# Measures of Atmospheric Composition

*<u>Required</u> Reading: Jacob Chapter 1*

Atmospheric Chemistry
ATOC-5151 / CHEM-5151
Spring 2013
Prof. Jose-Luis Jimenez

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## Business Items

- EVERYTHING should be linked from http://tinyurl.com/AtmChem (e.g. office hours)
- Will assign HW #2 later today:
  - http://tinyurl.com/hw-5151
- I keep adding clarifications to HW as people ask questions. Double-check the page before turning in the HW
- Clicker questions: I'll wait 45 s, or # seconds in question, or until all have answered, whichever is shorter
- Questions or items that need clarification?

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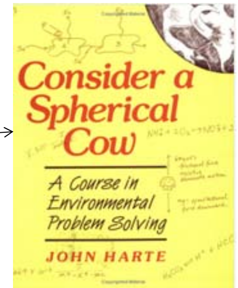
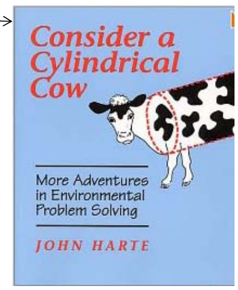
# Intro to order-of-magnitude calculations

- Often we need to get an estimate about whether something is important or negligible, or whether to quantities are comparable or not
- Correct "Order of magnitude":
  - Strictly: within a factor of 3.3
  - 3.3 or less → 1; 3.4 or more → 10
  - Approx. OoM: round each number
  - Formula: $10^{\text{Round}(\log(x))}$
- Correct within a "Factor of 2"
- Unknown quantities: quick search or most reasonable assumption
  - Neglect if variation is less than level of approximation
- Clicker Q: OoM of the mass of the Earth (Given Earth diameter = 12,740 km)
  - A: $10^{25}$ kg  B: $10^{20}$ kg  C: $10^{17}$ kg
  - D: $10^{-25}$ kg  E: I don't know

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# What are the components of the atmosphere?

- Gaseous envelope surrounding the Earth

- Mixture of gases, also contains suspended solid and liquid particles (*aerosols)*

  "Aerosol"= dispersed condensed phase suspended in a gas

We will use "species" as a generic term to describe a constituent of the atmosphere

**Aerosols are the "visible" components of the atmosphere**

**California fire plumes**

**Pollution off U.S. east coast**


**Dust off West Africa**


*From Jacob*

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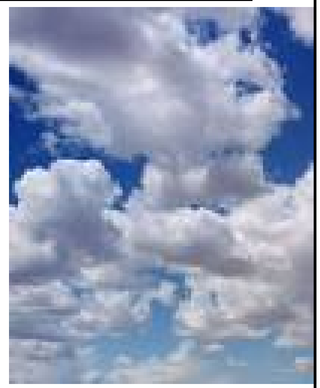
# What about Clouds?

- Clouds are made up of water droplets or ice crystals (1-100 mm)
- Much larger than typical aerosols (0.01-10 μm)
- They are technically aerosols but have unique properties and are in practice considered separately.



From Jacob

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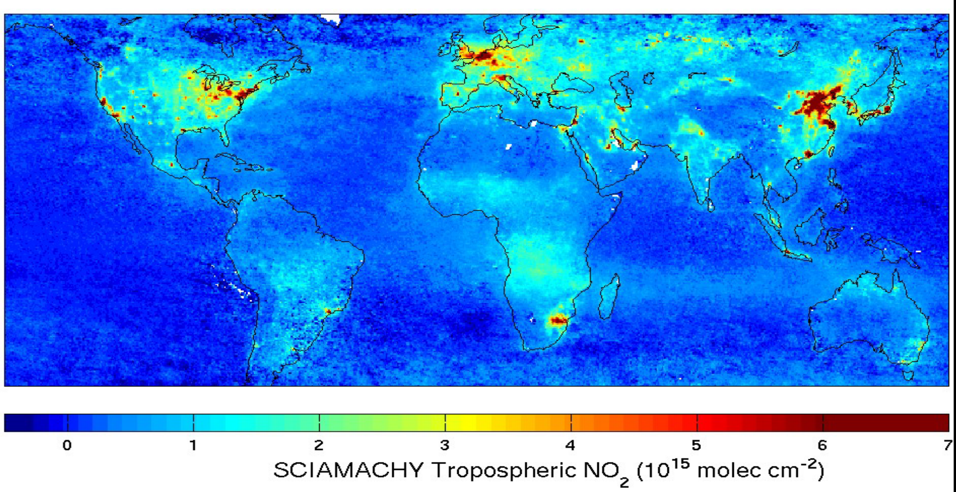
# Gases are visible in the IR or UV

$NO_2$ Columns Observed from the SCIAMACHY Satellite Instrument




From Jacob

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# Main Species & Mixing Ratio

**Table 1-1 Mixing ratios of gases in dry air**

| Gas | Mixing ratio (mol/mol) |
|---|---|
| Nitrogen ($N_2$) | 0.78 |
| Oxygen ($O_2$) | 0.21 |
| Argon (Ar) | 0.0093 |
| Carbon dioxide ($CO_2$) | $365 \times 10^{-6}$ |
| Neon (Ne) | $18 \times 10^{-6}$ |
| Ozone ($O_3$) | $0.01\text{-}10 \times 10^{-6}$ |
| Helium (He) | $5.2 \times 10^{-6}$ |
| Methane ($CH_4$) | $1.7 \times 10^{-6}$ |
| Krypton (Kr) | $1.1 \times 10^{-6}$ |
| Hydrogen ($H_2$) | $500 \times 10^{-9}$ |
| Nitrous oxide ($N_2O$) | $320 \times 10^{-9}$ |

