Atmospheric Chemistry

Topics

- What is air?
  - How did it get here?
- Solar Radiation
- The Flow of Air on Earth
  - Weather
- Energy Movement Based on Weather
- Ozone
  - Tropospheric Ozone,
  - Stratospheric Ozone
  - Fluorocarbons, Stratospheric Ozone Effects
- Greenhouse Effect (Positive and Negative)
- Photochemical Reactions
- Images of Illustrating some examples
  - “Env. Sci. CD-11
  - See filename: Photo CD SEPM Photo CD Air List

<u>The Sun –</u>
<u>The Atmospheric Energy Driver</u>

All energy driven reactions on Earth are a result of large amounts of energy form the Sun.

The atmosphere has different temperatures at different heights due to chemical reactions driven by the Sun's energy of **~1 Kw/m^2/ day at surface** and

1,340 watts/m^2/ day on earth's atmosphere –
in the upper atmosphere perpendicular to the Sun.

READIATION WINDOW

- UV
- VISIBLE
- INFRA-RED

What did the original composition of air look like?

Probably?

Originally there was outgasing of the earth:

N_2 and CO_2 with traces of H_2, CO, H_2O an d O_2.

Formation of O_2 from CO_2 may have been by this mechanism:

$CO_2 + hv \rightarrow CO + O$ Then, $O + O + M \rightarrow O_2 + M$

Where:
hv is Sun radiation energy and
M is a particle that can remove some energy from the reaction.

The formation of plant material yields as the byproduct Oxygen.

$6H_2O_{(l)} + 6CO_{2(g)} + hv \rightarrow 6O_{2(g)} + C_6H_{12}O_{6(s)}$

At present most O_2 on earth is stored as oxides in the earth's crust (Fe_2O_3, Al_2O_3 or as Ca or $MgCO_3$, etc).

What did the earth's atmosphere start like?
How did it develop (A hypothesis).

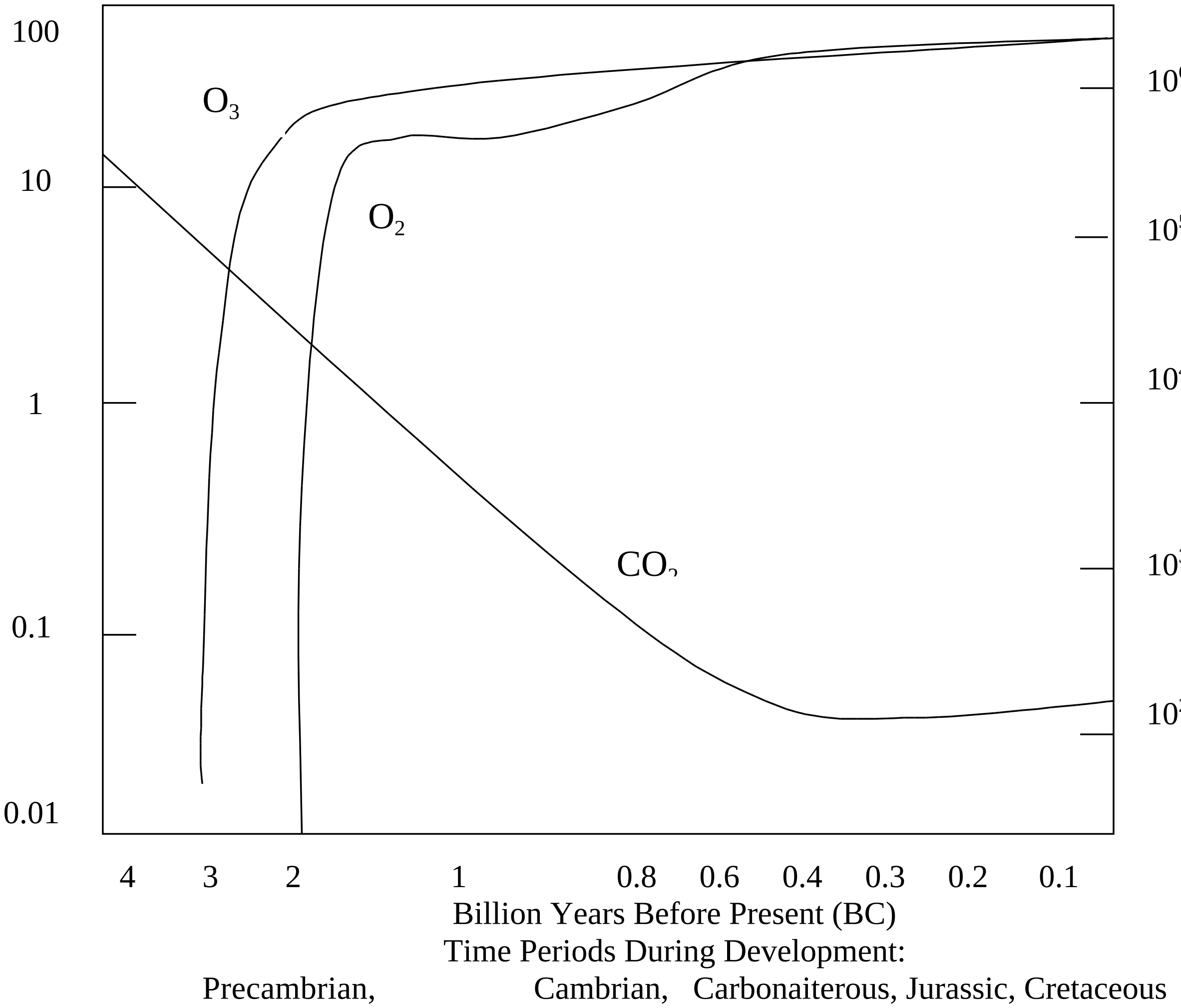


Figure: Schematic diagram showing predictions of the evolution of oxygen, Ozoone and carbon dioxide to present atmosphereic levels (PAL).

