

Chapter-4

STATES OF MATTER

Gases

Matter: Any thing that has mass as well as volume is called matter. Matter exists in four states i.e. solid, liquid, gas and plasma.

Comparison of three states of matter:

S.No	Gas	Liquid	Solid
1.	<i>Shape:</i> Gas has no definite shape.	<i>Shape:</i> Liquid has no definite shape.	<i>Shape:</i> Solid has definite shape.
2.	<i>Volume:</i> Gas has no definite volume.	<i>Volume:</i> Liquid has definite volume.	<i>Volume:</i> Solid has definite volume.
3.	<i>Compressibility:</i> Gases are highly compressible due to large empty spaces between their molecules.	<i>Compressibility:</i> Liquids are comparatively less compressible because their molecules are closer.	<i>Compressibility:</i> Solids have very low compressibility because their molecules are much closer.
4.	<i>Forces:</i> Forces of attraction are negligible.	<i>Forces:</i> Forces of attraction are stronger.	<i>Forces:</i> Forces of attraction are strongest.
5.	<i>Diffusion:</i> Gases have high ability to mixed up (diffuse) with one another.	<i>Diffusion:</i> Liquids have little ability to diffuse into one another.	<i>Diffusion:</i> Diffusion of solids into one another is negligible.
6.	<i>Fluidity:</i> They are fluid i.e. they can flow very easily.	<i>Fluidity:</i> They are fluid i.e. they can flow very easily.	<i>Fluidity:</i> They are not fluid i.e. they cannot flow.
7.	<i>Density:</i> Gases have very low density this is due to more volume of the gas. Gas has 1000 time less density than same mass of liquid e.g. $O_{2(g)}$ has density 0.00142 g/cm^3 .	<i>Density:</i> Liquids have very more density than gases this is due to less volume of liquids e.g. $O_{2(l)}$ has density 1.149 g/cm^3 .	<i>Density:</i> Solids have very high density than liquids and gases this is due to very less volume of solids e.g. $O_{2(s)}$ has density 1.426 g/cm^3 .

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Science, Society Relationship:

Some Important Uses of Liquid Gases:

- *Compressed natural gas (CNG) is used as fuel in vehicles.*
- *Liquid oxygen is used in hospitals for patients suffering from breathing problems.*
- *Liquid nitrogen is used by dermatologists and by inseminators to freeze semen.*
- *Liquid chlorine is used for purification of water, sanitation of industrial waste, sewage and swimming pools. It is also used to bleach paper pulp and textile. It is used in manufacturing of chloroform, carbon tetra chloride etc.*
- *Liquefaction of helium below 2.17 K, liquid has many amazing properties, such as climbing the walls of vessel, exhibition of zero viscosity.*
- *Liquefaction of air done to obtain nitrogen, oxygen and argon.*

Kinetic Molecular Theory of Gases:

Kinetic molecular theory of gases explains the physical behaviour of gases. It has following postulates.

1. All gases consist of molecules which are widely separated from each other.
2. Space occupied by gas molecules is negligible as compared to space among gas molecules. i.e. volume of gas molecules is negligible as compared to volume of the gas.
3. The gas molecules are in constant and random motion, while doing so they collide with each other as well as with wall of container.
4. Gases exert pressure due to collision of their molecules with wall of the container.
5. Gas molecules make elastic collisions.
6. No forces of attraction among gas molecules exist.
7. Average kinetic energy of gas molecules is directly proportional to absolute temperature. $\text{Av. K. E} \propto T$
8. Two gases at same temperature have equal average kinetic energy.
9. Gravity has no influence on gas molecules.

Four Variables of Gas:**1. Pressure:**

It is defined as "Force per unit area." $P = F/A$

Units: Various units of pressure and their inter relations ships are:

$$1 \text{ atm} = 1 \text{ bar} = 760 \text{ mmHg (Torr)} = 1.01 \times 10^5 \text{ N/m}^2 \text{ (Pa)} = 1.01 \times 10^6 \text{ dyne/cm}^2 = 14.7 \text{ PSI (Lb/in}^2\text{)}$$

(S.I unit) (CGS system) (British system)

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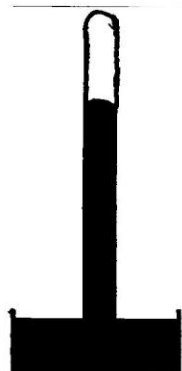
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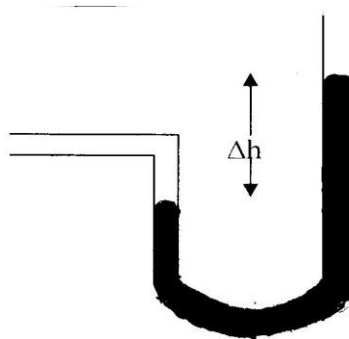
Instruments or Devices: Barometer and Manometer are used to measure the pressure.

Barometer measures the pressure of atmosphere (i.e. open gas or air)

Manometer measures the pressure of the gas enclosed in a container.



