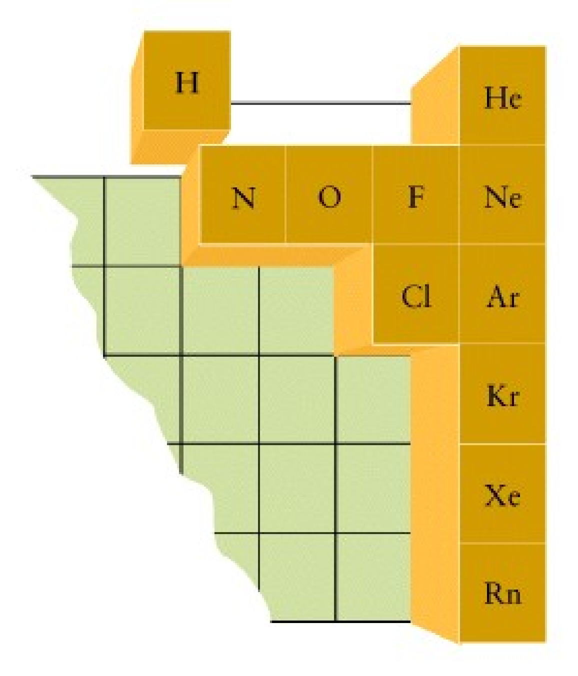
Gases



11 gaseous elements

Rare gases

He, Ne, Ar, Kr, Xe, Rn

Diatomic gaseous elements

H_2, N_2, O_2, F_2, Cl_2

Gas	**T_{boil}, K**
H_2	20
He	4.4
Ne	27
Ar	87
Kr	120
Xe	165
Rn	211
N_2	77
O_2	90
F_2	85
Cl_2	238

Gas

Large part of chemical and physical theories was developed on experiments with gases.

Different kinds of "air"
→ studies on gases, concept of gas

Gas sylvestre = CO_2

CO_2 is formed:

- Burning coal with KNO_3 (salpeter)
- Fermentation of beer and wine
- Action of vinegar on limestone
- Grotto del Cane

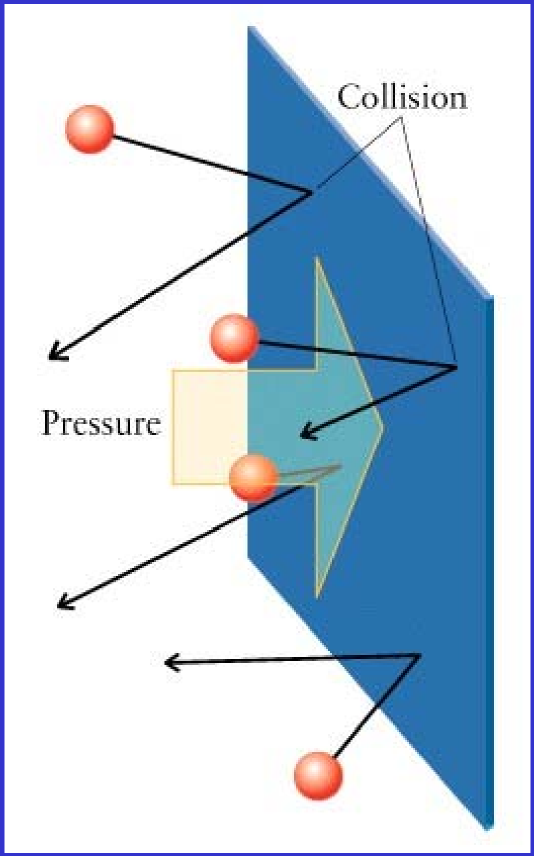
Johann Baptista van Helmont
(1579-1644)

Pressure

Collisions of gas molecules with container walls

F = force, N
A = area, m^2

$$p = \frac{F}{A}$$



101325 Pa
760 mm Hg
760 torr
(Torricelli)
1 atm

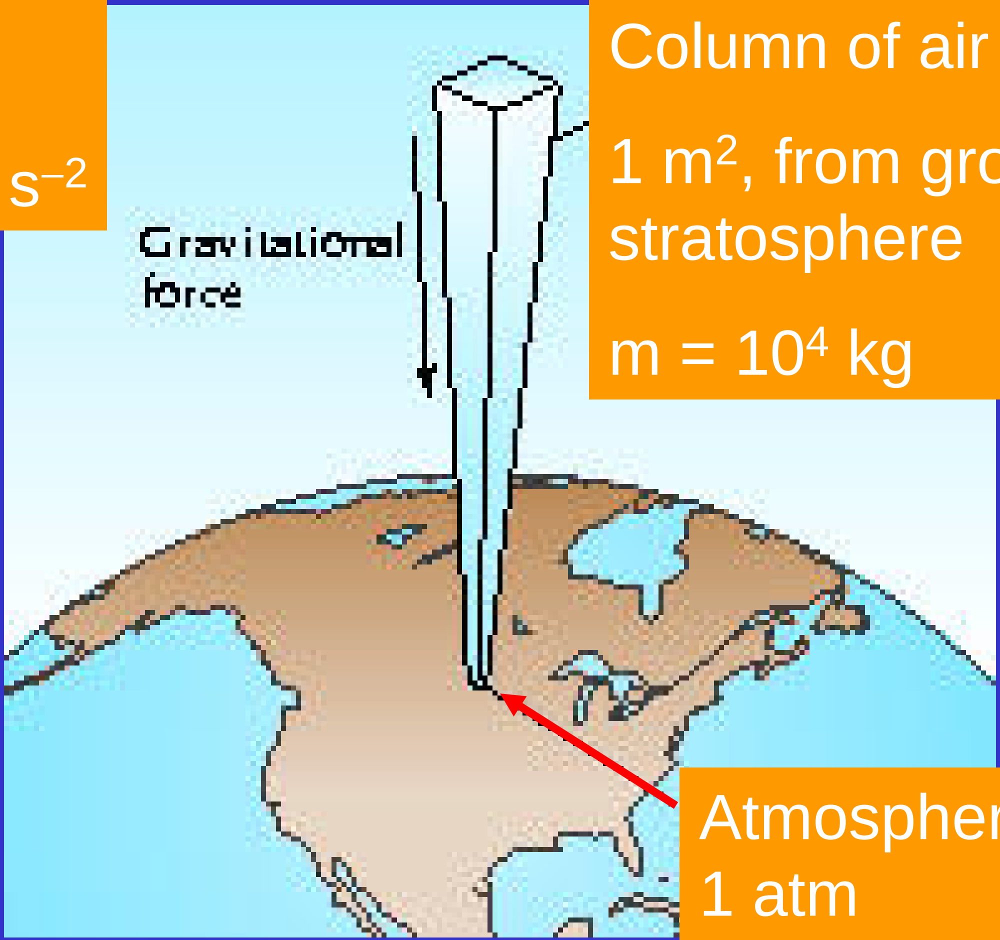
Evangelista Torricelli
(1608-1647)

barometer 1643

Atmospheric Pressure

$F = m\,g$

$g = 9.80665\ \mathrm{m\ s^{-2}}$



Column of air

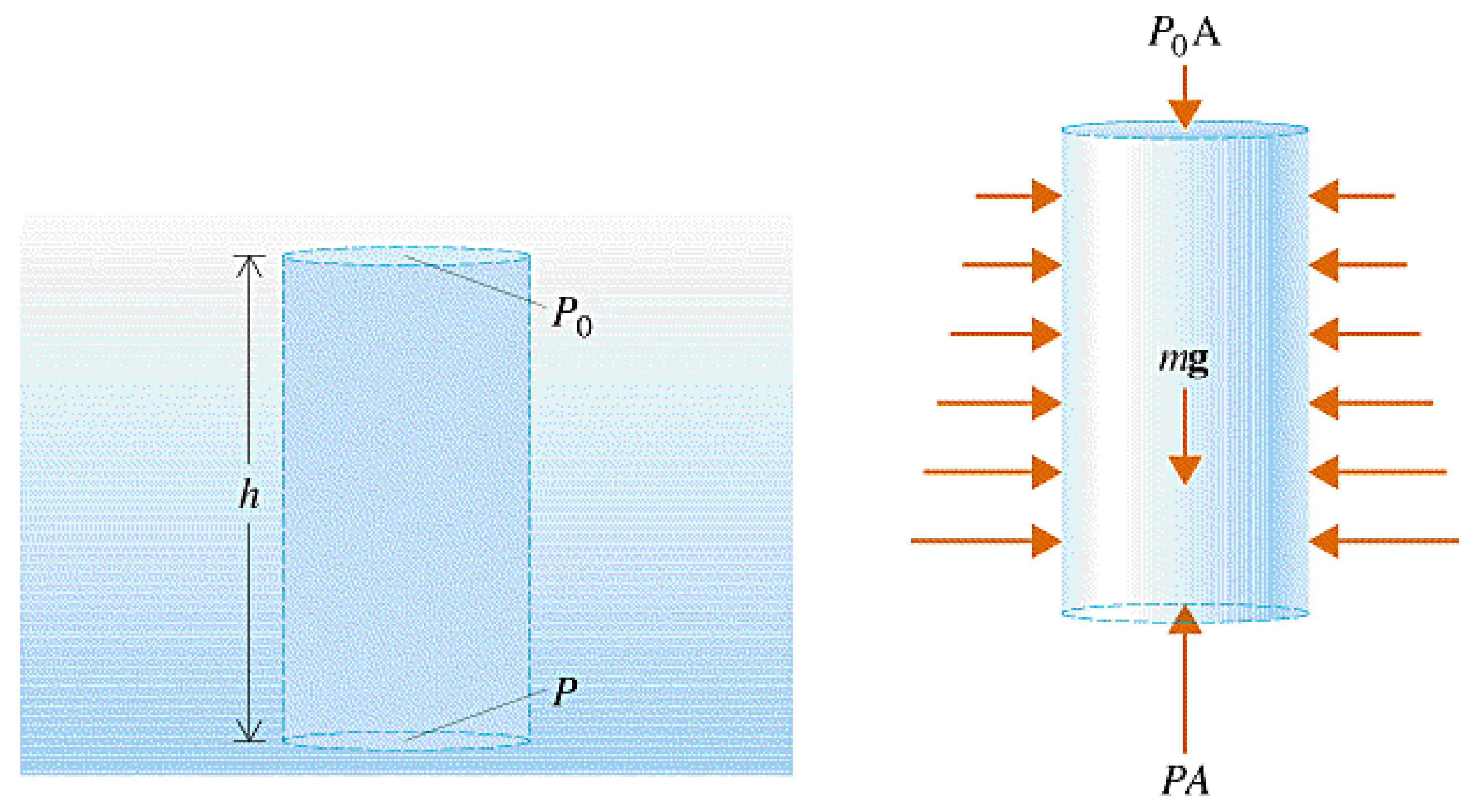
1 $\mathrm{m^2}$, from ground to stratosphere

$m = 10^4\ \mathrm{kg}$

Atmospheric Pressure
1 atm

Hydrostatic Pressure

$p = h \rho g$



Boyle's Law

1662

Product of gas pressure and its volume is a constant for a given amount of gas at constant temperature

