Welcome to

Aakash + BYJU'S LIVE

States of matter

Something that occupies **space** and has **mass**

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

Matter

- Solid
- Liquid
- Gas

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

Intermolecular Forces

Intermolecular Forces

Attractive

Repulsive

Intermolecular Attractive Forces

Attractive Forces

- Dipole-dipole attraction → Between polar molecules
- Instantaneous dipole-induced dipole attraction → Between non-polar molecules
- Ion-induced dipole attraction → Between ion and non-polar molecule
- Ion-dipole attraction → Between ion and polar molecule
- Dipole-induced dipole attraction → Between polar and non-polar molecules

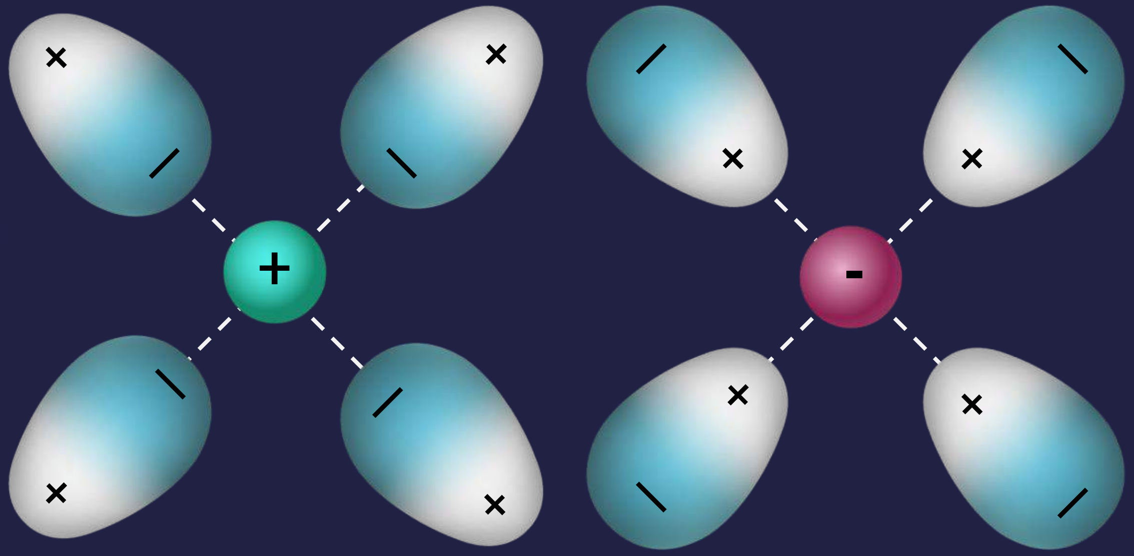
Ion-Dipole Attraction

Ion ← Electrostatic Force → Polar Molecule (Dipole)

Strength of attraction $\propto$ **Charge density** on the ion

Strength of attraction $\propto$ **Dipole moment** of the polar molecule

Ion-Dipole Attraction



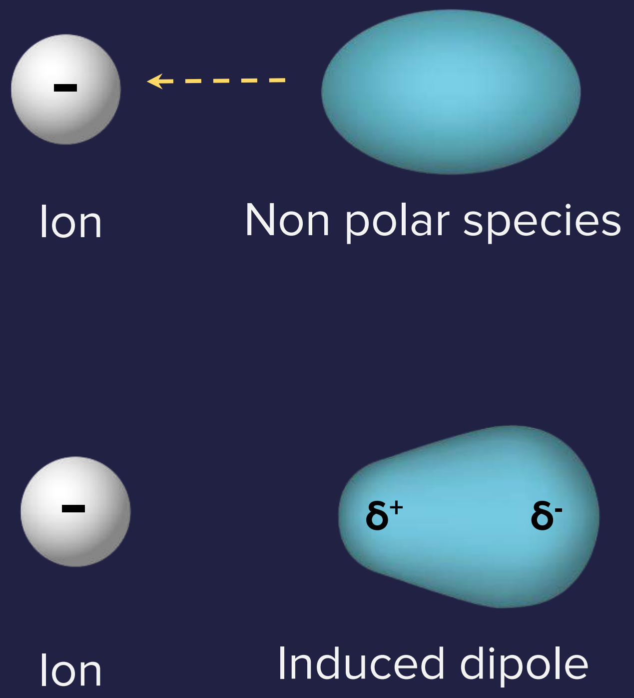
Cation-dipole attractions

Anion-dipole attractions

Ion - Induced Dipole Attraction

Ion ← Electrostatic Force → Non polar Molecule (Induced Dipole)

Ion - Induced Dipole Attraction



van der Waals Forces

van der Waals forces

Dipole-dipole forces	Dipole-induced dipole forces	Dispersion forces
Keesom forces	**Debye forces**	**London forces**

Dipole-Dipole Attraction

Exists between **polar molecules**

Electrostatic attractions between the **oppositely charged** ends of permanent dipoles

Due to this force, gases can be **liquified**

Dipole-Dipole Attraction

For stationary polar molecules → Interaction energy $\propto \frac{1}{r^3}$

For rotating polar molecules → Interaction energy $\propto \frac{1}{r^6}$

r — Distance between the polar molecules

Dipole-Induced Dipole Attraction

Exists between a **polar** and a **non-polar molecule**

Permanent dipole **deforms the electron cloud** of the non polar molecule

Induced dipole gets developed in the non polar molecule

Dipole-Induced Dipole Attraction

Permanent dipole

Non-polar species

Permanent dipole

Induced dipole

Induced dipole moment depends upon

Dipole moment present in the **permanent dipole**

Polarizability of the non-polar molecule

Dipole-Dipole Attraction

Exists between **polar molecules**

Electrostatic attractions between the **oppositely charged** ends of permanent dipoles

Due to this force, gases can be **liquified**

Dispersion Forces

London forces $\propto$ Molecular mass

London forces $\propto$ Molecular volume (or surface area)

Dispersion Forces

Molecular mass ↑

- F_2, Cl_2 → Gases
- Br_2 → Liquid
- I_2 → Solid

Exists in **atoms & non-polar molecules** like H_2, O_2, Cl_2, etc,. in **solid or liquid states**

↓

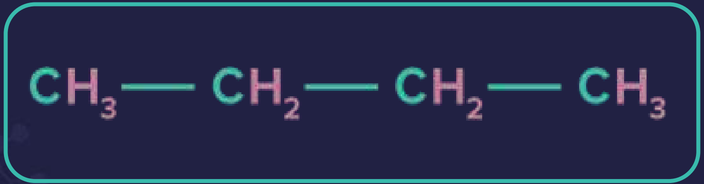
Which are **electrically symmetrical** & have **no permanent dipole**

Strength of London Forces

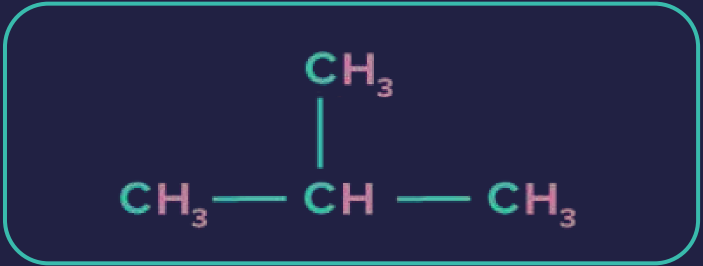
If **molecular mass** is **same**, then the factor responsible is **molecular surface area**

van der Waals force $\propto$ Surface area

Strength of London Forces



A



B

Surface Area	A	>	B
Boiling Point	A	>	B

Interaction Energy v/s Distance

Type of interaction	Interaction energy $\propto \frac{1}{r^x}$
Ionic bond	$\frac{1}{r}$
Ion-dipole	$\frac{1}{r^2}$
Dipole-dipole	$\frac{1}{r^3}$

Interaction Energy v/s Distance

Type of interaction	Interaction energy $\propto \frac{1}{r^x}$
Ion-induced dipole	$\frac{1}{r^4}$
Dipole-induced dipole	$\frac{1}{r^6}$
London forces	$\frac{1}{r^6}$

Strength of Intermolecular Forces

Ion-dipole attraction

Dipole-dipole attraction

Ion-induced dipole attraction

Dipole-induced dipole attraction

Instantaneous dipole - induced dipole attraction

Strength ↓

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

Gas $\longrightarrow$ Liquid $\longrightarrow$ Solid

Predominance of **intermolecular Forces**

Gas $\longleftarrow$ Liquid $\longleftarrow$ Solid

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

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

Volume (V)

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 is the measure of hotness of the system.

Temperature (T)

T (K)	=	t (°C) + 273.15

Standard Temperature & Pressure (STP)

T	=	273.15 K
P	=	1 bar

$\left.\begin{array}{l} T = 273.15\ \text{K} \\ P = 1\ \text{bar} \end{array}\right\}$ **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

$\underbrace{\text{pressure, volume, temperature \& amount}}$ of gases

Interdependent properties,

describes the state of the gas

Gas Laws

Gas laws

- Boyle's Law
- Charles' Law
- 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

Pressure-Density Relation

According to Boyle's law,

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

Density (d) is given by,

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

m Mass

V Volume

Pressure-Density Relation

$$d = \frac{m \times P}{k_1}$$

$$d = \left(\frac{m}{k_1}\right) P$$

$$d = k'P$$

$$d \propto P$$

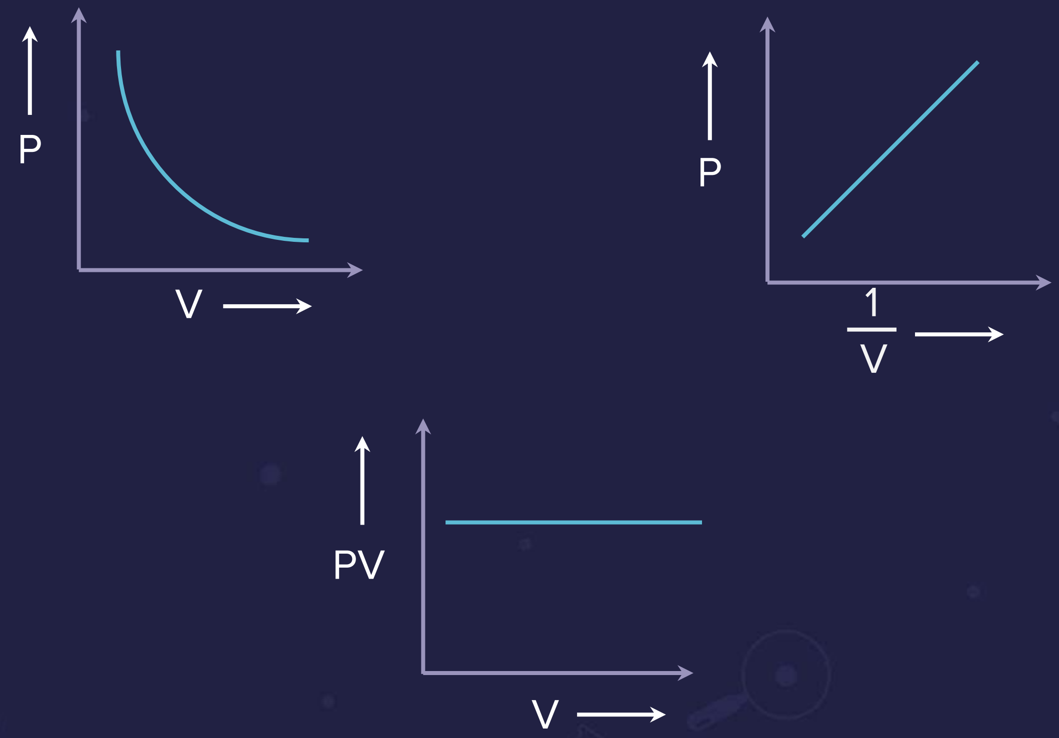
(n, T constant)

Pressure ↑

Gases become denser
(**Density** ↑)

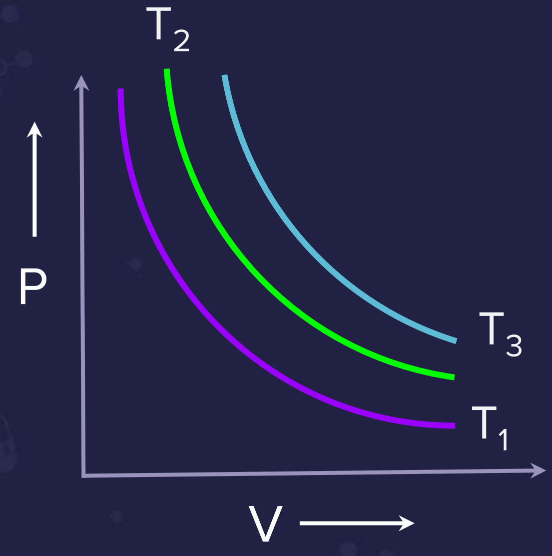
Same number of
molecules
occupy smaller space