A Typical barometer



A Typical Manometer

Temperature:

It is defined as “Measure of average kinetic energy of a system” Or
“Degree of hotness or coldness of a body”

Units: Usually three scales are commonly used, Celsius or centigrade, Fahrenheit and Kelvin. Their inter relationships are

- (i) $K = ^\circ C + 273$
(S.I unit)
- (ii) $1.8 \times ^\circ C = ^\circ F - 32$

Instruments or Devices:

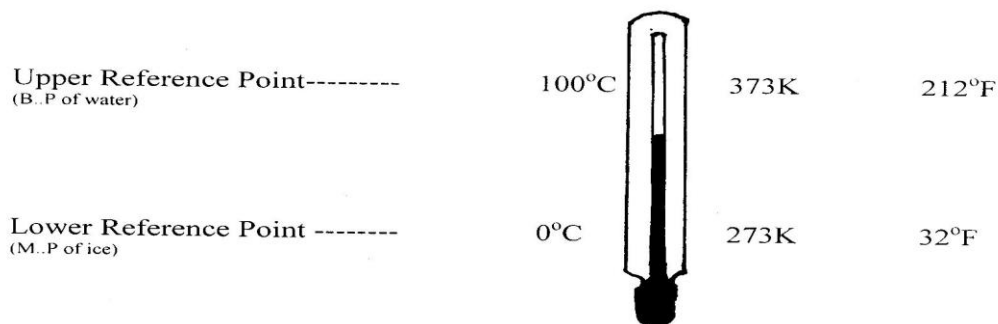
Thermometer

To calibrate thermometer two reference points are chosen the upper reference point is boiling point of water while lower reference point is melting point of ice.

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2. **Volume:** The space occupied by a substance is called its volume.

Units: Most commonly used units or their submultiples are

$$1 \text{ m}^3 = 1000 \text{ dm}^3 \text{ or Litres}$$

(S.I unit) (MKS System)

$$1 \text{ dm}^3 \text{ or Litre} = 1000 \text{ cm}^3 \text{ or milliliters or c.c}$$

(CGS System)

Instruments or Devices: Burette, pipette, cylinder, beaker, flasks etc.

3. **Mass:** Quantity of matter in a body is called mass.

Units: Most commonly used units or their submultiples are

$$1 \text{ kg} = 1000 \text{ g}$$

(S.I unit)

$$1 \text{ g} = 1000 \text{ mg}$$

Instruments or Devices: Physical balance.

Ideal Gas Laws:

I Boyle's Law:

Robert Boyle, in 1662, gave this law. It relates pressure and volume of ideal gases at constant temperature and mass. It states

“For fixed mass of a gas, the volume is inversely proportional to pressure at constant temperature.”

$$V \propto \frac{1}{P} \dots\dots\dots (1)$$

This shows that when pressure increases, volume decreases to same fold and vice versa.

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

$$\boxed{PV = K_b} \dots\dots\dots (2)$$

Thus law can also be stated as:

“For fixed mass of a gas, the product of pressure and volume remains constant at constant temperature.”

It means volume changes with change in pressure but product PV remains same.

Let volume of a gas is V_1 at pressure P_1 . Then

$$P_1V_1 = K_b \dots\dots\dots (3)$$

If pressure changes to P_2 then volume will change to V_2 such that product remains same

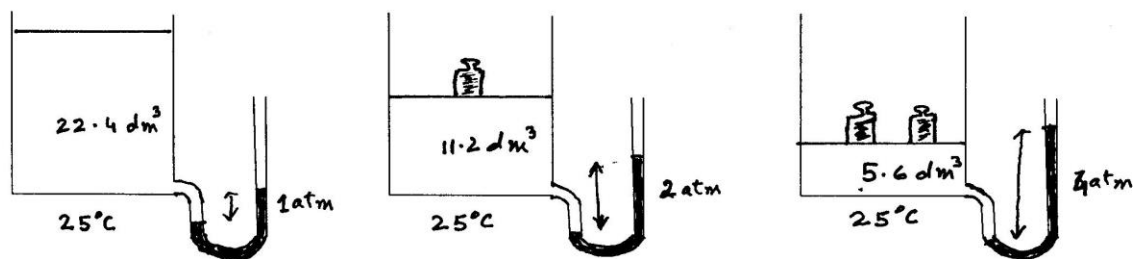
$$P_2V_2 = K_b \dots\dots\dots (4)$$

Comparing equation (3) and (4), we can write

$$\boxed{P_1V_1 = P_2V_2} \dots\dots\dots (5)$$

Experimental Verification of Boyle's law:

Consider a gas present in a cylinder fitted with a movable and weightless piston. A manometer is attached with cylinder to measure pressure. Let the initial volume of gas is 22.4 dm^3 and pressure on it is 1 atmosphere (as piston has no weight on it and only air is exerting pressure on it). Now place one weight on piston, pressure will become double and it can be observed that volume is reduced to half i.e 11.2 dm^3 . Similarly by putting more and more weights on piston pressure goes on increasing while volume goes on decreasing to same extent to which pressure increases. In this way a data can be collected and then by plotting graphs the law can be verified.



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The experimental data collected is given in the following table.

Expt. No	P (atm)	V (dm ³)	PV	1/P
1	1	22.4	1 x 22.4 = 22.4	1/1 = 1
2	2	11.2	2 x 11.2 = 22.4	1/2 = 0.5
3	3	7.47	3 x 7.47 = 22.41	1/3 = 0.33
4	4	5.6	4 x 5.6 = 22.4	1/4 = 0.25
5	0.5	44.8	0.5 x 44.8 = 22.4	1/0.5 = 2

Knowing that:

- (i) Plot of inversely proportional quantities is hyperbolic curve.
- (ii) Plot of directly proportional quantities is straight line.
- (iii) Plot of a constant quantity against a variable quantity, is horizontal line.

We can verify the law by following three graphs.

