States and properties of matter.

Pure compounds or their mixtures can assume, depending on temperature and pressure, three physical states:

Solid

Liquid

Gaseous

States of the matter

- Every compound, if it does not undergo a chemical reaction, changes reversibly its state of aggregation upon variations in temperature and/or pressure.

- The three states of aggregation result, in a first approximation, from the competition between the kinetic energy of the particles that make up the substance and the energy of interaction between the particles themselves.

Gas and their properties:

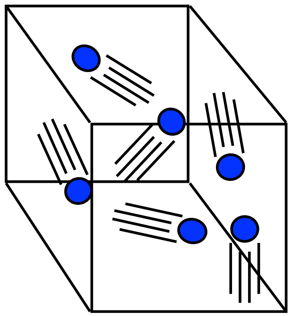
- Can be compressed
- Exerts and uniform pressure on the walls of its container
- Occupies all the available volume
- Does not have a defined shape or volume
- Two gases easily diffuse and mix reciprocally
- All gases have low density
  - air 0.0013 g/ml
  - water 1.00 g/ml
  - iron 7.9 g/ml

I_2

Br_2

NO_2

Ideal gas.



- The gas consists of a large number of particles called atoms / molecules.

- The volume physically occupied by a molecule of an ideal gas is equal to zero (each molecule is much smaller than the volume occupied by gas).

- The molecules of a given mass of ideal gas move in the available volume with a chaotic motion, according to laws of probability (Brownian motion).

- There is no attractive or repulsive force between gas molecules.

- Collisions between molecules and between molecules and containers are fully elastic (ie momentum before and after each collision is conserved).

- A gas is fully described by 4 parameters:
  - number of moles
  - pressure
  - volume
  - temperature

Ideal gas laws

- Avogadro's principle and concept of mole.
- Boyle's law: $PV=k$ (isotherm, $T=const$)
- Charles law: $P/T=k$ (isocore, $V=cont$)
- Gay-Lussac's law: $V/T=k$ (isobaric, $P=const$)
- Ideal gas law: $PV=nRT$
- Dalton's law: $P_{TOT}=P_1+P_2+\ldots+P_i$
- Henry's law: $c=kP$
- Graham's law

Avogadro's principle

- In 1811, Amedeo Avogadro outlined a clear distinction between atoms and molecules.
- Avogadro hypothesized that: "two given samples of an ideal gas, at the same temperature, pressure and volume, contain the same number of molecules."
- Avogadro's work was ignored until Stanislao Cannizzaro showed that the principle could be used to determine the molar masses and indirectly the atomic masses (Karlsruhe Conference in 1860) which set the mole concept.

1776 -1856

1826 -1910

$$\frac{V}{N} = k$$

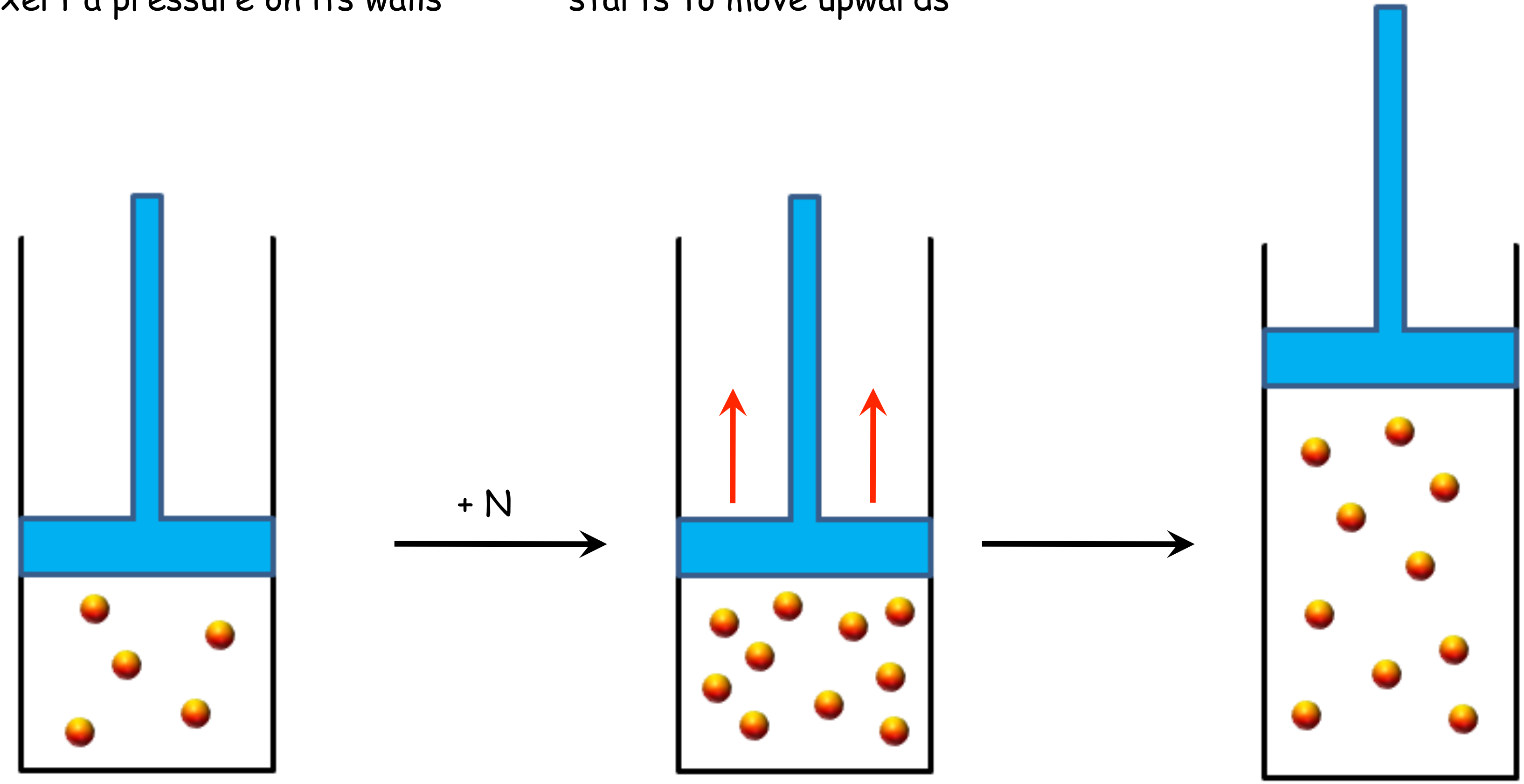
At constant pressure and temperature

A cylindrical vessel fitted with a movable piston is immersed in a water bath that keeps temperature constant.

The container is filled with N particles of a gas that exert a pressure on its walls

N gas particles are added. The pressure doubles and the piston starts to move upwards

Upon equilibration the volume doubles



volume = V
particles = N

volume = V
particles = 2N

volume = 2V
particles = 2N

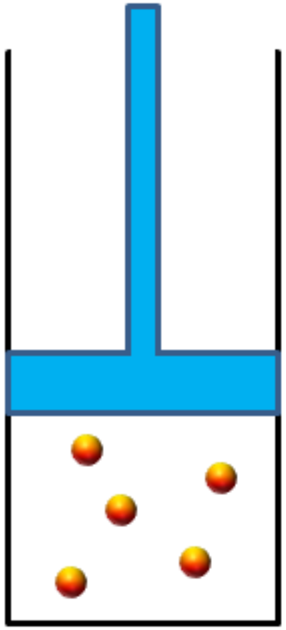
The ratio between the number of particles an the volume is constant.

The ratio between the gas volume and the number of particles is constant if P and T are constant.

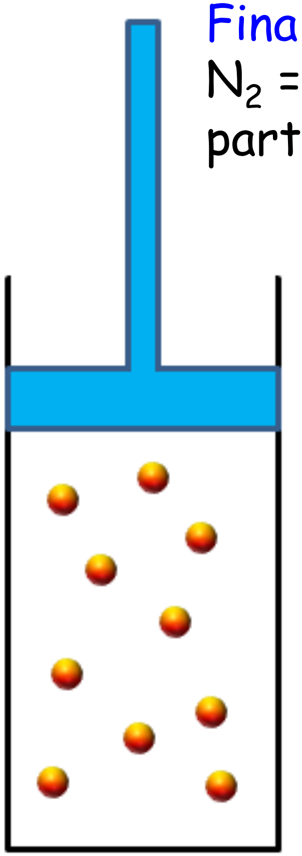
$$\frac{V}{N} = k$$

$$\frac{V_1}{N_1} = \frac{V_2}{N_2} = \frac{V_3}{N_3} = \ldots$$

Initial state:
N_1 particles
V_1



Final state:
$N_2 = 2N_1$
particles $V_2 = ?$



$$\frac{V_1}{N_1} = \frac{V_2}{N_2} \longrightarrow V_2 = \frac{N_2}{N_1} V_1 \longrightarrow V_2 = \frac{2N_1}{N_1} V_1 = 2V_1$$

The mole (greek = quantità), milestone of chemistry

The mole (mol) is the SI unit to measure the amount of a compound:

A mole is the amount of substance containing a number of particles (atoms, molecules, ions, electrons, etc..) equal to the number of atoms in 12 grams of the C isotope C_{12}.

The key to the concept of mole is to recognize that it always contains the same number of particles, regardless of the substance. It is the Avogadro N_A:

N_A= 6.02214199x10^{23} particles

$$n = \frac{N}{N_A}$$

602 214 199 000 000 000 000 000 particelle

If one mole of euros was divided by the world's population (5.5 billion people) about each of us would. 1000000 million euros!

- *Problem:* Take 1 liter of water from the ocean and somehow label each molecule of water in the glass. Dump the water back into the ocean and wait a long period of time for the labeled molecules to mix and disperse evenly throughout the entire body of water. (volume 1.68×10^{16} cubic meters). Now take a second 1 liter sample of water from the body of water. How many of the original labeled molecules are in the second 1 liter container?

Calculate the number of molecules in a liter of water = number of labeled molecules.

* 1 L water= 1000 g *
* Molecular weight H_2O= 18 g/mole
* 1000 g = 1000g/18 g/mole =55.55 moles di H_2O*
* 55.62 moles x 6.02 x 10^{23} molecules/mole = 3.35 x 10^{25} labeled molecules*

Number of liters of water in the ocean:
1.68 x 10^{16} m^3 x (10^3 L/m^3) = 1.68 x 10^{19} L

Divide the number of labeled molecules by the number of liters of water in oceans, by the number of labeled molecules per liter in the second sample.

3.35 x 10^{25} molecole/1.68 x 10^{19} liters = 2.0 x 10^6 molecules
= 2.000.000 molecules = 2 millions of molecules

The mass in grams of one mole of any element (molecule, ion, etc..) represents the molar mass of that element.
The molar mass of an element (molecule) is the quantity in grams numerically equal to its atomic weight (molecular).

E.g.: Molar mass of Na = mass of 1 mole of atoms of Na
= 22.99 g/mol
= mass of 6.02214199×10^{23} atoms of Na

$$n_{MOLE} = \frac{mass\ in\ grams}{atomicweight}$$

In conclusion:

$$\frac{V}{N} = k$$

$$\frac{V_1}{N_1} = \frac{V_2}{N_2} = \frac{V_3}{N_3} = \ldots$$

$$n_{MOLES} = \frac{mass\ in\ grams}{atomic\ weight}$$

$$\mathrm{n} = \frac{\mathrm{N}}{\mathrm{N_A}} \rightarrow \mathrm{N} = \mathrm{n} \cdot \mathrm{N_A}$$

Density

The density δ of a body is equal to its mass divided by the volume it occupies.
In the IS density is measured in kg/m^3 (g/cm^3 or equivalently the g/ml).
In fluids, objects with lower density float, when subjected to a gravitational field.