Left Scale Ground-Level O2 Concentration or O3 Concentration Abundance (% PAL)
Right Scale Ground-Level CO2 Concentration (% PAL)

(Ref. Introduction to Atm. Chem. By Peter V. Hobbs, Cambridge Univ. Press. 2000)

The atmosphere most likely formed from degassing of the planet and then evolved through different stages of development.

The reservoirs now exist in the following spheres:

Atmosphere,	Biosphere,	Hydrosphere,	Crust,	Mantle,	Core
N	H	H	O	O	Fe
O	O	O	Si	Si	Ni
H	C	Cl	Al	Mg	C
Ar	N	Na	Fe	Fe	S
C	Ca	Mg	Mg/Ca	Al	Si

Atmosphere	5.2×10^{18} in no. of Kg of reservoirs
Biosphere	4.2×10^{15}
Hydrosphere	2.4×10^{21}
Crust	2.4×10^{22}
Mantle	4.0×10^{24}
Core	1.9×10^{24}

Estimate of inventory of carbon near the Earth's surface,
Units in Gigatoms (10^{15} g) of Carbon.

Sphere:	(10^{15} g) of Carbon
Biosphere:	
Marine	2-5
Terrestrial (land, plants)	600
Atmosphere (as CO2)	750
Ocean (as dissolved CO2)	38,000
Fossil Fuels	8,000
Shales	8,000,000
Carbonate rock	65,000,000

What is "Air"?

Air is a non-homogenous mixture of gases, solid particles, and liquids.

Air is characterized as an aerosol.

Gases and particles with small settling velocity that exhibit stability in a gravitational field.

Recall atmosphere layers	KM
Troposphere	0-17 kilometers (Sea Level ≤ 11 miles)
Stratosphere	17-50
Mesosphere	50-90
Ionosphere	90-100

<u>95% of the air by weight is contained in the Troposphere.</u>

The Troposphere is where we live and where all of our activity and most of our weather is compartmentalized.

5% of the air on earth is located in the:

Stratosphere
Mesosphere and
Ionosphere

Nominal Composition

Major Components (99%) in % by wt or fraction of total molecules*)

N_2	75.51% by w	(0.7808)
O_2	23.14%	(0.2095)
^{40}Ar	1.28%	(0.0093)
Water Vapor		(0.0004)

Minor Components

Carbon dioxide CO_2	355 ppm (parts per million**)
Ne	18
He	5
CH_4	2
Kr	1
H_2	0.5
N_2O	0.5
Xe	0.1

* Fractions of total molecules
** 355 ppm means that 355 of each 1 million particles is CO_2

Physical and Chemical Function of the Atmosphere

How it functions to provide energy and composition of equilibrium that are vital to life on our planet!

Evaluation through –

Charts, graphs and lists give some relevance of the following:

1. Residence times of some atmospheric gases

2. Mean Free Path of molecules and atoms

3. Energy consumption and distribution of incoming energy

4. Energy balance and incoming solar radiation

5. Redistribution of energy by the atmosphere
   - Water vapor
   - Wind
   - Evaporation and condensation

6. Homogeneity of the atmosphere

Ref. Introduction to Atmospheric Chemistry, Peter V. Hobbs, Cambridge University Press, 0-521-77143-9, 2000)
"The Greenhouse Effect, New Scientist, 22 October 1988, pg. 1-4.
Manhan, - Text -

The Atmospheric Pressure at a given height is given designated by P_h and are related by

$$P_h = P_0 e^{-\frac{Mgh}{RT}}$$

Where:
P_h is the atmospheric pressure at a given hight
P0 is the pressure at zero altitude or sea level
G is the acceleration of gravity (981 cm x sec^{-2} at sea level)
H is the altitude in cm
R is the gas constant (8.314 x 10^7 erg x deg^{-1} x $mole^{-1}$)
P_h units are cm-g-sec

Troposphere
(95% of the air molecules are in the Troposphere)

Above the Troposphere
(5% of the air molecules and other ions are in the remaining upper atmosphere)

Energy Balance – the Greenhouse Effect

What is the greenhouse effect?

Like glass in a greenhouse or in your car in the sun

Earth maintains its temperature because of its atmosphere.
Between 0 °C and < 100 °C, average about 15 °C .

Why?

The moon is at the same place in the solar system and it is at an average of -18 °C (0°F), with extremes of -150 °C to +100° C

Average temperature of Earth is 15 °C (59 °F)

<u>What wavelengths are involved?</u>
The Sun surface temperature is 6000°C and radiates primarily in the visible region.
The sun is our only source of energy.
The Sun transmits ~ 86 % of this energy at (0.4 to 0.7 µm (micrometers) (400-700 nm), Visible Light with a maximum at 0.5 µm.

