The Properties Of Gases

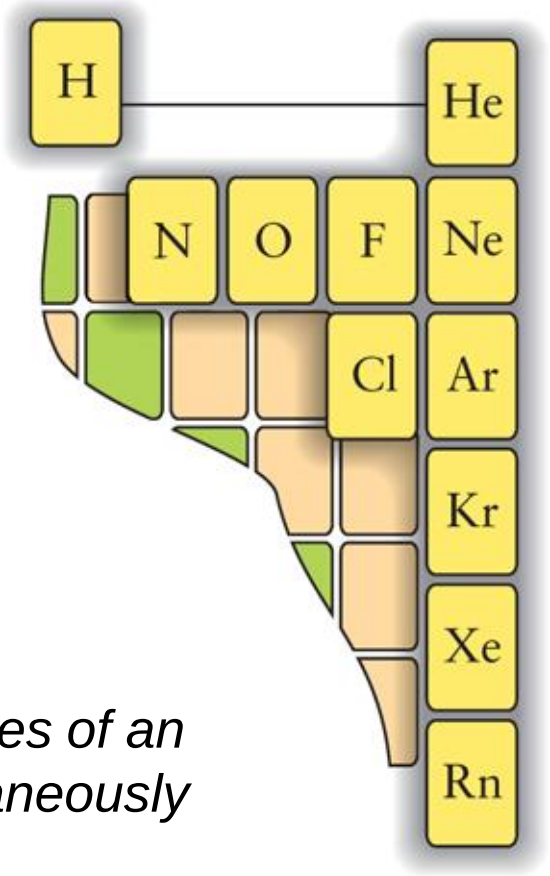
The Nature of Gases

Eleven (11) elements are gases under normal conditions.

H_2, N_2, O_2, F_2, Cl_2,

Low molar mass compounds such as carbon dioxide, hydrogen chloride are also gases.

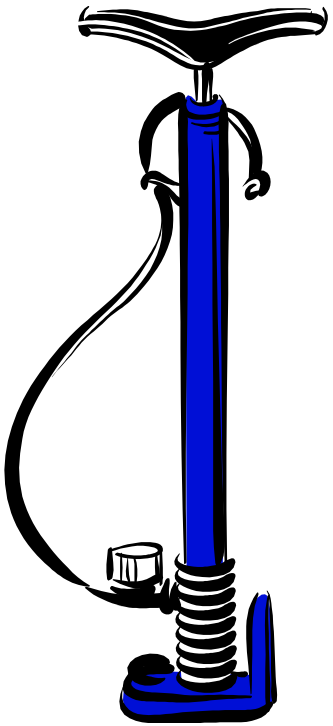
Remarkable gases have similar physical properties at low pressures.



Describing one properties of an individually gas, simultaneously describes them all.

1. Compressibility

Pushing on a bicycle pump - with your finger over the valve - we can feel the pressure build, as we confine the gases into smaller and smaller volumes.

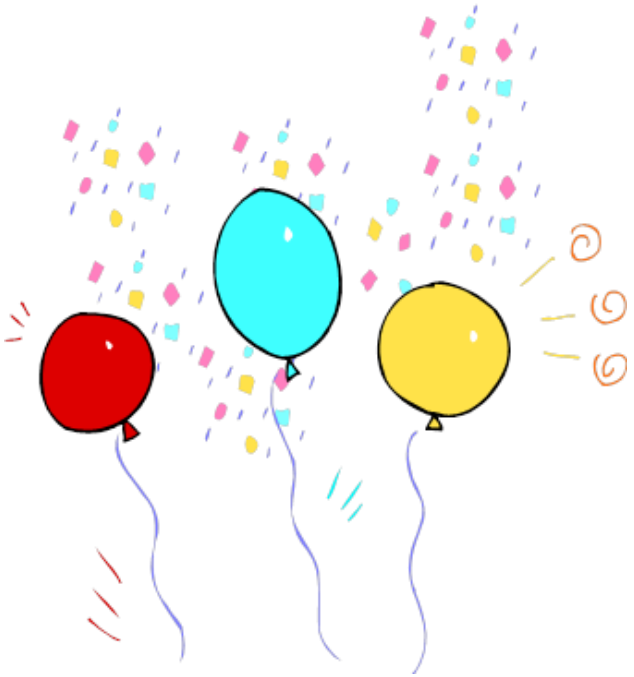


The observation that gases are more compressible than solids and liquids suggests that there is a lot of space between the molecules of gases .

2. Motion

Releasing air from an inflated balloon, we know the gas expands rapidly to fill the space available to it.

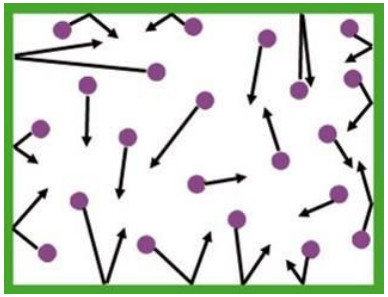
Also, because balloons are spherical we can infer that the motion of the molecules is chaotic, not favoring any single direction.



Our first primitive picture of a gas could be gasses are a collection of widely spaced molecules in ceaseless rapid chaotic motion.

Pressure (P)

$$\text{Pressure (P)} = \frac{\text{Force (F)}}{\text{Area (A)}}$$



F: constant

A ↓ ➡ P ↑

A: constant

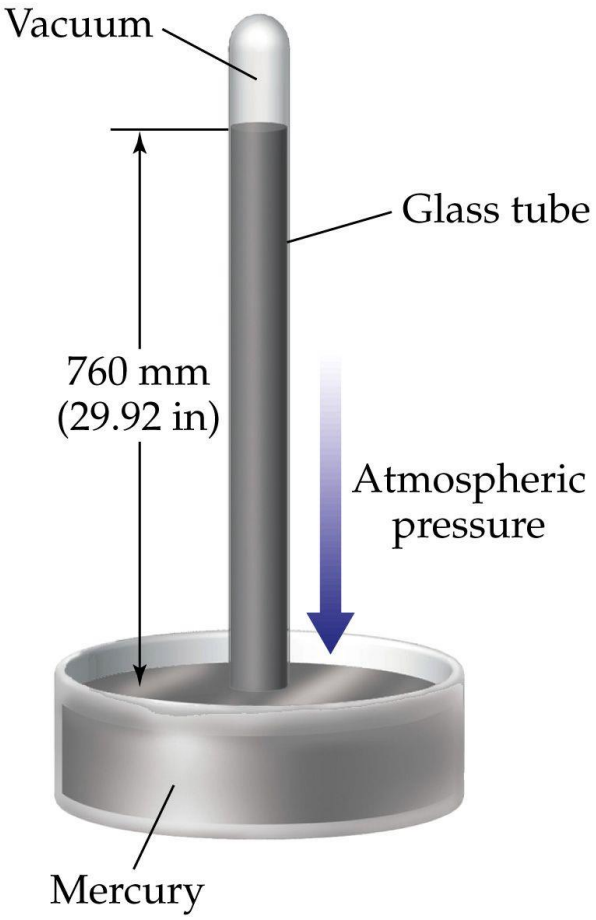
F ↑ ➡ P ↑

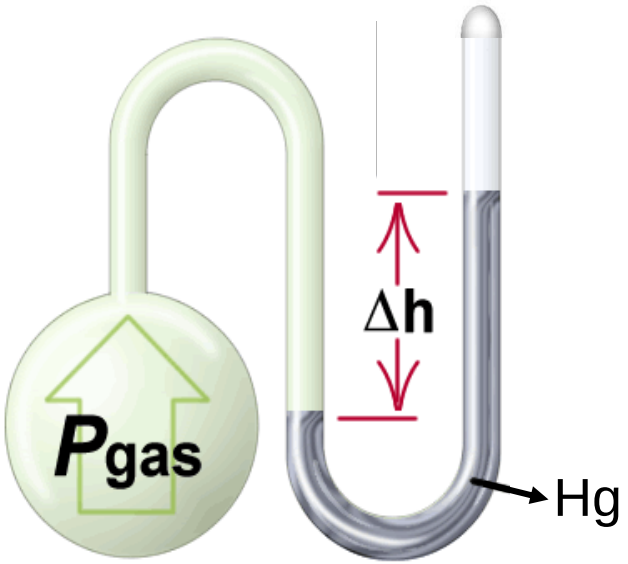
Atmosphere (atm)
Millimeters of mercury (mm Hg)
Torr
Inches of mercury (in. Hg)
Pascal (Pa)
Pound per square (psi)

1.000 atm = 760.0 mm Hg
= 760.0 Torr
= 101,325 Pa
= 29.92 in. Hg
= 14.69 psi

1 Pa = 1 $kg \cdot m^{-1} \cdot s^{-2}$

Pressure (P)





barometer

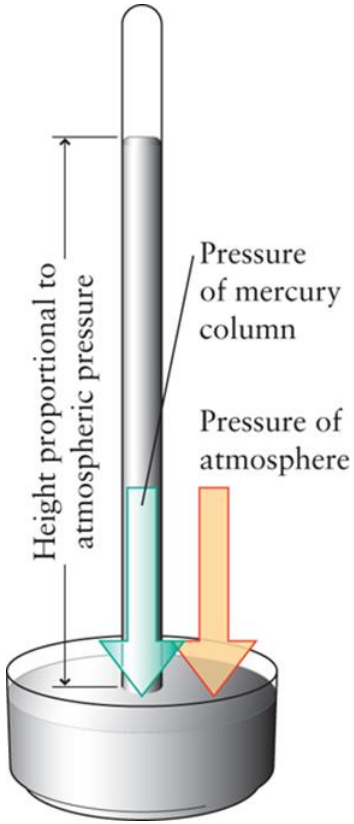
atmospheric pressure

manometer

pressure of gas in a container

Barometer

Evangelista Torricelli, 17th century, a student of Galileo, made the first barometer (Torricelli means "little tower" in Italian).



$$P = \frac{F}{A} = \frac{\text{weight}}{cm^2} = \frac{d \times h \times cm^2 \times g}{cm^2} = d \times h \times g$$

P = pressure (Pa) , F = Force ~ weight, A = Surface area (cm^2),
d = density (kg/m^3), h = height, *g* = gravity (9.80665 $m.s^{-1}$).

