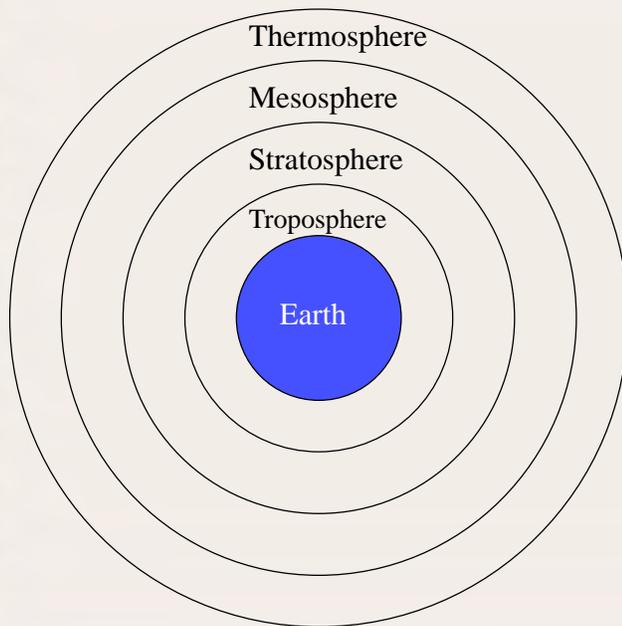


# Regions of the Atmosphere



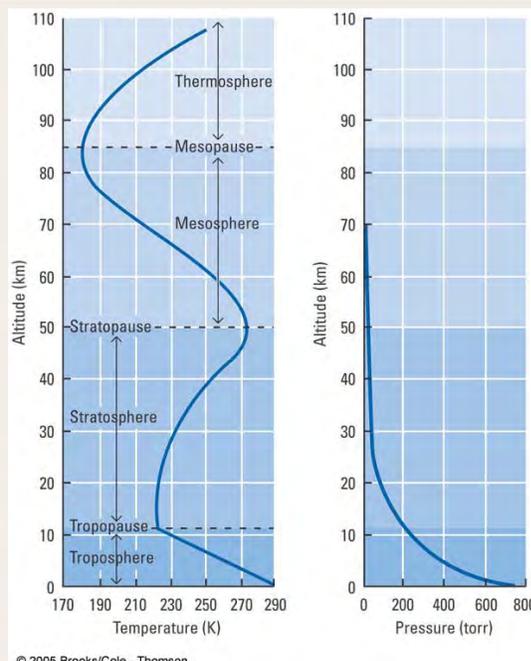
Troposphere: 0 – 15 km;  
layer of the atmosphere in  
which we live

Stratosphere: 15 – 50 km;  
contains ozone layer

Mesosphere: 50 – 80 km;  
coldest layer; photolysis of  
 $O_2$ ,  $N_2$ , etc.

Thermosphere: 80 – 250  
km; chemistry dominated  
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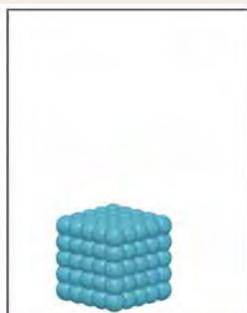
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## Tropospheric Chemistry

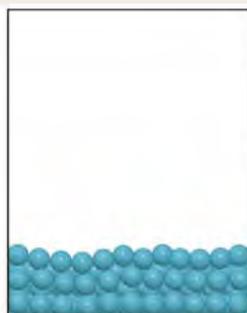
- The troposphere is the most chemically complicated layer of the atmosphere—there are literally thousands of chemical species in the troposphere.
- Weather plays a big role in the troposphere—high concentration of water forms clouds and smaller aerosol droplets, wind patterns provide rapid mixing of trace components, and temperature variations are quite large.

## Behavior of Gases

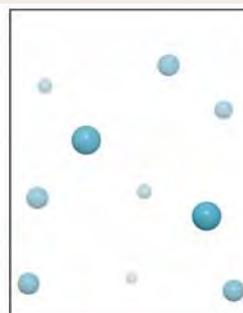
- Gas-phase molecules and atoms are free to move about their container—they fill the entire volume of the container unlike a liquid or a solid.



