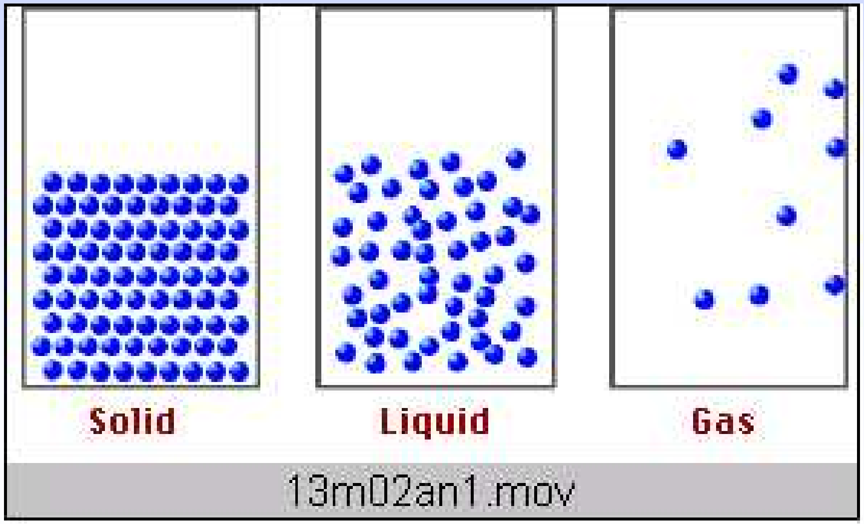
BEHAVIOR OF GASES

Chapter 12

Importance of Gases

- Airbags fill with N_2 gas in an accident.
- Gas is generated by the decomposition of sodium azide, NaN_3.
- $2\ NaN_3 \dashrightarrow 2\ Na + 3\ N_2$

THREE STATES OF MATTER



General Properties of Gases

- There is a lot of “free” space in a gas.
- Gases can be expanded infinitely.
- Gases occupy containers uniformly and completely.
- Gases diffuse and mix rapidly.

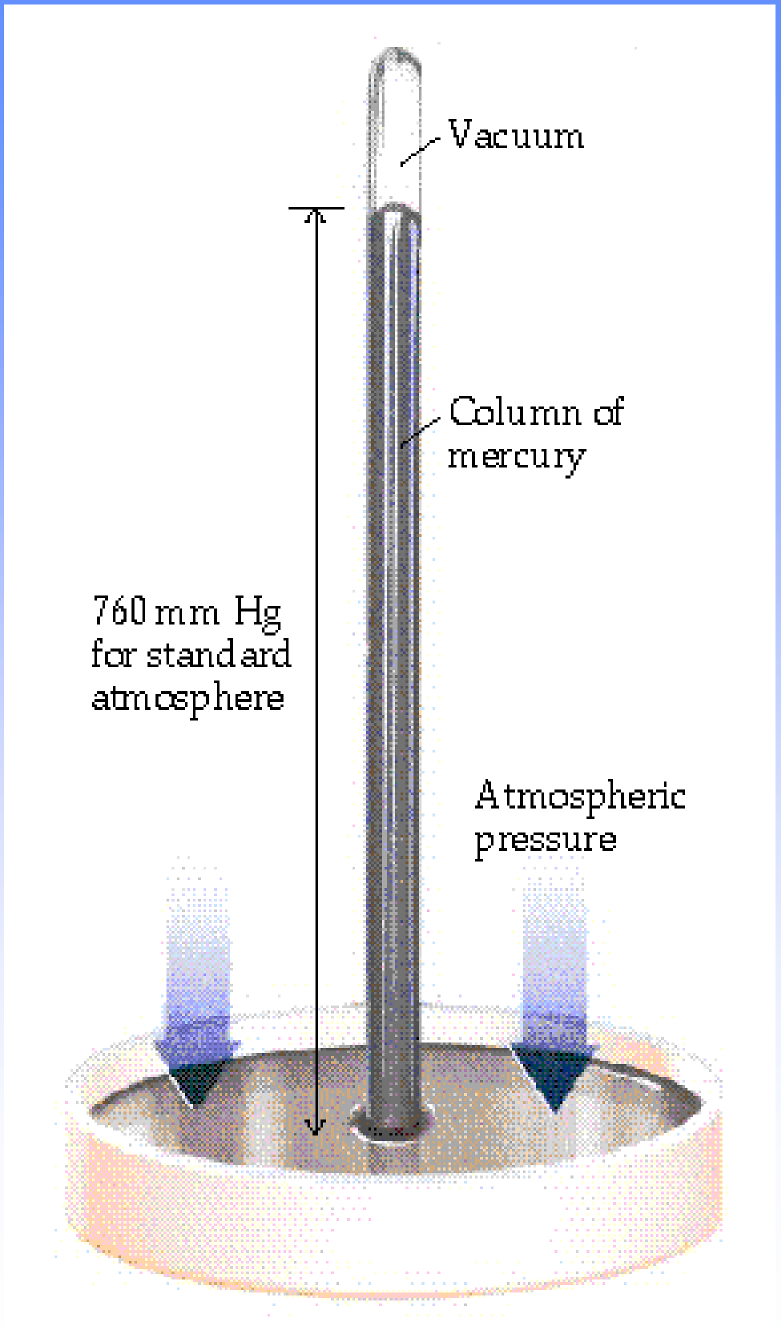
Properties of Gases

Gas properties can be modeled using math. Model depends on—

- V = volume of the gas (L)
- T = temperature (K)
- n = amount (moles)
- P = pressure (atmospheres)

Pressure

Pressure of air is measured with a **BAROMETER** (developed by Torricelli in 1643)

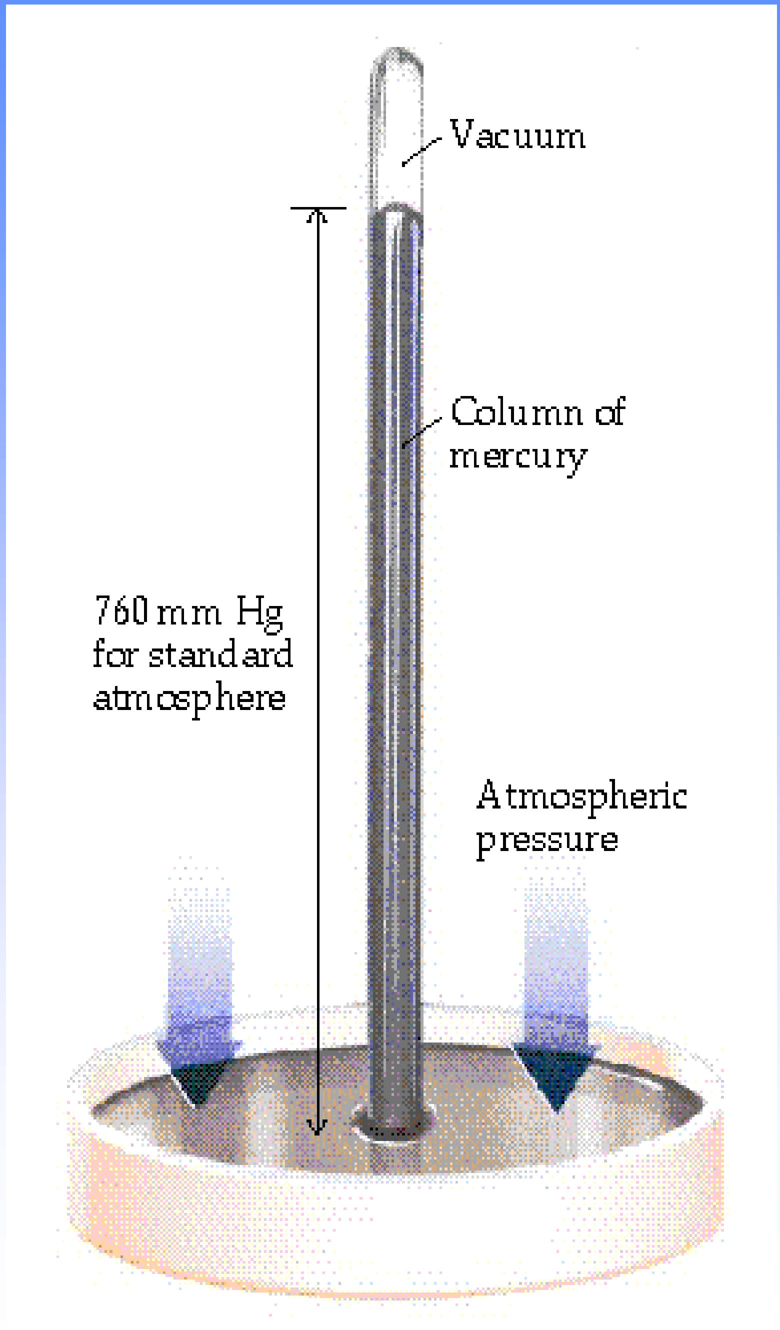


Pressure

Hg rises in tube until force of Hg (down) balances the force of atmosphere (pushing up).

