Welcome to

Aakash + BYJU'S LIVE

States of matter

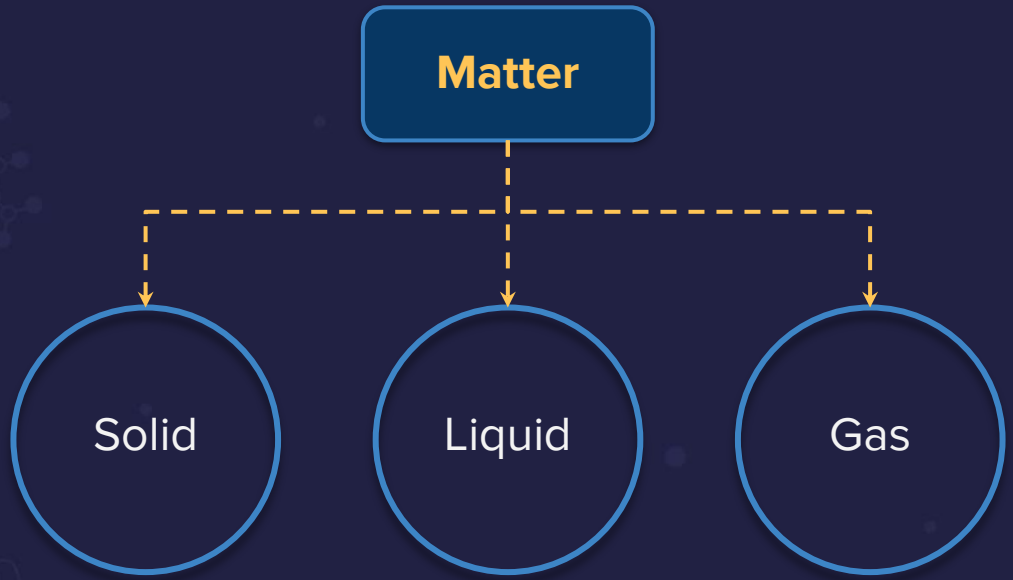
States of Matter

Bulk Properties

Most of the **observable characteristics** of chemical systems represent **bulk properties** of matter

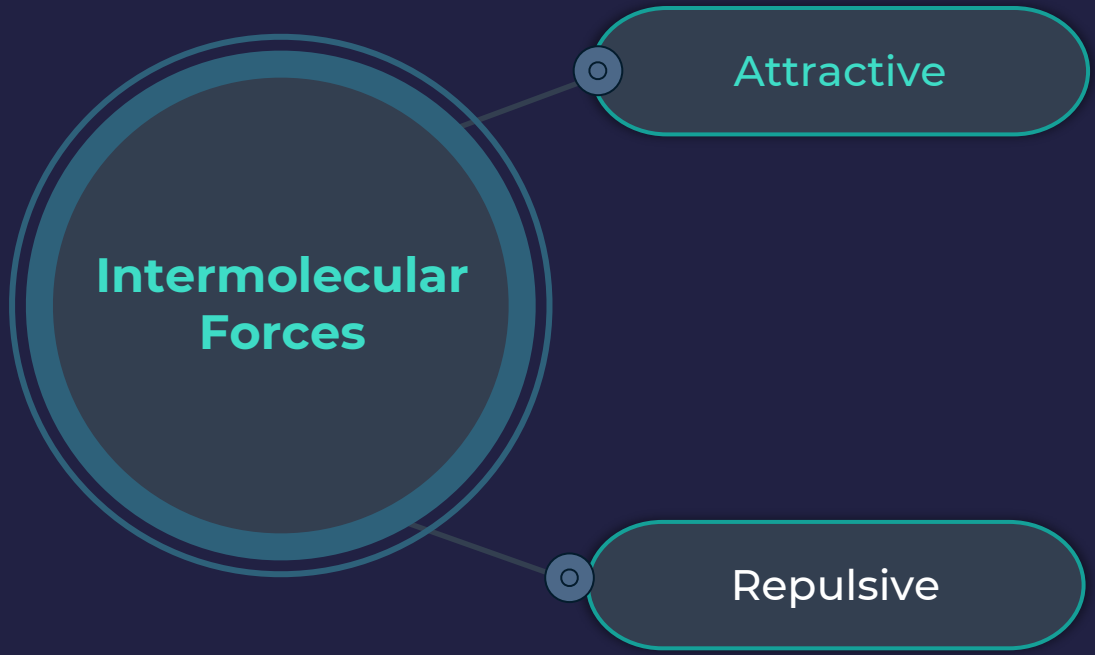
Properties associated with a **collection of a large number of atoms, ions or molecules**

Classification of Matter

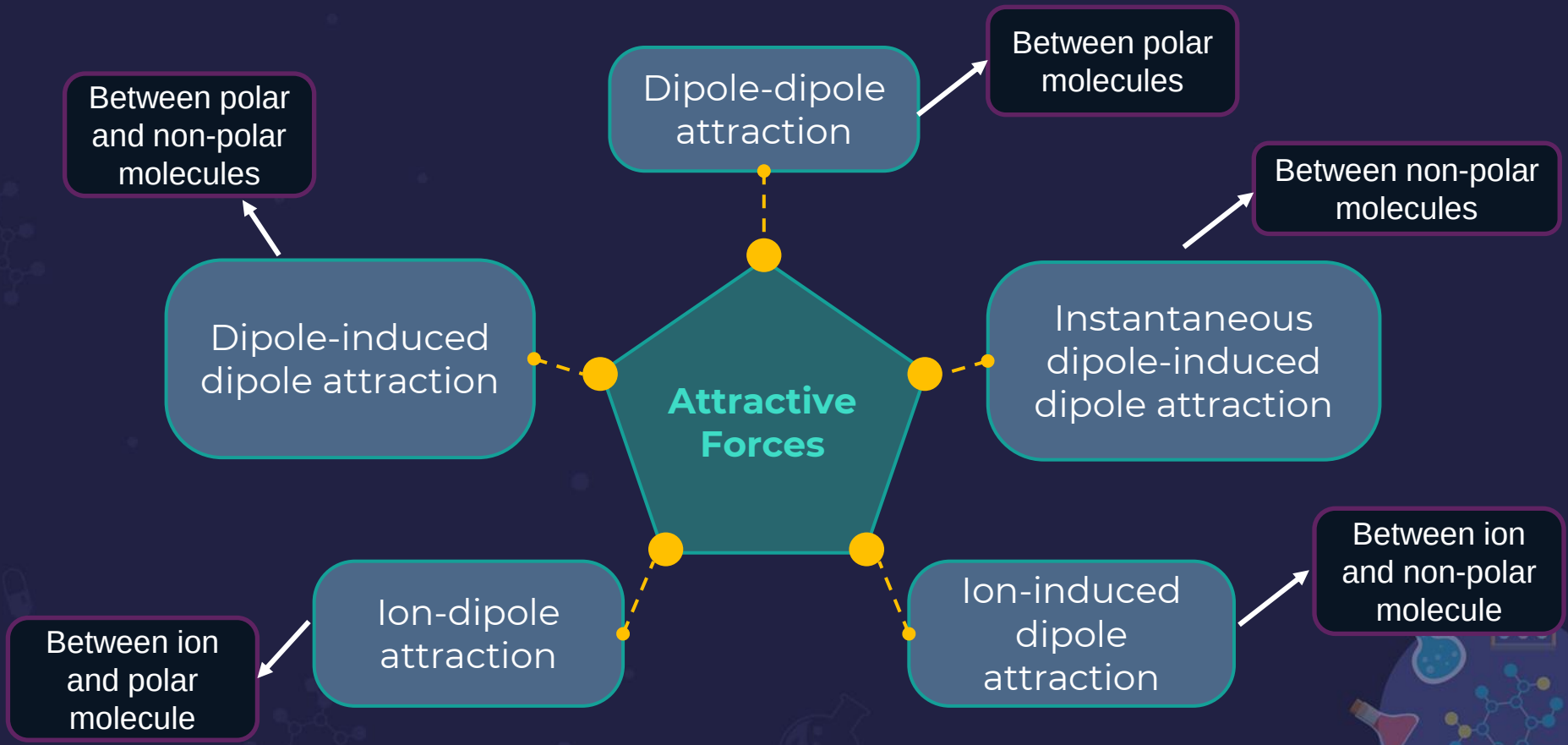


States of Matter depends upon **Intermolecular forces** & **thermal energy**

Intermolecular Forces



Intermolecular Attractive Forces



Thermal Energy

Energy of a body arising from **motion of its atoms or molecules**

It is the measure of **average K.E.** of the particles of the matter

Thermal Energy $\propto$ Temperature (T) of substance

Intermolecular Forces vs Thermal Energy

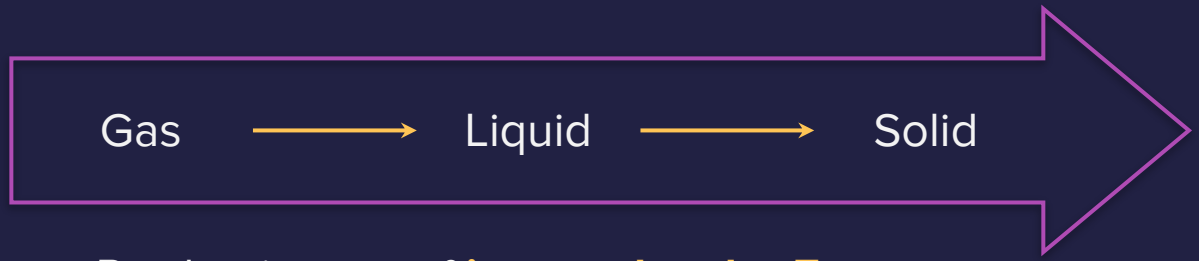
Intermolecular forces tend to keep the **molecules together** but

Thermal energy tends to **keep them apart**

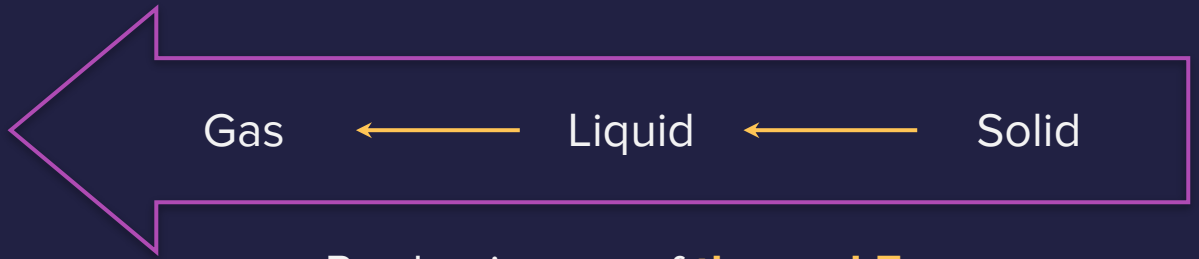
The result of balance between these two forces

Three states of matter

Intermolecular Forces vs Thermal Energy



Predominance of **intermolecular Forces**



Predominance of **thermal Energy**

General Properties of Gaseous State

01 No fixed **shape & volume**

02 Much **lower density** than the solids & liquids

03 Weak forces of **attraction**

04 Exerts **pressure** equally in all directions

05 Infinite **expansibility** & high **compressibility**

06 Forms **homogeneous mixtures**

Pressure

Pressure of the gas is the force exerted by the gas per unit area on the walls of the container in all directions.

Pressure (P)

1 atm	=	1.01325×10^5 Pa
1 bar	=	10^5 Pa = 750 torr = 750 mm of Hg
1 atm	=	760 torr = 760 mm of Hg = 76 cm of Hg
1 atm	=	1.01325 bar
1 N/m^2	=	1 Pa = 10 dyne/cm^2

Volume & Temperature

Volume (V)

The **volume** of the container is the volume of the gas sample as gases occupy the entire space available to them.

$1\ m^3$	=	$10^3\ L$
$1\ L$	=	$10^3\ cm^3$ or c.c. or mL
$1\ m^3$	=	$10^6\ cm^3$

Temperature (T)

Temperature is the measure of hotness of the system.

T (K)	=	t (°C) + 273.15

Standard Temperature & Pressure (STP)

T	=	273.15 K
P	=	1 bar

STP

Molar Volume of an ideal gas = **22.71098 L mol^{-1}**

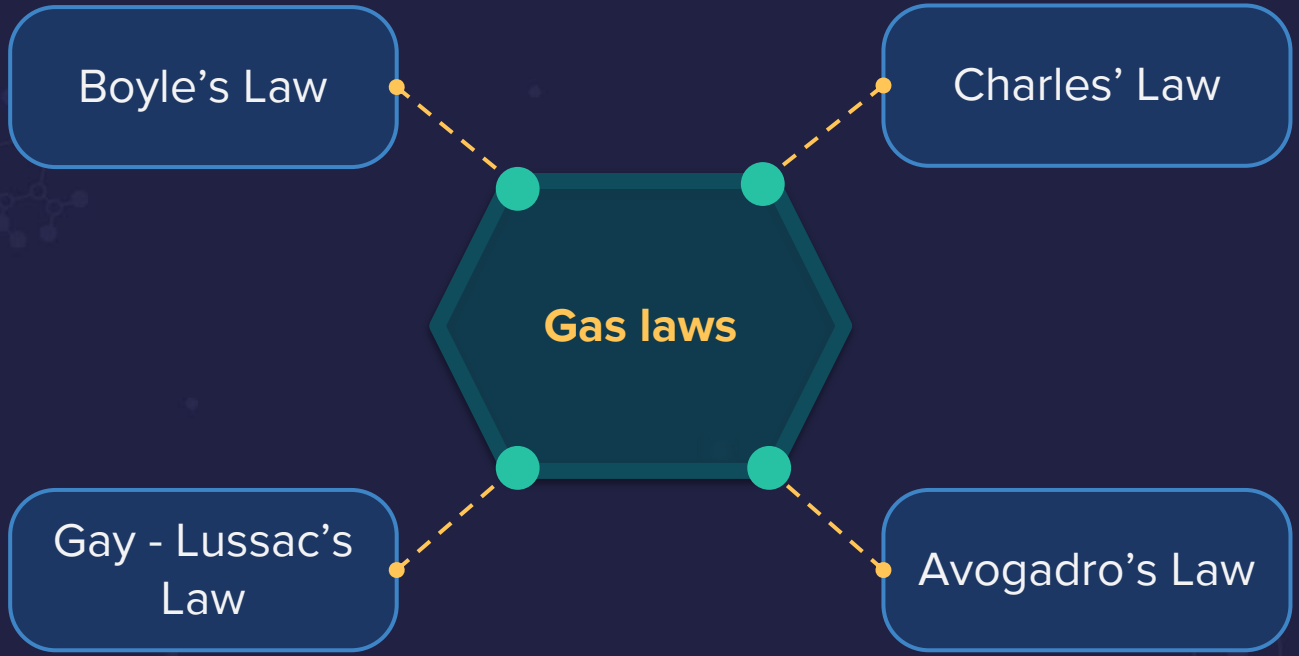
Gas Laws

Behaviour of gases is governed by some laws

Relationships between measurable properties **pressure, volume, temperature & amount** of gases

Interdependent properties, **describes the state of the gas**

Gas Laws


Boyle's Law
Charles' Law
Gas laws
Gay - Lussac's Law
Avogadro's Law

Boyle's Law

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

- T = Constant
- Amount of gas = Constant

At **constant temperature**

The **volume** of a fixed amount (number of moles 'n') of gas **varies inversely with its pressure**

Boyle's Law

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

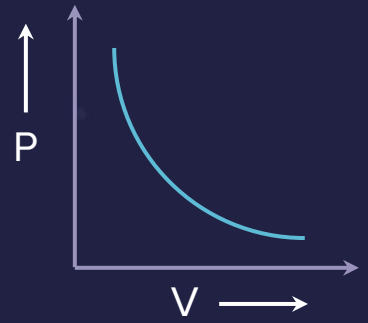
(n, T constant)

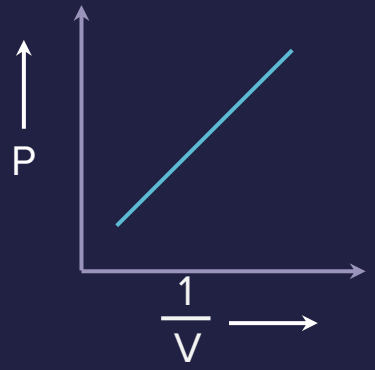
$$P = k_1 \frac{1}{V} \longrightarrow PV = k_1$$

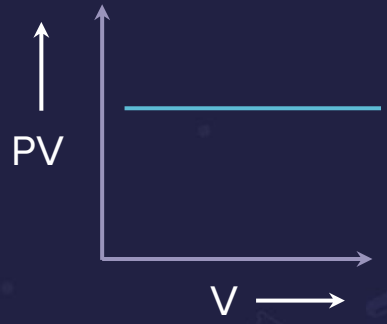
$$P_1V_1 = P_2V_2 \quad \text{or} \quad \frac{P_1}{P_2} = \frac{V_2}{V_1}$$

k_1 depends on **amount** & **temperature (T)** of gas

Boyle's Law

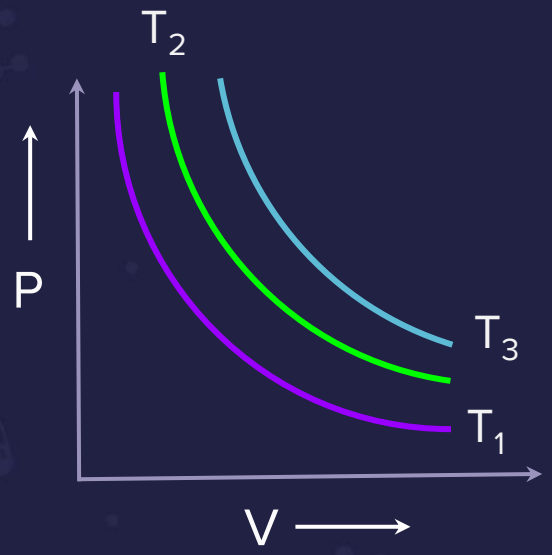


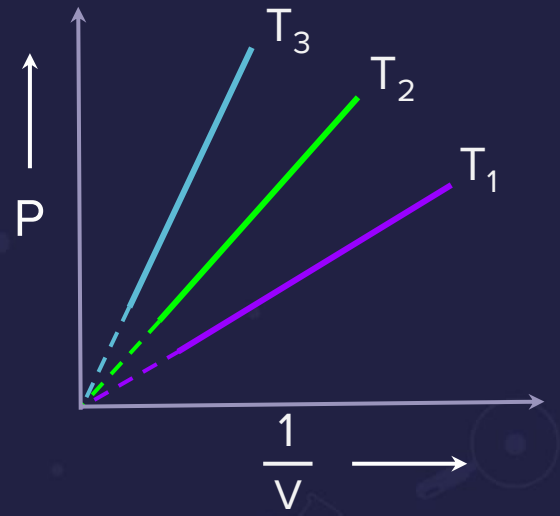




Boyle's Law at Different Temperatures

P-V Isotherms - - - → **Constant temperature** curves





$T_3 > T_2 > T_1$

Charles' Law

$$V \propto T$$

- P = Constant
- Amount of gas = constant

At **constant pressure**

The **volume** of a fixed amount of gas is directly proportional to its **absolute temperature.**