Solid



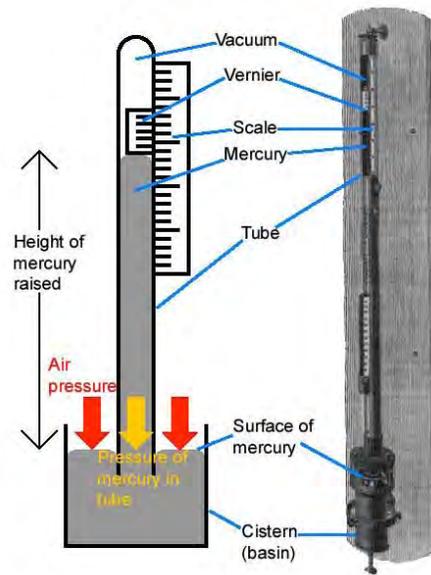
Liquid



Gas

# Pressure

- Pressure is defined as force per unit area.
- Pressure is measured with a device called a barometer.
- A mercury barometer uses the weight of a column of Hg to determine the pressure of gas pushing on a reservoir— atmospheric pressure corresponds to a column height of 760 mm.



# Pressure Units

- Pressure may be measured in a number of different units:
  - atmosphere (atm): barometric pressure at sea level
  - Torr: mm of Hg—comes from use of Hg barometers
  - psi: pounds per square inch
  - Pascal (Pa): official SI units for pressure—1 pascal =  $1 \text{ N m}^{-2}$

## Pressure Units

Pressure conversion factors:

$$760 \text{ Torr} = 1 \text{ atm}$$

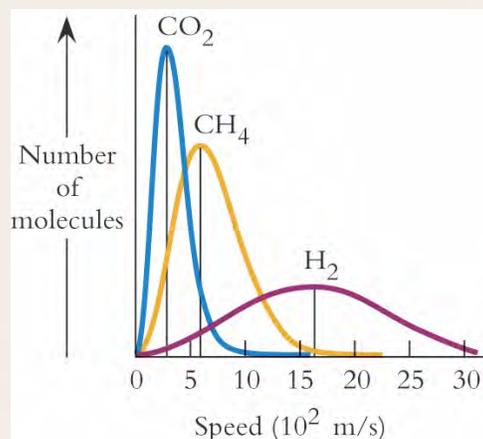
$$760 \text{ mm Hg} = 1 \text{ atm}$$

$$14.7 \text{ psi} = 1 \text{ atm}$$

$$101,325 \text{ Pa} = 1 \text{ atm}$$

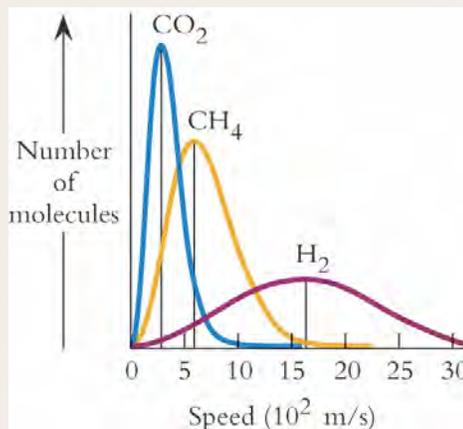
## Molecular Speed and Energy

- Gas molecules travel at a range of speeds —some molecules move much faster than others.
- The average speed of a gas depends on its molar mass—the lighter the mass, the faster the average speed.



## Molecular Speed and Energy

- Average speed can be defined several ways for molecules:
- The most probable speed corresponds to the speed at the maximum in a plot of molecules vs speed—if we could measure the speed of individual gas molecules, more of them would have this value than any other value.



## Molecular Speed and Energy

Kinetic energy is given by

$$E_K = \frac{1}{2}mu^2$$

$m$  = mass  $u$  = velocity (speed)

$$\begin{aligned} m_{\text{H}_2} &= (2.0158 \text{ g mol}^{-1}) / (6.022 \times 10^{23} \text{ H}_2 \text{ mol}^{-1}) \\ &= 3.347 \times 10^{-24} \text{ g} = 3.347 \times 10^{-27} \text{ kg} \end{aligned}$$

$$u_{\text{mp}} = 1.57 \times 10^3 \text{ m s}^{-1}$$

$$\begin{aligned} E_K &= \frac{1}{2}(3.347 \times 10^{-27} \text{ kg})(1.57 \times 10^3 \text{ m s}^{-1})^2 \\ &= 4.13 \times 10^{-21} \text{ kg m}^2 \text{ s}^{-2} = 4.13 \times 10^{-21} \text{ J} \end{aligned}$$

