## Some of the more abundant “variable” trace gases:

| Species | Mixing ratio |
|---|---|
| Water vapor ($H_2O$) | 4% (tropics) - 0.00001% (South Pole) |
| Carbon dioxide ($CO_2$) | 380 ppmv (increasing ~0.4% per year due to fossil fuel burning) |
| Methane ($CH_4$) | 2 ppmv |
| Hydrogen ($H_2$) | 0.6 ppmv |
| Ozone ($O_3$) | 0.4 ppmv |
| Nitrous oxide ($N_2O$) | 0.3 ppmv |
| Carbon monoxide (CO) | 0.09 ppmv (90 ppbv) |
| Fluorocarbon-12 ($CF_2C_{12}$) | 0.0005 ppbv (0.5 pptv) |

## Carbon Dioxide Mixing Ratio

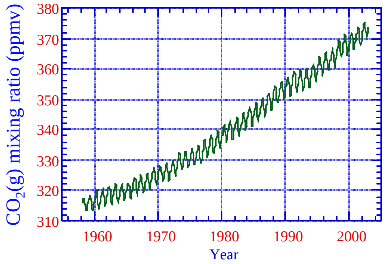


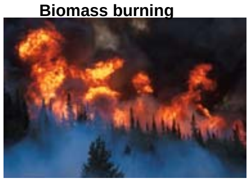
Figure 3.11

## Main sources of methane ($CH_4$)

**Termites**

**Rice Paddies**

**Biomass burning**



**Wetlands**

**Ruminants**

**Natural Gas Leakage**

## Change in $CH_4$(g) Mixing Ratio

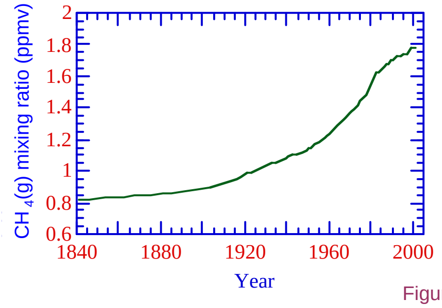


Figure 12.7

## Ozone ($O_3$) non-attainment areas

Federal 8-hour ozone standard: 0.08 ppmv averaged over 8 hours
(recently changed to 0.075 ppmv)

Source: US EPA, Office of Air and Radiation, AQS Database

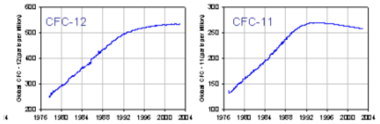
Thursday, March 27, 2008

## Chloroflourocarbons (CFCs)

**Refrigeration**

**Propellant**

**Trends in atmospheric CFC concentrations**



## Thomas Midgley (1889-1944)

Edgar Fahs Smith Collection, U. Penn. Library

Invented leaded gasoline and CFCs

## Thomas Midgley

- 1916: Joined Dayton Eng. Laboratory Companies (DELCO)
- 1919: DELCO main research lab for General Motors (GM)
- 1921: Invented leaded gasoline, which he named Ethyl
  Lead reduced knock, increased power to vehicles
- 1923: VP of Ethyl Gas. Co., a GM and Standard Oil subsidiary
- 1923: Midgley suffered lead poisoning, but he defended lead:

  "The exhaust does not contain enough lead to worry about, but no one knows what legislation might come into existence fostered by competition and fanatical health cranks."

## Thomas Midgley

- 1923-5: 17 workers died, 149 injured due to lead poisoning
- 1924: 5 of the workers became suddenly insane from poisoning
- 1925: Despite working on ethanol/benzene blends, iron carbonyl alternatives, Midgley countered,

  "...tetraethyl lead is the only material available which can bring about these (antiknock) results, which are of vital importance to the continued economic use by the general public of all automotive equipment, and unless a grave and inescapable hazard exists in the manufacture of tetraethyl lead, its abandonment cannot be justified"

- 1924: Forced to step down as VP due to managerial problems
- 1924: Returned to research on synthetic rubber in Dayton for GM
- 1925: U.S. Surgeon General organized committee to investigate lead
  Observed drivers/garage workers did not experience poisoning
  --> “no grounds for prohibiting the use of Ethyl gasoline.”
  though cautioned that further studies should be carried out (they weren’t)

## Leaded Gasoline

- 1930s: 90 percent of vehicles leaded
- 1936: Federal Trade Commission issued a restraining order forbidding commercial criticism of tetraethyl lead:

  "...entirely safe to the health of (motorists) and to the public in general when used as a motor fuel, and is not a narcotic in its effect, a poisonous dope, or dangerous to the life or health of a customer, purchaser, user or the general public."