Charles' Law

$V \propto T$ (P, n constant)

$V = k_2 T$

k_2 depends on the **amount** & **P** of the gas

$\frac{V}{T} = k_2$

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

Charles' Law

For **each degree** rise in **temperature**, the **volume** of a gas **increases** by **1 /273.15** of the original volume of the gas at 0 °C.

$$V_t = V_o + \frac{t}{273.15} V_o$$

$$V_t = V_o \left[1 + \frac{t}{273.15}\right]$$

$$V_t = V_o \left[\frac{t + 273.15}{273.15}\right]$$

V_o Initial volume (at 0 °C)

V_t Final volume (at t °C)

Charles' Law

$$V_t = V_o + \frac{t}{273.15} V_o$$

$$V_t = V_o \left[1 + \frac{t}{273.15}\right]$$

$$V_t = V_o \left[\frac{t + 273.15}{273.15}\right]$$

V_o Initial volume (at 0 °C)

V_t Final volume (at t °C)

Absolute Scale of Temperature

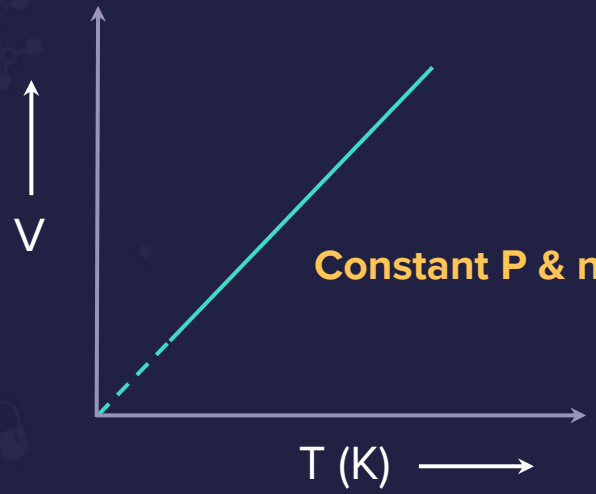
$$V_t = V_o\left(\frac{T_t}{T_o}\right)$$

T	Absolute scale or Kelvin scale or thermodynamic scale of temperature

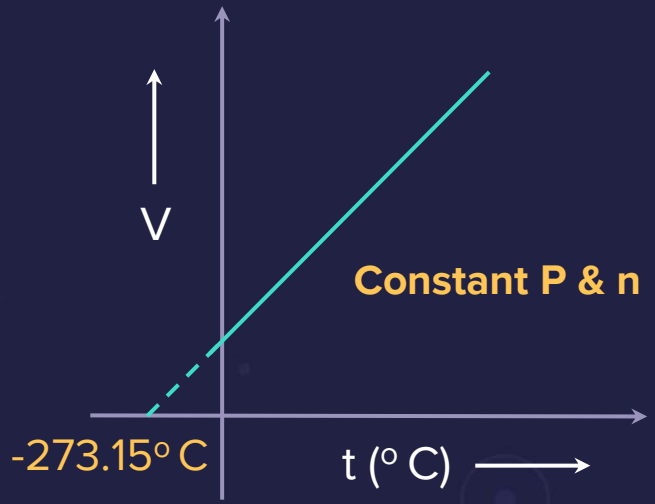
$$t\ ^oC \Rightarrow T_t = (273.15 + t)\ K$$

Charles' Law

Volume vs Temperature (K)

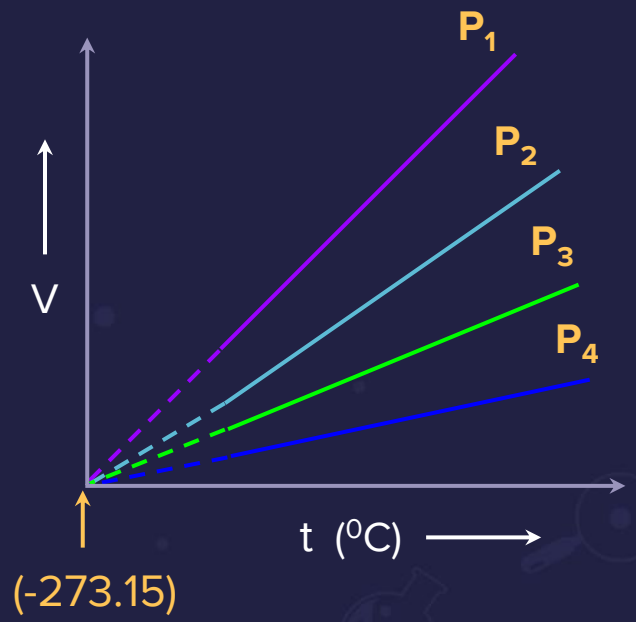


Volume vs Temperature (°C)



Charles' Law

T - V Isobars ----→ **Constant pressure** curves



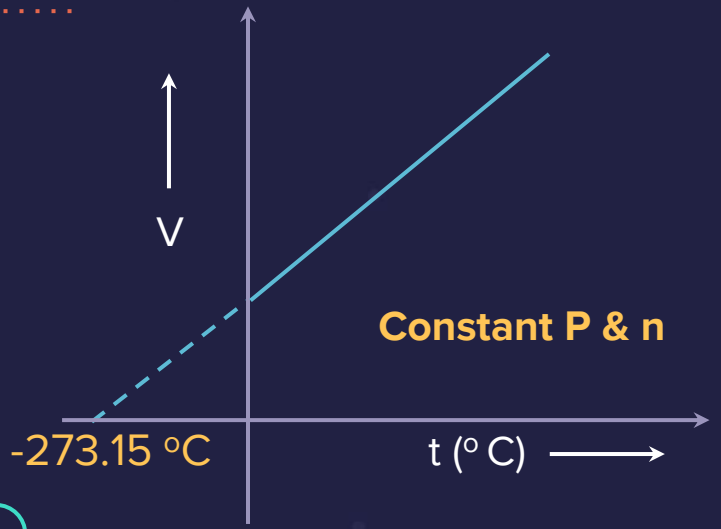
$P_1 < P_2 < P_3 < P_4$

What Happens at Absolute Zero?

$$V_t = V_o\left[\frac{t + 273.15}{273.15}\right]$$

Let value of **t = -273.15**

$$V_t = V_o\left[\frac{-273.15 + 273.15}{273.15}\right] = 0$$



It means volume of gas becomes zero at -273.15 °C

Volume of Gas is Zero!

Absolute zero

Lowest **hypothetical** or imaginary T at which gases supposedly occupy **zero volume**

Gas will **not exist**

All the gases get **liquified** before this temperature is reached

Gay-Lussac's Law

$$P \propto T$$

- V = Constant
- Amount of gas = Constant

At **constant volume**

The **pressure** of a fixed amount of a gas is **directly proportional to the temperature.**

Gay-Lussac's Law

$$P \propto T \quad (V, n \text{ constant})$$

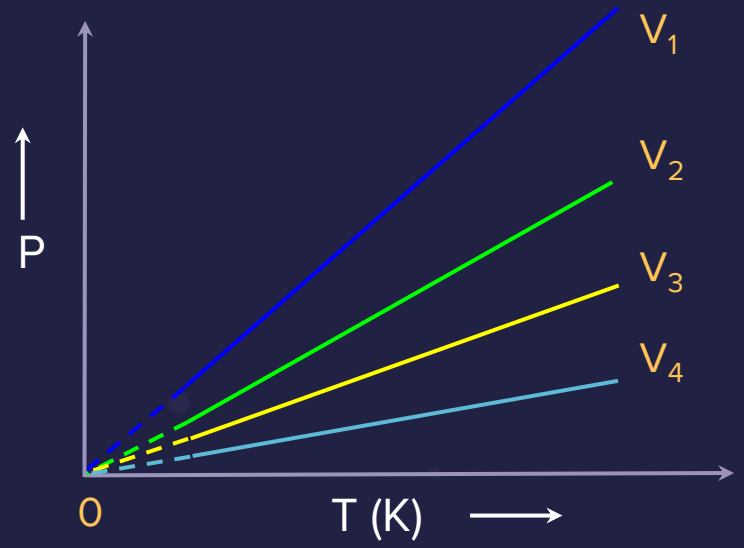
$$P = k_3 T \dashrightarrow \frac{P}{T} = k_3$$

$$\frac{P_1}{T_1} = \frac{P_2}{T_2} = k_3$$

k_3 depends on **amount** & **V** of gas

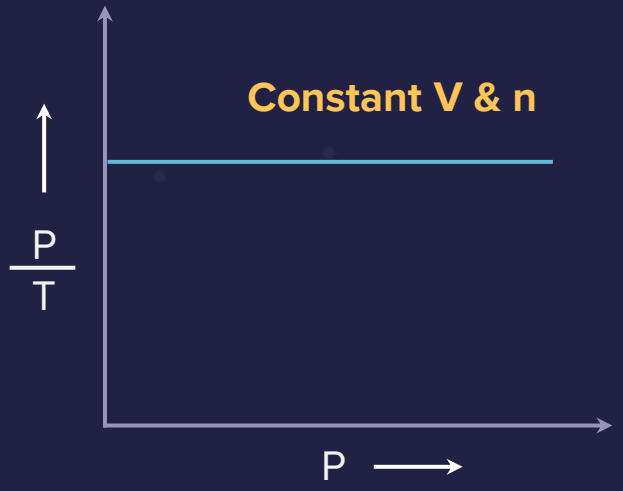
Gay-Lussac's Law

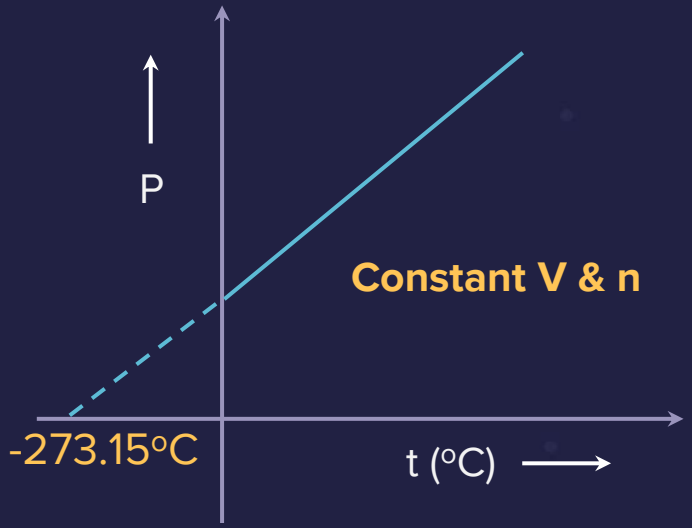
P - T **Isochores** - - - → **Constant volume** curves



$V_1 < V_2 < V_3 < V_4$

Gay-Lussac's Law





Avogadro's Law

$V \propto n$

- Same conditions of P & T

Same **conditions of P & T**

Equal volume of all gases contains **equal number of molecules**

Avogadro's Law

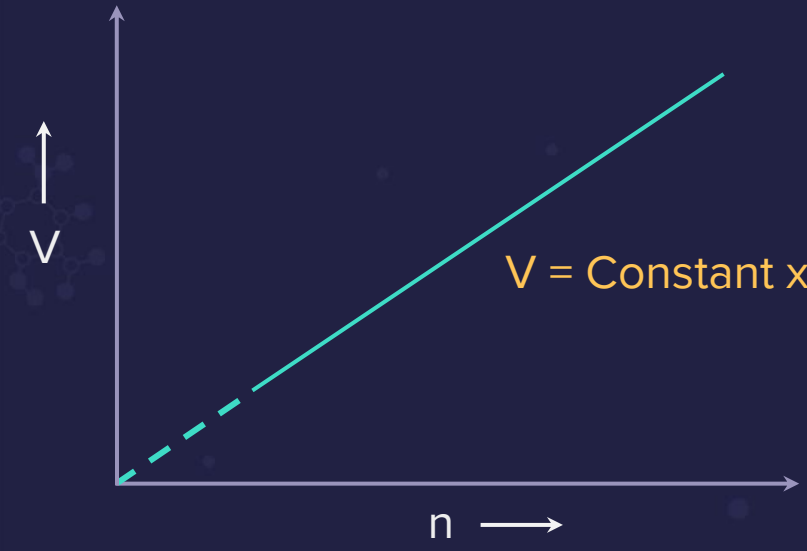
$$V \propto n \quad (P, T \text{ constant})$$

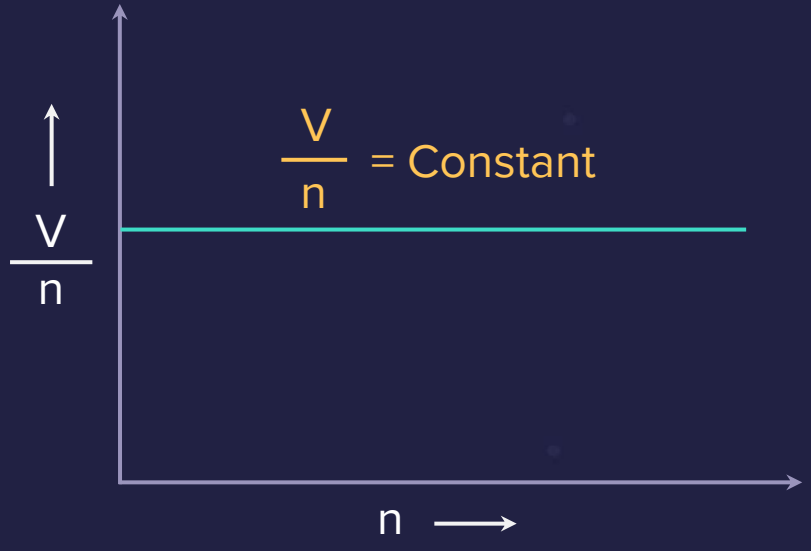
$$V = k_4 n \dashrightarrow \frac{V}{n} = k_4$$

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

k_4 depends on **P & T** of gas

Avogadro's Law





Combining Different Gas Laws

Boyle's Law

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

At constant n, T

Charles' Law

$V \propto T$

At constant n, P

Avogadro's Law

$V \propto n$

At constant T, P

Gay Lussac's Law

$P \propto T$

At constant n, V

Combining Different Gas Laws

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

$$\Rightarrow V = R\frac{nT}{P}$$

R: Universal Gas Constant

Remember!

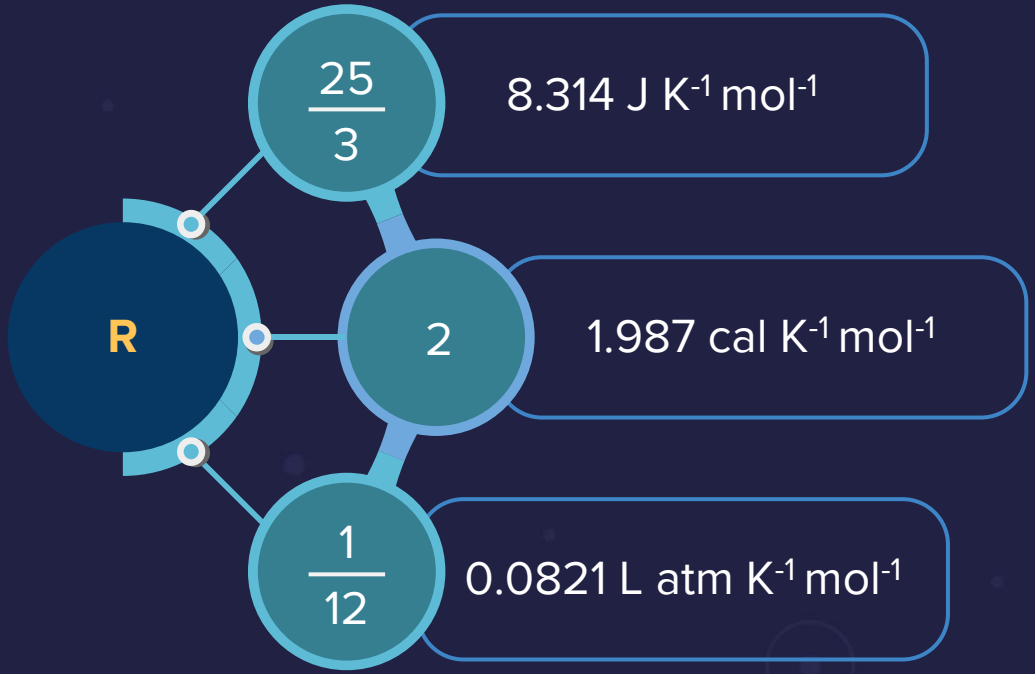
Ideal gas is hypothetical.
The **real gas** follows the gas laws and ideal gas equation only under specific condition **(Low P and high T).**

Ideal gas equation

PV = nRT

Ideal gas equation **(PV = nRT)** is a relation between four variables and it describes the state of any ideal gas. Due to this, it is also known as the **equation of state.**

Values of R


R
$\frac{25}{3}$
8.314 J K^{-1} mol^{-1}
2
1.987 cal K^{-1} mol^{-1}
$\frac{1}{12}$
0.0821 L atm K^{-1} mol^{-1}