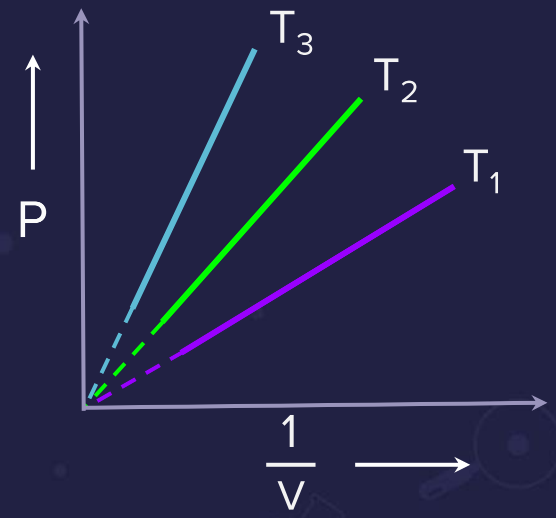
Boyle's Law



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)

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

$V = k_2 T$

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

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

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

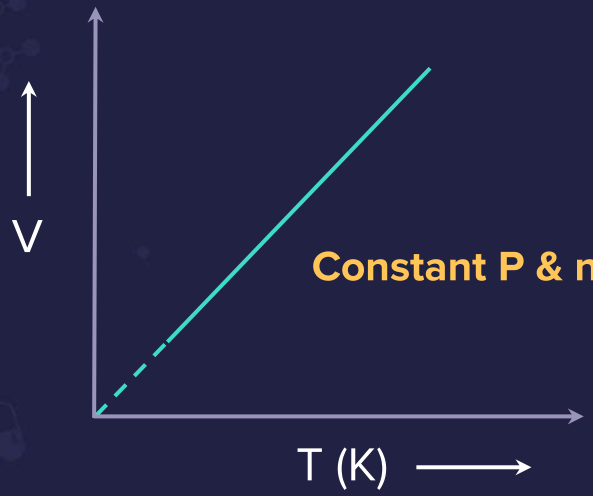
$$V_t = V_o\left(\frac{T_t}{T_o}\right)$$

T — Absolute scale or Kelvin scale or thermodynamic scale of temperature

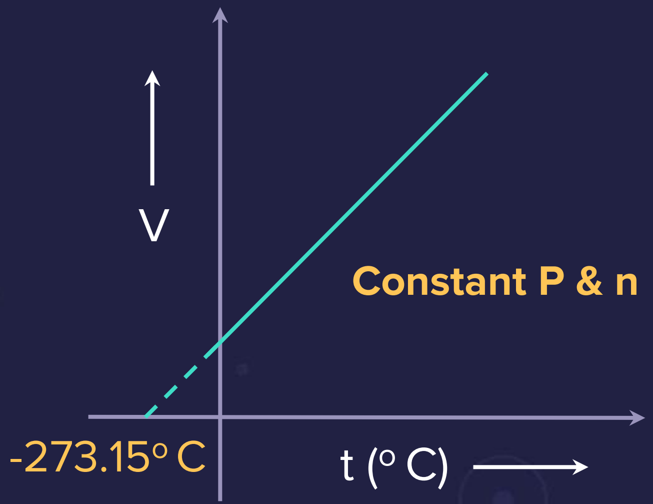
$t\ ^{o}C \Rightarrow T_t = (273.15 + t)\ K$

Charles' Law

Volume vs Temperature (K)

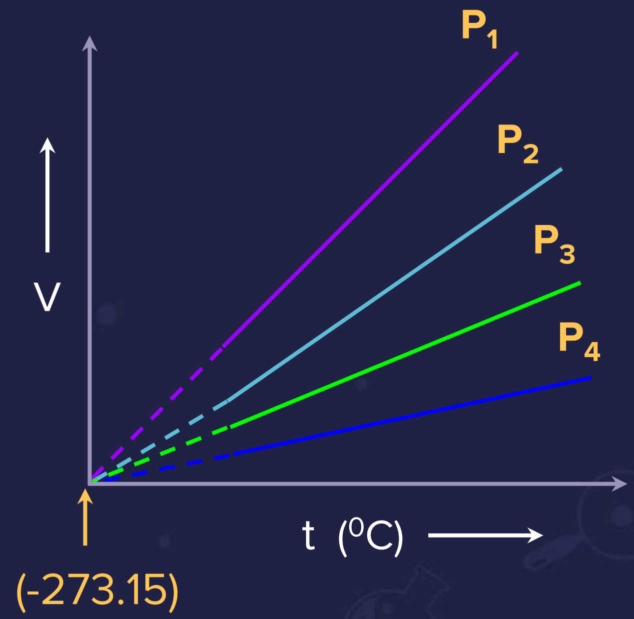


Volume vs Temperature (°C)



Charles' Law

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



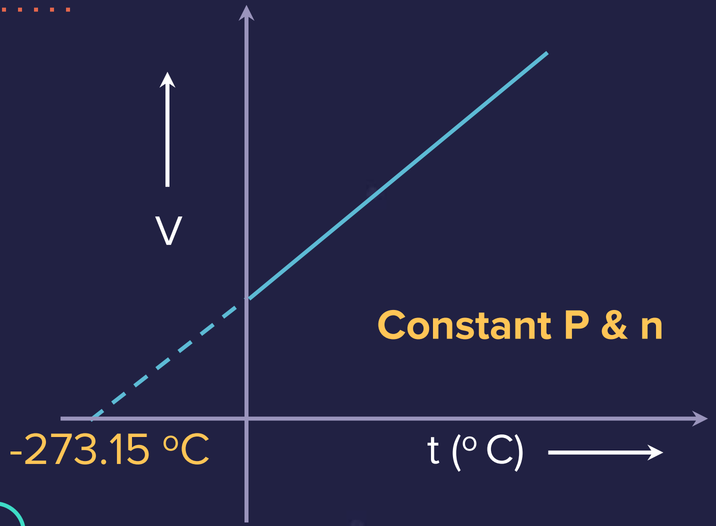
$P_1 < P_2 < P_3 < P_4$

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

Applications of Charles' Law

Athletes find it more difficult to perform in winter season!!!

When the weather is **cool**

the capacity of human lungs **decreases**

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

$$P \propto T$$

(V , n constant)

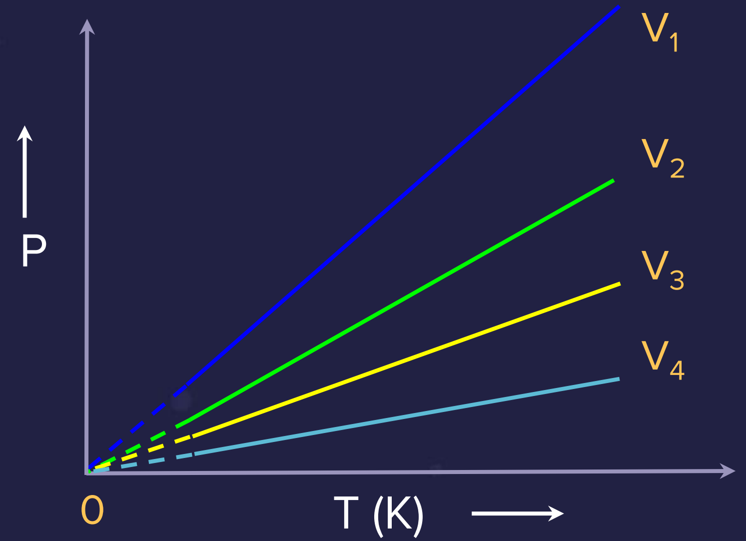
$$P = k_3 T \dashrightarrow \frac{P}{T} = k_3$$

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

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

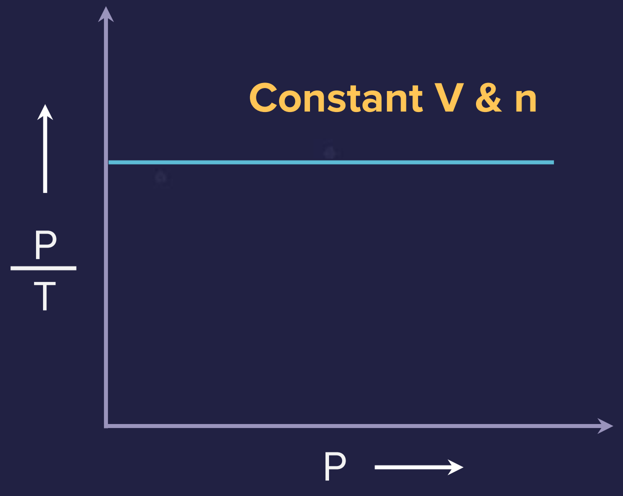
Gay-Lussac's Law

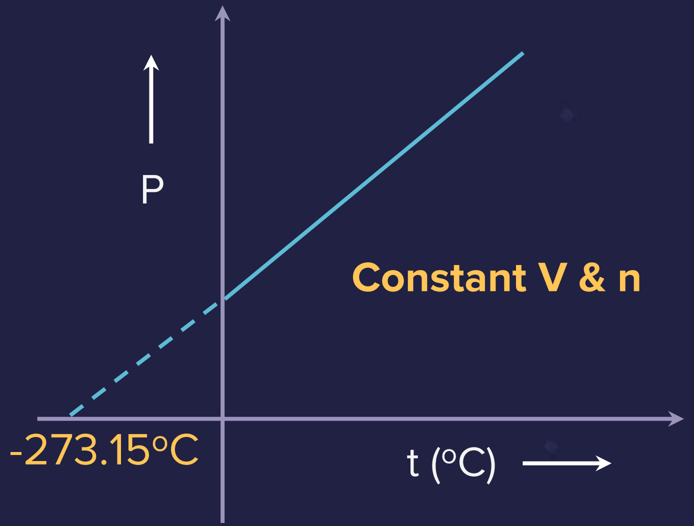
P - T **Isochores** → **Constant volume** curves



$V_1 < V_2 < V_3 < V_4$

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

$$V \propto n$$

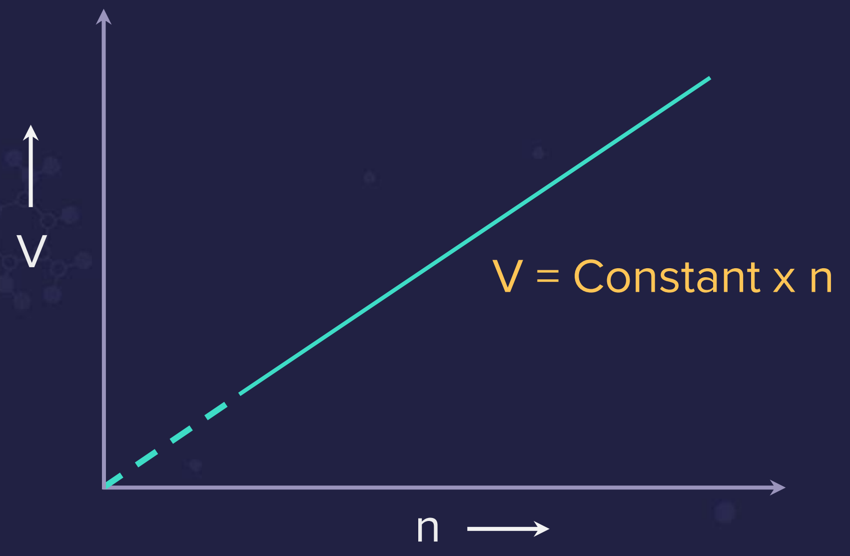
(P , T constant)