P = dgh

Practice 1: The density of water at 20°C is 0.998 g·cm^{-3}. What height would the column of liquid be in a water barometer when the atmospheric pressure corresponds to 760. mm of mercury?

$$P = dhg$$

760. mm = 1.01×10^5 Pa = 1.01×10^5 kg·m^{-1}·s^{-2}

$$h = \frac{P}{dg} = \frac{1.01 \times 10^5 \text{ kg·m}^{-1}\text{·s}^{-2}}{998 \text{ kg·m}^{-3} \times 9.80665 \text{ m·s}^{-2}} = 10.3 \text{ m or } 33.8 \text{ ft}$$

It would be a very long climb to read a barometer using water instead of mercury; the equivalent of climbing a 3 story building.

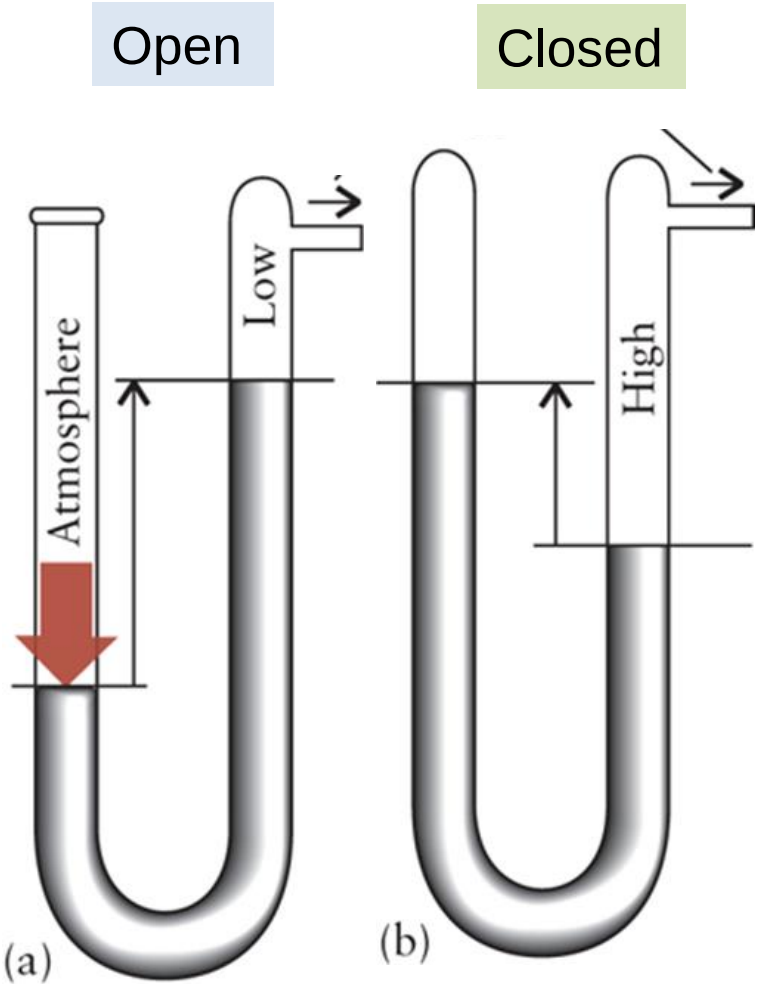
Manometer in a Lab

An **open-tube** manometer, is a measure of a gas against atmospheric pressure (proportional to atmospheric pressure).

(a) Shown is where the atmospheric pressure is greater than the gas at the other end.

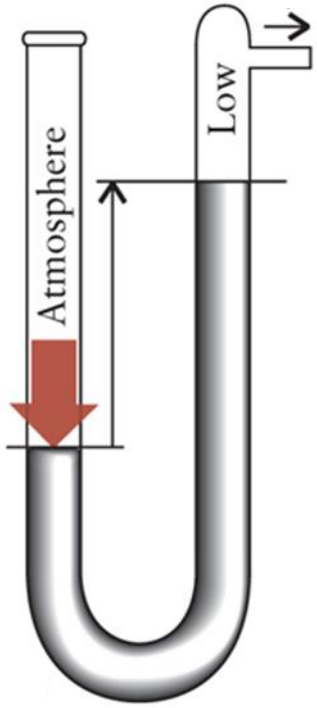
In a **closed-tube** manometer, the difference in heights of the two columns is <u>proportional</u> to the pressure in the system.

Height difference is pressure in both cases.



Practice 2: The height difference of the mercury in an open-tube mercury manometer was 10. mm when the atmospheric pressure is 756 mmHg and at 15 °C. What is the pressure inside the apparatus in mmHg and in pascals?

Higher atmospheric pressure pushes the mercury level lower, so the internal pressure is less than atmospheric.



756 mm - 10. mm = 746 mm of mercury

$P = dhg = 13{,}595\ kg \cdot m^{-3} \times 0.746\ m \times 9.80665\ m \cdot s^{-2}$

$= 9.95 \times 10^4\ kg \cdot m^{-1} \cdot s^{-2} = 9.95 \times 10^4\ Pa$

Boyle's Law

Robert Boyle

Boyle's law: m,T: constant

Isothermal change is one that takes place at **constant temp**.

$P \propto 1/\alpha\ V \Longrightarrow PV = k$ (a constant)

P_1V_1 = k (a constant)

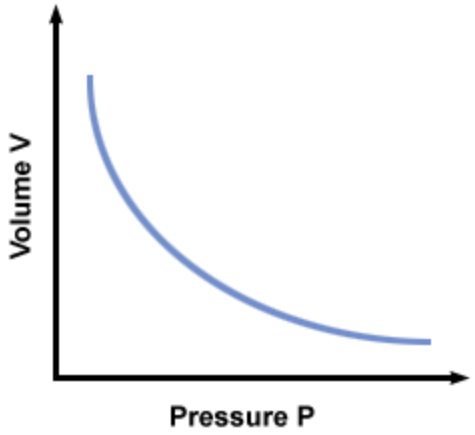
P_2V_2 = k (a constant)

$$\Longrightarrow \boxed{P_1V_1 = P_2V_2}$$

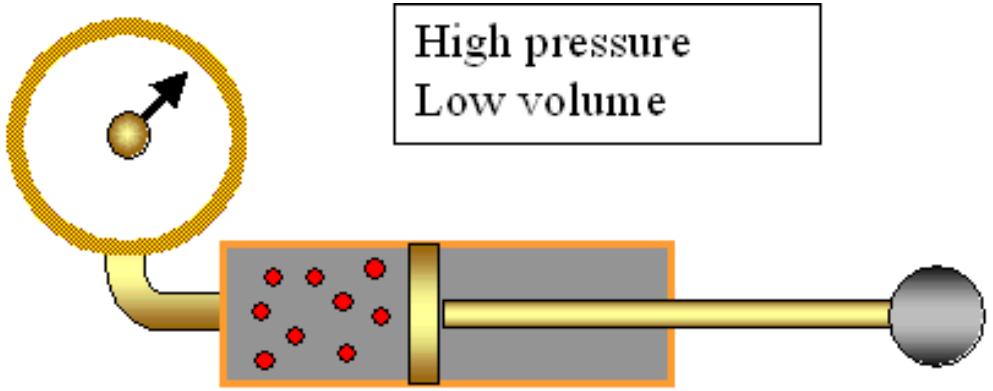
$$P_2 = \frac{P_1V_1}{V_2}$$

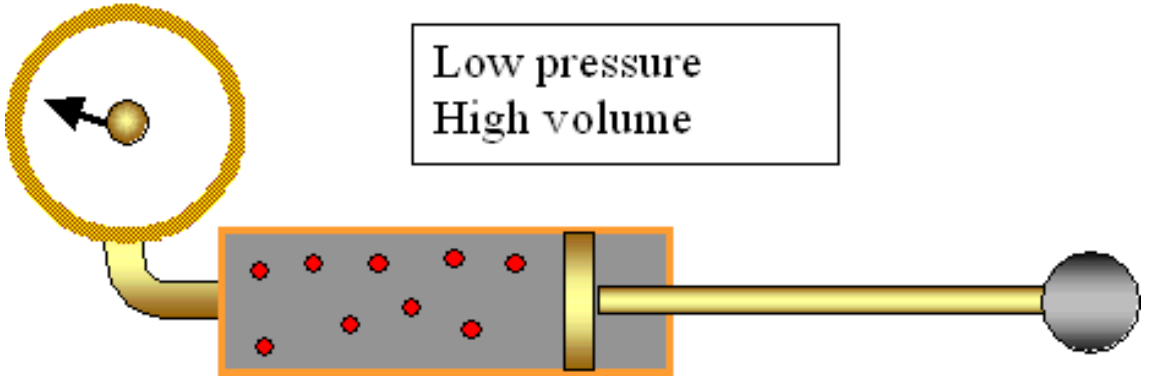
$$V_2 = \frac{P_1V_1}{P_2}$$

Boyle's Law



decreasing the volume of a gas sample means increasing the pressure.