Ideal Gas Equation in Terms of Density

$PV = nRT$

$n = \frac{m}{M}$

$PV = \frac{m}{M}RT$

$PM = \frac{m}{V}RT$

$PM = dRT$

$d = \frac{m}{V}$

- m = Mass of gas
- M = Molar mass of gas
- V = Volume of the gas
- d = Density of gas

Density of Gases on Compression

Pressure ↑

↓

Gases become denser (**Density** ↑)

↓

Same number of molecules occupy smaller space

Balloon squeezes → Volume of gas inside it ↓ → Pressure inside ↑

As the balloon cannot withstand the added pressure, it bursts

Gauge Pressure (P_g)

The difference of the actual pressure (P) & the atmospheric pressure (P_a)

$$P - P_a = P_g$$

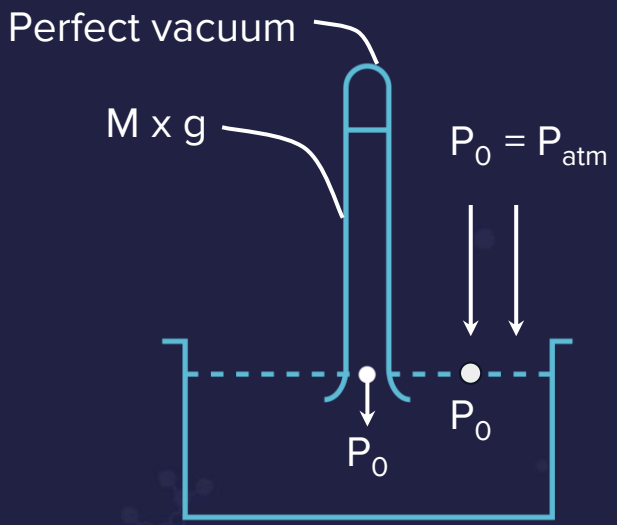
Measurement of Pressure: Barometer

Measures atmospheric pressure by

Determining the **height of a mercury column** supported in a **sealed glass tube**

Mercury Barometer

Downward pressure of mercury in the column	=	Outside atmospheric pressure



At equilibrium
$P_{atm} A = Mg$

Mercury Barometer

Mercury column inside the capillary comes to rest ⟶ Net forces are balanced

Applying force balance

$P_{atm} \times A = M \times g$

$M = \rho \times V$ &
$V = A \times h$

$\Rightarrow P_{atm} \times A = (\rho \times g \times h) \times A$

$\Rightarrow P_{atm} = \rho g h$

Faulty Barometer

In a **faulty barometer**, the region above the mercury column is **not completely** a **vacuum** and **contains trapped air** that creates some **additional pressure.**

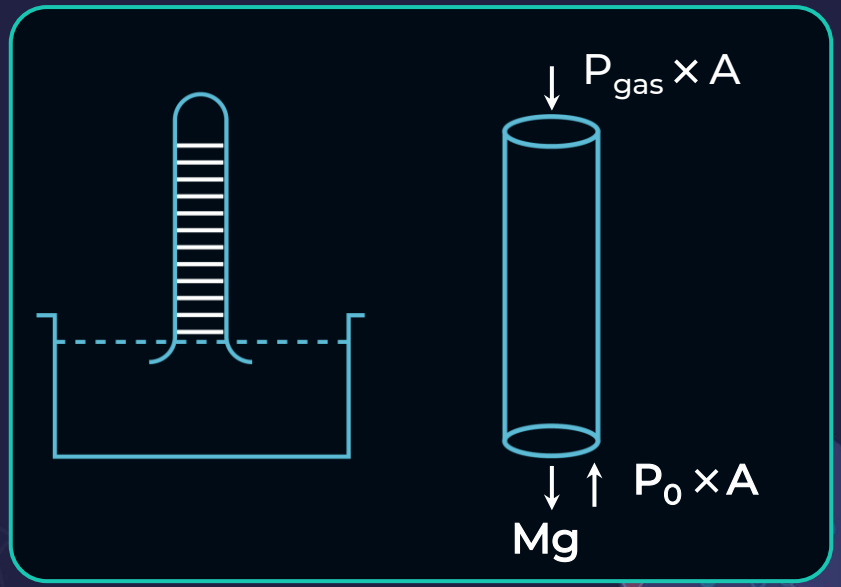
Actual Pressure if some gas is trapped instead of vacuum?

$P_oA = mg + P_{gas}A$

Pressure due to trapped air

where, $P_0 = \rho gh + P_{gas}$

Hence, $\rho gh = P_0 - P_{gas}$



Manometer

Instrument used for measurement of pressure of gas

Manometer

$$|P_{External} - P_{Gas}| \propto \Delta \text{ Height of mercury column}$$

Partial Pressure of a Gas Component

The pressure that a **component** of gas would exert if it occupies the **same volume** as the **mixture** at the same temperature

Mixture of non reacting gases

Dalton's Law of Partial Pressures

For a **non reacting** gaseous mixture **total pressure** of the mixture is the **summation of partial pressure** of the different component gases.

$$P_T = P_1 + P_2 + ...$$

Partial pressure of a gas is **independent** of the other gases present in the mixture

Partial Pressure in Terms of Mole Fraction

- Suppose at temperature T, three gases enclosed in volume V, exert partial pressures P_1, P_2 and P_3

$$P_1 = \frac{n_1RT}{V}$$

$$P_2 = \frac{n_2RT}{V}$$

$$P_3 = \frac{n_3RT}{V}$$

Partial Pressure in Terms of Mole Fraction

Dalton's law

$$P_{Total} = P_1 + P_2 + P_3$$

$$P_{Total} = \frac{n_1RT}{V} + \frac{n_2RT}{V} + \frac{n_3RT}{V}$$

$$P_{Total} = (n_1 + n_2 + n_3)\frac{RT}{V}$$

$$n_{Total} = n_1 + n_2 + n_3$$

Partial Pressure in Terms of Mole Fraction

On dividing P_1 by P_{Total},

$$\frac{P_1}{P_{Total}} = \frac{n_1}{n_1 + n_2 + n_3} \times \frac{RT}{V} \times \frac{V}{RT}$$

$$\frac{P_1}{P_{Total}} = \frac{n_1}{n_{Total}} = \chi_1$$

χ_1 Mole fraction of gas 1

Partial Pressure in Terms of Mole Fraction

Similarly,

$$\frac{P_2}{P_{Total}} = \chi_2 \quad \text{and} \quad \frac{P_3}{P_{Total}} = \chi_3$$

$$P_i = \chi_i P_{Total}$$

χ_i Mole fraction of the i^{th} component gas in the gaseous mixture

Average Molar Mass of Gaseous Mixture

$$M_{avg} = \frac{M_1 n_1 + M_2 n_2}{n_1 + n_2}$$

- M_1 = Molar mass of first gas
- M_2 = Molar mass of second gas
- n_1 = Moles of first gas
- n_2 = Moles of second gas

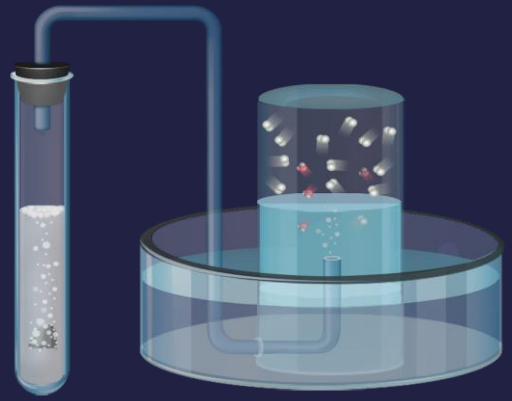
Vapour Pressure

Pressure exerted by the
vapour in equilibrium with liquid,
at a given temperature

Vapour pressure **doesn't change** if
the **temperature** remains **constant**

Utility of Dalton's Law

Gases are generally collected over water and thus, become **moist.** In such cases, **Dalton's law** is useful in calculating the **pressure of gas.**



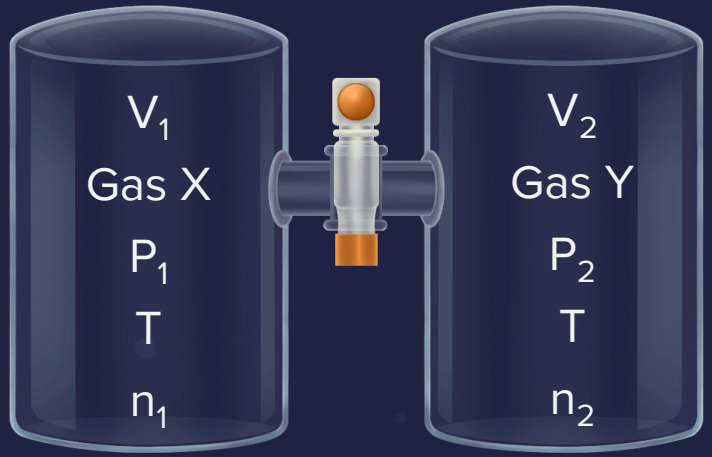
$$P_T = P_g + P_w$$

- P_T: Pressure of water vapour
- P_g: Pressure of dry gas

Pressure exerted by saturated water vapour is called **Aqueous tension**

Connecting Vessels

n_1 & n_2 are moles of two non-reacting gases X & Y



Connecting Vessels

Before opening valve;

$$(n_1 + n_2) = \frac{P_1V_1}{RT} + \frac{P_2V_2}{RT}$$

After opening valve;

$$P_{final}(V_1 + V_2) = (n_1 + n_2)RT$$

Gas flows till its **Partial pressure becomes equal** in both container

Connecting Vessels

To calculate moles of gas ‘X’ in each container

$$\left[P_X \right]_1 = \left[P_X \right]_2$$

- P_x: Partial pressure of X

Let ‘a’ moles of gas ‘X’ flow from container 1 to 2

$$\left(n_1 - a \right) \frac{RT_1}{V_1} = \frac{a\,RT_2}{V_2}$$

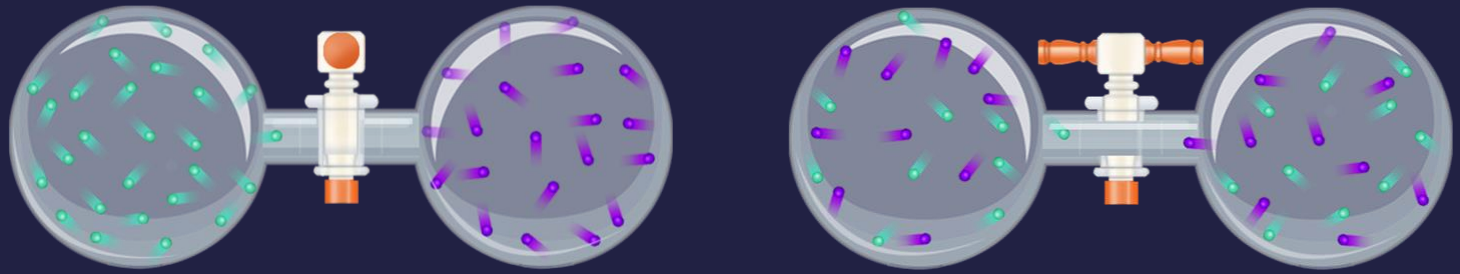
Remember!!

Open rigid container: $n_1T_1 = n_2T_2$ P & V are constant

Closed rigid container: $\frac{n_1RT_1}{P_1} = \frac{n_2RT_2}{P_2}$ V is constant

For Ballon: $P_{external} = P_{internal}$

Diffusion



Net spontaneous flow of gaseous molecules from a region of **higher concentration** (higher partial pressure) to a region of **lower concentration** (lower partial pressure)

Diffusion

Flow of gaseous molecules

Region of high concentration to lower concentration

Region of higher partial pressure to lower partial pressure

Effusion

Gas escapes through a small orifice

Graham's Law of Diffusion

Under similar conditions of pressure & temperature, the **rate of diffusion** of gases are **inversely proportional** to the **square roots** of their **densities (d)**

$$\text{Rate of diffusion } (r_{gas}) \propto \frac{1}{\sqrt{d}}$$

Graham's Law of Diffusion

General form of Graham's law

$$r_{gas} \propto \frac{PA}{\sqrt{MT}}$$

P	Partial pressure of gas
A	Area of orifice
M	Molar mass of gas
T	Temperature of gas

Graham's Law of Diffusion

Since, $PM = dRT$

P and T constant

$$\frac{r_A}{r_B} = \sqrt{\frac{d_B}{d_A}} = \sqrt{\frac{M_B}{M_A}} = \sqrt{\frac{(V.D.)_B}{(V.D.)_A}}$$

V.D. Vapour density

Importance of Graham's Law

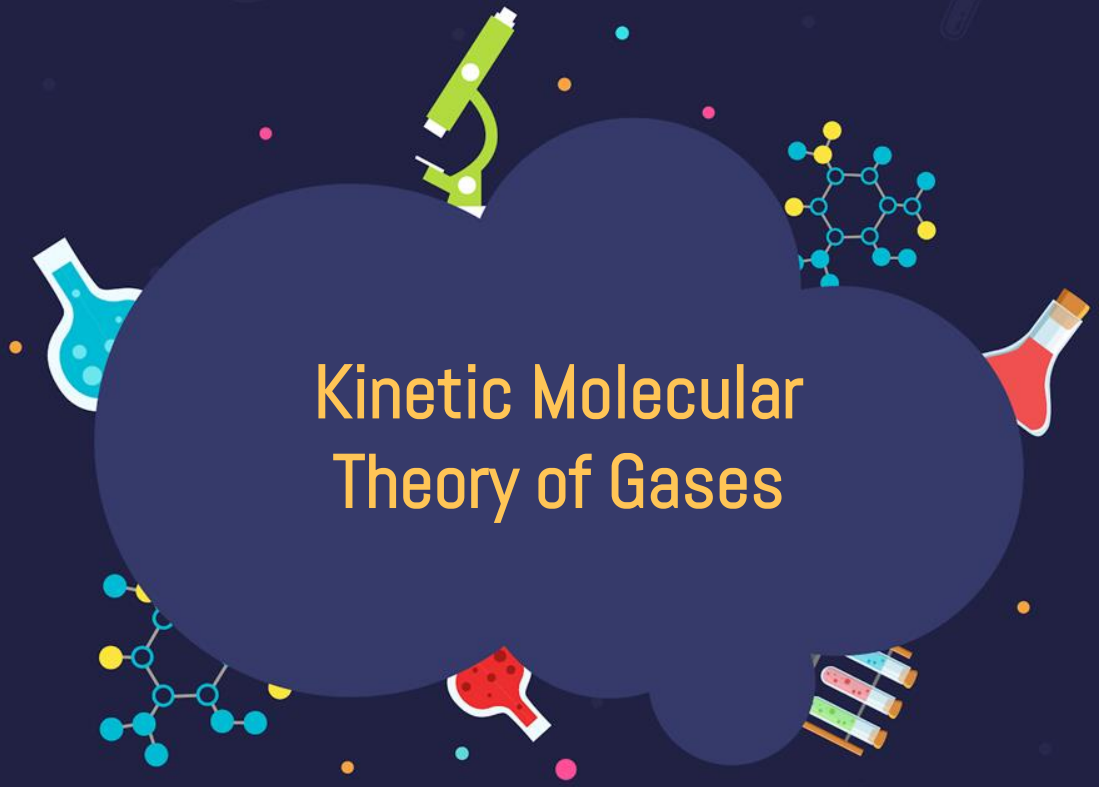
Separation of isotopes

Separation of gases having different densities

Rate of diffusion is inversely proportional to square root of molar mass. So, after doing diffusion, we get a mixture which is rich in lighter isotope. If we repeat process of diffusion several times, then we get a mixture which is very rich in lighter isotope. Hence, we can separate lighter gas and heavier gas

In determining densities and molecular masses of unknown gases

Molecular masses of unknown gases can be determined by comparing its diffusion rate with that of any known gas.