"Trace" gases (Carbon dioxide through Nitrous oxide)

*Table From Jacob's book*

Air also contains variable $H_2O$ vapor ($10^{-6}$-$10^{-2}$ mol mol$^{-1}$) and aerosol & cloud particles

- Mixing ratio: moles of species/moles air
  - Constant when air expands or contracts, cools or warms: *robust measure*
- Units of mixing ratio:
  - Mol fraction = Volume fraction
  - ppm: 1 molec in $10^6$ = 1 μmol mol$^{-1}$
  - ppb: 1 molec in $10^9$ = 1 nmol mol$^{-1}$
  - ppt: 1 molec in $10^{12}$ = 1 pmol mol$^{-1}$
  - ppq: 1 molec in $10^{15}$ = 1 fmol mol$^{-1}$
  - Sometimes written ppmv, ppbv, pptv
  - xmol mol$^{-1}$ is proper SI unit

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# Business Items

- Will keep clicker points same as until now (1 point per answer)
- HW due on Thu
  - 1 vs 2 weeks
- Continue "measures" lecture, then 35 min discussion of Igor and HW & Q&A
- HW#1
  - Plot altitude in vertical axis
  - Turning in Pxp
  - Size of text in procedure
    - Pasting procedures
    - Axes that allow seeing info

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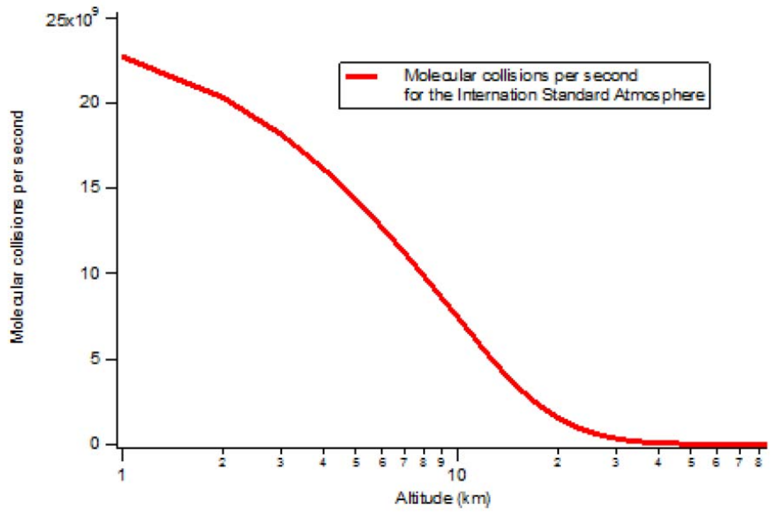
# Graph from last HW

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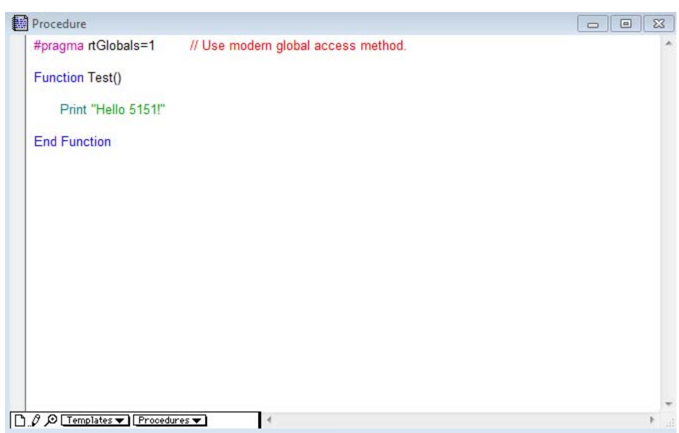


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# Clicker Questions

What is the molecular weight of air? (30s)

a. 28.0 g/mole  b. 28.8 g/mole

c. 32.2 g/mole  d. 44.0 g/mole

e. I don't know

Q: approximate mass fraction of Kr (atomic mass ~ 84) in air? (45s)

A: $84 \times 10^{-6}$  B: $1.1 \times 10^{-6}$

C: $3.4 \times 10^{-6}$  D: $0.38 \times 10^{-6}$

E: I don't know

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# Reference for more species

**TABLE 1.1 Atmospheric Gases**

| Gas | Molecular Weight | Average Mixing Ratio (ppm) | Cycle | Status |
|---|---|---|---|---|
| Ar | 39.948 | 9340 | No cycle | Accumulation during Earth's history |
| Ne | 20.179 | 18 | | |
| Kr | 83.80 | 1.1 | | |
| Xe | 131.30 | 0.09 | | |
| $N_2$ | 28.013 | 780,840 | Biological and microbiological | ? |
| $O_2$ | 32 | 209,460 | | |
| $CH_4$ | 16.043 | 1.72 | Biogenic and chemical | Quasi-steady-state or equilibrium |
| $CO_2$ | 44.010 | 355 | Anthropogenic and biogenic | |
| CO | 28.010 | 0.12 (NH)<br>0.06 (SH) | Anthropogenic and chemical | |
| $H_2$ | 2.016 | 0.58 | Biogenic and chemical | |
| $N_2O$ | 44.012 | 0.311 | Biogenic and chemical | |
| $SO_2$ | 64.06 | $10^{-5}$–$10^{-4}$ | Anthropogenic, biogenic, chemical | |
| $NH_3$ | 17 | $10^{-4}$–$10^{-3}$ | Biogenic and chemical | |
| NO | 30.006 | $10^{-6}$–$10^{-2}$ | Anthropogenic, biogenic, chemical | |
| $NO_2$ | 46.006 | | | |
| $O_3$ | 48 | $10^{-2}$–$10^{-1}$ | Chemical | |
| $H_2O$ | 18.015 | Variable | Physicochemical | |
| He | 4.003 | 5.2 | | |