## Molecular Speed and Energy

$$u_{\text{mp}}(\text{CH}_4) = 557 \text{ m s}^{-1}$$

$$E_{\text{K}}(\text{CH}_4) = \frac{1}{2}(2.664 \times 10^{-26} \text{ kg}) (557 \text{ m s}^{-1})^2 \\ = 4.13 \times 10^{-21} \text{ J}$$

$$u_{\text{mp}}(\text{CO}_2) = 337 \text{ m s}^{-1}$$

$$E_{\text{K}}(\text{CO}_2) = \frac{1}{2}(7.308 \times 10^{-26} \text{ kg}) (337 \text{ m s}^{-1})^2 \\ = 4.15 \times 10^{-21} \text{ J}$$

- Even though the three gases ( $\text{H}_2$ ,  $\text{CH}_4$ , and  $\text{CO}_2$ ) have different speeds, they all possess the same amount of kinetic energy at temperature  $T$ .

## Molecular Speed and Energy

- The average kinetic energy of a gas is determined by its temperature:

$$E_{\text{K}}(T) = \frac{3}{2} RT/N_{\text{A}}$$

$R$  is the *gas constant*

$$R = 8.314 \text{ J mol}^{-1} \text{ K}^{-1} = .08206 \text{ L atm mol}^{-1} \text{ K}^{-1}$$

- The kinetic energy of the gas depends only on its temperature, not the identity of the gas.

## Molecular Speed and Energy

- We can equate the two expressions for kinetic energy:

$$E_{K,avg} = \frac{1}{2} m u_{avg}^2 = \frac{3}{2} RT/N_A$$

$$\frac{1}{2} u_{avg}^2 = \frac{3}{2} RT/mN_A$$

$$u_{avg}^2 = 3 RT/mN_A$$

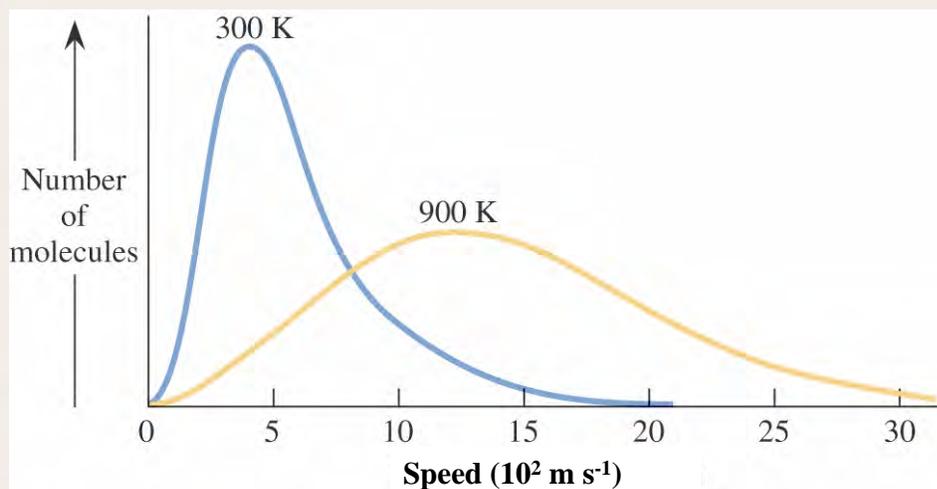
$$u_{avg} = [3 RT/mN_A]^{1/2}$$

$$mN_A = M \text{ (molecular weight)}$$

$$u_{avg} = [3 RT/M]^{1/2} \quad \text{root-mean-square speed}$$

## Molecular Speed and Energy

- The average speed of a gas increases with increasing temperature:



## Molecular Speed and Energy

The average speed of a gas is important because it determines a number of properties of a gas:

- pressure exerted by a gas—pressure depends on the rate of collision with the walls of a vessel and the force of those collisions.
- collision rate—how frequently gas molecules collide, and for reactive collisions, have the opportunity to undergo reaction.
- rate of diffusion—how fast one gas mixes with another

## Ideal Gases

An *Ideal Gas* has two unique properties that distinguish it from real gases

1. An ideal gas particle has no volume—it is simply a point moving through space.
2. An ideal gas has no intermolecular attractive forces—collisions with other ideal gas molecules or the walls of a container are perfectly elastic—no energy is lost in collisions.