Kinetic Molecular Theory of Gases

Postulates / Assumptions of KTG

A gas consists of **tiny spherical particles** called **atoms/molecules of the gas** which are **identical in shape & size (mass)**

The **volume occupied** by the particles is **negligible** in comparison to the **total volume** of the gas

Gaseous molecules are always in **random motion** and **collide with each other** and with the **walls of the container**

Postulates / Assumptions of KTG

Pressure is due to the **collisions of the particles** with the **walls of the container** --→ **Elastic collisions**

Newton's laws of motion are applicable on the **motion of the gaseous particles**

For an Ideal gas; Attractive or repulsive forces = zero

Postulates / Assumptions of KTG

Effect of gravity is negligible on the **molecular motion**

The **average K.E.** of the gaseous molecules $\propto$ **Absolute temperature** of the gas

Postulates / Assumptions of KTG

Average K.E. $\propto$ T

Average K.E. $= \frac{3}{2} k_B T$

Depends only on temperature and not on nature of the gas

k_B Boltzmann constant

T Temperature (K)

Boltzmann Constant

$$k_B = \frac{R}{N_A}$$

$$k_B = 1.3807 \times 10^{-23}\ J/K$$

R Universal gas constant

N_A Avogadro number

Molecular Speed

Gas molecules are always in **continuous motion**

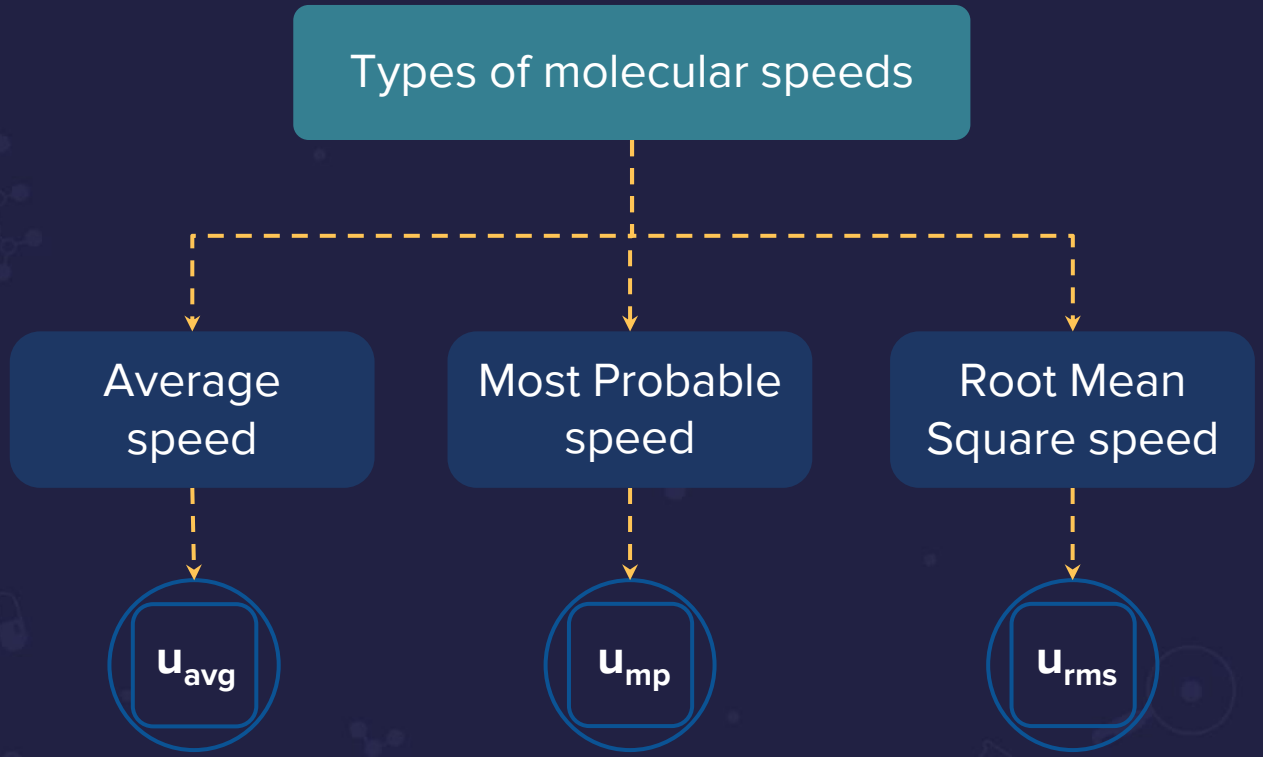
They **collide** with each other and with the walls of the container

Change in their **speed** & redistribution of **energy**

Speed & **energy** of all the molecules at any instant are **not the same**

Measuring **speed** of an individual molecule is not possible

Molecular Speeds



Average Speed

Arithmetic mean of the **speeds of different molecules** of the gas

$$u_{avg} = \left[\frac{u_1 + u_2 + ...+ u_N}{N}\right]$$

$$u_{avg} = \left[\frac{8RT}{\pi M}\right]^{\frac{1}{2}}$$

u_{avg} Average speed of molecules

N Total number of molecules

Most Probable Speed

Speed possessed by the **maximum number** of **gas molecules**

$$u_{mp} = \left[\frac{2RT}{M}\right]^{\frac{1}{2}}$$

Root Mean Square Speed

Square root of the **mean of the squares of the speeds** possessed by the gas molecules

$$u_{rms} = \left[\frac{3RT}{M}\right]^{\frac{1}{2}}$$

$$u_{rms} = \left[\frac{u_1^2 + u_2^2 + ...+ u_N^2}{N}\right]^{\frac{1}{2}}$$

u_{rms}	Root of mean of square of speeds
N	Total number of molecules

Relationship Between the Different Types of Speeds

For a particular gas at the same temperature (T),

u_{rms}	:	u_{avg}	:	u_{mp}
$\left[\frac{3RT}{M}\right]^{\frac{1}{2}}$	:	$\left[\frac{8RT}{\pi M}\right]^{\frac{1}{2}}$	:	$\left[\frac{2RT}{M}\right]^{\frac{1}{2}}$
$\sqrt{3}$	:	$\left[\frac{8}{\pi}\right]^{\frac{1}{2}}$	:	$\sqrt{2}$
1.224	:	1.128	:	1

- T = Temperature in Kelvin
- M = Molar mass in kg
- R = 8.314 J/mol K

Conclusion:

$u_{rms} > u_{avg} > u_{mp}$

Maxwell-Boltzmann Distribution of Speeds

Based on the theory of **probability**

Gives the **statistical average of the speeds** of the whole collection of the gas molecules

Maxwell's Distribution of Molecular Speeds

Fraction of molecules with speed between 'u' & 'u + du'

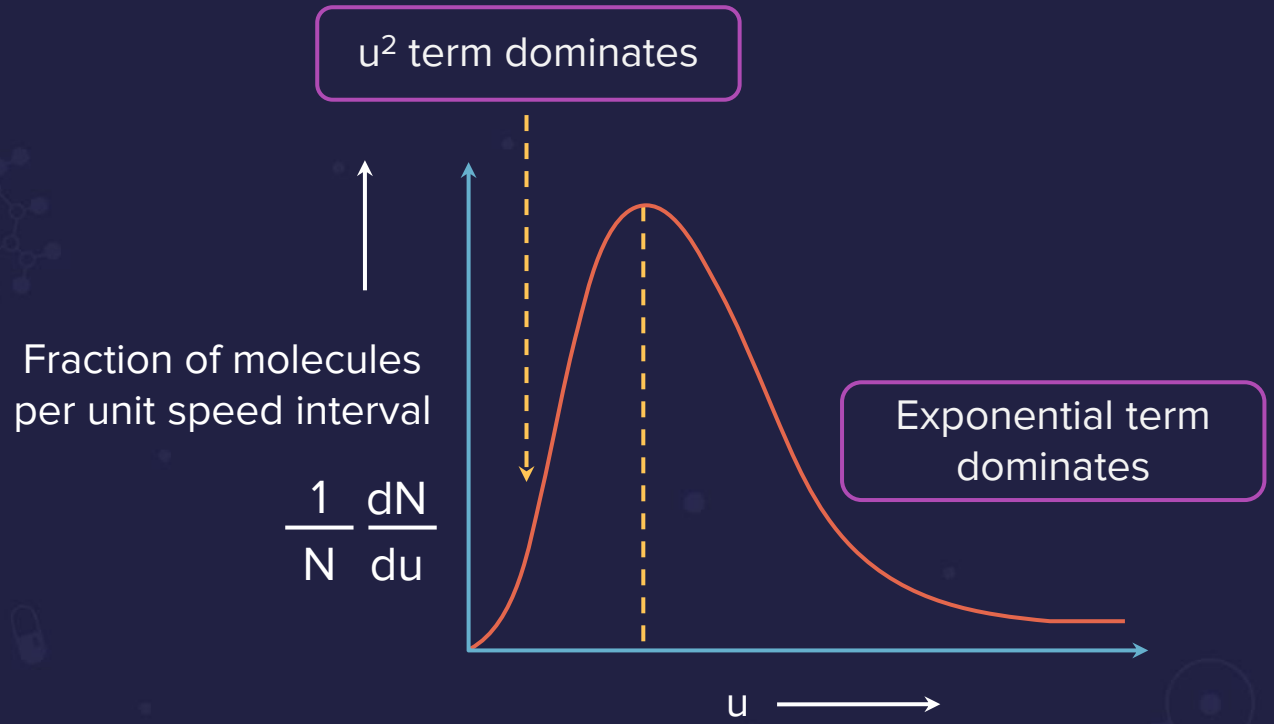
$$\frac{1}{N}\frac{dN}{du} = 4\pi\left[\frac{M}{2\pi RT}\right]^{\frac{3}{2}} e^{-\frac{Mu^2}{2RT}} u^2$$

N Total number of gas molecules

M Molar mass

u Speed

Maxwell-Boltzmann Distribution of Speeds



Maxwell-Boltzmann Distribution of Speeds

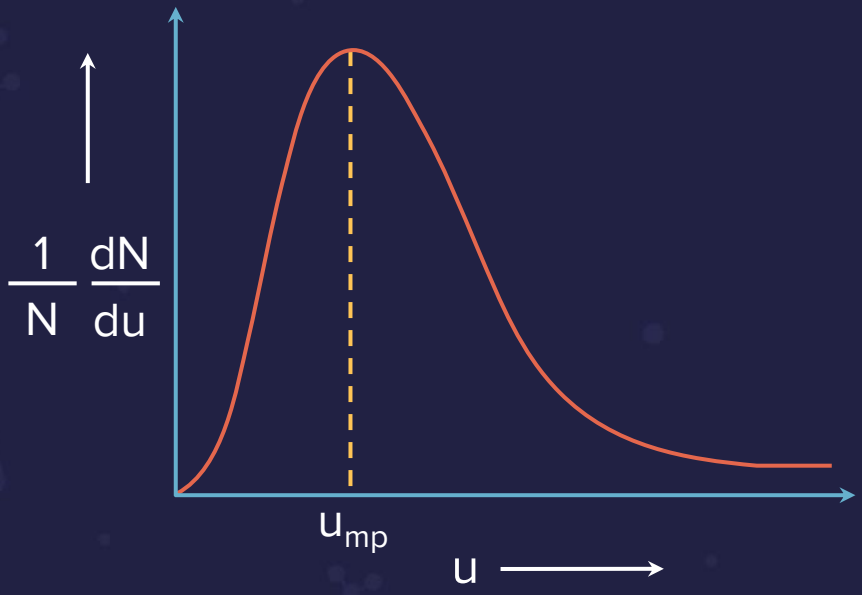
At a particular temperature,

Individual speed of molecules **keeps changing**

Distribution of speeds remains the same

Maxwell-Boltzmann Distribution of Speeds

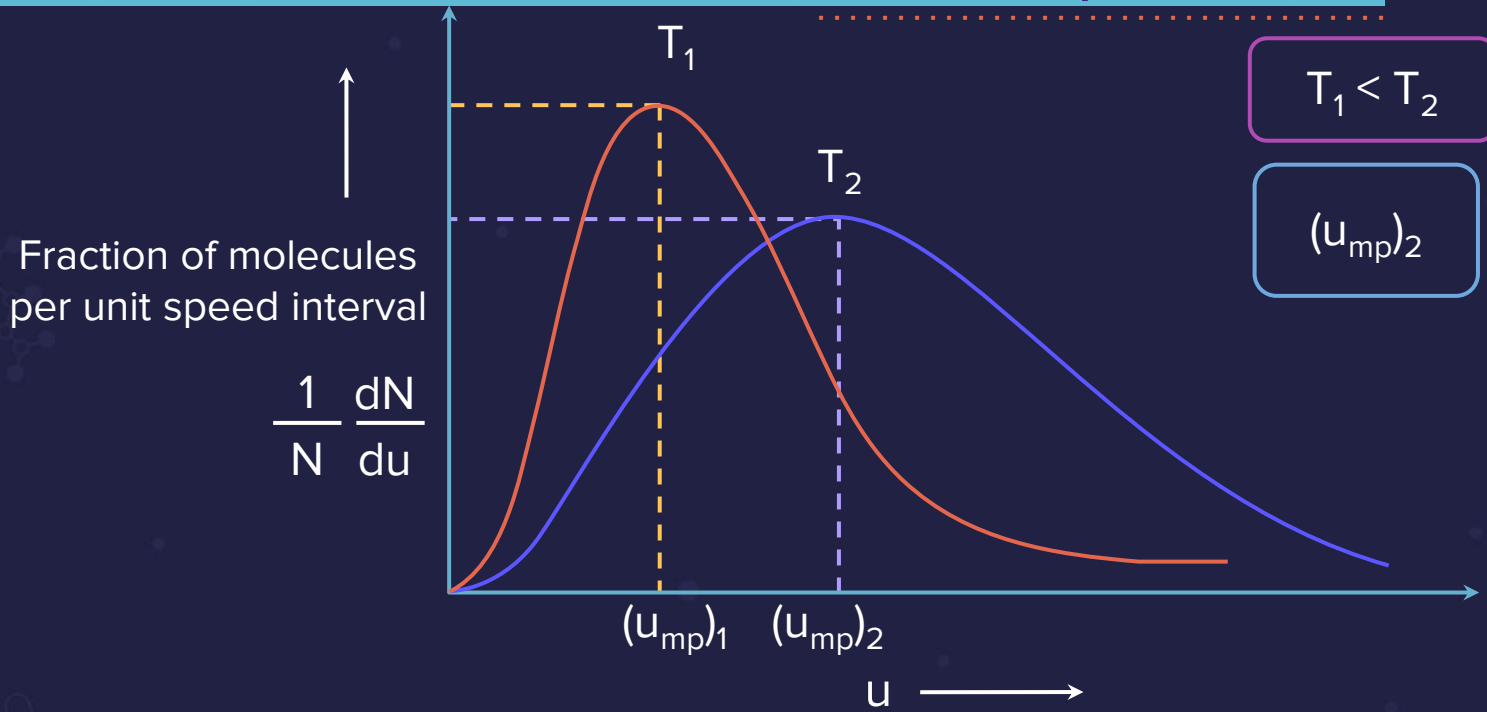
Maximum fraction of molecules possess a **speed** corresponding to the **peak of this curve** referred to as u_{mp}



Actual distribution of **molecular speeds** in a gas depends on

- Temperature
- Molar Mass

Maxwell-Boltzmann Distribution of Speeds

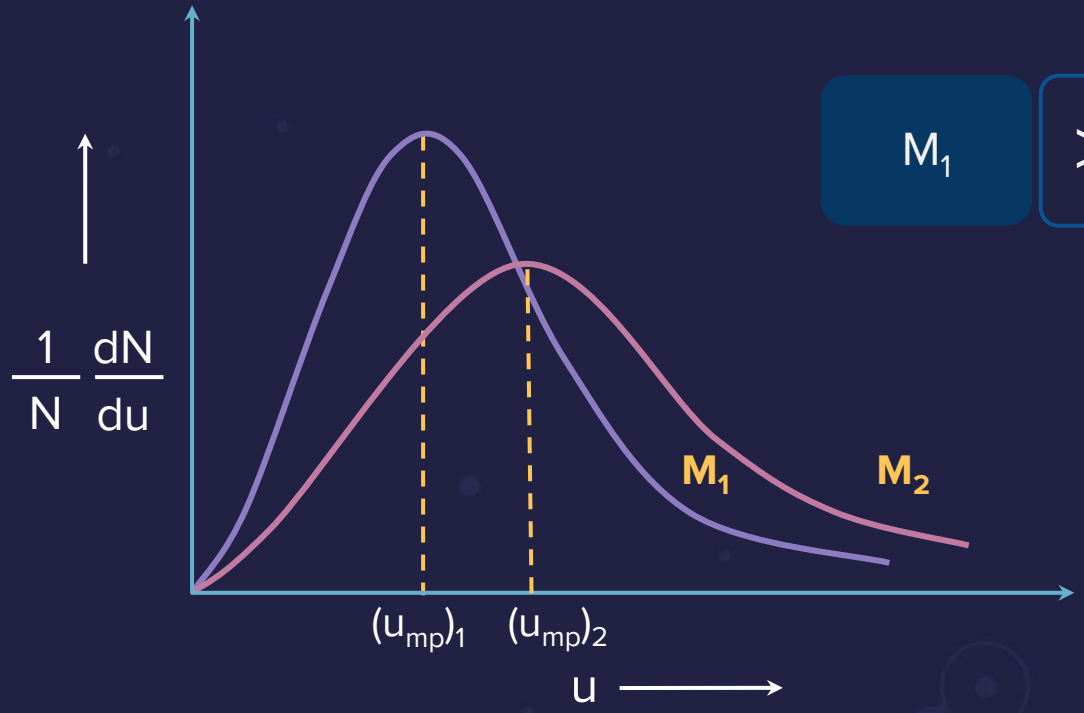


$T_1 < T_2$

$(u_{mp})_2 > (u_{mp})_1$

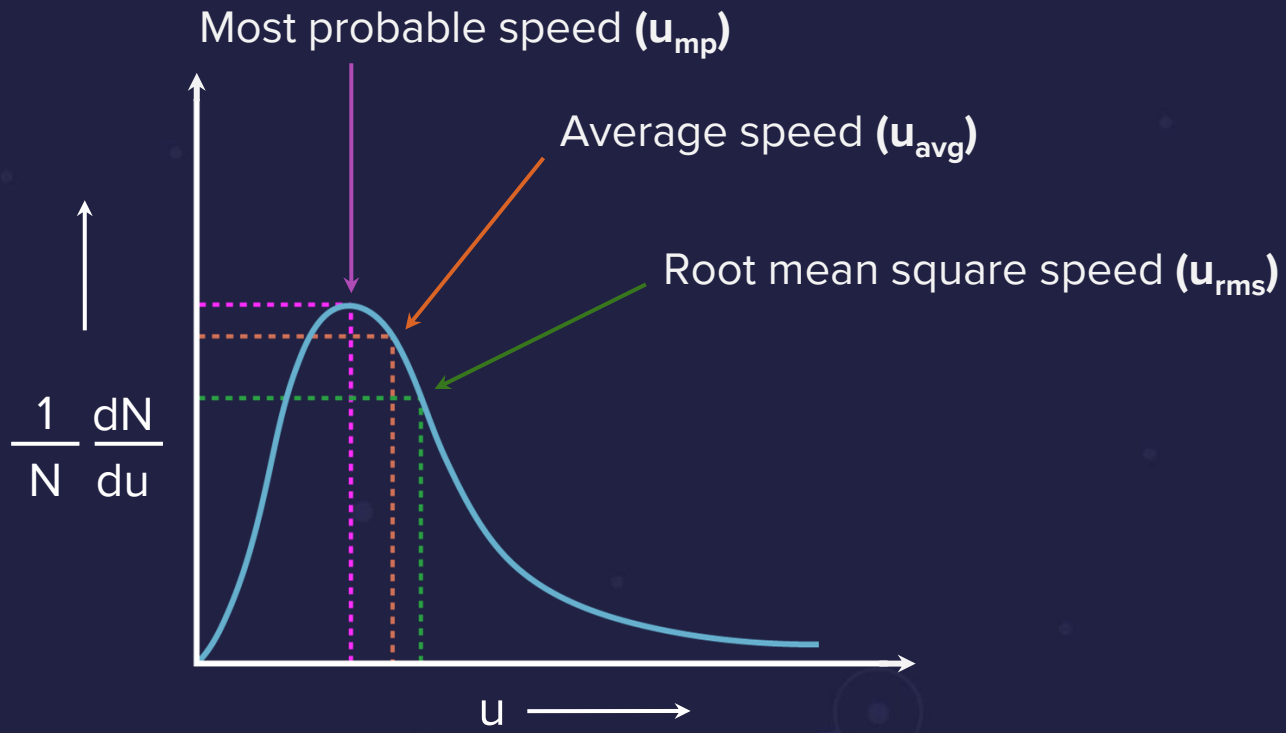
Temperature ↑ → Molecular motion becomes rapid → Entire curve shifts towards the right