P of Hg pushing down related to

- Hg density
- column height



Pressure

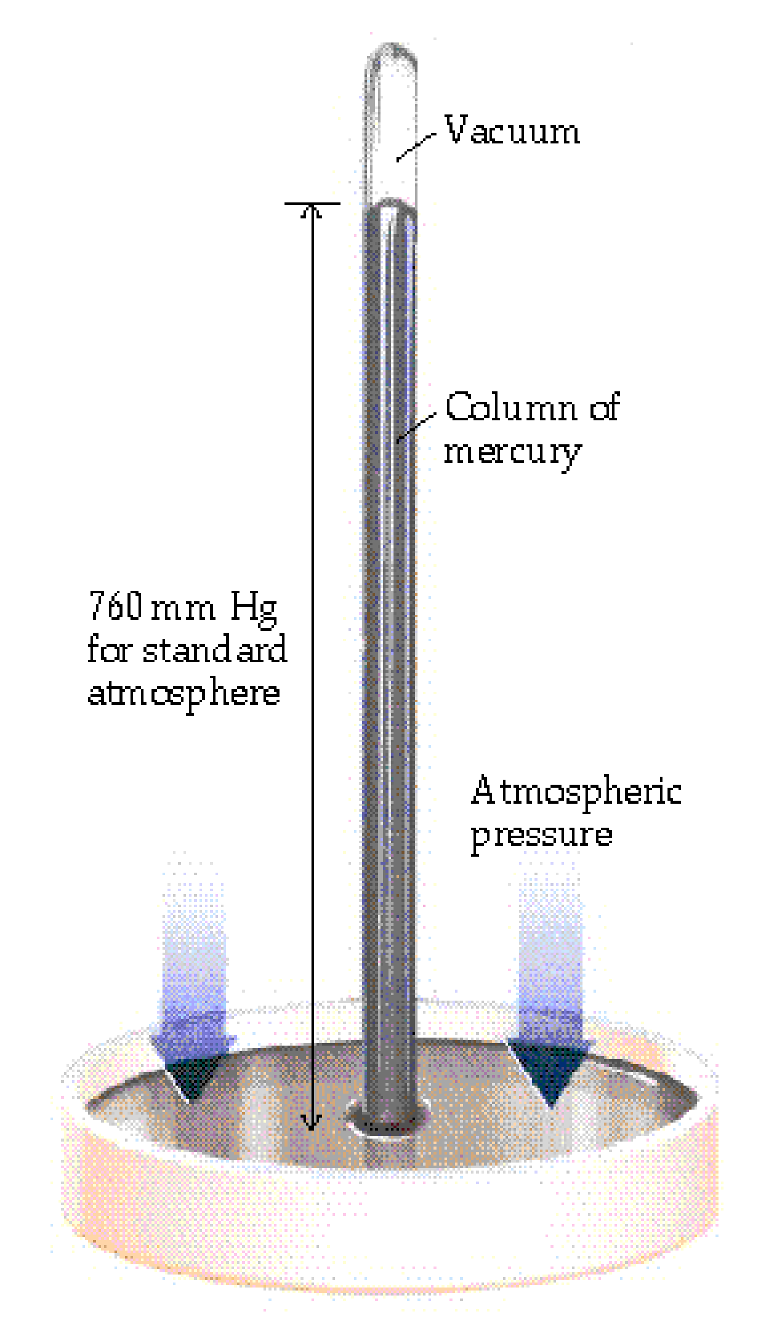
Column height measures P of atmosphere

- 1 standard atm = 760 mm Hg

= 29.9 inches

= about 34 feet of water

SI unit is PASCAL, Pa, where 1 atm = 101.325 kPa

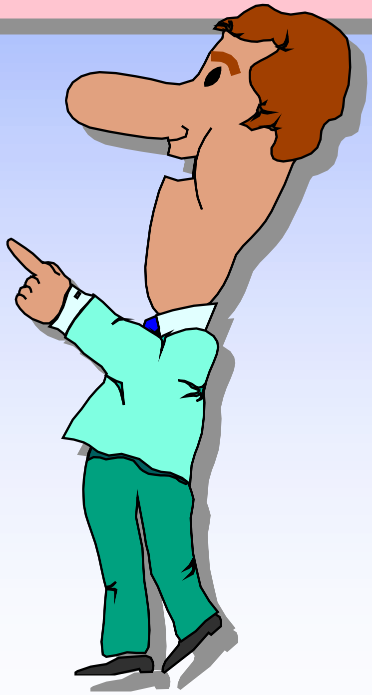


IDEAL GAS LAW

$$PV = nRT$$

Brings together gas properties.

Can be derived from experiment and theory.



Boyle's Law

If n and T are constant, then

$$PV = (nRT) = k$$

This means, for example, that P goes up as V goes down.

Robert Boyle (1627-1691). Son of Early of Cork, Ireland.

Boyle's Law

A bicycle pump is a good example of Boyle's law.

As the volume of the air trapped in the pump is reduced, its pressure goes up, and air is forced into the tire.

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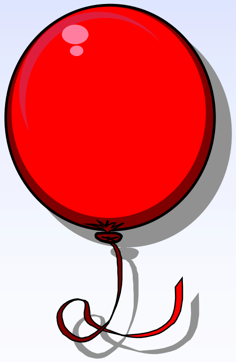
Charles's Law