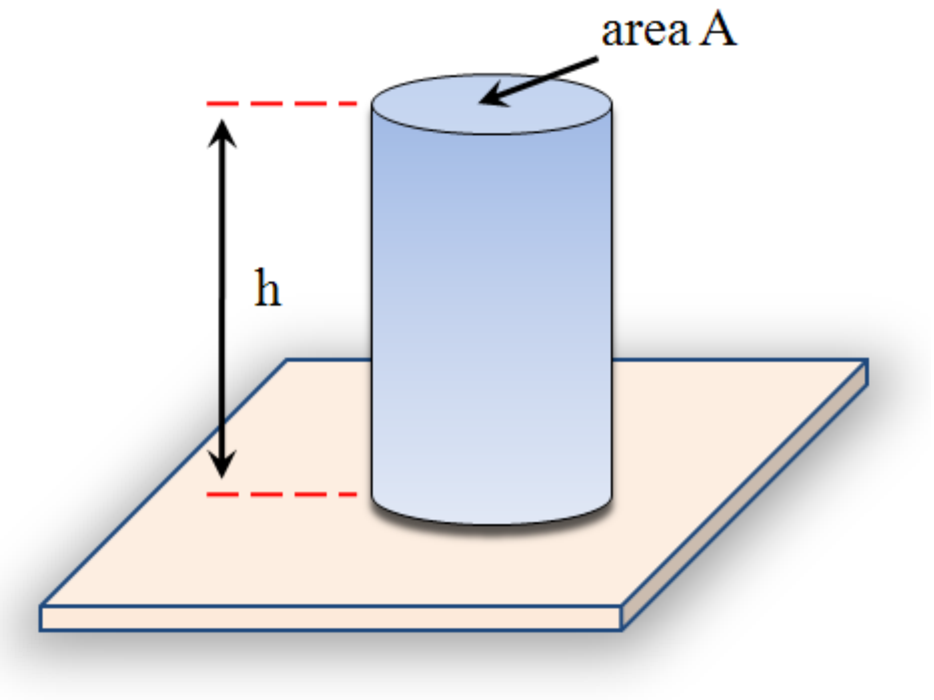
$$\boxed{\delta = \frac{mass}{volume}}$$

As the volume usually varies with temperature, this must be specified.

Pressure

Pressure is a physical quantity, defined as the ratio of the force acting perpendicularly on a surface and the surface itself. The pressure exerted by an object depends on its weight and the area on which it is distributed.

$$\text{pressure} = \frac{\text{force}}{\text{surface}}$$



If we consider a cylinder of height h, area A and volume $V=Ax\ h$
The weight of the cylinder is given by its mass m multiplied by the acceleration of gravity g ($9.8\ m/s^2$). This is the force exerted by the cylinder on the plane:
$F = m\,g$
Pressure P is this force divided by the area A of the base of the cylinder:
$p = F/A$
The mass of the cylinder is given by the density of the material by its volume.
$m = d\,V$.

$$P = \frac{m\,g}{A} = \frac{\delta\,V\,g}{A} = \frac{\delta\,A\,h\,g}{A} = \delta\,h\,g$$

Mass is an intrinsic property of a body, while its weight depends on gravity.

Pressure units.

	pascal (Pa)	bar (bar)	atmosphere (atm)	torr (torr o mmHg)	Pound / square inch(psi)
1 Pa	≡ 1 N/m^2	10^{-5}	9.8692×10^{-6}	7.5006×10^{-3}	145.04×10^{-6}
1 bar	100000	≡ 10^6 $dyne/cm^2$	0.98692	750.06	14.5037744
1 atm	101325	1.01325	≡ 1 atm	760	14.696
1 torr	133.322	1.3332×10^{-3}	1.3158×10^{-3}	≡ 1 torr;	19.337×10^{-3}
1 psi	6,894.76	68.948×10^{-3}	68.046×10^{-3}	51.715	≡ 1 lbf/in^2

Blood pressure

Blood pressure is the force exerted by circulating blood on blood vessels and is one of the principal vital signs.

Blood pressure decreases as the blood flows through arteries, arterioles, capillaries and veins. The term "blood pressure" refers to blood pressure of arteries and is measured with a sphygmomanometer.

Anaeroid sphygmomanometer

Mercury sphygmomanometer

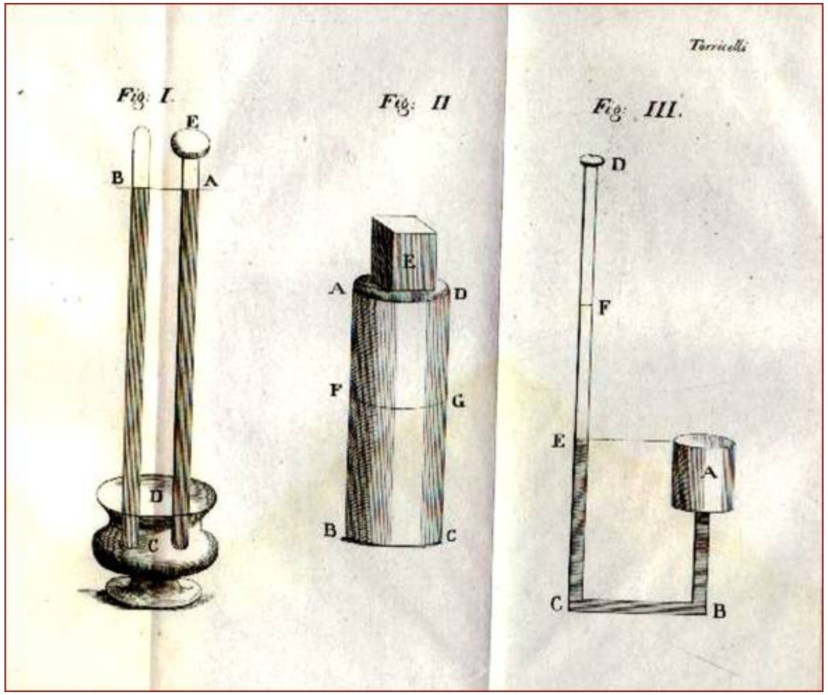
Normal values for an healthy human:
systolic: 115 mmHg
diastolic: 75 mmHg

Evangelista Torricelli (1608-1647)

Barometer

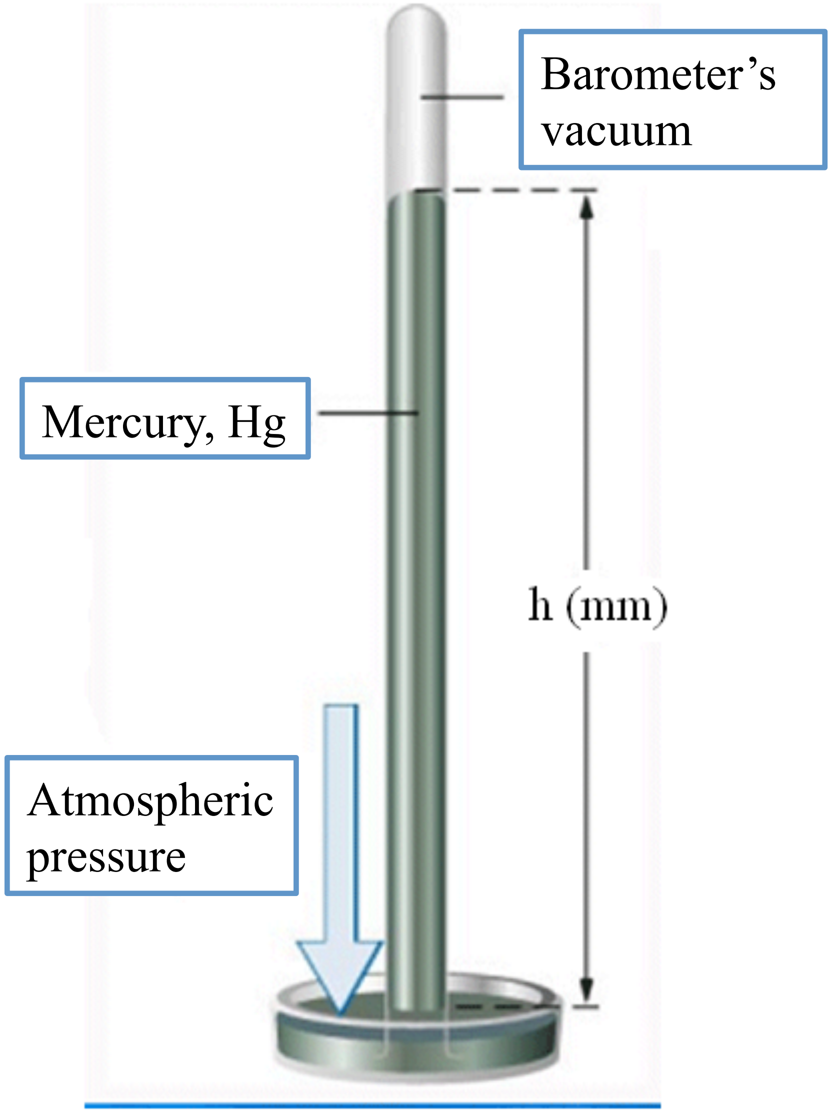
The first barometer was a 10 m high water column H_2O.

Torricelli used Hg instead of H_2O (13.6 times more dense) using a tube 0.9 m long.

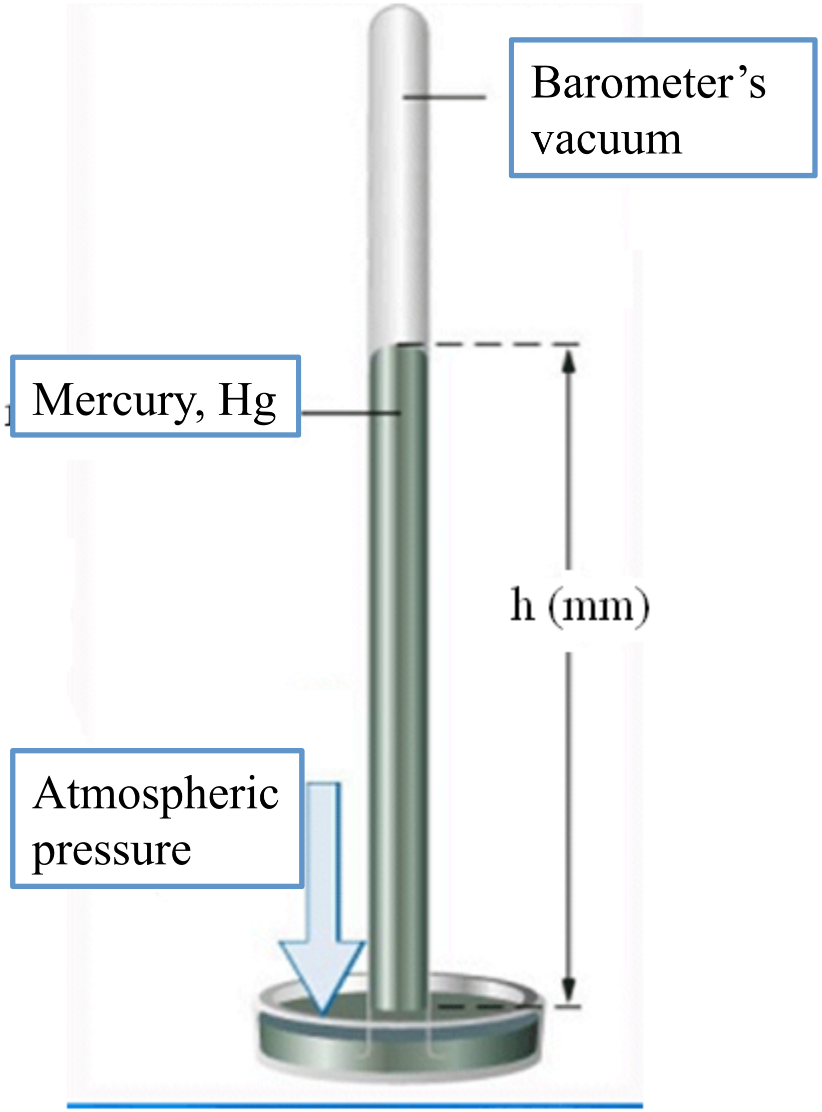


Drawing by Torricelli

Torricelli’s barometer.



Sea level P = 760 mm Hg



1600 m above sea levelP = 620 mm Hg

Gas compressibility: Boyle's law (Isotherm)

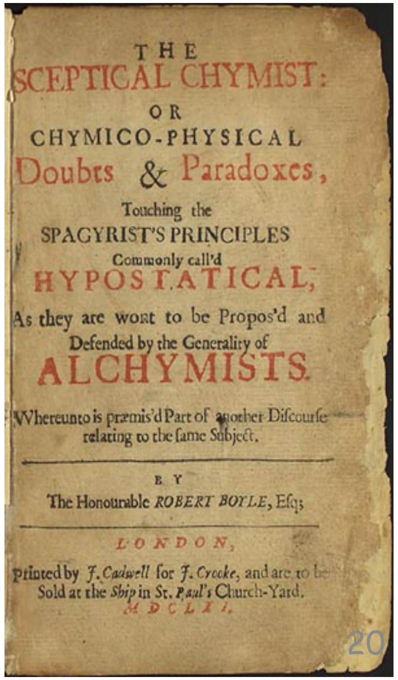
When you inflate a bicycle tyre, the pump compresses air into a smaller volume. This property is called compressibility.