Energy as radiation can travel through the vacuum of space to contact the Earth.

The radiation from the sun includes 3 regions Visible, ultra-violet and infra-red light.

All of the Visible and small parts of the UV and IR

86% Transmitted as The Visible Light Spectrum. [0.4 µm blue and 0.7 µm red]
~7 % is transmitted at < 0.4 µm or as ultraviolet (UV).
~7 % is transmitted at > 0.7µm or as Infrared (IR).

Light from Sun enters Earth as

- Visible (86%, VIS), (0.4 to 0.7 µm)
- Ultra-Violet (7%, UV) (0.1 to 0.4 µm)
- Infra-Red (7%, IR) (0.7 to 50 µm)

An equilibrium is reached between the energy kept and re-radiated back to space.

To accomplish this the Visible light is transformed into IR as it strikes the earth and re-radiated.

A portion of the re-radiated IR is kept by

- Water,
- Carbon dioxide
- Ozone
- Methane
- Nitrous Oxides
- And other Greenhouse gasses

Greenhouse Effect (Cont.)

Overview:
"Sunlight is degraded and shifted from UV-VIS on interaction with Earth to IR and spectral differences cause absorption of IR by atmospheric components the shift in the components changes the % of IR retained in the atmosphere"

<u>How are these conversions accomplished?</u>
Radiation depends on the temperature of the object doing the radiation. The Sun {surface} temperature is 6000 °C yielding radiation primarily in the visible radiation band.

Earth is 10-30 °C and radiates at 4 to 100 µm in the IR band {4,000 to 100,000 nm}.

H_2O vapor strongly absorbs radiation 4-7 µm
{4,000 nm to 7,000 nm }

CO_2 gas strongly absorbs radiation 13 - 19 µm {13,000 – 19,000 nm }

About 70 % of the IR radiation does escape the earth, but about 30 % is absorbed by CO_2, H_2O (and other greenhouse gases) and warms the troposphere and the earth's surface. Greenhouse gasses radiate IR in all directions to earth & to space.

An <u>equilibrium</u> is established which accounts for the earth's surface temperature this is the greenhouse effect.

The greenhouse effect is necessary. It is an increase in absorbency and a shift of this equilibrium that may increase the average temperature of the earth's surface.

Remember Le Chatelier's principle and shifting equilibrium 30/70

Major Greenhouse Gases and Their Characteristics
(other than water)

GAS	LIFE SPAN (years)	GREENHOUSE EFFICIENCY (CO_2 =1)	GREENHOUSE CONTRIBUTION (%)	SOURCES OF GAS
Carbon Dioxide (fossil fuels and biological)	3-4	1	57	coal, oil, natural gas, deforestation
CFC's	75-111	15,000	25	foams, aerosols, refrigerants, solvents
Methane	11	25	12	wetlands, rice, fossil fuels, livestock
Nitrous Oxide	150	230	6	fossil fuels, fertilizers, deforestation

See absorption of molecules in the IR region *charts*.

Absorption of air (water vapor) is week in IR region between
7 - 8.5 µm and
11 – 14 µm

Very little absorption occurs between
8.5 – 11 µm

Carbon Dioxide absorbs strongly between 12 – 16.3 µm

CO_2 occupies a critical space in the IR absorption region.

Reflected readiation:

A portion reflected by clouds, water surfaces, ice is called the "**albedo**".

The albedo of freshly fallen snow is 90%.
The albedo of plowed earth and black-top is 2 to 1%.

Energy and Heat are moved around in the Troposphere by air circulation and water evaporation.

Energy exchanged as the heat of vaporization or heat of fusion of water is called **"latent heat"**

Water vapor plays a significant role in moving heat and is a significant part of weather.

Weather:

Horizontal air = (wind)
Vertical air = (air currents)
Convection columns establish patterns on the Earth's surface establishing patterns of convection columns as described in weather patterns known as **Hadley Cells.**

Hadley Cells move based on the **Coriolis** effect (caused by the rotation of the earth)

Fronts are masses of air differing in Temperature, density and water content.

These moving fronts contact one another.

The energy in the Hadley Cells and Fronts are due to Solar radiation and Latent heat from water. Note Solar radiation is a maximum in the Equatorial regions and causes initial updrafts. **See Hadley Cells Diagram**

Clouds:

The water content of air is **"humidity"**.

“Relative humidity” is the % water in the air as compared to the maximum amount of water the air can hold at that temperature.

The **“dew point”** is the temperature below which the water in the air will condense if it is cooled below that point if there are condensation nuclei present.

Clouds are made up of liquid water in aerosol droplet form 0.04 mm diameter (not larger than 0.2 mm). (rain 0.5 to 4.0 mm).

Inversions and Air Pollution

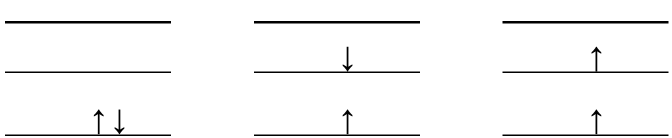
Air temperature usually increases the closer to the Earth’s surface you are. However when air is warmer above the Earth’s surface the air movement stops and a stable non-moving air mass results. This is known as a “Temperature Inversion”.