Robert Boyle
(1627 - 1691)

$$p\,V = \text{const.}$$

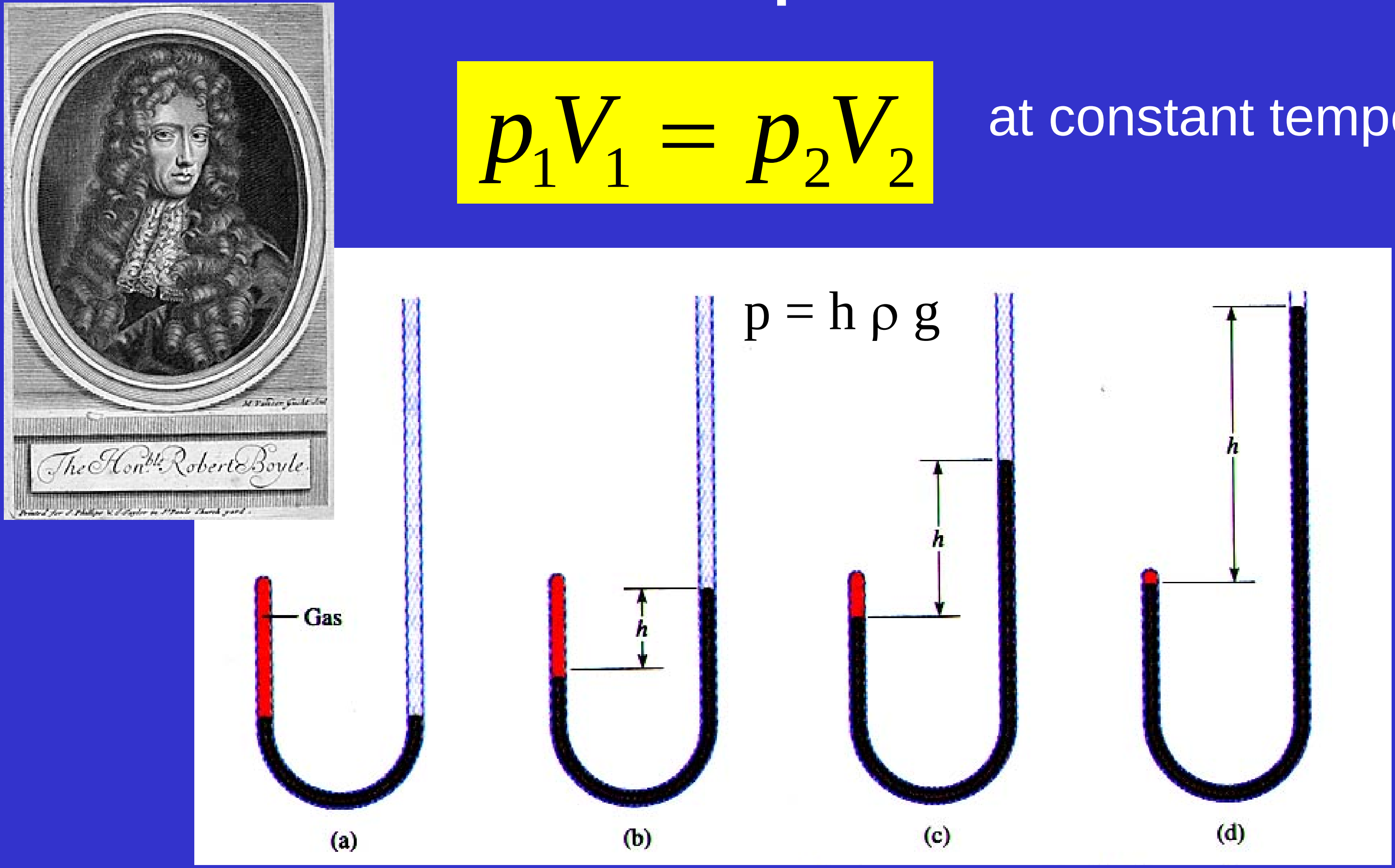
Isothermic

Does not depend on the kind of gas, mixture of gases

Exceptions NO_2

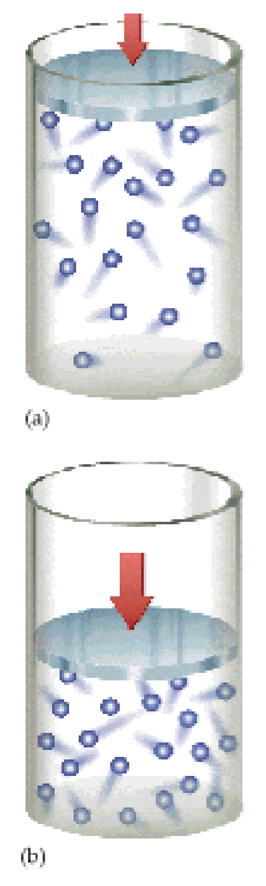
Gas Compression

$$p_1V_1 = p_2V_2$$ at constant temperature



p = h ρ g

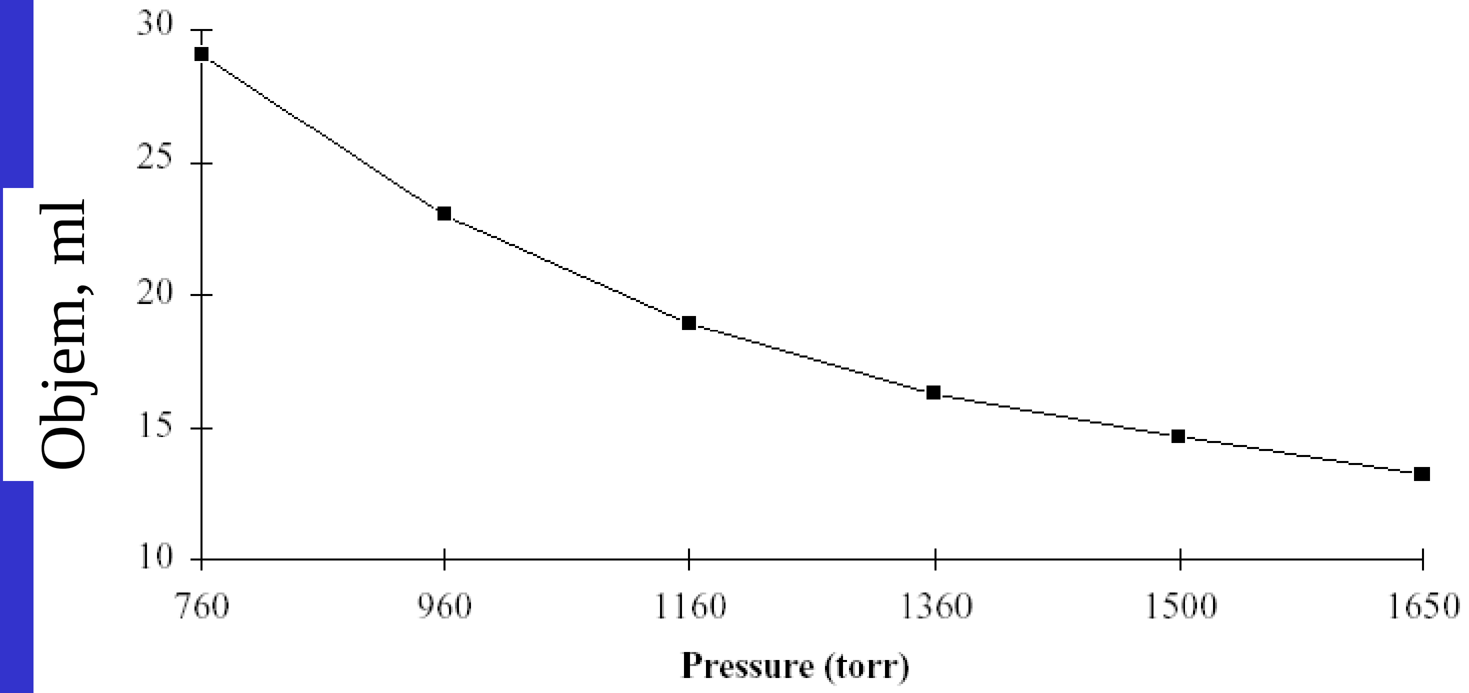
tlak roste →

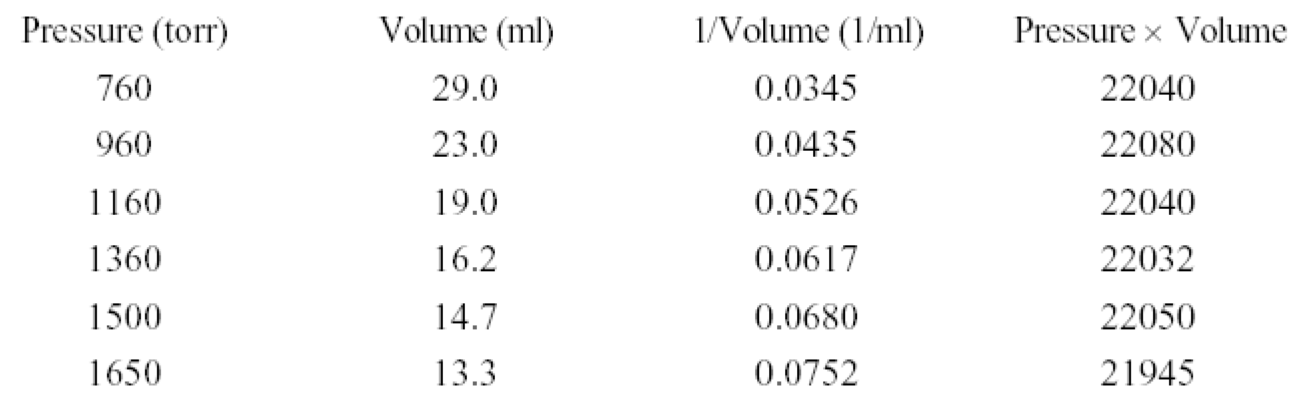


Boyle’s Law

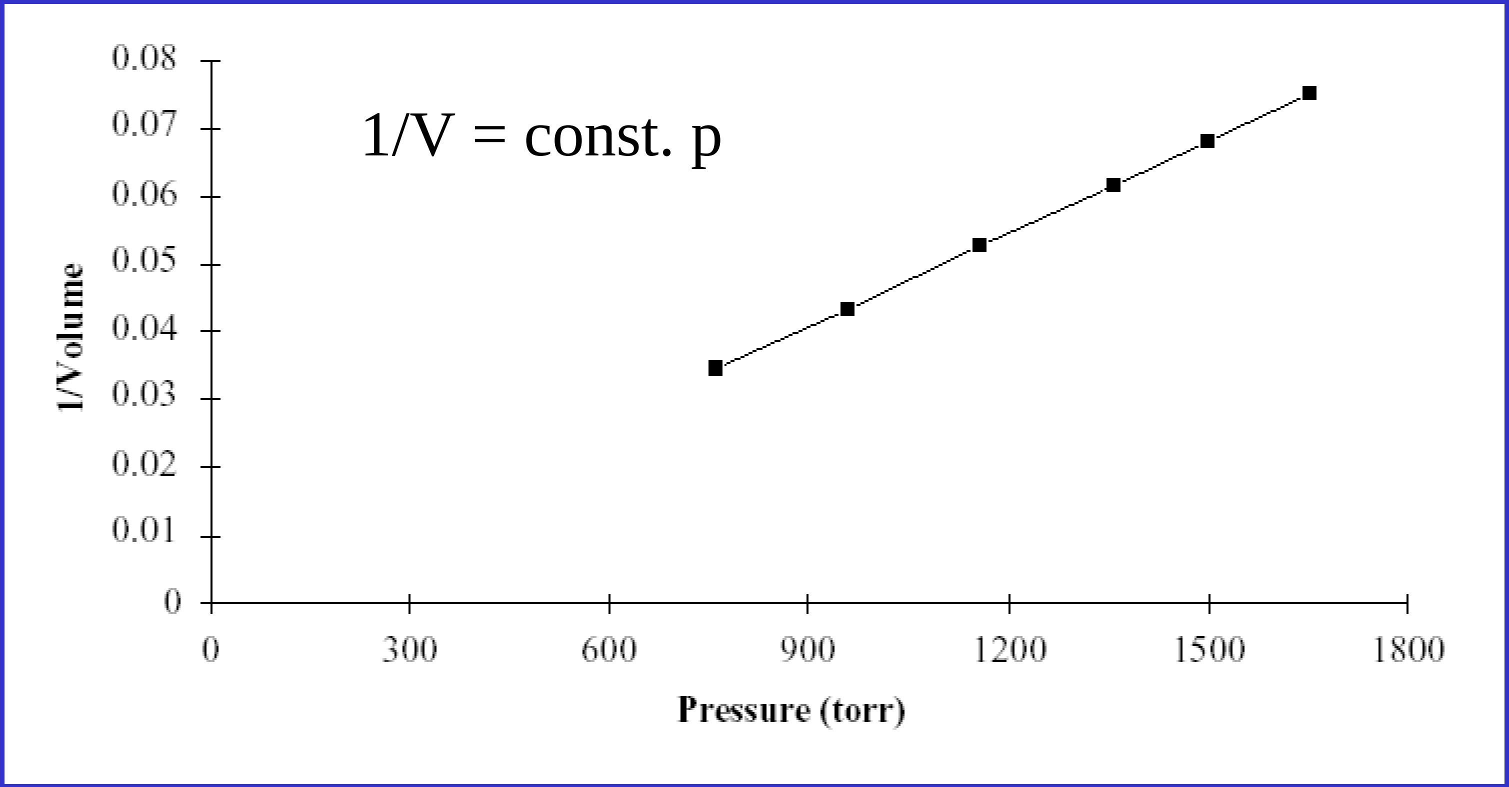
V = const. / p

Pressure (torr)	Volume (ml)
760	29.0
960	23.0
1160	19.0
1360	16.2
1500	14.7
1650	13.3