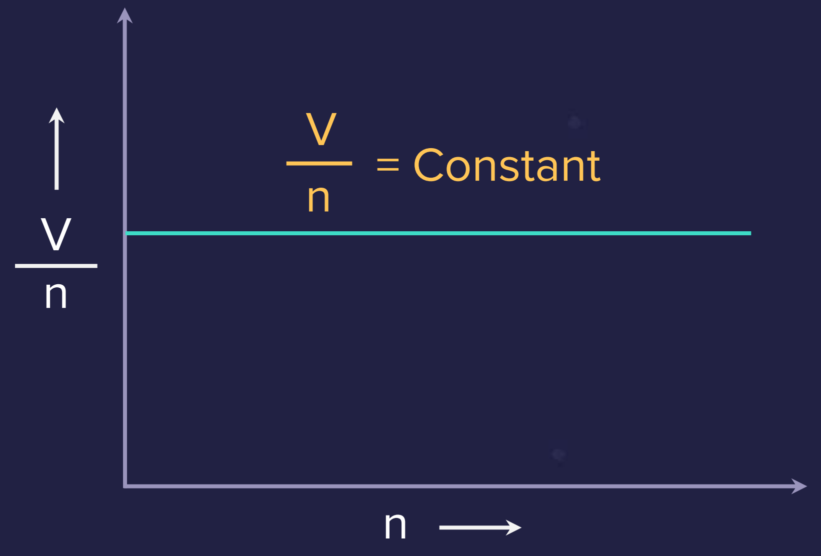
$$V = k_4 n \dashrightarrow \frac{V}{n} = k_4$$

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

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

$$PV = nRT$$

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

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

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

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

$$PM = dRT$$

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

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

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.

$$P_T = P_1 + P_2 + \ldots..$$

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

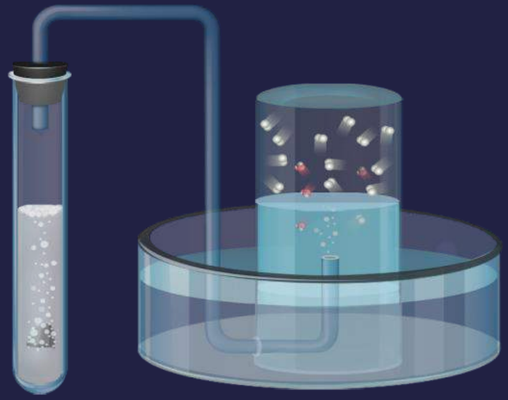
Vapour Pressure

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.**



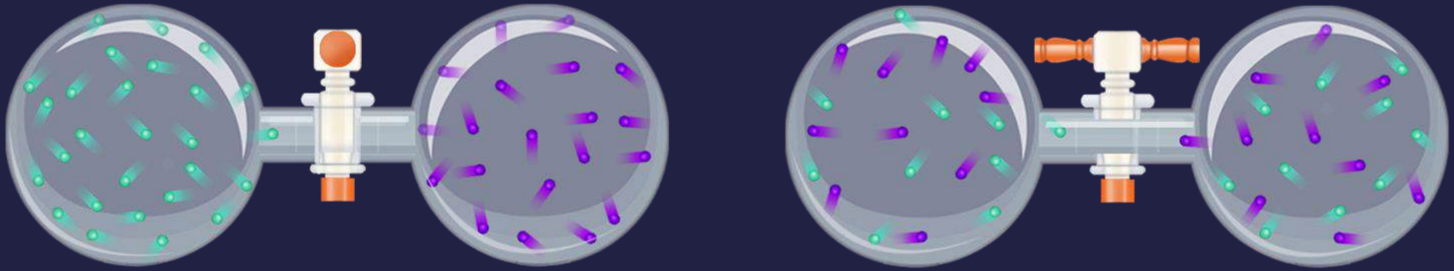
$P_T = P_g + P_w$

Pressure of dry gas

Pressure of water vapour

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

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

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

Separation of gases having different densities

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

Types of molecular speeds

- Average speed → u_{avg}
- Most Probable speed → u_{mp}
- Root Mean Square speed → u_{rms}

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} Average speed of molecules

N Total number of molecules

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

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

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

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

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'

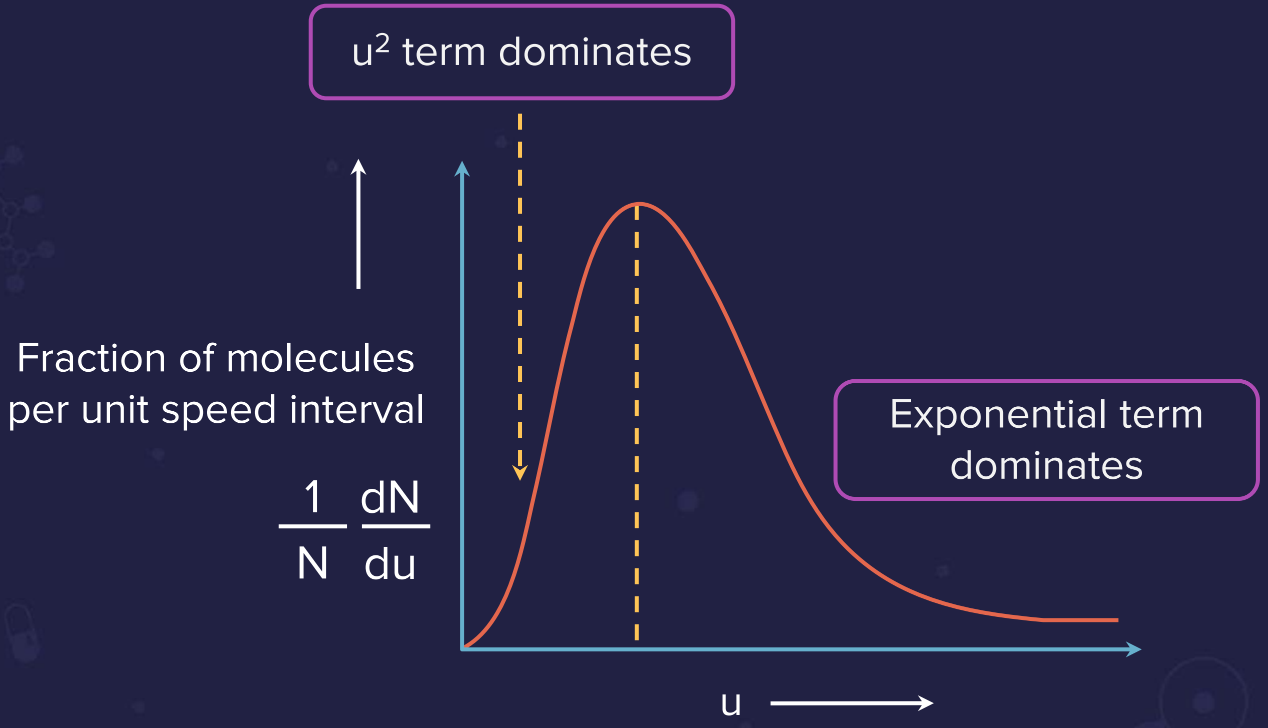
$$\frac{1}{N}\frac{dN}{du} = 4\pi\left[\frac{M}{2\pi RT}\right]^{\frac{3}{2}} e^{\frac{-Mu^2}{2RT}} u^2$$