## Ideal Gas Equation

- The properties of an ideal gas lead to an equation that relates the temperature, pressure, and volume of the gas:

$$PV = nRT \quad (\text{pivnert})$$

P = pressure (atm)

V = volume (L)

n = number of moles of gas

T = temperature (K)

R = 0.08206 L atm mol<sup>-1</sup> K<sup>-1</sup>

## Ideal Gas Equation

What volume would 2.00 mol of an ideal gas with a pressure of 1000 Torr and a temperature of -25.0 °C occupy?

$$(1000 \text{ Torr}) (1 \text{ atm}/760 \text{ Torr}) = 1.32 \text{ atm}$$

$$-25.0 \text{ }^\circ\text{C} + 273.2 \text{ }^\circ\text{C} = 248.2 \text{ K}$$

$$V = nRT/P$$

$$= \frac{(2.00 \text{ mol})(.08206 \text{ L atm mol}^{-1} \text{ K}^{-1})(248.2 \text{ K})}{(1.32 \text{ atm})}$$

$$V = 30.9 \text{ L}$$

## Variations of the Ideal Gas Law

- If the system is closed (no input or removal of gas from the container), the number of moles of gas cannot change— $n$  is fixed.
- At constant temperature:

$$nRT = \text{a constant}$$

$$\therefore P_1V_1 = P_2V_2 \quad \text{Boyle's Law}$$

If the pressure [volume] is increased, the volume [pressure] will decrease.

If the pressure [volume] is decreased, the volume [pressure] will increase.

## Variations of the Ideal Gas Law

- At constant volume:

$$nR/V = \text{a constant}$$

$$\therefore P_1/T_1 = P_2/T_2$$

If the pressure [temperature] is increased, the temperature [pressure] will increase.

If the pressure [temperature] is decreased, the temperature [pressure] will decrease.

## Variations of the Ideal Gas Law

- At constant pressure:

$$nR/P = \text{a constant}$$

$$\therefore V_1/T_1 = V_2/T_2 \quad \text{Charles' Law}$$

If the volume [temperature] is increased, the temperature [volume] will increase.

If the volume [temperature] is decreased, the temperature [volume] will decrease.

## Variations of the Ideal Gas Law

- At constant temperature and pressure:

$$V/n = \text{a constant}$$

$$\therefore V_1/n_1 = V_2/n_2 \quad \text{Avagadro's Law}$$

If the volume of a gas at constant T and P is increased, the amount of gas must increase.

If the volume of a gas at constant T and P is decreased, the amount of gas must decrease.

## Variations of the Ideal Gas Law

Determination of molar mass:

$$n = m/M \quad M = \text{molecular weight}$$

Substituting into the Ideal Gas Law:

$$PV = mRT/M$$

Rearranging gives:

$$M = mRT/PV$$

## Determination of Molecular Weight

A sample of hydrocarbon with  $m = 1.65$  g exerts a pressure of 1.50 atm in a 945 mL container at 21.5 °C. What is the chemical formula of the hydrocarbon?

$$T = 21.5 \text{ }^\circ\text{C} + 273.2 \text{ }^\circ\text{C} = 294.7 \text{ K}$$

$$M = \frac{(1.65 \text{ g}) (.0821 \text{ L atm mol}^{-1} \text{ K}^{-1}) (294.7 \text{ K})}{(1.50 \text{ atm}) (.945 \text{ L})}$$

$$= 28.1 \text{ g mol}^{-1}$$

formula:  $\text{C}_2\text{H}_4$  (ethylene— $M = 28.1 \text{ g mol}^{-1}$ )

## Dalton's Law of Partial Pressures

- When a container is filled with a mixture of gases, Dalton hypothesized that each individual gas behaved as if it were in a vacuum, *i.e.*, there is no interaction between different types of gas molecules that would affect the resulting pressure within the container.
- Each gas in the mixture exerts a pressure equal to the pressure it would exert if no other gases were in the container
- *Partial pressure* is the pressure exerted by a gas in a mixture as if it were in a vacuum.