If n and P are constant, then

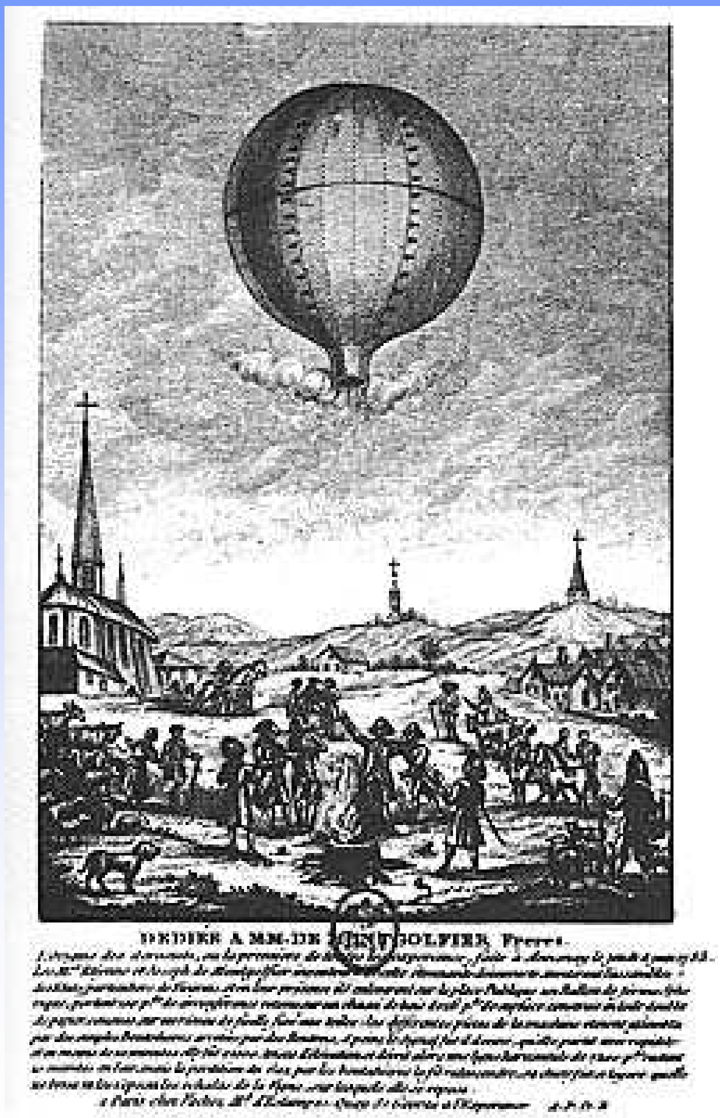
$V = (nR/P)T = kT$

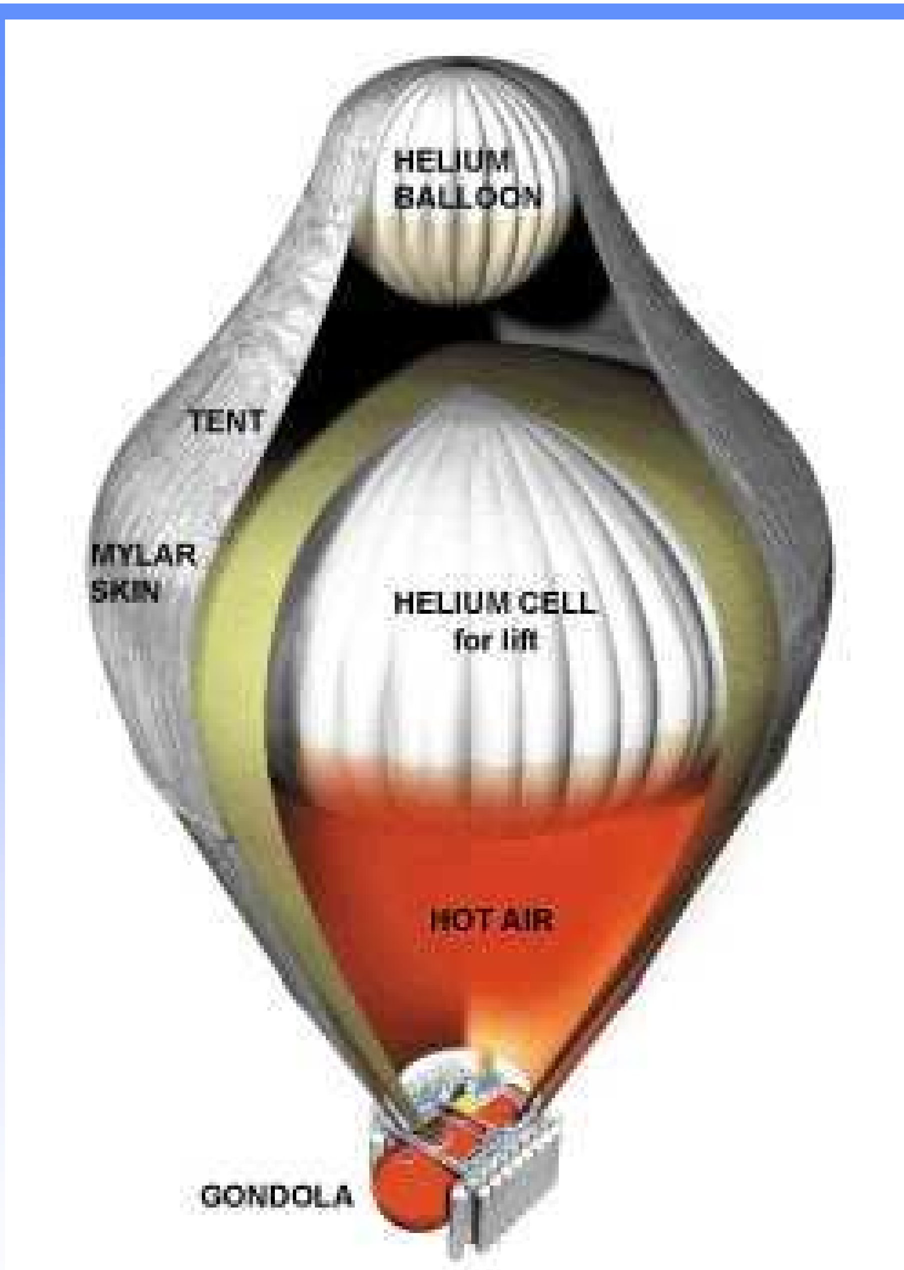
V and T are directly related.



Jacques Charles (1746-1823). Isolated boron and studied gases. Balloonist.

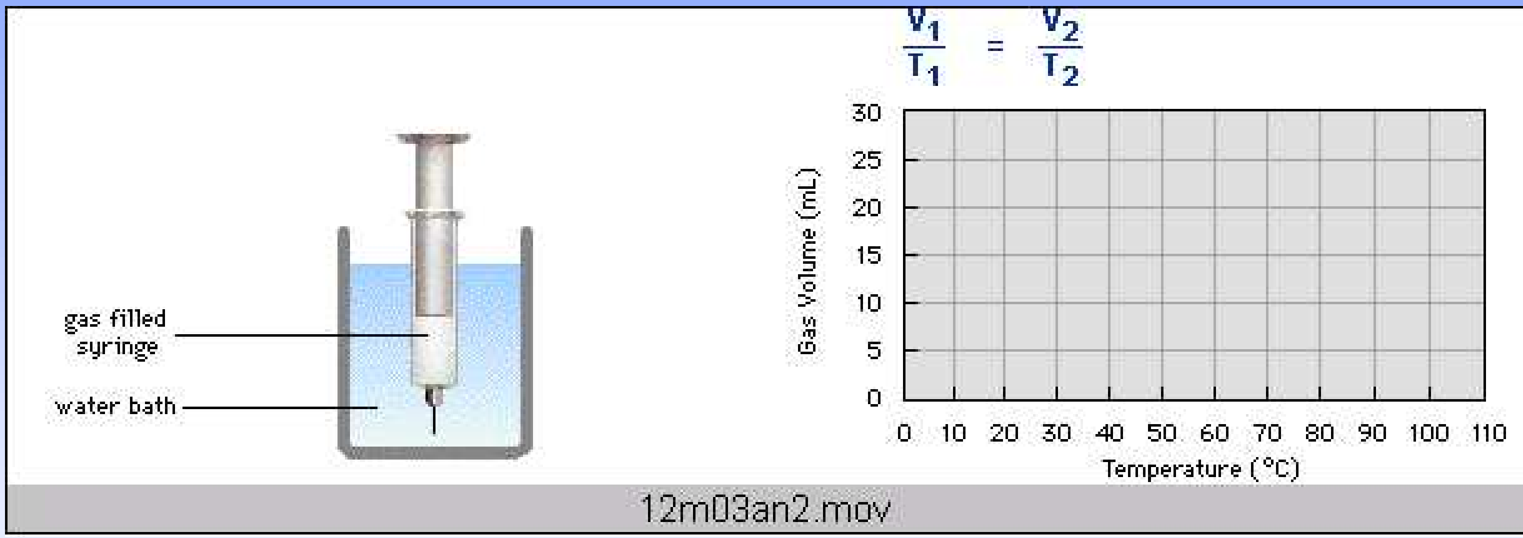
Charles's original balloon





Modern long-distance balloon

Charles's Law

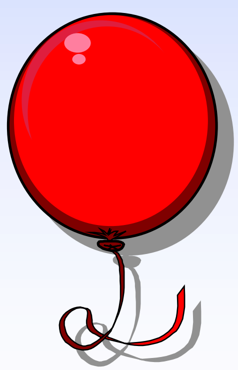


Avogadro's Hypothesis

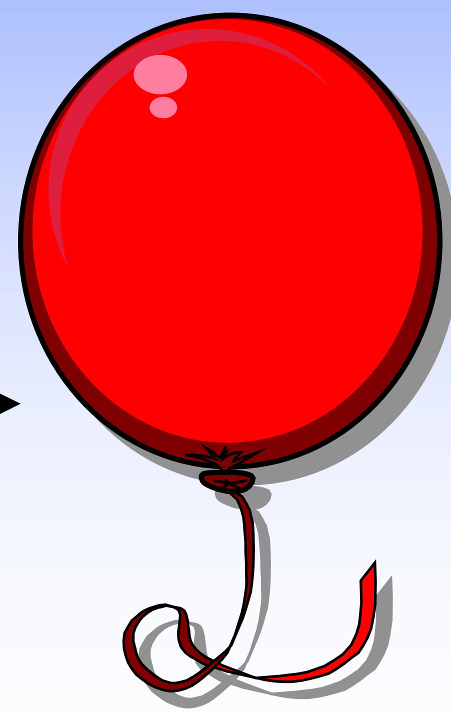
Equal volumes of gases at the same T and P have the same number of molecules.