N Total number of gas molecules

M Molar mass

u Speed

Maxwell-Boltzmann Distribution of Speeds



Maxwell-Boltzmann Distribution of Speeds

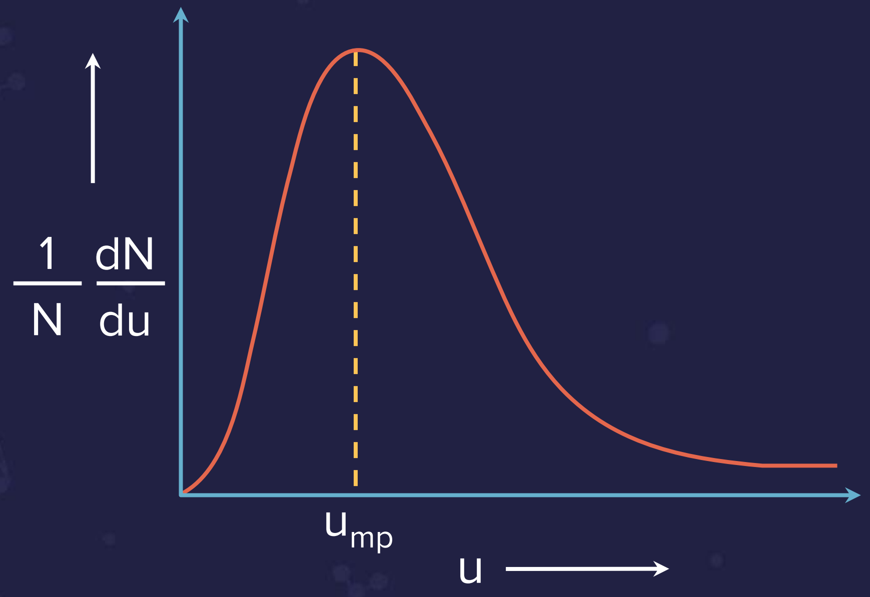
At a particular temperature,

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}

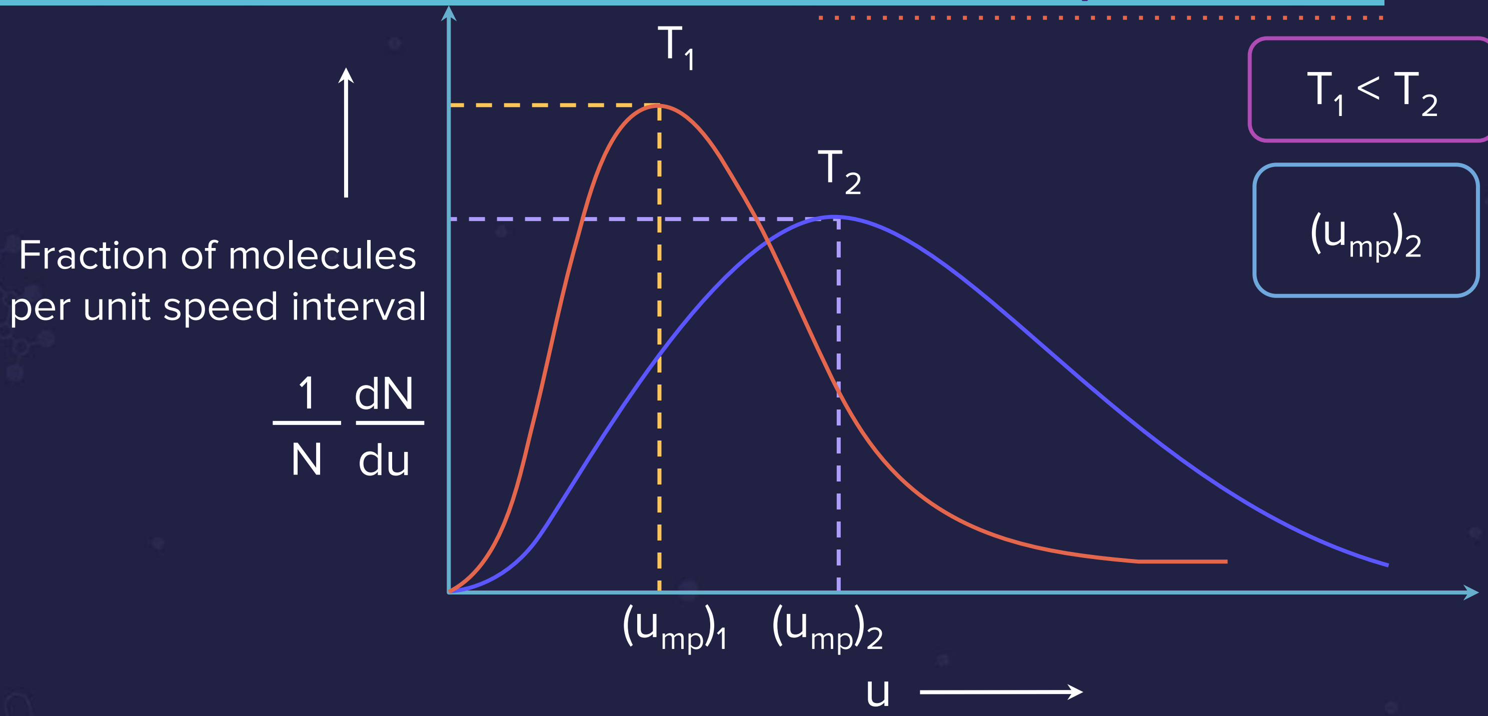


Actual distribution of **molecular speeds** in a gas depends on

Temperature

Molar Mass

Maxwell-Boltzmann Distribution of Speeds

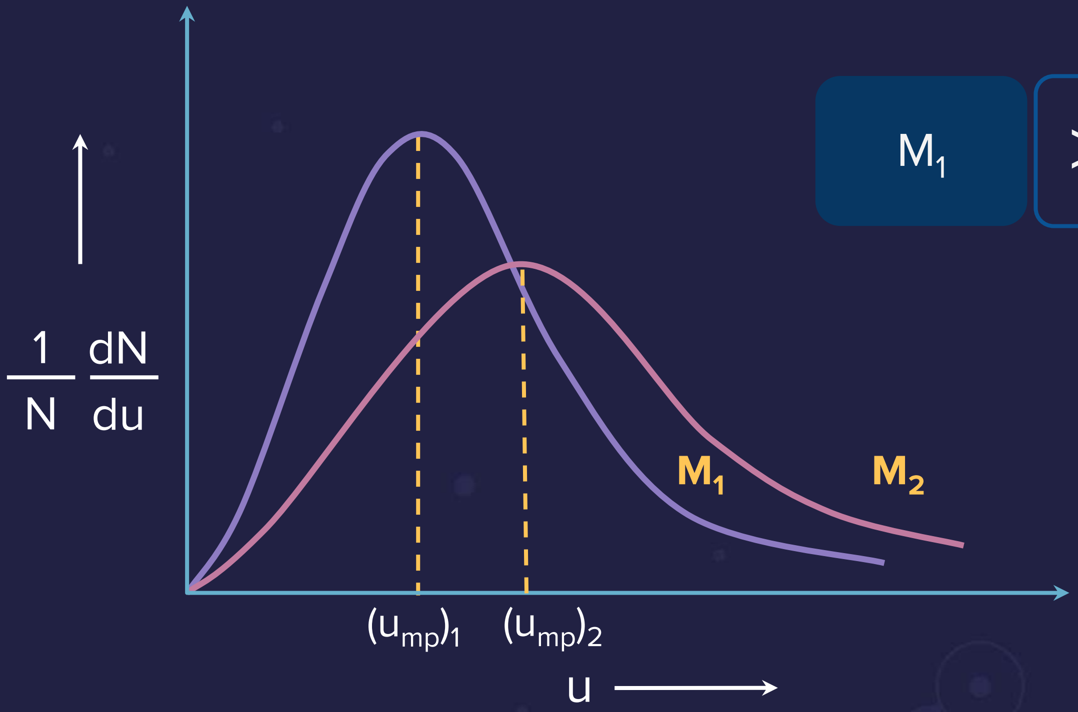


$T_1 < T_2$

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

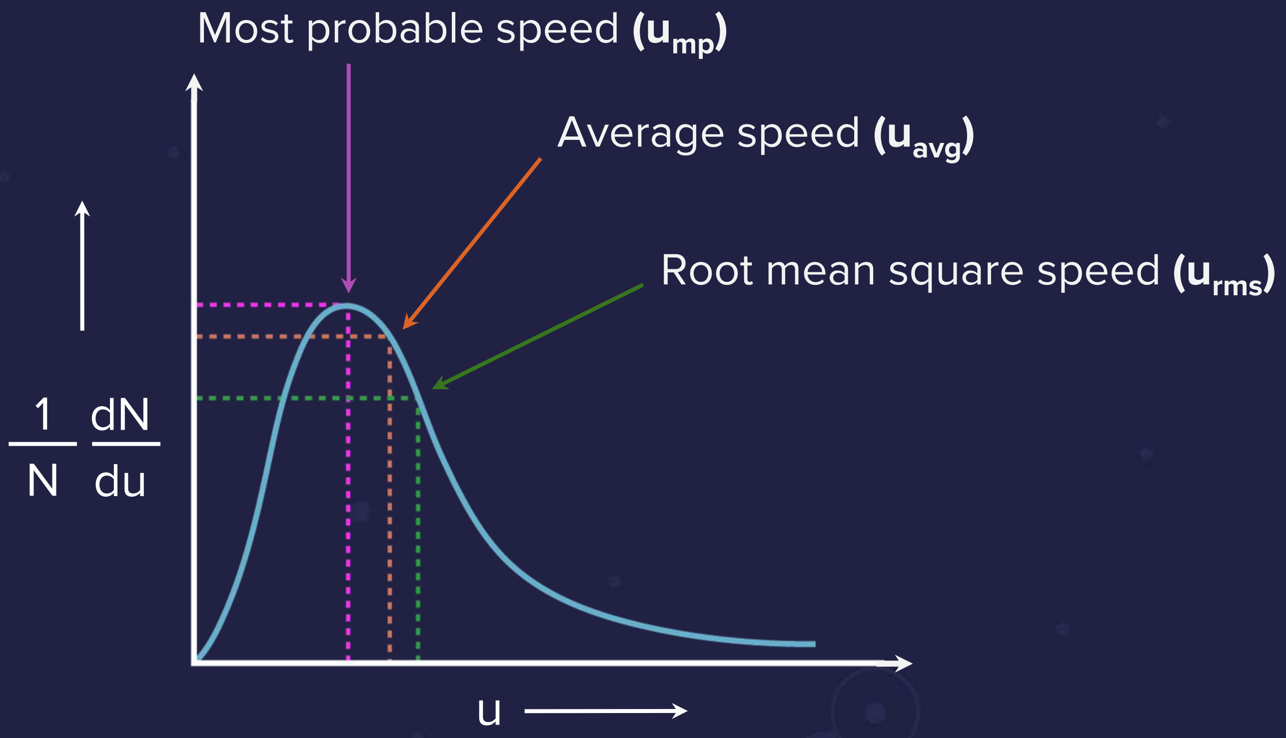
Temperature ↑ → Molecular motion becomes rapid → Entire curve shifts towards the right

Distribution of Speeds for Different Molar Masses

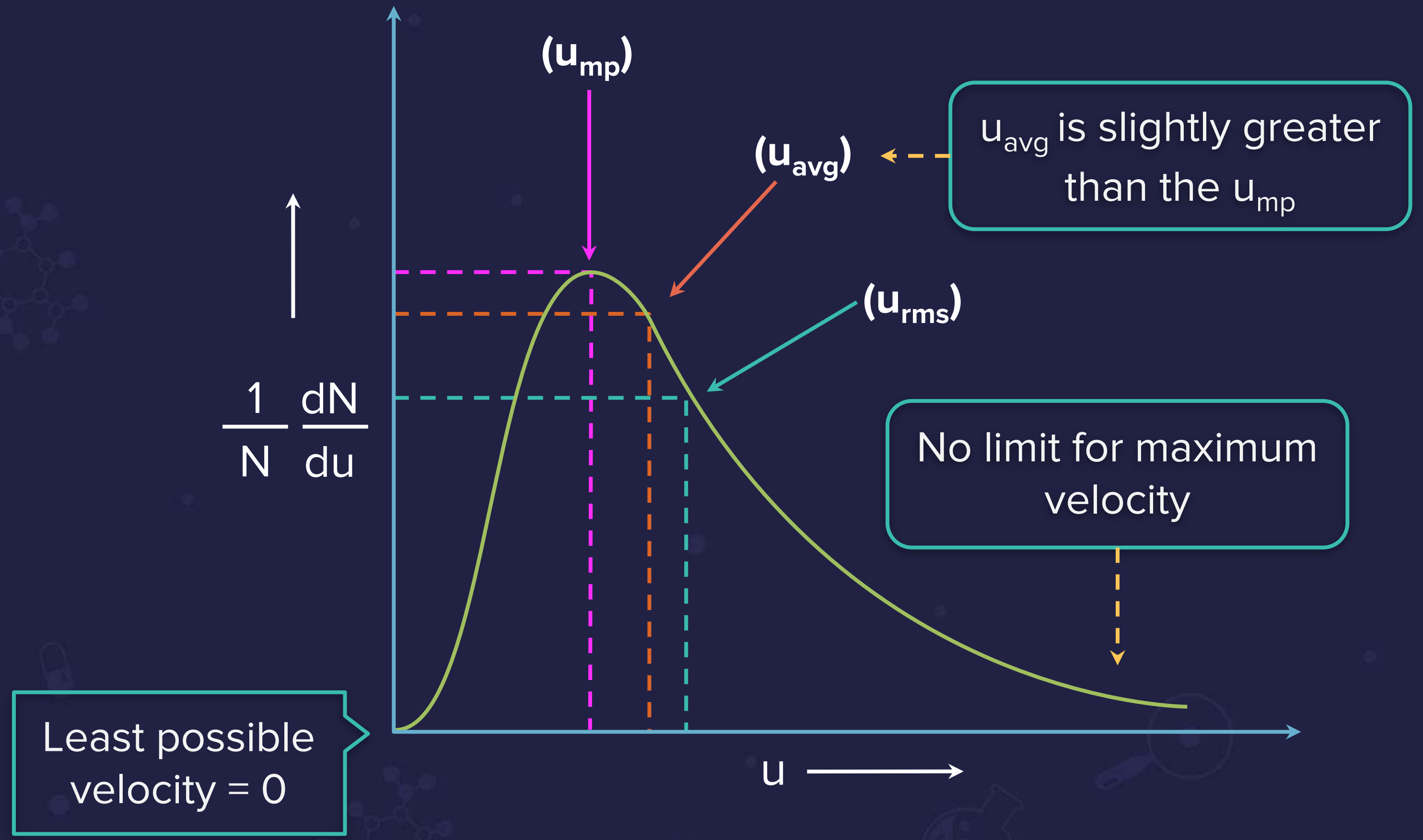


M_1 > M_2

Maxwell's Distribution of Molecular Speeds

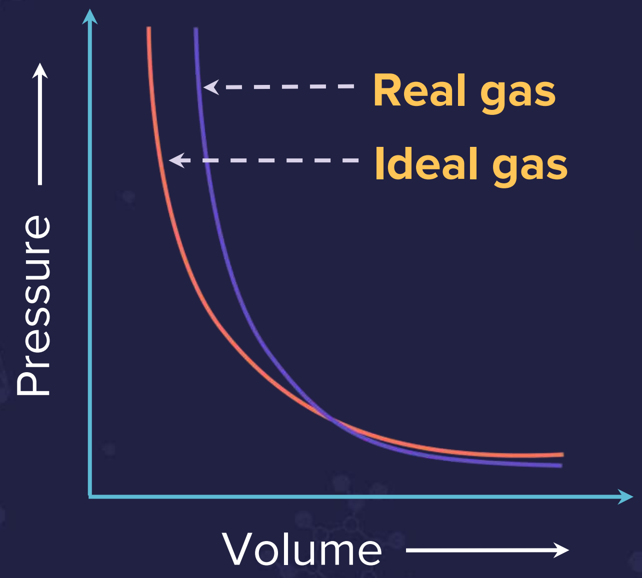


Why Average Velocity is Towards the Right?



Real Gas

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



All gases found in **universe are real gases**. Real gases can behave like ideal gas at **low pressure and high temperature.**

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

Z

- $Z = 1$ — $PV_m = RT$ — **Ideal gas behaviour**
- $Z \neq 1$ — $PV_m \neq RT$ — **Deviation from ideal behaviour**

Compressibility Factor (Z)

At very low pressure

$Z \approx 1$

Attractive forces $\approx$ Repulsive forces

At intermediate pressure

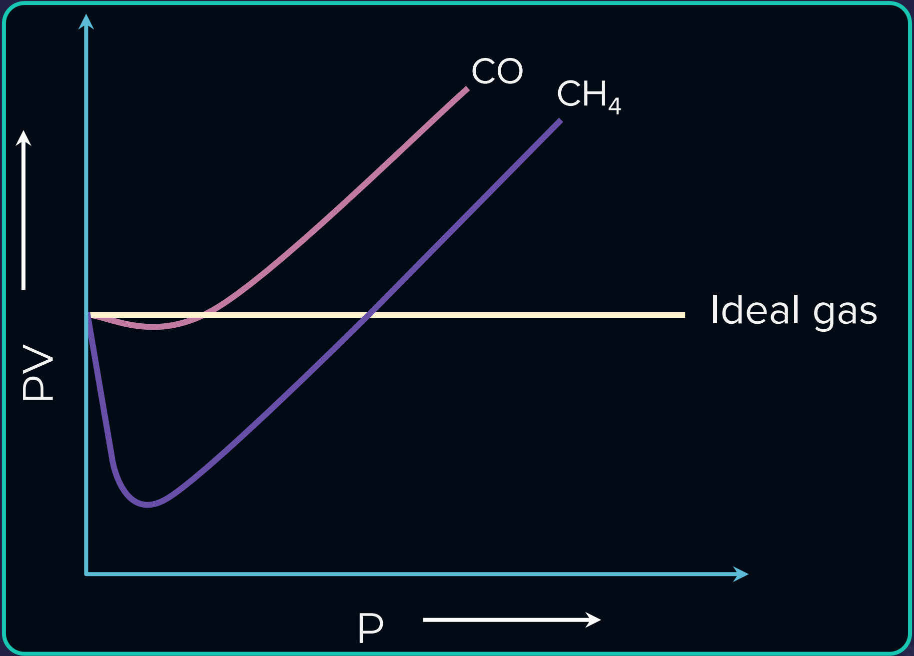
$Z < 1$

Negative deviation

Attractive forces > Repulsive forces

Gas easy to compress

Inferences from the Plot



First there is a **negative deviation** & then a **positive deviation**

Compressibility Factor (Z)