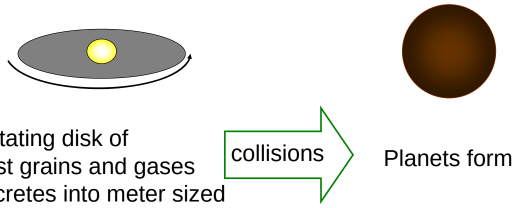
- 1959: U.S. Public Health Service

  "...regrettable that the investigations recommended by the Surgeon General's Committee in 1926 were not carried out by the Public Health Service."

- 1975: Catalytic converter invented; lead deactivates catalyst
- 1976: Lead regulated as criteria air pollutant in the U.S.
- Between 1970 and 1997, total lead emissions in the U.S. decreased from 219,000 to 4,000 tons per year.
- Today, largest sources of lead in the U.S. are from lead-ore crushing, lead-ore smelting, and battery manufacturing.

## How did it start?

Big Bang 15 billion years ago

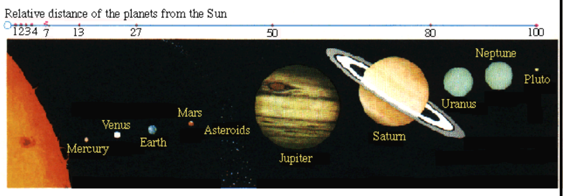


Rotating disk of dust grains and gases accretes into meter sized "planetesimals" around sun

collisions

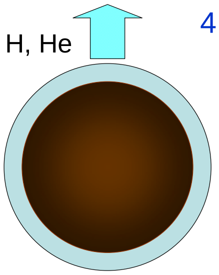
Planets form

## Our Solar System



4.5 billion years ago

## 1. Prebiotic atmosphere – 1st Stage



4.5 billion years ago

Atmosphere initially contains light gases, such as Hydrogen (H) and Helium (He), that can escape the atmosphere due to the solar wind and gravitational escape.

Earth looses its primordial atmosphere.

## 1. Prebiotic atmosphere – 2nd Stage

After a few hundred million years

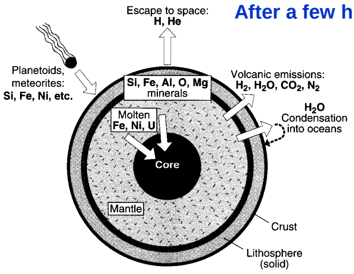


Figure 4.2 The differentiated structure of the early Earth and the principal geophysical and geochemical processes that contributed to the evolution of the atmosphere.

Densest elements (iron, nickel) form the core.

Atmosphere formed by outgassing of the interior (volcanoes) as well as bombardment by planetoids and meteorites.

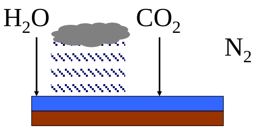
## 1. Prebiotic atmosphere – 2nd Stage

4.5 billion years ago

**Earth cools down…**

- Condensation of $H_2O$ → rain → oceans form
- $CO_2$ forms carbonates in the ocean → sedimentary rocks
- $N_2$ left as most abundant component in the atmosphere

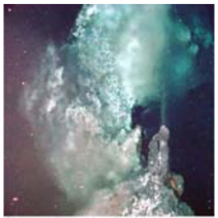
**No Oxygen!**



## 2. Biotic atmosphere before $O_2$

**Life develops** **3.5 billion yrs ago**

- No oxygen → no ozone layer → life not possible on surface
- Life can only develop in the ocean
  water protects from sun's ultraviolet radiation

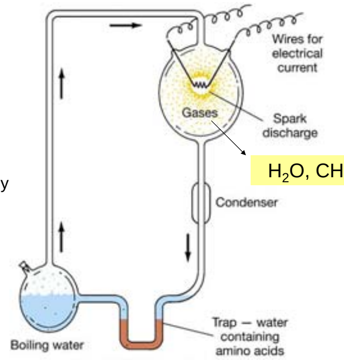


From NOAA: Erupting Volcanic Deep Ocean Vent

- Early microbes did not require oxygen (anaerobic)

