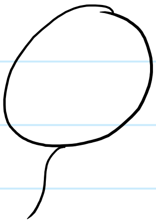
Thermal Properties of Matter I

Terminology: $1 \text{ mole} = N_A = 6.022 \times 10^{23}$

$\boxed{\underline{\text{def}} \quad 1 \text{ mole of carbon-12} = 0.012 \text{ kg carbon-12}}$

molar mass = mass in 1 mole

<u>Equation of state</u> (EOS)



thermodynamic quantities : P, V, T, n
(macroscopic)

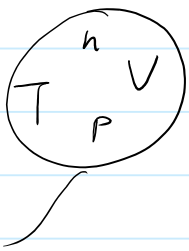
define the state of matter

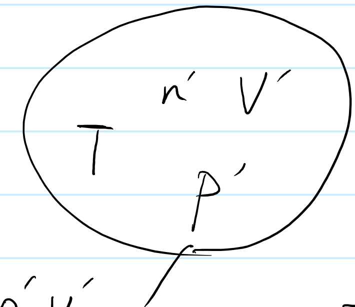
EOS = relation among thermodynamic quantities.

In general, $f(P, V, T, \ldots) = 0$

for <u>ideal gas</u> (inert gas, point-like molecules)

ideal gas #1





ideal gas #2

same T

if $\frac{pV}{n} = \frac{p'V'}{n'} \Rightarrow T$ is a function of $\left(\frac{pV}{n}\right)$

simple choice $T \propto \frac{pV}{n}$

$\Rightarrow \boxed{pV = nRT}$ where $\underline{R} = 8.314 \ \mathrm{J\,mol^{-1}\,K^{-1}}$

<u>universal gas constant</u>

number of molecules $= N = nN_A$

Ideal gas law becomes

$$pV = \frac{N}{N_A} RT \equiv N k_B T$$

k_B = Boltzmann constant $= 1.381 \times 10^{-23}$ J/K.
(or k)

Ideal gas law is valid for all ideal gas disregard the species of gas; i.e., H_2, N_2, O_2, CO, CO_2, Ne, ...
$pV = nRT = Nk_BT$ works for all.

For fixed amount of gas

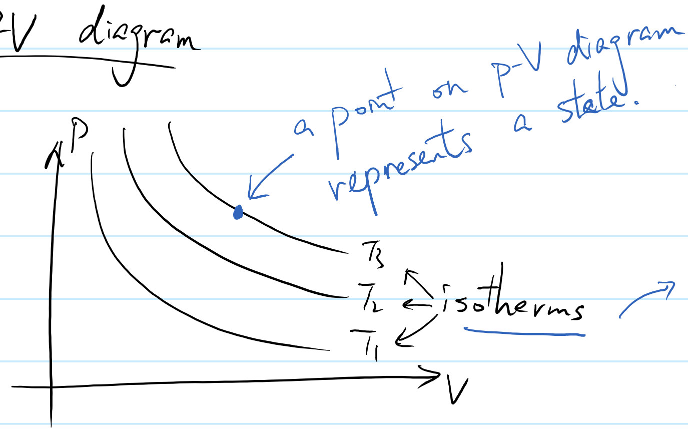
$$\frac{pV}{T} = nR = \text{constant} \Rightarrow \frac{p_1V_1}{T_1} = \frac{p_2V_2}{T_2} \text{ for any states } 1, 2$$

Standard temp. and pressure. (STP)

$$T = 0°C = 273.15 \text{ K}$$
$$p = 1 \text{ atm} = 1.013 \times 10^5 \text{ Pa}$$

for 1 mole ideal gas, $V = \frac{RT}{p} = 0.0224 \text{ m}^3 = 22.4$ Litre.

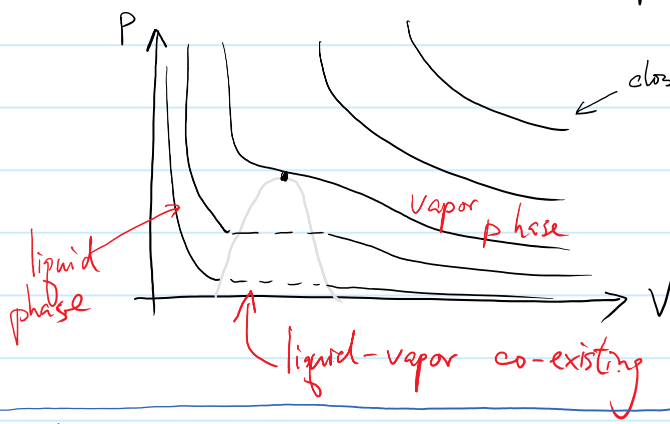
<u>P-V diagram</u>



states with the same temperature

$$pV = nRT \Rightarrow p = \frac{nRT}{V} \propto \frac{1}{V}$$

Real Gas : more than one phase (liquid, gas)



low density ⇒ intermolecular force is weak.