These stall air permitting pollution build up and are due to several mechanisms such as:
cold air over-riding a cold air mass,
Cool air flowing at night into vallies (Radiation inversion)
Etc.

Photochemical Processes:

The absorption of sunlight by airborne molecular species and its chemistry is the origin of Photochemical Processes.

Electrons are promoted to empty orbitals and either retain their spin or reverse their spin producing excited state molecules that are very reactive.



↑↓	↑↓	↑↓
Ground State	Singlet State	Triplet State

Excited states are energized and chemically much more reactive.

These “energized” species now undergo a reaction to reduce the energy. If UV or VIS absorption was involved one of the following reactions will result.

Physical Quenching

$NO_2^* + M \rightarrow NO_2 + M$(high transnational energy)

$O_2^* + M \rightarrow O_2 + M$(high transnational energy)

Dissociation

$NO_2^* \rightarrow NO + O$

$O_2^* \rightarrow O + O$

Direct Reactions with other species

$O_2^* \; O_3 \rightarrow 2O_2 + O$

$O^* + H_2O$ ¾¾¾→ 2 OH• (hydroxyl radical production)

Luminescence or Fluorescence or Phosphorescence

$NO_2^* \rightarrow NO_2 + hv$

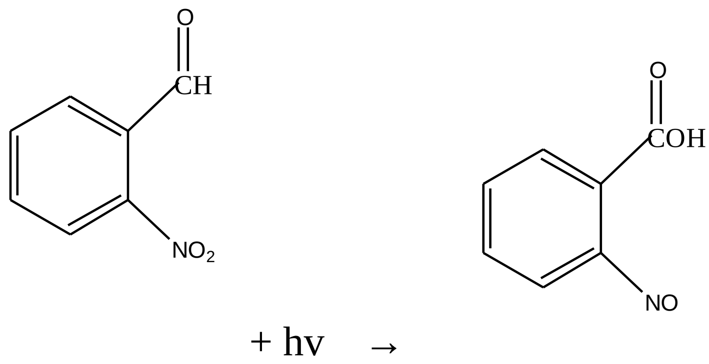
Intermolecular energy transfer

$O_2^* \; Na \rightarrow O_2 + Na^*$

Intramolecular transfer

$XY^* \rightarrow XY^*$ Where the second is another excited state

Spontaneous isomerization (internal molecular modifications



Photoionization (ion production)

$N_2^* \rightarrow N_2^+ + e^-$

These reactions usually require hv to be UV or VIS but not IR as it is less energetic and usually initiates vibrational energy releases only (energy released as heat).
These are the initiators of many photochemical reactions

Ions and Radicals in the Atmosphere

The Mean Free Path of molecules is the distance before the molecule or species hits another atom or molecule. In the Troposphere it is as high a 10^{-7} meters.

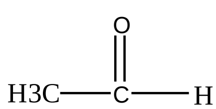
In the Stratosphere it can be 10^{-1} to 10^{1} meters.

Ions, electrons, free radicals, charged particles all exist for long periods of times and in high concentrations.

The low pressures of the upper belts stabilize and make possible the accumulation of these existence these ions.

Free Radicals

The presence of an unpaired electron produced in the same way by solar radiation produces a free radical, for example:



+ hv → H3C• + •CH=O

These are very reactive species and initiate many additional important ractions

Free Radicals

One of the most important Free Radicals is the Hydroxide Reacical.

The Hydroxyl Radical

Natural Troposphere atmospheric cleansers.

The single most important intermediate reactant in photochemical processes.

The average concentration of hydroxyl radical is 2 x10^5 to 1x10^6 radicals per cm^3

Fromed by

$$H_2O(g) \xrightarrow{\text{sunlight}} H(g) + OH(g)\bullet$$

(hydroxyl radical)

or

$$O^* + H_2O \longrightarrow 2\ OH\bullet \text{ (hydroxyl radical)}$$

Carbon monoxide is converted to carbon dioxide

$$CO(g) + HO(g)\bullet \longrightarrow CO_2(g) + H(g)$$

=

VOCs are removed by hydroxyl radical

$$CH_4(g) + HO(g)\bullet \longrightarrow H_3C\bullet(g) + H_2O$$

The hydroxyl radical is the Tropospheric cleansing agent.

Formation of Hydroperoxyl radical

H + O_2 ¾¾¾¾¾→ HOO•(g) (Hydroperoxyl radical)

and

HCHO + hv ¾¾¾¾¾→ H + HOC•

HOC• + O2 ¾¾¾¾¾→ HOO•(g) + CO(g)

Termination reactions

HOO•(g) + HO(g) • ¾¾¾¾¾→ H_2O(g) + O_2

HOO•(g) + HOO•(g) ¾¾¾¾¾→ H_2O_2(g) + O_2

Regeneration of Hydroxyl radical

HOO•(g) + NO(g) ¾¾¾¾¾→ NO_2(g) + HO(g) •

HOO•(g) + O_3(g) ¾¾¾¾¾→ $2O_2$(g) + HO(g) •

Transformation from primary to secondary molecules in the atmosphere

Acid-base atmospheric reactions:

Transformation to secondary pollutants also takes place

$CO_{2(g)}$ + water ¾¾→ $CO_{2(aq)}$

$CO_{2(aq)}$ + H_2O ¾¾→ H_2CO_3 ¾¾→ H^+ + HCO_3^-

$SO_{2(g)}$ + H_2O ¾¾→ H^+ + HSO_3^-

$NO_{2(aq)}$ + H_2O ¾¾→ HNO_3 + H^+

Biodegradation forms ammonia
$NO_{3\ (aq)}^-$ + 2{CH_2O} + H ¾→ $NH_{3(g)}$ + $2CO_2$ + H_2O
(biomass)
The only water soluble base in the atmosphere
Ammonia can neutralize acid in the air.
Neutralization of Nitric Acid

$NH_{3(aq)}$ + $HNO_{3(aq)}$ ¾→ $NH_4NO_{2(aq)}$
Neutralization of Sulfuric Acid
$NH_{3(aq)}$ + $H_2SO_{4(aq)}$ ¾→ $NH_4HSO_{4(aq)}$

Reactions of Oxygen in the atmosphere

Oxygen cycles in the atmosphere are extremely important in many areas.

Reactions of Tropospheric Oxygen

CH_4 (natural gas) + $2O_2$ ¾¾→ $CO_2(g)$ + $2H_2O(g)$

Formation of Ozone in the Stratosphere

Keys Points; 1. Mean Free Path, 2. 95% more UV light

Photodissociation Reaction

Step a

Ultraviolet

$O_2(g)$ ¾¾¾¾¾¾→ $2O(g)$ (or O + O)

120 Kcal/Mol

Step b 240 - 300 nm

Ultraviolet

$O(g)$ + $O_2(g)$ + $M(g)$ ¾¾¾¾¾¾→ $O_3(g)$ + $M(g)$

where M(g) is another molecule such as O_2 or N_2 to carry away thermal energy (Unchanged chemically)

Step c < 308 nm

Ultraviolet

$O_3(g)$ ¾¾¾¾¾¾→ $O_2(g)$ + $O(g)^*$ 636, 630, 558 nm

26 Kcal/mol

Back to Step b again

Absorbs UV light O_3 200 - 360 nm

Other Oxygen reactions

Detoxification

CO from volcanos + O_2 ¾¾¾¾¾→ CO_2

Oxygen consumed as primary reagents in:

1. respiration for animals

$\{CH_2O\}$ O_2 ¾¾→ $CO_2 + 2H_2O$

2. in combustion of carbon based fuels

CH_4 (natural gas or fuel) + $2O_2$ ¾¾→ $CO_2(g) + 2H_2O(g)$

3. Photosynthesis

$CO_2 + H_2O + hv$ ¾¾→ $\{CH_2O\} + O_2$

4. Oxygen in sediment

$Ca^{2+} + CO_3^{2-}$ ¾¾→ $CaCO_{3(s)}$

Stratospheric and Tropospheric Ozone Revisited <u>Later</u>

Photochemical Nitrogen Reactions in the Atmosphere - At altitudes above 100 Km

N2 + hv ¾¾→ N + N

Other reactions that produce mono-atomic

$N_2^+ + O$ ¾¾→ $NO^+ + N$

$NO^+ + e^-$ ¾¾→ $N + O$

$O^+ + N_2$ ¾¾→ $NO^+ + N$

$N_2 + hv$ ¾¾→ $N_2 + N$

$NO + hv$ ¾¾→ $NO^+ + e^-$ (Ionosphere)

In the Ionosphere (upto 10^3 mean free path)

$N_2 + hv$ (cosmic ray) ¾¾→ $N_2^+ + e^-$

Key in photochemical smog

$NO_2 + hv$ ¾¾→ $NO + O$

Note:

Perspective on “Solar Energy”

If we could burn all the Coal, Oil, Natural Gas and All the trees on earth it would equal about 10 days worth of Solar energy that is captured by the Earth.

Burning fossil fuels at our current rate undoes the photosynthesis by oxidizing carbon at the rate of one year of fossil fuel use equals 1000 years of photosynthesis.

(source: NASA in a Video on Solar Energy, Worldscope Media “Solar Energy: Science in Action”)

Through The Haze:
Clarifying The Ground Level Ozone

"Scientific Basis of Good and Bad Ozone"

What is the Atmosphere?

Air is a **non-homogenous mixture** of gases, solid particles, and liquids.

Air is characterized as an **aerosol**.

Nominal Composition

Major Components (99%) in % by wt.

N_2	75.51% by w	(0.7808)
O_2	23.14%	(0.2095)
^{40}Ar	1.28%	(0.0093)
Water Vapor		(0.0004)

Minor Components

Carbon dioxide CO_2	325 ppm (parts per million)
Ne	18
He	5
CH_4	2
N_2O	0.5
Xe	0.1

** 325 ppm means that 325 of each 1 million particles is CO_2

The Atmosphere is Divided into Four Major Regions

Recall atmosphere layers

Troposphere		0-17, Km (≤ 11 mi.)	> -56°C
Stratosphere		17-50	> -2°C
Mesosphere		50-90	> -85°C
Ionosphere	(thermosphere)	90-100	

95% of the air by weight is contained in the Troposphere.