Charles's Law

Jacques Charles

Charles's law: m,P: constant

$$T \ \alpha \ V \quad \Longrightarrow \quad \frac{V}{T} = k \text{ (a constant)}$$

$$\frac{V_1}{T_1} = k \text{ (a constant)}$$

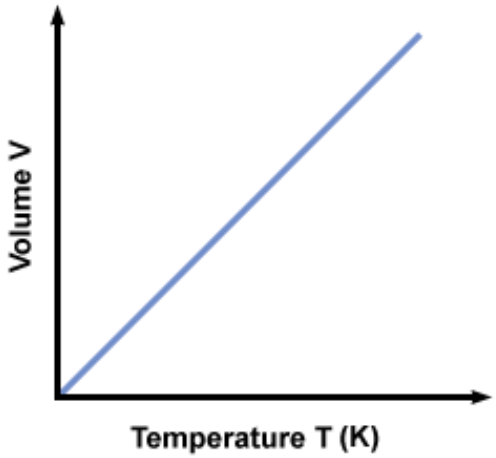
$$\frac{V_2}{T_2} = k \text{ (a constant)}$$

$$\Longrightarrow \quad \boxed{\frac{V_1}{T_1} = \frac{V_2}{T_2}}$$

$$V_2 = \frac{V_1 T_2}{T_1} \qquad T_2 = \frac{T_1 V_2}{V_1}$$

gas-properties_en.jar

Charles's Law



an increase in temperature at constant pressure results in an increase in volume.

Gay-Lussac's Law

Gay-Lussac's law: m,V: constant

$$P \propto T \Longrightarrow \frac{P}{T} = k \text{ (a constant)}$$

$$\frac{P_1}{T_1} = k \text{ (a constant)}$$

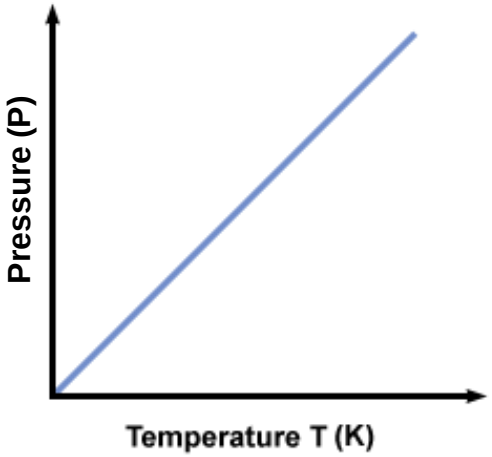
$$\frac{P_2}{T_2} = k \text{ (a constant)}$$

$$\Longrightarrow \boxed{\frac{P_1}{T_1} = \frac{P_2}{T_2}}$$

$$P_2 = \frac{P_1 T_2}{T_1}$$

$$T_2 = \frac{T_1 P_2}{P_1}$$

Gay-Lussac's Law



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Avogadro's Principle

Avogadro's principle: P,T: constant

$$V \ \alpha \ n \quad \Longrightarrow \quad \frac{V}{n} = k \text{ (a constant)}$$

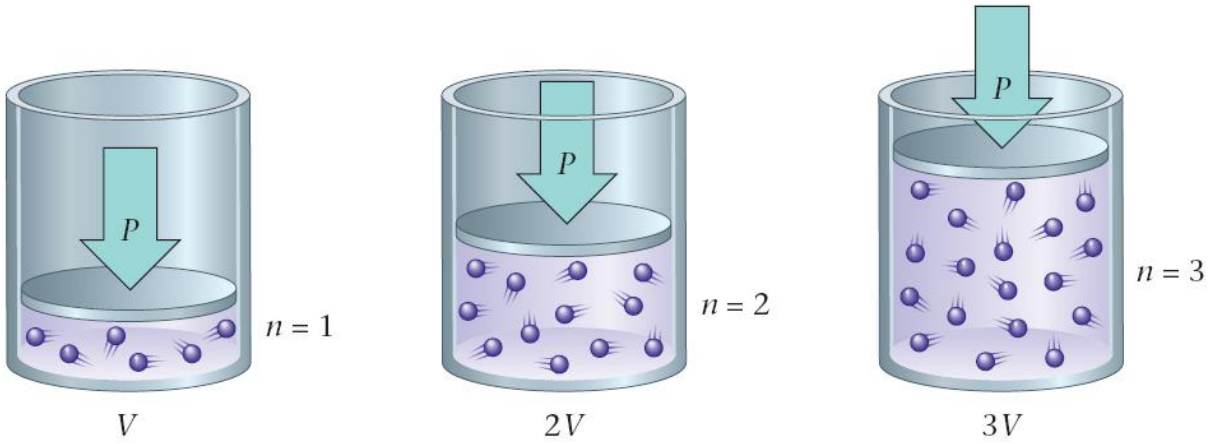
$$\frac{V_1}{n_1} = k \text{ (a constant)}$$

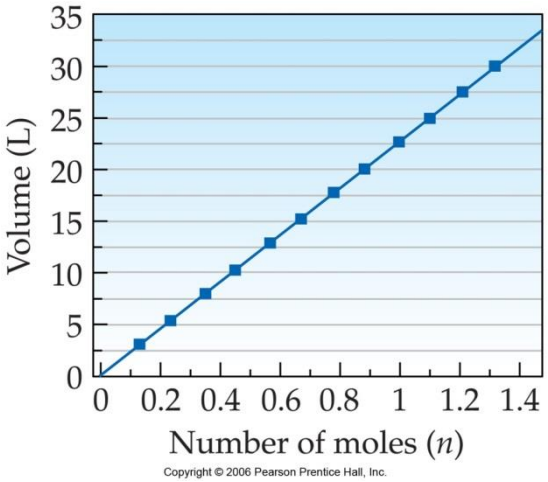
$$\frac{V_2}{n_2} = k \text{ (a constant)}$$

$$\Longrightarrow \quad \boxed{\frac{V_1}{n_1} = \frac{V_2}{n_2}}$$

Avogadro's Principle

increasing the moles of gas at constant pressure means more volume is needed to hold the gas.





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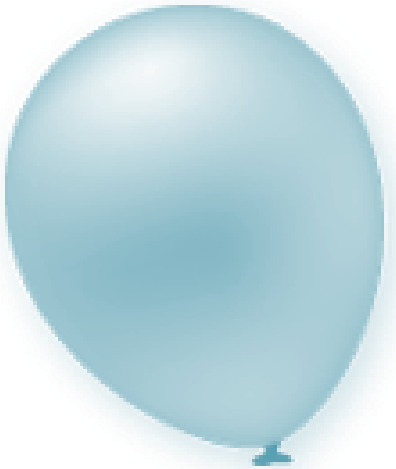
Avogadro's Law

Practice 4:

- If 0.105 mol of helium gas occupies a volume 2.35 L at a certain temperature and pressure, what volume would 0.337 mol of helium occupy under the same conditions?

$$\frac{V_1}{n_1} = \frac{V_2}{n_2}$$

$$\frac{2.35\ \text{L}}{0.105\ \text{mol}} = \frac{V_2}{0.337\ \text{mol}}$$



$$\mathbf{V_2 = 7.54\ L}$$

Combined Gas Law

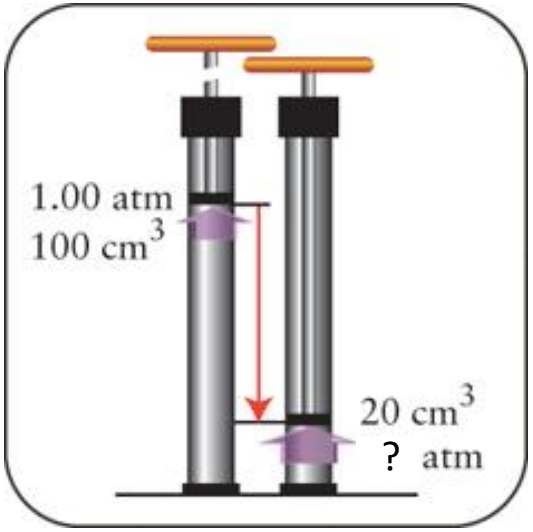
Combined gas law:

$$\frac{PV}{nT} = k \text{ (a constant)}$$

$$\frac{P_1V_1}{n_1T_1} = \frac{P_2V_2}{n_2T_2}$$

Practice 5: You press on the piston of a bicycle pump, the volume inside the pump is decreased from about 100. cm^3 to 20. cm^3 before the air flows into the tire. Suppose that the compression is isothermal; estimate the final pressure of the compressed air in the pump, given an initial pressure of 1.00 atm.