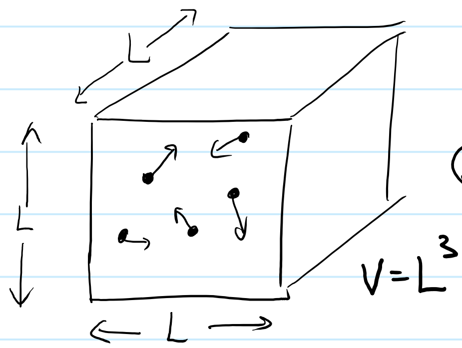
Kinetic Theory of ideal gas

model assumption : ① Ideal gas , non-interacting.

② collisions between the gas molecules are elastic

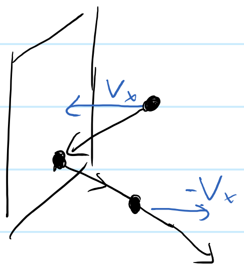
⇒ Total energy is conserved

③ molecules are moving at different velocities.



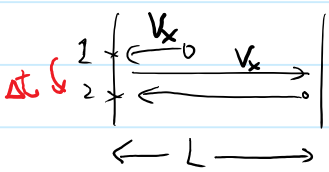
$V = L^3$

Collisions on the boundary cause the pressure of the gas.



Consider the wall perpendicular to x-axis.

F_x = Average force exerted on the wall in duration T by one ball.



$= \dfrac{\text{momentum changes on the ball bouncing off}}{T}$

$= \dfrac{\text{no. of collisions } (n) \times \text{momentum change of one ball } (\Delta P_x)}{T}$

$n = \dfrac{T}{\text{time between 2 collisions}} = \dfrac{T}{2L/V_x}$

$\Delta P_x = mV_x - (-mV_x) = 2mV_x$

$$F_x = \frac{T}{2L/V_x}\,\frac{2mV_x}{T} = \frac{mV_x^2}{L}$$

Pressure on the wall $p = \frac{\sum F_x}{A} = \frac{1}{L^2} \sum \frac{m V_{ix}^2}{L} = \frac{1}{L^3} \sum m V_{ix}^2$

$$p = \frac{1}{V} \sum m V_{ix}^2$$

$$pV = \sum_i m V_{ix}^2$$

Similarly, $pV = \sum m V_{iy}^2$, $pV = \sum m V_{iz}^2$

$\Rightarrow$ Total translational kinetic energy of the gas.

$$K_{tran}^{tot} = \sum \frac{1}{2} m |\vec{V}_i|^2 = \frac{1}{2} \sum_i \left(m V_{ix}^2 + m V_{iy}^2 + m V_{iz}^2 \right)$$

$$= \frac{1}{2} \cdot 3 \cdot pV$$

$$= \frac{3}{2} pV$$

for ideal gas, $pV = N k_B T = nRT$.

$$\boxed{K_{tran.}^{tot} = \frac{3}{2} N k_B T = \frac{3}{2} nRT.}$$

depends only on T.

Average K per molecule.

$$K_{avg} = \frac{K_{tr}^{tot}}{N} = \frac{3}{2} k_B T$$

Speed associated with average kinetic energy.

Let $K_{avg} = \frac{1}{2} m V_{rms}^2$

V_{rms} = Root-mean-square speed.

$$V_{rms}^2 = \frac{2}{m}\frac{\sum K_i}{N} = \frac{\cancel{2}}{\cancel{m}}\frac{\cancel{\frac{1}{2}}\cancel{m}\sum v_i^2}{N}$$

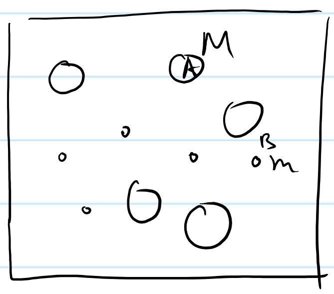
$$= \frac{1}{N}\sum v_i^2 = (v^2)_{avg}$$

$$\Rightarrow \quad V_{rms} = \sqrt{\frac{1}{N}\sum_i v_i^2} = \sqrt{(v^2)_{avg}}$$

$$V_{avg} = \frac{1}{N}\sum_i V_i \neq V_{rms}$$

relating to temperature $\quad \frac{1}{2} m V_{rms}^2 = K_{avg} = \frac{3}{2} k_B T$

$$\Rightarrow \quad V_{rms} = \sqrt{\frac{3 k_B T}{m}}$$



suppose a mixture of two gases is in thermal equilibrium.

Which molecule has a higher kinetic energy?

ANS: same $\because K \propto T$

Which molecule has a higher speed on average?

ANS: lighter molecule.