

Ideal gas  $\rightarrow$  a gas of non-interacting atoms or molecules (ideal = simple to describe)

Thermodynamic description uses state variables

temperature	$T$ (in K)	The amount of gas
Pressure	$P$	(# of moles $n$ )
Volume	$V$	often assumed constant

These variables uniquely describe the state of the gas

Universal gas law  $PV = nRT$   
derived phenomenologically, from observations  
(Robert Boyle)

Boyle's law (1627-1691)  $V \propto 1/p$  @ constant  $T$   
(Jacques Charles)

Charles' law (1746-1823)  $V \propto T$  @ constant  $P$   
(Joseph Gay-Lussac)

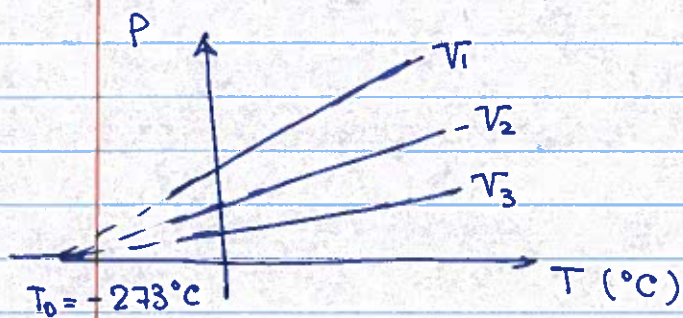
Gay-Lussac's law (1778-1850)  $P \propto T$  @ constant  $V$

$R = 8.314 \text{ J/mol}\cdot\text{K}$  - universal gas constant  
(needed to properly connect SI units)

$PV = nRT$  is valid only for  $T$  in Kelvin scale!

$$P = \frac{nR}{V} \cdot T$$

and can be used to measure absolute zero

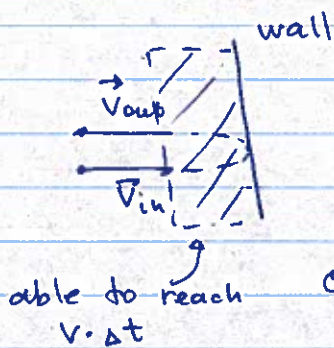


$P \propto T$  for a constant volume

# Microscopic picture - the kinetic theory of gases

Ideal gas: no internal structure  
 large number of molecules  $N$   
 random motion  
 all molecules are identical  
 elastic collision with walls and each other  
 molecule separation  $\gg$  their size

First step  $\rightarrow$  crude model: all molecules move with same velocity  $v$  in ~~random~~ <sup>one</sup> directions



elastic collision  $v_{in} = v_{out}$   
 Transferred momentum  $\Delta p_{\perp} = 2mv$   
 To calculate a force on the wall, we need to know how many collisions happen during time  $\Delta t$

Particle density  $\frac{N}{V}$ , and molecules within  $v \cdot \Delta t$  near the wall can hit it,  $\frac{1}{2}$  moves away  
 transferred momentum =  $\Delta p_{\perp} \cdot \frac{N}{V} \cdot v \cdot \Delta t \cdot A \cdot \frac{1}{2}$  (area)  
 $= 2mv \cdot \frac{N}{V} \cdot v \Delta t \cdot A \cdot \frac{1}{2} = mv^2 \cdot \frac{N}{V} \cdot \Delta t \cdot A$

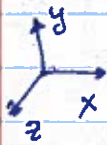
$$\text{Pressure } P = \frac{F}{A} = \frac{\text{transferred momentum}}{A \Delta t} = \frac{N}{V} \cdot mv^2$$

$$PV = N \cdot mv^2 \quad \text{related to temperature}$$

More realistic 3D model  $v^2 \rightarrow v_x^2$

also, all velocities are different

$v_x^2 \rightarrow \langle v_x^2 \rangle$  average  $v_x$



$$PV = N m \langle v_x^2 \rangle$$

Random motion  $\rightarrow$  any dimension is equally possible

$$\langle v_x^2 \rangle = \langle v_y^2 \rangle = \langle v_z^2 \rangle = \frac{1}{3} \langle v^2 \rangle$$

$$PV = N \frac{1}{3} m \langle v^2 \rangle = \frac{2}{3} N \underbrace{\left\langle \frac{mv^2}{2} \right\rangle}_{\text{average kinetic energy}} = \frac{2}{3} N \cdot k_B \cdot T$$