Combined gas law: $\frac{P_1V_1}{n_1T_1} = \frac{P_2V_2}{n_2T_2}$



A table of variables and values:

$T_1 = T_2$ (isothermal) and $n_1 = n_2$

$P_1V_1 = P_2V_2$

P_2 = ? P_1 = 1.00 atm

V_2 = 20. cm^3 V_1 = 100. cm^3

$1.00\ atm \times 100.\ cm^3 = P_2 \times 20.\ cm^3 \rightarrow P_2 = 5.0\ atm$

Practice 6: A weather balloon is filled with helium gas at 20.°C and 1.00 atm. The volume of the balloon is 250. L. When the balloon rises to a layer of air where the temperature is -30.°C, it has expanded to 800. L. What is the pressure of the atmosphere at that point?

$$\frac{P_1V_1}{\cancel{n_1}T_1} = \frac{P_2V_2}{\cancel{n_2}T_2}$$

This problem has three changing variables pressure, volume and temperature, therefore, we can use the combined gas law.

A table of variables and values:

$n_1 = n_2$

P_2 = ?	P_1 = 1.00 atm
V_2 = 800. L	V_1 = 250. L
T_2 = 273.15 + -30.°C = 243 K	T_1 = 273.15 + 20.°C = 293 K

Solve our equation for our variable

$$\frac{1.00\ \text{atm} \times 250.\ \text{L}}{293\ \text{K}} = \frac{P_2 \times 800.\ \text{L}}{243\ K} \rightarrow P_2 = 0.259\ \text{atm}$$

Avogadro's principle

Avogadro's principle: All gases occupy the same volume, under the same conditions of temperature and pressure.

Avogadro's principle is **molar volume**:

$$V_m = \frac{V}{n}$$

This is a principle rather than law, because it is based not on observation alone but also on a model of matter-namely that matter consists of molecules. Even though there is no longer any doubt that matter consists of atoms and molecules, it remains a principle rather than a law.

Practice 3: A helium weather balloon was filled at -20.°C and a certain pressure to a volume of 2.5×10^4 L with 1.2×10^3 mol He. What is the molar volume of helium under those conditions?

Our units are molar volume or $L\cdot mol^{-1}$ which means we can use

Avogadro's principle $V_m = \frac{V}{n}$.

$$V_m = \frac{2.5 \times 10^4\ L}{1.2 \times 10^3\ mol} = 20.83\ L\cdot mol^{-1}$$

2.5×10^4 L and 1.2×10^3 are each a 2 sig. fig number: 21 $L\cdot mol^{-1}$

Ideal Gas Law

Ideal gas law:

we learned: $\frac{PV}{nT} = k$ (a constant)

$$PV = nRT$$

n: number of moles (mol)
R: universal gas constant
V: volume (L)
P: pressure (atm)
T: temperature (K)

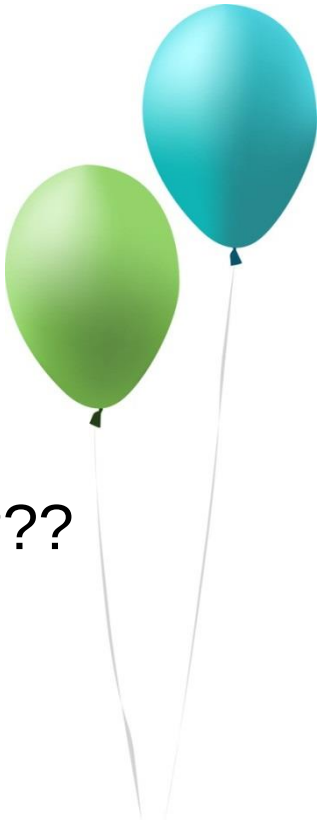
Standard Temperature and Pressure (STP)

T = 0.00°C (273 K)
P = 1.000 atm

⇨ 1 mole → V = 22.4 L

$$R = \frac{PV}{nT} = \frac{(1.000\ \text{atm})\ (22.4\ \text{L})}{(1\ \text{mol})\ (273\ \text{K})} = 0.082106\ \frac{\text{L.atm}}{\text{mol.K}}\ \text{or}\ \frac{\text{J}}{\text{mol.K}}$$

Ideal Gas Law



Practice 7:

- Given three of the variables in the Ideal Gas Law, calculate the fourth, unknown quantity.
- P = 0.98 atm, n = 0.1021 mol, T = 302 K. V = ???

$$PV = nRT$$

$$(0.98\ \text{atm})V = (0.1021\ \text{mol})(0.08206\ \frac{\text{L atm}}{\text{mol K}})(302\ \text{K})$$

$$\mathbf{V = 2.6\ L}$$

Ideal Gas Law

Practice 8:

- At what temperature will a 1.00 g sample of neon gas exert a pressure of 500. Torr in a 5.00 L container?

$$PV = nRT$$

$$1.00\ \text{g} \times \frac{1\ \text{mol}}{20.18\ \text{g}} = 0.0496\ \text{mol}$$

$$500.\ \text{Torr} \times \frac{1\ \text{atm}}{760\ \text{torr}} = 0.658\ \text{atm}$$

$$(0.658\ \text{atm})\ (5.00\ \text{L}) = (0.0496\ \text{mol})(0.08206\ \frac{\text{L atm}}{\text{mol K}}) \times \text{T}$$

$$\text{T} = 809\ \text{K}$$

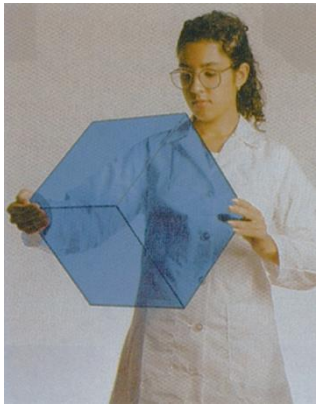
Standard Temperature and Pressure (STP)

STP means 0°C (273.15 K) and 1 atm (both exactly). At STP, the molar volume of an ideal gas is **22.41 L·mol^{-1}**.

A beach ball is about 22 L.

Standard Ambient Temperature and Pressure (SATP)

SATP means exactly 25°C (298.15 K) and exactly 1 bar (≈ 1 atm), the molar volume of an ideal gas is **24.79 L·mol^{-1}**, which is about the volume of a cube, 1ft on a side.



Note: the temperature is lower and the pressure is slightly higher for STP conditions, and so the same amount of gas molecules occupies a smaller volume than at SATP.

Gas Density

$PV = nRT$

$M \text{ (molar mass)} = \frac{m \text{ (mass)}}{n \text{ (mole)}}$

$$d = \frac{m}{V} = \frac{nM}{V} = \frac{(PV/RT)M}{V} = \frac{MP}{RT}$$

$$\boxed{d = \frac{MP}{RT}}$$

When a gas is compressed (V↓ and P↑), its density increases (d↑) because the molecules are confined in a smaller volume.

Upon heating (T↑) the pressure increases the volume occupied by the gas and therefore reduces its density (d↓).

Practice 9: The volatile organic compound geraniol, a component of oil of roses, is used in perfumery. The density of the vapor at 260.°C and 103 Torr is 0.480 $g \cdot L^{-1}$. What is the molar mass of geraniol ?

When working with density's of gases we use: $d = \frac{MP}{RT}$

Since we're solving for M, we'll need R to match our pressure, so we use 62.364 $Torr \cdot K^{-1} \cdot mol^{-1}$ and change the temperature to K,

273.15 + 260.°C = 533 K

Solve for the variable in question, $M = \frac{dRT}{P}$

Replace variables with data,

$$\frac{0.480\ g \cdot L^{-1} \times 62.364\ Torr \cdot K^{-1} \cdot mol^{-1} \times 533\ K}{103\ Torr} = 155\ g \cdot moL^{-1}$$

Stoichiometry of Reacting Gases

Practice 10: The reaction of H_2 and O_2 gases to produce liquid H_2O is used in fuel cells on the space shuttles to provide electricity. What mass of water is produced in the reaction of 100.0 L of oxygen stored at 25°C and 1.00 atm?