## Dalton's Law of Partial Pressures

- The total pressure of a gas mixture is given by:

$$P_{\text{tot}} = n_{\text{tot}}RT/V$$

$n_{\text{tot}}$  = total number of moles of all gases in container

Also

$$P_{\text{tot}} = P_A + P_B + P_C + \dots$$

Dalton's Law of Partial Pressures

$$P_A = n_A RT/V \quad \text{partial pressure of A}$$

$$P_B = n_B RT/V \quad \text{partial pressure of B}$$

$$P_C = n_C RT/V \quad \text{partial pressure of C}$$

## Partial Pressure and Mole Fraction

- The mole fraction of a mixture component is defined as the number of moles of that component divided by the total number of moles:

$$X_A = n_A/n_{\text{tot}}$$

- For a gas mixture:

$$\frac{P_A}{P_{\text{tot}}} = \frac{\frac{n_A \cancel{RT}}{\cancel{V}}}{\frac{n_{\text{tot}} \cancel{RT}}{\cancel{V}}} = \frac{n_A}{n_{\text{tot}}} = X_A$$

## Relative Humidity

- The amount of water in air is frequently expressed as relative humidity.

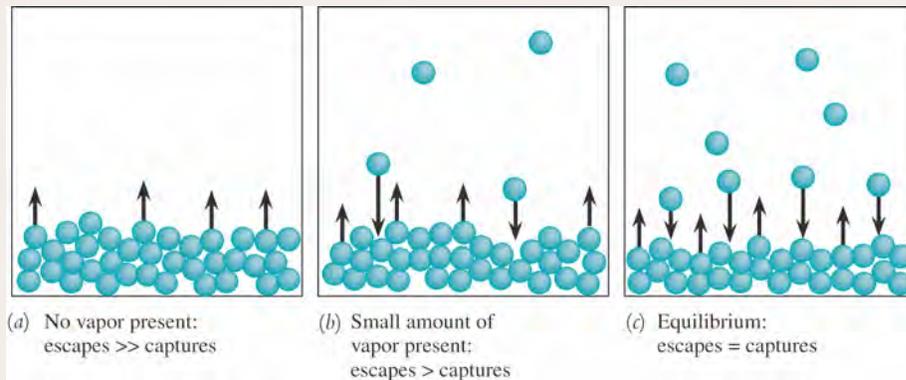
$$\text{RH} \equiv (P_{\text{H}_2\text{O}} / \text{VP}_{\text{H}_2\text{O}}) \times 100\%$$

$P_{\text{H}_2\text{O}}$  is partial pressure of water in air

$\text{VP}_{\text{H}_2\text{O}}$  is vapor pressure of water at a specific temperature

- Vapor pressure is the pressure exerted by  $\text{H}_2\text{O}(\text{g})$  over a water sample in which equilibrium with the liquid is established. Vapor pressure depends on the temperature of the liquid—the higher the temperature, the higher the vapor pressure.

# Relative Humidity



# Relative Humidity

At 30 °C (86 °F),  $VP_{H_2O} = 31.8$  Torr. If the RH = 60%, what is the partial pressure of water in air?

$$RH = (P_{H_2O}/VP_{H_2O}) \times 100\%$$

$$P_{H_2O} = (RH/100) \times VP_{H_2O}$$

$$= (60/100) \times 31.8 \text{ Torr} = 19.1 \text{ Torr}$$

2.5% of air is water

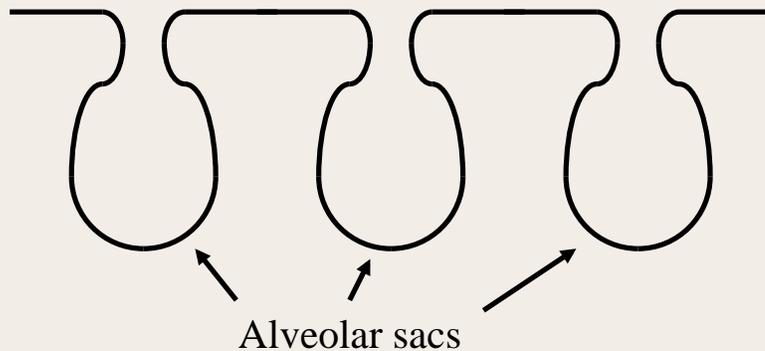
At 15 °C (59 °F),  $VP_{H_2O} = 12.8$  Torr

If temperature drops from 30 °C to 15 °C, the air becomes saturated with water, and the remainder must condense out as dew or fog. RH = 100%