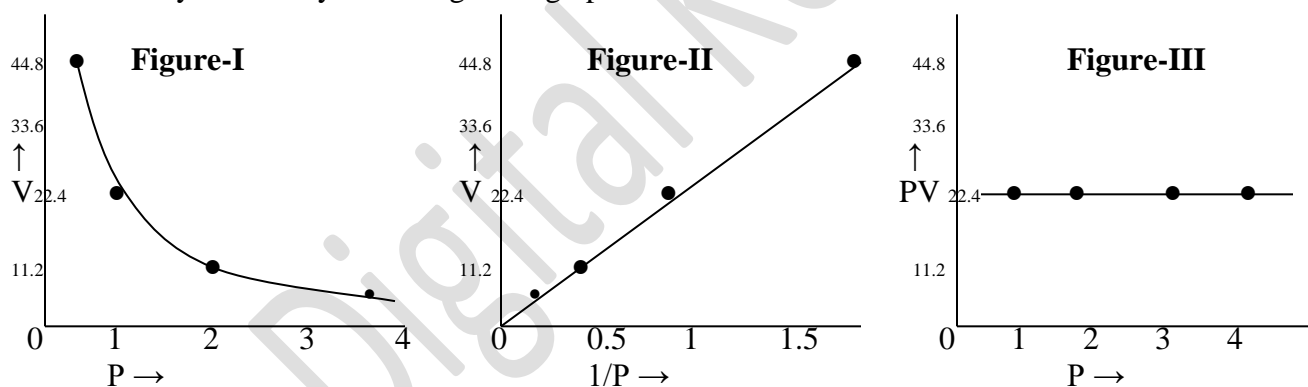


Figure-I shows a hyperbolic curve which means volume is inversely proportional to pressure. Thus law is verified.

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

Figure-II shows a straight line which means volume is directly proportional to reciprocal of pressure. Law is again verified.

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

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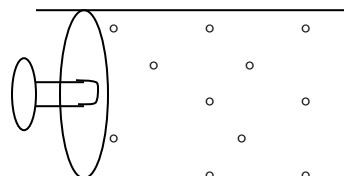
Figure-III shows a horizontal line which means product of pressure and volume (PV) is constant. Thus law is further verified.

$$PV = \text{Constant}$$

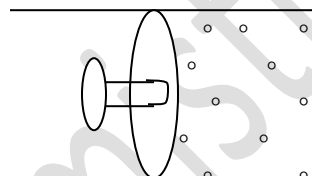
All the three plots have verified the law.

Explanation of Boyle's Law on the basis of KMT:

Consider a cylinder fitted with fixed piston. Let the cylinder contains 'n' number of molecules at temperature 'T', volume is 'V' and pressure exerted by molecules is 'P'.



T, V, n, P



T, V/2, n, 2P

Further consider that piston is moved to a place where volume is reduced to half. As temperature remained same so av. K.E remains same and in turn velocity remains same. But now molecules have to travel half distance, so number of collisions become double and in turn pressure becomes double. It means when volume reduces to half, pressure becomes double i.e.

$$V \propto 1/P$$

And this is the statement of Boyle's law.

II Charles's Law:

JAC Charles, in 1662, gave this law. It relates volume and absolute temperature of ideal gases at constant pressure and mass. It states

“For fixed mass of a gas, the volume is directly proportional to absolute temperature at constant pressure.”

$$\boxed{V \propto T} \quad \dots\dots\dots (1)$$

This shows that when absolute temperature increases, volume increases to same fold and vice versa.

$$V = K_c T$$

Or
$$\boxed{\frac{V}{T} = K_c} \quad \dots\dots\dots (2)$$

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Thus law can also be stated as:

“For fixed mass of a gas, the ratio of volume and absolute temperature remains constant at constant pressure.”

It means volume changes with change in absolute temperature but ratio V/T remains same.

Let volume of a gas is V_1 at absolute temperature T_1 . Then

$$V_1/T_1 = K_c \dots\dots\dots (3)$$

If pressure changes to P_2 then volume will change to V_2 such that ratio remains same

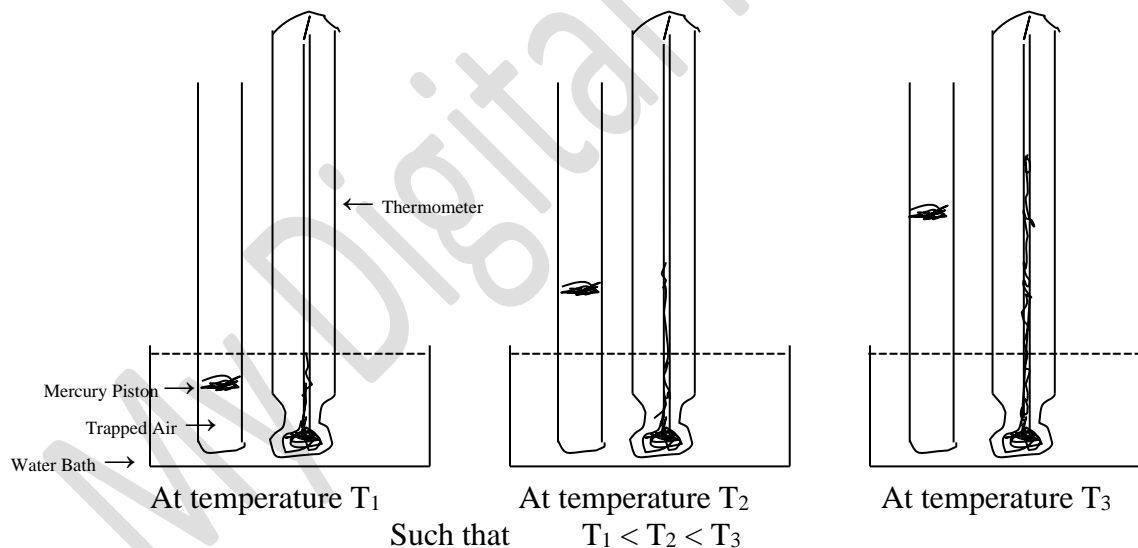
$$V_2/T_2 = K_c \dots\dots\dots (4)$$

Comparing equation (3) and (4), we can write

V_1	=	V_2	\dots\dots\dots (5)
T_1		T_2	

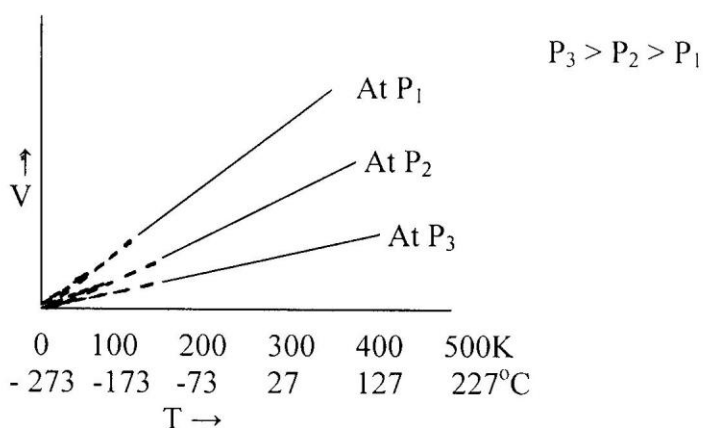
Experimental Verification of Charle's law:

The law can be verified by using the apparatus as shown in figure. A glass tube closed at one end is taken in which some mercury is poured. The air present in the tube will be trapped at close end and mercury will act as frictionless piston. The tube will be placed in thermostat.



By increasing the temperature it can be seen that volume increases. Thus law is verified.

Law is further verified by plotting graph for temperature versus volume it gives a straight line which verifies the law.



J.L Gay Lussac also showed a similar relationship of Celsius temperature and volume. It states

“For each one degree centigrade rise or fall in temperature, the increase or decrease in volume is $1/273$ of volume of gas at 0°C .”

Let volume of a gas at $0^{\circ}\text{C} = V_0$

$$\text{Increase in volume for } 1^{\circ}\text{C rise in temperature} = \frac{1}{273} \times V_0 = \frac{V_0}{273}$$

$$\text{Increase in volume for } 2^{\circ}\text{C rise in temperature} = \frac{V_0}{273} \times 2 = \frac{2V_0}{273}$$

$$\text{Increase in volume for } 3^{\circ}\text{C rise in temperature} = \frac{V_0}{273} \times 3 = \frac{3V_0}{273}$$

$$\text{Increase in volume for } t^{\circ}\text{C rise in temperature} = \frac{V_0}{273} \times t = \frac{V_0 t}{273}$$

Thus volume of a gas at $t^{\circ}\text{C} = V_t = V_0 + \frac{V_0 t}{273}$

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$$\text{Volume of a gas at } -273^{\circ}\text{C} = V_0 + \frac{V_0(-273)}{273} = V_0 - V_0 = 0$$

This temperature at which volume of a gas becomes hypothetically zero is called absolute zero (i.e. zero of absolute or Kelvin scale).

It shows that Charle's law and Gay Lussac's law are one and the same.

Explanation of Charle's Law on the basis of KMT:

Consider a cylinder fitted with freely movable piston. Let the cylinder contains 'n' number of molecules at temperature 'T', volume is 'V' and pressure exerted by molecules is 'P'.



Further consider that temperature is raised to double. As temperature became double so av. K.E also becomes double and in turn collisions also become double. Thus piston will be pushed up to double volume, so that internal and external pressure again becomes equal. It means when temperature increases twice, volume also increases twice. i.e.

$$V \propto T$$

And this is the statement of Charle's law.

III Avogadro's Law:

Avogadro, in 1813, gave this law. It relates volume and number of particles of ideal gases at constant temperature and pressure. It states

“Equal volumes of all gases at same temperature and pressure contain same number of molecules.”

It means if two gases have same volume, same temperature and same pressure then their number of molecules will also be same.

Mathematically law can be written as $V \propto n$

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$$\text{Or} \quad V = Kn$$

On the bases of this law Avogadro pointed that

22.4 dm³ of any gas at STP contain 6.02 x 10²³ molecules.

Or 24 dm³ of any gas at RTP contain 6.02 x 10²³ molecules.

Or in other words

Volume of 6.02 x 10²³ molecules of any gas at STP = 22.4 dm³

Or Volume of 6.02 x 10²³ molecules of any gas at RTP = 24 dm³

Ideal Gas Equation:

Boyle's law, Charle's law and Avogadro's law can relate only two parameters (or variables). But by combining all the three laws we can relate all the four variables.

$$V \propto \frac{1}{P} \dots\dots\dots \text{(Boyle's law)}$$

$$V \propto T \dots\dots\dots \text{(Charle's law)}$$

$$V \propto n \dots\dots\dots \text{(Avogadro's law)}$$

By combining

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

$$V = R n T \frac{1}{P} \quad \text{where R is universal gas constant}$$

$$\boxed{PV = nRT \dots\dots\dots (1)}$$

This is ideal gas equation in terms of number of moles.

We know that

$$n = \frac{m}{M} \quad \text{where 'm' is mass in grams & 'M' is molar mass}$$

$$\boxed{PV = \frac{m}{M} \times RT \dots\dots\dots (2)}$$

This is ideal gas equation in terms of mass.

On rearranging above equation we can write

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

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But $m/V = d$
So

$$PM = dRT \dots\dots\dots (3)$$

This is ideal gas equation in terms of density.

Value of R:

Knowing from Avogadro's law that volume of one mole of any gas at STP is 22.4 dm^3 we can find value of R by using ideal gas equation.

$$PV = nRT$$

Or

$$R = \frac{PV}{nT} = \frac{1 \text{ atm} \times 22.4 \text{ dm}^3}{1 \text{ mole} \times 273 \text{ K}}$$

$$R = 0.08205 \text{ atm} \cdot \text{dm}^3 \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$$

In mmHg or torr

$$R = 0.08205 \times 760 = 62.36 \text{ mmHg} \cdot \text{dm}^3 \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$$

Or $\text{torr} \cdot \text{dm}^3 \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$

In S.I Units

$$R = \frac{PV}{nT} = \frac{1.01 \times 10^5 \text{ N/m}^2 \times 0.0224 \text{ m}^3}{1 \text{ mole} \times 273 \text{ K}}$$

In Calories

$$R = 8.3143 \text{ Nm} / \text{K} \cdot \text{mol} = 8.3143 \text{ JK}^{-1} \cdot \text{mol}^{-1}$$

$$R = 8.3143 / 4.1846 = 1.99 \approx 2 \text{ Cal} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$$

Real Gases and their Deviation from Ideal Behaviour:

To obey all the gas laws and all the postulates of kinetic molecular theory of gases at all temperatures and pressures, is called ideal behaviour. Thus ideal gases obey ideal gas equation.

$$PV = nRT$$

$$\frac{PV}{nRT} = Z = 1$$

Where Z is compressibility factor. It is always constant and one for ideal gases.