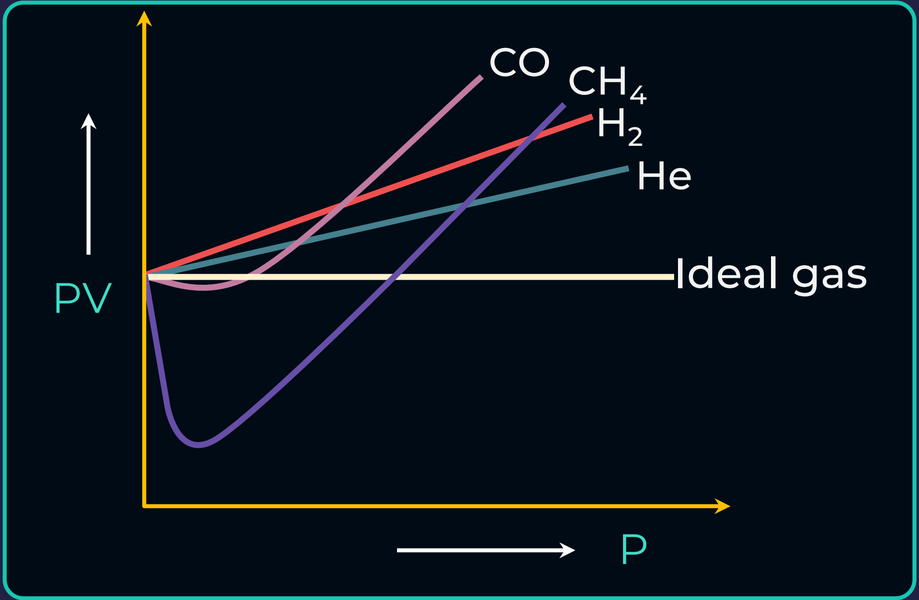
At high pressure

Z > 1 **Positive deviation**

Attractive forces < Repulsive forces

Gas difficult to compress

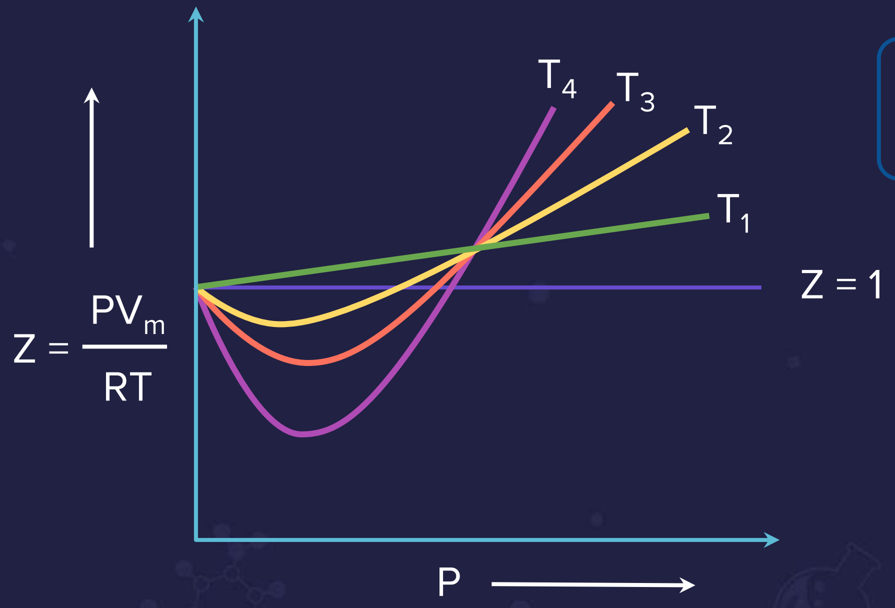
Inferences from the Plot



Ideal gas: PV vs P will be a straight line parallel to x-axis
Real gas: PV vs P is not a horizontal straight line

Different T, Same Gas

T ↑ → Collision ↑ → Repulsion ↑ → Z ↑



$T_1 > T_2 > T_3 > T_4$

For a given real gas, at very low pressure($P \to 0$), the compressibility factor, z=1 and the gas behaves ideally. At intermediate pressure where attraction dominates, z<1 and at very high pressure, where repulsion dominates, z>1.

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

$Z = 1$

- Ideal gas
- Real gas at $T = T_b$
  - Low pressure region

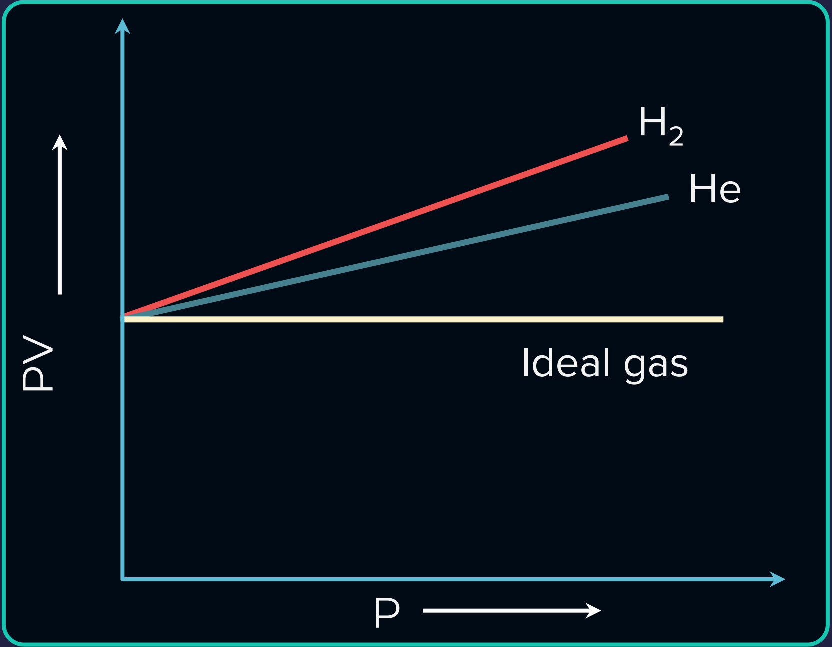
Exceptional Behaviour of H_2 and He

$Z > 1$

$T\ (273\ K) > T_{b,\ gas}$

Repulsive forces dominate

Exceptional Behaviour of H_2 and He



Ideal gas: PV vs P will be a straight line parallel to x-axis
Real gas: PV vs P is not a horizontal straight line but above x-axis

Conclusion

$Z < 1$

Real gas

High P → Never

Low P → If $T < T_{b,\ gas}$

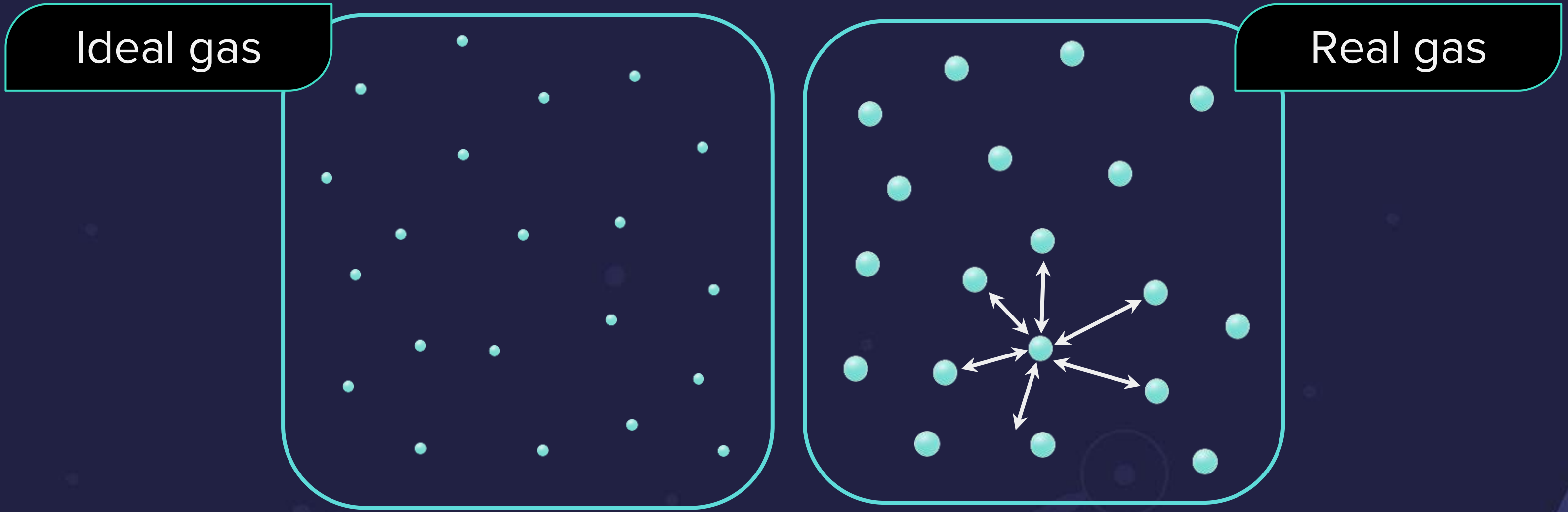
Real Gases

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



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

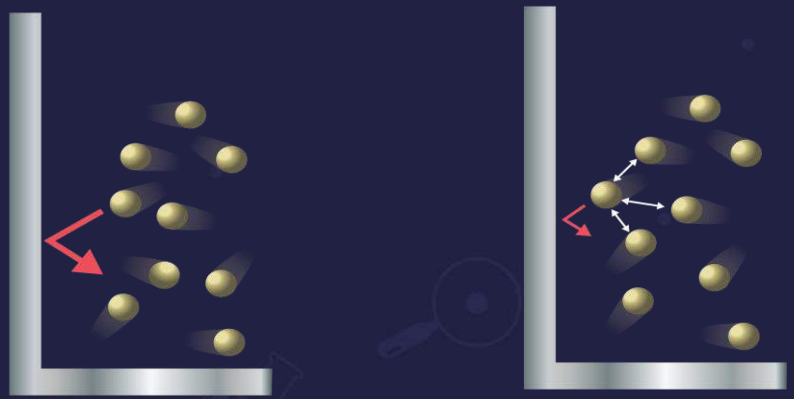
Molecular volume

Pressure Correction

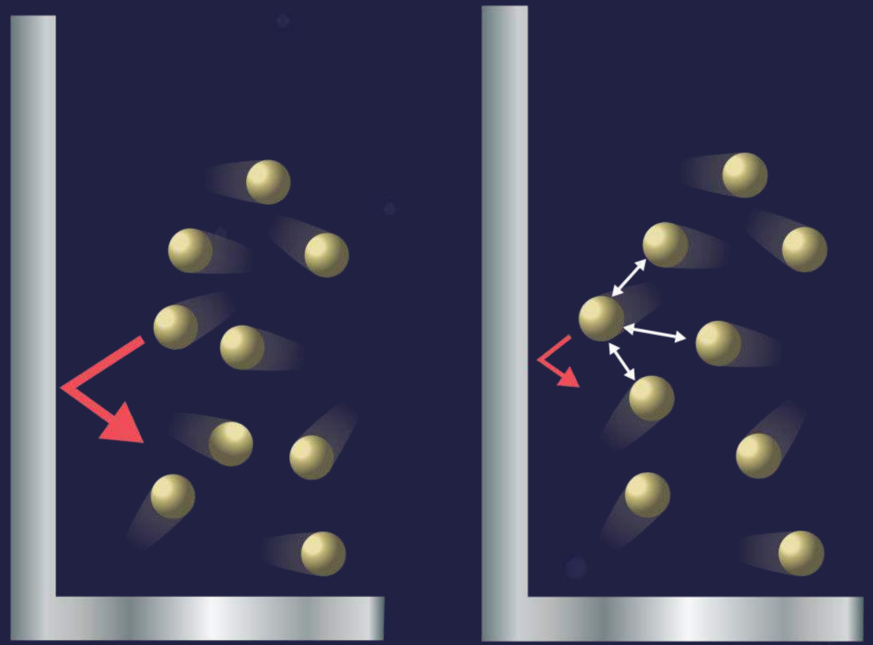
Intermolecular **Attractive forces** are present