*Table from S&P*

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# Earth's Atmosphere in Perspective

- All major planets (except Pluto and Mercury) and some large satellites (Titan) have atmospheres.
- Properties of atmospheres on neighboring Mars, Venus, and Earth are amazingly different!
- Earth is unique in:
  - Very high $O_2$ content (close to spontaneous combustion limit)
  - High $H_2O$ content
  - Existence of graduate students and professors on the surface

*Comparison between Venus, Mars, and the Earth*

| *Characteristic* | *Venus* | *Earth* | *Mars* |
|---|---|---|---|
| Total mass ($10^{27}$ g) | 5 | 6 | 0.6 |
| Radius (km) | 6049 | 6371 | 3390 |
| Atmospheric mass (ratio) | 100 | 1 | 0.06 |
| Distance from Sun ($10^6$ km) | 108 | 150 | 228 |
| Solar constant (W $m^{-2}$)[a] | 2613 | 1367 | 589 |
| Albedo (%) | 75 | 30 | 15 |
| Cloud cover (%) | 100 | 50 | Variable |
| Effective radiative (°C) temperature | −39 | −18 | −56 |
| Surface temperature (°C) | 427 | 15 | −53 |
| Greenhouse warming (°C) | 466 | 33 | 3 |
| $N_2$ (%) | <2 | 78 | <2.5 |
| $O_2$ (%) | <1 ppmv | 21 | <0.25 |
| $CO_2$ (%) | 98 | 0.035 | >96 |
| $H_2O$ (range %) | $1 \times 10^{-4} - 0.3$ | $3 \times 10^{-4} - 4$ | <0.001 |
| $SO_2$ (fraction) | 150 ppmv | <1 ppbv | Nil |
| Cloud composition | $H_2SO_4$ | $H_2O$ | Dust, $H_2O$, $CO_2$ |

[a]The intensity of the solar radiation over a square meter of surface at a distance equal to that from the Sun to the planet's orbit.
From Graedel and Crutzen, 1995.

*Slide from S. Nidkorodov, UCI*
*Table From Brasseur, 1999*

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# Atmospheric Evolution: The Imprint of Life

*The evolution of Earth's atmosphere is intricately tied to the evolution of life. Biological processes are responsible for many disequlibria in today's atmosphere (e.g., unusually high $O_2$ content). In the past, the atmosphere was not anywhere close to what it is now.*

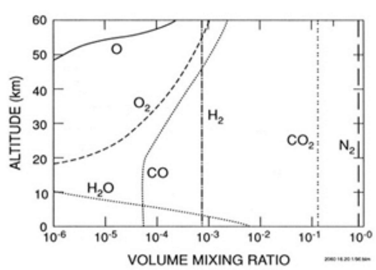


***Figure 16.2.*** *Vertical distribution of major atmospheric constituents in a weakly reduced, prebiotic atmosphere. The major gases are $N_2$ and $CO_2$. Photochemical destruction of $CO_2$ leads to the production of O and $O_2$ in the upper atmosphere (Kasting, 1990).*

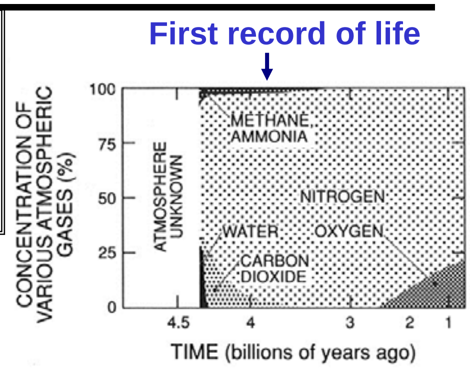


***Figure 16.1.*** *Probable evolution of the relative abundance (in percent) of chemical composition of the atmosphere during the Earth's history (Allègre and Schneider, 1994).*

Atmospheric chemistry and Global Change, NCAR, 1999

# Number density $n_X$ [molecules cm$^{-3}$]

$$n_X = \frac{\text{\# molecules of X}}{\text{unit volume of air}}$$

**Proper measure for**
- **reaction rates**
- **optical properties of atmosphere**

Column concentration $\Omega_X = \int_0^\infty n_X(z)dz$ Proper measure for absorption of radiation by atmosphere

***$n_X$* and *$C_X$* are related by the ideal gas law:**

$$n_X = n_a C_X = \frac{A_v P}{RT} C_X$$

**Also define the mass concentration (g cm$^{-3}$):**

$$\rho_X = \frac{\text{mass of X}}{\text{unit volume of air}}$$

*$C_x$ = mixing ratio*
*$n_a$ = air density [molec cm$^{-3}$]*
*$A_v$ = Avogadro's number*
*P = pressure [Pa]*
*R = Universal gas constant*
*= $A_v$*k, where k=Boltzmann cnst*
*T = temperature [K]*
*$M_X$= molecular weight of X [g/mol]*

