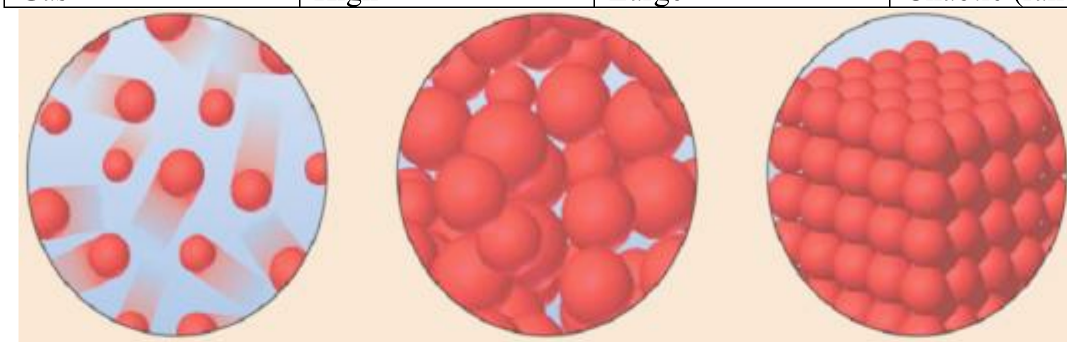
Gases

States of Matter

States of Matter	Kinetic E (motion) Potential E(interaction)	Distance Between (size)	Molecular Arrangement
Solid	Small	Small	Ordered
Liquid	Unity	Unity	Local Order
Gas	High	Large	Chaotic (random)



(http://www.chem.neu.edu/Courses/1105Tom/05Lecture19_files/image002.jpg

Individual Molecules in Gas

Gas is made of molecules in motion –

can be pure He or CH_4 etc.

or mixture of molecules Air contains Ar, CO_2, O_2, H_2O, N_2

Gas Properties and Ideal Gas Law

Pressure p (atm)
Volume V (L)
Temperature T (K)
Moles n (mol)
Gas Constant R (0.08206 L atm/mol K)

Ideal Gas Law **p V = n R T** links properties together

Always use Kelvin temperature scale in pV = nRT

$^oC = (\ ^oF - 32)/1.8$

$K = {}^oC + 273.15$

Atmospheric Pressure Measured with a Barometer

Pressure = Force/ Area

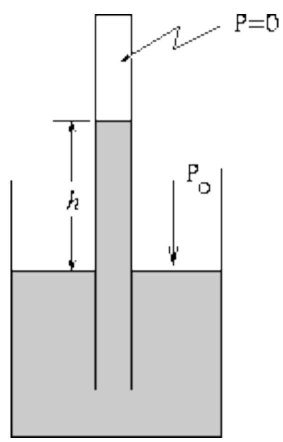
Height of column of Mercury (Hg) is way to measure pressure.
Mercury can expand with temperature but effect is small in wide bore column.
Careful measurements correct for temperature expansion.

Pressure units used:
1.01×10^5 Pa = 1.01 bar = 760 mm Hg =760 torr = 1 atm = 14.7 lbs/in^2 psi

Note:Pa = Pascal (N/m^2) and bar is 10^5 Pa

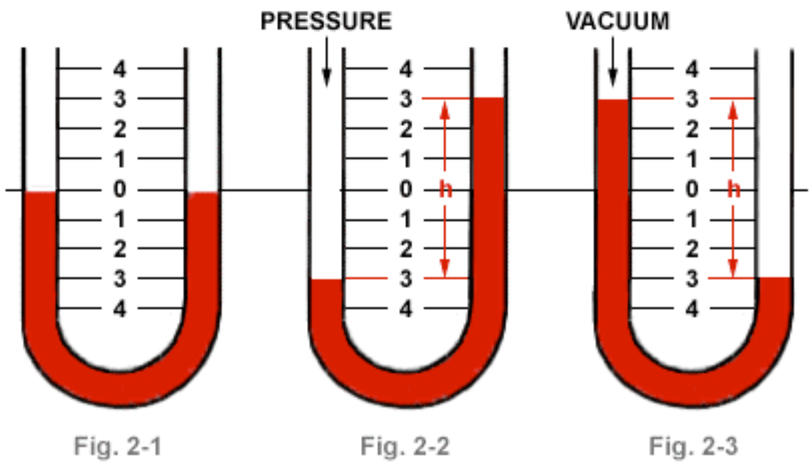
Atmospheric Pressure Measured with a Barometer