## One theory on how life began…

Miller and Urey
1953



$H_2O, CH_4, NH_3, H_2$

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## Life without oxygen

**Anaerobic respiration**

Fermentation

$C_6H_{12}O_6$ → …→ 2 $C_2H_5OH$ + 2 $CO_2$
Sugar → alcohol + carbon dioxide

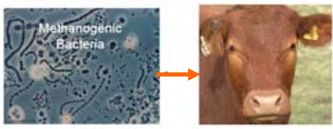
# Life without oxygen

**Anaerobic respiration**

Methanogenic bacteria converted hydrogen gas ($H_2$) into methane ($CH_4$)

$CO_2 + 4H_2 \rightarrow CH_4 + 2H_2O$

Source of $CH_4$ in the atmosphere



**Today: cows+wetlands**

---

# Life without oxygen

**Autotrophic photosynthesis**

2-3 billion yrs ago

Microscopic bacteria use sunlight as energy source (purple bacteria)

$$CO_2 + H_2S \xrightarrow{\text{sunlight}} \text{“}CH_2O\text{”} + SO_4^{2-}$$

Organic matter

Currently live near volcanic vents rich in $CO_2$ and $H_2S$

---

# 3. Oxygen Age

2-3 billion yrs ago

Oxygen producing photosynthesis develops

Microscopic algae (cyanobacteria, blue-green algae)

Organic matter

$CO_2 + H_2O$ ☀ $\rightarrow$ “$CH_2O$” + $O_2$

**Hot Spring in Yellowstone National Park**

Different colored photosynthetic cyanobacteria grow at in hot spring due to different temperatures.

## How was the ozone layer formed?

→ illuminate Oxygen ($O_2$) with UV-Radiation

$O_2$ + ultraviolet (UV) light → O + O

$O_2 + O \rightarrow O_3$

The stratospheric ozone layer formed, protecting the Earth's surface from harmful UV radiation, and allowing life on land to develop.

## Coevolution of life and the atmosphere

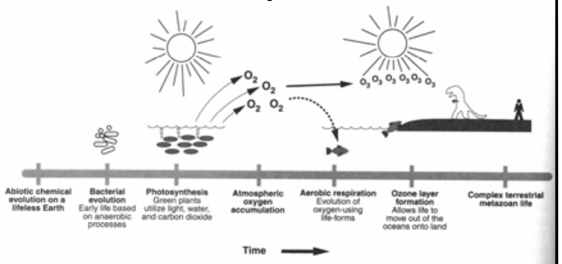


Figure 4.6 Milestones in the coevolution of life and the environment. Living organisms have become increasingly complex over time, and biological processes have had a major impact on the composition of the atmosphere. Evolution, in turn, has responded to changes in the atmosphere's composition by producing life-forms that could utilize atmospheric gases.

Figure 4.6

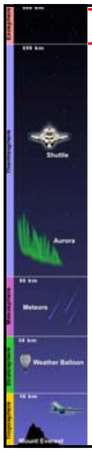
## The Atmosphere

Circumference
~40,000 km

Depth of Atmosphere: ~100 km

Depth of Habitable Part: ~5 km

Diameter: ~12,750 km
(~8,000mi)



Exosphere (lighter, faster molecules such as H that are moving in the right direction can escape the Earth's gravitational pull)

Mean free path in exosphere > 10 km

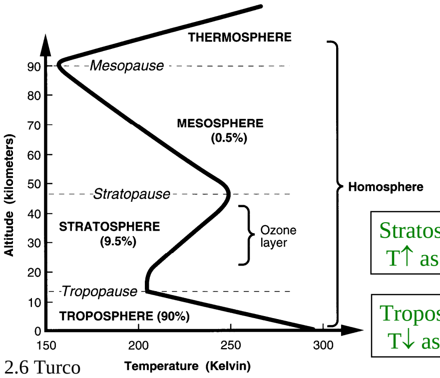
Thermosphere (collisions infrequent, heavier atoms and molecules settle to bottom of layer)

Mean free path in thermosphere > 1 km

Homosphere (well mixed because collisions are frequent: 78% $N_2$, 21% $O_2$)