$V = n\,(RT/P) = kn$

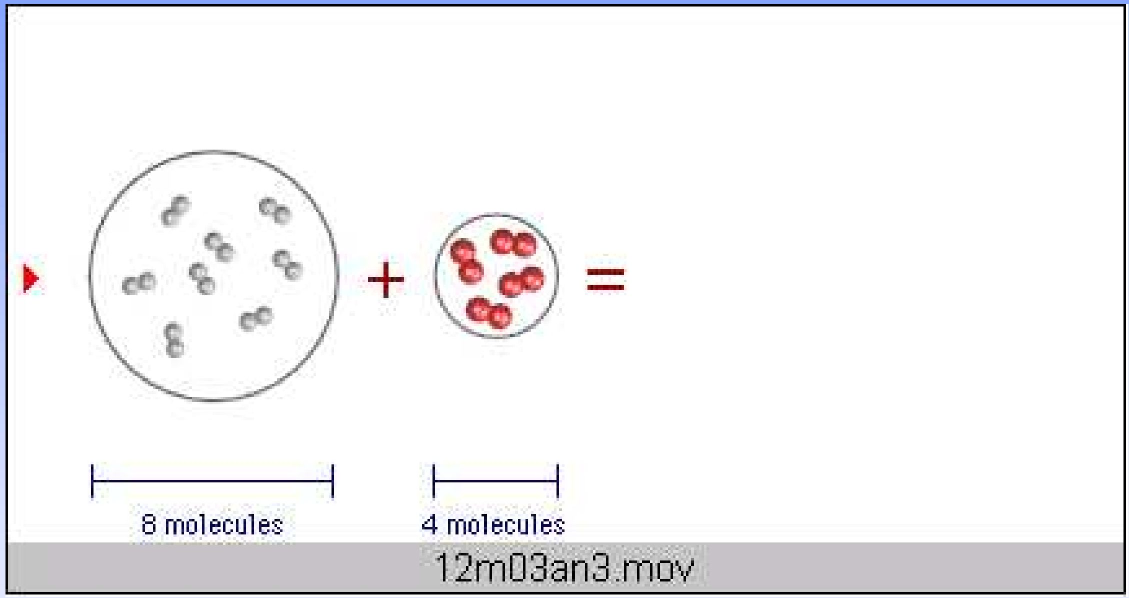
V and n are directly related.



twice as many molecules



Avogadro's Hypothesis



The gases in this experiment are all measured at the same T and P.

Using PV = nRT

How much N_2 is req'd to fill a small room with a volume of 960 cubic feet (27,000 L) to P = 745 mm Hg at 25 ^oC?

R = 0.082057 L•atm/K•mol

Solution

1. Get all data into proper units

V = 27,000 L

T = 25 ^oC + 273 = 298 K

P = 745 mm Hg (1 atm/760 mm Hg)
= 0.98 atm

Using PV = nRT

How much N_2 is req'd to fill a small room with a volume of 960 cubic feet (27,000 L) to P = 745 mm Hg at 25 ^oC?

R = 0.082057 L•atm/K•mol

Solution

2. Now calc. n = PV / RT

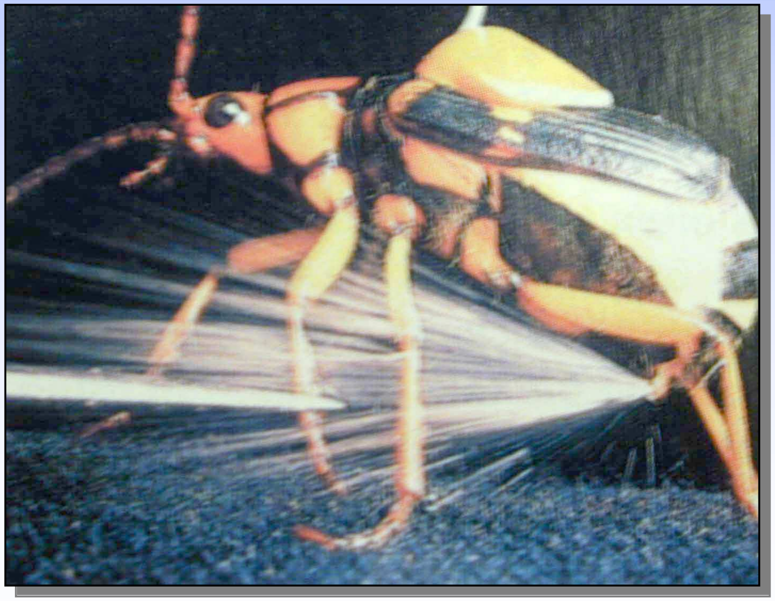
$$n = \frac{(0.98\text{ atm})(2.7 \times 10^4\text{ L})}{(0.0821\text{ L} \cdot \text{atm/K} \cdot \text{mol})(298\text{ K})}$$

n = 1.1 x 10^3 mol (or about 30 kg of gas)

Gases and Stoichiometry

$2\ H_2O_2(liq)$ ---> $2\ H_2O(g)$ + $O_2(g)$

Decompose 1.1 g of H_2O_2 in a flask with a volume of 2.50 L. What is the pressure of O_2 at 25 ^oC? Of H_2O?



Bombardier beetle uses decomposition of hydrogen peroxide to defend itself.

Gases and Stoichiometry

$2\ H_2O_2(liq)$ ---> $2\ H_2O(g)$ + $O_2(g)$

Decompose 1.1 g of H_2O_2 in a flask with a volume of 2.50 L. What is the pressure of O_2 at 25 ^oC? Of H_2O?

Solution

Strategy:

Calculate moles of H_2O_2 and then moles of O_2 and H_2O.

Finally, calc. P from n, R, T, and V.

Gases and Stoichiometry

$2\ H_2O_2(liq)\ \text{--->}\ 2\ H_2O(g)\ +\ O_2(g)$

Decompose 1.1 g of H_2O_2 in a flask with a volume of 2.50 L. What is the pressure of O_2 at 25 °C? Of H_2O?

Solution

$$1.1\ g\ H_2O_2 \bullet \frac{1\ mol}{34.0\ g} = 0.032\ mol$$

$$0.032\ mol\ H_2O_2 \bullet \frac{1\ mol\ O_2}{2\ mol\ H_2O_2} = 0.016\ mol\ O_2$$

Gases and Stoichiometry

$2\ H_2O_2(liq) \longrightarrow 2\ H_2O(g) + O_2(g)$

Decompose 1.1 g of H_2O_2 in a flask with a volume of 2.50 L. What is the pressure of O_2 at 25 ^oC? Of H_2O?

Solution

$$P \text{ of } O_2 = nRT/V$$

$$= \frac{(0.016 \text{ mol})(0.0821 \text{ L} \cdot \text{atm/K} \cdot \text{mol})(298 \text{ K})}{2.50 \text{ L}}$$

P of O_2 = 0.16 atm

Gases and Stoichiometry

$$2\ H_2O_2(liq) \longrightarrow 2\ H_2O(g) + O_2(g)$$

What is P of H_2O? Could calculate as above. But recall Avogadro's hypothesis.

V $\propto$ n at same T and P

P $\propto$ n at same T and V

There are 2 times as many moles of H_2O as moles of O_2. P is proportional to n. Therefore, P of H_2O is twice that of O_2.

P of H_2O = 0.32 atm

Dalton's Law of Partial Pressures

$$2\ H_2O_2(liq) \longrightarrow 2\ H_2O(g) + O_2(g)$$

0.32 atm   0.16 atm

What is the total pressure in the flask?