Distribution of Speeds for Different Molar Masses

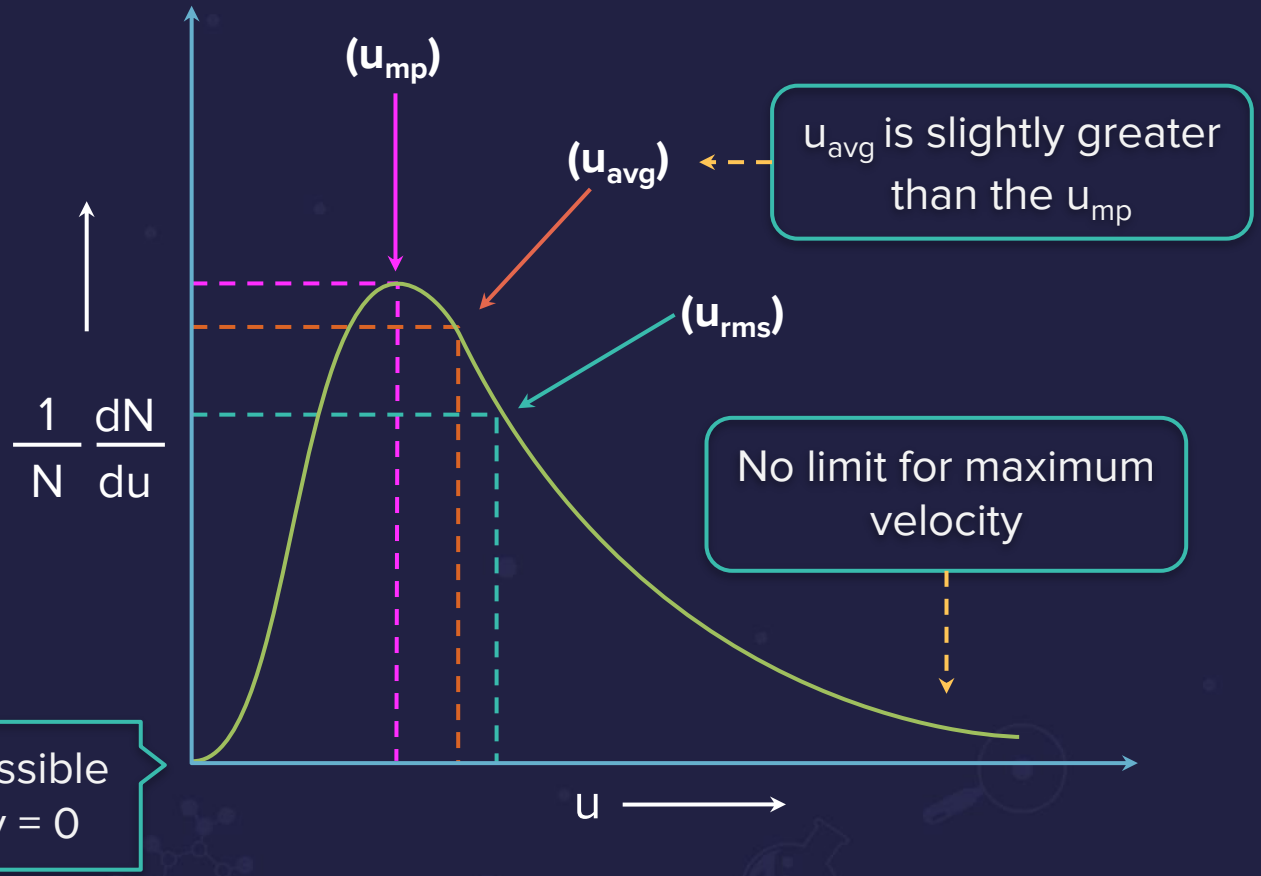


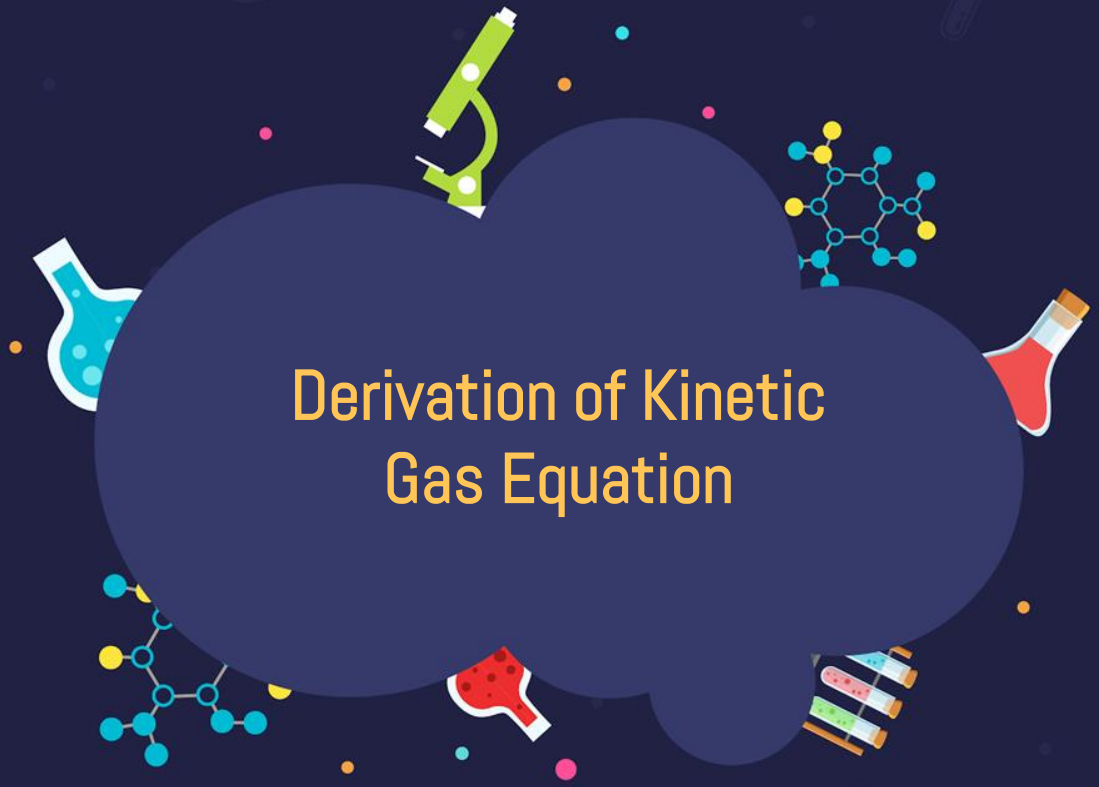
$M_1 > M_2$

Maxwell's Distribution of Molecular Speeds



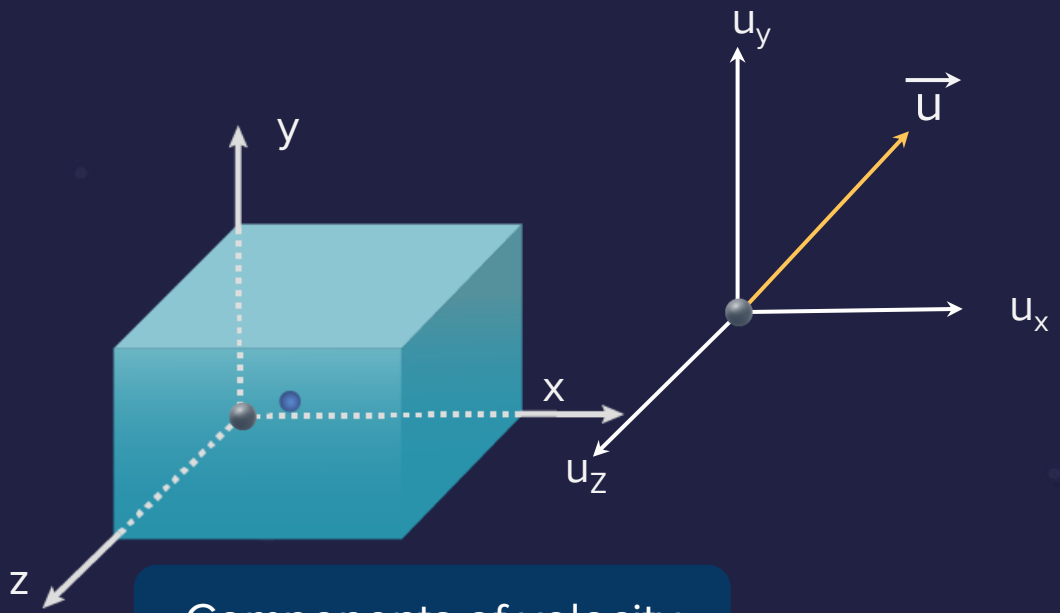
Why Average Velocity is Towards the Right?





Derivation of Kinetic Gas Equation

Derivation of Kinetic Equation



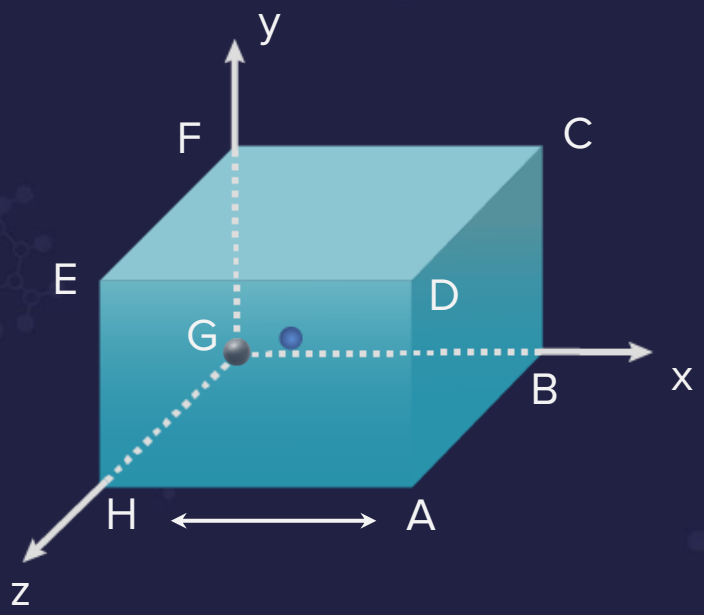
Components of velocity

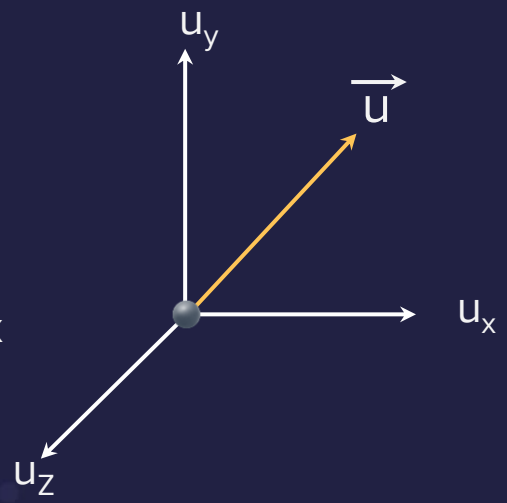
$$\vec{u} = u_x\hat{i} + u_y\hat{j} + u_z\hat{k}$$

Abbreviation / Symbol Used

Length of an edge of the cube	=	l
Number of molecules	=	N
Mass of a molecule	=	m

Consider Collision with Face ABCD





$$\vec{p_i} = mu_x \hat{i}$$

$$\vec{p_f} = -mu_x \hat{i}$$

$$|\Delta p| = 2mu_x \hat{i}$$

Between Two Successive Collisions with Face ABCD

Distance travelled	=	$2l$
Time taken	=	$\frac{2l}{u_x}$
Frequency	=	$\frac{u_x}{2l}$

Derivation of Equation

$$F = \frac{\Delta p}{\Delta t} \dashrightarrow 2mu_x \frac{u_x}{2l} \dashrightarrow \frac{mu_x^2}{l}$$

$$F_{x,\,Total} = \frac{m}{l}\{u_{x_1}^2 + u_{x_2}^2 + \ldots\ldots\ldots\ldots\ldots\ldots u_{x_N}^2\}$$

Derivation of Equation

Average value of u_x^2 = $\overline{u_x^2}$ = $\dfrac{u_{x_1}^2 + u_{x_2}^2 + \ldots\ldots\ldots u_{x_N}^2}{N}$

Force due to all the molecules (F_x) = $\dfrac{m}{l}\{N\overline{u_x^2}\}$

Derivation of Equation

Average of all **three components** of **velocity** are **equal** as the **motion** is **totally random** in **all directions**

$$\overline{u_x^2} = \overline{u_y^2} = \overline{u_z^2}$$

$$u^2 = \overline{u_x^2} + \overline{u_y^2} + \overline{u_z^2} = 3\overline{u_x^2}$$

Derivation of Equation

$$F = \frac{m}{l} N \frac{1}{3} \overline{u^2}$$

$$P = \frac{F}{l^2} = \frac{1}{3} \frac{mN}{l^3} \overline{u^2}$$

Volume of the container 'V' = l^3

$$PV = \frac{1}{3} mN\overline{u^2}$$

Derivation of Equation

Root mean square speed

$$u_{rms} = \sqrt{\overline{u^2}}$$

$$\sqrt{\overline{u^2}} = \sqrt{\frac{u_1^2 + u_2^2 + u_3^2 + \ldots\ldots\ldots\ldots + u_N^2}{N}}$$

Deriving u_{rms} from Kinetic Gas Equation

$$PV = \frac{1}{3} mNu_{rms}^2$$

Kinetic Gas Equation

$$u_{rms}^2 = \frac{3PV}{mN} = \frac{3PV}{mnN_A}$$

$N = nN_A$

$$u_{rms}^2 = \frac{3nRT}{mnN_A}$$

For an ideal gas

$PV = nRT$

$$u_{rms}^2 = \frac{3RT}{mN_A}$$

Deriving u_{rms} from Kinetic Gas Equation

$$u_{rms}^2 = \frac{3RT}{M}$$

$$mN_A = M$$

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

Deriving u_{rms} from Kinetic Gas Equation

$J = Nm$

$N = kgms^{-2}$

R in $JK^{-1}mol^{-1}$

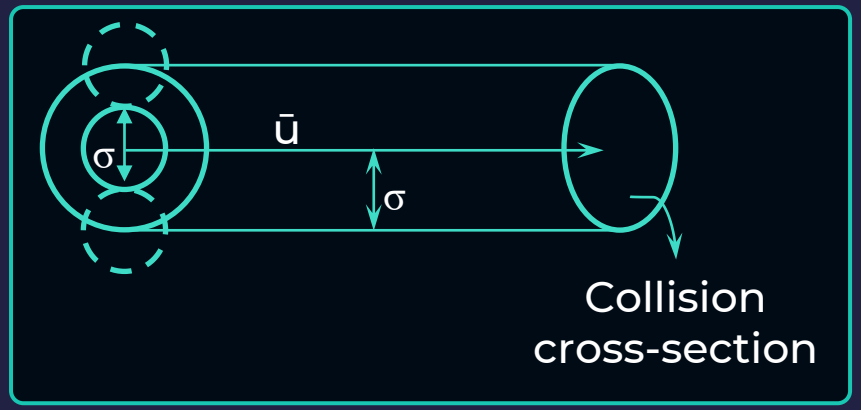
M in $kg\ mol^{-1}$

$$\text{Unit of } u_{rms} = \sqrt{\frac{(Nm)K^{-1}mol^{-1} \times K}{kg\ mol^{-1}}} = \sqrt{\frac{(kgms^{-2}m)}{kg}}$$

$$= \sqrt{m^2s^{-2}} = ms^{-1}$$

Collision Frequency (Z)

Collision cross-section is an area of an imaginary sphere of radius 'σ' around the molecule within which the center of another molecule **cannot** penetrate.



The **volume swept** by a single molecule in unit time is

$$V = (\pi\sigma^2)\bar{u}$$

$\bar{u}$: Average speed

Collision Frequency (Z)

If N^* is the number of molecules per unit volume, then the number of molecules within the volume V is:

$$N = VN^*$$
$$= (\pi\sigma^2\bar{u})N^*$$

The number of collision made by a single molecule in unit time will be

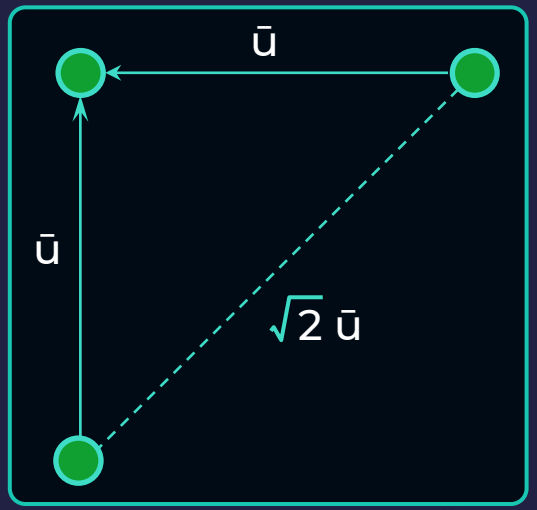
$$Z = N$$
$$= (\pi\sigma^2\bar{u})N^*$$

Collision Frequency (Z)

In order to account for the movements of all molecules, we must consider the **average velocity** along the line of centers of two colliding molecules instead of the **average velocity** of a single molecule.