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Thus a plot of PV/nRT vs P will be horizontal line for ideal gases.

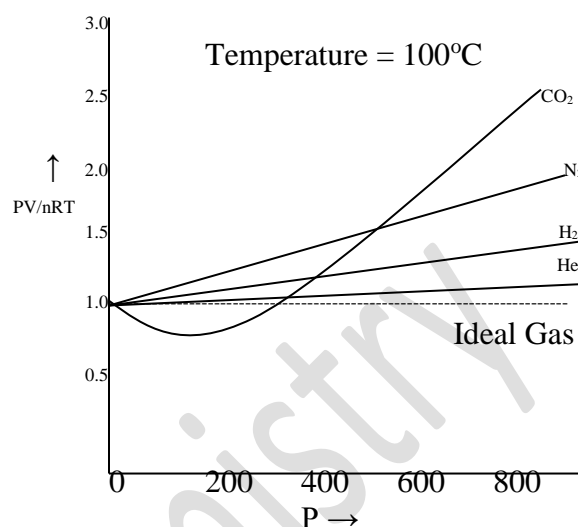
But for real gases it is not horizontal line as is clear from figure.

This shows that real gases deviate from ideal behaviour.

Further it can be shown that real gases deviate more:

1. At low temperature
2. At high pressure

The reasons for deviation of real gases from ideal behaviour are due to two wrong assumption of kinetic molecular theory of gases.



(i) There are no forces of attraction among gas molecules.

(ii) The actual volume of gas molecules is negligible as compared to volume of gas (volume of container).

Attractive forces:

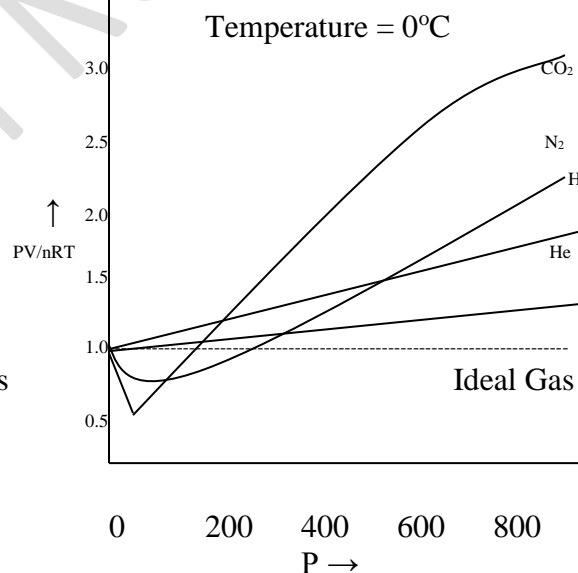
Forces of attraction in gases are negligible but when pressure is high and molecules are forced to come close to each other then these forces are no more negligible. Further more when temperature is low molecules become slow, so forces become more affective.

Volume:

When pressure is high then volume of gas decreases and thus volume of gas molecules will no more be negligible.

It is this reason that real gases deviate from ideal behaviour and they do not obey ideal gas equation.

Van der Waal made corrections in ideal gas equation to make it suitable for real gases.



Van der Waals' equation:

In 1873, a Dutch scientist, J.D. Van der waal derived an equation for real gases.

Volume Correction: For ideal gases, volume of molecules is neglected. But for real gases, volume of molecules can not be neglected.

$$\begin{aligned} \text{Therefore } V_{\text{free or } V_{\text{gas}}} &= V_{\text{vessel}} - V_{\text{molecules}} \\ \text{Or } V_{\text{gas}} &= V_{\text{vessel}} - b && \text{for one mole} \\ V_{\text{gas}} &= V_{\text{vessel}} - nb && \text{for n moles} \end{aligned}$$

Where, "b" is volume of one mole molecule of a gas. V_{vessel} is same as V in ideal gas equation.

Therefore Van der Wall made correction in volume:

$$\begin{aligned} V_{\text{free or } V_{\text{gas}}} &= V_{\text{vessel}} - nb && \text{for n moles} \\ V_{\text{free or } V_{\text{gas}}} &= V_{\text{vessel}} - b && \text{for one moles} \end{aligned}$$

Pressure Correction: As molecules of real gases attract each other so the molecule striking the wall of container will be attracted by the molecules behind to it. This will decrease the impact of its collision with the wall of container. Thus observed pressure P, consequently will be less than the ideal pressure P_i .

$$P = P_i - P' \quad \text{Where } \begin{array}{l} P = \text{observed pressure} \\ P' = \text{correction factor for pressure or total inward force} \\ P_i = \text{ideal pressure} \end{array}$$

$$\text{Or } P_i = P + P' \dots\dots\dots (1)$$

The total inward force away from the wall is proportional to the product of the number of molecules at the surface of container (molecules being pulled) and the number of molecules in next layer (those engaged in pulling).