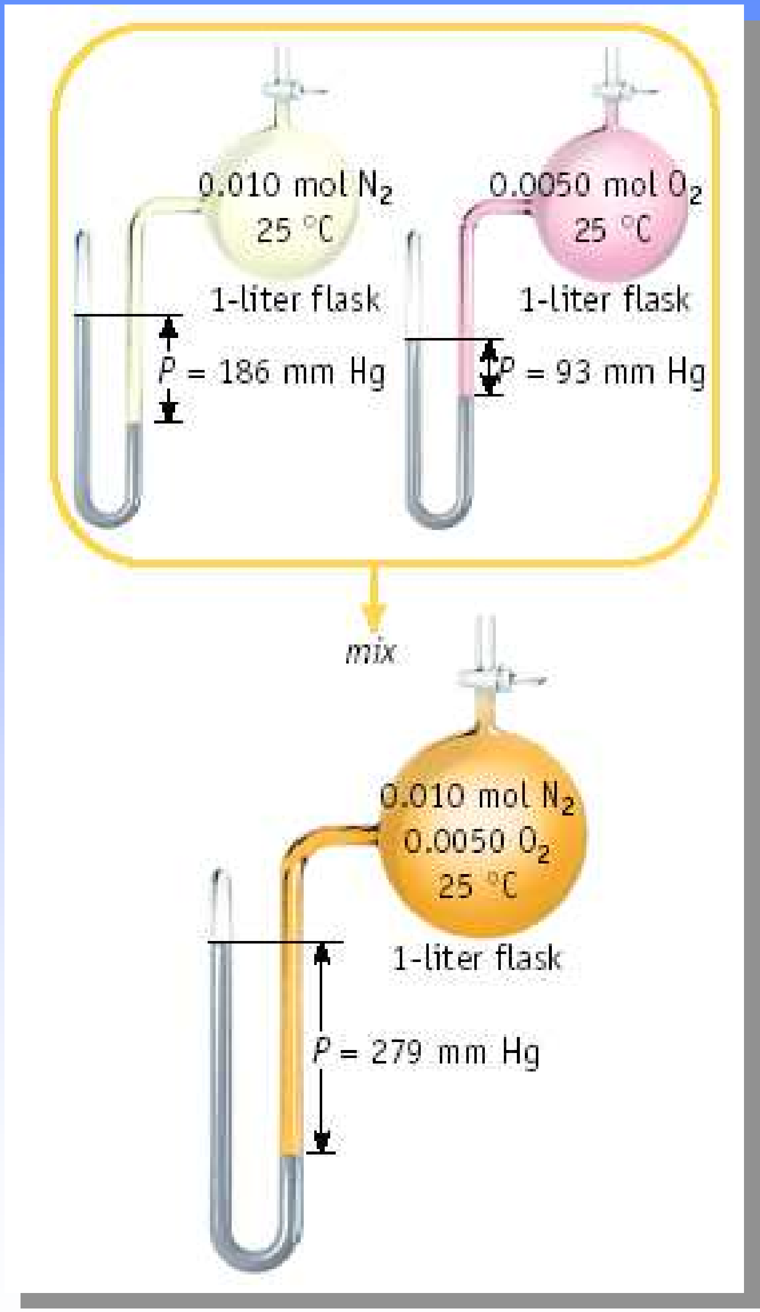
P_{total} in gas mixture = $P_A + P_B + ...$

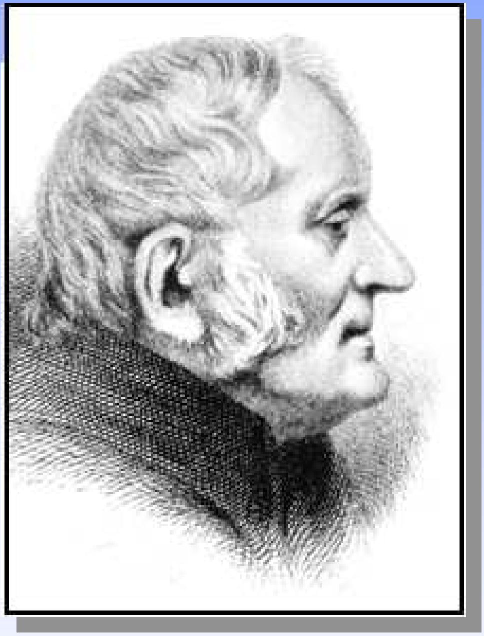
Therefore,

$P_{total} = P(H_2O) + P(O_2) = 0.48$ atm

Dalton's Law: total P is sum of PARTIAL pressures.

Dalton's Law





John Dalton
1766-1844

GAS DENSITY

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Low density

High density

GAS DENSITY

Screen 12.5

$$PV = nRT$$

$$\frac{n}{V} = \frac{P}{RT}$$

$$\frac{m}{M \cdot V} = \frac{P}{RT}$$

where M = molar mass

$$d = \frac{m}{V} = \frac{PM}{RT}$$

d and M proportional

USING GAS DENSITY

The density of air at 15 ^{o}C and 1.00 atm is 1.23 g/L. What is the molar mass of air?

1. Calc. moles of air.

   V = 1.00 L P = 1.00 atm T = 288 K

   n = PV/RT = 0.0423 mol

2. Calc. molar mass

   mass/mol = 1.23 g/0.0423 mol = 29.1 g/mol

KINETIC MOLECULAR THEORY (KMT)

Theory used to explain gas laws. KMT assumptions are

- Gases consist of molecules in constant, random motion.
- P arises from collisions with container walls.
- No attractive or repulsive forces between molecules. Collisions elastic.
- Volume of molecules is negligible.

Kinetic Molecular Theory

Because we assume molecules are in motion, they have a kinetic energy.

$$KE = (1/2)(mass)(speed)^2$$

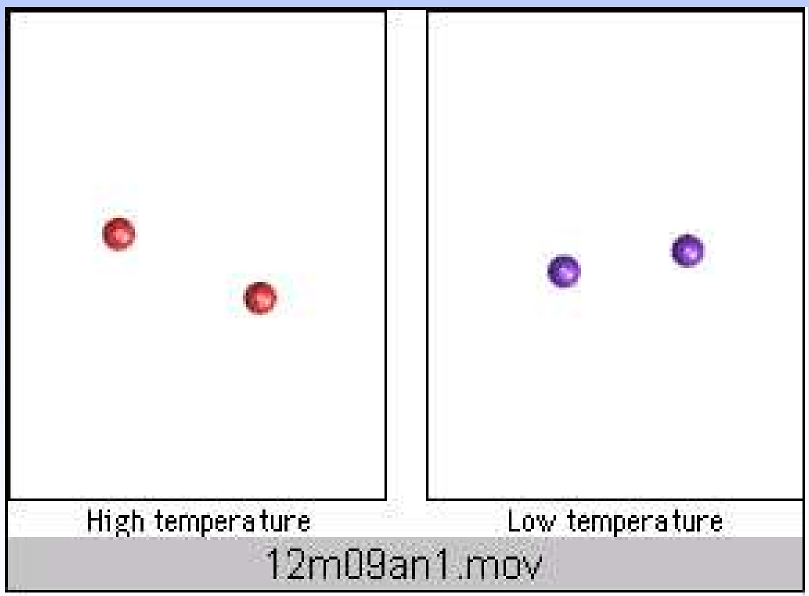
At the same T, all gases have the same average KE.

As T goes up, KE also increases — and so does speed.

Kinetic Molecular Theory

At the same T, all gases have the same average KE.

As T goes up, KE also increases — and so does speed.