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

Our plan moles O_2 → moles H_2O → g H_2O

Information for O_2 is for SATP, Vm = 24.47 $L \cdot mol^{-1}$

To find moles of O_2 we use $V_m = \frac{V}{n}$ or $n = \frac{V}{V_m}$, or $\frac{100.0\ L\ O_2}{24.47\ L \cdot mol^{-1}\ O_2} = 4.087\ mol\ O_2$

we can use the mole ratio: 2 mol H_2O = 1 mol O_2

molar mass to find grams H_2O, 1 mol H_2O = 18.016 g H_2O

$$4.087\ mol\ O_2 \times \frac{2\ mol\ H_2O}{1\ mol\ O_2} \times \frac{18.016\ g\ H_2O}{1\ mol\ H_2O} = 147.2\ g\ H_2O$$

Two measured numbers, both with 4 sig figs: 100.0 and 24.47

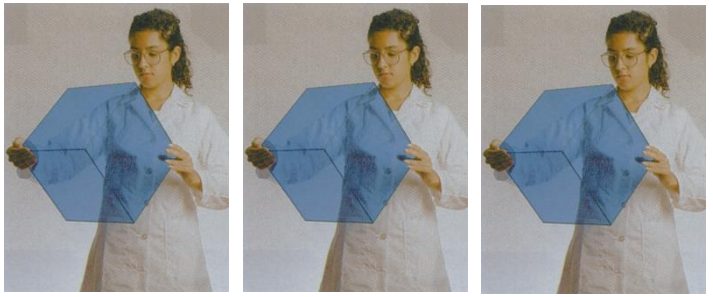
An example of a gas reaction

Sodium azide, NaN_3, forms large volume of nitrogen gas; a reaction triggered electrically in air bags.

$$2\ NaN_3\ (s) \rightarrow\ 2\ Na\ (s) + 3\ N_2\ (g)$$

$NaN_3 = 65.01\ g \cdot mol^{-1}$

130.02 g NaN_3 → 3 moles of N_2 gas



Mixtures of Gases

The atmosphere or air, is a mixture of nitrogen, oxygen, argon, carbon dioxide, and many other gases.

A mixture of gases behaves like a single pure gas.

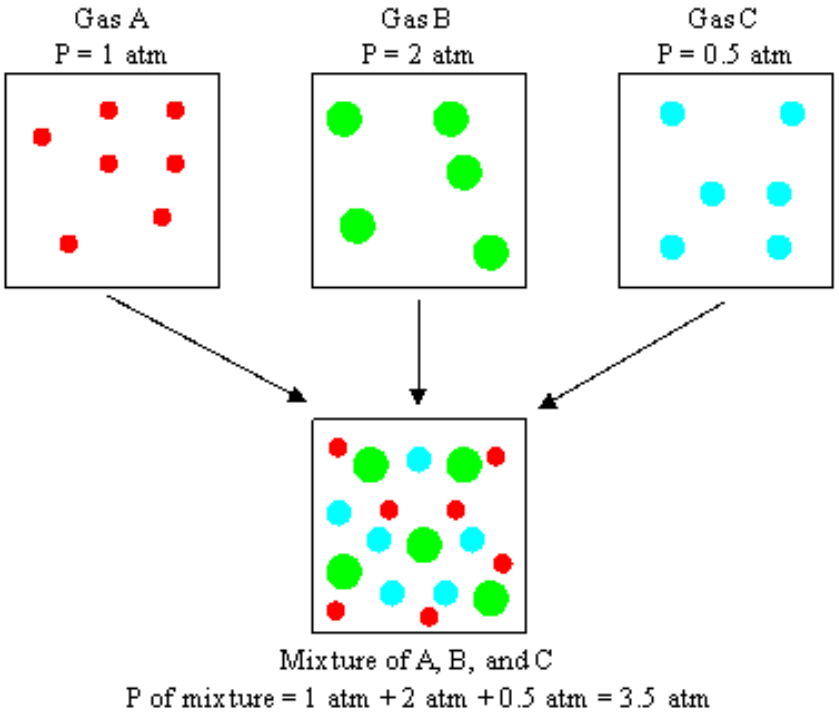
Dalton concluded that the total pressure is the sum of the individual pressures of each gas.

Dalton's Law

Dalton's law of partial pressure:

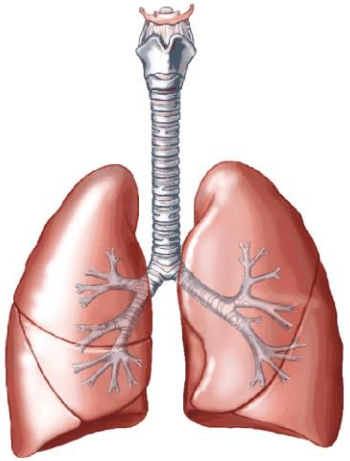
The **total pressure** of a mixture of gases is the **sum** of the **partial pressures** of its components:

$$P_T = P_1 + P_2 + P_3 + \ldots$$



Dalton's Law

We use partial pressures to describe the composition of damp air in our lungs is,



$P = P_{dry\ air} + P_{water\ vapor}$

Water vaporizes, in our lungs, until its partial pressure has reached a ***certain value***, called its ***vapor pressure***. The vapor pressure of water at normal body temperature is 47 Torr. The partial pressure of the ***air*** itself in our lungs is therefore,

$P_{dry\ air} = P - P_{water\ vapor}$ or at sea level where the total pressure is 760. Torr

$P_{dry\ air} = 760\ Torr - 47\ Torr = 713\ Torr.$

More on Dalton's Law of partial pressures: P ∝ n

The easiest way to express the relation between the *total pressure* of a mixture and the *partial pressures of its components* is to introduce the mole fraction, **χ**.

The moles of each gas n_A, n_B expressed as a mole fraction of gases A and B are:

$$\chi_A = \frac{n_A}{n_A + n_B + \cdots} \quad \text{and} \quad \chi_B = \frac{n_B}{n_A + n_B + \cdots}$$

Note that: $\chi_A + \chi_B + \ldots + \chi_N = 1$

More on Dalton's Law of partial pressures: $P \propto n$

In terms of total pressure and moles of all gasses:

$$P_T = \frac{n_T RT}{V} = (n_A + n_B + \ldots)\frac{RT}{V} \quad \text{and} \quad P_A V = n_A RT$$

Combine and rearrange $\frac{RT}{V}$ to: $\frac{P_T}{(n_A + n_B + \ldots)} = \frac{P_A}{n_A}$

Rearrange to get $P_A = \frac{n_A P_T}{(n_A + n_B + \ldots)}$

Then assign $\chi_A = \frac{n_A}{n_A + n_B + \ldots}$ we arrive at $\boxed{P_A = \chi_A P}$

(the same applies to each gas)

$$\boxed{P_T = n_{total}\left(\frac{RT}{V}\right)}$$

Practice 11: Students collecting hydrogen and oxygen gases by electrolysis of water failed to separate the two gases. If the total pressure of the dry mixture is 720. Torr, what is the partial pressure of each gas?

Balanced chemical equations: $2\ H_2O(g) \rightarrow\ 2\ H_2(g)\ +\ O_2(g)$

Other than the total pressure, the only piece of information we have is the mol ratio.

We know from Avogadro's principle that Pressure $\propto$ n

Since $P = P_A + P_B + ...$ and, mol total = mol A + mol B

Practice 11: Students collecting hydrogen and oxygen gases by electrolysis of water failed to separate the two gases. If the total pressure of the dry mixture is 720. Torr, what is the partial pressure of each gas?

$$P_A = \chi_A P$$

$$\chi_{H2} = \frac{2 \text{ mol } H_2}{2 \text{ mol } H_2 + \text{mol } O_2} \quad \text{and} \quad \chi_{O2} = \frac{1 \text{ mol } O_2}{2 \text{ mol } H_2 + \text{mol } O_2} .$$

Applying this to pressure

$$P_{H2} = 720. \text{ Torr} \times \frac{2 \text{ mol } H_2}{3 \text{ mol product}} = 480 \text{ Torr } H_2 \text{ and}$$

$$P_{O2} = 720. \text{ Torr} \times \frac{1 \text{ mol } O_2}{3 \text{ mol product}} = 240 \text{ Torr } O_2$$

Practice 12: Air is a source of reactants for many chemical processes. To determine how much air is needed for these reactions, it is useful to know the partial pressures of the components. A certain sample of dry air of total mass 1.00 g consists almost entirely of 0.760 g of nitrogen and 0.240 g of oxygen. Calculate the partial pressures of these gases when the total pressure is 0.87 atm.

For finding the partial pressure of a mixture of gasses we use: $P_A = \chi_A P$

Find the mol fraction of each gas $\chi_A = \frac{n_A}{n_A + n_B + \ldots}$ and for that, we'll need to find moles of each gas.

$$0.760 \text{ g } N_2 \times \frac{1 \text{ mol } N_2}{28.02 \text{ g } N_2} = 0.0271 \text{ mol } N_2 ,$$

$$0.240 \text{ g } O_2 \times \frac{1 \text{ mol } O_2}{32.00 \text{ g } O_2} = 0.00750 \text{ mol } O_2$$

$0.0271 \text{ mol } N_2 + 0.00750 \text{ mol } O_2 = 0.0346 \text{ mol total}$

… total pressure is 0.87 atm... $P_A = \chi_A P$

0.0271 mol N_2 + 0.00750 mol O_2 = 0.0346 mol total

$$\chi_{N2} = \frac{n_{N2}}{n_{N2} + n_{O2}} = \frac{0.0271 \text{ mol } N_2}{0.0346 \text{ mol}} = .783$$

$$\chi_{O2} = \frac{n_{O2}}{n_{N2} + n_{O2}} = \frac{0.00750 \text{ mol } O_2}{0.0346 \text{ mol}} = .217$$

$P_{N2} = \chi_{N2} P = .783 \times 0.87 \text{ atm} = .68 \text{ atm } N_2$

$P_{O2} = \chi_{O2} P = .217 \times 0.87 \text{ atm} = .19 \text{ atm } O_2$

A model of Molecular Motion

Summarizing the empirical results of gas laws suggests:

1. Gases are widely spaced;
2. None interacting;
3. Are in ceaseless motion;
4. Average speeds that increase with temperature.