Mean free path at surface = 1/10,000,000 = $10^{-7}$ km

## Vertical Temperature Profile



Stratosphere: T↑ as alt. ↑

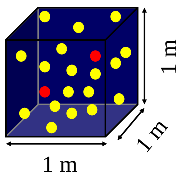
Troposphere: T↓ as alt. ↑

Figure 2.6 Turco

## Density

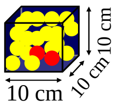
$$\text{Density:} \quad \rho = \frac{\text{Mass (i.e. g, kg)}}{\text{Volume (i.e. cm}^3\text{, m}^3\text{)}} = \frac{\text{M}}{\text{V}}$$

$$\rho = \frac{20 \times 100g}{1m^3} = 2000\frac{g}{m^3} = 2\frac{kg}{m^3}$$



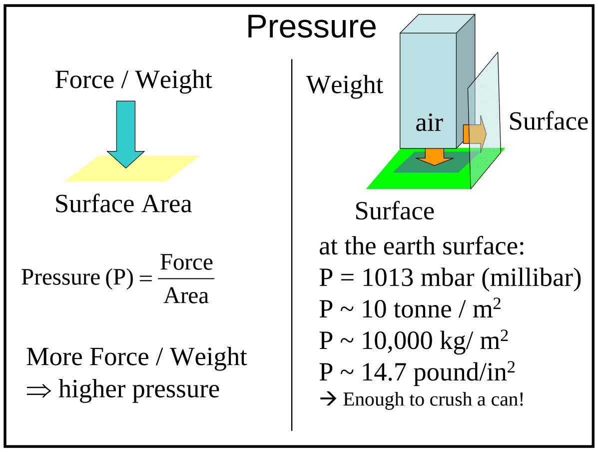
Each Tennis Ball: 100g

$$\rho = \frac{20 \times 100g}{10^{-3}m^3} = 2 \times 10^6\frac{g}{m^3} = 2 \times 10^3\frac{kg}{m^3}$$



**Density of air at surface:**
**1.3 kg/m$^3$ = 1.3 mg/cm$^3$**

ρ(water) = 1000 kg/m$^3$

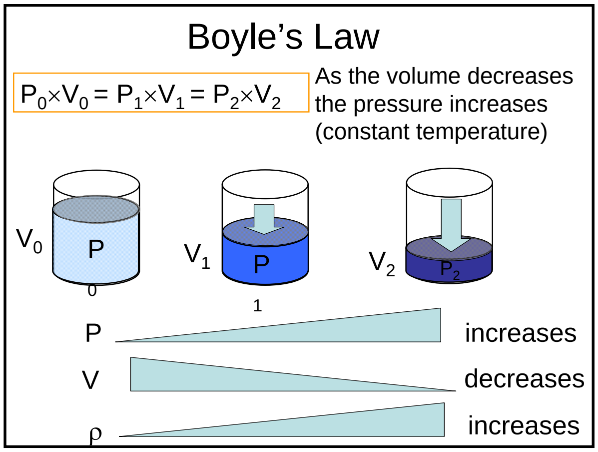


## Pressure

$$\text{Pressure (P)} = \frac{\text{Force}}{\text{Area}}$$

More Force / Weight
⇒ higher pressure

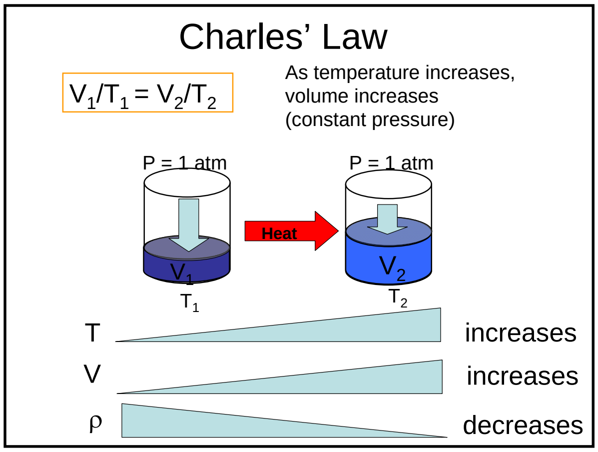
at the earth surface:
P = 1013 mbar (millibar)
P ~ 10 tonne / $m^2$
P ~ 10,000 kg/ $m^2$
P ~ 14.7 pound/$in^2$
→ Enough to crush a can!