- A thermal barrier to prevent Tropospheric mixing with Stratosphere
- Good Ozone layer is in the stratosphere also acts as a thermocline to prevent mixing (notice chart of atmospheric temperature)
- The Sun drives reactions and with the atmosphere sets the Earth's temperature
- Earth maintains its temperature because of its atmosphere.
  Between 0 °C and < 100 °C

Why?

Positive Greenhouse Effect

An equilibrium is established which accounts for the earth's surface temperature, this is the positive greenhouse effect.

It is an increase in the shift of this equilibrium that will increase the average temperature of the earth's surface and result in a
negative greenhouse effect.

The Sun - The Atmospheric Energy Driver

All energy driven reactions on Earth are a result of large amounts of energy form the Sun.

The atmosphere has different temperatures at different heights due to chemical reactions driven by the Sun's energy of **~1 Kw/m^2/ day at surface** and

1,340 watts/m^2/ day in the upper atmosphere perpendicular to the Sun.

What wavelengths are involved with the conversion of energy?
The sun is our only source of energy. It transmits ~ 86 % of this energy at 400-700 nm (0.4 to 0.7 {µm} micrometers)
The visible light spectrum. [400 nm blue and 700 nm red]
~7 % is transmitted at < 400 nm or as ultraviolet (UV).
(remember O_3)
~7 % is transmitted at > 700 nm or as Infrared (IR).

Outdoor Air Pollutants

(Bold denotes sources involved in ground level ozone)
Sources and Types:

1. Carbon Oxides - Carbon Monoxide (CO), Carbon Dioxide (CO_2)

2. Sulfur Oxides - Sulfur Dioxides (SO_2) & Sulfur Trioxide (SO_3)
{contributor to ground level Ozone, (O_3)}

3. Nitrogen Oxides - Nitric Oxide (NO), Nitrogen Dioxide (NO_2), & Nitrous Oxide (N_2O)
{contributor to ground level Ozone, (O_3)}

4. Volatile Organic Compounds (VOCs) - Most organic compounds
Example: Methane (CH_4), Methanol (CH_3OH), Benzene (C_6H_6), Chlorofluorocarbons (CFCs), formaldehyde (CH_2O), Propane (C_3H_8).
{contributor to ground level Ozone, (O_3)}

5. Suspended Particulate Matter (SPM) - Solid and liquid particles both suspended in air. Example: dust, soot, pollen, asbestos, ash, conglomerates, soil, salts, etc.
{contributor to ground level Ozone, (O_3)}

6. Photochemical Oxidants - Ozone (O_3), Peroxide (H_2O_2), Complex interactions with VOCs and NOx. **<u>Photochemical reactions</u>**

7. Radioactive Isotopes - Radon - 222, Iodine - 131, Strontium - 90, Plutonium - 239, Potassium - 40,

8. Heat - Waste energy from fossil fuels; most energy sources and uses produce waste energy as heat, Ex.: cars, power, plants,

9. Noise - A byproduct of energy: airplanes, cars, industry, lawn mowers, mechanical, radios, wind, electrical power line discharge, etc.

Outdoor Air Pollutants

Figure 22-2 (Primary Pollutants)

Primary Pollutants Anthropogenic (Directly Emitted)

CO	Carbon Monoxide
CO_2	Carbon Dioxide
NO	Nitrogen Monoxide (Nitric Oxide)
NO_2	Nitrogen Dioxide
SO_2	Sulfur Dioxide
VOC	Volatile Organic Carbon

SPM, Suspended Particulates Matter
or PM-10

Secondary Pollutants (Transformed in the environment)

SO_3	Sulfite (Sulfur Trioxide)
HNO_3	Nitric Acid
H_2SO_4	Sulfuric Acid
H_2O_2	Hydrogen Peroxide
O_3	Tropospheric (not Stratospheric)

Methane (CH_4) {a primary VOC}, Contributor to Photochemical Smog and Greenhouse Gas Emissions from <u>Anthropogenic</u> Sources

World	270,000,000 metric tons

By World Region

Asia	130,000,000
North and Central America	45,000,000
Europe	26,000,000
USSR	34,000,000
Africa	19,000,000
South America	18,000,000
Oceannia (Australia, Fiji, etc.)	6,200,000

<u>Outdoor Air Pollutants</u>

Pollution Emissions

Anthropogenic compositional alterations to the atmosphere:

From 1989 Compilation (from United Nations Reference)

Emissions of Chlorofluorocarbons (CFCs)

World	580,000 metric tons

By World Region

Asia	140,000
North and Central America	150,000
Europe	180,000
USSR	67,000
Africa	16,000
South America	15,000
Oceannia (Australia, Fiji, etc.)	9,000

Ozone depletion is the main effect, remember on average each Cl atom destroys 100,000 (10^5) O_3 molecules (4 per molecule of CFC).

Pollutant Trends

From 1900 to 1970 the U.S. had a dramatic increases in some pollutants

NO_x	690%
VOC	260%
SO_2	210%

From 1986-1995 U.S. concentrations of key pollutants decreased by

NO_x	14%	
Ozone	6%	
PM-10	22%	(Particulate Matter, <10 µm)
SO_2	37%	
lead	78%	
CO	37%	

From 1986-1995 U.S. Emissions of key pollutants decreased by

NO_x	3%	
VOC	9%	
PM-10	17%	(Particulate Matter, <10 µm)
SO_2	18%	
lead	32%	
CO	16%	

While you can measure Troposhperic Ozone, it is not (generally) a direct emission but is the result of reactions catalyzed or caused by other pollutants.