Ex:	Miami	760 mm Hg
	Denver	628 mm Hg
	Chattanooga	740 mm Hg



(http://theory.uwinnipeg.ca/physics/fluids/node9.html)

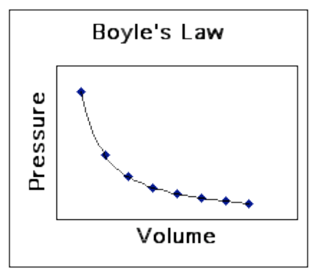
Difference in Pressure with a Manometer



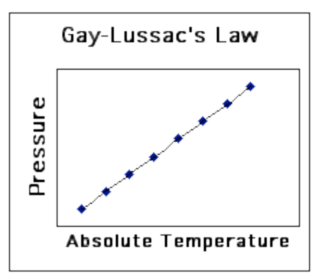
(http://www.dwyer-inst.com/htdocs/pressure/ManometerIntroduction.cfm)

High pressure can be measured with metal diaphragm

Development of Ideal Gas Law

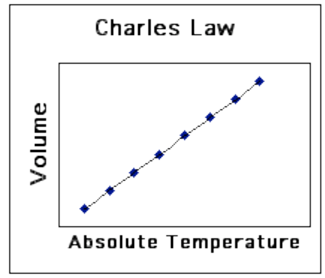


1660 Boyle's Law $V \alpha 1/P$



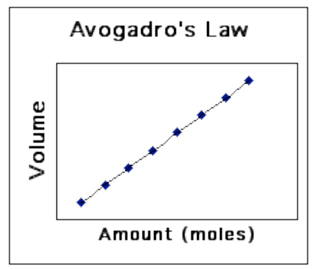
1703 Amonton's Law *(Gay-Lussac)* $P \alpha T$

$P= (const)\ (T)$



1787 Charles' Law $V \alpha T$

$V = (const)(T)$



1811 Avogadro' Law $V \alpha n$

Equal number of molecules in equal volumes

(http://dwb.unl.edu/Teacher/NSF/C09/C09Content.html)

Summarize Ideal Gas Law

$$V \sim (1/P)(T)(n)$$

$$V = R(1/P)(T)(n)$$

p V = n R T where R is gas constant

Absolute Zero

Charles' Law introduces idea of lowest possible temperature

V is proportional to T and plotting data for helium gas shows that

$V = 0$ at $T = -273^{o}C$ which we call Absolute Zero

$T = -273.15\ ^{o}C$ (Celsius) = 0 K (zero Kelvin)

Standard Temperature and Pressure (STP)

At $T = 0^{o}C = 273$ K and P = 1 atm = 760 mmHg

1 mole occupies 22.4 L

6.02×10^{23} molecules occupy 22.4L at STP but have different densities

O_2	32 g/mol	1.43 g/L
Ar	40 g/mol	1.79 g/L
CH_4	16 g/mol	0.72 g/L

Different weight but the same mass

Density = w/V (g/L) or (g/cm^3)

V, P, T → moles   use V, P, T to determine the # of moles

Molecular Weight   M = w/n (weight / moles)

<u>Gas Constant R</u>

pV = nRT   Ideal Gas Law   where R= gas constant

R= pV/nT
R= (22.414 L) (1.000 atm)/ (1.000 mol) (273.15 K)
R = 0.08206 L atm/ K mol

or

R= (2.21×10^{-2} m^3) (1.01×10^5 Pa) / (273.15 K) (1 mol)
R= 8.31 m^3 Pa / K mol   and Pa = (N / m^2) x m^3 = N x m = J so
R= 8.31 J/ K mol