Robert Boyle (1627-1691)

"The volume of a fixed quantity of gas at a given temperature is inversely proportional to the pressure exerted by the gas"

$$P \propto \frac{1}{V}$$

PV = k   N and T costant

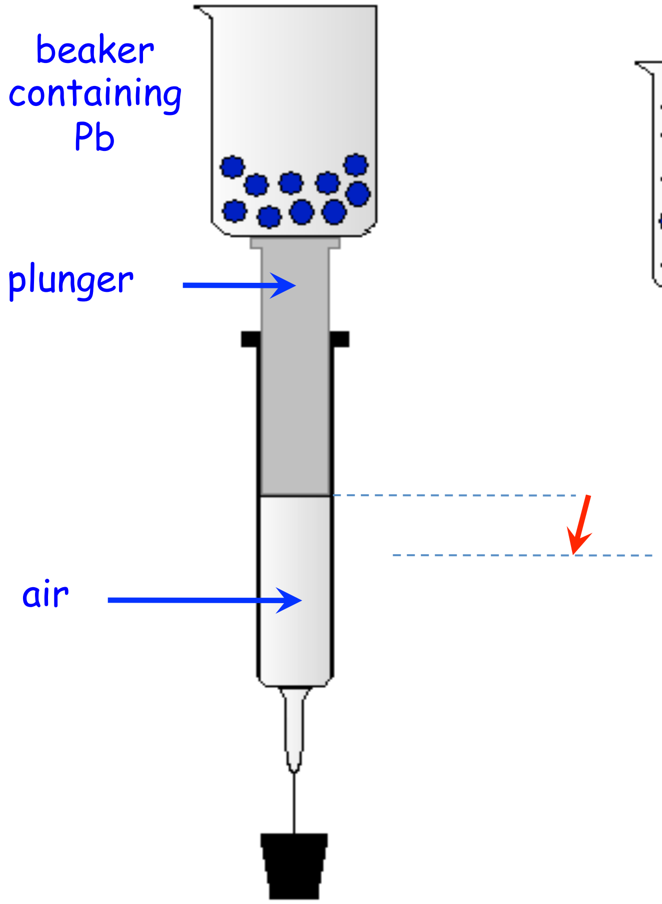


THE
SCEPTICAL CHYMIST:
OR
CHYMICO-PHYSICAL
Doubts & Paradoxes,
Touching the
SPAGYRIST'S PRINCIPLES
Commonly call'd
HYPOSTATICAL;
As they are wont to be Propos'd and
Defended by the Generality of
ALCHYMISTS.
Whereunto is præmis'd Part of another Diſcourſe
relating to the ſame Subject.

BY
The Honourable ROBERT BOYLE, Eſq;

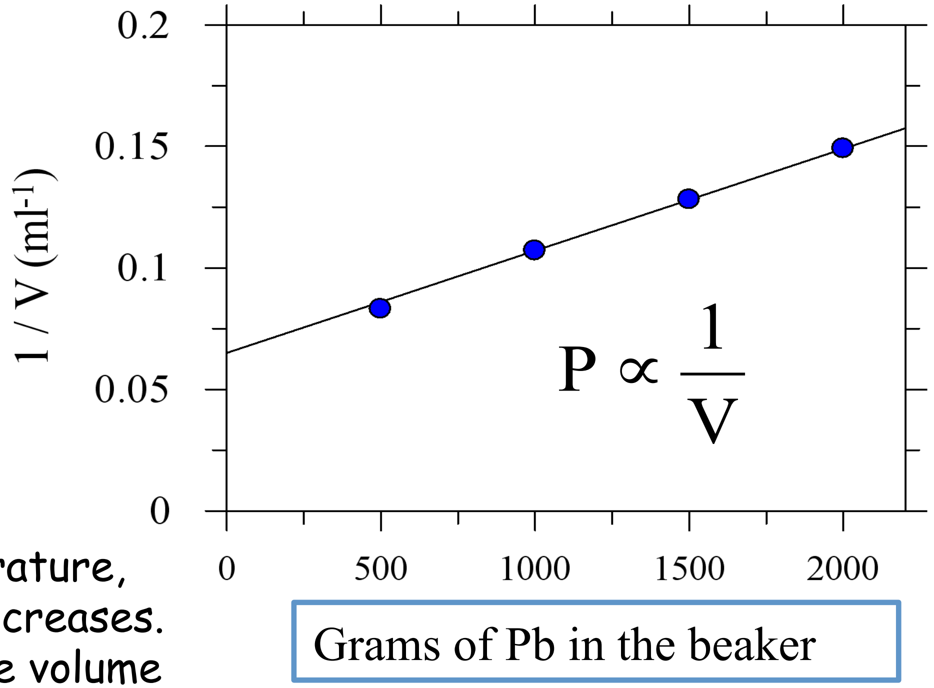
LONDON,
Printed by J. Cadwell for J. Crooke, and are to be
Sold at the Ship in St. Paul's Church-Yard.
MDCLXI.

Boyle's law can be demonstrated by the following experiment:



Adding increasing amounts of Pb, the air pressure in the syringe increases (and decreases the volume) and the gas is compressed.

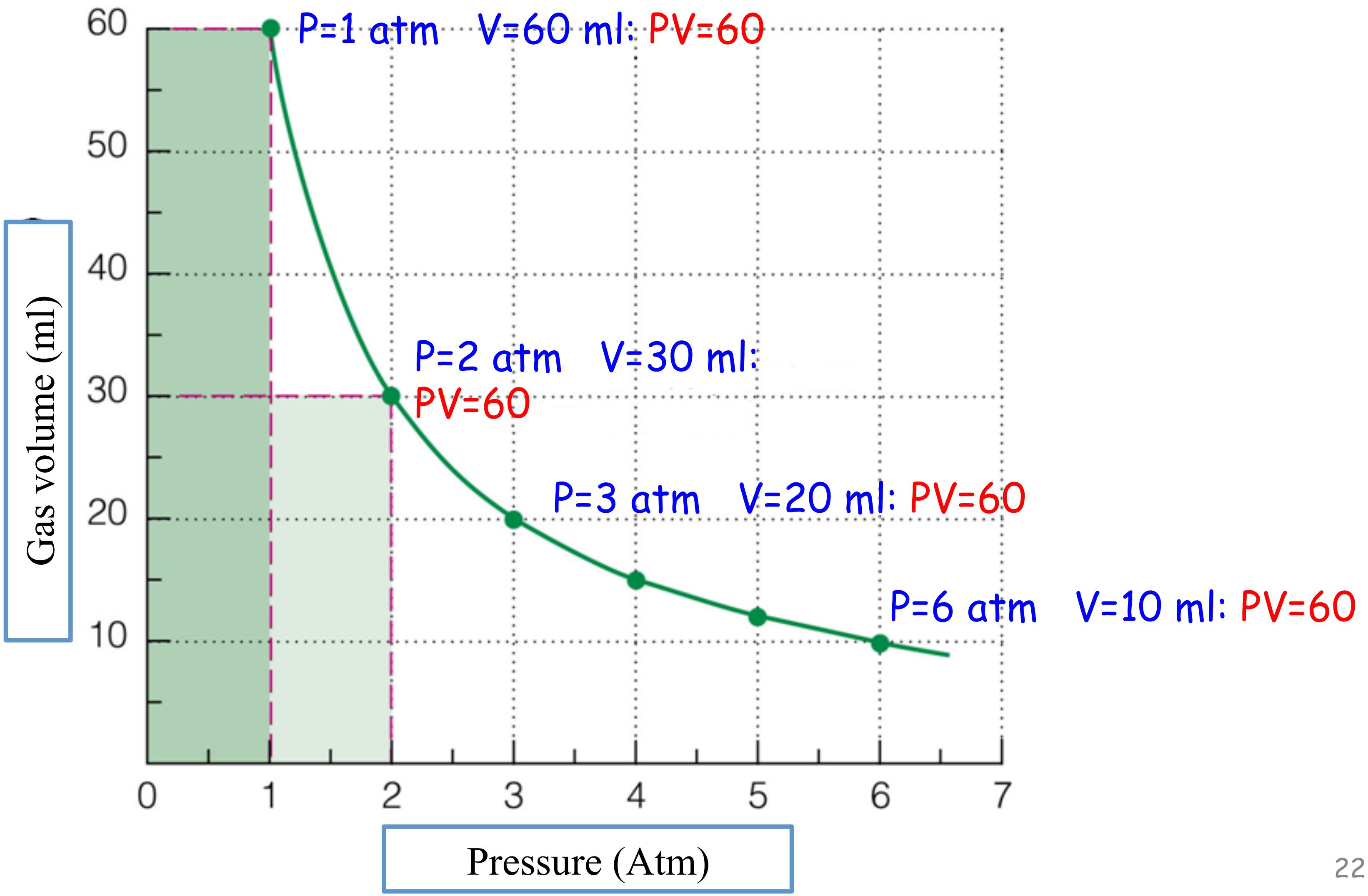
A graph of 1/V as a function of pressure yields a linear trend.



For a given amount of gas at a fixed temperature, the gas volume decreases if the pressure increases. Alternatively, if the pressure decreases the volume of gas increases.

Boyle's law states that for a given mass of gas, at a given temperature, the product of pressure for the volume is a constant.

$$PV = k$$



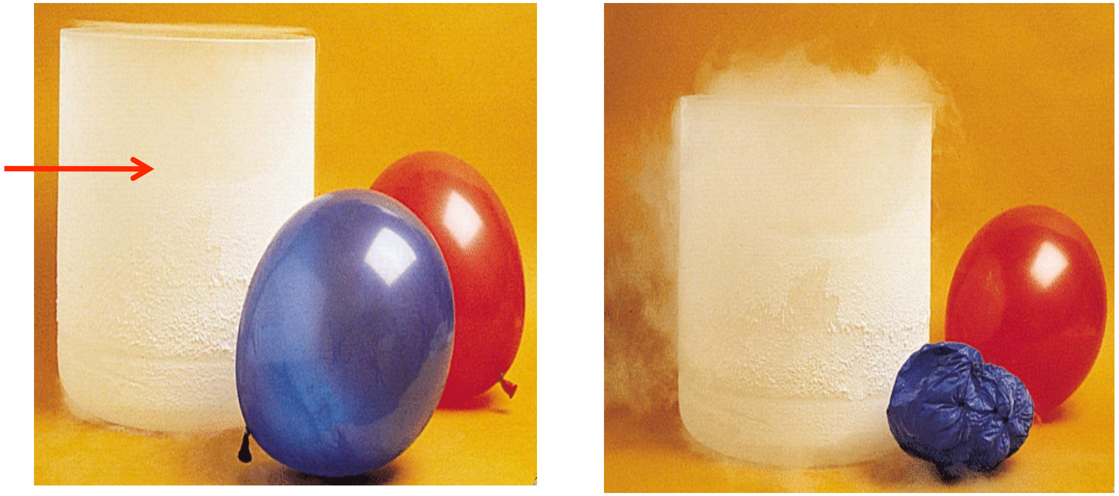
This means that if the pressure-volume product is known under certain conditions (P_1 and V_1),it is also known at all other conditions (P_2 and V_2). For each set of conditions the product PV is constant:

$$P_1 V_1 = P_2 V_2 \quad \text{for N and T constant}$$

This form of Boyle's law is useful when we want to know, for example, what happens to V of a given amount of gas when its pressure changes (T constant).