Both these numbers of molecules are, in turn, proportional to the density of the gas, ρ (rho).

$$\begin{aligned} \text{Total inward force or } P' &\propto \rho^2 \\ \text{But } \rho &= \frac{n}{V} \\ \text{Then } \rho^2 &= \frac{n^2}{V^2} \end{aligned}$$

$$\text{So } \text{Total inward force or } P' \propto \frac{n^2}{V^2}$$

$$\text{Or } \text{Total inward force or } P' = \frac{a n^2}{V^2} \quad \text{Where a is van der waal constant}$$

Putting in equation (1)

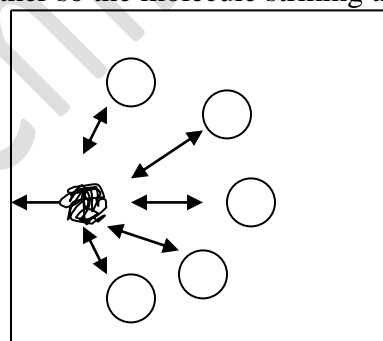
$$P_i = P + \frac{an^2}{V^2}$$

Therefore Van der Wall made correction in pressure

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$$P_i = P + \frac{an^2}{V^2} \quad \text{for } n \text{ moles}$$

$$P_i = P + \frac{a}{V^2} \quad \text{for one mole}$$

Putting corrected values of pressure and volume in ideal gas equation

$$\left(P + \frac{a}{V^2} \right) (V - b) = RT \quad \text{for one mole}$$

$$\left(P + \frac{an^2}{V^2} \right) (V - nb) = nRT \quad \text{for } n \text{ moles}$$

Above two equations are called *Van der Waal equations*. They are applicable to real gases. 'a' and 'b' are Van der Waal constants. Value of 'a' depends upon strength of intermolecular forces, stronger are intermolecular forces higher will be the value of 'a' and vice versa. Value of 'b' depends upon size of molecules of gases, bigger is the size of molecules of gases high will be the value of 'b' and vice versa.

For ideal gases value of "a" and "b" is zero.

S.I unit for Van der Waal's constant "a" is: $\text{N m}^4 \text{mol}^{-2}$

S.I unit for Van der Waal's constant "b" is: $\text{m}^3 \text{mol}^{-1}$

Gas →	Cl ₂	H ₂ O _(g)	NH ₃	CO ₂	CH ₄	CO	N ₂	O ₂	Ar	H ₂	He
Constant "a" (Nm ⁴ mol ⁻²)	0.659	0.553	0.423	0.365	0.229	0.151	0.141	0.138	0.137	0.025	0.0035
Constant "b" (m ³ mol ⁻¹)	5.64	3.3	3.72	4.28	4.3	4.0	3.92	3.19	3.23	2.67	2.38

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IV Dalton's Law of Partial Pressure:

John Dalton gave this law. It states

“The total pressure exerted by a mixture of non-reacting gases is equal to the sum of their partial pressures which they would exert if were present alone in same volume and at same temperature.”

$$P_t = P_1 + P_2 + P_3 + \dots \dots \dots (1)$$

Where as P_t = total pressure of mixture of gases

While P_1, P_2, P_3 etc are partial pressures of individual gases.

e.g. Air is a mixture of gases. It contain $N_2 = 78\%, O_2 = 21\%, Ar = 0.9\%, CO_2 = 0.03\%,$ Trace gases = 0.07%.

So total pressure of air is

$$P_{air} = P_{atm} = P_{N_2} + P_{O_2} + P_{Ar} + P_{CO_2} + P_{Trace\ gases}$$

Partial pressure of any gas 'I' can be calculated by applying ideal gas equation to it

$$P_i V = n_i RT$$

$$P_i = n_i \times \frac{RT}{V} \dots \dots \dots (2)$$

Similarly total pressure of a mixture of gases can also be calculated by applying ideal gas equation to the mixture.

$$P_t = n_t \times \frac{RT}{V} \dots \dots \dots (3)$$

By dividing equation (2) by equation (3)

$$\frac{P_i}{P_t} = \frac{n_i RT}{V} \times \frac{V}{n_t RT}$$

$$\frac{P_i}{P_t} = \frac{n_i}{n_t}$$

$$P_i = \frac{n_i}{n_t} \times P_t \dots \dots \dots (4)$$

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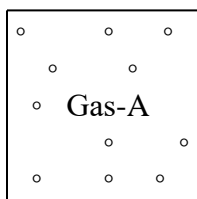
$\frac{n_i}{n_t}$ is mole fraction, further more mole fraction of a gas is proportional to its volume fraction, hence

$$P_i = \frac{V_i}{V_t} \times P_t \dots \dots \dots (5)$$

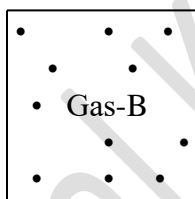
Thus partial pressure of any gas 'i' could be calculated by using equation (2), (4) or (5).

Explanation of Dalton's Law on the basis of KMT:

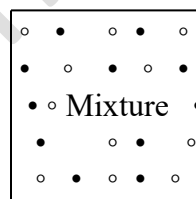
Consider a cylinder of volume 'V' containing 'n' number of molecules of a Gas-A at temperature 'T'. Let the pressure exerted by molecules is 'P'.



T, P, V, n



T, P, V, n



T, 2P, V, 2n

Consider an other cylinder of same volume 'V' containing 'n' number of molecules of an other Gas-B at same temperature 'T'. Then the pressure exerted by molecules of Gas-B will also be 'P'. Let both gases are transferred to a single container of same volume 'V'. Double number of molecules will exert double pressure. i.e.

$$\begin{array}{l} P + P = 2P \\ \text{Or } P_A + P_B = P_t \end{array}$$

This is Dalton's law of partial pressures.