## Boyle's Law

$P_0 \times V_0 = P_1 \times V_1 = P_2 \times V_2$

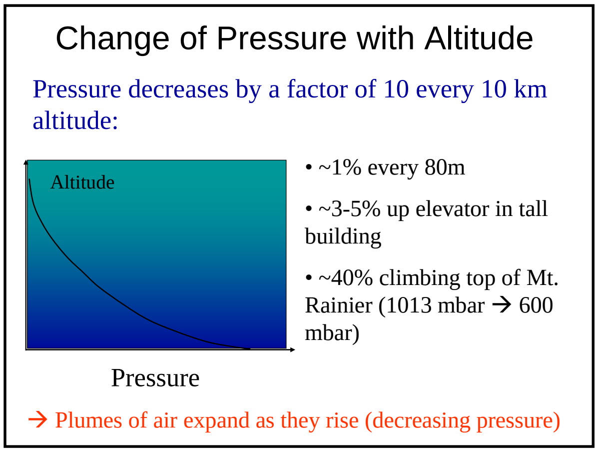
As the volume decreases
the pressure increases
(constant temperature)



## Charles' Law

$V_1/T_1 = V_2/T_2$

As temperature increases,
volume increases
(constant pressure)

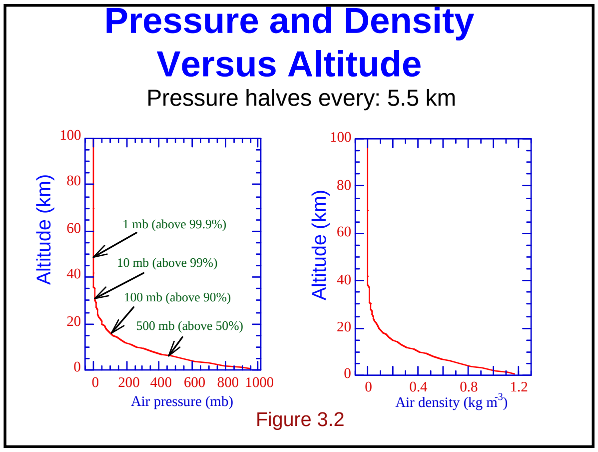


## Change of Pressure with Altitude

Pressure decreases by a factor of 10 every 10 km altitude:

- ~1% every 80m
- ~3-5% up elevator in tall building
- ~40% climbing top of Mt. Rainier (1013 mbar → 600 mbar)

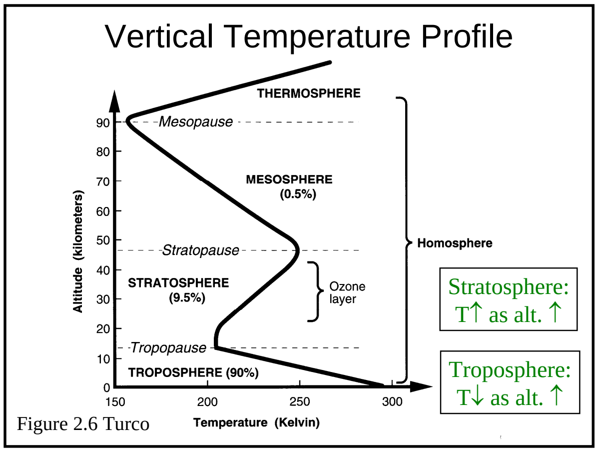
→ Plumes of air expand as they rise (decreasing pressure)



## Pressure and Density Versus Altitude

Pressure halves every: 5.5 km

Figure 3.2



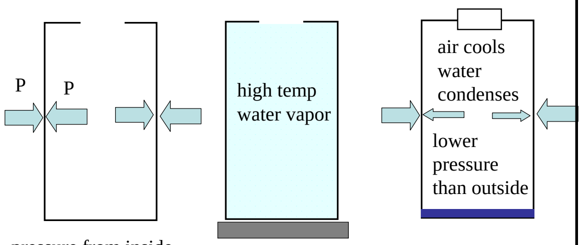
## Vertical Temperature Profile

Stratosphere: T↑ as alt. ↑

Troposphere: T↓ as alt. ↑

Figure 2.6 Turco

# The Can Experiment



P

P

high temp
water vapor

air cools
water
condenses

lower
pressure
than outside

pressure from inside
and outside balance
each other when can
open

heating

atmospheric
pressure crushes
can

# Can Crushing Video

http://www.atmos.washington.edu/~dargan/public.html

http://www.youtube.com/watch?v=8rLAxPe9Fis