$k_B$  - Boltzmann's constant  $k_B = 1.38 \cdot 10^{-23}$  J/K

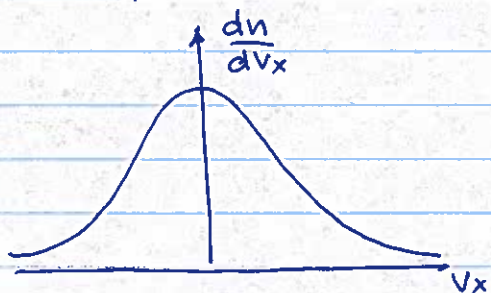
$R = k_B \cdot N_A$   $N_A = 6.022 \cdot 10^{23}$  # of atoms/molecule  
in one mole of  
a substance

Average kinetic energy depends only on its temperature

Do we know anything about velocity distribution for a given temperature?

Boltzmann law  
 a fraction of atoms with a given energy  $E$   
 $\propto e^{-E/k_B T}$

One component  $v_x \rightarrow \propto e^{-mv_x^2/2k_B T}$   
 $v_x = 0$  is most probable  $dn(v_x) \propto N e^{-mv_x^2/2k_B T} dv_x$



symmetric distribution around  $v_x = 0$

3D:  $dn(\vec{v}) = dn(v_x) dn(v_y) dn(v_z) \propto$

$$= N e^{-mv_x^2/2k_B T} e^{-mv_y^2/2k_B T} e^{-mv_z^2/2k_B T}$$

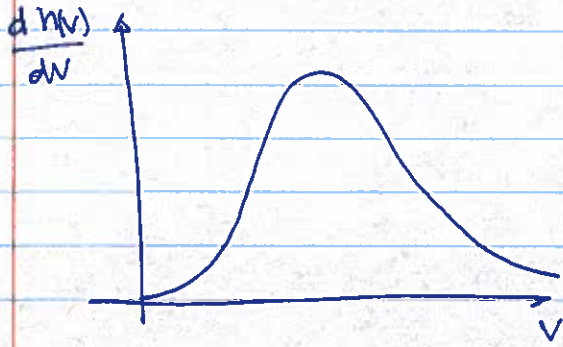
$$= N e^{-mv^2/2k_B T} v^2 dv \underbrace{d\Omega}_{\text{solid angle}}$$

$dv_x dv_y dv_z =$   
 can write in spherical coordinates

If we are not interested in the direction of motion, only velocity magnitude, we can average over all directions  $d\Omega \rightarrow 4\pi$

$$dn(v) = 4\pi N \underbrace{\left(\frac{m}{2\pi k_B T}\right)^{3/2}}_{\text{normalization constant}} v^2 e^{-mv^2/2k_B T} dv$$

so that  $\int_{v=0}^{\infty} dn(v) = N$



$$\frac{dn(v)}{dv} = 4\pi N \left( \frac{m}{2\pi k_B T} \right)^{3/2} v^2 e^{-mv^2/2k_B T}$$

small  $v$ :  $\frac{dn(v)}{dv} \sim v^2$

large  $v$ :  $\frac{dn(v)}{dv} \sim v^2 e^{-v^2/(2k_B T/m)}$

Most probable velocity (max  $\frac{dn}{dv}$ )

$$v_{mp} = \sqrt{\frac{2k_B T}{m}} = 1.41 \sqrt{\frac{k_B T}{m}}$$

Average velocity  $v_{ave} = \langle v \rangle = \int_0^{\infty} v \cdot dn(v) = \sqrt{\frac{8k_B T}{\pi m}} = 1.6 \sqrt{\frac{k_B T}{m}}$

Root mean square velocity

$$v_{RMS} = \sqrt{\langle v^2 \rangle} = \int_0^{\infty} v^2 dn(v) = \sqrt{\frac{3k_B T}{m}} = 1.73 \sqrt{\frac{k_B T}{m}}$$