Smog & Acid Deposition Concentration

Photochemical smog is the interaction of electromagnetic radiation from the Sun and Primary Pollutants to form photochemical smog.

Table of Atmospheric Trace Gases in Dry Air Near Ground Level

Gas or Species	Volume Percent	Major Source	Process for Removal
CH_4	$1.6x10^{-4}$	Biogenic	Photochemical
CO	$\sim 1.2x10^{-5}$	Photochemical, Anthro.	Photochemical
N_2O	$3x10^{-5}$	Biogenic	Photochemical
NO & NO_2	$10^{-10}-10^{-6}$	Photochemical, Lightning, Antho.	Photochemical
HNO_3	$10^{-9}-10^{-7}$	Photochemical	Precipitation, rain
NH_3	$10^{-8}-10^{-7}$	Biogenic	Photochemical, rain
H_2	5x10-5	Biogenic, Photochem.	Photochemical
H_2O_2	$10^{-8}-10^{-6}$	Photochemical	Precipitation
HO•	$10^{-13}-10^{-10}$	Photochemical	Photochemical
HO_2•	$10^{-11}-10^{-9}$	Photochemical	Photochemical
H_2CO	$10^{-8}-10^{-7}$	Photochemical	Photochemical
SO_2	$\sim 2x10^{-8}$	Anthropogenic, Photochem., volcanic	Photochemical
CCl_2F_2	$2.8x10^{-5}$	Anthropogenic	Photochemical
H_3CCCl_3	$\sim 1 x 10^{-8}$	Anthropogenic	Photochemical

Good Ozone

Hypotheses of CFC Effect on Ozone Presented

The possible depletion of Ozone by Anthropogenic gases was first proposed by H. S. Johnson of the U. of CA, Berkeley in the 1960s.

Effect on ozone of CFCs was theorized in 1974 by two chemists, Sherwood Rowland and Mario Molina from the University of California, Irvine.
(Noble Prize for this contribution)

Uses of CFCs

Coolants in air conditioning and refrigerating
Cleaning of electrical parts
Fumigants for granaries and cargo holds
Bubbles in polystyrene plastic foam packaging & insulation (DuPont - Styrofoam)
Propellants in aerosol spray cans (not in US since 1978s)

Demographics

By year 2000, 75 countries phased out all CFC use.

MDCs (industrialized countries) use 84% of CFCs
US is 25% of global consumption of CFCs

Vehicle air conditioners account for about 3/4 of US CFC emissions

Why is Cl from CFCs so devastating to Stratospheric Ozone?

How long does a CFC last in the atmosphere?
Over 50-200 years.

Freons without any hydrogen atoms have an average life time of 100 years in the atmosphere.

Time is needed to transcend the Troposphere thermal barrier and get into the Stratosphere reach the Ozone layer and enter it.

One Cl atom can convert 10,000 to 100,000 O_3
to O_2 and O.

Hydrogen containing CFCs only last a relatively short time and probably never make it to the Stratosphere. CH_3CCl_3 and $CHClF_2$ only last 6-7 years. This is the change in CFC formulation.

What is the difference between hydrogen containing (H)CFCs and halogen saturated CFCs?

Method of destruction in Troposphere.

$$CHClF_2 + OH\bullet \longrightarrow H_2O + CClF_2\bullet$$

The hydroxyl radical is the natural air cleanser of the Troposphere and can work on (H)CFCs (not CFCs).

<u>Mechanism of Ozone Decomposition by CFCs</u>

CFC travels just above the O3 layer in the Stratosphere.

Ultraviolet - UV

CF_2Cl_2 ¾¾¾¾¾¾→ $CF_2Cl + Cl$ <u>Eq-1</u>

It then drifts back into the lower Stratosphere where O_3 is in high concentrations

$Cl + O_3$ ¾¾¾¾¾¾→ $ClO + O_2$ <u>Eq-2</u>

Direct destruction of Ozone

$ClO + O$ ¾¾¾¾¾¾→ $Cl + O_2$ <u>Eq-3</u>

Short circuit of Step a and c of Ozone UV protection cycle.

Life of Cl atom in atmosphere is 1-2 years.

In 1-2 years, one Cl atom will repeat Eq-2
100,000 times.

One Cl atom destroys ~ 10^5 the # of O_3 atoms.
(A very efficient reaction mechanism)

Why Ozone absorb UV energy?

Ozone is a resonance structure.

$$P_h = P_0 e^{-\frac{Mgh}{RT}}$$

This resonance gives it the unique UV energy (< 308 nm) absorbing property.