Effect of temperature on gas volume: Charles Law (isobaric)

"The volume of a fixed quantity of gas kept at constant pressure, decreases with decreasing temperature"



Liquid N_2
(-196 °C)

$$V \propto T$$

$$\frac{V}{T} = k$$ for constant N and P

Jacques Charles
(1746-1823)

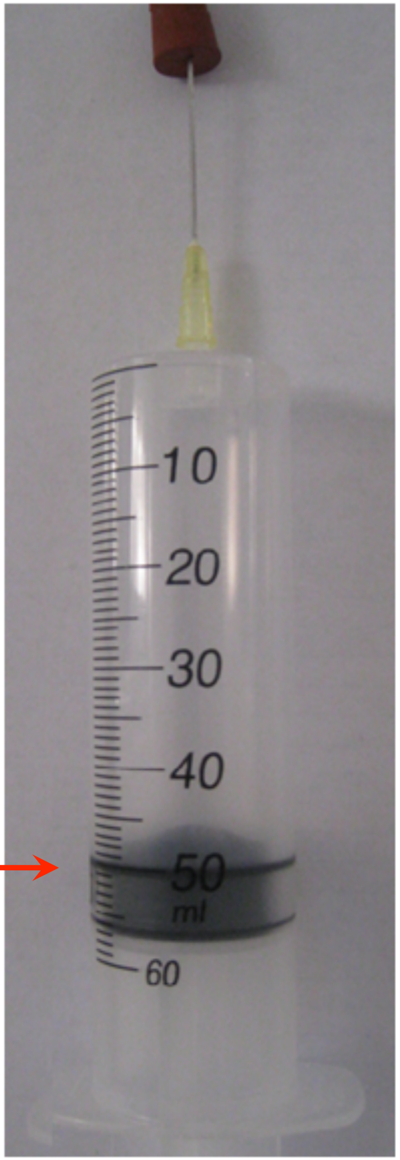
Charles law (isobaric)

Plastic bottle filled with air at 25 °C

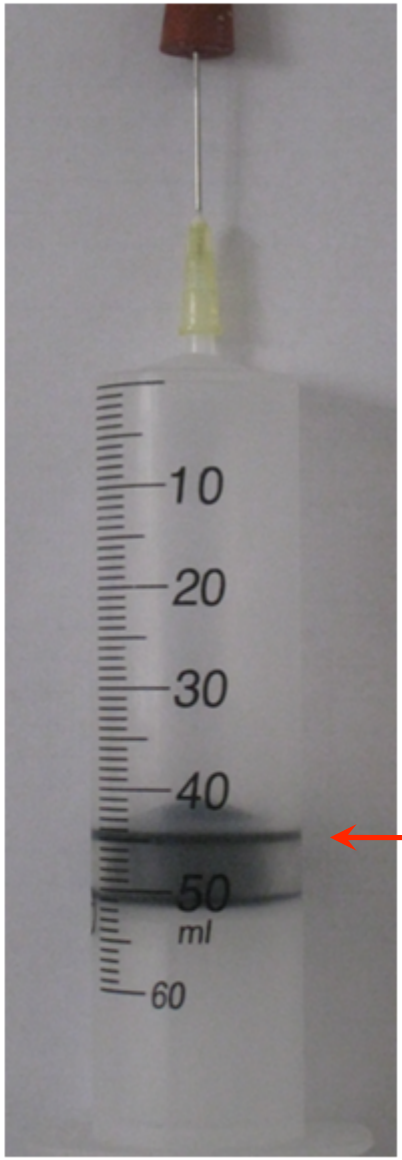
After storage in a freezer at -20 °C for 20 minutes.

Charles law (isobaric)

Syringe filled with
air at 25 °C



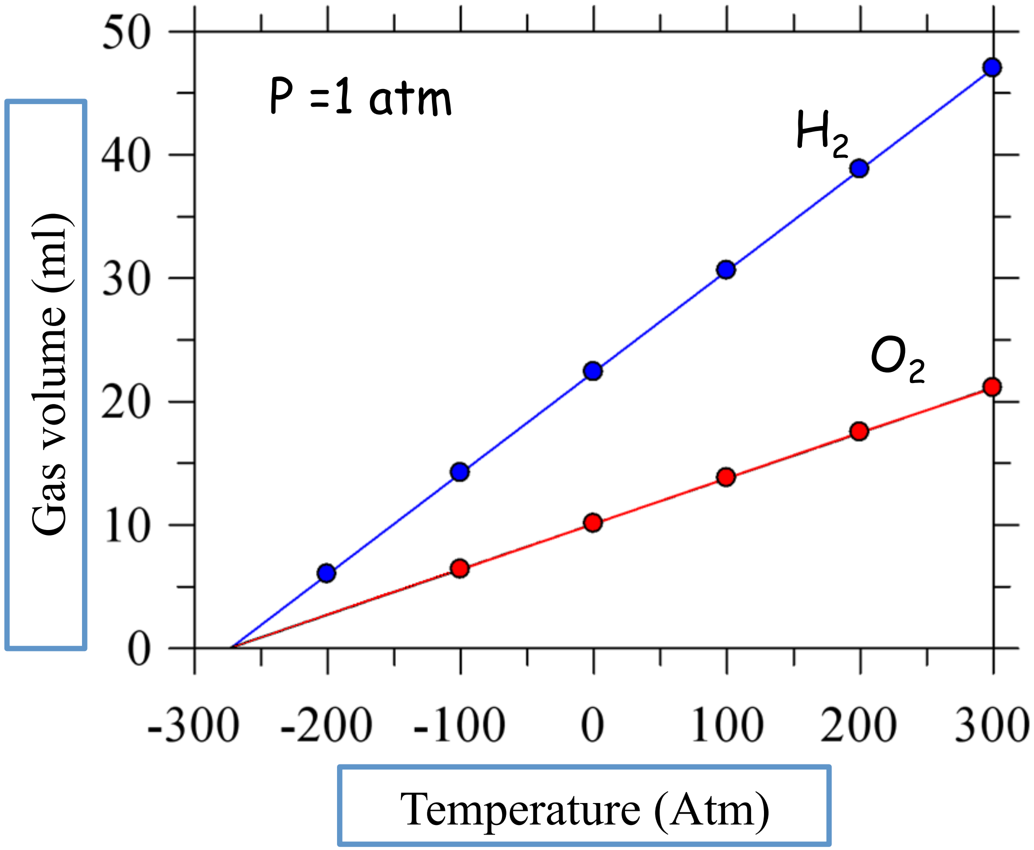
V = 50 ml



After storage in a
freezer at -20 °C
for 20 minutes.

V = 44.5 ml

Charles's law states that if a given quantity of gas is maintained at constant pressure, its volume is directly proportional to the temperature (Kelvin or absolute)



This leads us to conclude, for example, that the V of a gas doubles when T doubles.

If, we know the volume and temperature of a gas (V_1 and T_1), we can find the new volume V_2 at the new temperature T_2:

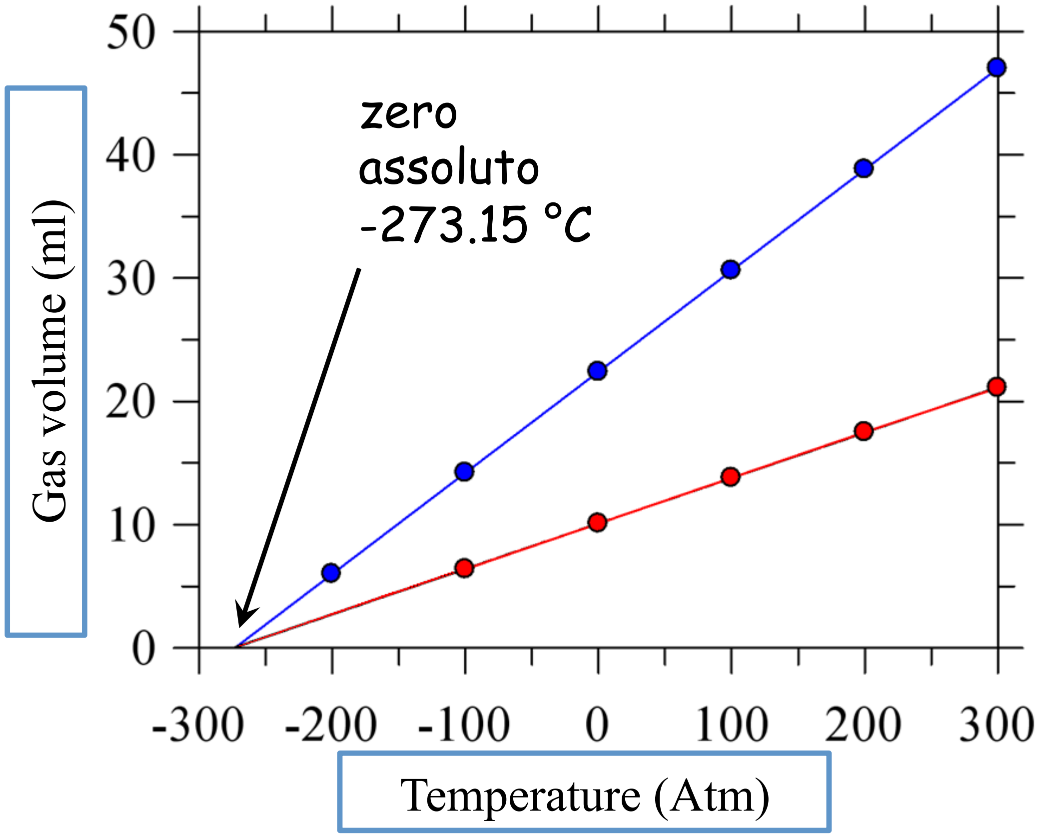
$$\frac{V_1}{T_1} = \frac{V_2}{T_2}$$

For constant N e P

Kelvin temperature

Since all the graphs of the law of Charles intersect the axis of temperatures at -273.15 ° C, Lord Kelvin proposed to use this value as zero absolute temperature scale: the Kelvin scale.

0 Kelvin (K) is the temperature at which the volume of an ideal gas is zero, and molecular motion ceases.



1 K = 1 °C

K = °C + 273.15

The effect of temperature on gas pressure: Gay-Lussac law (isochore).

Joseph Louis Gay-Lussac
(1778 – 1850)

"The pressure of a gas kept at constant volume, decreases with decreasing temperature"

$$P \propto T$$

$$\frac{P}{T} = k$$

For constant N and V

If the temperature of a gas doubles, so does its pressure.
If we know the pressure and temperature of a gas (P_1 and T_1), we can find the new pressure P_2 for T_2 following the equation:

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

For constant N and V.

Ideal gas state law: $P V = n R T$

Avogadro's law	Boyle's law	Charles law	Gay-Lussac's law
$V/n=k$	$PV=k$	$V/T=k$	$P/T=k$
T and P = cost.	T and n= cost.	P and N = cost	V and N = cost

The experiments of Avogadro, Boyle, Charles and Gay-Lussac suggest that 4 variables are sufficient to completely describe the behavior of a gas atequilibrium:

- pressure, P
- vlume, V
- particle number, N
- abslolute temperature

Combining these laws we obtain the ideal gas state law

$$P V = N k T$$

What is the value of the constant k?

The constant k is a fundamental quantity and it is called Boltzmann constant ($k_B = 1.38 \times 10^{-23}$ J/K)

$$\boxed{P\,V = N\,k_B\,T}$$

This equation fully describes the behavior of N gas particles at given conditions of T, V and P.

since $n = \dfrac{N}{N_A} \rightarrow N = n \cdot N_A$

$$\boxed{P\,V = n\,N_A\,k_B\,T = n\,R\,T}$$

dove $R = N_A\,k_B$

This equation is called the equation of state of an ideal gas.

It describes the behaviour of gases in all possible conditions.

$$P\,V = n\,R\,T$$

- P and T= constant $V = n\,k$ dove $k = R\,T / P$ (L. Avogadro)
- T = constant $PV = k$ dove $k = n\,R\,T$ (L. Boyle)
- P= constant $V = k\,T$ dove $k = n\,R / P$ (L. Charles)
- V = constant $P = k\,T$ dove $k = n\,R / V$ (L Gay-Lussac)

Ideal gas state law

$$PV = nRT$$

The numerical value of the universal gas constant R depends on the unit of pressure, volume and temperature:

$R = 8.314\ \mathrm{J\ mol^{-1}\ K^{-1}}$ (P in Pa, V in m^3, T in K)

$R = 0.08206\ \mathrm{L\ atm\ mol^{-1}\ K^{-1}}$ (P in atm, V in L, T in K)

$R = 62.36\ \mathrm{torr\ L\ mol^{-1}\ K^{-1}}$ (P in torr, V in L, T in K)

R represents the work exerted at P=1 atmosphere following the increase in temperature of 1 Kelvin.

This plastic bottle with a volume of 500 ml was closed at 2000 m altitude where atmospheric pressure is 595 mmHg at a temperature of 0 ° C. It was then brought to sea level where atmospheric pressure is 760 mmHg and a temperature of 20 ° C. What has happened to the bottle?

- Particle number did not change, (the bottle is selaed)
- at 1600 m: $P_1 V_1 = n R T_1$
- at sea level: $P_2 V_2 = n R T_2$
- since n = k

$$n = \frac{P_1 V_1}{RT_1} = \frac{P_2 V_2}{RT_2} \rightarrow \frac{P_1 V_1}{T_1} = \frac{P_2 V_2}{T_2}$$

$$V_2 = \frac{P_1}{P_2}\frac{T_2}{T_1}V_1 = \frac{595}{760}\frac{(273.15+20)}{273.15}500 = 420 \text{ mL}$$

Air pressure has squeezed the bottle.

Dalton Law

1766–1844

The total pressure exerted by a mixture of ideal gases is equal to the sum of the partial pressures exerted by the gas if it was the only one in that volume.

The partial pressure P_i of a component of a mixture of gases is the pressure that it would exert if it occupied the volume available to the entire mixture. The pressure P of a mixture of n gases can be defined as the sum of:

$$P = P_1 + P_2 + \dots + P_n$$

the partial pressures must all be expressed in the same units

Each gas in the mixture behaves as if the other gases were not present and therefore the pressures of each gas can be simply summed.
It is assumed that the gases do not react or interact via intermolecular forces with each other.