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 $\propto$ $\dfrac{n}{V}$

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

Pressure Correction

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

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

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

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’

As a $\uparrow$, Liquefaction $\uparrow$

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

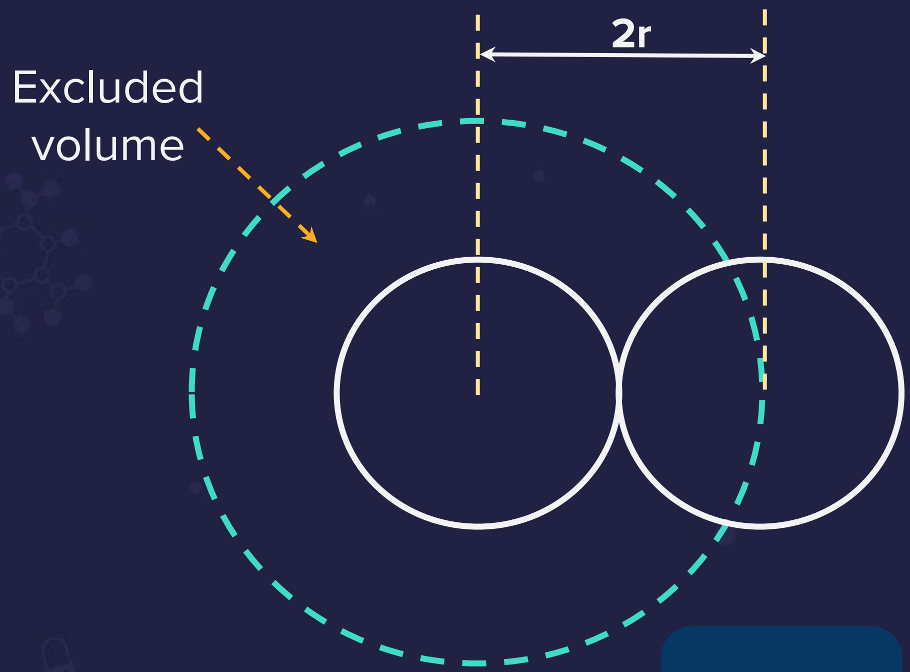
Remember!!

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

For **real** gas $\underbrace{V_i \neq V}$

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

$$b = 4 \times \text{Volume of individual molecules} \times N_A$$

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

$$b \propto \text{Size of the molecules}$$

Volume Correction and Unit of "b"