Photochemical Formation of Ozone in the Stratosphere and Its Interaction with UV light

Photodissociation Reaction

Step a

Ultraviolet

$O_2(g)$ ¾¾¾¾¾→ $2O(g)$

120 Kcal/Mol

Step b

240 - 300 nm
Ultraviolet

$O(g) + O_2(g) + M(g)$ ¾¾¾¾¾→ $O_3(g) + M(g)$

where $M(g)$ is another molecule such as O_2 or N_2 or particle to carry away thermal energy
(unchanged chemically)

How Ozone absorbs ultraviolet light

Step c

< 308 nm
Ultraviolet

$O_3(g)$ ¾¾¾¾¾→ $O_2(g) + O(g)^*$ + 636, 630, 558 nm

26 Kcal/mol (yellow to red light)

Back to Step b again to be regenerated if no pollutants are present

<u>Photochemical Formation of Ozone in the Troposphere and Its Interaction with UV light, VOC and NOx</u>

Primarily a Summer time phenomena in U.S. due to heat needed in the reactions.

Tropical climates have the potential in all seasons.

NOx + VOC + <u>Heat</u> + Sunlight ¾¾¾→ Ozone

Specific important reactions:

<u>Step a:</u> NO_2 decomposes to produce oxygen atoms

NO_2 + Sunlight (<430 nm) ¾¾¾→ O + NO

(NO2 must be regenerated)

<u>Step b:</u> oxygen atom combines with oxygen molecule to form ozone with heat carried away

O + O_2 (+N_2, O_2, M) ¾¾¾→ O_3 (+N_2, O_2, M)

Other Important Ozone building step and intermediates:

(Formation of hydroxyl radical and it cleansing effect)

Ozone participates in keeping the reaction going

O_3 + light (<320 nm) ¾¾¾→ O*(O* Excited) + O_2

Ozone creates hydroxyl radicals

O* + H_2O ¾¾¾→ 2 OH• (hydroxyl radical)

Hydroxyl radical creates an intermidiate from VOCs

OH• + RH (VOC) (+ O_2) ¾¾¾→ H_2O + RO_2

VOCs regenerate NO_2

RO_2 + NO ¾¾¾→ RO + NO_2 (back to Step a:)

Tropospheric Ozone requires

NO_2,

VOCs,

water,

Sunlight, and

heat

to reach high levels.

Thus NO_2 is the main ingredient. However, NO_2 must be regenerated by something other than Ozone itself to increase the Ozone concentration above that of NO and this is where the VOCs through the hydroxyl radical (OH•) do their part.

The following reaction is minimized by the regeneration of NO_2 by the VOCs and water and Ozone.

$$NO + O_3 \longrightarrow NO_2 + O_2$$

Thus formation of the hydroxyl radicals generate oxidized VOCs (RO_2) that regenerate NO_2 and prevent NO destruction of Ozone which prevent an Ozone concentration higher than that of NO_2.

Thus Ozone buildup and high concentrations depends on having all of the following factors

NO_2, H_2O, VOC, heat and Sunlight

to reach high Tropospheric level.

Why is Tropospheric chemistry radically different from Stratospheric chemistry?

- The mean free path for a reactive molecule is 10^4 to 10^9 different in these two regions of the atmosphere. Mean free path in the Troposphere is only 1×10^{-6} cm while at 500 km it can be as long as 1×10^6 cm a 10^{12} difference.

- < 5% of the UV light is available in the Troposphere due to the Ozone in the Stratosphere absorbing it and changing the Sunlight's spectrum.

- Water vapor exists in liquid form in the Troposphere to promote chemical reactions which do not occur in solid phase ice in the Stratosphere.

- Both NOx and VOCs are not significantly present in the Stratosphere as they are destroyed by the hydroxyl radical in the Troposphere.

The Hydroxyl Radical

Natural Troposphere atmospheric cleansers.

The single most important intermediate reactant in photochemical processes

sunlight

$H_2O(g)$ ¾¾¾¾¾→ $H(g) + OH(g)$ •

or

$O^* + H_2O$ ¾¾¾→ 2 OH• (hydroxyl radical)

Carbon monoxide is converted to carbon dioxide

$CO(g) + HO(g)$ • ¾¾¾¾¾→ $CO_2(g) + H(g)$

VOCs are removed by hydroxyl radical

$CH_4(g) + HO(g)$ • ¾¾¾¾¾→ H_3C•$(g) + H_2O$

Summary

Increases in NOx and VOC concentration on hot days (due to Sunlight) when water vapor is high the Sunlight drives the reactions that produce the O_3 level due to a complex series of reactions.

These reactions in general do not occur in the Stratosphere because NOx and VOCs do not persist (they are not stable enough) to migrate to this atmospheric level.

Since NOx and VOC can be transported they can contribute to O_3 concentrations in other locations where water and Sunlight find them on a warm Summer day.

What can we reduce or eliminate to reduce Ozone?

Agent or Contributor	**Reduction/Elimination**
Sunlight	No
Water vapor	No
Heat	No
Inversions	No
VOCs	Some
NOx	Some
Intermediates (ex. OH•)	No
Air Movement	No

End

Notes:

1. Many graphics to be integrated
2. CD of graphics

Do not use below this point.!!!

Storage

Electrical discharge:

$$3O_2(g) \xrightarrow{\text{Electrical Discharge}} 2O_3(g)$$

Blue liquid with distinct odor

<u>Why is there an Ozone hole over Antarctic and a similar effect over the Arctic?</u>

Catalysis

Ice crystals absorb CFCs and provide a surface for Ozone molecule interaction (catalyst effect) in effect speeding up the reaction.