Pressure (torr)	Volume (ml)	1/Volume (1/ml)	Pressure × Volume
760	29.0	0.0345	22040
960	23.0	0.0435	22080
1160	19.0	0.0526	22040
1360	16.2	0.0617	22032
1500	14.7	0.0680	22050
1650	13.3	0.0752	21945



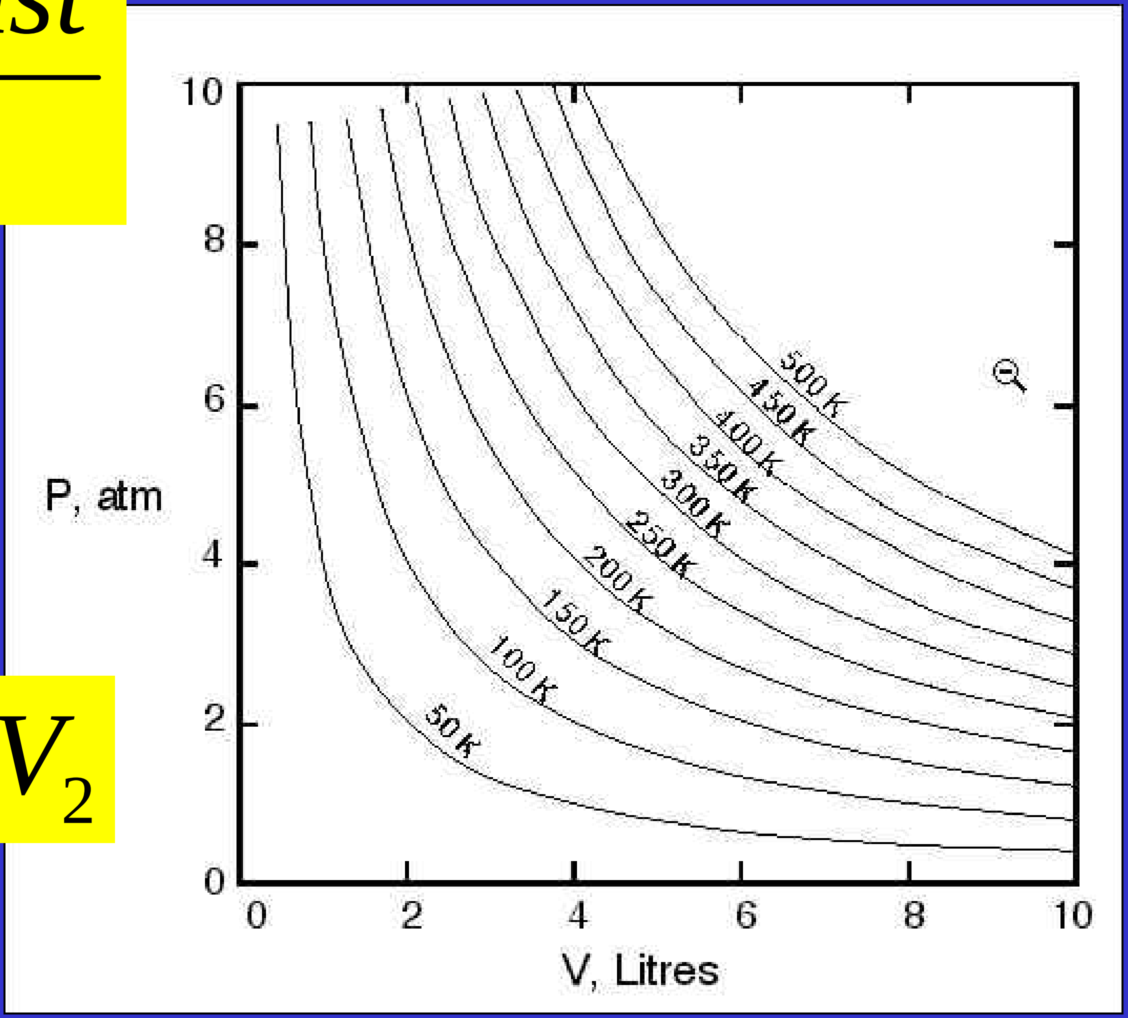
$1/V = \text{const. } p$

$$p = \frac{konst}{V}$$

Isotherms

T = const.

$$p_1 V_1 = p_2 V_2$$

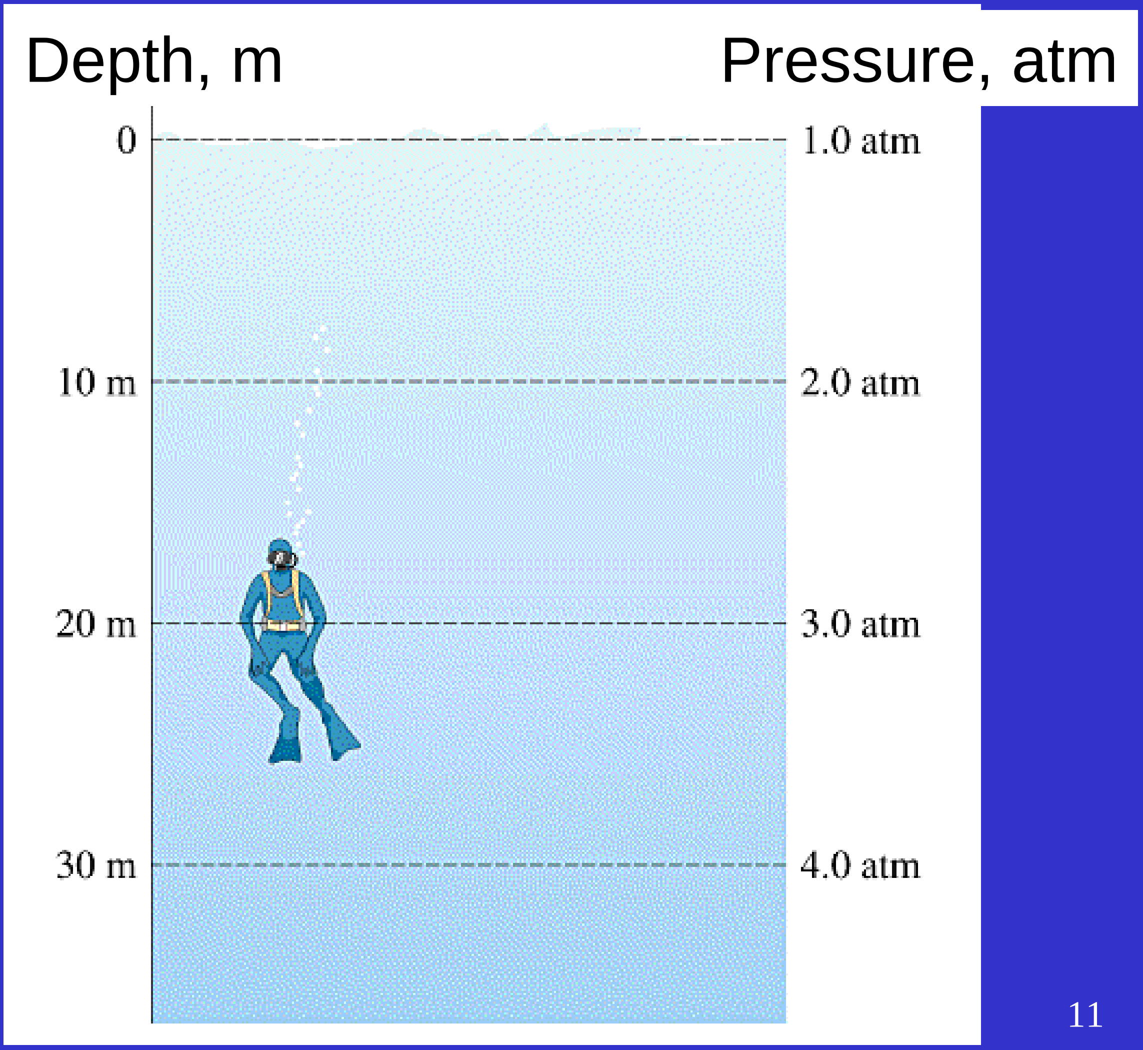


Scuba Diving

Air in a tank for a 60 minute dive at surface

How much air ?

X minutes in 30 m



Charles-Gay-Lussac Law

p = const. Isobaric

1787

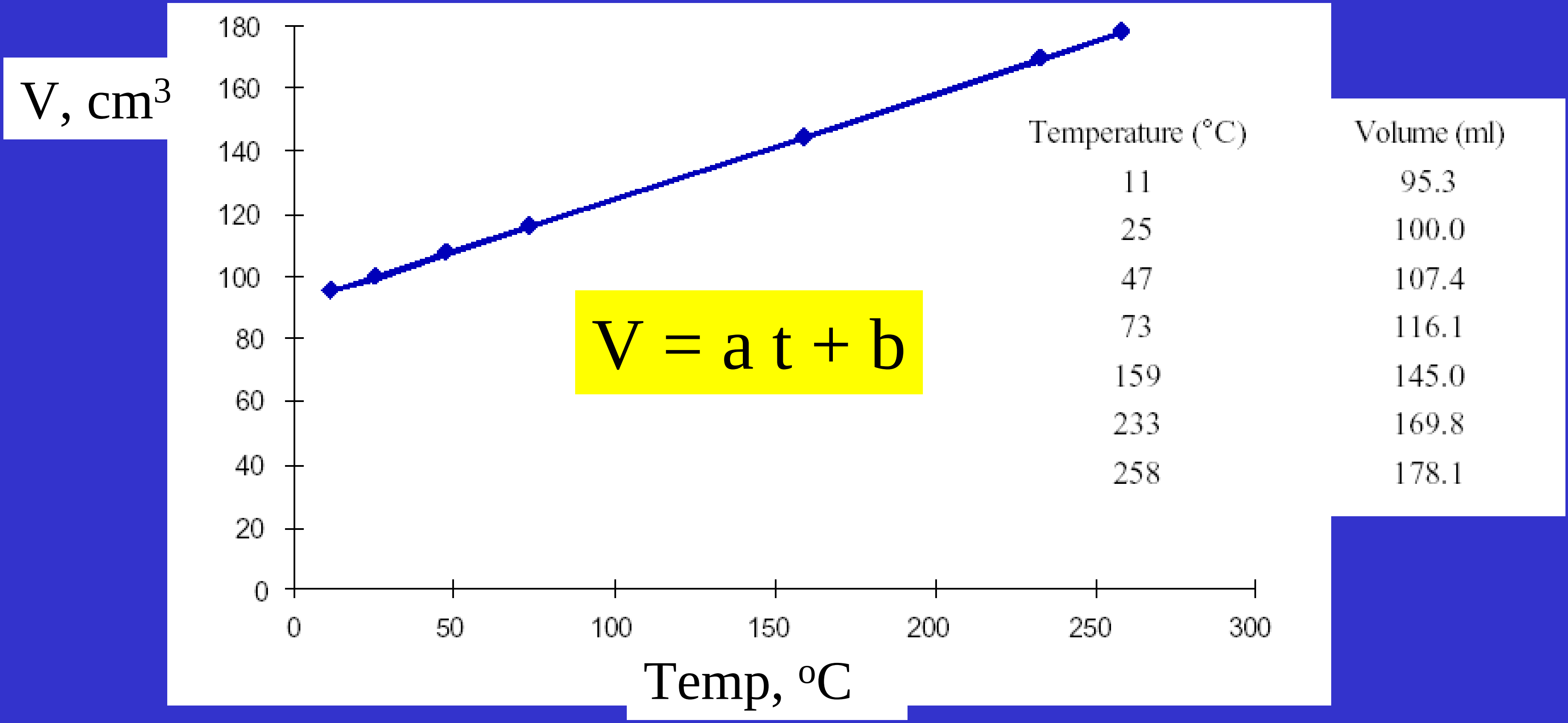
Different gases expand by the same fraction of volume on heating by the same degree