*From Jacob* 15

# Ideal Gas Law: Molecular vs Molar forms

**PV = N' kT or PV = N RT**

**N' = number of molecules in the air parcel**

**N = number of moles; N' = N x $A_v$**

**k = Boltzmann constant**

**R = Universal Gas Constant; R = k x $A_v$**

==================================

*(In meteorology texts:* **P = ρ RT** - *different "R" = 287 J/kg/K)*

*$k = 1.3806503 \times 10^{-23}$ m$^2$ kg s$^{-2}$ K$^{-1}$*

*R = 8.31 J mole$^{-1}$ K$^{-1}$*

*From Heald* 16

# Atm. Comp: Unit Conversions

TABLE 2.5 Conversion between Units of Concentration in ppm, pphm, ppb, ppt, and Molecules $cm^{-3}$, Assuming 1 atm Pressure and 25°C[a]

| Parts per | Unit | Molecules, atoms, or radicals per $cm^3$ |
|---|---|---|
| $10^6$ | 1 ppm | $2.46 \times 10^{13}$ |
| $10^8$ | 1 pphm | $2.46 \times 10^{11}$ |
| $10^9$ | 1 ppb | $2.46 \times 10^{10}$ |
| $10^{12}$ | 1 ppt | $2.46 \times 10^{7}$ |

[a] 1 ppm in units of mass per cubic meter = $40.9 \times$ (MW) $\mu g\ m^{-3}$. (at 1 atm and 25C)

Table from FP²

- Clicker Q: number of atoms of Ar at 0.1 atm and 25C? (1 min.)
  - A: $2.46 \times 10^{16}$ B: $2.46 \times 10^{15}$ C: $2.46 \times 10^{14}$
  - D: $2.46 \times 10^{11}$ E: I don't know

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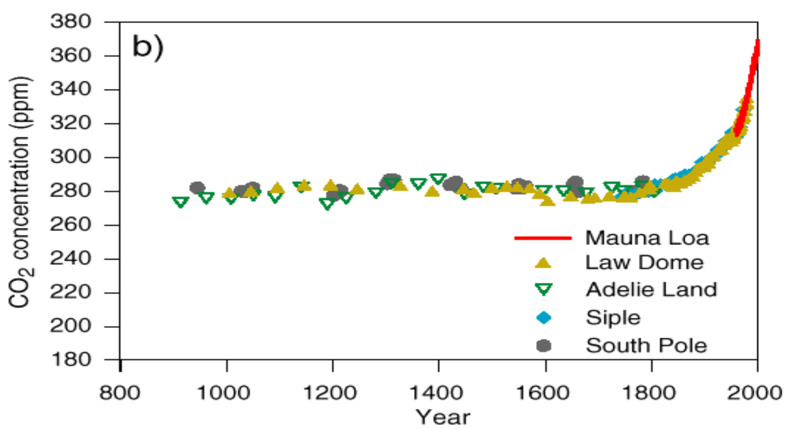
# Atmospheric $CO_2$ over last 1000 yrs

**Intergovernmental Panel on Climate Change (IPCC), 2005**




**Concentration units: parts per million (ppm)**
**number of $CO_2$ molecules per $10^6$ molecules of air**

*$CO_2$ CONCENTRATION IS MEASURED AS MIXING RATIO*

From Jacob

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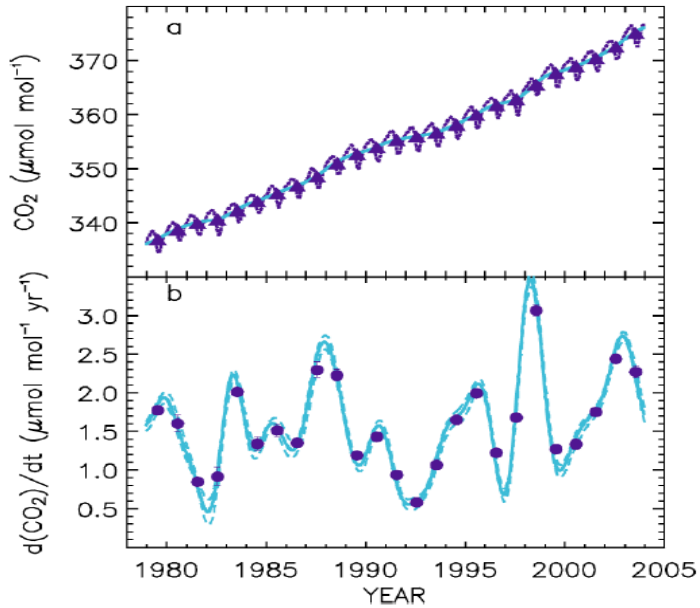
# Atmospheric $CO_2$ in recent decades




IPCC [2005]

