6.02 × 10 ²³ molecules
1 mol		1 mol	1 mol
12.01g		16.00g	28.01g

Other Green House Gases: CH₄, N₂O, O₃, CFCs,...

Gas	Source
CH ₄	Natural (~40%). Wetlands by anaerobic bacteria, melting permafrost, from oceans release of trapped exist as methane hydrates, termites metabolism, generate methane instead of CO ₂ , agriculture (rice) by anaerobic bacterial action, cattle and sheep digestive process, landfills by anaerobic bacterial action, <u>extraction of fossil fuels - oil and coal mining releases trapped methane.</u>
N ₂ O	Bacterial action on nitrates, ammonia fertilizer, nitrogen compounds reacting with O atoms in stratosphere, <u>auto catalytic converters, biomass burning, industrial processes (nylon, HNO₃)</u>
CFCs, halons etc.	
O ₃	

Effect of green house gases depend on their concentration, atmospheric lifetime and effectiveness of IR absorption defined as GWP.

Global Warming Potential (GWP) represents the relative contribution of a molecule of an atmospheric gas to global warming.

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Name and Chemical Formula	Preindustrial Concentration (1750)	Concentration in 2008	Atmospheric Lifetime (years)	Anthropogenic Sources	Global Warming Potential
carbon dioxide CO ₂	270 ppm	388 ppm	50-200*	Fossil fuel combustion, deforestation, cement production	1
methane CH ₄	700 ppb	1760 ppb	12	Rice paddies, waste dumps, livestock	21
nitrous oxide N ₂ O	275 ppb	322 ppb	120	Fertilizers, industrial production, combustion	310
CFC-12 CCl ₂ F ₂	0	0.56 ppb	102	Liquid coolants, foams	8100

Effectiveness = Concentration × Lifetime × GWP 3.8

Amplification of Greenhouse Effect: Global Warming

What we know:

1. CO₂ contributes to an elevated global temperature.
2. The concentration of CO₂ in the atmosphere has been increasing over the past century.
3. The increase of atmospheric CO₂ is a consequence of human activity.
4. Average global temperature has increased over the past century.

3.2

All natural and anthropogenic factors influencing the earth's energy in's and out's are accounted in models; **'radiative forcings' (negative forcings has a cooling effect, positive forcings a warming effect).**

Radiative Forcings are factors that affect the balance of Earth's incoming and outgoing radiation.

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	Climate Change	Ozone Depletion
region of atmosphere	primarily the troposphere	the stratosphere
major players	H ₂ O, CO ₂ , CH ₄ , and N ₂ O	O ₃ , O ₂ , and CFCs
interaction with radiation	Molecules absorb IR radiation. This causes them to vibrate and return heat energy to the Earth.	Molecules absorb UV radiation. This causes one or more bonds in the molecule to break.
nature of problem	Greenhouse gases are increasing in concentration. In turn this is trapping more heat, causing an increase in the average global temperatures.	CFCs are causing a decrease in concentrations of O ₃ in the stratosphere. In turn, this is causing an increase in the UV radiation at the surface of the Earth.

What might be true:

1. CO₂ and other gases generated by human activity are responsible for the temperature increase.
2. The average global temperature will continue to rise as emissions of anthropogenic greenhouse gases increase.

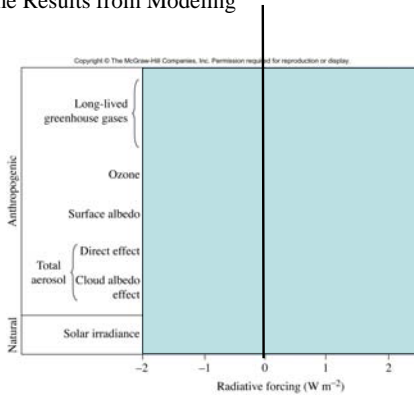
Prediction of future is accomplished with mathematical models that includes all factors that contribute to climate change! THIS IS A VERY DIFFICULT TASK.

3.9

Factors considered in Computer models:

1. Solar irradiance
2. Greenhouse gases
3. Land use (surface albedo)
4. Aerosols

Some Results from Modeling



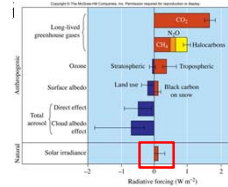
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Solar irradiance

Overall global irradiance is unchanged over the year.