In the next three sections, we refine our model in two steps.

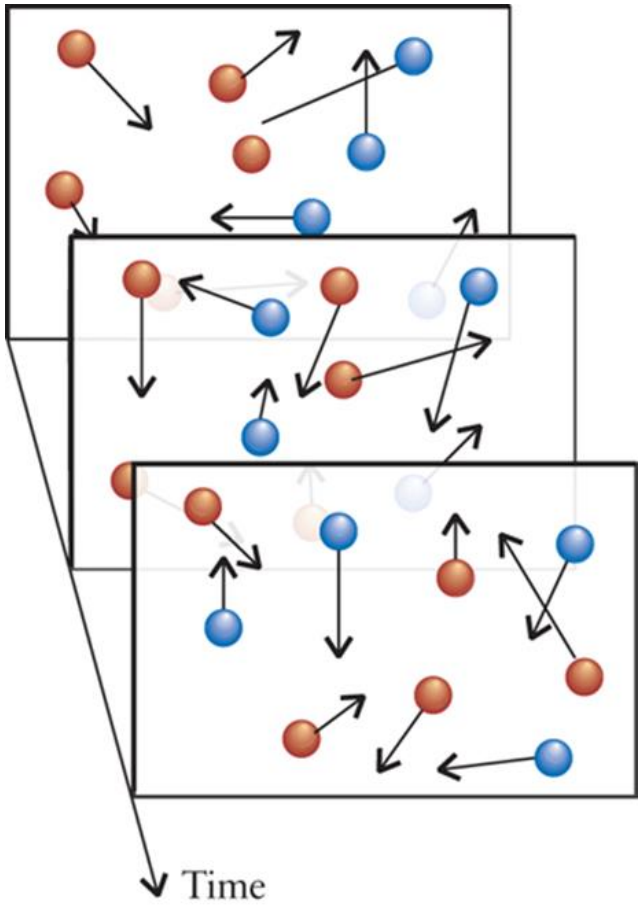
First, we discover how to determine the average speeds of gas molecules.

Then we use these average speeds in an ideal gas to find detailed information about the proportion of molecules having any specified speed.

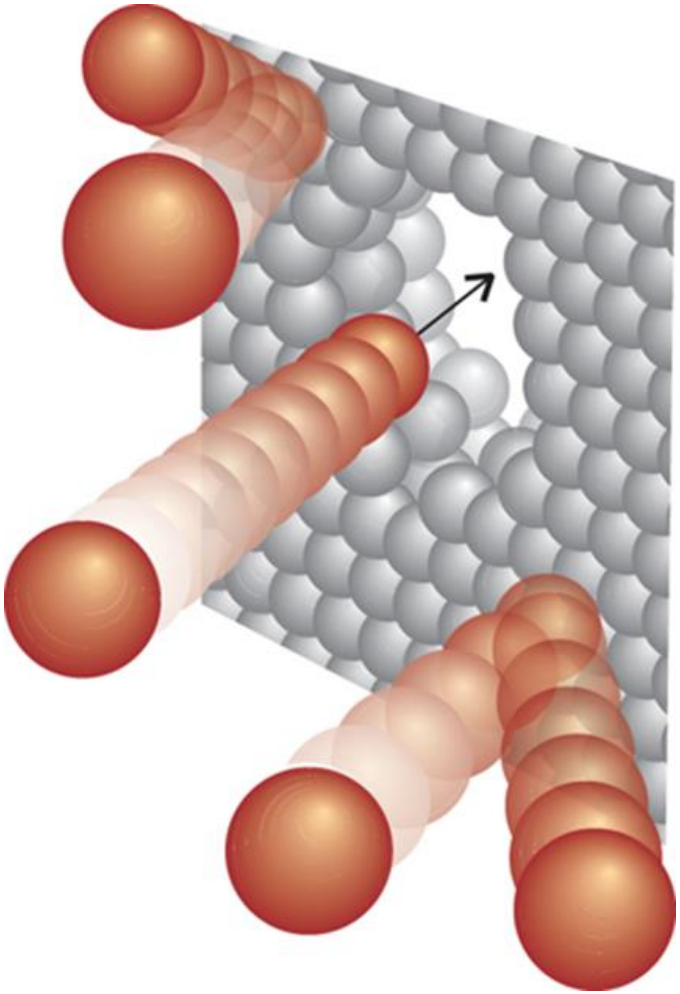
Diffusion & Effusion

Two kinds of processes, diffusion and effusion, show how the **average speeds** of gas molecules are related to **molar mass** and **temperature**.

In **diffusion**, molecules spread into regions in a series of random steps, undergoing collisions as they move.



Diffusion & Effusion



In **effusion**, molecules escape through a small hole in a barrier into a region of low pressure.

Graham's law

The nineteenth-century Scottish chemist Thomas Graham carried out experiments on the rates of gas effusion.

At constant temperature, the rate of effusion is inversely proportional to the square root of its molar mass:

$$\text{rate of effusion} = \frac{1}{\sqrt{\text{molar mass}}}$$

This is now known as Graham's law of effusion.

Since the average speed of molecules determines the rate they approach the hole we conclude:

$$\text{Average speed} \propto \frac{1}{\sqrt{\text{molar mass}}}$$

Graham's law with 2 gasses

Rewriting Graham's law for two gases A and B with molar masses M_A and M_B, we would obtain,

$$\frac{\text{rate of effusion for A}}{\text{rate of effusion for B}} = \frac{\sqrt{\text{molar mass B}}}{\sqrt{\text{molar mass A}}}$$

Since time is proportional to rate and rate increases as the square root of T:

$$\frac{\text{Time for A to effusion}}{\text{Time for B to effusion}} = \frac{\sqrt{\text{molar mass B}}}{\sqrt{\text{molar mass A}}}$$

$$\frac{\text{rate of effusion at } T_1}{\text{rate of effusion at } T_2} = \frac{\sqrt{T_2}}{\sqrt{T_1}}$$

Practice 13: It takes a certain amount of helium atoms 10. s to effuse through a porous barrier. How long does it take the same amount of methane, CH_4, molecules to effuse through the same barrier under the same conditions?

$$\frac{\text{Time for A to effusion}}{\text{Time for B to effusion}} = \frac{\sqrt{\text{molar mass B}}}{\sqrt{\text{molar mass A}}}$$

Graham's law is useful for solving effusion problems.

Given: 4.00 g·mol^{-1} He at 10. s, and 16.04 g·mol^{-1} CH_4

$$\frac{\text{Time for } CH_4 \text{ to effusion}}{\text{Time for He to effusion}} = \frac{\sqrt{\text{molar mass He}}}{\sqrt{\text{molar mass } CH_4}}$$

$$\text{Time for } CH_4 \text{ to effusion} = \frac{\sqrt{4.00\ \text{g·mol}^{-1}\ \text{He}}}{\sqrt{16.04\ \text{g·mol}^{-1}\ CH_4}} \times 10.\ \text{s} = 5.0\ \text{s}$$

An interesting feature of Graham's law is heavier molecules move more slowly, in this case rate He = $\frac{\sqrt{16}}{\sqrt{4}}$ or He is 2 times faster than CH_4.

Molar volume

Graham's law is helpful to describe an interesting feature of molar volume 22 L·mol^{-1}, the idea that <u>all gases</u> *occupy* the **same volume**.

This seems to be at odds with gases having different densities, different sizes, and different masses.

Ideal gas	22.41
Argon	22.09
Carbon dioxide	22.26
Nitrogen	22.40
Oxygen	22.40
Hydrogen	22.43

However, Graham's law, explains that larger, heavier, slower moving gases (big rabbits) can cover the same distance as smaller, lighter, faster moving gas molecules (small rabbit).

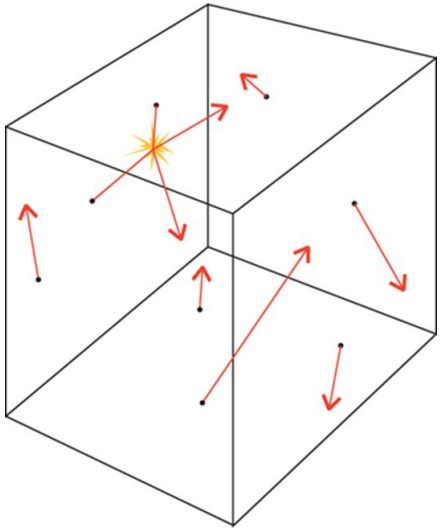
Smaller molecules need to travel a longer time to cover the same distance; *all gases cover the same area but at different rates*.