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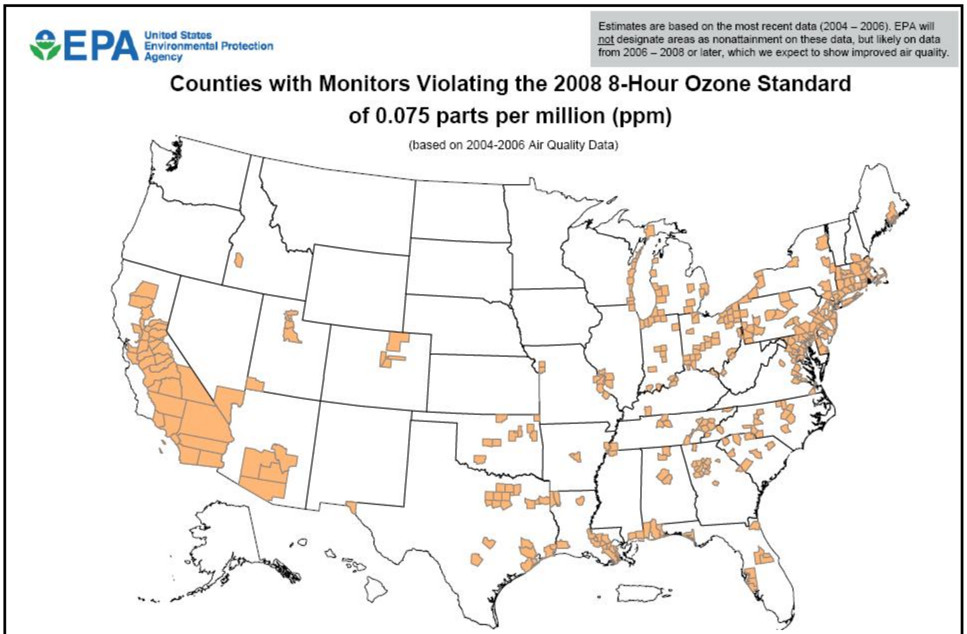



**EPA air quality standard for surface ozone is 75 ppb**

*From Heald* 20

# Concentration units vs. vertical dimension

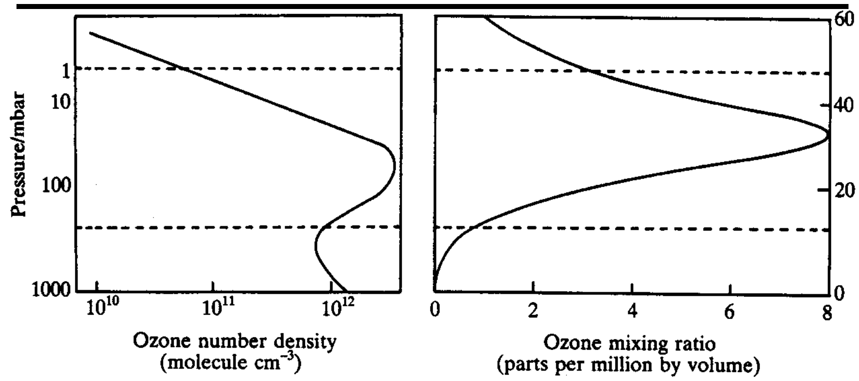
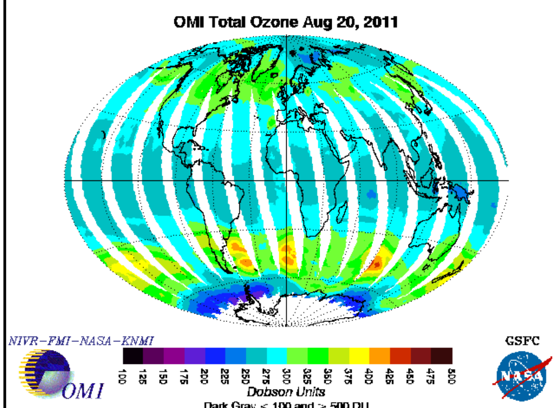


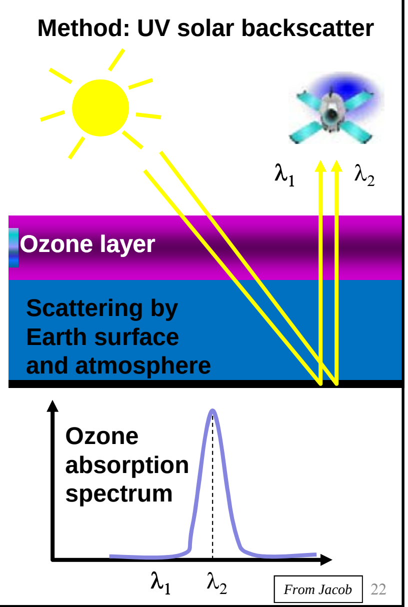

**Fig. 1.2.** Variation of atmospheric ozone concentration with altitude, expressed as an absolute number density and as a mixing ratio. From *Stratospheric Ozone 1988*, UK Stratospheric Ozone Research Group, HMSO, London, 1988.

- Units change the view very significantly
- Why is the stratospheric peak higher in mixing ratio vs n.d.?

*Adapted from Nidkorodov* 21

# Units for Stratospheric Ozone (DU)




**1 "Dobson Unit (DU)" = 0.01 mm ozone at STP**
**= 2.69x10$^{16}$ molecules cm$^{-2}$**

***"Thickness" of ozone layer is measured as a column concentration***

*From Jacob* 22

# In-Class Group Problem

- Solve in class in groups of 4: Dr. Evil decides to poison humankind by spilling 100,000 55-gallon drums of tetrachloromethane in Nevada (MW = 154 g mole$^{-1}$; $\rho$ = 1.59 g cm$^{-3}$, 1 gallon = 3.785 liters).
- Assuming that all $CCl_4$ evaporated and that it does not react with anything, calculate its mixing ratio after it gets uniformly distributed through the entire atmosphere.
- Did he accomplish his objective given that the present day $CCl_4$ mixing ratio is roughly 100 ppt?
- How many drums could one fill with all the $CCl_4$ in the atmosphere?