Periodic oscillations of the sun (affects its shape) tilt of earth's axis and direction. Both periodicity 100000 yr – do not explain the recent warming.

Sunspots (11-yr period, 0.1% activity) increases

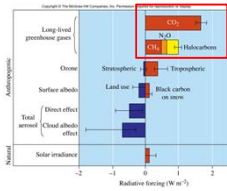


Greenhouse gases

Dominant anthropogenic forcings.

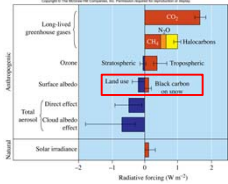
CO₂ main contributor.

Montreal Protocol (1990) keep CFC contribution low.



Land use

Changes in land use is significant in incident and reflection of sun's rays. (albedo - reflectivity of surface; 0.1 - 0.9). Decreasing albedo increase warming. Albedo depends on the season. Glacier retreat, loss of snow cover, and sea ice, deforestation decrease the albedo -warms. Crops increase albedo, cools.

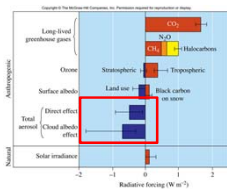


$$\text{albedo} = \frac{\text{reflected radiation}}{\text{incident radiation}}$$

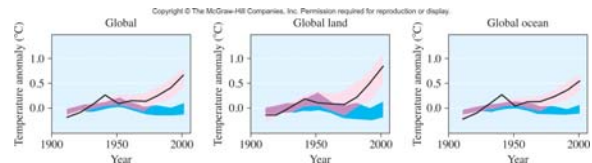
Aerosols Particle plumes, size <4μm, scatters radiation.

Origin: Dust storms, ocean spray, forest fires, volcanic activity, smoke, soot, coal combustion (sulfates).

Promotes cloud formation (condensation of water), reflection of radiation.



Climate Models are used to predict global mean surface temperatures (one measure of climate phenomena).



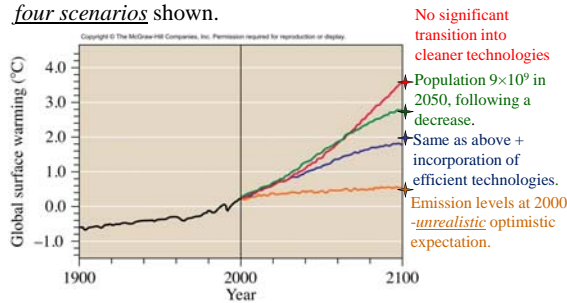
Blue bands = predicted temperature using natural forcings only

Pink bands = temperature with both natural and anthropogenic forcings

Future predictions – include rate of economic growth, 'green' technologies, population etc. in the future models.

3.9

Models can be used to predict future global temperatures, four scenarios shown.



Black line: data for the 20th century

Other lines: projected 21st century temperatures based on different socioeconomic assumptions

3.9

Intergovernmental Panel on Climate Change (IPCC)

Recognizing the problem of potential global climate change, the World Meteorological Organization (WMO) and the United Nations Environment Program (UNEP) established the intergovernmental Panel on Climate Change (IPCC) in 1988. It is open to all members of the UN and WMO.

In 2007, the IPCC stated in a report that scientific evidence for global warming was unequivocal and that human activity is the main cause.

AAAS, ACS recognize the threats posed by climate change.

3.10

Conclusions from the 2007 IPCC Report

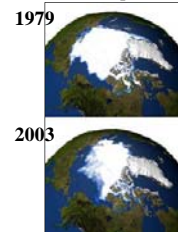
Table 3.6	IPCC Conclusions, 2007
Very Likely 90-99%	<ul style="list-style-type: none"> Human-caused emissions are the main factor causing warming since 1950. Higher maximum temperatures are observed over nearly all land areas. Snow cover decreased about 10% since the 1960s (satellite data); lake and river ice cover in the middle and high latitudes of the Northern Hemisphere was reduced by 2 weeks per year in the 20th century (independent ground-based observations). In most of the areas in the Northern Hemisphere, precipitation has increased.
Likely 60-90%	<ul style="list-style-type: none"> Temperatures in the Northern Hemisphere during the 20th century have been the highest of any century during the past 1000 years. Arctic sea ice thickness declined about 40% during late summer to early autumn in recent decades. An increase in rainfall, similar to that in the Northern Hemisphere, has been observed in tropical land areas falling between 108° North and 108° South. Summer droughts have increased.
Very Unlikely 1-10%	<ul style="list-style-type: none"> The observed warming over the past 100 years is due to climate variability alone, providing new and even stronger evidence that changes must be made to stem the influence of human activities.