Values of R will be given on exams
Use R= 0.08206 L atm/ K mol for gas law problems trying to find amounts of P, V, or T
Use R= 8.31 J/ K mol for calculations trying to find energy

<u>Problems using Gas Law</u>

a. Direct Substitution
b. Change
c. Stoichiometry

a. Direct Substitution

1. Write down what you know

   $p = 320$ mm Hg → (329)(1atm/ 760) = 0.421 atm
   $T = 27^{o}C$ → 300 K
   N = ½ mol → 0.5 mol
   R = 0.08206 L atm mol K
   V = ?

2. Convert to proper units

3. Find Symbolic Solution (rearrange pV=nRT for what you are seeking)

   $pV = nRT \qquad V = ?$

   $V = nRT/ P$

4. Substitute in Numbers and do math

$$V = \frac{(0.5\text{ mol})(0.08206\text{ L atm/ mol K})(300\text{ K})}{(0.421\text{ atm})} = 29.2\text{ L}$$

b. Change

1. Write Before	2. Write After (fix units if needed)
$P_1 = 1$ atm	$P_2 = ?$
$V_1 = 2.0$ L	$V_2 = 6.0$ L
$T_1 = 200$ K	$T_2 = 400$ K

3. Find Symbolic

   $P_1V_1/ n\,T_1 = P_2V_2 / n\,T_2$

   Cross out any property that is constant

   $P_2 = (V_1/ V_2)\,(T_2/ T_1)\,P_1$

4. Substitute in Numbers and do math

   $P_2 = (2.0L/6.0L)\,(400K/200K)\,(1\text{ atm}) = 0.67$ atm

c. Stoichiometry

1. Do regular stoichiometry problem
2. Do gas law problem with answer from part 1

Ex. Water is converted to gas by electrolysis. Starting with 100g H_2O produces what volume of H_2, O_2, at STP?

$2H_2O\ (l) \rightarrow 2H_2\ (g) + O_2\ (g)$

100g x (1.00 mol / 18.0g) = 5.56 mol H_2O

5.56 x (2/2) = 5.56 mol H_2

5.56 x (1/2) = 2.78 mol O_2

at STP 22.4 L/ mol so 125 L H_2 and 62.5 L O_2

from pV = nRT

$$V = ? \quad V = (nRT/p) = \frac{(2.78\ \text{mol})(0.08206\ \text{L atm / mol K})(273\ \text{K})}{(1\ \text{atm})} = 62.3\text{L}$$

Partial Pressure

Based on Mixture of Gases that don't react chemically

Ex. Air is mixture of N_2, O_2, CO_2, Ar, H_2O

Total Pressure of the mixture is the sum of the components

$P_{TOTAL} = P_A + P_B + P_C$ in general for gases A, B, and C

$P_{TOTAL} = P_{N2} + P_{O2} + P_{CO2} + P_{Ar} + P_{H2O}$ for gases in air
= 5.75 + 134 + 12 + 4 + 20
=745 mm Hg

Keep track of relative number of molecules

Mole fraction X_A

$X_A = (n_A / n_{TOTAL}) = (n_A) / (n_A + n_B + n_C + ...)$

Sum of the mole fractions (components) is one

$$1 = X_A + X_B + X_C + \ldots$$

To calculate partial pressure from mole fraction

Can use ideal gas law with partial pressure as do for pressure

Volume is total volume of container

$p_AV = n_ART$ $\qquad$ $p_BV = n_BRT$ $\qquad$ etc.

p_A = Pressure of A
n_A = Moles of A

Molecular Speed

Higher temperature → Higher speed → Higher kinetic energy

Typical room temperature values

Speed ~ 180 m/s
~ 400 mph

Collisions ~ 10^{10} collisions/second (collisions are random)