On an average, molecules collide while approaching each other **perpendicularly** then the average velocity along their centers is $\sqrt{2}\ \bar{u}$

Collision Frequency (Z)

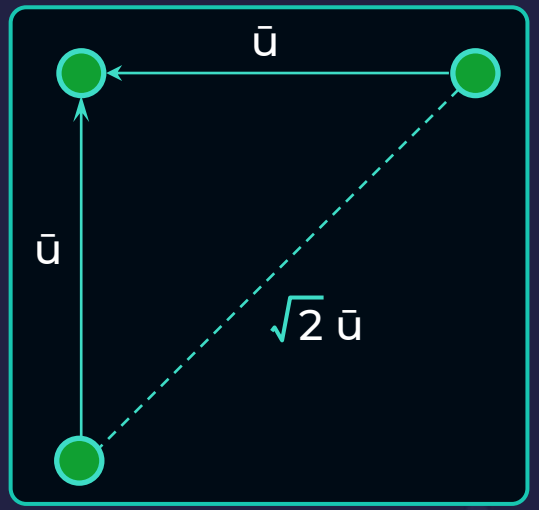


Number of collision made by a single molecule with other molecules per unit time is:

$$Z_1 = \pi\sigma^2 (\bar{u}_{rel}) N^*$$

$$= \sqrt{2}\, \pi\sigma^2 \bar{u} N^*$$

Collision Frequency (Z)



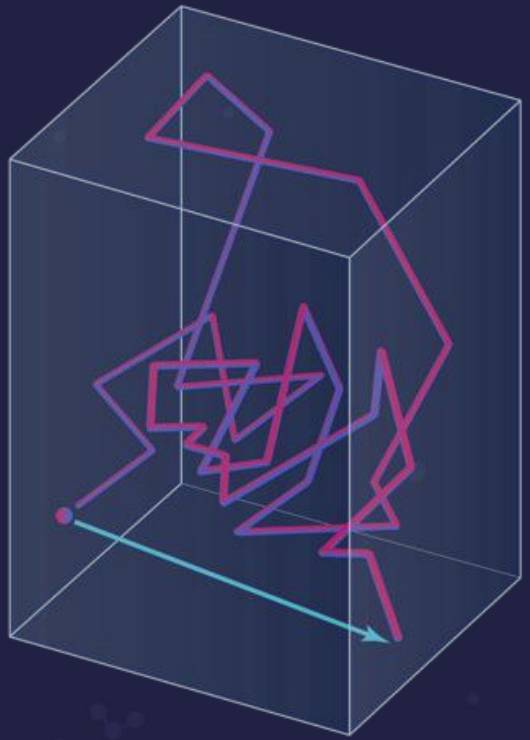
The total number of **bimolecular collisions Z11** per unit volume per unit time is:

$$Z_{11} = \frac{1}{2}(Z_1 N^*)$$

$$= \frac{1}{2}(\sqrt{2}\,\pi\sigma^2 \bar{u} N^*)N^*$$

$$= \frac{1}{\sqrt{2}}\pi\sigma^2 \bar{u}(N^*)^2$$

Mean Free Path



Average distance travelled by a particle between two successive collision

Between two collisions, particles travel in linear path

Mean Free Path

$$\lambda = \frac{\text{Average distance travelled per unit time}}{\text{Number of collisions made by a single molecule per unit time}}$$

$$\lambda = \frac{\bar{u}}{Z_1}$$

or

$$\lambda = \frac{\bar{u}}{\sqrt{2}\pi\sigma^2\bar{u}N^*}$$

$$\lambda = \frac{1}{\sqrt{2}\pi\sigma^2N^*}$$

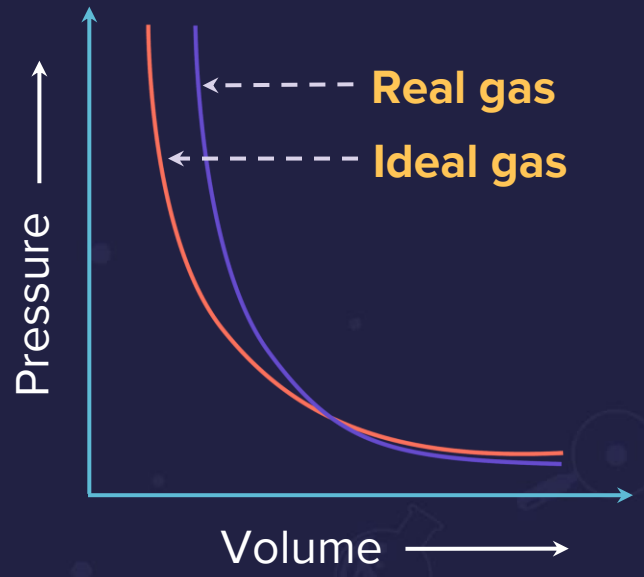
Mean Free Path

At constant V → $P \propto T$ → $\frac{T}{P}$ = constant → λ = constant

No effect of T or P variation on λ at constant V

Real Gas

Gases which **do not obey Ideal gas law** under all conditions of **T & P**



What is Compressibility Factor (Z)?

A measure of the **deviation of** real gases from ideal behaviour

V_m is the Molar Volume

$$\frac{V_{m,\,real}}{V_{m,\,ideal}} = Z$$

Measured at the same T & P

Compressibility Factor

Since, $V_{m,\,ideal} = \frac{RT}{P}$ $Z = \frac{V_{m,\,real}}{V_{m,\,ideal}} = \frac{PV_m}{RT}$

Compressibility Factor (Z)

At very low pressure

Z ≃ 1

Attractive forces ≃ Repulsive forces

At intermediate pressure

Z < 1 **Negative deviation**

Attractive forces > Repulsive forces **Gas easy to compress**

Compressibility Factor (Z)

At high pressure

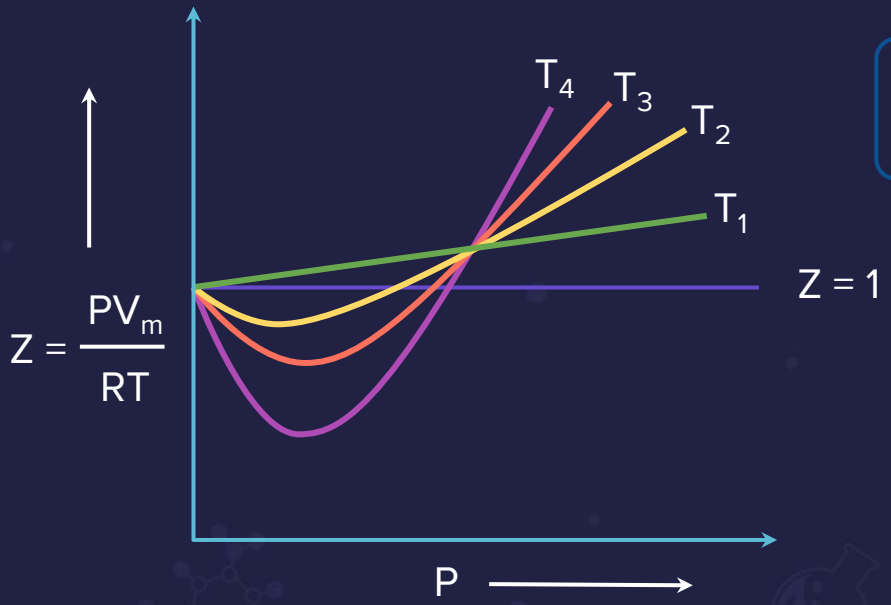
Z > 1 **Positive deviation**

Attractive forces < Repulsive forces

Gas difficult to compress

Different T, Same Gas

T ↑ → Collision ↑ → Repulsion ↑ → Z ↑



$T_1 > T_2 > T_3 > T_4$

Boyle Temperature (T_b)

Boyle point or temperature

Temperature at which a **real gas behaves like an ideal gas** at low pressure

Boyle Temperature

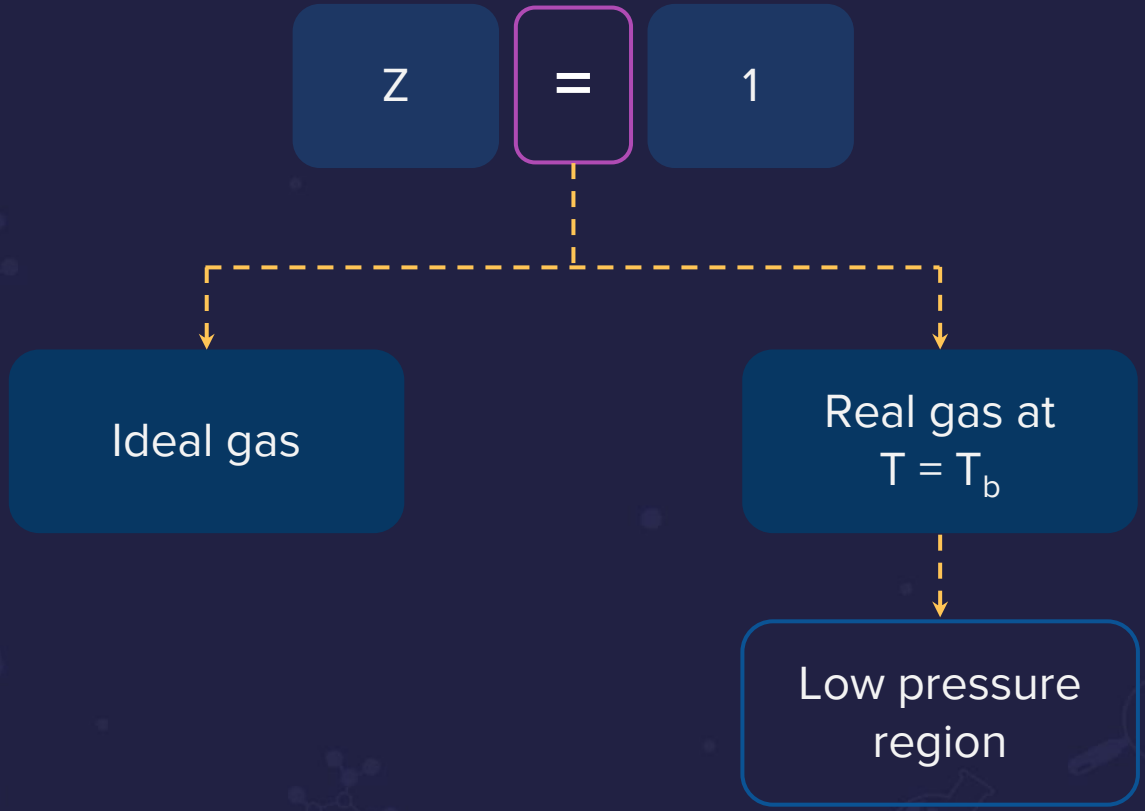
$T_b \propto$ Attraction between molecules

T_b depends on the **nature of the gas**

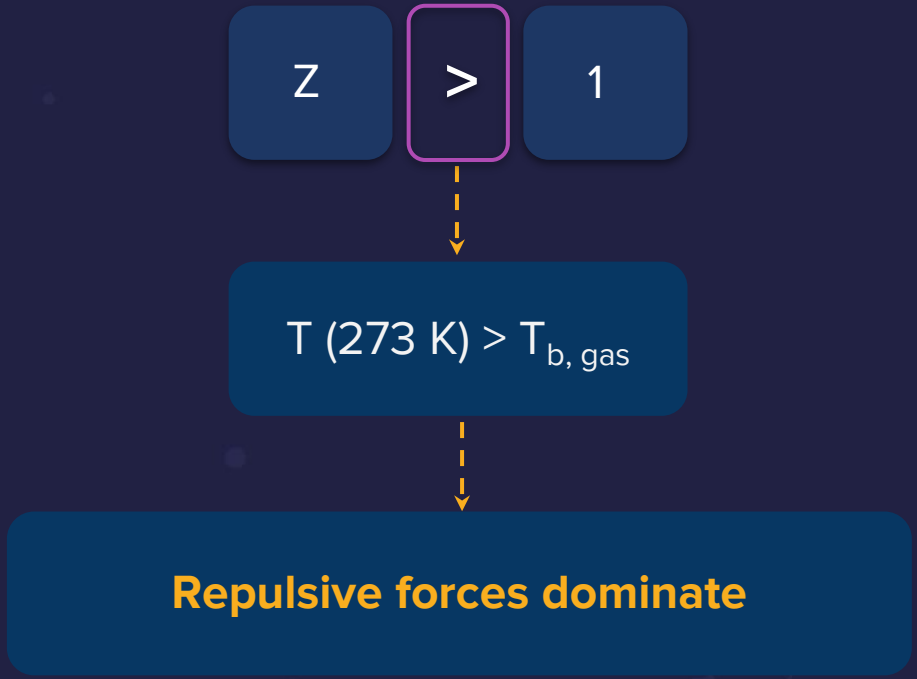
$(T_b)_{CO,\ CH_4} > 273\ K$

$(T_b)_{H_2,\ He} < 273\ K$

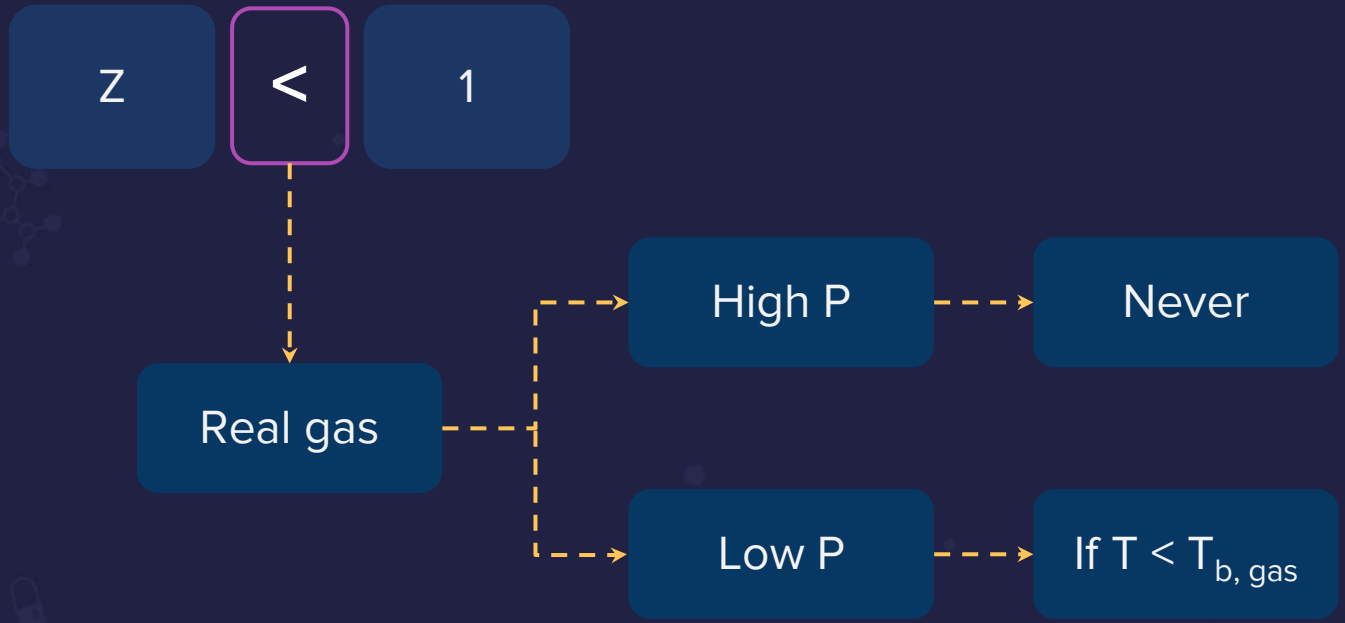
Conclusion



Exceptional Behaviour of H_2 and He



Conclusion



Real Gases

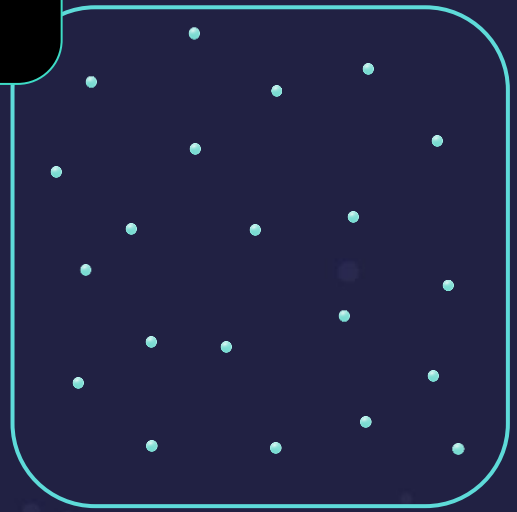
Volume of gas particles is **not negligible** w.r.t the container

On liquefaction, occupy a finite volume

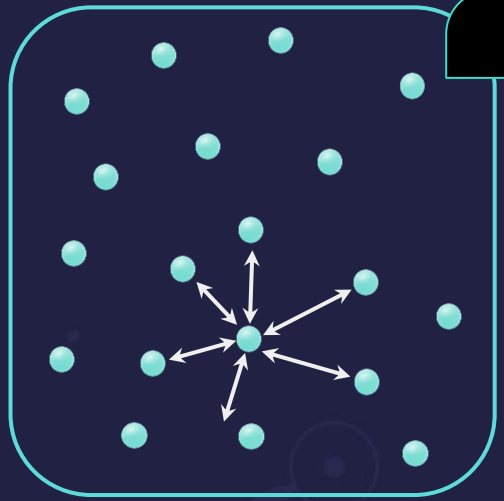
Real Gases

Interparticle forces of attraction are present

Ideal gas



Real gas



van der Waals Equation of Real Gases

$P_{ideal}\ V_{ideal} = nRT$

$P_{real}\ V_{real} \neq nRT$

$(P_{real} \pm __)\ (V_{real} \pm __) = nRT$

Ideal gas equation is affected by

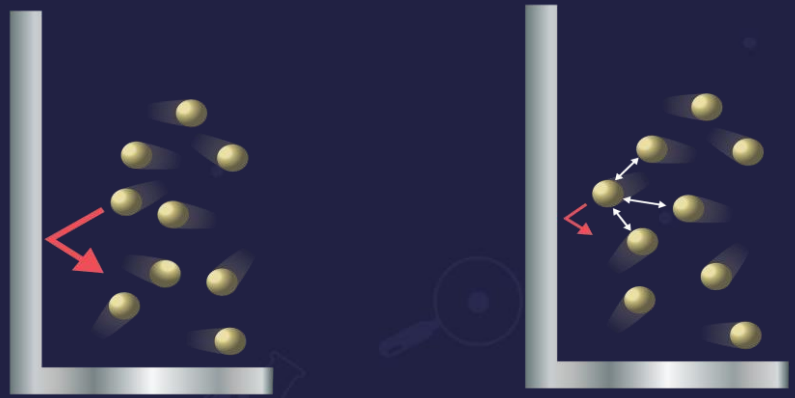
- Intermolecular forces
- Molecular volume