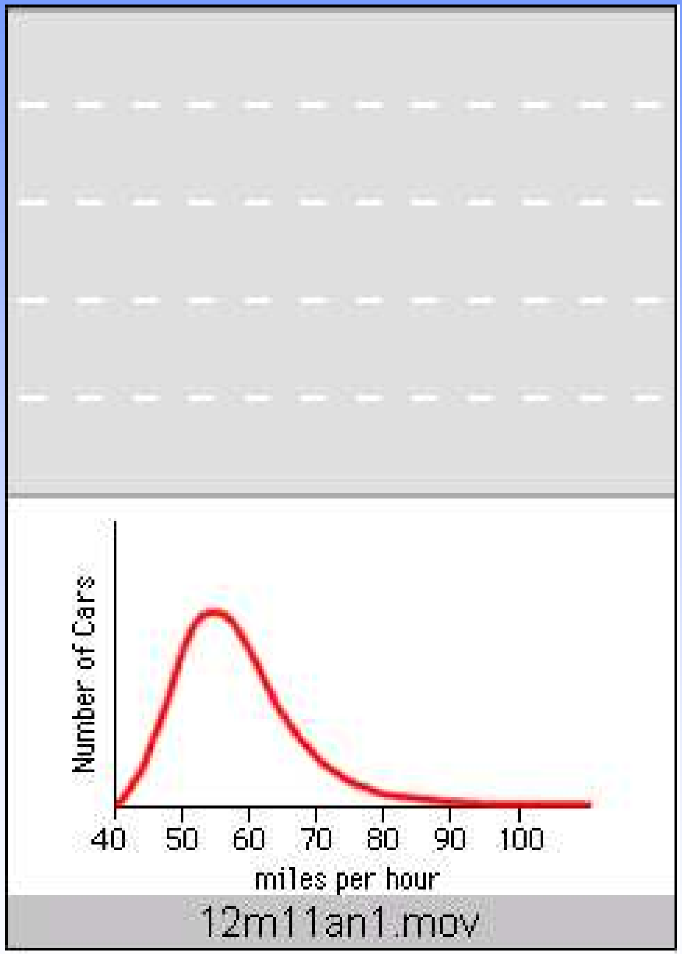
Kinetic Molecular Theory

Maxwell's equation

$$\underbrace{\sqrt{\overline{u^2}}}_{\text{root mean square speed}} = \sqrt{\frac{3RT}{M}}$$

where u is the speed and M is the molar mass.

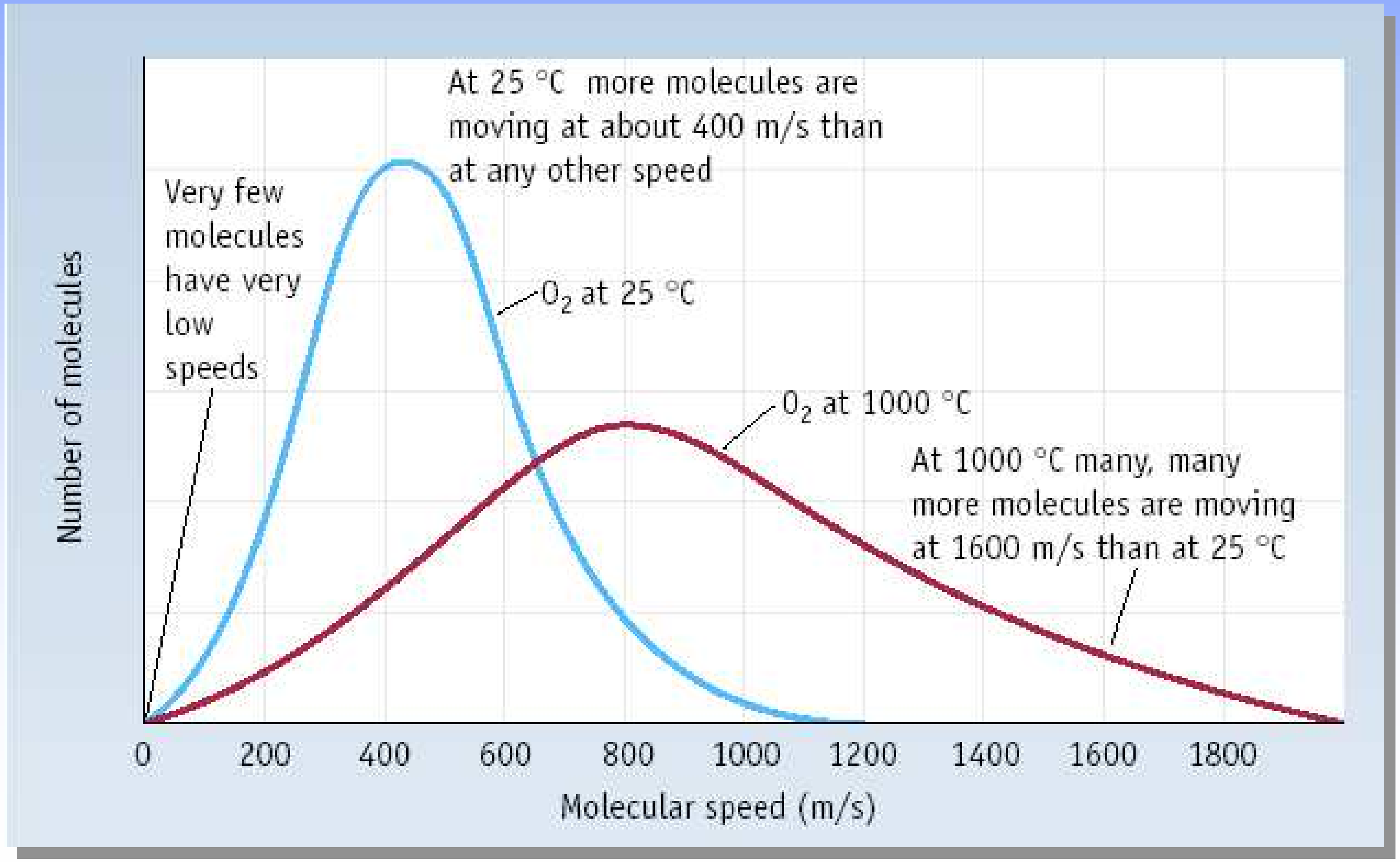
- speed INCREASES with T
- speed DECREASES with M



Distribution of Gas Molecule Speeds

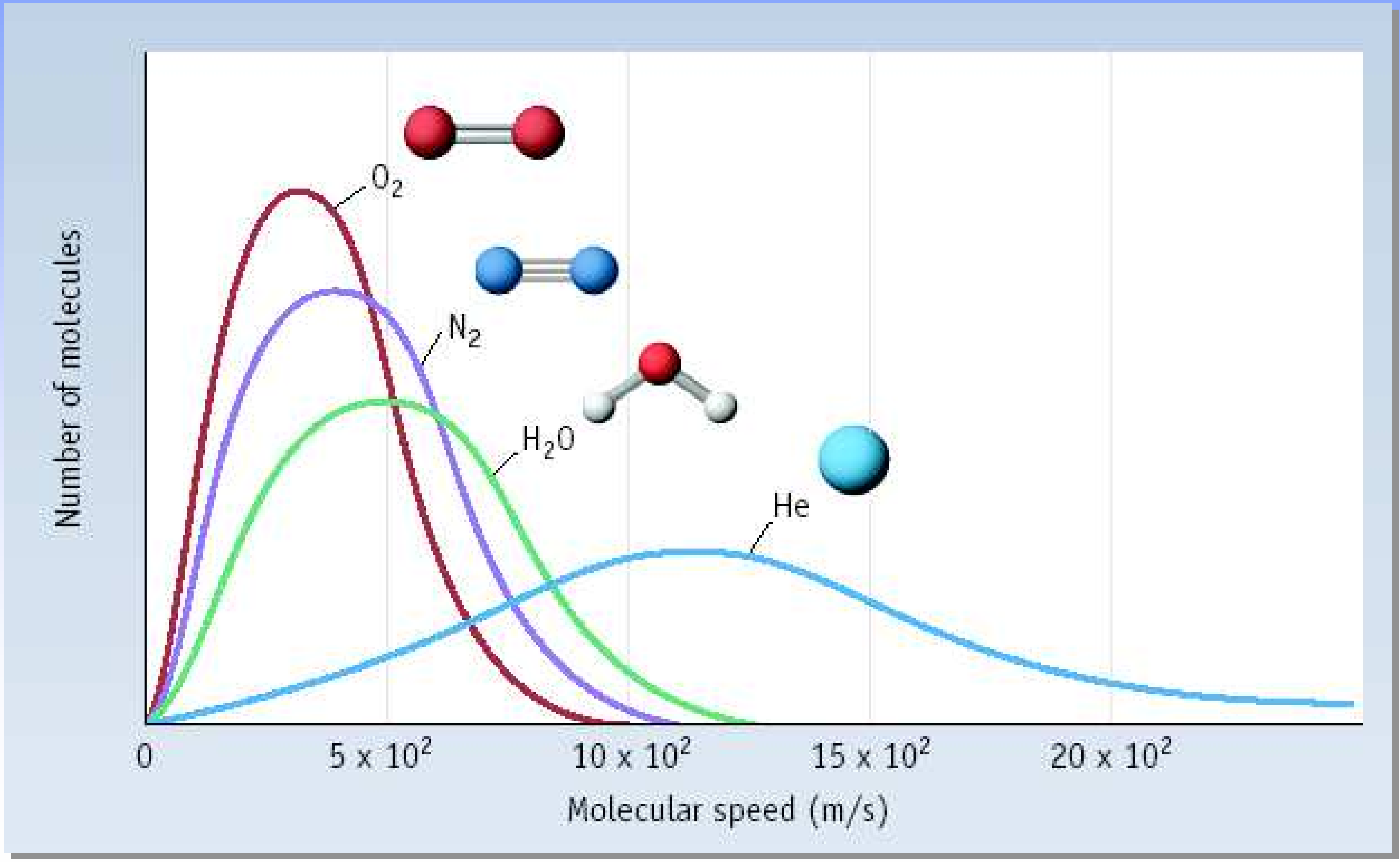
Velocity of Gas Molecules

Molecules of a given gas have a **range** of speeds.