Jacques A. C. Charles
(1746 - 1823)

The first solo flight in ballon
The first H_2 ballon

Joseph Louis Gay-Lussac
(1778 - 1850)

Charles-Gay-Lussac Law



$$V = a\,t + b$$

Temperature (°C)	Volume (ml)
11	95.3
25	100.0
47	107.4
73	116.1
159	145.0
233	169.8
258	178.1

p = const. Isobaric

Charles-Gay-Lussac Law

$V = a\,t + b$ p = const. Isobaric

$V = a\,t + b$

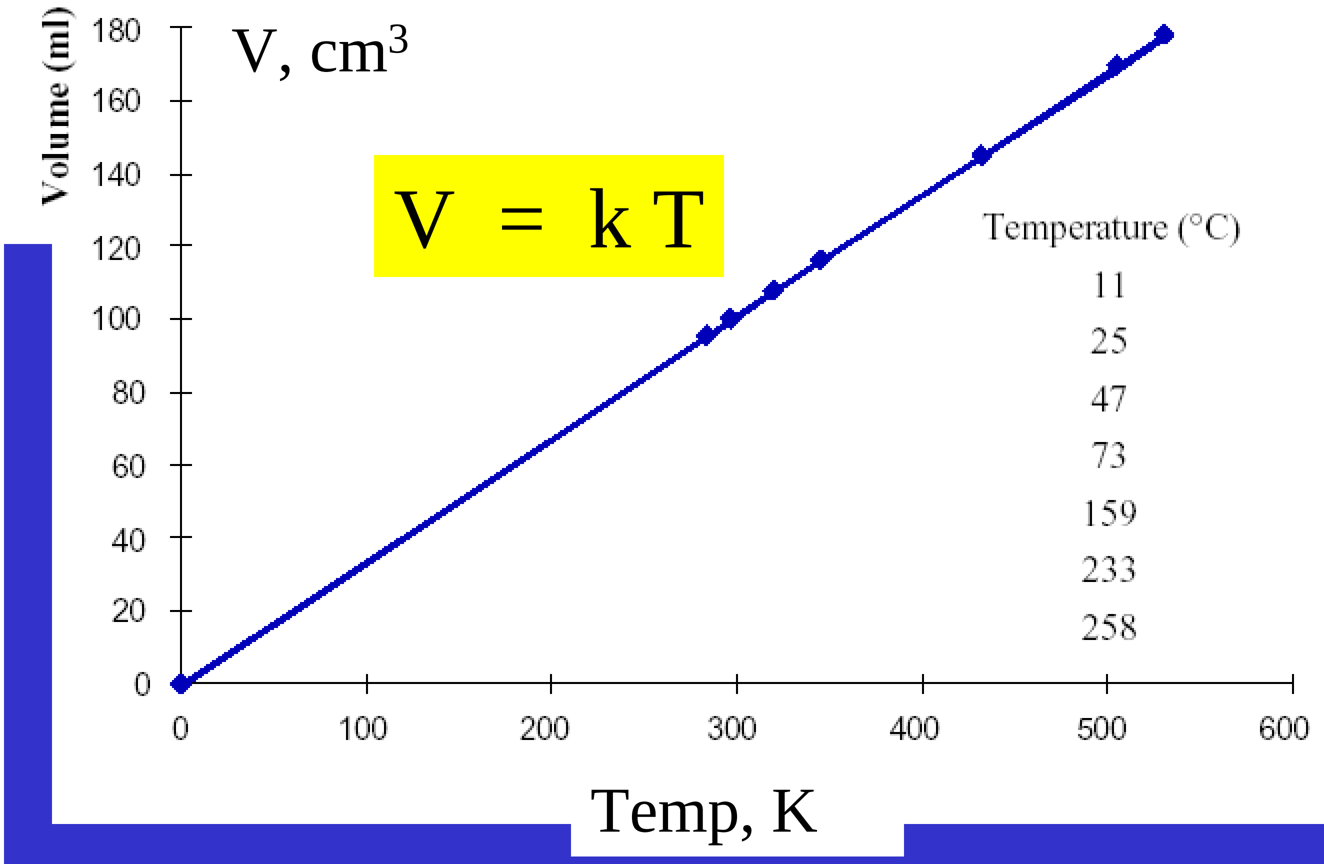
$V = a\,(t + b/a)$

b/a = 273 °C absolute temperature scale

$V = k\,T$ T = absolute temperature [K]

Concept of absolute zero temperature

Charles-Gay-Lussac Law

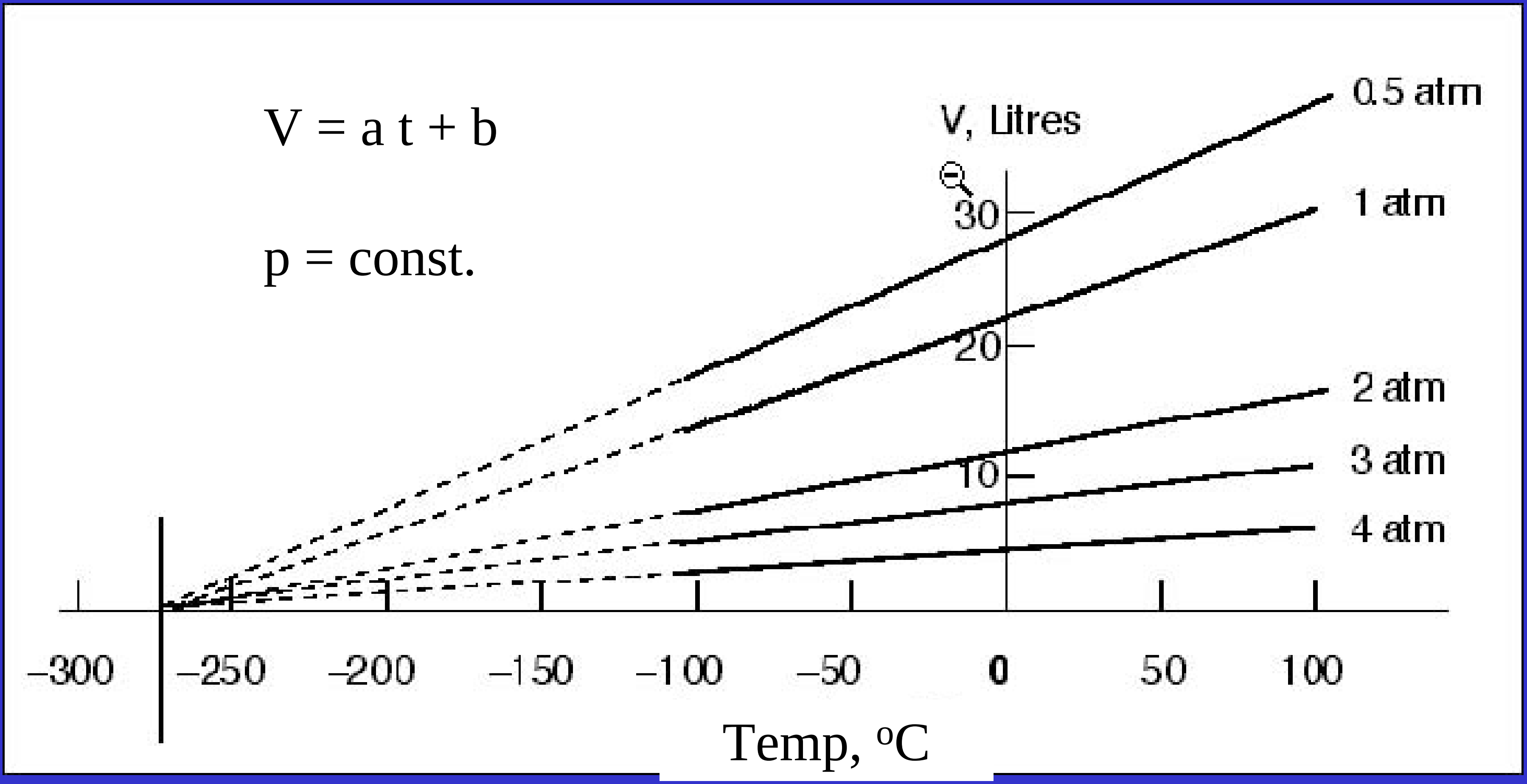


$$V = kT$$

p = const. Isobaric

Temperature (°C)	Temperature (K)	Volume (ml)
11	284	95.3
25	298	100.0
47	320	107.4
73	350	116.1
159	432	145.0
233	506	169.8
258	531	178.1

Isobars



$V = a\,t + b$

$p = \text{const.}$

Charles-Gay-Lussac Law

$$V = V_0 \, (1 + \alpha \, t)$$

α = 1/273 coefficient of thermal expansion

t = temp. in °C

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

const. *n* and *p*

Amonton's Law

$$p = p_0 (1 + \alpha\ t)$$

α = 1/273 coefficient of thermal expansion

$$\frac{p_1}{T_1} = \frac{p_2}{T_2}$$

const. n and V

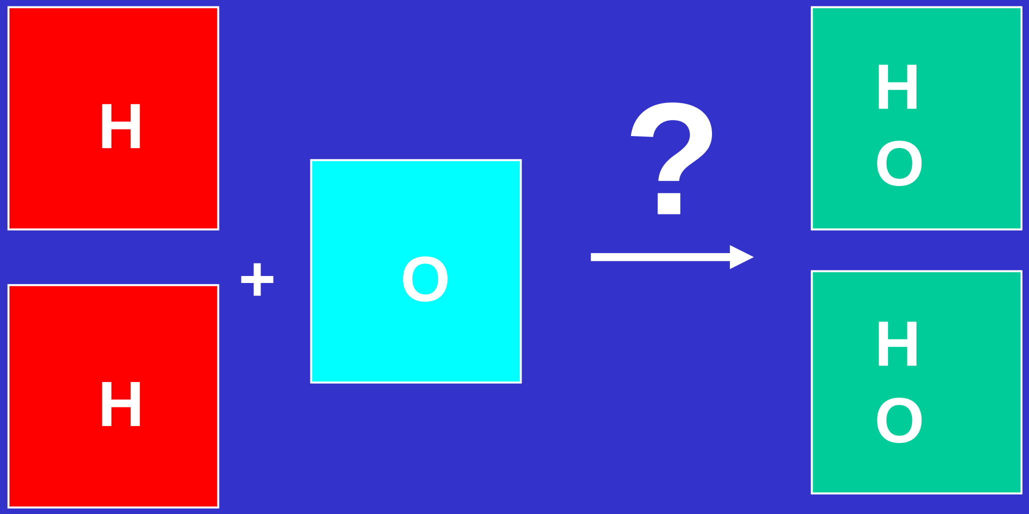
isochore

Law of Constant Volumes (Gay-Lussac)

1809 Gases combine in simple volume ratios

2 volumes of hydrogen + 1 volume of oxygen

→ 2 volumes of water vapor



Joseph Louis Gay-Lussac
(1778 - 1850)

Avogadro's Hypothesis

1811 A. Avogadro deduced from Dalton's atomic theory and from Gay-Lussac's law:

At the same temperature and pressure, the same volumes of different gases contain the same number of particles.