Pressure Correction

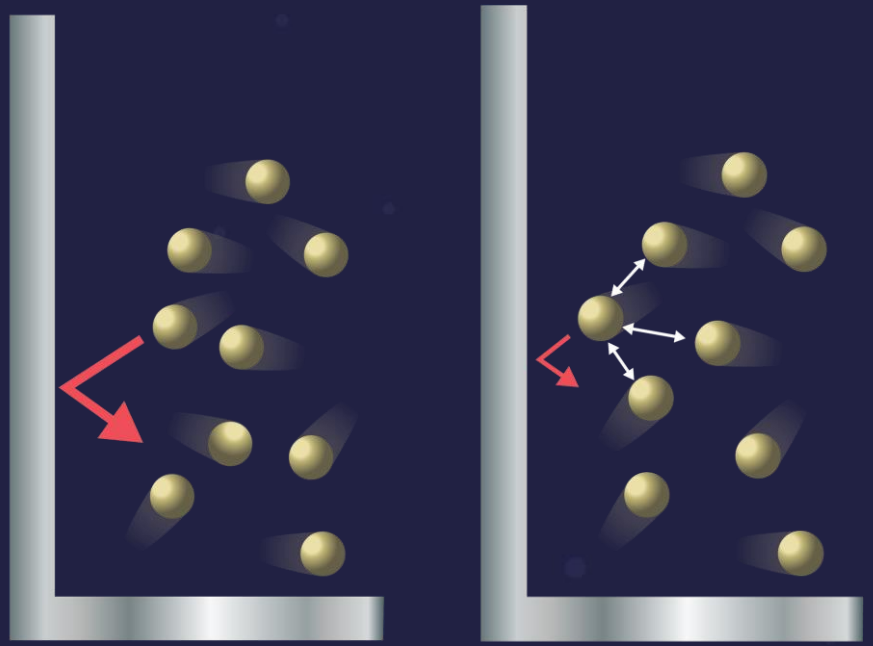
Intermolecular **Attractive forces** are present

Speed during collisions will be reduced → Momentum ↓ → Force applied ↓ → **Pressure** ↓

$P_{ideal} > P_{real}$



Pressure Correction



Molecules are dragged back by other molecules due to **intermolecular attractive forces**

$P_{ideal} = (P_{actual} + __)$

$P_{ideal} = P_{actual} +$ **Pressure correction term**

Pressure Correction

Correction term $\propto$ **Number of molecules** attracting the colliding molecule $\propto \frac{n}{V}$

Correction term $\propto$ **Concentration** of the colliding molecules $\propto \frac{n}{V}$

Pressure Correction

Correction term $\propto \frac{n}{V} \times \frac{n}{V}$

Correction term $\propto \frac{n^2}{V^2}$

Correction term $= \frac{an^2}{V^2}$

a van der Waals constant

'a' depends on force of attraction

Unit of "a"

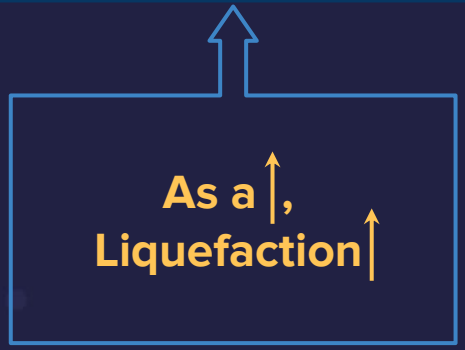
$$P_{correction} = \left[\frac{an^2}{V^2}\right]$$

$$a = \frac{P_{correction}\,[V]^2}{n^2}$$

$$\text{Unit} = \text{atm } L^2 \text{ mol}^{-2}$$

Significance of 'a'

Stronger the forces of attraction, greater will be 'a'



Value of 'a' depends on the nature of the gas

Remember!!

a ↑ → Boiling Point ↑

a (Polar molecules) > a (Non polar molecules)

For **non polar** molecules

Surface area ↑ → van der Waals forces ↑ → a ↑

Volume Correction

V_{ideal} = Volume available for free movement of the gaseous molecules

V Volume of container

V_{ideal} = V - Volume not available for free movement

$V_{ideal} = V_{container} - V_{excluded}$

$V_{excluded}$ Volume that is **not available** for free movement is called excluded volume

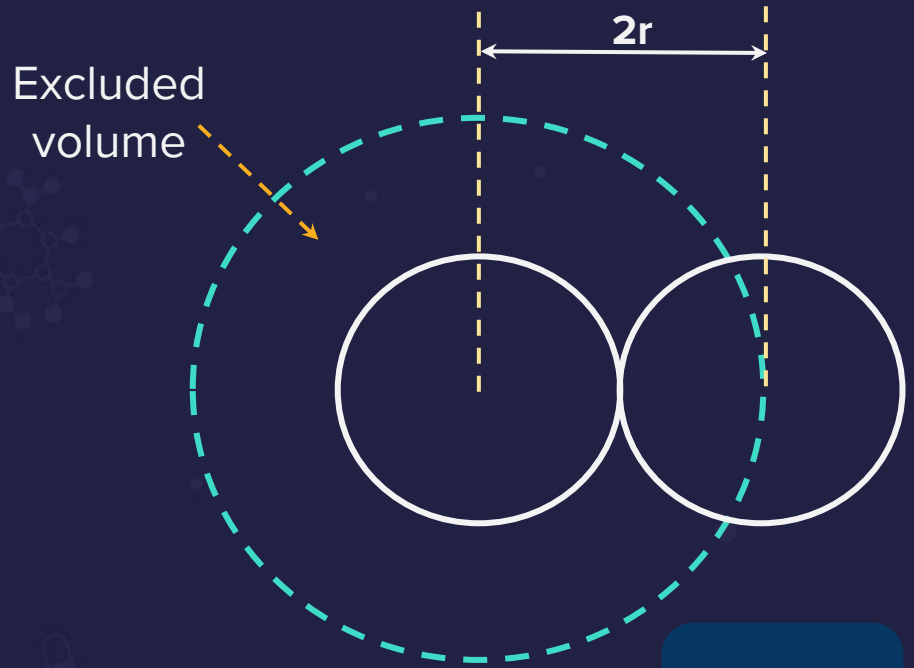
Remember!!

For **ideal** gas $V_i = V$

For **real** gas $V_i \neq V$

All volume is not available for free movement

Volume Correction



For a pair of molecules

$$V_{excluded} = \frac{4}{3}\pi (2r)^3$$

For a molecule,

$$V_{excluded} = \frac{1}{2}\left[\frac{4}{3}\pi (2r)^3\right] = 4\left[\frac{4}{3}\pi r^3\right]$$

Volume Correction

b Excluded volume per mole of gas

b van der Waals constant

'b' depends on size of the gas molecules

$b = 4 \times$ Volume of individual molecules $\times N_A$

$b = 4 \times \frac{4}{3} \pi r^3 \times N_A$

$b \propto$ Size of the molecules

Volume Correction and Unit of "b"

For n moles

$V_{excluded} = nb$

$V_{ideal} = V - nb$

$[V] = [nb]$

$b = \frac{[V]}{n}$

$Unit = L\ mol^{-1}$

Remember!!

If two gases have the **same 'b'** but **different 'a'** then

Gas having the **larger value of 'a'** will occupy **lesser volume**

Force of attraction ↑ ⇢ Distance between the molecules ↓

van der Waals Equation of Real Gases

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

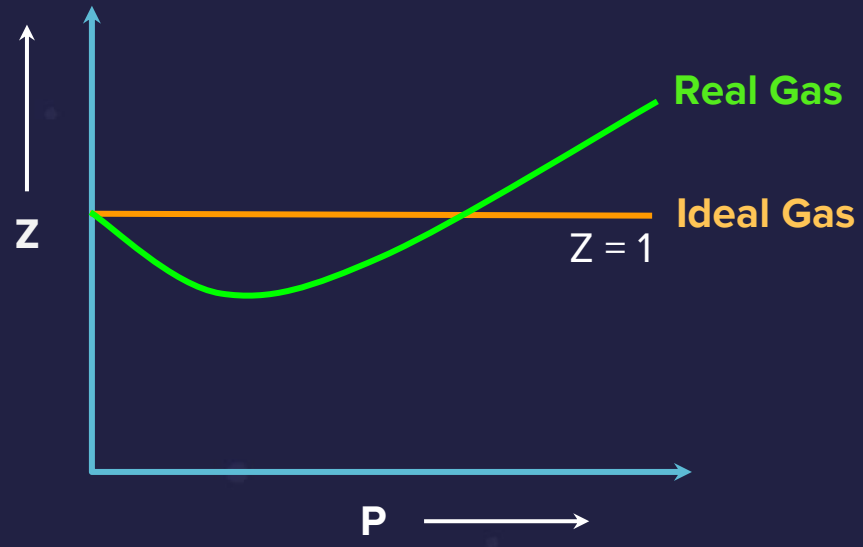
Pressure correction term

Volume correction term

- a & b = van der Waals constants
- n = Number of moles of gas

Verification of
van der Waals equation

Compressibility Factor



van der Waals Equation

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

$$V_m = \frac{V}{n} = \text{Volume of 1 mole of gas}$$

Verification of van der Waals Equation

1

At Low pressure (moderate temperature)

Pressure ↓ V_m ↑ b can be neglected in comparison to V_m

$$\left[P + \frac{a}{V_m^2}\right] V_m = RT$$

$$PV_m + \frac{a}{V_m} = RT$$

$$\frac{PV_m}{RT} + \frac{a}{V_m RT} = 1$$

Verification of van der Waals Equation

$$\frac{PV_m}{RT} \longrightarrow Z = 1 - \frac{a}{V_m RT}$$

$$Z < 1$$

Real gas is **more compressible** as compared to an **Ideal gas**

Verification of van der Waals Equation

2 At high pressure (moderate temperature)

Pressure ↑ V_m ↓

b can't be neglected in comparison to V_m

Pressure ↑ $\frac{a}{V_m^2}$ can be neglected

Verification of van der Waals Equation

$$P\ (V_m - b) = RT$$

$$Z = 1 + \frac{Pb}{RT}$$

$$PV_m - Pb = RT$$

$$Z > 1$$

$$\frac{PV_m}{RT} = 1 + \frac{Pb}{RT}$$

Real gas is **less compressible** as compared to an **Ideal gas**

Verification of van der Waals Equation

3 Real gas having very large molar volume

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

b ⇢ can be neglected in comparison to V_m

V_m is very large ⇢ $\frac{a}{V_m^2}$ can be neglected

Verification of van der Waals Equation

$PV_m \simeq RT$

$Z \simeq 1$

Ideal gas condition

4 H_2 / He

$a \simeq 0$

$Z = 1 + \frac{Pb}{RT} > 1$

Liquefaction of Gases

Phenomenon of converting a **gas into liquid**

Occurs when the **intermolecular forces of attraction become high**

Gas liquification

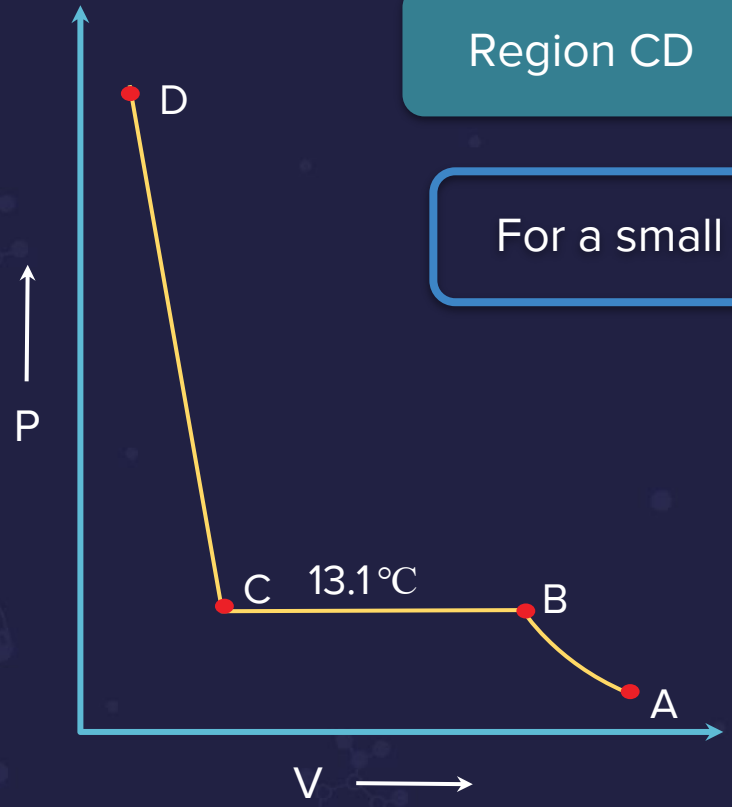
Pressure ↑

Temperature ↓

Andrew's Isotherm

P - V relationship
(isotherms)
for CO_2

Andrew's Isotherm

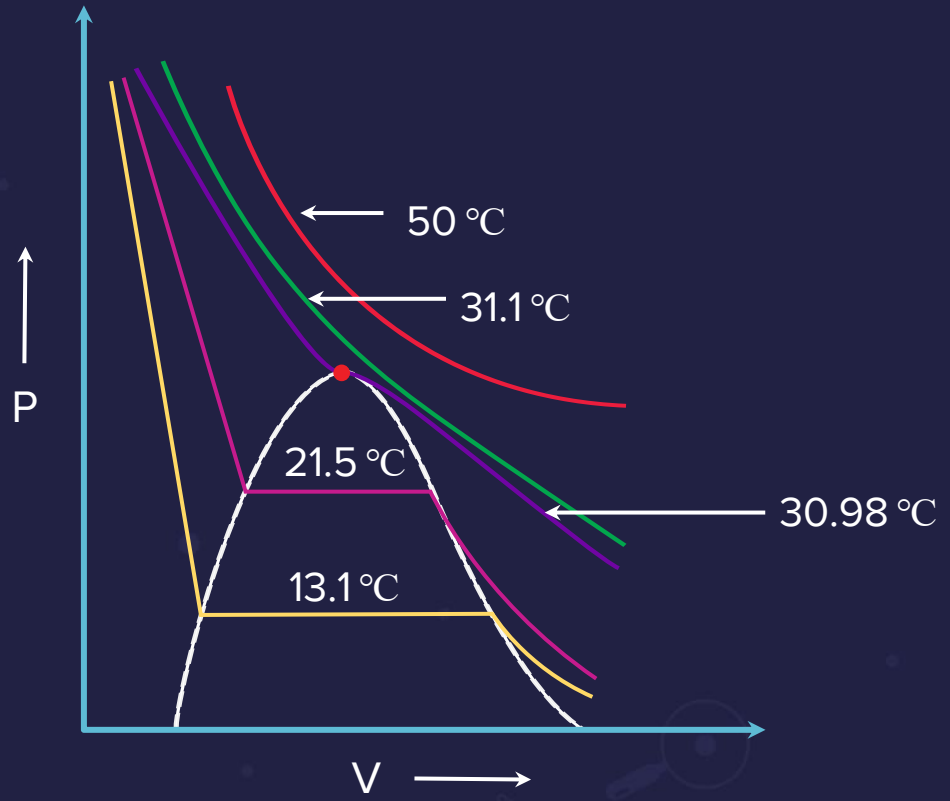


Region CD ---> Compression of liquid at constant T

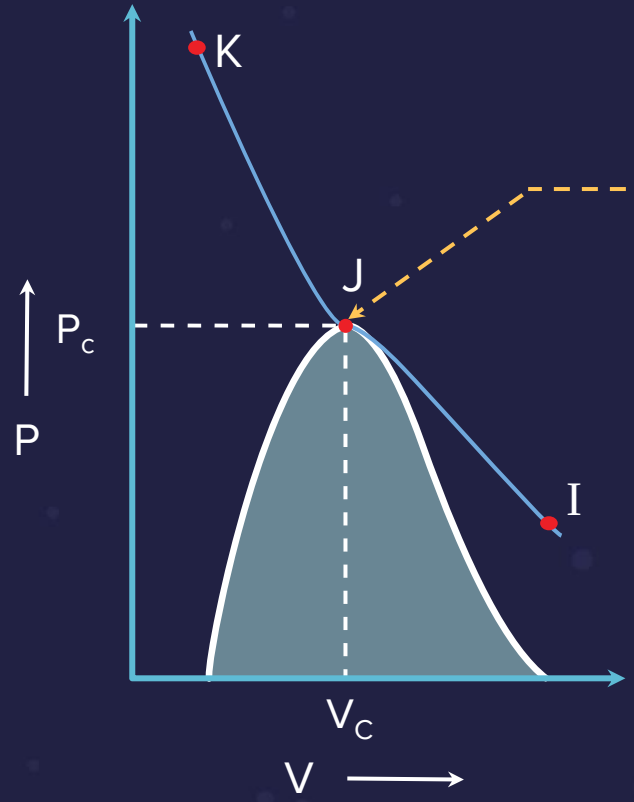
For a small volume change, high pressure is required