For n moles

$V_{excluded} = nb$

$V_{ideal} = V - nb$

$[V] = [nb]$

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

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

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

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

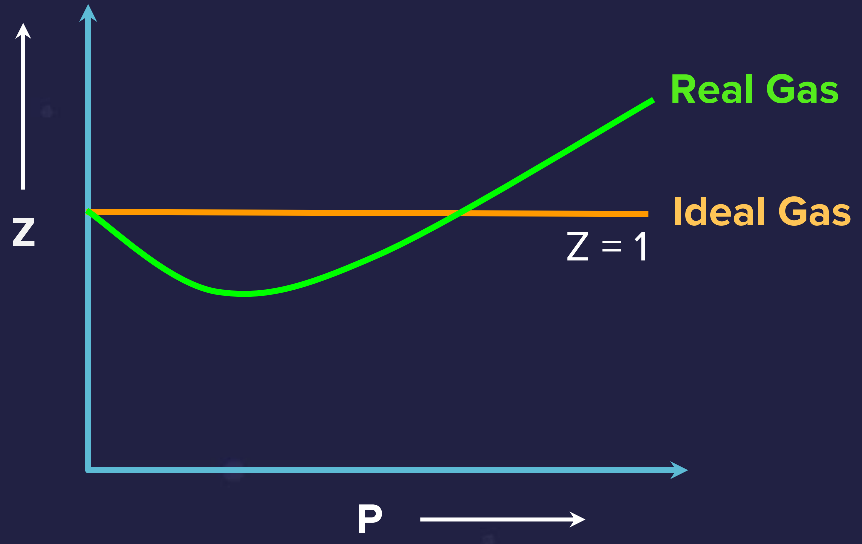
Pressure correction term

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

$$\frac{PV_m}{RT} \dashrightarrow Z = 1 - \frac{a}{V_mRT}$$

$$Z < 1$$

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

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

$$PV_m - Pb = RT$$

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

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

$$Z > 1$$

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

$PV_m \approx RT$

$Z \approx 1$

Ideal gas condition

4 H_2 / He

$a \approx 0$

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

Liquefaction of Gases

Phenomenon of converting a **gas into liquid**

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

Gas liquification

Pressure ↑

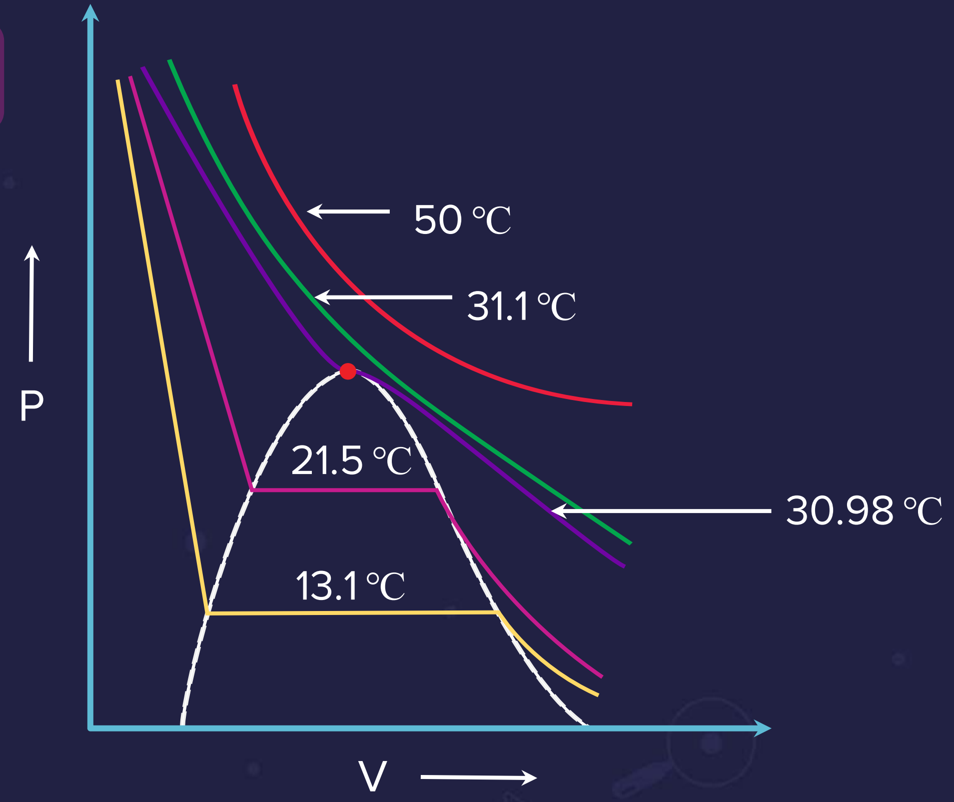
Temperature ↓

Andrew's Isotherm

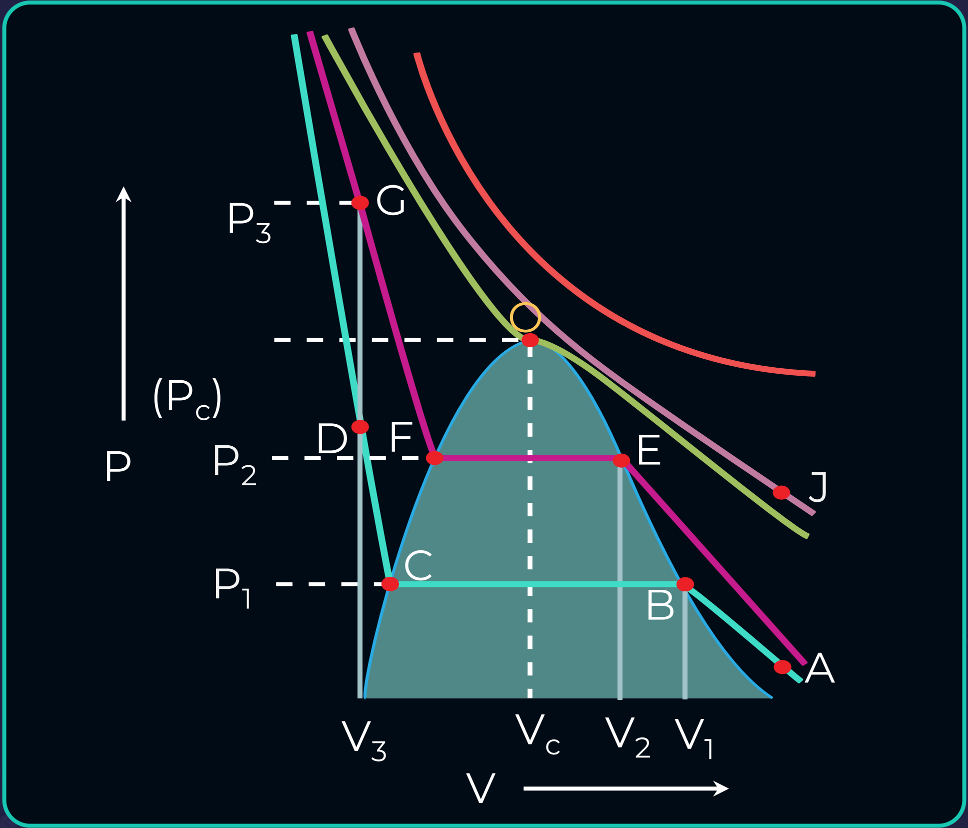
P - V relationship
(isotherms)
for CO_2

The 'Dome' of Andrew's Isotherm

Different isotherms for the same gas

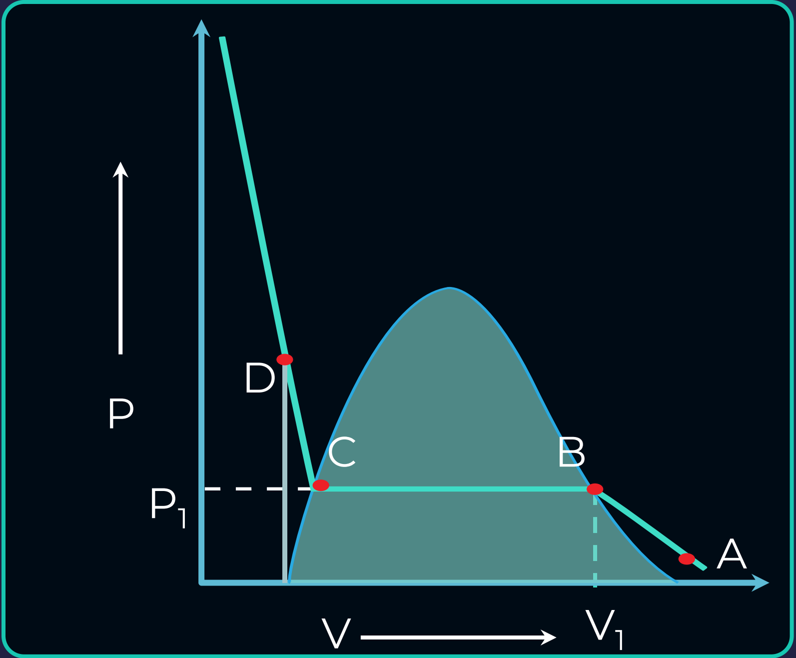


Isotherm of CO_2

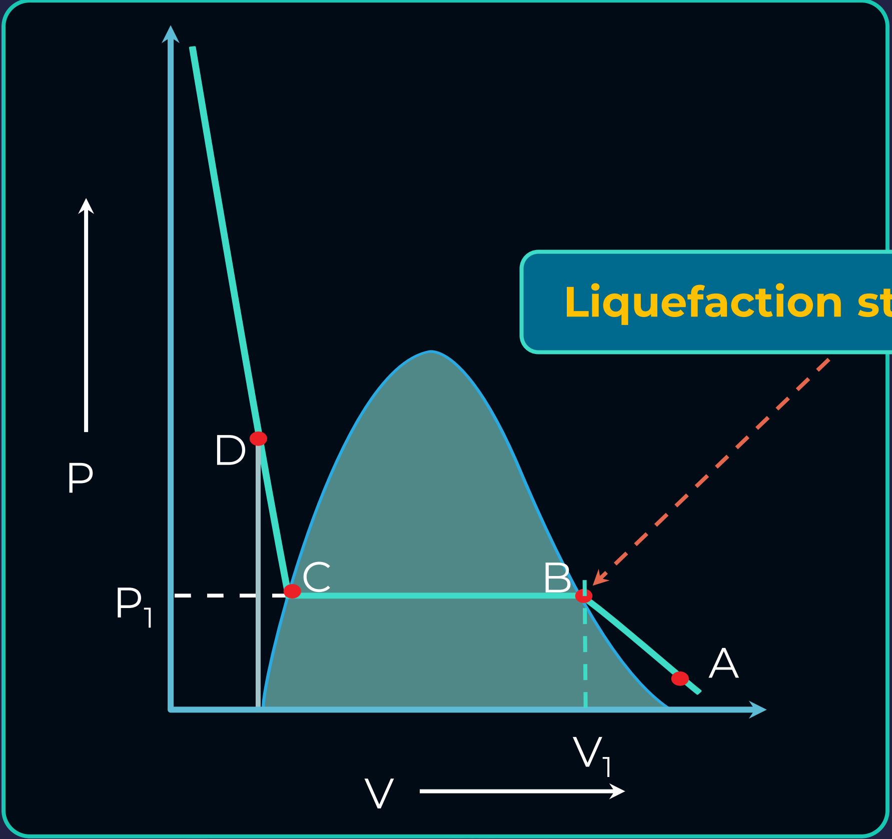


Isotherm of CO_2

Region AB ⟶ Gaseous phase
⟶ Compression at constant T



Isotherm of CO_2



Liquefaction starts at B

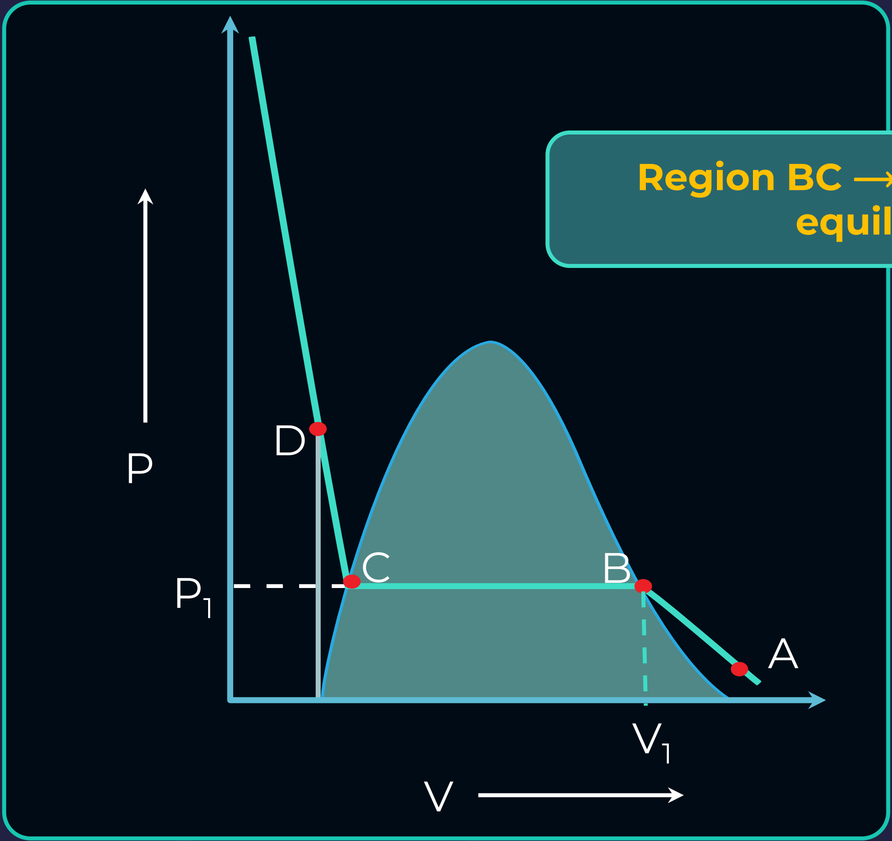
Isotherm of CO_2

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

$n \downarrow$ $V \downarrow$

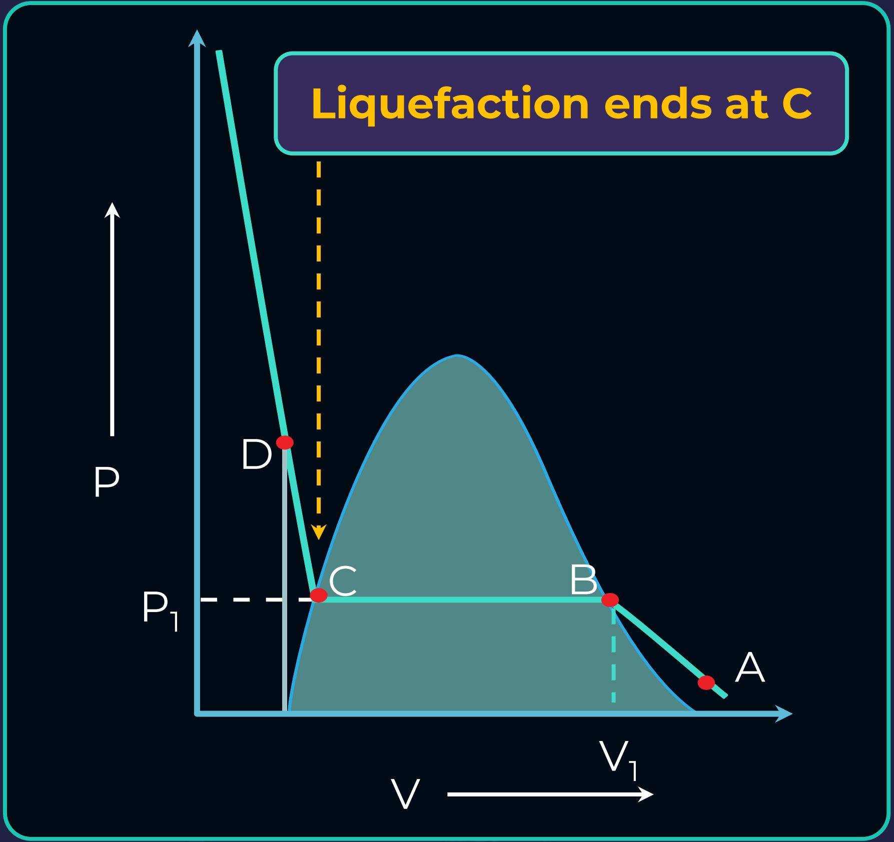
$\Downarrow$

Pressure remains constant

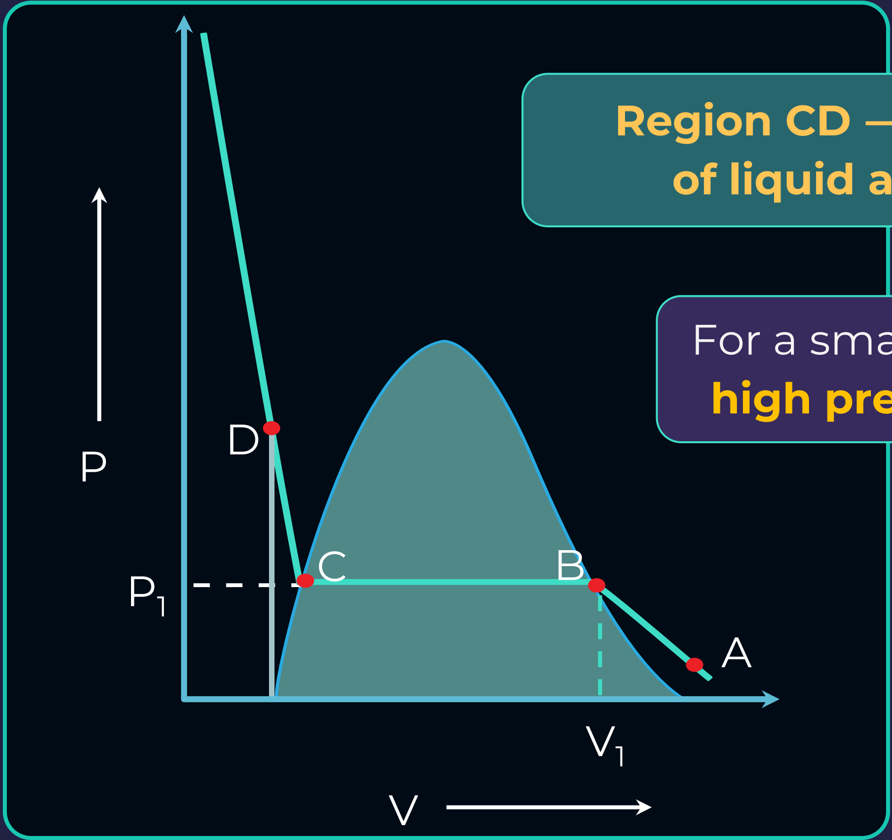


Region BC ⟶ Liquid-vapour equilibrium

Isotherm of CO_2



Isotherm of CO_2

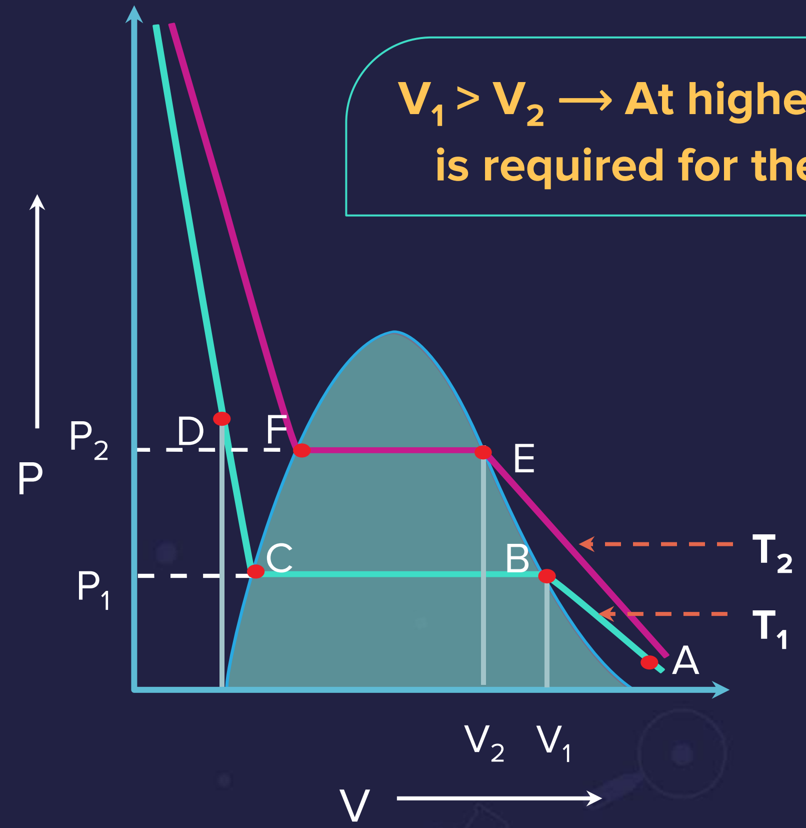


Region CD ⟶ Compression of liquid at constant T

For a small volume change, **high pressure** is required

Isotherm of CO_2

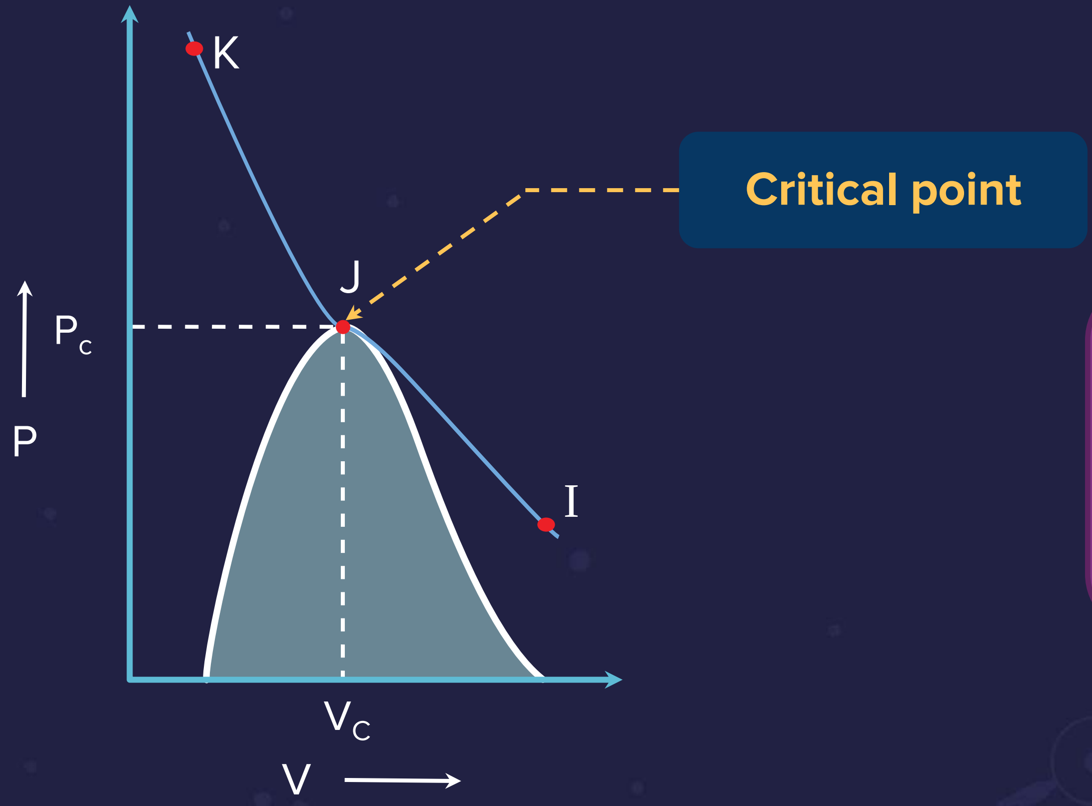
$V_1 > V_2 \longrightarrow$ At higher T, more compression is required for the liquefaction to start



Region BC > Region EF

$T_2 > T_1$

Critical Isotherm



Critical Point

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

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

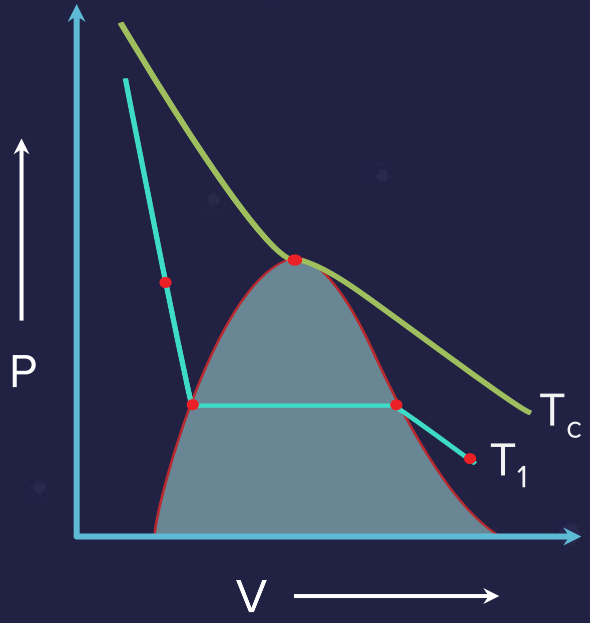
Liquid passes into the **gaseous phase** continuously and the boundary between the two phases disappears

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

Temperature ↑

Density of liquid ↓

Density of vapour ↑

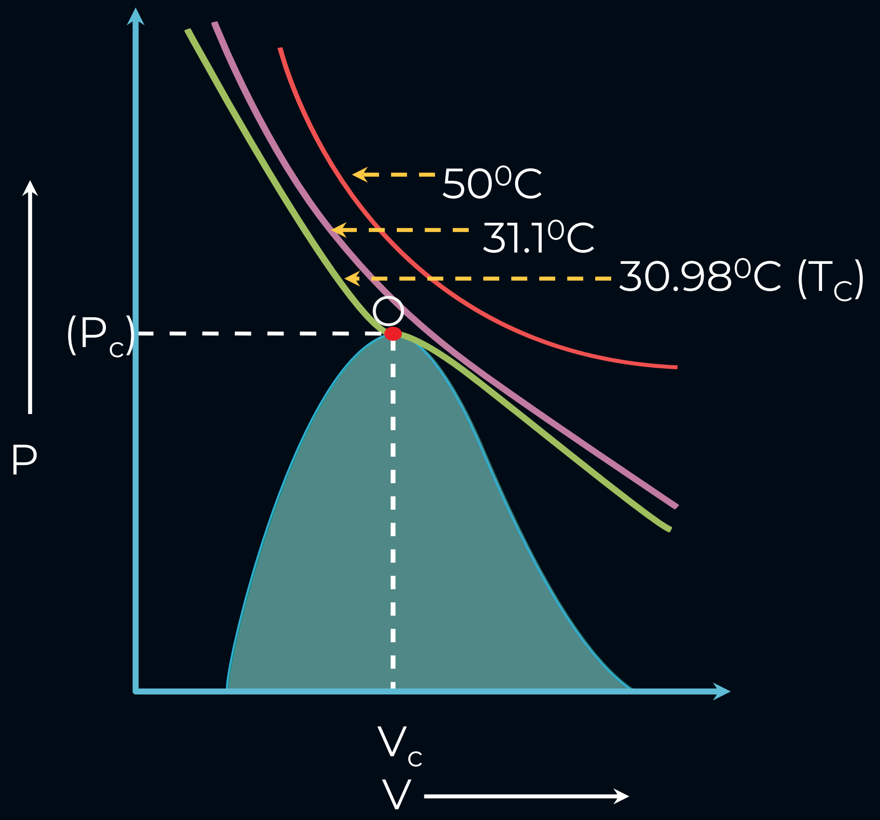