Gases are diatomic molecules

H_2, N_2, O_2

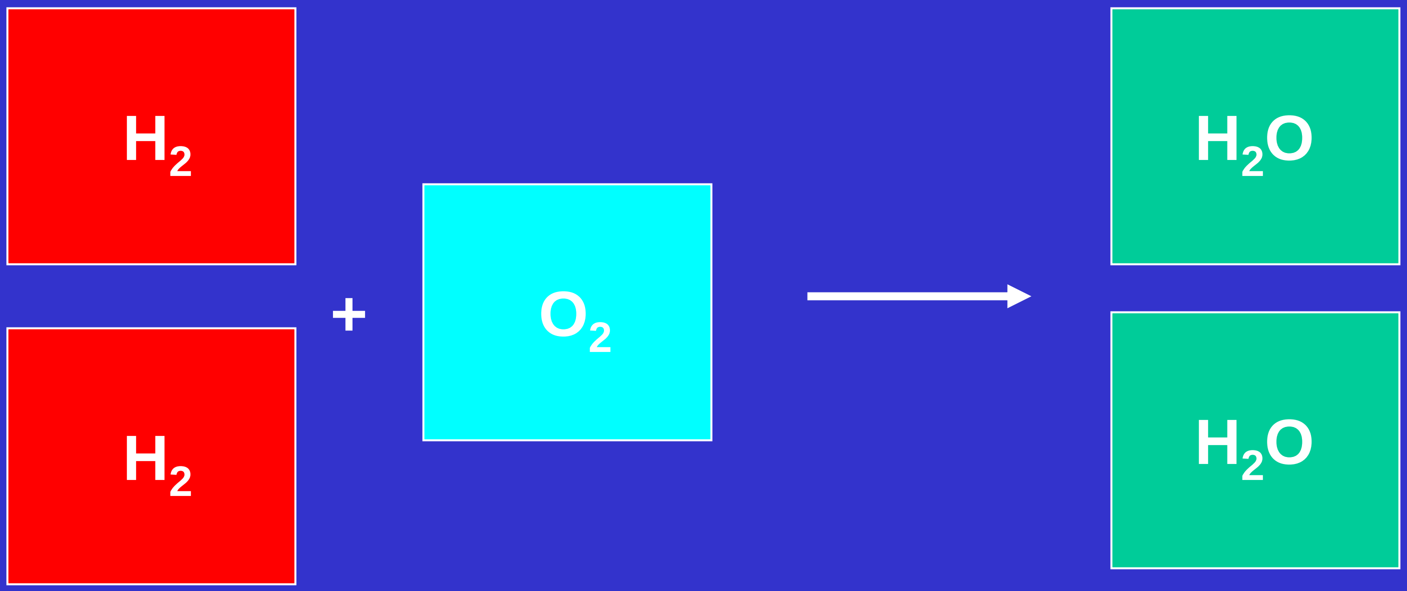
Not accepted till 1858, Cannizzaro
Water till that time was considered
as OH, M(O) = 8
after 1858 H_2O, M(O) = 16

Amadeo Avogadro
(1776 - 1856)

Law of Constant Volumes

At the same temperature and pressure, the same volumes of different gases contain the same number of particles.

Gases are diatomic molecules



Avogadro's Law

1811

The same volumes of different gases contain the same number of particles

(at const. p, T)

$V = n$ const.

Volume of 1 mole of gas = **22.4 liter**

$V/n =$ const.

at 0 °C and 101 325 Pa (STP)

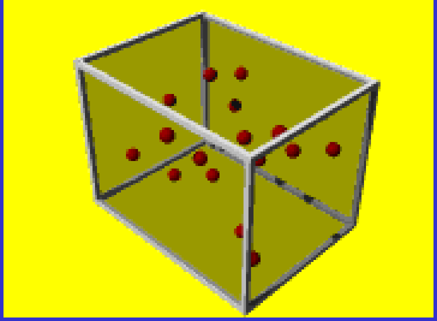
$V_M = 22.4\ \text{l mol}^{-1}$ **molar volume of ideal gas**

(at 0 °C and 100 000 Pa (1 bar) $V_M =$ **22.71** l mol^{-1})

Pressure depends on the number of molecules, temperature and volume

$p\,V = f\,(n, T)$

Ideal Gas



- Composed of small particles (atoms, molecules) that are in constant motion along **linear trajectories** in random directions with high velocities.

- Dimensions of particles are very small in comparison to their distances

- They do not exert attractive or repulsive forces.

- Collisions are **elastic**, no loss of energy.

- Kinetic energy of a particle depends on temperature (but not on pressure).

$E_{kin} = ½ m v^2$

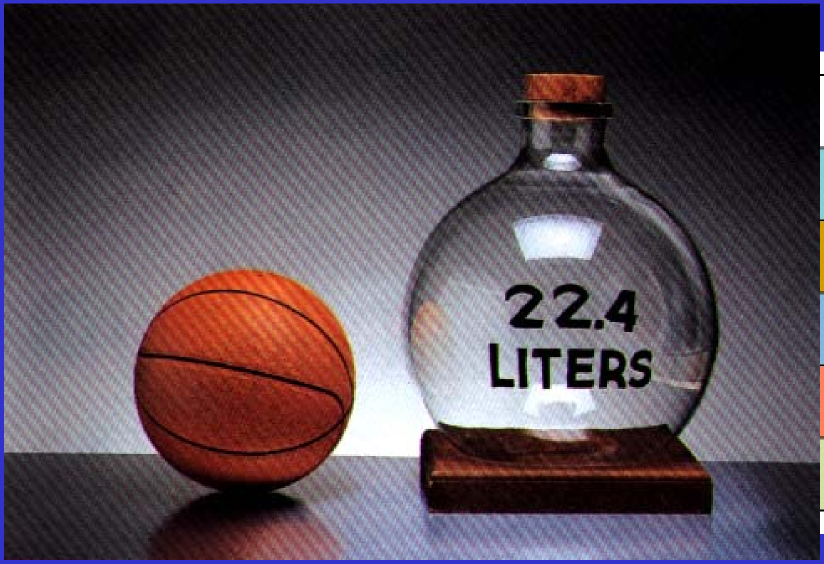
$$E_{kin} = \frac{1}{2} m \langle v^2 \rangle = \frac{3}{2} k_B T$$

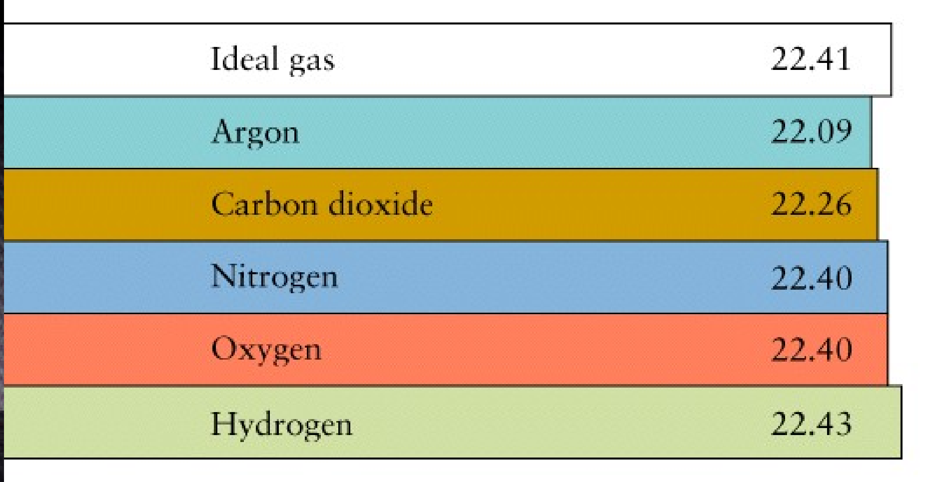
1 mole of a Real Gas

V = n const.

V/n = const.

$V_m = 22.41 \quad l\ mol^{-1}$





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

At standard temperature and pressure (STP)
p = 101.325 kPa = 1 atm = 760 torr
t = 0 °C

Ideal Gas Equation

Ideal gas

- Molecular volume is zero (very small in comparison to gas volume)
- No intermolecular forces

$$\boxed{p\,V = n\,R\,T}$$

n = amount of substance

$V = (n\,R\,T) / p$

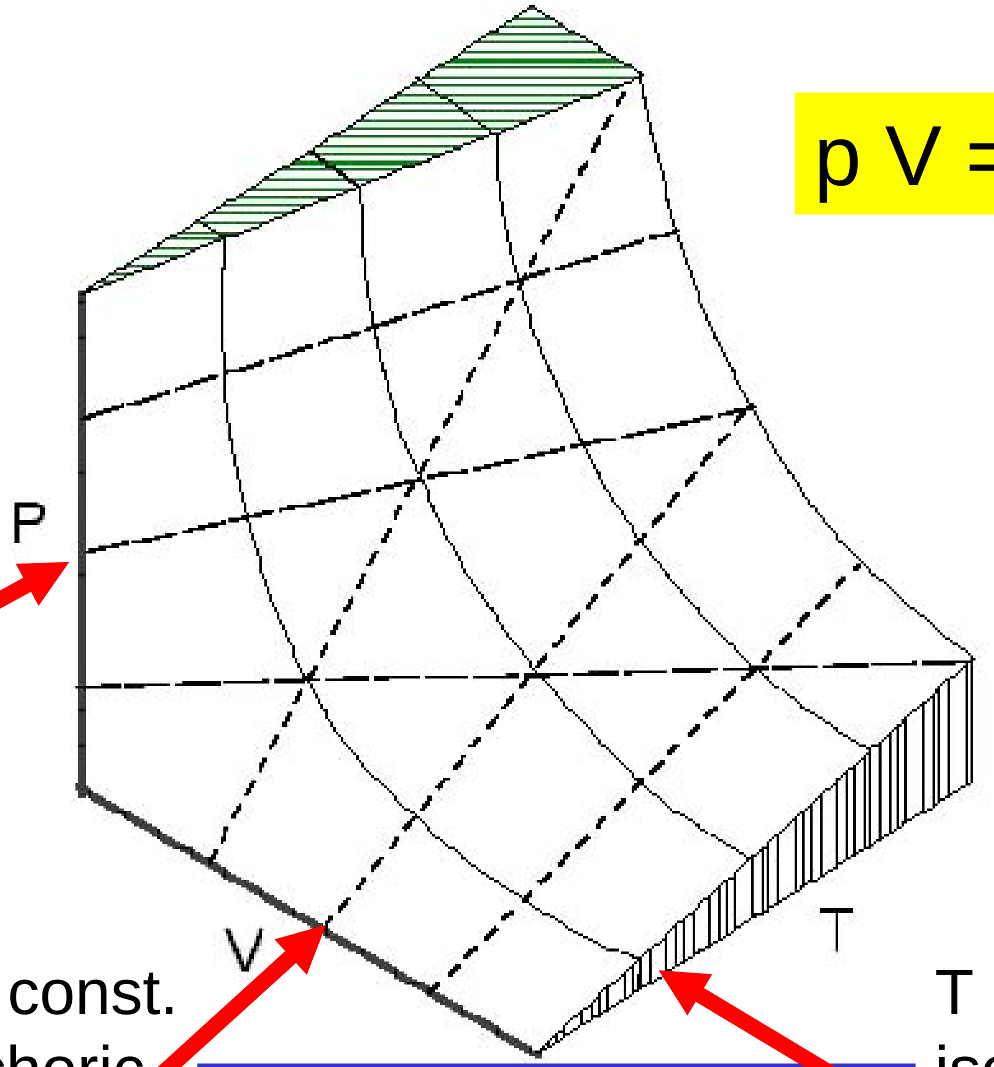
$p = (n\,R\,T) / V$

$n/V = p / RT$

R = gas constant

$R = 8.314\ \mathrm{J\ K^{-1}\ mol^{-1}}$

Ideal Gas Equation



$pV = nRT$

p = const.
isobaric

V = const.
isochoric

T = const.
isothermal

Calculation of Gas Density and M_r

$p V = n R T = (m/M) R T$

$r = m/V = p M / R T$ Gas Density

$M = r RT / p = r V_m$ Gas molar mass

$V_m = R T / p$

Partial Pressure, p_i

p_i = Pressure of a component of a mixture if it was alone in a given volume.