Diffusion is much slower than molecular speed

Distance between collisions ~ 10^{-7} m

Speeds of molecules is greater for lighter molecules and greater at higher temperatures

http://en.wikipedia.org/wiki/Image:MaxwellBoltzmann.gif#file

Kinetic Molecular Theory of Gases

Explain behavior of gases in terms of molecule assumptions:

1. Size of gas molecules is negligible (molecules small compared distances between)

2. Attractive forces between molecules are negligible

3. Molecules are in constant random motion, collide with each other and walls

4. Kinetic energy proportional to temperature

Ideal gas law NOT followed

At high pressure – size important, molecules packed together

At low temperature – interactions become important

There are other equations of state more complicated

Science observations → Law → Model

Results of Kinetic Molecular Theory

$pV = nRT$ pressure depends on number of collisions per area

p increases if...

V decreases	small volume, less wall area → more collisions
T increases	each a collision has more energy
n increases	more molecules → more collisions

Mathematical Derivation of Ideal Gas Law from Kinetic Theory

We will not cover these math details and you are not responsible for
-(discussed in some GChem textbooks)

Average Molecular Speed

Ex. What is the average speed of nitrogen gas molecules?

$3/2\ (RT) = 1/2\ (Mu^2)$ where M = molar mass

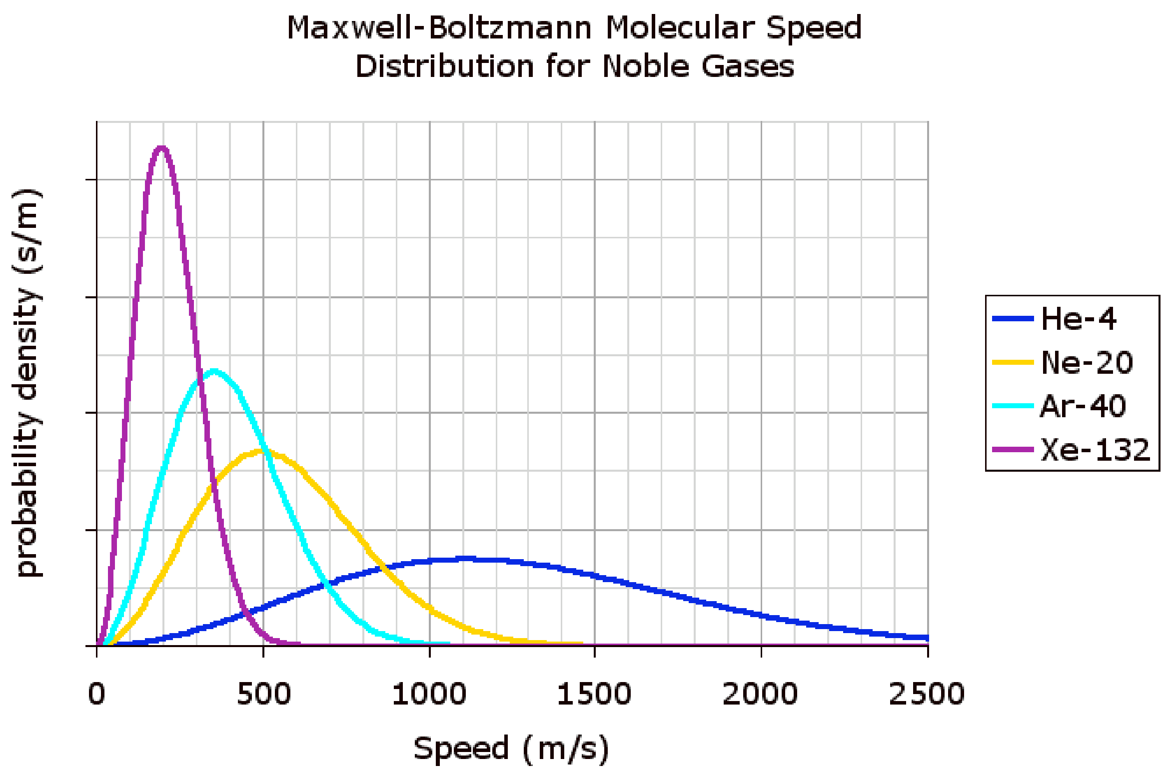
$u_{avg} = (3RT/M)^{1/2}$

$= (3 (8.31 J/mol K) (300K)) / (0.028 kg/mol))^{1/2}$

$= 517$ m/s since $(J/kg)^{1/2} = (m^2/ s^2)^{1/2}$

$= 517$ m/s (mi/1609 m)(3600s/ hr)