Dalton's law

In a mixture of gases, the total pressure is the sum of the partial pressures of each gas.

$$p_{tot} = \sum_{1}^{N} p_i$$

$P_{tot} = P_a + P_b$; $P_a = P_{tot} \times n_a/n = P_{tot} \times X_a$

The partial pressure of a gas is the pressure that the gas would exert if it occupied the whole volume available.

X_a = molar fraction = Moles$_a$/total moles

36

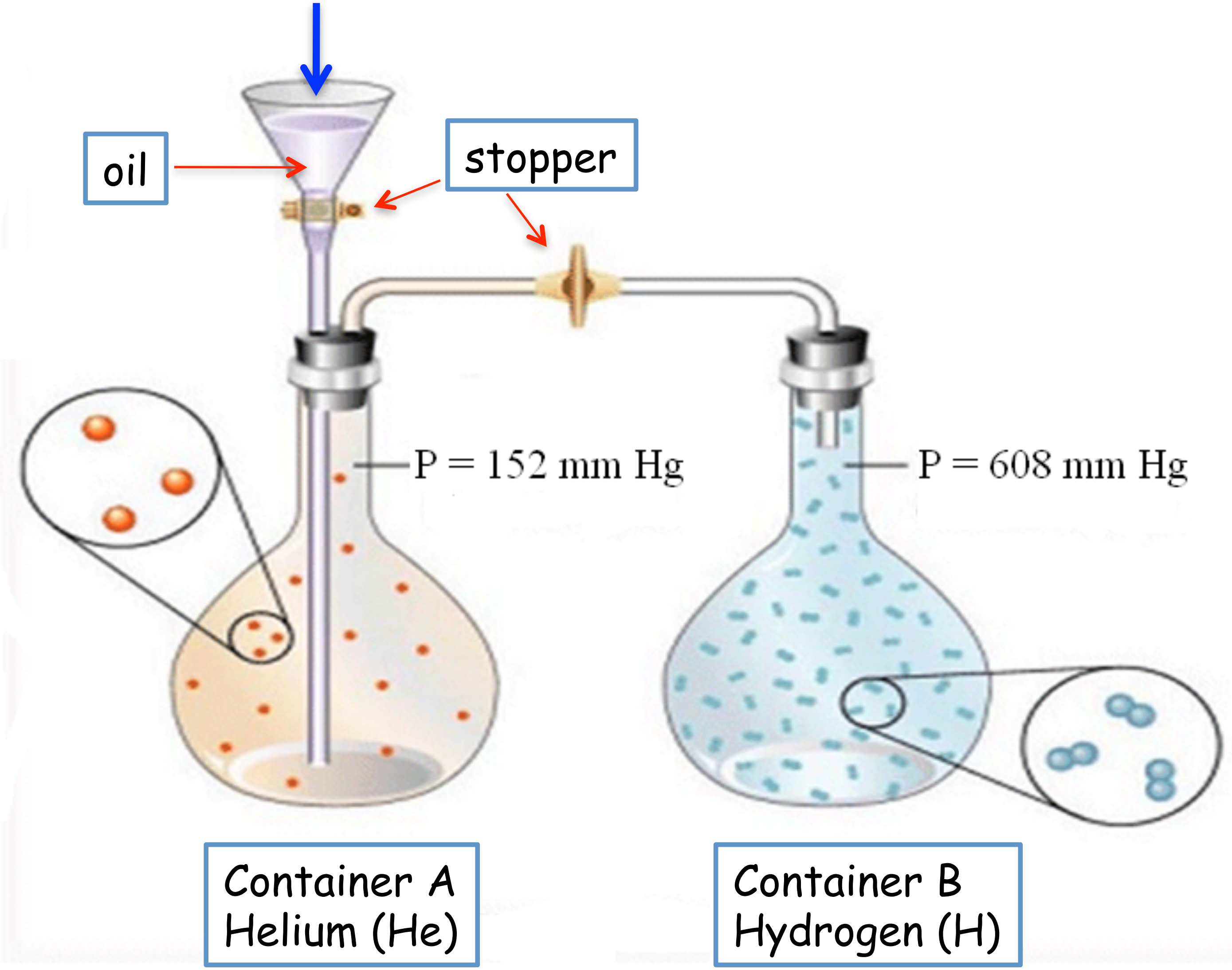
Composition of dry air at sea level

Gas	%V	Gas	%V
azoto (N_2)	78.084	Kripton (Kr)	0.0001
oxygen (O_2)	20.948	Carbon monoxide	0.00001
argon (Ar)	0.934	xenon (Xe)	0.00008
Carbon dioxide (CO_2)	0.033	Ozone (O_3)	0.00002
neon (Ne)	0.00182	ammonia (NH_3)	0.00001
hydrogen (H_2)	0.0010	Nitrogen dioxide(NO_2)	0.000001
helium (He)	0.00052	Sulphur dioxide (SO_2)	0.0000002
methane (CH_4)	0.0002		

Partial pressure due to $N_2 = 760 \times 0.78 = 593.4$ mm Hg = 0.78 atm
Partial pressure due to $O_2 = 760 \times 0.21 = 159.6$ mm Hg = 0.21 atm

Experimental demonstration of Dalton Law

The first container is filled with oil.



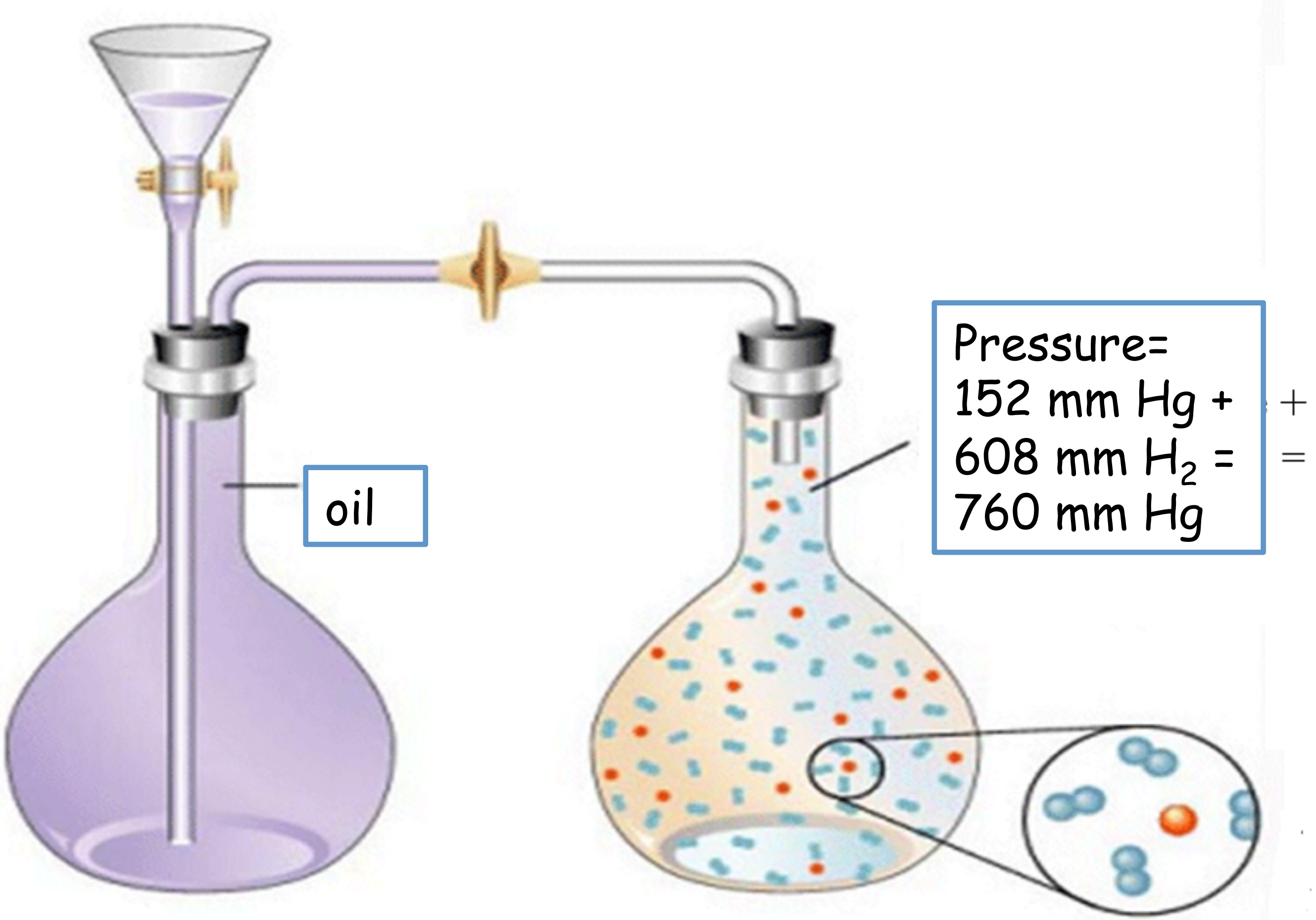
oil

stopper

Container A
Helium (He)

Container B
Hydrogen (H)

After mixing



oil

Pressure=
152 mm Hg +
608 mm H_2 =
760 mm Hg

Container A
oil

Container B
He + H

Henry's Law and the solubility of gases into liquids.

1775-1836

It was formulated by W. Henry in 1803:
a gas that exerts a pressure on the surface of a liquid passes into solution until it has reached inside the liquid the same pressure exerted on it.

$$\boxed{c = k \times P}$$ a T= constant

P is the gas partial pressure, c is its concentration in the liquid and k is a constant typical of each liquid. In water at 298 K:

O_2 : k = 2.30×10^{-5} mol/atm
CO_2 : k = 6.09×10^{-4} mol/atm
H_2 : k = 1.42×10^{-5} mol/atm

Note that the value of the coefficient k varies with the solvent and temperature. An increase in temperature increases the kinetic energy of the gas and causes a decrease in solubility of the gas molecules.

Boyle and Henry's law and patholgies

Decompression sickness (DCS): Air bubbles precipitate out into the bloodstream if the gas dissolved in the blood at pressure is not allowed sufficient time to out-gas on ascent. The symptoms may be subtle and not immediately noticeable. Recompression is the most effective treatment of an air embolism.

Normally this is carried out in a recompression chamber. This is because as pressure increases, the solubility of a gas increases. Additionally, owing to Boyle's law, the size of the gas bubble or bubbles decreases in proportion to the increase in atmospheric pressure. In the hyperbaric chamber the patient breathes 100% oxygen. Under hyperbaric conditions, oxygen diffuses into the bubbles, displacing the nitrogen from the bubble and into solution in the blood.

Ideal gas *vs.* real gas

The particles of an ideal gas have no volume.
Matter, however, occupies a physical space. In fact, given the nature of the atomic or molecular gas particles, their volume can be considered negligible compared to the total volume. This approximation becomes less effective reducing the volume of the gas.

The particles of a gas move in a random way.
This is a realistic assumption: the tendency of gases to occupy all the volume available in a uniform manner proves it.

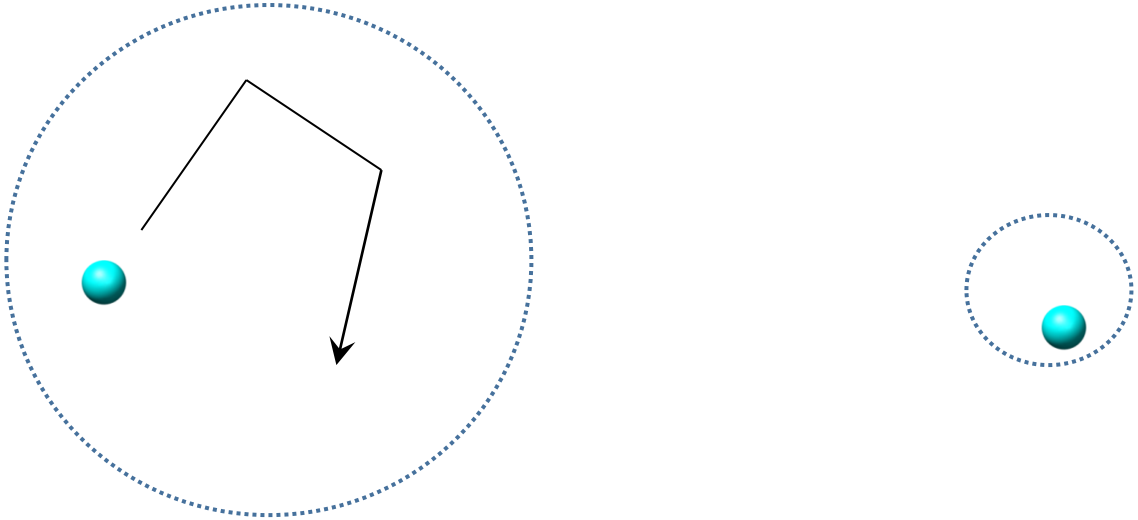
The particles do not interact with each other, or with the container.
The interactions between the particles are small but not absent.
The collisions with the walls of the container have a macroscopic effect on pressure.