Molární zlomek

$x_i = n_i / \Sigma n_i$

$\Sigma x_i = 1$

$$\boxed{x_i = \frac{n_i}{\Sigma n_i}}$$

Pressure of gas trapped above a liquid

$p = p(\text{gas}) + \text{vapor pressure}$

Dalton’s Law of Partial Pressures

$p_{tot} = p_1 + p_2 + p_3 + ...+ p_n = \Sigma\ p_i$

$p(air) = p(O_2) + p(N_2) + p(Ar) + p(CO_2) + p(other)$

Partial Pressure

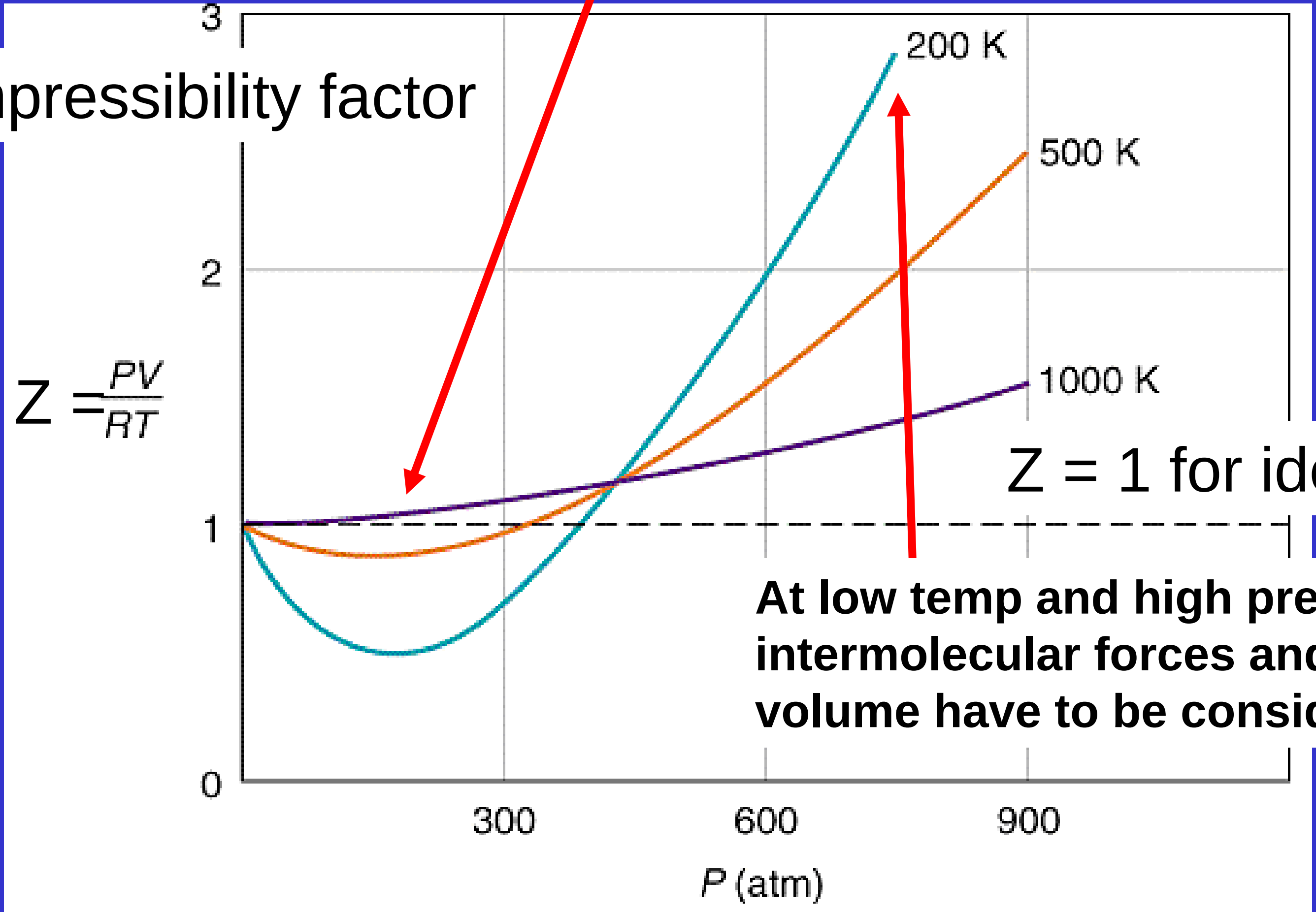
Pressure of a component of a mixture if it was alone in the given volume.

$P_{He} = x_{He}\ P_{tot}$ $P_{Ne} = x_{Ne}\ P_{tot}$

$P_{tot} = P_{He} + P_{Ne}$

Nonideal (Real) Gas

Nonideal gas behavior approaches ideal gas behavior at high temp and low pressure



Z = compressibility factor

$$Z = \frac{PV}{RT}$$

Z = 1 for ideal gas

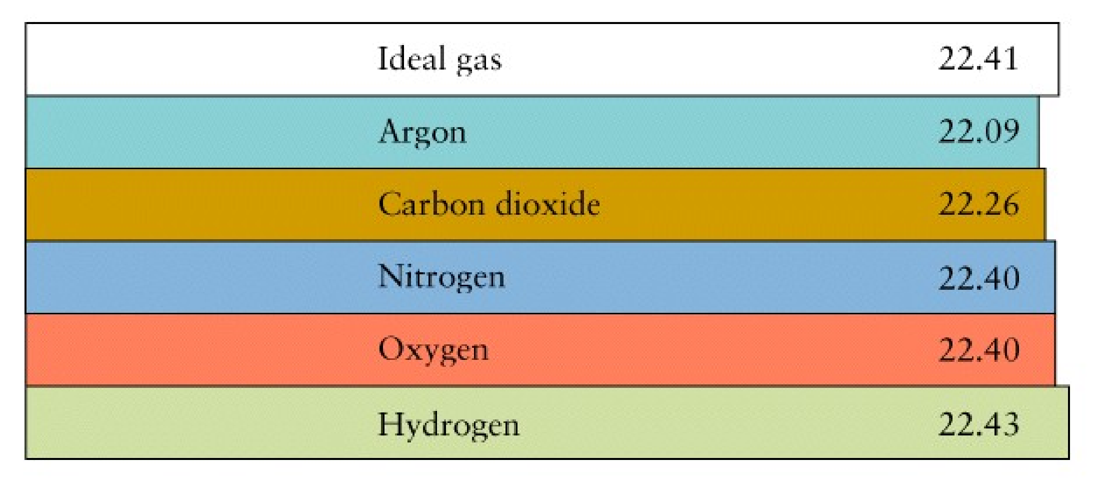
At low temp and high press, intermolecular forces and molecular volume have to be considered

Nonideal (Real) Gas

Z = compressibility factor

Z > 1   Molar volume of nonideal gas is bigger than ideal gas
Repulsive intermolecular interactions prevail

Z < 1   Molar volume of nonideal gas is smaller than ideal gas
Attractive intermolecular interactions prevail



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

Van der Waals State Equation of Real Gases

$$\left(p+\frac{a}{V_m^2}\right)\left(V_m-b\right)=RT$$

J. D. van der Waals
(1837-1923)
NP in Chemistry 1910

V_m = molar volume of gas

b = volume of molecules of gas
(must be substracted)

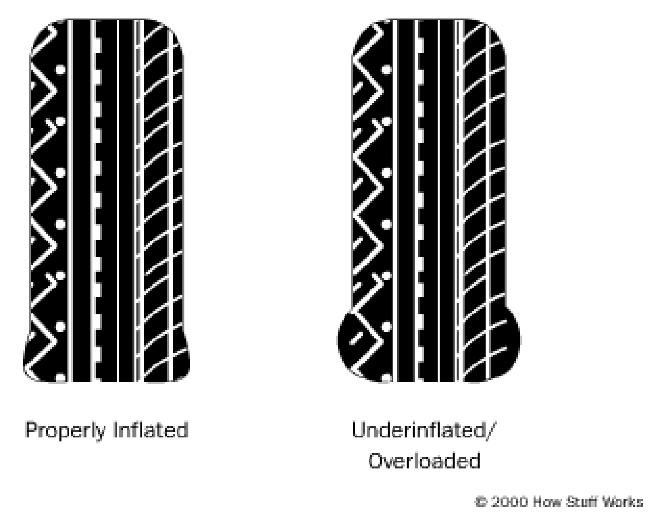
a = intermolecular attraction
(must be added to p)

Van der Waals State Equation of Real Gases

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

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

Gas	**a (l^2 bar mol^{-2})**	**b (l mol^{-1})**
Helium	0.034598	0.023733
Hydrogen	0.24646	0.026665
Nitrogen	1.3661	0.038577
Oxygen	1.3820	0.031860
Benzene	18.876	0.11974



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Liquification of Gases

Condensation requires vdW forces

Low T, high p, decrease of E_{kin}, close approach of molecules

Ideal gas cannot be liquified

Critical temperature = above critical temperature, gas cannot be liquified by any high pressure

Joule-Thompson Effect

Joule-Thompson effect = change of temperature during adiabatic expansion of compressed gas thru an orifice (pressure drops $dp < 0$)

$\mu = dT/dp$ Joule-Thompson coeficient

$\mu > 0$ cooling ($dT < 0$) breaking of vdW bonds, required energy is taken from E_{kin}, T drops.

Below J-T inversion temp. O_2, N_2, NH_3, CO_2, freons

N_2 (348 °C) O_2 (491 °C)

$\mu = 0$ ideal gas, real gas at J-T inversion temp.