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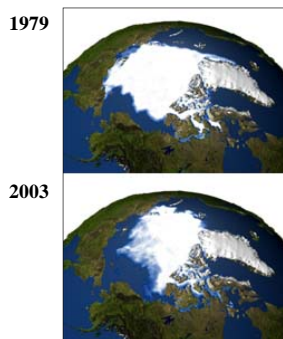
(Possible) outcomes of a warmer planet:

- Sea ice disappearance
- Rising ocean and surface temperatures
- Sea level rise
- More extreme weather
- Changes in ocean chemistry
- Loss of biodiversity
- Vulnerability of fresh water resources
- Human health

Loss of Polar Ice Cap



Loss of Polar Ice Cap



3.10

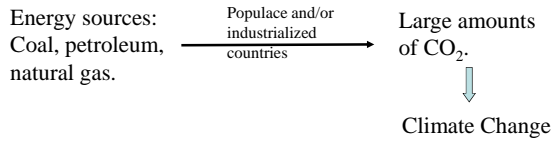
NASA: The Arctic warming study, appearing in the November 1, 2003, issue of the American Meteorological Society's *Journal of Climate*, showed that compared to the 1980s, most of the Arctic warmed significantly over the last decade, with the biggest temperature increases occurring over North America.

Perennial, or year-round, sea ice in the Arctic is declining at a rate of **9%** per decade.

As the oceans warm and ice thins, more solar energy is absorbed by the soil surface and water, creating positive feedbacks that lead to further melting.

Such dynamics can change the temperature of ocean layers, impact ocean circulation and salinity, change marine habitats, and widen shipping lanes.

3.10

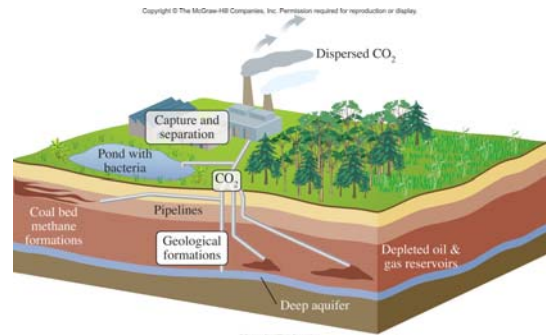


Options: mitigation (eliminate/reduce emissions) and adaptation – must be global.

Mitigation – increase efficiency generation and utilization of energy (mandatory), CCS (expensive), reverse de-forestation and planting trees

Adaptation – system adjustments to climate change, new crops, public health systems, coastline protection.

One potential method for *mitigation* (to moderate or alleviate) is CO₂ sequestration.



3.11

Problem: lack of political will, inability to agree on basics by countries (major polluters).

Kyoto Protocol – 1997 Conference (legally binding)

- Intergovernmental Panel on Climate Change (IPCC) certified the scientific basis of the greenhouse effect.
- Kyoto Protocol established goals to stabilize and reduce atmospheric greenhouse gases.
- Emission targets set to reduce emissions of six greenhouse gases from 1990 levels. (CO₂, CH₄, NO, HFCs, PFCs, and SF₆)
- Trading of emission credits allowed.
- Effective 2005, US never opted to participate.

3.11

IPCC determined greenhouse gases must peak by 2020 and be reduced to half the current levels. Annual global emissions must be decreased by 9 billion tons.

Practically to reduce by 1 billion tons:

- reduce energy use in buildings by 20-25%
- all cars – 60 mpg
- CCS at 800 coal burning power plants
- replace 700 coal-burning power plants by renewables

A Cap-and-Trade System can be used to limit CO₂ emissions.



3.11