All gasses occupy about the same molar volume 22 $L \cdot mol^{-1}$.

The Kinetic Model of Gases

From our kinetic model ("**kinetic molecular theory**", KMT):

1. A gas is in continuous random motion;
2. Gas molecules are infinitesimally small;
3. They move in straight lines until collision;
4. Gas molecules do not influence one another except during collisions.

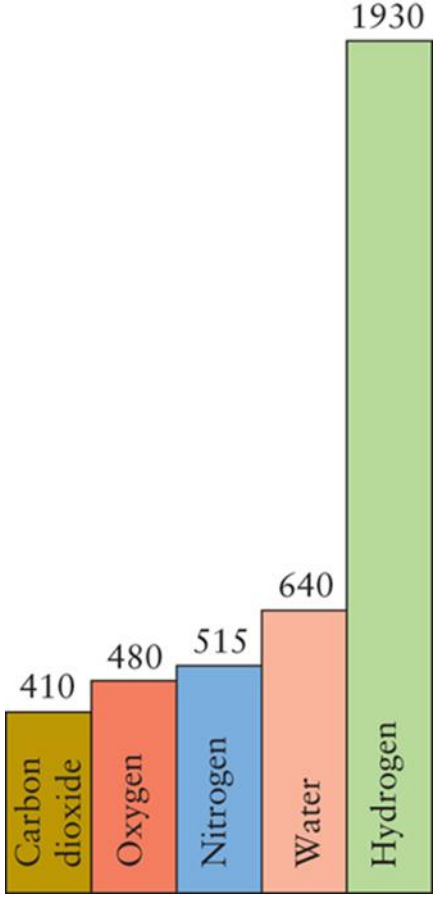


The kinetic model of a gas allows us to derive the **quantitative** relation between pressure and the speeds of the molecules.

Root mean Square Speed of molecules (v_{rms})

$$v_{rms} = \sqrt{\frac{v_1^2 + v_2^2 + \cdots + v_n^2}{N}}$$

$$P = \frac{nN_A m v^2_{rms}}{3V} = \frac{nMv^2_{rms}}{3V}$$



m: mass is of one molecule
M: is the molar mass of the molecules. $M = mN_A$
N_A: Avogadro's constant
n: number of moles
v_{rms}: root mean square speed of molecule
V: volume

Root mean Square Speed of molecules (v_{rms})

$$P = \frac{nN_A m v^2_{rms}}{3V} = \frac{nMv^2_{rms}}{3V}$$

Since PV = nRT, we set $PV = \frac{1}{3}nMv^2_{rms} = nRT$ and rearrange to get:

$$v_{rms} = \sqrt{\frac{3RT}{M}}$$

And from $v_{rms}^2 = 3RT/M$ it follows:

$$T = \frac{Mv_{rms}^2}{3R}$$

That temperature is proportional to the mean square speed of the molecules.

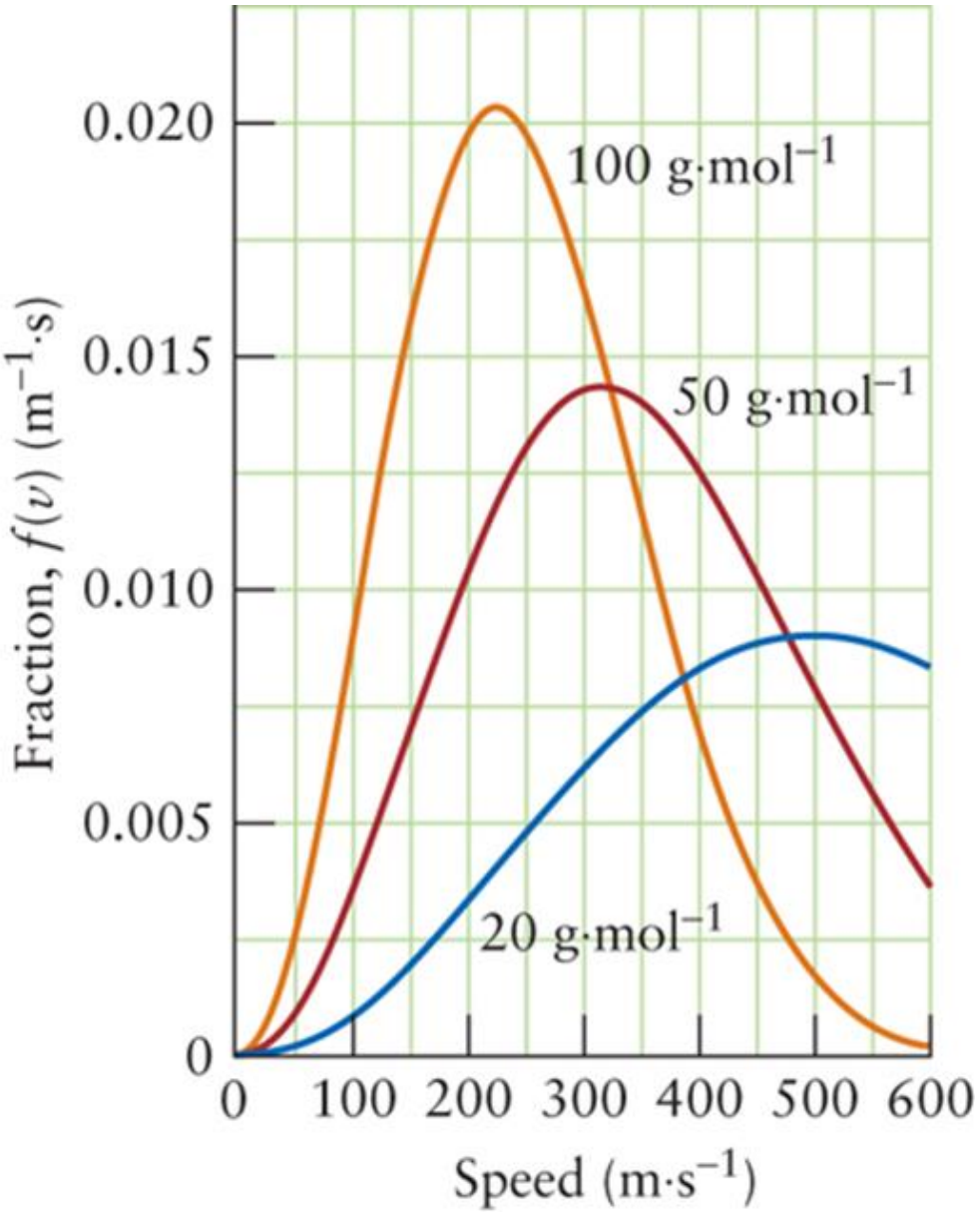
Practice 14: Estimate the root mean square speed of CH_4 molecules at 25°C.

$$v_{rms} = \left(\frac{3RT}{M}\right)^{\frac{1}{2}}$$

The temperature is 298 K and the molar mass of CH_4 is 16.04 g·mol^{-1} (corresponding to1.604×10^{-2} kg·mol^{-1}) and R = 8.314 J·K^{-1}·mol^{-1}.

$$v_{rms} = \left(\frac{3 \times 8.314\ \text{J·K}^{-1}\text{·mol}^{-1} \times 298\ \text{K}}{1.604 \times 10^{-2}\ \text{kg·mol}^{-1}}\right)^{\frac{1}{2}} = 681\ \text{m·s}^{-1}$$