Joule-Thompson Effect

Joule-Thompson effect = change of temperature during adiabatic expansion of compressed gas thru an orifice (pressure drops $dp < 0$)

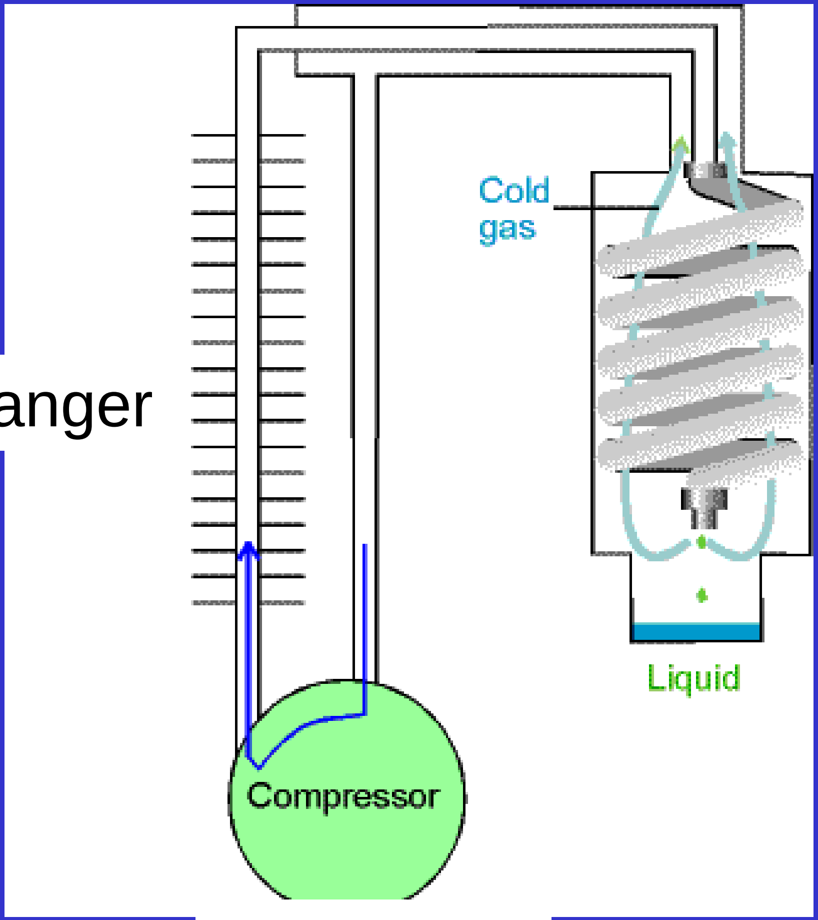
$\mu = dT/dp$ Joule-Thompson coeficient

$\mu < 0$ heating ($dT > 0$) Above J-T inversion temp. H_2, He, Ne.

He (-222 °C)

There are repulsive interactions in compressed gas that are removed upon expansion, energy is released = heating

Liquification of Gases



Heat exchanger

Jet

Compresor

Kinetic-Molecular Theory of Gases

1738

Daniel Bernoulli
(1700-1782)

Atoms and molecules are in perpetual motion, temperature is a measure of intensity of this motion

Statistical mechanics, Clausius, Maxwell, Boltzmann

Average velocity of molecules of H_2 at 0 °C

$\langle v \rangle = 1.84\ 10^3\ \mathrm{m\ s^{-1}} = 6624\ \mathrm{km\ h^{-1}}$

Kinetic-Molecular Theory of Gases

Average kinetic energy of gas molecules

$E_{kin} = {}^{1}/_{2}\ m \langle v^2 \rangle$

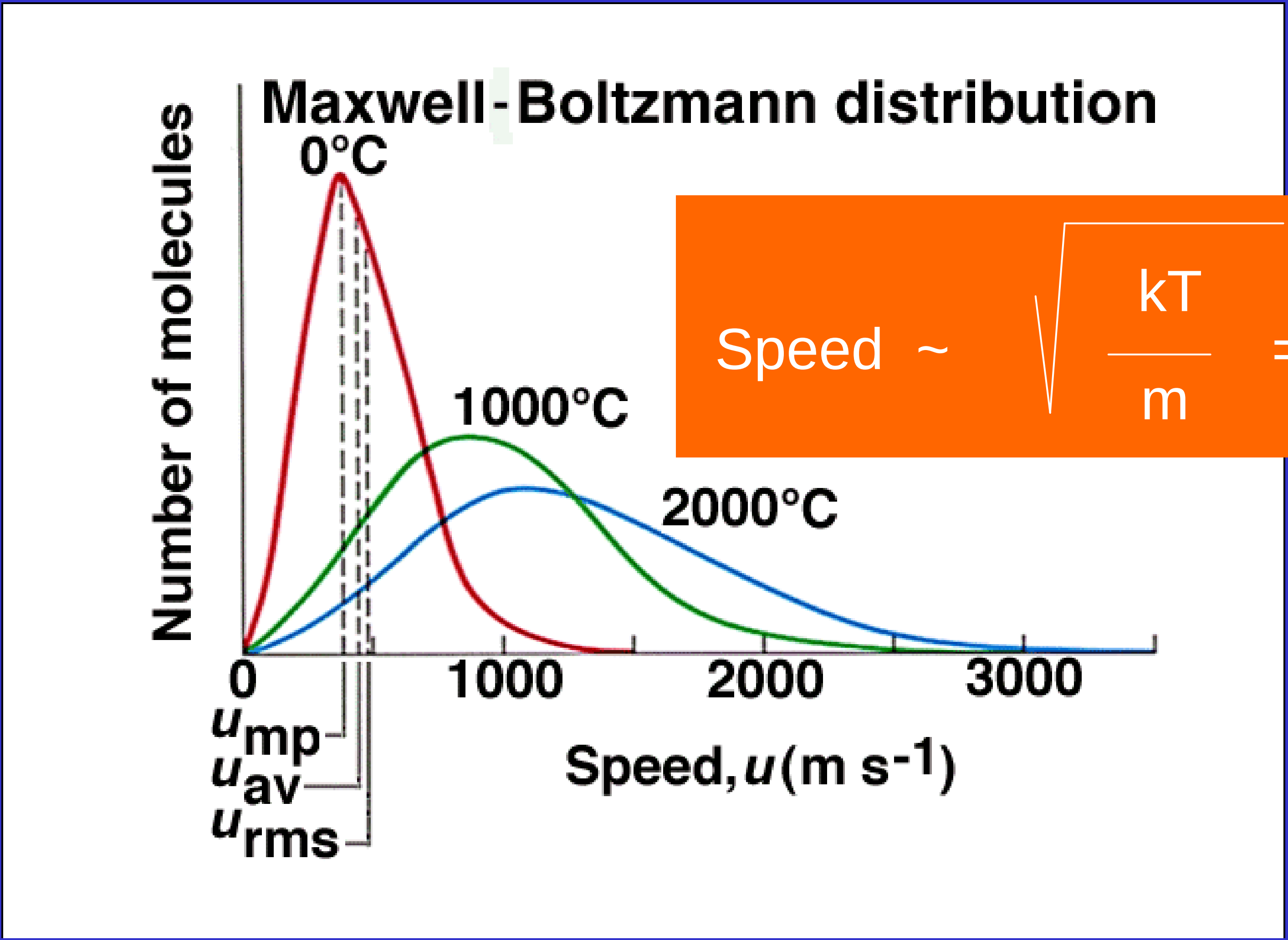
m = gas molecule mass

<v> = Root-mean-square speed

Average kinetic energy of all gases at a given temperature is the same

$$\boxed{E_{kin} = \frac{3}{2} k_B T}$$

Maxwell-Boltzmann Distribution



$$\text{Speed} \sim \sqrt{\frac{kT}{m}} = \sqrt{\frac{RT}{M}}$$

Maxwell-Boltzmann Distribution

$$dN = 4\pi N\,(m / 2\,\pi\,kT)^{3/2}\,\exp(-\tfrac{1}{2}\,mv^2 / kT)\,v^2\,dv$$

Most probable speed $v_{mp} = (2kT / m)^{½}$

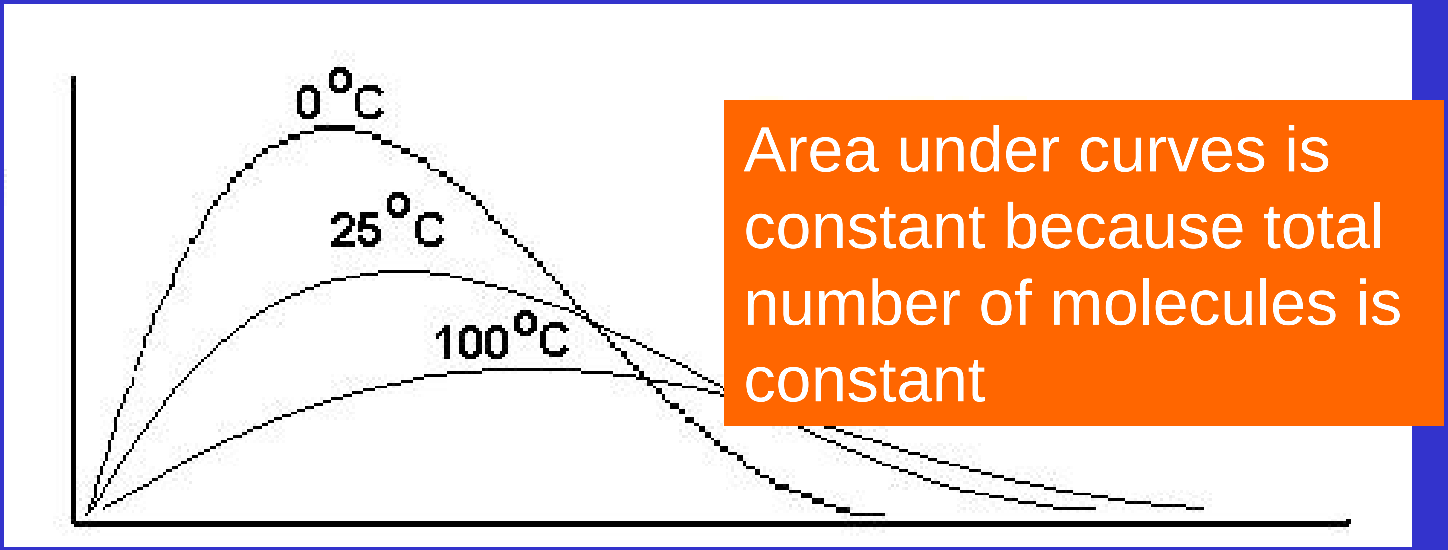
Average speed $v_{av} = (8kT / \pi\,m)^{½}$