Gases behave ideally at low pressures and high temperatures.

1 atom of He: r = 31 pm = $3.1\text{x}10^{-11}$ m
1 atom of He: $V = 4 \pi r^3 / 3 = 1.25 \cdot 10^{-31}$ m^3 = $1.25\text{x}10^{-28}$ L
1 mole of He $V_{He} = 4 \pi r^3 N_A / 3 = 7.5 \text{ x}10^{-5}$ L

At 0° C e 1 atm 1 mole of He has a volume of 22.4 l.
% of V occupied by the gas molecules: $7.5 \text{ x}10^{-5}\text{x}100 / 22.41 = 3.3 \text{ x}10^{-4}$ %
Each He can move in a sphere with a radius of 2000 pm (a lentil in basketball)

If the gas is compressed at 1000 atm V = 0.02241 L
% del V occupied by the gas molecules: $7.5 \text{ x}10^{-5}\text{x } 100 / 0.02241 = 0.33$ %
Each He atom can move in a sphere with a radius of 200 pm (a lentil in golf ball



The volume of gas particles

- If $P V = n R T$, for $T = 0$, the only solution for all P is $V = 0$.

  A gas should disappear at 0 K.

- The influence of the finite size of the molecules reduces the actual volume of gas available by a term b (covolume) that is related to the volume actually occupied by the molecules

$$V_{ideale} = V_{reale} - \mathrm{n\,b}$$

Interactions between particles

- Since interactions exist, the pressure of a real gas is lower than that of an ideal gas: there is a lower number of collisions against the walls per unit area

- The force exerted on molecules by other molecules as they collide on the container, is greater as they get closer. Moreover the number of molecules that collide with the container is inversely proportional to the volume of gas.

$$P_{ideale} = P_{reale} + \frac{a}{V^2} n^2$$

Volume available to a real gas < volume available to an ideal gas

$$V_{ideal} = V_{real} - \mathrm{n\,b}$$

Real gas pressure < ideal gas pressure

$$P_{ideal} = P_{reae} + \frac{\mathrm{a}}{V^2}\mathrm{n}^2$$

van der Waals equation for real gases

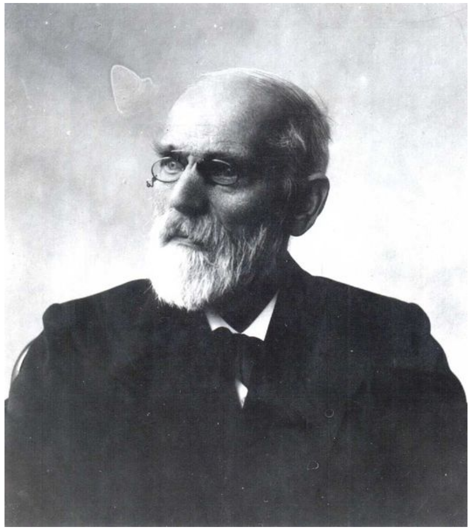
$$P_{ideal}V_{ideal} = \mathrm{n}RT$$

$$\left(P + \frac{\mathrm{a}}{V^2}n^2\right)\left(V - \mathrm{n\,b}\right) = \mathrm{n}RT$$

State law for real gases: van der Waals equation

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

gas	a (atm L^2·mol^{-2})	b (L·mol^{-1})
He	0.034	0.0237
Ar	1.34	0.0322
H_2	0.244	0.0266
N_2	1.39	0.0391
O_2	1.36	0.0318
CO_2	3.59	0.0427
Cl_2	6.49	0.0562
H_2O	5.46	0.0305



Johannes Diderik
van der Waals
1837-1923

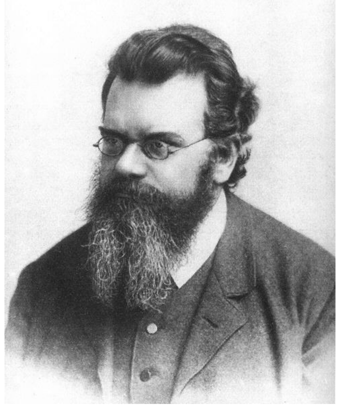
$$PV=nRT$$

For high temparatures
and low pressure

Kinetic gas theory

Gas laws provide a macroscopic description of gas properties (pressure, volume, density, etc…). The kinetic molecular theory provides a description at the atomic or molecular level.

J.C. Maxwell
(1831–1879)



L.E. Boltzmann
(1844-1906)

A) Gases consist of particles (atoms or molecules) whose mutual distance is much larger than the size of the particles themselves.

N_2 (liq) boils
a -196 °C

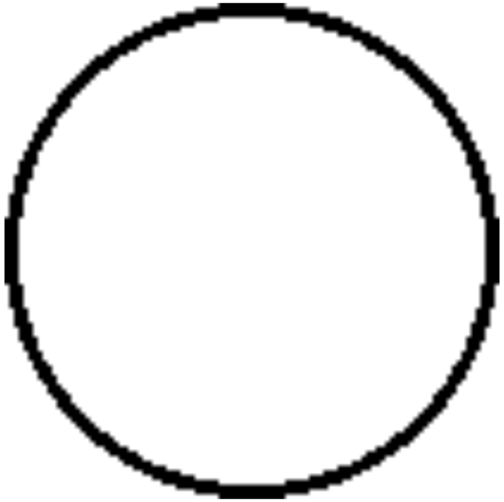
1 g of H_2O at 100° C and 1 Atm

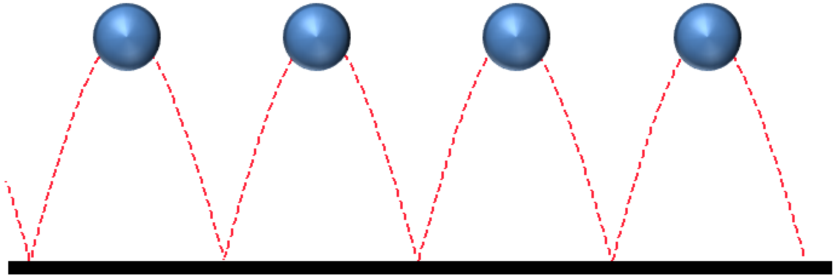
$V_{liquid} = m / \delta = 1.0\ cm^3$

$V_{gas} = nRT/P = 1700\ cm^3$

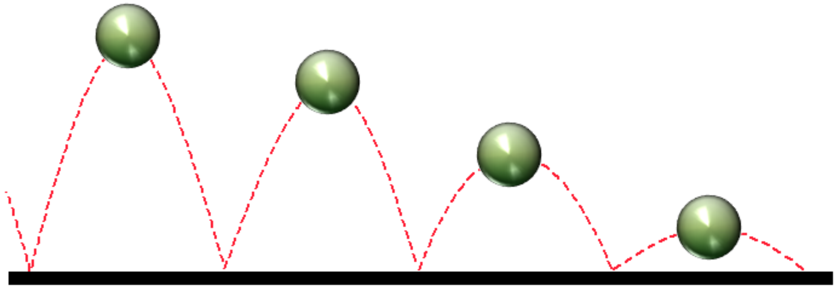
V_{liquid} / V_{vapour} ~1700

Gas particles move with a fast, random motion. They collide with each other and with the walls of their container, without loss of kinetic energy.





Elastic collision

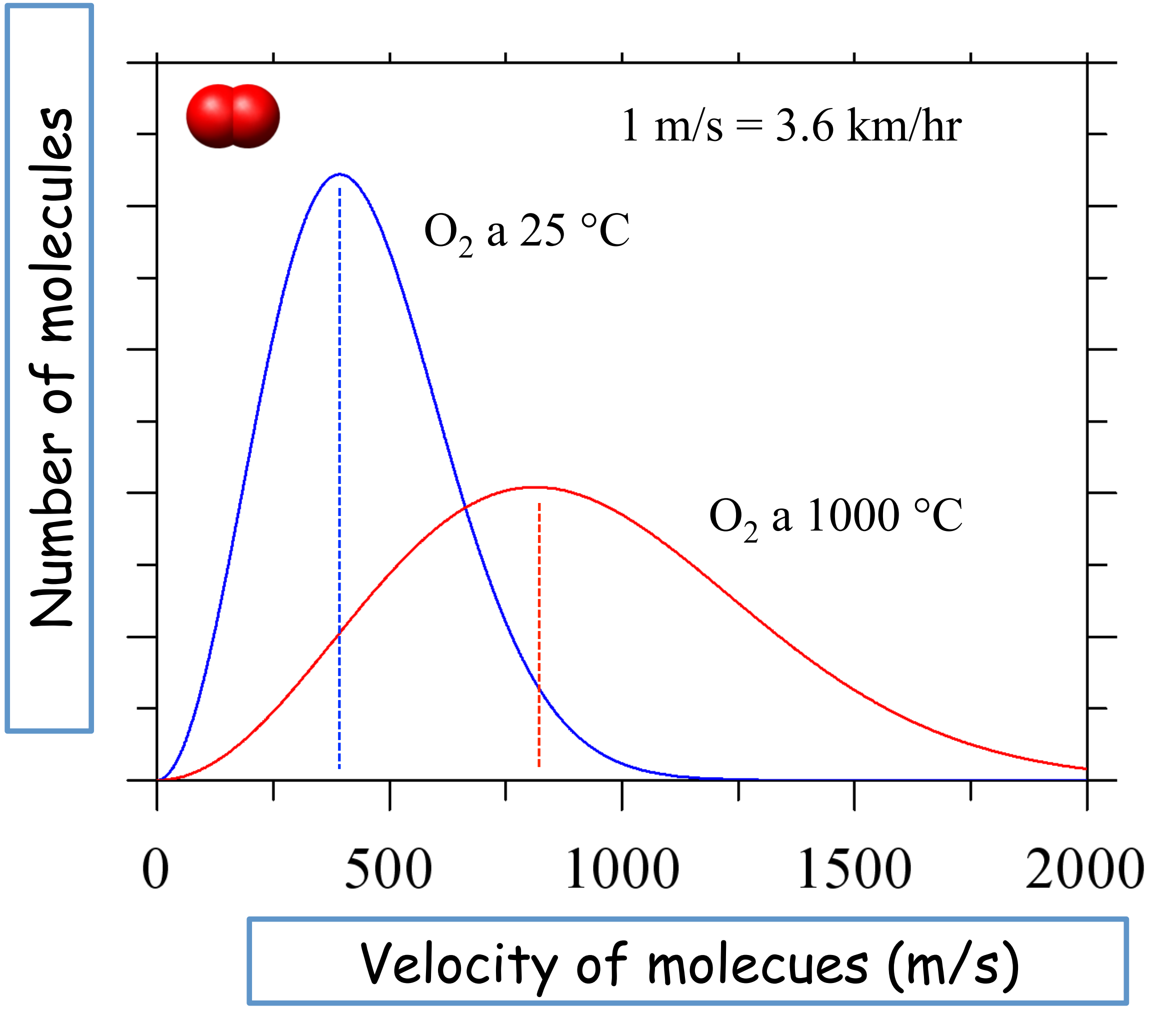


Anelastic collision

C) Average kinetic energy is proportional to temperature.

$$\overline{E_k} = \frac{3}{2}RT$$

Maxwell-Boltzmann distribution



NH_3 (g) + HCl (g)