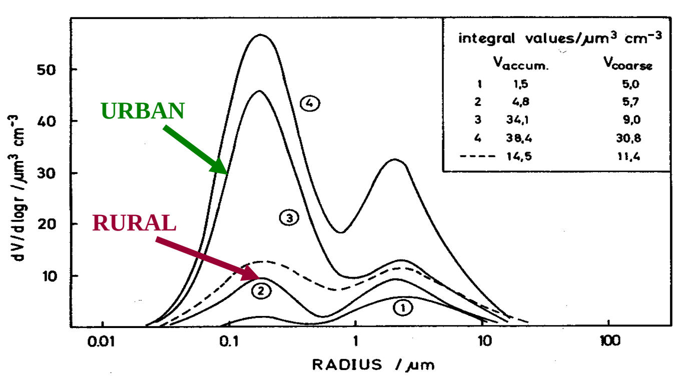
*Adapted from Nidkorodov* 23

# Specific Issues for Aerosol Concentrations

**• A given aerosol particle is characterized by its size, shape, phase, and chemical composition – large number of variables!**

**• Measures of aerosol concentrations must be given in some integral form, *by summing over all particles present in a given air volume that have a certain property***

**• The aerosol size distribution must be treated as a continuous function**



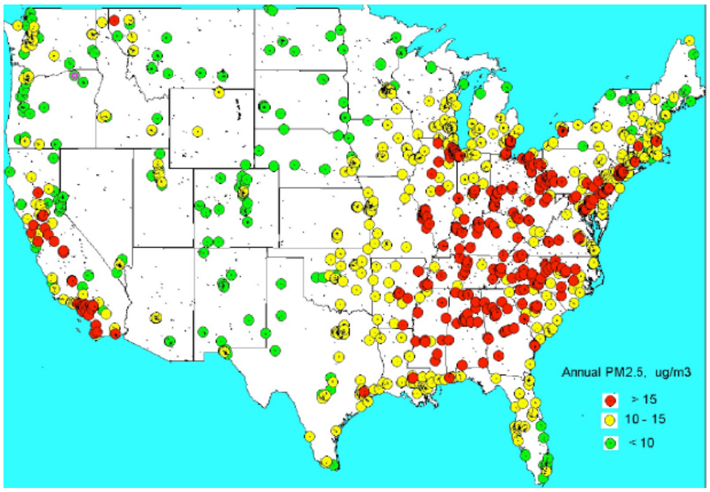

**Typical U.S. aerosol size distributions by volume**

*From Jacob* 24

# Annual Avg. PM at U.S. Sites 1995-2000

EPA particulate matter assessment document (NARSTO), 2003

**$PM_{2.5}$ (aerosol particles < 2.5 $\mu$m diameter)**




U.S. air quality standard: $PM_{2.5}$ = 15 $\mu$g $m^{-3}$ (annual mean)

**Red circles indicate sites in violation of the standard**

*Air Quality Standard is expressed in $\mu g\ m^{-3}$ (mass per unit volume)*

From Jacob 25

# Business Items

- No need to warn Jordan if you are coming to office hours, he will be in the room regardless
  - Any exceptions will be listed in course web page
- Any other questions?

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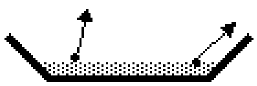
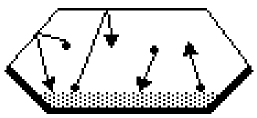
# Partial pressure $P_x$ [Pa]

**Dalton's law:** $P_X = C_X P$ **Proper measure for phase change (such as condensation of water vapour)**

**Evaporation of liquid water from a pan:**



No lid: water molecules escape from pan to atmosphere (evaporation)



**Add a lid:**

- **escaping water molecules collide on lid and return to surface; collision rate measures $P_{H2O}$**
- **eventually, flux escaping = flux returning : saturation ($P_{H2O,SAT}$)**
- **cloud formation in atmosphere requires $P_{H2O} > P_{H2O,SAT}$**
- **$P_{H2O,SAT}$ increases with T**

*From Jacob* 27

# Clicker Question

When the pan does NOT have a cover, does the evaporation rate (molec. evaporated / s) change if above the pan we have vacuum OR dry air?

