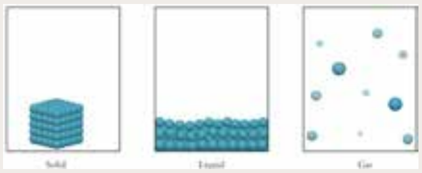
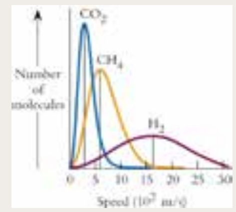
Behavior of Gases

- 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.



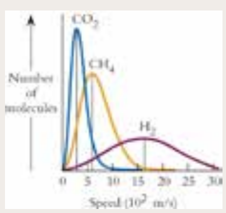
Molecular Speed and Energy

- 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

$E_T = ½mu^2$

m = mass u = velocity (speed)

$m_{H2} = (2.0158 \text{ g mol}^{-1}) / (6.022 \times 10^{23} \text{ H}_2 \text{ mol}^{-1})$

$= 3.347 \times 10^{-24} \text{ g} = 3.347 \times 10^{-27} \text{ kg}$

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

$E_T = ½(3.347 \times 10^{-27} \text{ kg}) (1.57 \times 10^3 \text{ m s}^{-1})^2$

$= 4.13 \times 10^{-21} \text{ kg m}^2 \text{ s}^{-2} = 4.13 \times 10^{-21} \text{ J}$

Molecular Speed and Energy

$u_{mp}(CH_4) = 557 \text{ m s}^{-1}$

$E_T(CH_4) = ½(2.664 \times 10^{-26} \text{ kg}) (557 \text{ m s}^{-1})^2$

$= 4.13 \times 10^{-21} \text{ J}$

$u_{mp}(CO_2) = 337 \text{ m s}^{-1}$

$E_T(CO_2) = ½(7.308 \times 10^{-26} \text{ kg}) (337 \text{ m s}^{-1})^2$

$= 4.15 \times 10^{-21} \text{ J}$

- Even though the three gases (H_2, CH_4, and CO_2) have different speeds, they all possess the same amount of kinetic energy.

Molecular Speed and Energy

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

  $E_T(T) = 3/2 \, RT/N_A$

  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:

$E_{T,avg} = ½ mu_{avg}^2 = 3/2\ RT/N_A$

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

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

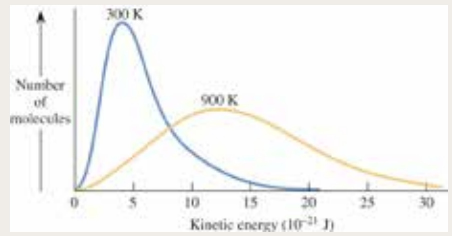
$u_{avg} = [3\ RT/mN_A]^{1/2}$

$mN_A = M$ (molecular weight)

$u_{avg} = [3\ RT/M]^{1/2}$ 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:

$PV = nRT$ (pivnert)

P = pressure (atm)

V = volume (L)

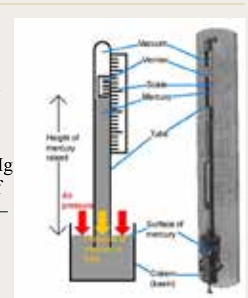
n = number of moles of gas

T = temperature (K)

$R = 0.08206\ L\ atm\ mol^{-1}\ K^{-1}$

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 N m^{-2}

Bar: 10^5 Pa

Pressure Units

Pressure conversion factors:

1 bar = 1.01325 atm

760 Torr = 1 atm

760 mm Hg = 1 atm

14.7 psi = 1 atm

101,325 Pa = 1 atm

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 ^oC occupy?

(1000 Torr) (1 atm/760 Torr) = 1.32 atm

-25.0 ^oC + 273.2 ^oC = 248.2 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 L

Variations of the Ideal Gas Law

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

nRT = a constant

$\therefore P_1V_1 = P_2V_2$ 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 = 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 = a constant

$\therefore V_1/T_1 = V_2/T_2$ 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 = a constant

  $\therefore V_1/n_1 = V_2/n_2$ 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:

$n = m/M$ M = 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?

$T = 21.5\ ^oC + 273.2\ ^oC = 294.7$ K

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

$= 28.1$ g mol^{-1}

formula: C_2H_4 (ethylene—M = 28.1 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 exerted by a specific gas in 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 the only gas in the container.