## Urban Smog

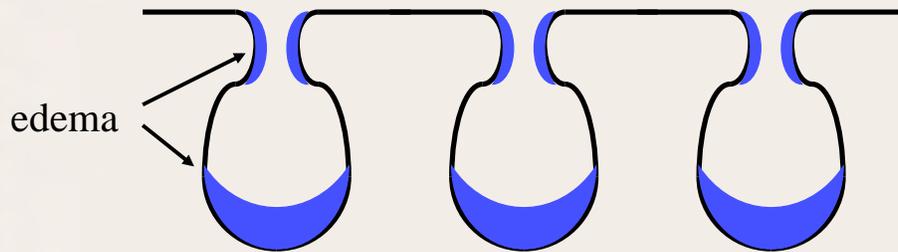
- Polluted troposphere contains a large number of anthropogenic species including hydrocarbons, nitrogen oxides, sulfur oxides, and particulate matter.
- The most damaging component of smog to human health is ozone ( $O_3$ ).

## Urban Smog



Alveoli: exchange of oxygen across the lung lining and into the blood as well as expiration of carbon dioxide occurs in the alveoli

## Urban Smog



Ozone reacts with the lung lining in the alveoli which results in the formation of edema (build up of fluid) at the entrance to the alveoli and with the alveoli themselves.

## Urban Smog

Results of reaction of ozone within alveoli:

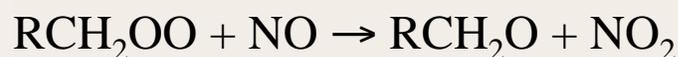
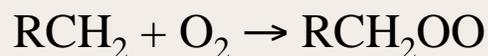
- ➔ Decreased *tidal volume*—the total volume available in the lungs.
- ➔ Increased *residual volume*—because of constriction at alveolar entrance less air can be exchanged on breath-by-breath basis resulting in increased volume of “used” air in lungs.
- ➔ Decreased rate of transport of oxygen across lung lining.

## Formation of Ozone in Smog

- Ozone is not a primary pollutant—species emitted directly into air. It is formed by a series of chemical reactions involving primary pollutants and sunlight.
- The following things are necessary for production of ozone:
  - Hydrocarbons
  - Nitrogen monoxide (NO)
  - Sunlight
  - Hydroxyl radical (OH)

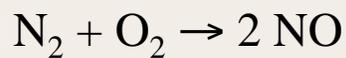
## Formation of Ozone in Smog

- The following reactions produce ozone:



## Sources of Primary Pollutants

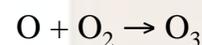
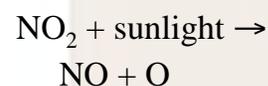
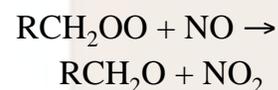
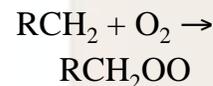
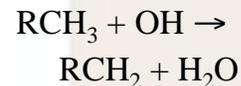
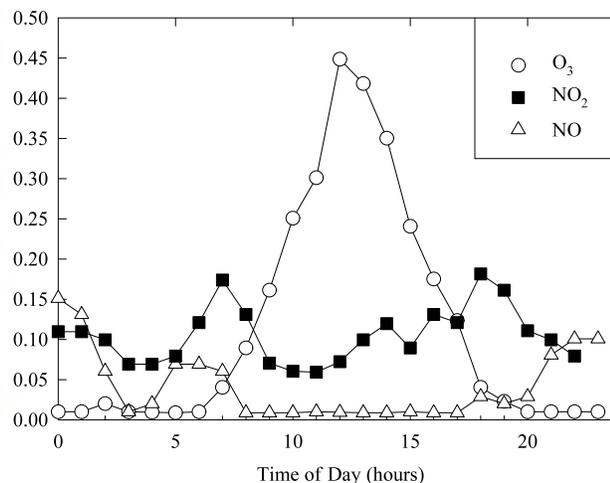
- Hydroxyl radical: formed in several chemical systems including aerosols.
- Hydrocarbons: industrial and transportation emissions.
- Nitrogen monoxide: ~70% of NO in LA Basin comes from car and truck engines



Reaction only occurs at very high temperatures found, for example, within combustion cylinders of engines.