A. Yes

B. No

C. Only above the critical point of water

D. Only above the critical point of air

E. I don't know

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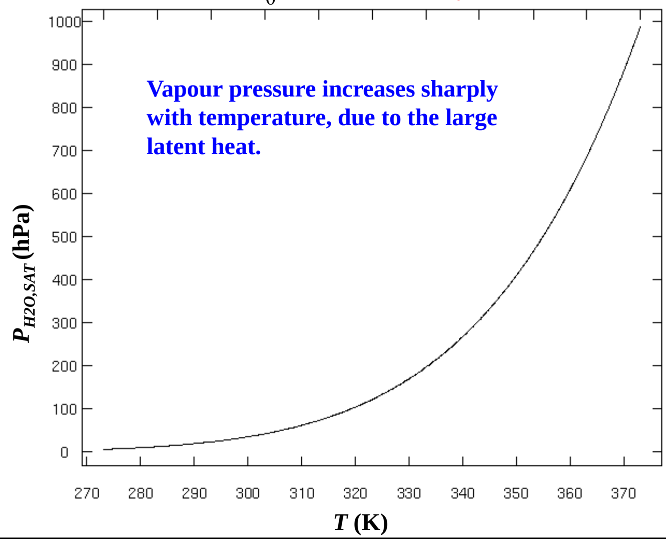
# Vapor pressure of water vs Temperature

$$P_{H2O,SAT} = A\exp[B(\frac{1}{T_0} - \frac{1}{T})]$$

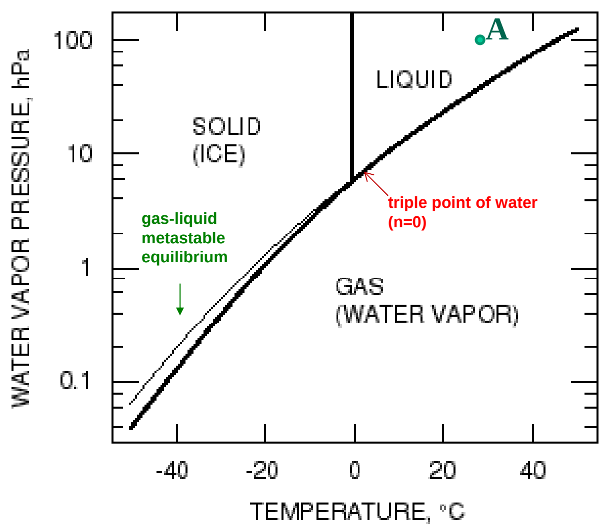
***A* = 6.11 hPa (= $P_{vap}$ at 0C)**
***B* = 5310 K**
**$T_o$ = 273 K**

Clausius-Clapeyron equation




From Jacob 29

# Phase Diagram for Water




CQ: on point A we have
a. Only liquid
b. Liquid and vapor
c. Liquid and solid
d. Liquid and solid and vapor
e. I don't know

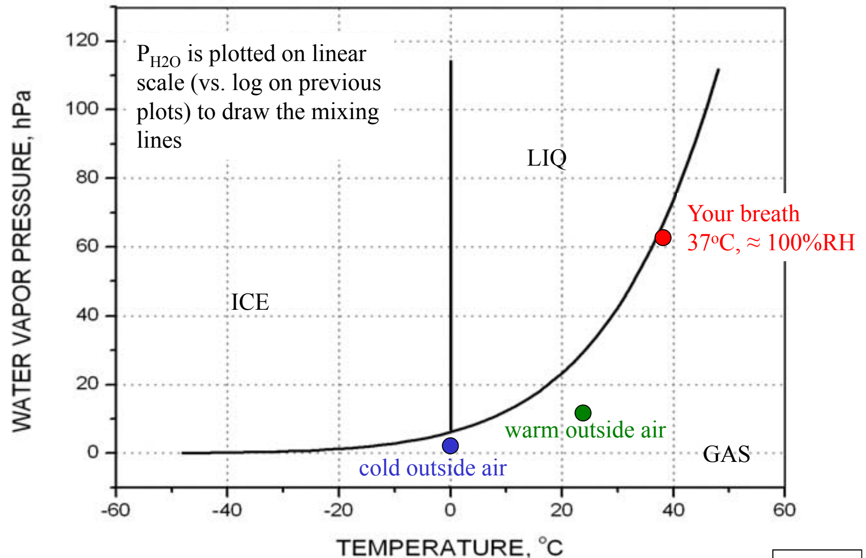
$$RH(\%) = 100\frac{P_{H_2O}}{P_{H_2O,sat}(T)}$$

**Dew point: Temperature $T_d$ such that $P_{H2O} = P_{H2O,SAT}(T_d)$**

From Jacob 30

## Why can you see your breath in cold mornings?

Draw mixing lines (dashed) to describe dilution of your breath plume w/outside air




From Heald 31

## Clicker Questions

What is RH for the "warm outside air" point in the previous slide?

A. 100% B. 80% C. 60%

D. 30% E. I don't know

What is the dewpoint for the same point?

A. 100% B. 10C C. 20C

D. 30% E. I don't know

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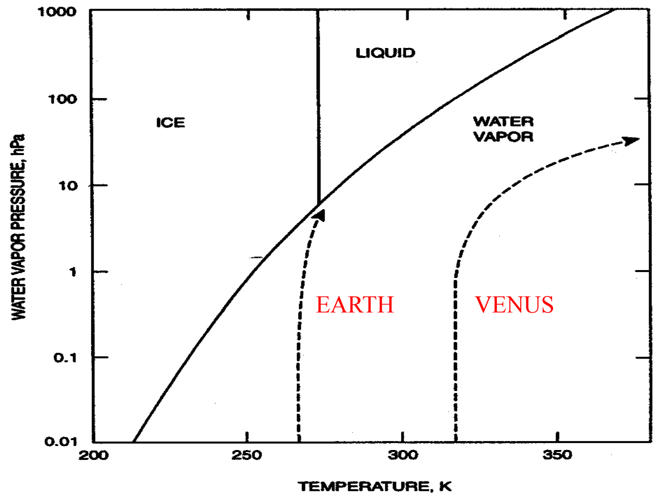
# Greenhouse Effect on Earth vs Venus