Root-mean-square speed $v_{rms} = (3kT / m)^{½}$

$$\text{Speed} \sim \sqrt{\frac{kT}{m}} = \sqrt{\frac{RT}{M}}$$

Kinetic-Molecular Theory of Gases

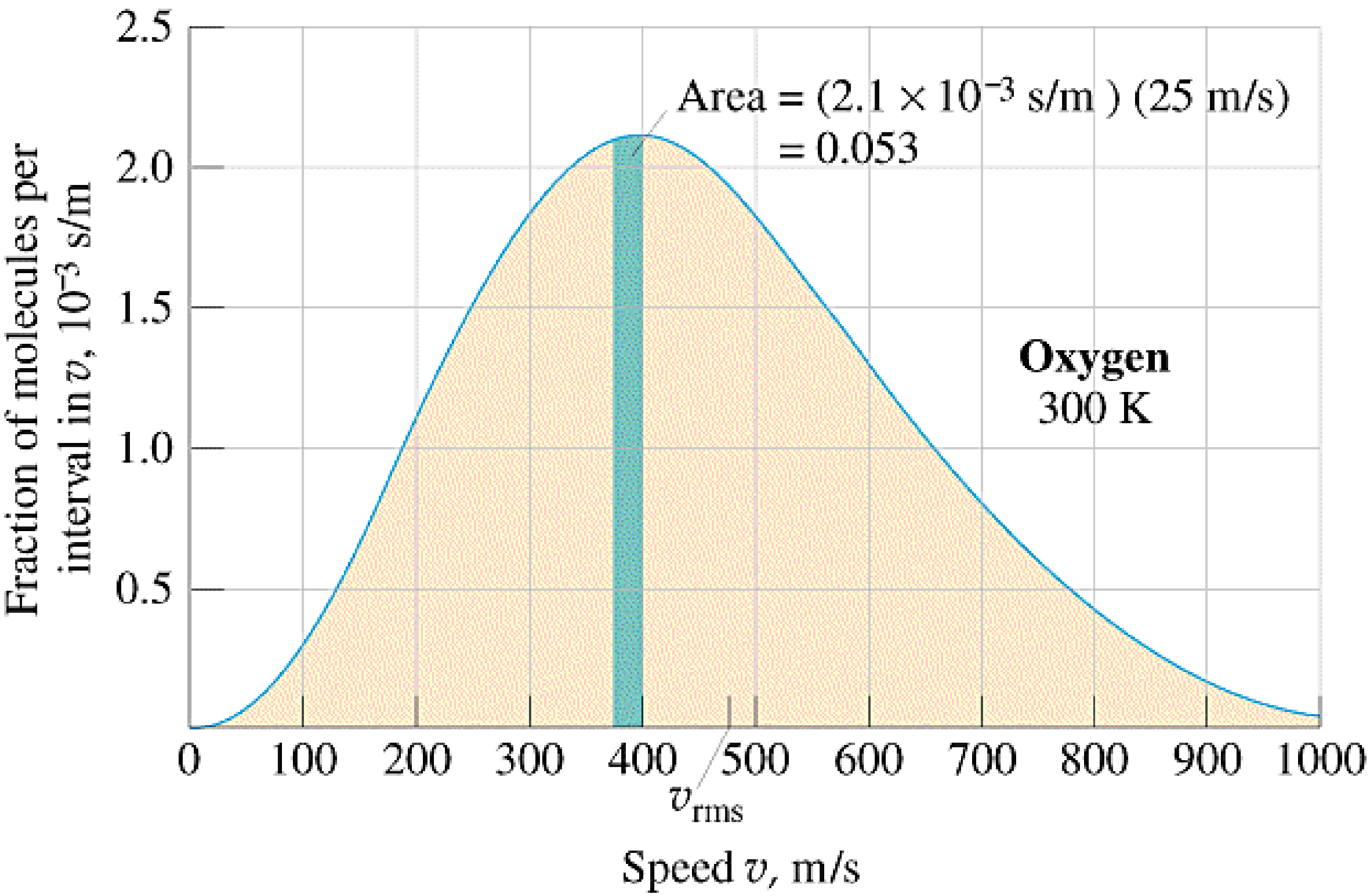
Number
of
molecules



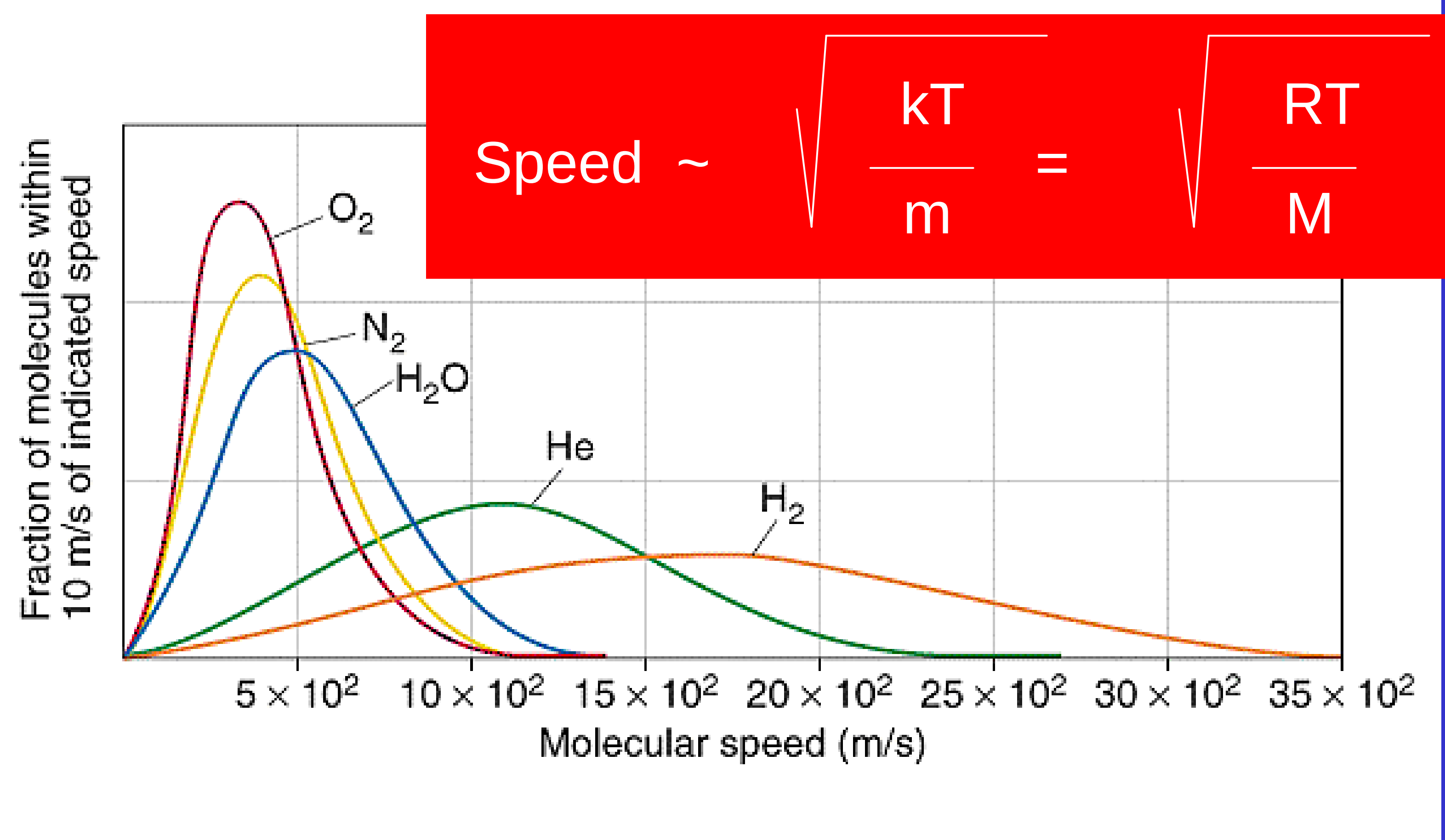
Area under curves is constant because total number of molecules is constant

Speed, m s^{-1}

No molecule has zero speed
Maximum speed → ∞
The higher the speed, the less molecules

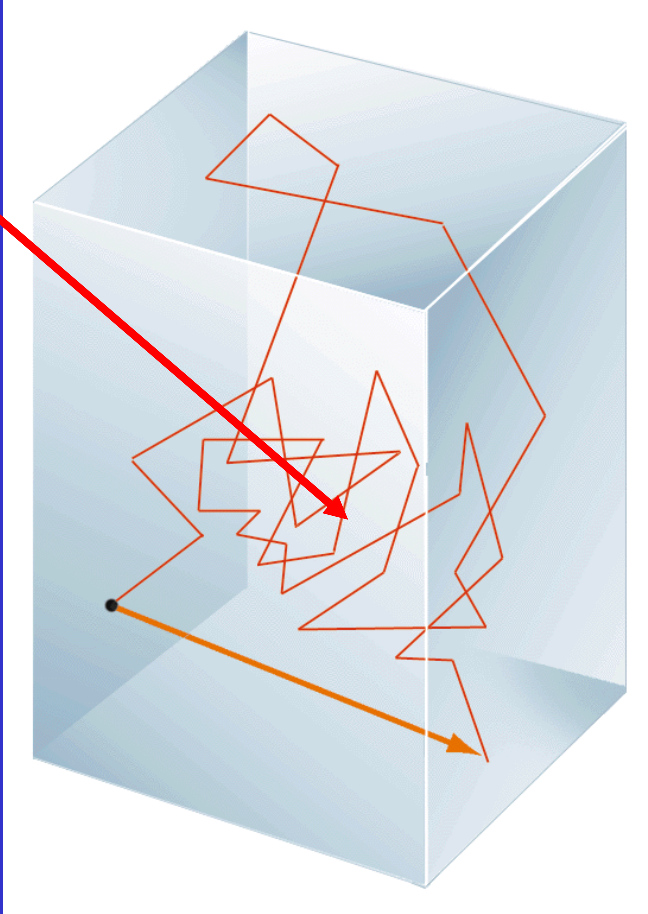

Area = (2.1 × 10^{-3} s/m) (25 m/s)
= 0.053
Oxygen
300 K
Fraction of molecules per interval in v, 10^{-3} s/m
2.5
2.0
1.5
1.0
0.5
0
100
200
300
400
500
600
700
800
900
1000
v_{rms}
Speed v, m/s

Maxwell-Boltzmann Distribution



$$\text{Speed} \sim \sqrt{\frac{kT}{m}} = \sqrt{\frac{RT}{M}}$$

Diffusion



Mean free path, *l*, average distance between collisions

Depends on p and T

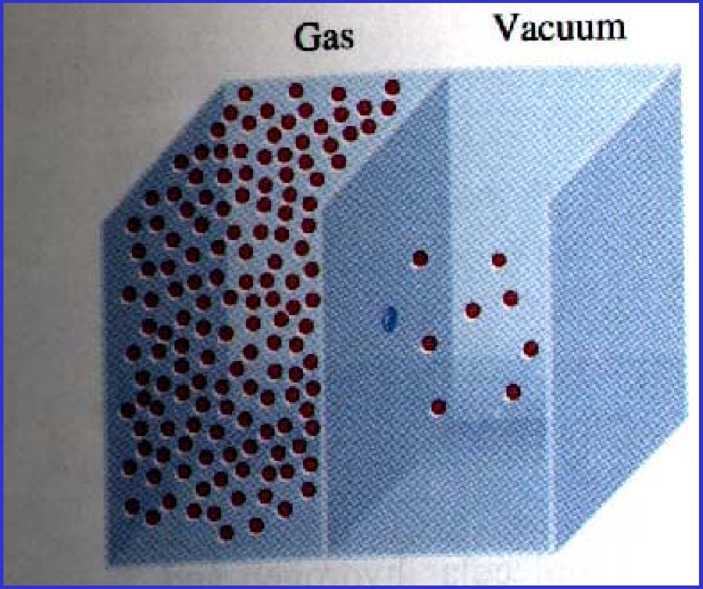
l = const T/ p = const /n $\pi\ (2r)^2$

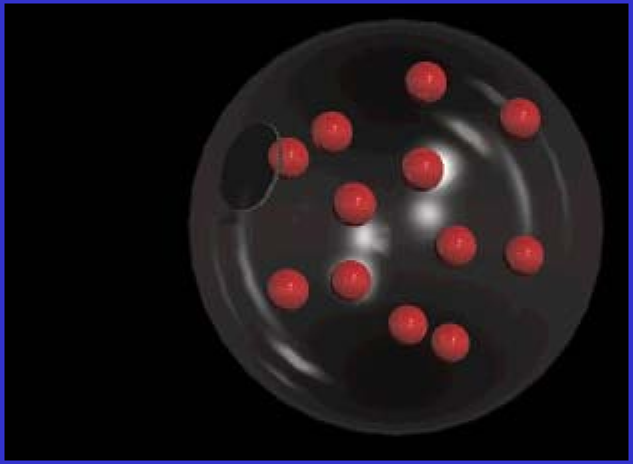
n = number of particles in m^3
r = molecular radius

l = 500 – 1000 Å
At normal p,T

Viscosity, thermal conductivity

Effusion





Graham's Law

$$v_1/v_2 = (\rho_2/\rho_1)^{½} = (M_2/M_1)^{½}$$