$= 517$ mi/s (2.24) = 1160 mph !



Effusion

The movement of molecules through hole is effusion
Movement of molecules through gas or liquid is diffusion

In general relative rate of effusion is given by:

$Rate_A / Rate_B = \sqrt{(M_B/M_A)}$ where M = mass

Ex. Comparison of rate of He to N_2
He faster than N_2 since mass less

Rate He/ Rate N_2 = 2.65 = $\sqrt{(M_{N2} / M_{He})} = \sqrt{(28/4)}$ = 2.65

Can use to determine molar mass of one gas relative to known gas

Real Gases

Kinetic Molecular Theory for Ideal Gas must be modified to account for real gas behavior

1. Gas Molecules do have interactions
   attractions for each other (collisions are sticky)

2. Gas Molecules do have volume
   can only be compressed so far
   can not be squeezed together too close

Van der Waals Equation of State includes parameters that relate to size and interactions

$$P = (nRT / (V - nb)) - (a\, n^2 / V^2)$$

P is less due to attractions of molecules

Weaker interactions between molecules mean lower temperatures required to convert from gas to liquid (at 1 atm, the normal boiling point)

He bp = 4K and N_2 bp = 77 K
Therefore N_2 has stronger interactions than He

Generally larger molecules have stronger interactions but water is unusual because small molecule with high boiling point H_2O bp = 373 K dipole

Extra Stoichiometry Problem
Ex. 50g of $CaCO_3$ heated produces what volume of CO_2 at STP?
$CaCO_3$ (s) heat→ CaO(s) + CO_2 (g)

?mol $CaCO_3$ = 50g $CaCO_3$ (mol/ 100 g)
= 0.50mol$CaCO_3$
and CO_2 is same moles as CaCO3 therefore use 0.50 mole of CO_2

PV=nRT → V = nRT/P
V = (0.50mol)(.08206 L atm/mol K) (273K)/(1.00atm) = 11.2 L

Extra Problem to find Molar Mass

Find the molecular weight of CO_2 from observing the mass of CO_2 produced and the volume it occupies.

Experiment $CaCO_3$ (s) + heat → CaO (s) + CO_2 (g)
CO_2 (g) collected at 1.00 atm and 300 K and mass or of CO_2 was 11g
And volume of CO_2 was 6.15 L

1) Convert volume to moles pV = nRT

$$n = pV/RT = \frac{(1\ \text{atm})(6.15\ \text{L})}{(0.08206\ \text{L atm/mol K})(300\text{K})} = 0.25\ \text{mol}$$

2) Calculate the molecular weight W (molar mass) of CO_2

and use Density = m/V in (g/cm^3) or (g/L) Heavier the molecule the larger the density

W = m / n (g/mol)

W = 11g / 0.25 mol = 44 g/mol for CO_2

Example Gas Density Calculation

Density d = m/v

Moles of Gas n = m/W m = mass (g) W = molecular weight (g /mol)

n = pV/ RT

Combining above gives

n = m/W = pV/ RT

And simplifying

m/V = pW/RT

d density = m/V = pW/ RT

Example for NO_2

$$d = [(1\ \text{atm})(46\ \text{g/mol})] / [(0.08206\ \text{L atm/ mol K})(273\ \text{K})] = 2.05\ \text{g/L}$$

Note that liquid densities are measured in g/mL and gas densities in g/L so about a factor of 1000 different. Gases are much less dense than liquids.