Ran away in Venus due to accumulation of water vapor from volcanoes early in its history

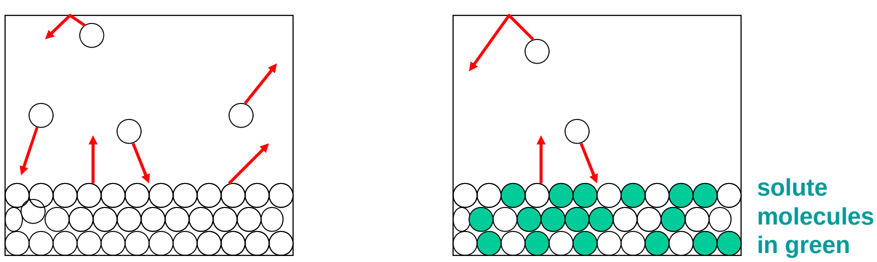
…did not happen on Earth because farther from Sun; as water accumulated it reached saturation and precipitated, forming the oceans




From Jacob 33

# Raoult's Law

$P^{o}_{H2O,SAT}$ $\qquad$ $P_{H2O,SAT} = x_{H2O} P^{o}_{H2O,SAT}$




**water saturation vapor pressure over pure liquid water surface**

**water saturation vapor pressure over aqueous solution of water mixing ratio $x_{H2O}$**

**An atmosphere of relative humidity *RH* can contain at equilibrium aqueous solution particles of water mixing ratio**

$$x_{H2O} = \frac{P_{H2O,SAT}}{P^{o}_{H2O,SAT}} = \frac{RH}{100}$$

From Jacob 34

# Air Pollution Haze

•

**Views of Acadia National Park**

**http://www.hazecam.net/**

**“clean” day**

**“moderately polluted” day**

**Visibility is limited by high concentrations of aerosol particles that have swollen to large sizes due to high relative humidity**

*From Jacob* 35

# Particles must satisfy solubility equilibria

**Consider an aqueous sea salt (NaCl) particle: it must satisfy**

$$x_{Na+} x_{Cl-} \le K_s \quad \text{(solubility equilibrium)}$$

$$x_{Na+} = x_{Cl-} \quad \text{(electroneutrality)}$$

$$x_{Na+} + x_{Cl-} + x_{H2O} = 1 \quad \text{(closure)}$$

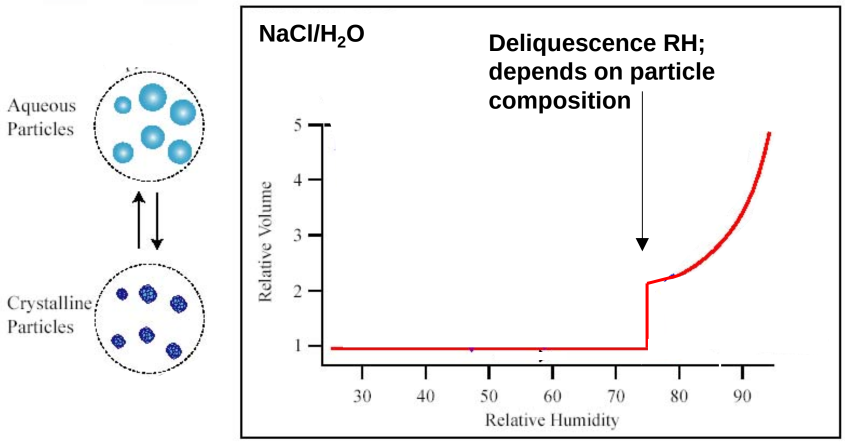
**This requires:**

$$RH \ge 100(1 - 2K_s^{\frac{1}{2}}) \quad \text{"deliquescence RH"}$$

**At lower RH, the particle is dry.**

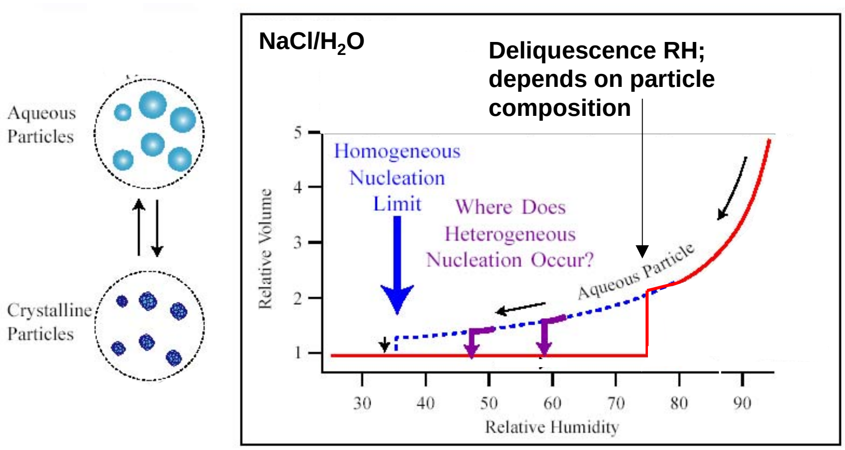
*From Jacob* 36

## Uptake of Water by Aerosols ("haze")




From Jacob 37

## Deliquescence and Efflorescence




Adapted from Jacob 38