Did you know?

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 cannot be liquefied



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

- Critical Temperature **(T_C)**
- Critical Pressure **(P_C)**
- Critical Volume **(V_C)**

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

Liquid State

Properties of Liquids

1. Have definite volume
2. Can flow
3. Denser than gases

Intermolecular forces are stronger than in gaseous state and weaker than that in solid state

Liquid State - Physical Properties

Properties

- Evaporation
- Vapor Pressure
- Boiling point
- Surface Tension
- Viscosity

Evaporation

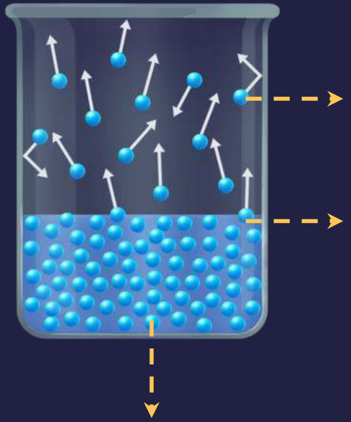
Liquid → Vapor

Below its boiling point

Molecules at the liquid's surface having **sufficient K.E.** → Escape into the vapor phase

Evaporation

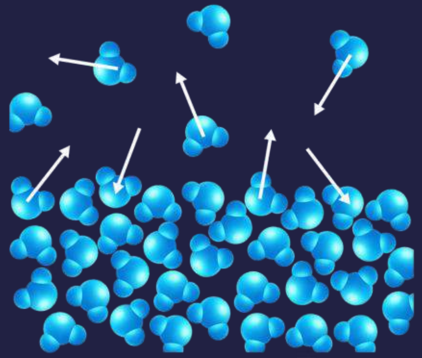
Requires energy to **overcome** the **intermolecular forces** between the molecules of the liquid



Gas particle

Particles with higher K.E. leaves the liquid surface

Liquid particles



Vapor Pressure (V.P.)

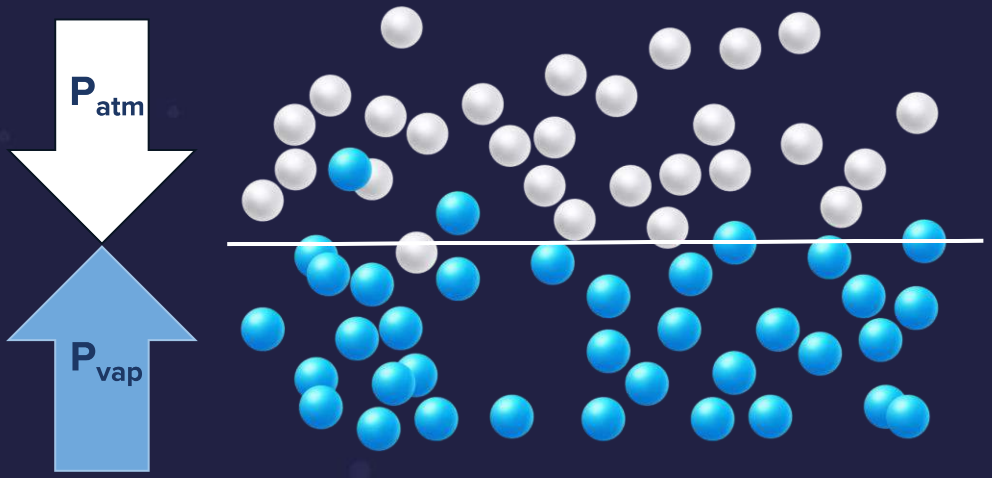
Pressure exerted by the **vapors** over its liquid when it is in equilibrium with the liquid

Initially, the molecules start going in vapour phase from the liquid surface but after some time some molecules start coming back to the liquid surface. At equilibrium, the number of molecules going from the surface and the molecules coming back becomes equal.

Boiling Point

Temperature at which the vapour pressure of liquid is equal to the external pressure

Boiling Point



$$P_{atm} = P_{vap}$$

Surface Tension

Surface tension is defined as the force acting per unit length perpendicular to the line drawn on the surface of liquid.

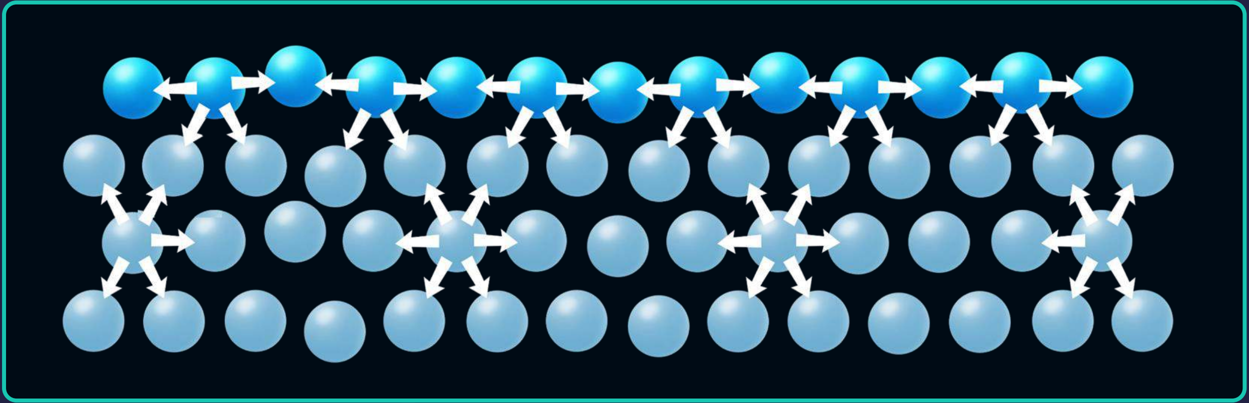
Surface Tension(γ) = $\frac{F}{L}$

S.I Unit of γ : $N\ m^{-1}$

The measure of **inward force** on the surface of the liquid. It tends to **minimize the surface area.**

Surface Tension

Surface molecule : Net attraction into the liquid (downwards)



Interior molecule : Attracted in all directions

Factors Affecting Surface Tension

Temperature $\uparrow$ Surface tension $\downarrow$

Intermolecular attractive forces $\uparrow$
Surface tension $\uparrow$

Applications of Surface Tension

Soaps and Detergents

Disinfectants

Industrial Processes

Human Health

Viscosity

Measure of resistance to flow of a liquid

Arises due to the **internal friction** between the layers of the fluid while it flows

Viscosity

Why does milk flow faster than honey?

Because of the difference in the intermolecular forces of attraction

More force of attraction in honey causes more viscosity as compared to milk.