## Formation of Smog

Variations in Concentration of  $\text{NO}_x$  and Ozone on a Smoggy Day in LA Basin

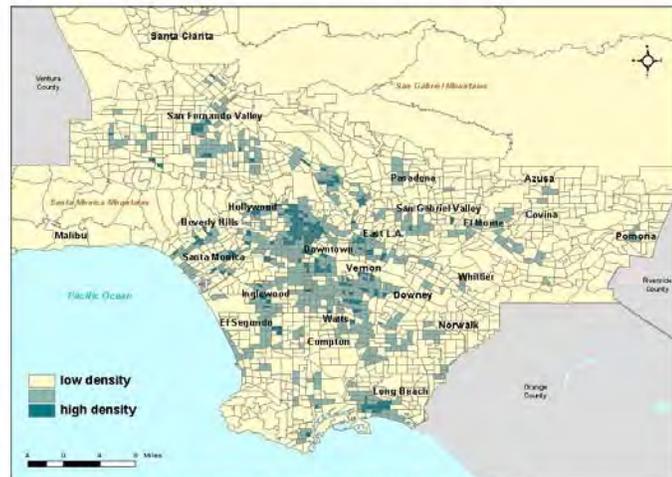


# Smog in Los Angeles

- There are four factors that make smog in LA consistently the worst in the country:

1. Topography—  
LA is a basin  
surrounded by  
relatively high  
mountains.

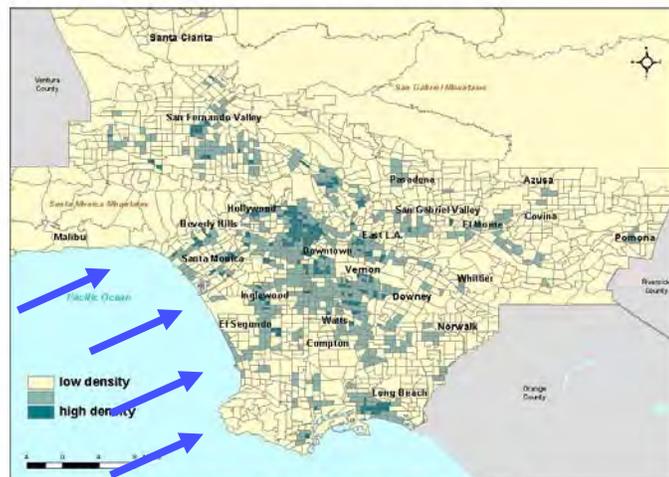
Los Angeles County: Population Density 2000



# Smog in Los Angeles

2. Predominant  
on-shore breeze  
—the warm land  
next to the cool  
ocean water  
produces an on-  
shore breeze that  
tends to push the  
air inland toward  
the mountains

Los Angeles County: Population Density 2000



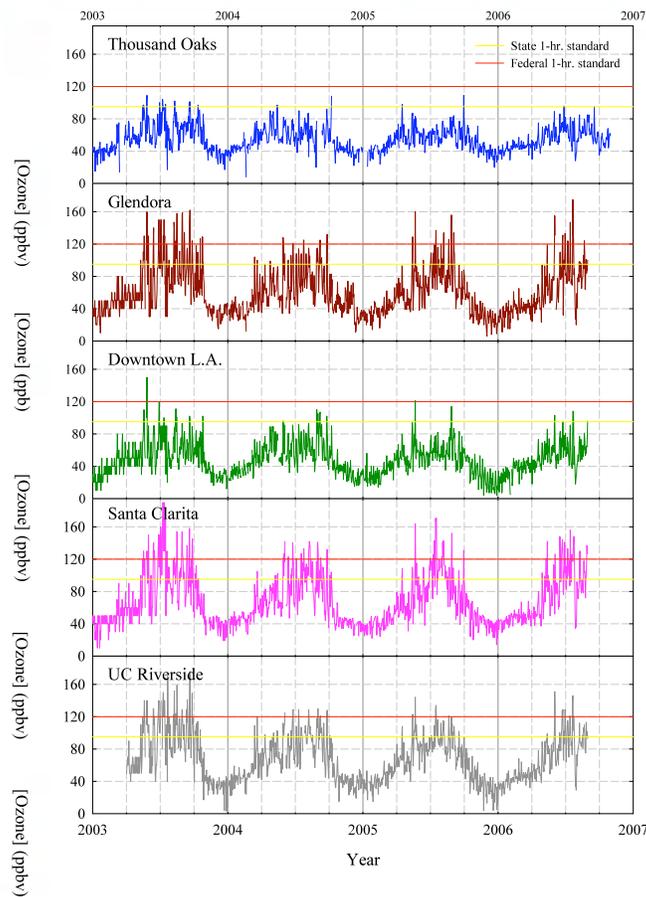
## Smog in Los Angeles

3. Large population base—the five counties that comprise the LA region have a total population nearing 17 million people. Those 17 million people produce a tremendous amount of anthropogenic emissions into the troposphere due to industrial, transportation, and other support activities.