Dalton's Law of Partial Pressures

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

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

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

  Also

  $P_{tot} = P_A + P_B + P_C + \ldots$

  Dalton's Law of Partial Pressures

  $P_A = n_ART/V$ partial pressure of A

  $P_B = n_BRT/V$ partial pressure of B

  $P_C = n_CRT/V$ partial pressure of C

Partial Pressure and Mole Fraction

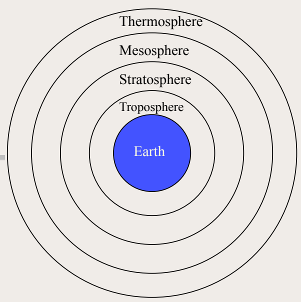
- The mole fraction of a mixture component is defined as the number of moles of that component divided by the total number of moles:

  $X_A = n_A/n_{tot}$

- For a gas mixture:

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

Regions of the Atmosphere



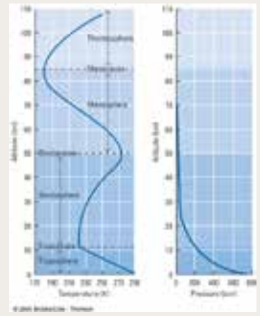
Troposphere: 0 – 15 km; layer of the atmosphere in which we live

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 by ionic photochemistry

Regions of the Atmosphere



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

Thermosphere: 80 – 250 km; chemistry dominated by ionic photochemistry

Tropospheric Chemistry

- The troposphere is the most chemically complex 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.

Relative Humidity

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

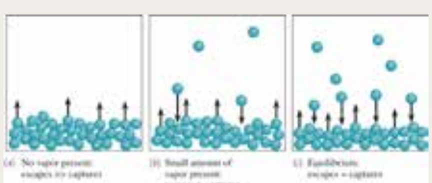
  RH ≡ (P_{H2O} / VP_{H2O}) x 100%

  P_{H2O} is partial pressure of water in air

  VP_{H2O} is vapor pressure of water at a specific temperature

- Vapor pressure is the pressure exerted by $H_2O(g)$ 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_{H2O} = 31.8 Torr. If the RH = 60%, what is the partial pressure of water in air?

RH = (P_{H2O}/VP_{H2O}) x 100%

P_{H2O} = (RH/100) x VP_{H2O}

= (60/100) x 31.8 Torr =19.1 Torr

2.5% of air is water

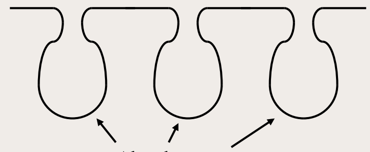
At 15 °C (59 °F), VP_{H2O} = 12.8 Torr

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

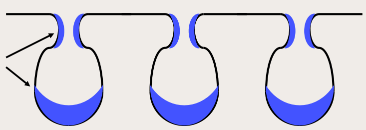


Alveolar sacs

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

edema



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.

Urban Smog

Background O_3 concentration is ~25 ppbv
note: ppbv is a mole fraction—in 1 billion "air" molecules, 25 will be O_3

Symptomatic effects: 20 – 50 ppbv
eye irritation, chest pain, coughing, wheezing, chest congestion, labored breathing, nausea, increased respiration rate, headache, decreased sensitivity to odors

Urban Smog

Irritant effects: 80 – 150 ppbv
aggravation of asthma/allergies, cough, eye/nose irritation, decreased pulmonary function, asthma attacks

Toxic effects: 400 ppbv
structural changes to lungs, increased airway reactivity, effects on lung permeability, inhibition of enzyme function, decreased lung protein synthesis, increased susceptibility to bacterial infection

Lethal poisoning: 2.25 ppmv

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:

$RCH_3 + OH \rightarrow RCH_2 + H_2O$ — alkyl radical formation

$RCH_2 + O_2 \rightarrow RCH_2OO$ — peroxy radical formation

$RCH_2OO + NO \rightarrow RCH_2O + NO_2$ — alkoxy radical & NO_2 formation

$NO_2 + \text{sunlight} \rightarrow NO + O$ — NO_2 photolysis

$O + O_2 \rightarrow O_3$ — ozone formation

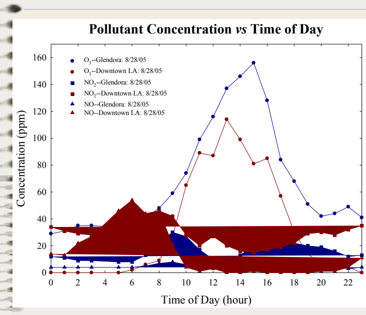
Sources of Primary Pollutants

- 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

$$N_2 + O_2 \rightarrow 2\ NO$$

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

Formation of Smog



$RCH_3 + OH \rightarrow RCH_2 + H_2O$

$RCH_2 + O_2 \rightarrow RCH_2OO$

$RCH_2OO + NO \rightarrow RCH_2O + NO_2$

$NO_2 + \text{sunlight} \rightarrow NO + O$

$O + O_2 \rightarrow O_3$

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.

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

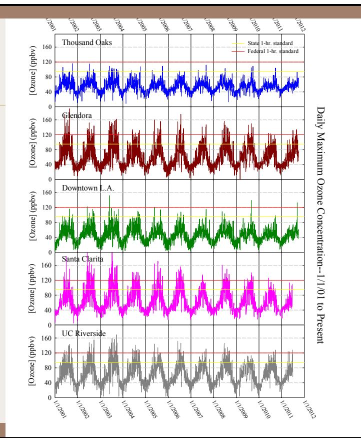
Smog in Los Angeles

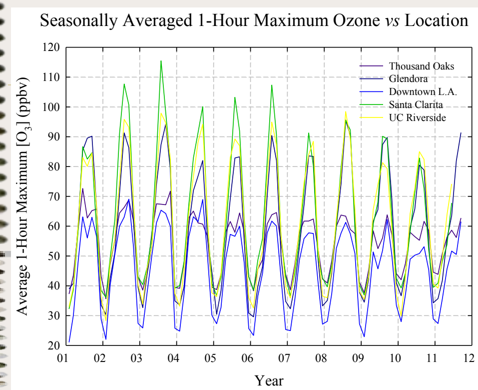
3. Large population base—the five counties that comprise the LA region have an estimated population of 17.8 million people. Those 18 million people produce a tremendous amount of anthropogenic emissions into the troposphere due to industrial, transportation, and other support activities.

County	Population (2010 census)
Los Angeles	9,848,605
Orange	3,010,232
Riverside	2,189,641
San Bernardino	2,035,210
Ventura	823,318

Smog in Los Angeles

4. Sunlight—light drives the photolysis of 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.





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:

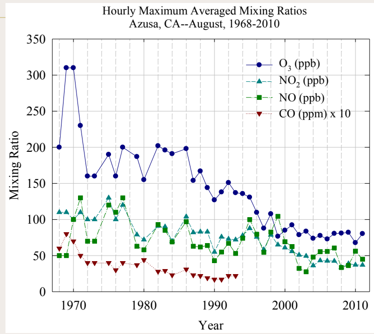
- Decreased automotive emissions
- Restrictions on solvent use—LA Times required to change type of ink used
- Severe restrictions on industrial emissions—refineries in South Bay
- Required change in barbecue lighter fluids

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 without useful work being done
- Impose strict emission technologies on dry-cleaners
- Further restrictions on industrial emissions
- 1 out of 7 vehicle must ZEV by 2025

Formation of Smog



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 acetylene (C_2H_2) determined by the ideal gas law and the van der Waals' equation under the following conditions:

n = 25.0 mol   T = 300 K   V = 20.0 L

$a(C_2H_2) = 4.390\ L^2 atm\ mol^{-2}$ $b(C_2H_2) = .05136\ L\ mol^{-1}$

Ideal gas: $P = \frac{nRT}{V} = \frac{(25.0\ mol)(.08206\ L\ atm\ mol^{-1}\ K^{-1})(300.\ K)}{20.0\ L} = 30.8\ atm$

van der Waals':

$$P = \frac{nRT}{V - nb} - \frac{an^2}{V^2} =$$

$$= \frac{(25.0\ mol)(.08206\ L\ atm\ mol^{-1}\ K^{-1})(300\ K)}{20.0\ L - (25.0\ mol)(.05136\ L\ mol^{-1})} - \frac{(4.390\ L^2\ atm\ mol^{-2})(25.0\ mol)^2}{(20.0\ L)^2}$$

$= 26.0\ atm$

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)