Diffusion and Effusion:

Mixing of different gases with one another due to random motion and collision of their molecules.

or

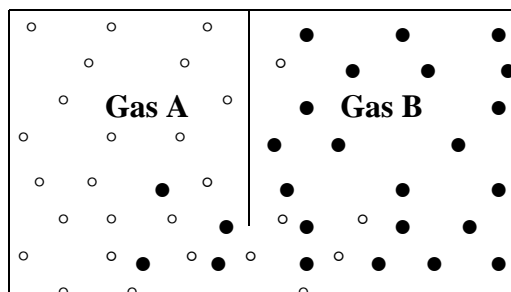
Movement of gas from high pressure to low pressure is called diffusion.

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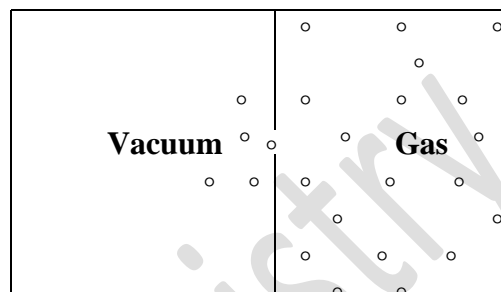
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e.g. if cap of ammonia bottle is removed we can feel its pungent smell in the other corner of laboratory within short time. Ammonia gas diffused into air and thus reached to other corner of laboratory and we felt its smell.



Diffusion



Effusion

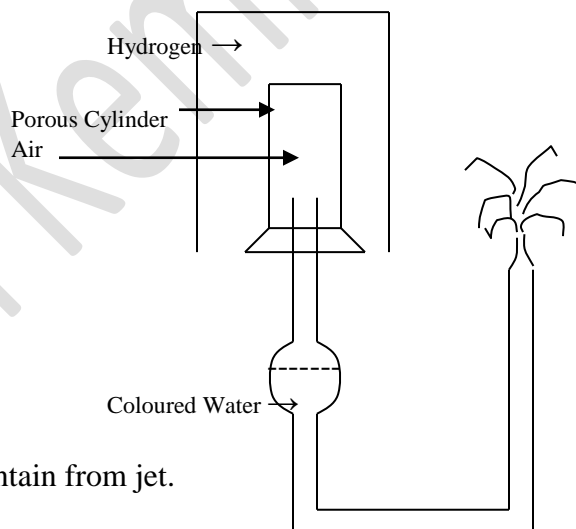
Process of diffusion can be showed by performing an experiment using apparatus as shown in figure. The U-shaped tube having a bulb in it, is

filled with coloured water.

The porous cylinder contains air in it.

On inverting Hydrogen gas jar on the porous cylinder a fountain is observed on the jet end of the U-shaped tube.

This is because Hydrogen quickly diffused into the porous cylinder than the air came out. So pressure inside increases and water is forced out in the form of fountain from jet.



“Escaping of gas molecules through small pores of molecular dimensions is called effusion.”

Diffusion	Effusion
<ol style="list-style-type: none"> 1. For diffusion molecular collisions are needed. 2. It is two way traffic 3. It takes place openly 	<ol style="list-style-type: none"> 1. For effusion no molecular collision are needed. 2. It is one way traffic 3. It takes place through a small hole of molecular dimensions.

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V Graham's Law of Diffusion and Effusion:

Thomas Graham, an English scientist, in 1829, gave this law. It relates relative rates of diffusion and effusion of gases with their densities or molecular masses, at constant temperature and pressure. It states

“At constant temperature and pressure, relative rates of diffusion or effusion of gases are inversely proportional to square roots of their densities or molecular masses.”

e.g. Hydrogen gas (mol.mass = 2) has 16 times less molecular mass than that of Oxygen gas (mol.mass = 32), So Hydrogen gas diffuses 4 times rapidly than oxygen gas.

Mathematically law can be written as

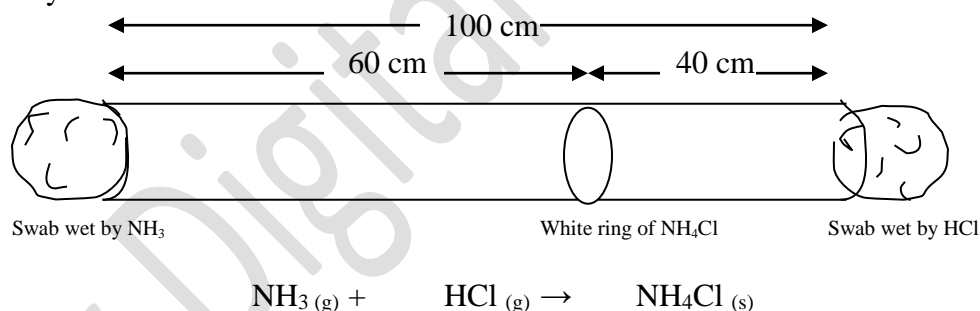
$$\frac{r_1}{r_2} = \sqrt{\frac{d_2}{d_1}}$$

or

$$\frac{r_1}{r_2} = \sqrt{\frac{M_2}{M_1}}$$

Experimental Verification of the law:

A 100 cm long glass tube is placed horizontally and is closed on both ends by two cotton swabs. HCl solution is poured on one swab and ammonia on the other swab by droppers simultaneously.



Vapours of the two substances traveled through tube and white ring is formed at the point of their contact. The two substances reacted and produced white (solid) ammonium chloride which get deposited on the inner wall of the tube and formed white ring. This ring is produced at distance of 60 cm from NH_3 end and 40 cm from HCl end. It means that NH_3 has covered 60 cm distance while HCl has covered 40 cm in same time 't' seconds.

$$\text{Rate of diffusion of } \text{NH}_3 = r_1 = \frac{\text{Distance covered by } \text{NH}_3}{\text{time}}$$

$$r_1 = \frac{60}{t} \dots \dots \dots (1)$$

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$$\text{Rate of diffusion of HCl} = r_2 = \frac{\text{Distance covered by HCl}}{\text{time}}$$

$$r_2 = \frac{40}{t} \dots\dots\dots (2)$$

dividing equation (1) by equation (2)

$$\frac{r_1}{r_2} = \frac{\frac{60}{t}}{\frac{40}{t}}$$

$$\frac{r_1}{r_2} = \frac{60}{t} \times \frac{t}{40}$$

$$\frac{r_1}{r_2} = 1.5$$

It means that NH₃ diffuses 1.5 times rapidly than HCl.