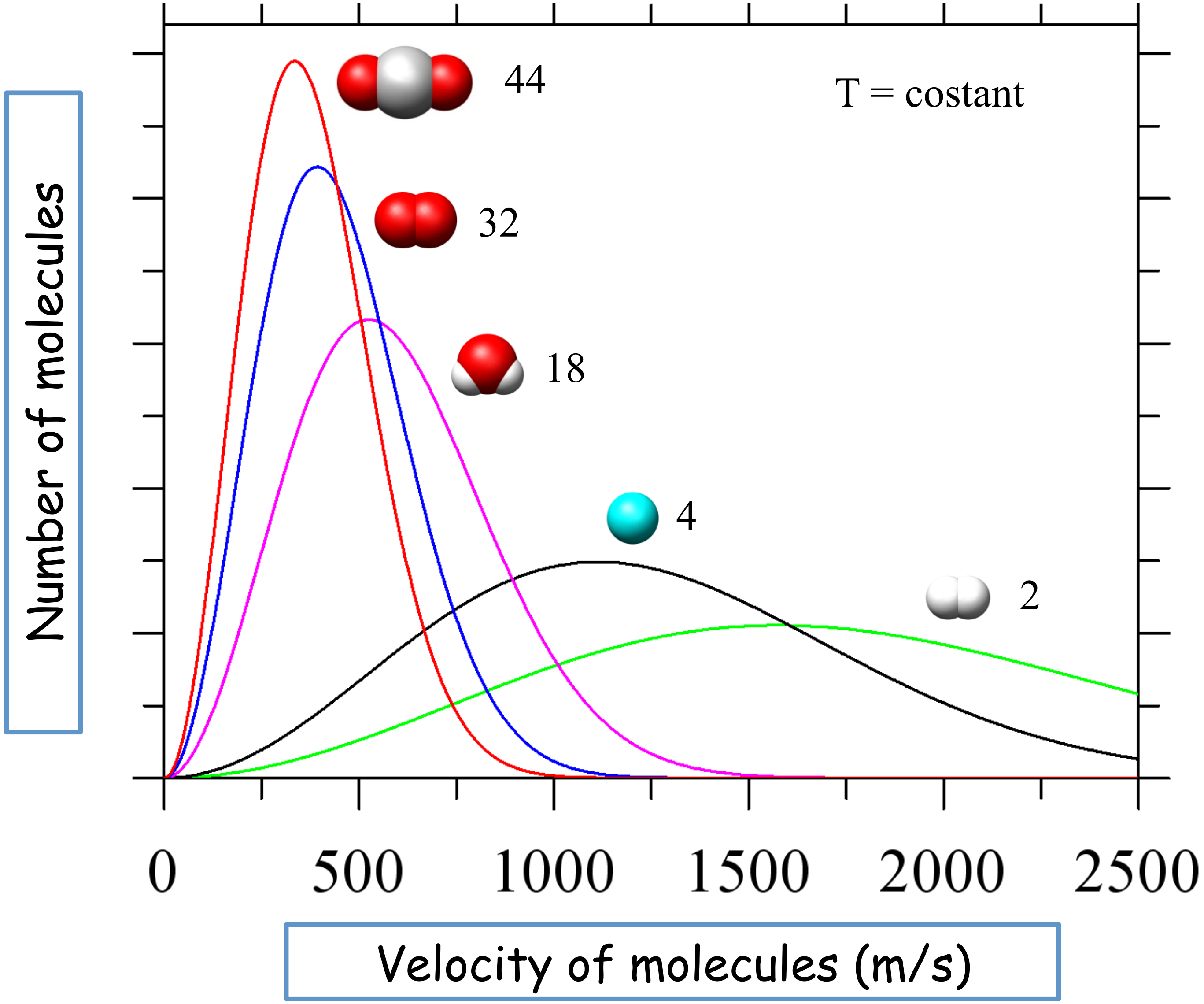
Since: $E_k=1/2 \times m \times v^2$

The average energy of a molecule

$$\overline{E}_k=1/2 \times m \times \overline{v}^2$$

If for all gases at the same temperature E is identical,
mass and velocity must have a an inverse relationship of proportionality.

Maxwell-Boltzmann distribution



Kinetic gas theory

Kinetic energy in a real gas

$$\bar{E}_k = \frac{3}{2}RT$$

and

$$\bar{E}_k = 1/2\ M\bar{v}^2$$

P = pressure (Pa)
V = volume (m^3)
T = temperature (K)
N = number of atoms or molecules
M = mass of a molecole (kg)
$\sqrt{\bar{v}^2} = c$ = square average velocity (m/s)

Therefore the square average velocity of a molecule is

$$c = \sqrt{\frac{3RT}{M}}$$

Maxwell Equation

Molecular description of gas laws

A molecular description of Boyle's Law

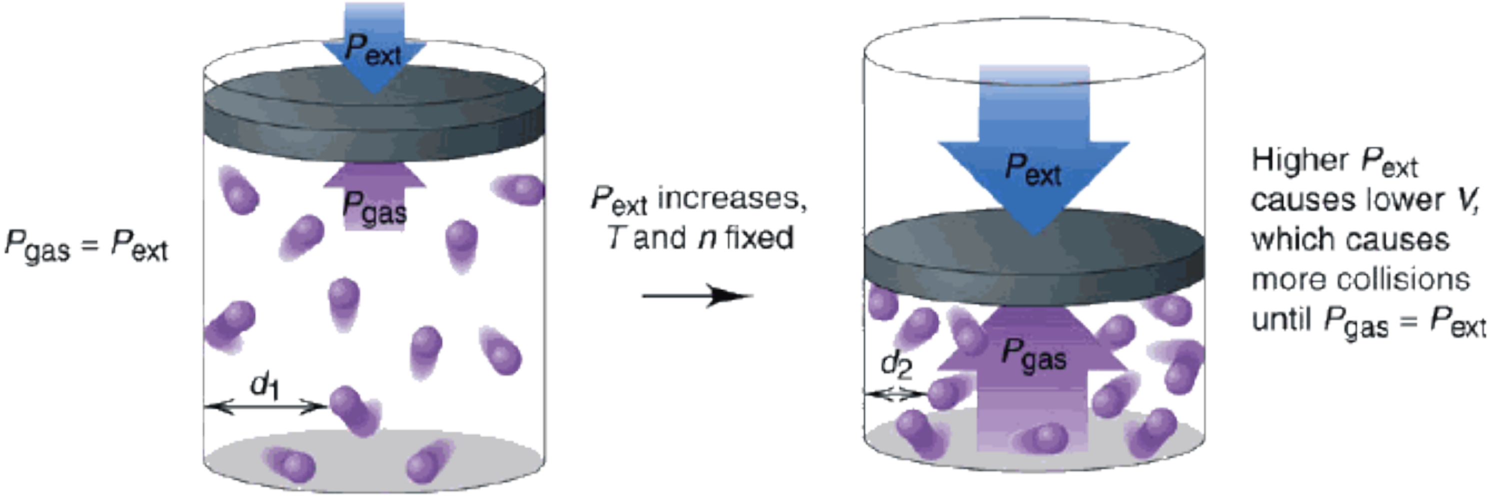
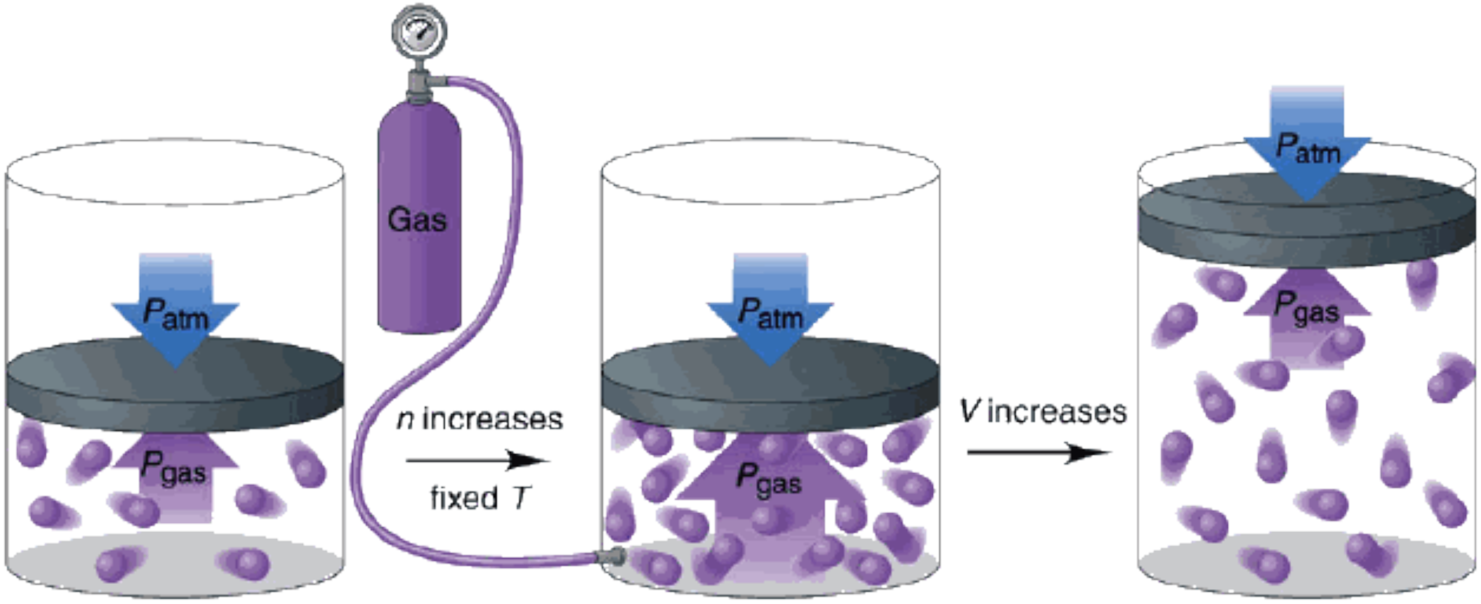