<u>County</u>	<u>Population (2000 census)</u>
Los Angeles	9,519,338
Orange	2,846,289
Riverside	1,545,387
San Bernardino	1,709,439
Ventura	753,197

## Smog in Los Angeles

4. Sunlight—light drives the photolysis of  $\text{NO}_2$  to form oxygen atoms that combine with molecular oxygen to create ozone. LA boasts some of the best weather of any large urban center in the world—more than 300 sunny days per year.



Daily Maximum Ozo

## AQMD Regulations to improve air quality

The South Coast Air Quality Management District (AQMD) is the governmental agency charged with improving air quality in the LA Basin.

Steps taken include:

- Decreased automotive emissions
- Restrictions on solvent use—LA Times required to change type of ink used
- Severe restrictions on industrial emissions—refineries in South Bay
- Required change in barbecue lighter fluids

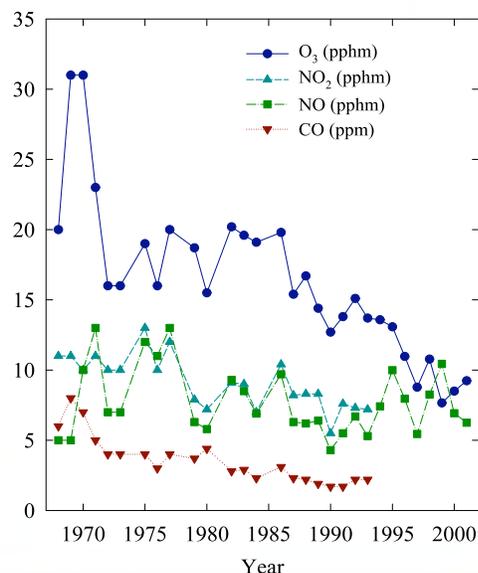
# AQMD Regulations to improve air quality

Proposed ideas for further improvement:

- Regulations on diesel engines—reduce emissions of both hydrocarbons and particulates
- Ban of “drive-thru” restaurants—idling cars emit hydrocarbons and NO with useful work being done
- Impose strict emission technologies on dry-cleaners
- Further restrictions on industrial emissions

## Formation of Smog

Hourly Maximum Averaged Mixing Ratios  
Azusa, CA--August, 1968-2001



## Real Gases vs Ideal Gases

- We made the following assumptions in defining an ideal gas:
  - no volume—gas behaves as a point
  - perfectly elastic collisions
- Real gases do not follow these rules—they occupy a volume of space, and there are intermolecular forces attracting colliding gas molecules

## The van der Waals' Equation

- To better describe real gases, we can use a different equation of state to predict their behavior:

$$P = \frac{nRT}{V - nb} - \frac{a n^2}{V^2} \quad \text{Van der Waals' Equation}$$

where  $a$  and  $b$  are measured constants

The vdw  $b$  constant is a measure of the volume of the gas molecules

The vdw  $a$  constant is a measure of the internuclear attractive forces

## The van der Waals' Equation

Example: Compare the pressure of oxygen determined by the ideal gas law and the van der Waals' equation under the following conditions:

$$n = 25.0 \text{ mol} \quad T = 375 \text{ K} \quad V = 20.0 \text{ L}$$

$$a(\text{O}_2) = 1.36 \text{ L}^2\text{atm mol}^{-2} \quad b(\text{O}_2) = .0318 \text{ L mol}^{-1}$$

Ideal gas:  $P = 38.5 \text{ atm}$

Van der Waals':  $P = 29.7 \text{ atm}$

## Real Gases vs Ideal Gases

- Gases tend to behave ideally under low pressure conditions
  - The time between collisions is much longer so there is less relative time for attractive forces to affect pressure (minimizes effect of a constant)
  - The volume occupied by the gas molecules is much smaller than the total volume of the container (minimizes effect of b constant)