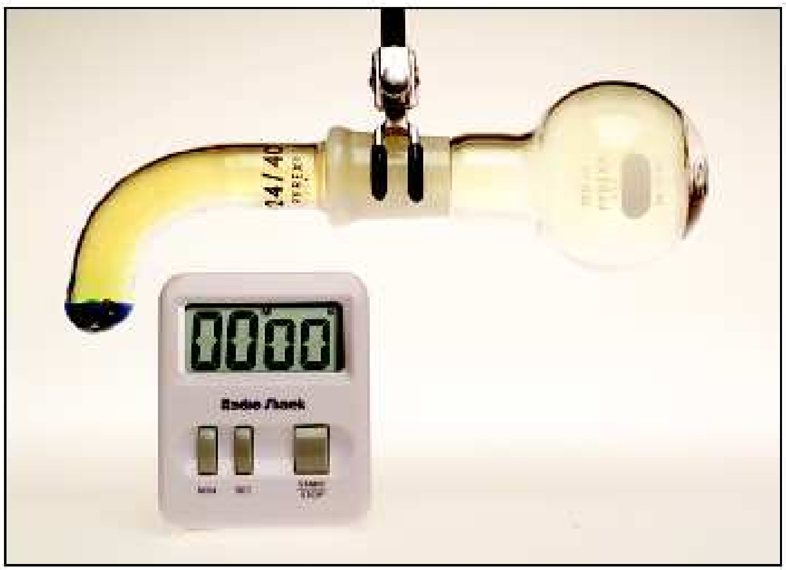
Velocity of Gas Molecules

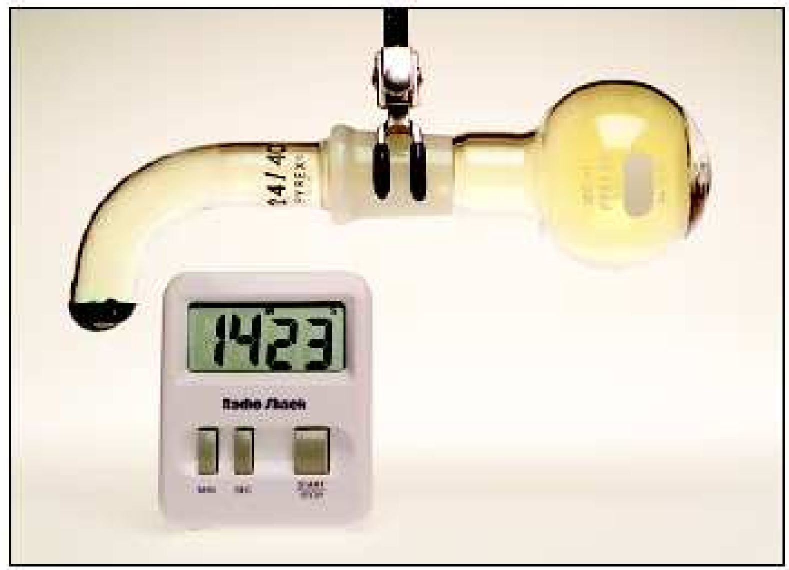
Average velocity decreases with increasing mass.



GAS DIFFUSION AND EFFUSION

- **diffusion** is the gradual mixing of molecules of different gases.
- **effusion** is the movement of molecules through a small hole into an empty container.



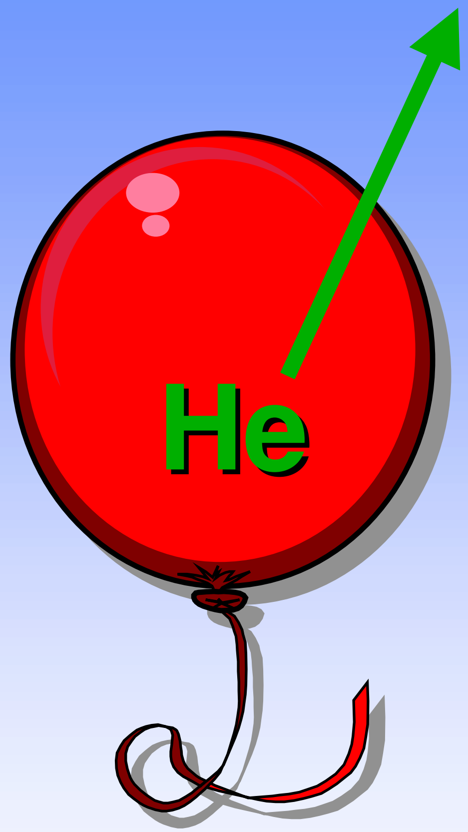


GAS DIFFUSION AND EFFUSION

Molecules effuse thru holes in a rubber balloon, for example, at a rate (= moles/time) that is

- proportional to T
- inversely proportional to M.

Therefore, He effuses more rapidly than O_2 at same T.



GAS DIFFUSION AND EFFUSION

Graham's law governs effusion and diffusion of gas molecules.

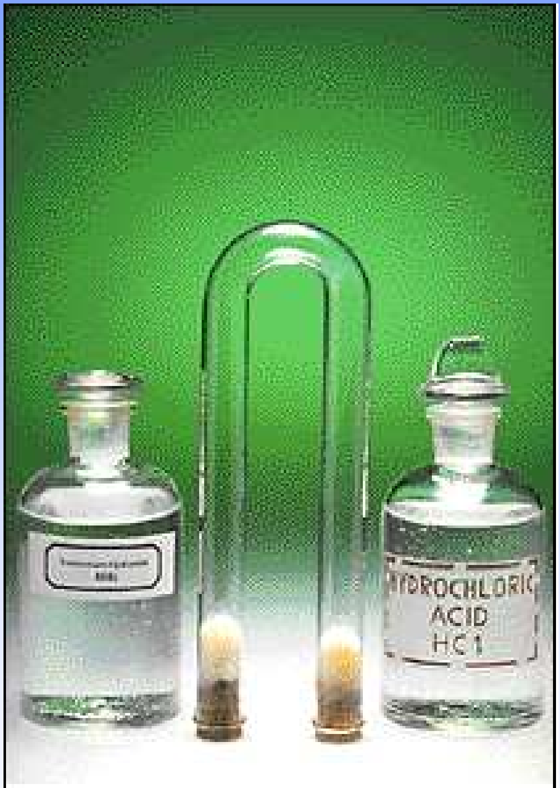
$$\frac{\text{Rate for A}}{\text{Rate for B}} = \sqrt{\frac{\text{M of B}}{\text{M of A}}}$$

Rate of effusion is inversely proportional to its molar mass.

Thomas Graham, 1805-1869. Professor in Glasgow and London.