Figure 5.15

A molecular description of Avogadro's Law



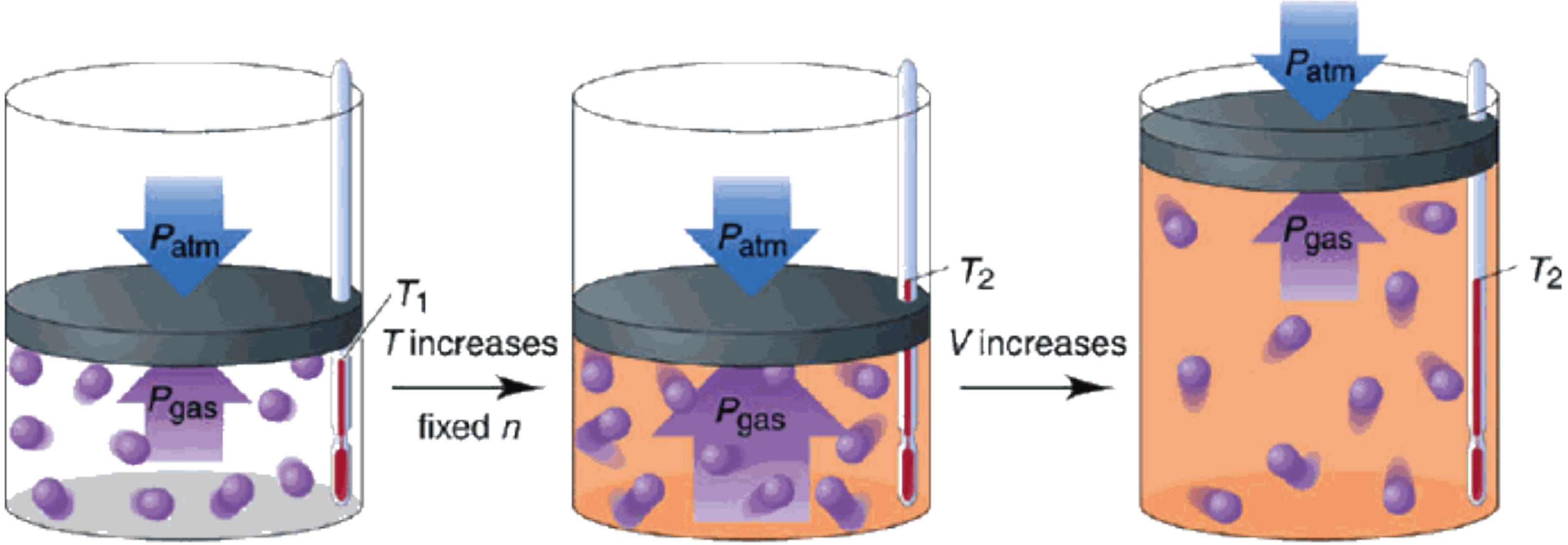
$P_{gas} = P_{atm}$

More molecules increase collisions: $P_{gas} > P_{atm}$

V increases until $P_{gas} = P_{atm}$

Figure 5.18

A molecular description of Charles's Law



$P_{gas} = P_{atm}$

Higher T increases collision frequency:
$P_{gas} > P_{atm}$

V increases until
$P_{gas} = P_{atm}$

Figure 5.17

A molecular description of Dalton’s law of partial pressures

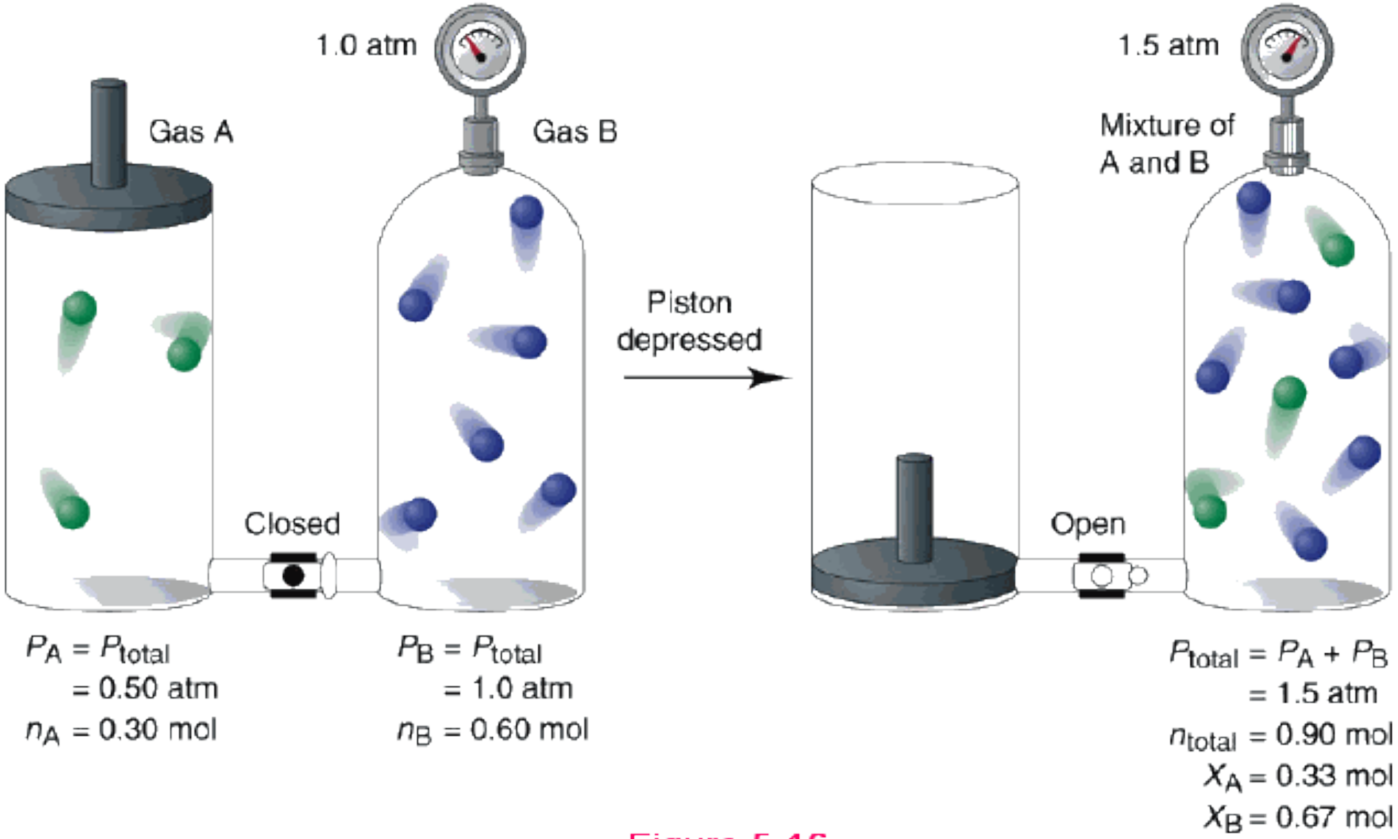
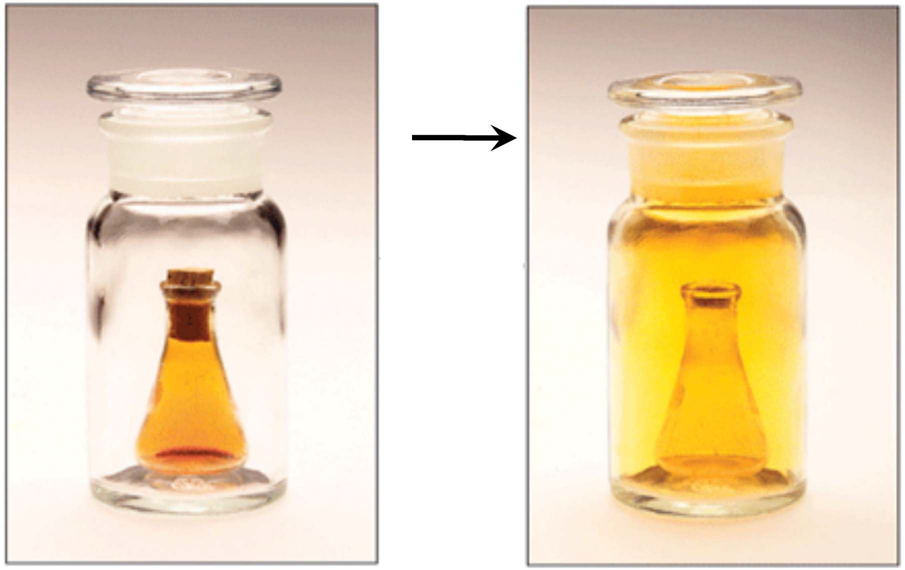


Figure 5.16

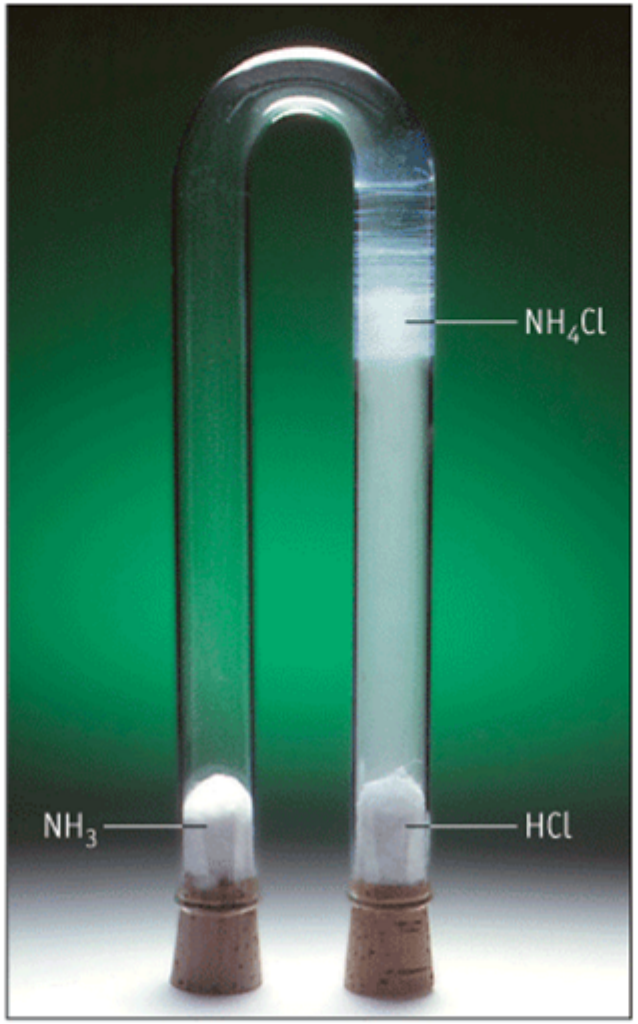
Diffusion of a gas

The mixing of molecules of two or more gas due to the random movements of molecules is called gaseous diffusion.



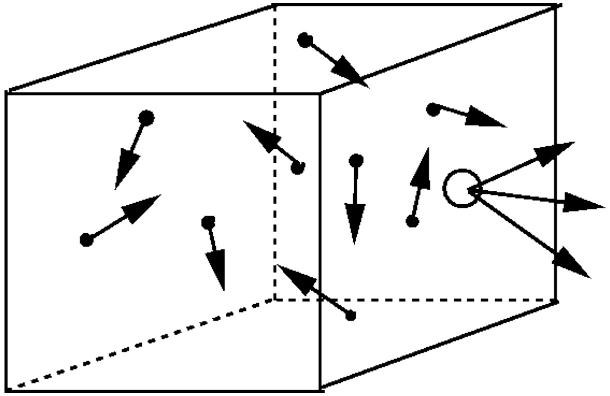
$Br_2\ (g)$

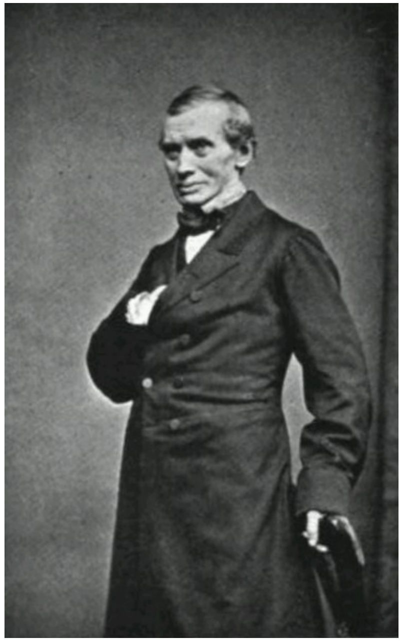
$$NH_3\ (g) + HCl\ (g) \rightarrow NH_4Cl\ (s)$$



Graham law

Diffusive motion of a gas through a narrow opening, from a container to another in which the pressure is very low.



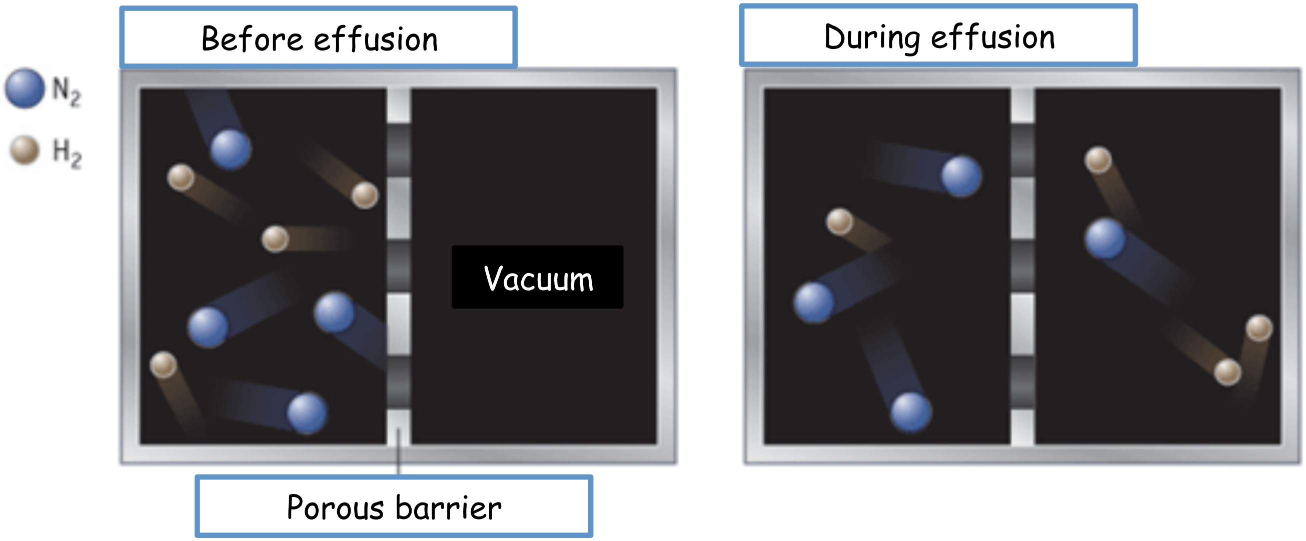


1805-1869

Thomas Graham (discoverer of dialysis) studied the diffusion of gases and found experimentally that the rate of effusion of two gases are inversely proportional to the square roots of their molar masses (in the same conditions of temperature and pressure):

$$\frac{\text{velocity of gas1}}{\text{velocity of gas2}} = \sqrt{\frac{M_2}{M_1}}$$

Molecules of H_2 e N_2 diffuse through a porous wall. Molecules of H_2 are lighter and faster than those of N_2, heavier and slower at the same temperature.



$$\frac{v_{H_2}}{v_{N_2}} = \frac{\sqrt{M_{N_2}}}{\sqrt{M_{H_2}}} = \frac{\sqrt{28}}{\sqrt{2}} = 3.74$$

according to Graham law H_2 molecules exit 3.74 faster than those of N_2.

$$v_{H_2} = 3.74 \cdot v_{N_2}$$

Example

If Ne has an average velocity of 400. m/s, evaluate the same parameter for butane (C_4H_{10}) at the same temperature

$$v_{C_4H_{10}} = v_{Ne}\frac{\sqrt{M_{Ne}}}{\sqrt{M_{C_4H_{10}}}} = 400\frac{\sqrt{20.18}}{\sqrt{58.12}} = 235.7\ m/s$$