Now using relations given by Graham's law

$$\frac{r_1}{r_2} = \sqrt{\frac{M_2}{M_1}} = \sqrt{\frac{36.5}{17}} = 1.465 \approx 1.5$$

$$\frac{r_1}{r_2} = \sqrt{\frac{d_2}{d_1}} = \sqrt{\frac{1.66}{0.76}} = 1.478 \approx 1.5$$

As result obtained experimentally is in good agreement with calculated results by relations given by Graham's law, so law is verified.

Explanation of Graham's Law of diffusion and effusion on the basis of KMT:

Consider two gases at same temperature 'T'.

Let Average kinetic energy of Gas-A at temperature-T = $\frac{1}{2} m_1 v_1^2$

And Average kinetic energy of Gas-B at temperature-T = $\frac{1}{2} m_2 v_2^2$

According to KMT two gases at same temperature have equal average kinetic energies, so

$$\frac{1}{2} m_1 v_1^2 = \frac{1}{2} m_2 v_2^2$$

$$\text{Or } m_1 v_1^2 = m_2 v_2^2$$

On rearranging

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$$\frac{v_1^2}{v_2^2} = \frac{m_2}{m_1}$$

Taking square root of both sides

$$\frac{v_1}{v_2} = \sqrt{\frac{m_2}{m_1}}$$

or

$$\frac{r_1}{r_2} = \sqrt{\frac{M_2}{M_1}}$$

This is Graham's law.

According to ideal gas equation

$$PM = dRT$$

For any gas 'i' at constant temperature and pressure

$$M_i = d_i \frac{RT}{P}$$

But RT/P is constant

So $M_i \propto d_i$

Therefore 'M' can be replaced by 'd'

$$\frac{r_1}{r_2} = \sqrt{\frac{d_2}{d_1}}$$

This is also Graham's law.

Liquefaction of Gases:

Gases are liquefied when they are cooled to their normal boiling points or below this temperature. But normal boiling points of gases are very low and need much cooling. So gases are usually liquefied at their critical temperatures and pressures.

“The maximum temperature above which a gas cannot be liquefied no matter what ever pressure may be applied, is called critical temperature (T_c)”.

“The pressure that is required to liquefy a gas at its critical temperature is called critical pressure (P_c)”.

“The volume of one mole of a gas at its critical temperature and critical pressure is called its critical volume (V_c)”.

⇒ Value of T_c and P_c depends upon intermolecular forces, stronger the forces high will be T_c & P_c

	H ₂ O	SO ₂	NH ₃	HCl	CO ₂	O ₂	N ₂	H ₂
Critical Temperature T_c	374.1°C	157.2°C	132.4°C	51.4°C	31.1°C	-118.8°C	-147.1°C	-239.9°C
Critical Pressure P_c	218.5atm	77.7 atm	112.0atm	81.55atm	73.0 atm	49.7 atm	33.5 atm	12.8 atm

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Gases are liquefied by applying Joule-Thomson effect. It states,

“When highly compressed gas is suddenly allowed to expand, it causes cooling.”

When gases are compressed, their molecules come closer and start attracting each other. When they are allowed to expand, they have to overcome forces of attraction, for which they use their own kinetic energy and thus their temperature decreases.

Two methods are usually used to liquefy gases.

- (i) **Linde’s Method:** Linde in 1895 successfully liquefied air by using Joule-Thomson effect. In this method gases are compressed and allowed to expand repeatedly thus ultimately they get liquefied.
- (ii) **Claude’s Method:** This method is based on the principle of cooling due to adiabatic expansion. In this method compressed gas is allowed to do work by expanding in the cylinder. Here cooling produced is greater than that produced in Linde’s method. This process is repeated again and again thus ultimately gas is liquefied.

Plasma:

Plasma is fourth state of matter. The term plasma was originally used by Langmuire in 1928 to ionized gas in electric discharge.

It is most abundant state of matter in the universe but is least abundant on the earth. On earth plasma is present in the upper atmosphere. 99% of universe consists of plasma. As plasma is the most abundant state of matter in the universe so it might be considered as first state of matter.

“The state of matter that consists of neutral molecules, cations and electrons is called plasma.”

Or

“The state of matter that consists of ionized gas is called plasma.”

At very high temperatures, electrons are knocked out from atoms or molecules so they are ionized and constitute plasma. Alternatively during electric discharge plasma is also produced. Plasma conduct electricity and it has many unique properties that are different from solid, liquid and gas.

Examples:

- (i) Neon signs are plasma.
- (ii) Electric arc used by welders contains plasma.
- (iii) During lightening plasma is produced.
- (iv) In discharge tube plasma is produced.
- (v) Flames contain plasma.
- (vi) Sun and most of other stars as well as space contain plasma.
- (vii) Luminous clouds contain plasma.

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Applications:

- (i) Plasma is used in fluorescent lamps.
- (ii) It is used for sterilization of food.
- (iii) It is used for sterilization of surgical tools and operation theaters.
- (iv) It is used to kill bacteria, viruses, fungi and spores.
- (v) It is used in Neon signs.
- (vi) Plasma display screens are used in televisions, monitors etc.
- (vii) Fluorine plasma is used for etching metal films.
- (viii) Oxygen plasma is used for cleaning laboratory glassware.
- (ix) Contact lenses can be improved by plasma treatment.
- (x) It is used for high power microwaves sources and pulse power switches.

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