Velocity of different masses, but at the same temperatures



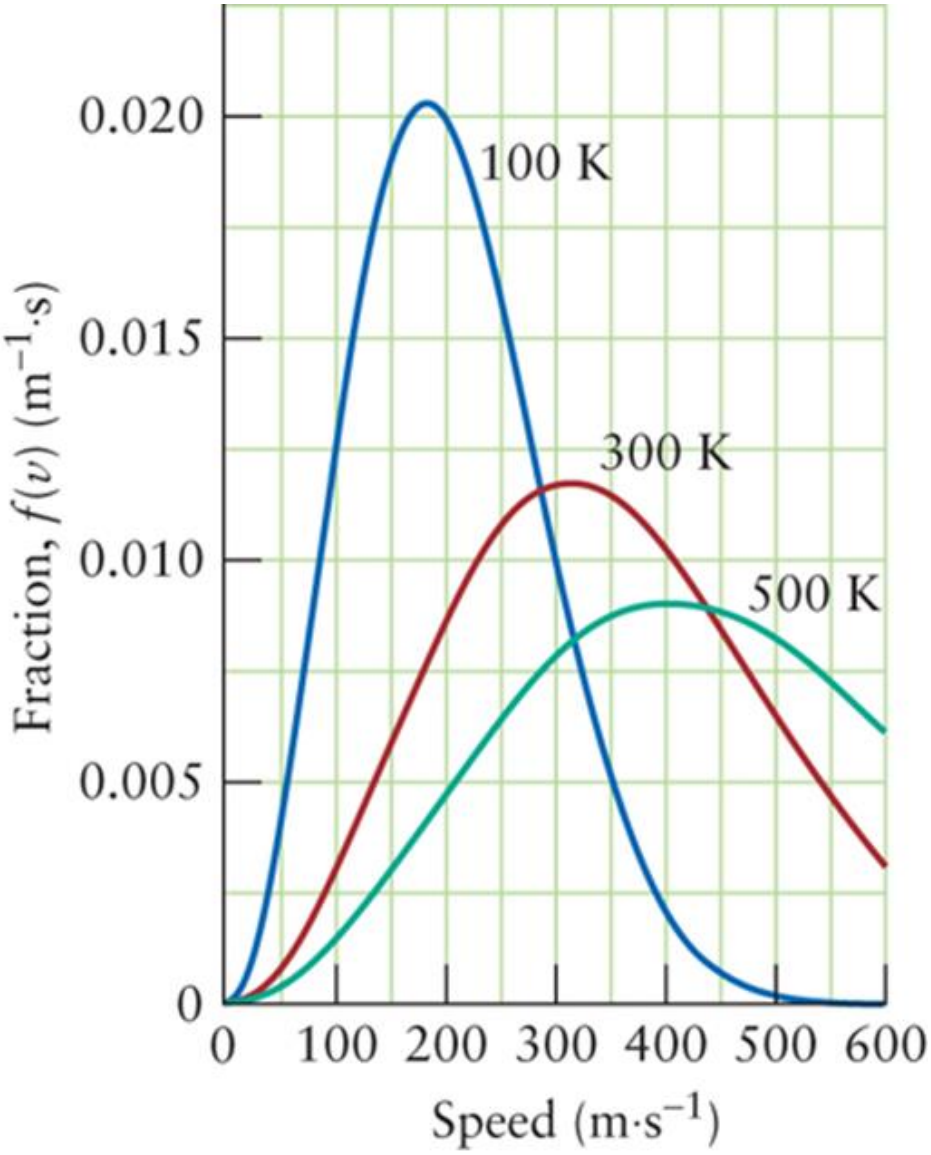
James Clerk Maxwell (Scottish scientist) distribution gives the range of molecular speeds for three gases.

All are for the same temperature 300K.

The greater the molar mass, the lower the speed.

The Maxwell distribution the curves correspond to the speeds of a single substance (of molar mass 50 g·mol^{-1}) at different temperatures.

The higher the temperature, the higher the average speed and the broader the spread of speeds.



Same mass, different temp

Ideal Gas law: deviations from ideality

In industry and in many research laboratories, gases must be used under high pressures, when the ideal gas law is not followed closely.

The ideal gas law is a limiting law, valid only as $P \rightarrow 0$.

All actual gases, which are called **real gases**, have properties that differ from those predicted by the **ideal gas** law.

These differences are significant at high pressures and low temperatures.

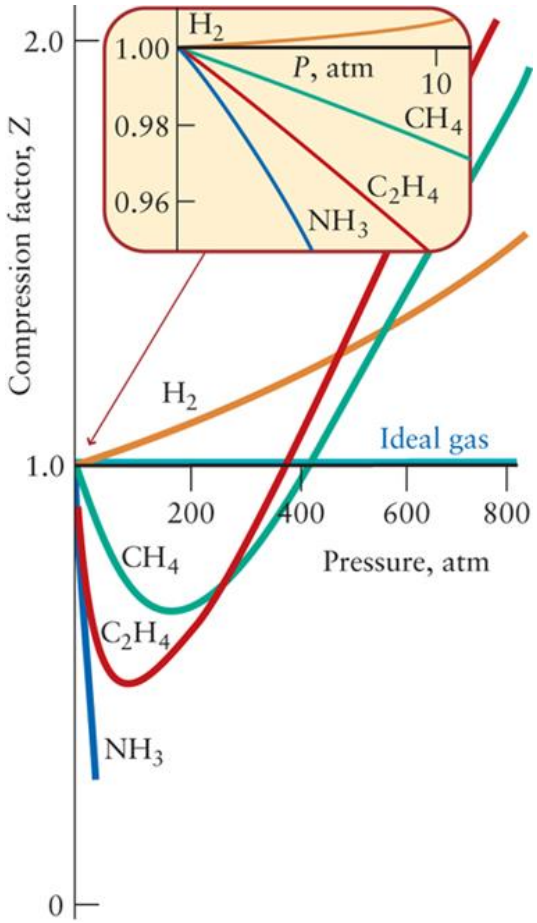
Deviations from ideality: compressibility

Gases can be condensed to liquids when cooled or compressed.

A measurement of the compression factor, Z,

$$Z = \frac{V_m}{V_m^{ideal}}$$, for Z = 1 under ideal conditions.

H_2 is an ideal gas with very weak intermolecular attractions, it's Z is always greater than 1.



For most gases, at low pressures the **attractive forces** are dominant and Z < 1 . At high pressures, **repulsive forces** become dominant and Z > 1 for all gases.

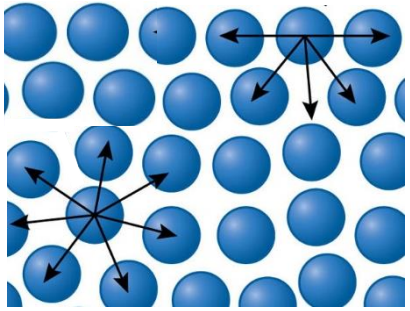
Deviations from ideality: intermolecular forces

All deviations from ideal behavior can be explained by the intermolecular forces.

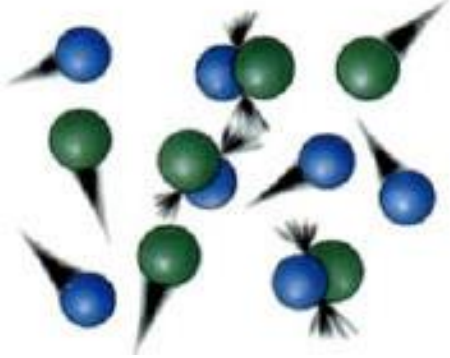
All molecules **attract** one another when they are a *few molecular diameters apart.*

They **repel** one another as soon as their *electron clouds come into contact*.

The **attractive intermolecular forces** accounts for the condensation of gases to liquids when they are compressed or cooled. If molecules are moving slow enough, there can be an attraction between the two.



The **repulsive forces** is an indication that molecules have definite volumes. When you touch a solid object, you feel its size and shape because your fingers cannot penetrate into it. The resistance to compression offered by the solid is due to the repulsive forces exerted by its atoms on the atoms in your fingers.

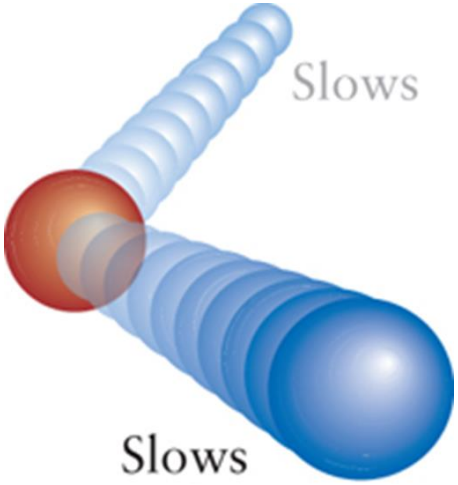


The Joule-Thomson Effect

It is used in some commercial refrigerators to liquefy gases (not Charles Law).

When molecules of a real gas climb away from each others attractive forces, (expand) they exert a force on each other just as a ball is pulling away the surface of Earth feels the gravitational pull.

For real gases, attractive forces dominant, slowing the molecules average speed and so they cool as they expands.



Joule-Thomson effect is named in honor of the scientists James Joule and William Thomson (later to become Lord Kelvin) who first observed this.

Equations of State of Real Gases

Van der Waals equation (temperature-independent equation):

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

(values for a and b are found experimentally or for well know molecules, in tables)

Parameter a represents the role of attractions; so it's large for strongly attracting molecules.

Parameter b represents the role of repulsions; it can be thought of as representing the volume.

Practice 15: Estimating the pressure of a real gas. Investigators are studying the physical properties of a gas to be used as a refrigerant in an air-conditioning unit. A table of van der Waals parameters shows that for this gas

$a = 16.2\ L^2 \cdot atm \cdot mol^{-2}$ and
$b = 8.4 \times 10^{-2}\ L \cdot mol^{-1}$

Estimate the pressure of the gas when 1.50 mol occupies 5.00 L at 0°C.

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

$$P = \frac{nRT}{(V - nb)} - a\frac{n^2}{V^2}$$ now apply the data

$$\frac{1.50\ mol \cdot\ 0.08206\ atm \cdot L \cdot mol^{-1} \cdot K^{-1} \cdot\ 273\ K}{(5.00\ L - 1.50\ mol \cdot\ 8.4 \times 10^{-2}\ L \cdot mol^{-1})} -$$

$$16.2\ L^2 \cdot atm \cdot mol^{-2}\ \frac{(1.50\ mol)^2}{(5.00\ L)^2} = 5.44\ atm.$$

Using ideal gas conditions PV=nRT, P = 6.72 atm.