Gas Diffusion

relation of mass to rate of diffusion



Gaseous diffusion of $NH_3(g)$ and $HCl(g)$

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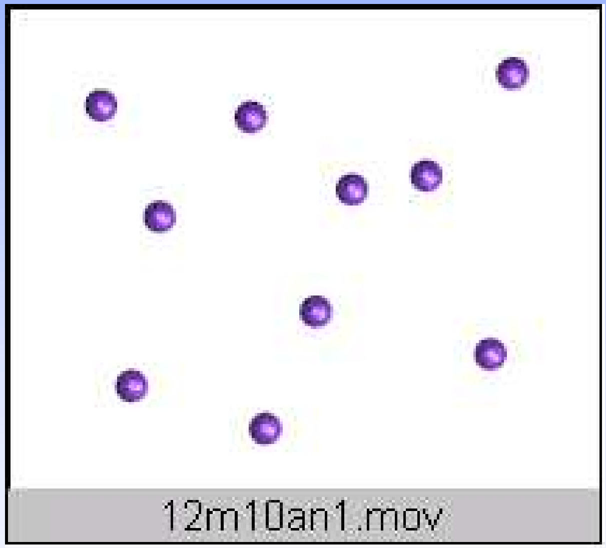
- HCl and NH_3 diffuse from opposite ends of tube.
- Gases meet to form NH_4Cl
- HCl heavier than NH_3
- Therefore, NH_4Cl forms closer to HCl end of tube.

Using KMT to Understand Gas Laws

Recall that KMT assumptions are

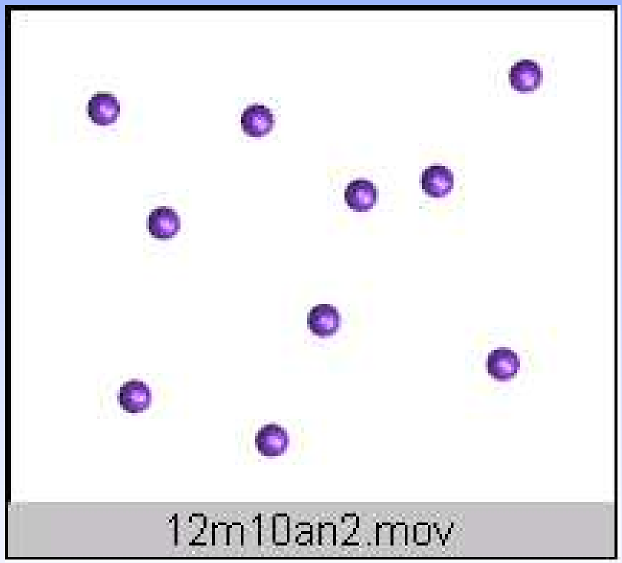
- **Gases consist of molecules in constant, random motion.**
- **P arises from collisions with container walls.**
- **No attractive or repulsive forces between molecules. Collisions elastic.**
- **Volume of molecules is negligible.**

Avogadro's Hypothesis and Kinetic Molecular Theory



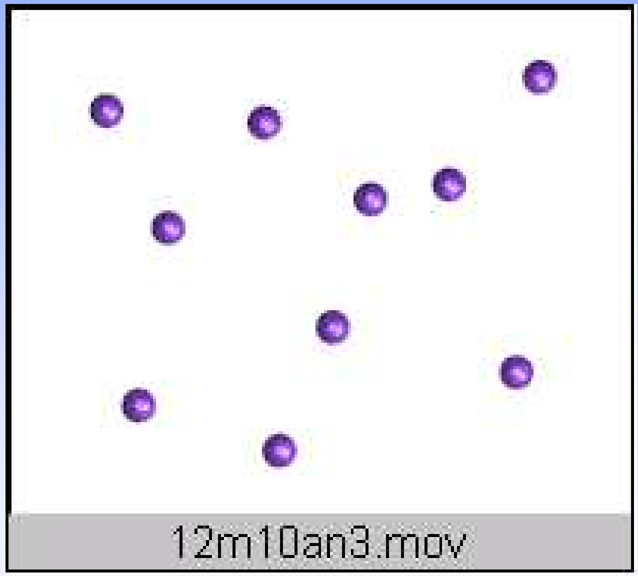
P proportional to n

Gas Pressure, Temperature, and Kinetic Molecular Theory



P proportional to T

Boyle's Law and Kinetic Molecular Theory



P proportional to 1/V

Deviations from Ideal Gas Law

- Real molecules have **volume**.
- There are **intermolecular forces**.
  - Otherwise a gas could not become a liquid.

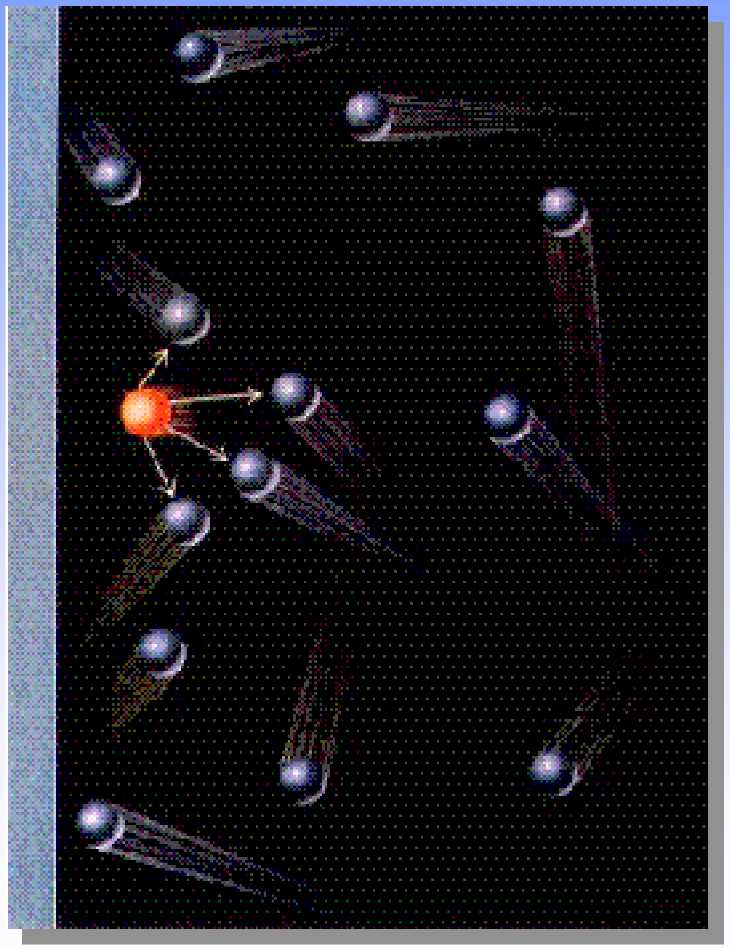


Fig. 12.20

Deviations from Ideal Gas Law

Account for volume of molecules and intermolecular forces with **VAN DER WAAL'S EQUATION**.

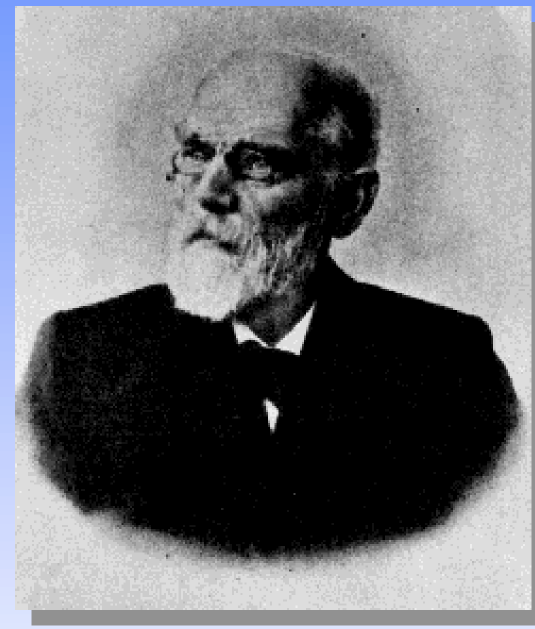
Measured P

Measured V = V(ideal)

$$\left(P + \frac{n^2 a}{V^2}\right)\left(V - nb\right) = nRT$$

intermol. forces

vol. correction



J. van der Waals, 1837-1923, Professor of Physics, Amsterdam. Nobel Prize 1910.

Deviations from Ideal Gas Law

Measured P

Measured V = V(ideal)

$$\left[P + \frac{n^2 a}{V^2}\right]\left(V - nb\right) = nRT$$

vol. correction

intermol. forces

Cl_2 gas has **a** = 6.49, **b** = 0.0562

For 8.0 mol Cl_2 in a 4.0 L tank at 27 ^oC.

P (ideal) = nRT/V = 49.3 atm

P (van der Waals) = 29.5 atm