The 'Dome' of Andrew's Isotherm

Different isotherms for the same gas



Critical Isotherm

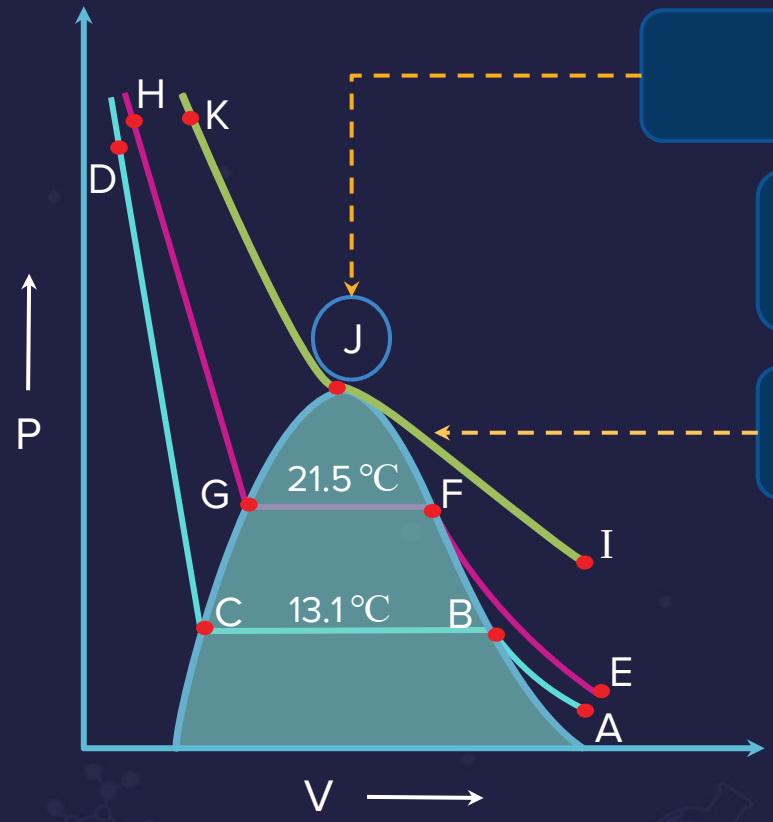


Critical point

Critical Point

A point on the critical isotherm where **gas & liquid are in equilibrium**

Critical Isotherm



Critical Point
(**Point of inflection**)

$$\frac{\partial P}{\partial V} = \frac{\partial^2 P}{\partial V^2} = 0$$

Critical isotherm

At critical point

ΔH_{vap} = 0

Critical Temperature (T_C)

Temperature **above** which the gas **cannot be liquefied**, regardless of the pressure

Below T_c

Two phases can be **distinguished**

At T_c

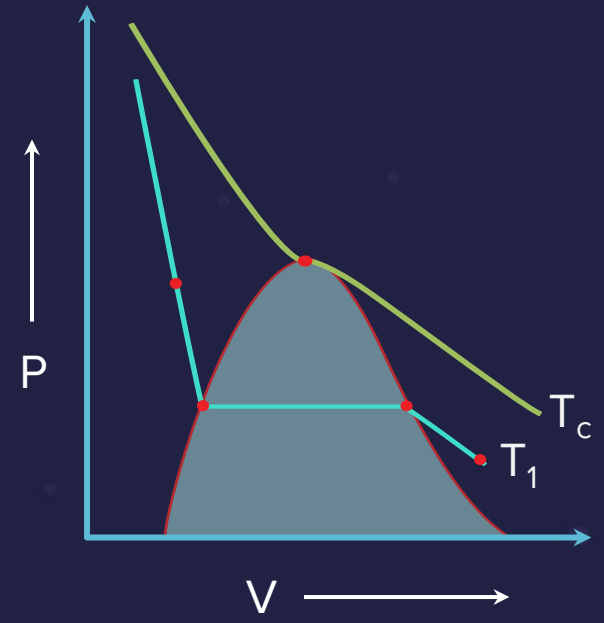
Liquid passes into the **gaseous phase** continuously and the boundary between the two phases disappears

Continuity of States

At the **critical temperature (T_C)**, the densities of the liquid & the vapour phase becomes identical

No distinction between vapour & liquid

Density Variation with Temperature



At T_1,

Density of liquid	>	Density of vapour

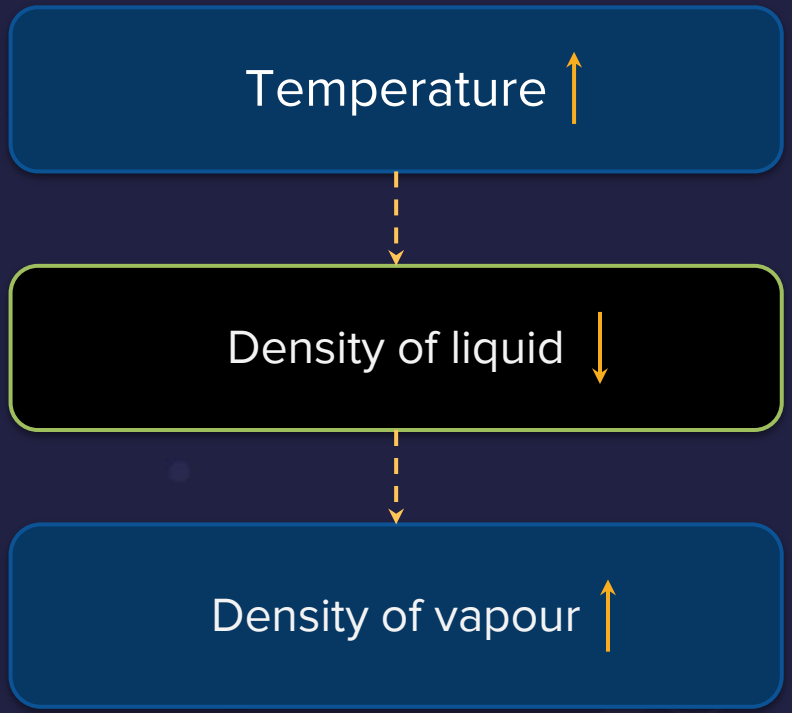
At T_C,

Density of liquid	=	Density of vapour

At $T_1 < T_C$ ⇢ **Gas can be liquefied**

Density Variation with Temperature

In liquid-vapour equilibrium region



Did you know?

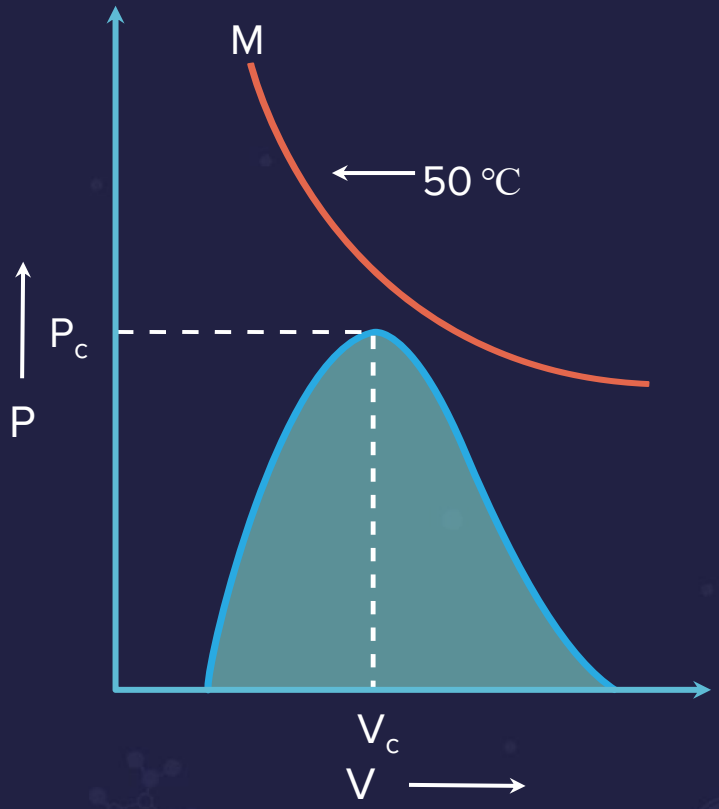
Term **vapour** is used when

$T < T_c$

Term **gas** is used when

$T > T_c$

Critical Temperature (T_C)



At $T > T_C$

Gas can't be liquefied for any amount of pressure

Significance of Critical Temperature

As **intermolecular forces** increase, T_c also increases

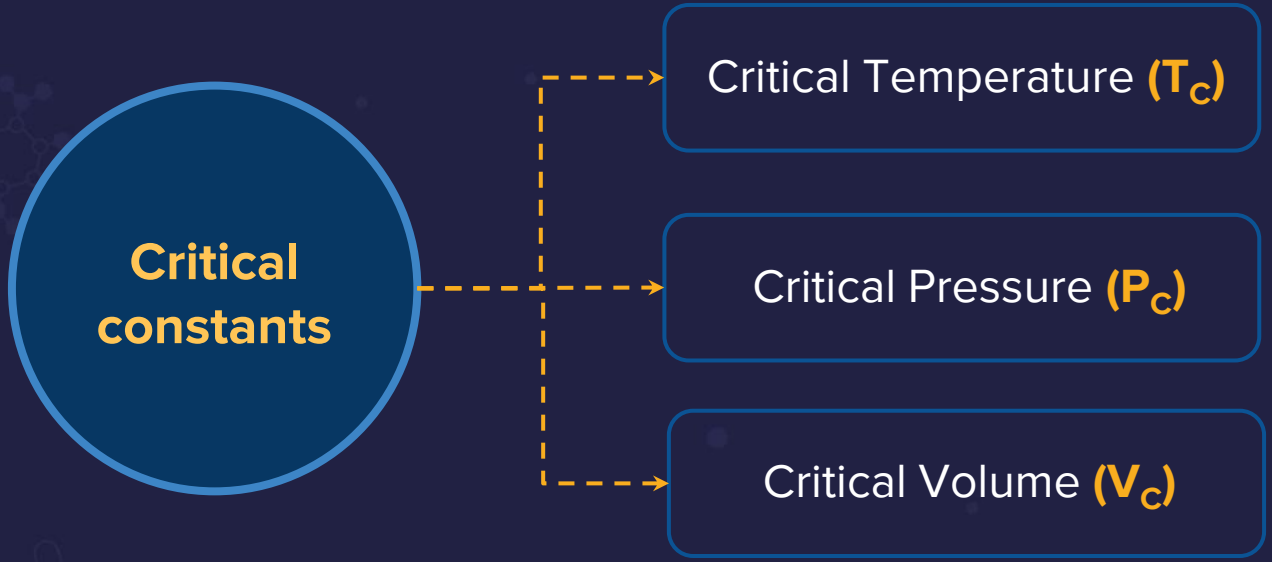
Ease of liquefaction ↑

Critical Pressure (P_C) and Critical Volume(V_C)

Minimum pressure which must be applied **at critical temperature** to convert a **gas into liquid**

Volume occupied by one mole of a gas **at critical temperature (T_C) & critical pressure (P_C)**

Critical Constants



Critical Constants in Terms of van der Waals Constants

$$V_C = 3b$$

$$P_C = \frac{a}{27b^2}$$

$$T_C = \frac{8a}{27Rb}$$

Value of V_C is not reliable as it can't be measured properly

Determine van der Waals constants ('a' & 'b') using T_C & P_C

Compressibility Factor & Critical Constants

For every gas,

$$Z_C = \frac{P_C V_C}{RT_C} = \frac{\frac{a}{27b^2} \times 3b}{R \times \frac{8a}{27Rb}} = \frac{3}{8} = 0.375$$

Virial Equation of State

Generalised equation
of gaseous state

Z is expressed in power series expansion of **P** or $\frac{1}{V_m}$

Virial Equation of State

$$Z = \frac{PV_m}{RT} = 1 + \frac{B}{V_m} + \frac{C}{V_m^2} + \frac{D}{V_m^3} + \ldots\ldots\ldots\ldots$$

- 1 ⇒ First virial coefficient
- B ⇒ Second virial coefficient
- C ⇒ Third virial coefficient
- D ⇒ Fourth virial coefficient

van der Waals Equation in Virial Form

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

For 1 mol, $V = V_m$

$$\left[P + \frac{a}{V_m^2} \right] [V_m - b] = RT$$

van der Waals Equation in Virial Form

$$P = \frac{RT}{V_m - b} - \frac{a}{V_m^2}$$

Multiplying both sides by $\frac{V_m}{RT}$

$$\frac{PV_m}{RT} = \frac{V_m}{V_m - b} - \frac{a}{V_m RT}$$

Also,

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

$$Z = \frac{V_m}{V_m - b} - \frac{a}{V_m RT}$$

van der Waals Equation in Virial Form

$$Z = \frac{1}{1 - \left[\frac{b}{V_m}\right]} - \frac{a}{V_m RT}$$

Using binomial expansion formula,

$$\frac{1}{1 - x} = (1 - x)^{-1} = 1 + x + x^2 + x^3 + \ldots.$$

where $x << 1$

van der Waals Equation in Virial Form

$$Z = \left[1 + \frac{b}{V_m} + \frac{b^2}{V_m^2} + \frac{b^3}{V_m^3} + \ldots\ldots\right] - \frac{a}{V_m RT}$$

$$Z = 1 + \frac{1}{V_m}\left[b - \frac{a}{RT}\right] + \frac{b^2}{V_m^2} + \frac{b^3}{V_m^3} + \ldots\ldots$$

van der Waals Equation in Virial Form

$$Z = 1 + \frac{1}{V_m}\left[b - \frac{a}{RT}\right] + \frac{b^2}{V_m^2} + \frac{b^3}{V_m^3} + ...$$

Comparing van der Waals equation with Virial equation

$$Z = 1 + \frac{B}{V_m} + \frac{C}{V_m^2} + \frac{D}{V_m^3} + ...$$

van der Waals Equation in Virial Form

$$B = b - \frac{a}{RT}$$

$$C = b^2$$

$$D = b^3$$

At **low pressure**, V_m will be very **large**.

Hence, $\frac{1}{V_m^2}$, $\frac{1}{V_m^3}$, ... and higher terms can be neglected.

$$Z = 1 + \left[b - \frac{a}{RT} \right] \frac{1}{V_m}$$

Only '**B**' is temperature dependent, all other virial coefficients are independent of temperature

van der Waals Equation in Virial Form

At **low pressure**, V_m will be very **large**.

Hence, $\frac{1}{V_m^2}$, $\frac{1}{V_m^3}$, ... and higher terms can be neglected.

$$Z = 1 + \left[b - \frac{a}{RT} \right] \frac{1}{V_m}$$

van der Waals Equation in Virial Form

If $\left[b - \frac{a}{RT} \right] = 0$

Then, $T = \frac{a}{Rb}$

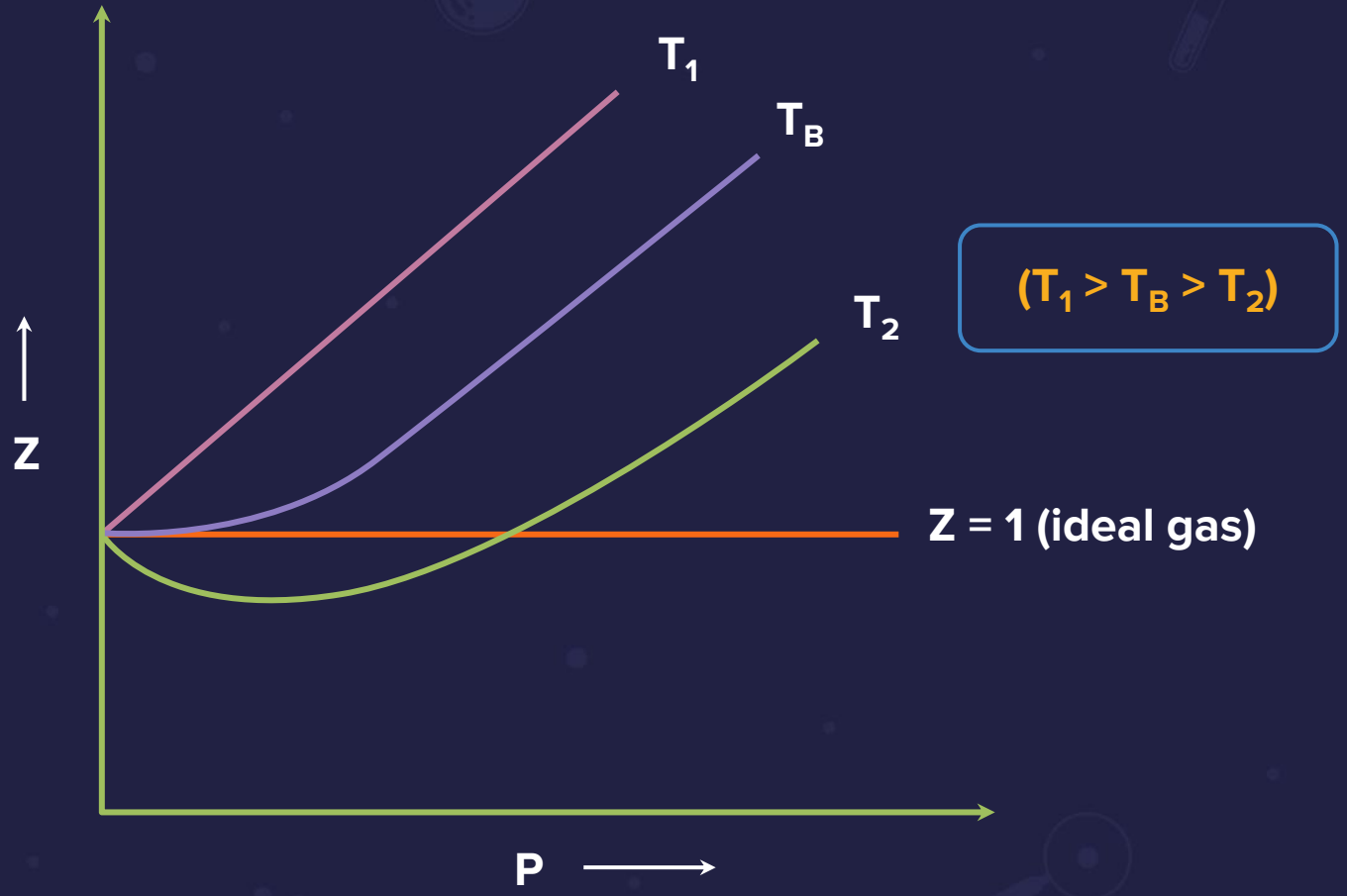
And $Z = 1$

van der Waals Equation in Virial Form

At $T = \frac{a}{Rb}$ ⇢ At low pressure

Gas will behave as an **ideal gas**

This **temperature** is known as the **Boyle temperature (T_b)**


T_1
T_B
T_2
Z
P
$(T_1 > T_B > T_2)$
Z = 1 (ideal gas)