Study of Gas Laws

The Gaseous State

A gas neither has a fixed shape nor a fixed volume. Hence, it does not have a fixed boundary. It can flow in all directions and can be easily compressed. In a given space, the number of particles in a gas is lesser than in the case of a solid or a liquid. The constituent particles of a gas show a random motion because of the presence of large spaces between them.

Consequently, the kinetic energy of the particles in a gas is more than in the case of a solid or a liquid. Due to the large distances between the particles, the forces of attraction between them are very low or negligible.

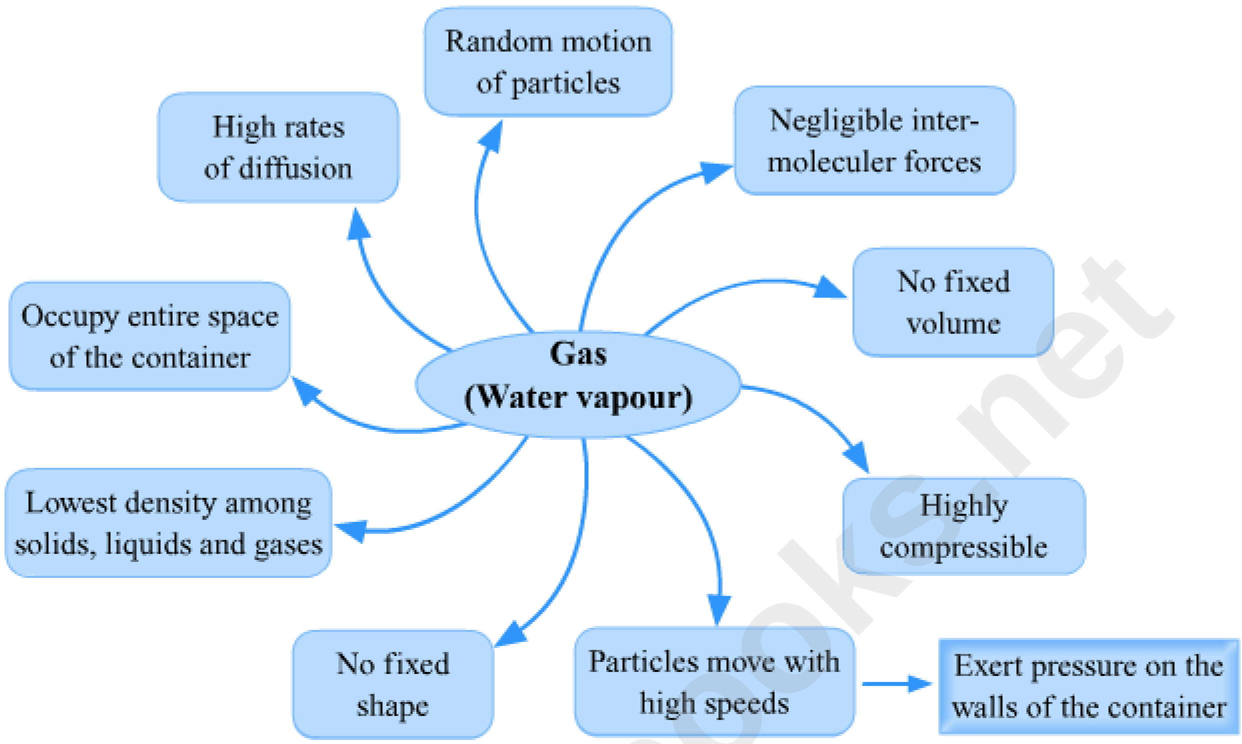
Activity Time

Procedure: Take three 100 mL syringes and remove their pistons. Close the nozzles of the syringes with rubber corks. Fill one syringe with chalk powder and another with water. Now, reinsert the pistons and push them.

Result: The force required to push the pistons of syringes containing chalk powder and water will be greater than that required to push the piston of the syringe containing air.

The Gaseous State

The following diagram illustrates the properties of a gas.



Boyle's Law and Charle's Law

Boyle's Law

- Relation between pressure (p) and volume (V)

- Statement − At constant temperature, the pressure of a fixed amount (number of moles, n) of a gas is inversely proportional to its volume.

- Explanation − Based on kinetic theory:
- Number of particles and their average kinetic energy is constant for a given mass of gas.
- When volume of a certain mass of gas is reduced to half, the particles have lesser space to move around.
- The number of collision of the particles with the walls of the container doubles, thus increasing the pressure to twice the original value.
- Mathematically,

$$p \propto \frac{1}{V} \text{(at constant } T \text{ and } n\text{)}$$

$\Rightarrow p = k_1 \frac{1}{V}$, where k_1 = Proportionality constant

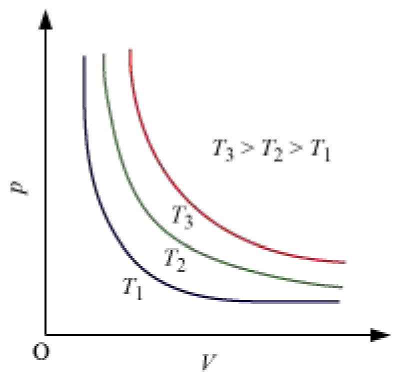
$$\Rightarrow pV = k_1$$

- From the above equation, it is found that at constant temperature, the product of pressure and volume of a fixed amount of a gas is constant.

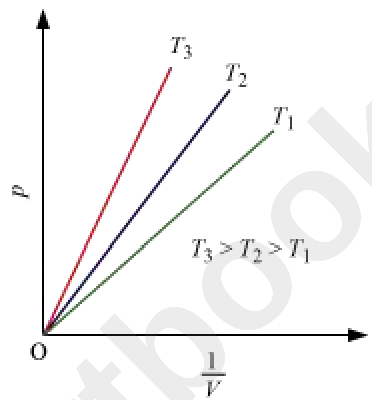
- The value of k_1 depends upon

  - amount of the gas
  - temperature of the gas
  - units of p and V

  Graphical representation of Boyle's law



p vs V graph



p vs $\frac{1}{V}$ graph

  - Each line is called isotherm (at constant temperature plot).

- If at constant temperature,

  V_1 = Volume of a gas at pressure p_1

  V_2 = Volume of the same gas at pressure p_2

  Then,

  $p_1V_1 = p_2V_2$ = Constant

  $$\Rightarrow \frac{p_1}{p_2} = \frac{V_2}{V_1}$$

- Relationship between density (d) and pressure (p):

  We know that,

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

Where, m = Mass of a gas

V = Volume of the gas

$$\Rightarrow d = \left(\frac{m}{k_1}\right)p \quad \left(\text{since } p = k_1 \frac{1}{V}\right)$$
$$\Rightarrow d = k'p$$
$$\Rightarrow d \propto p$$

- From the above equation, it is known that density is proportional to the pressure of a fixed amount of a gas.
- Significance of Boyle's law:
- Mountaineers carry oxygen cylinders with them as at higher altitudes as the pressure is low.

Example

Rita has two cylinders. One is empty and the other contains compressed nitrogen at 25 atm. She wants to distribute the gas in the two cylinders. To do so, she connects the two cylinders. If the volume of the cylinder containing the gas is 50 L and that of the empty one is 80 L, then what will be the pressure inside the two cylinders?

Solution:

According to Boyle’s law,

$$p_1V_1 = p_2V_2$$

Given, p_1 = 25 atm

V_1 = 50 L

V_2 = (50 + 80) L = 130 L

Now, 25 atm × 50 L = p_2 × 130 L

$$\Rightarrow p_2 = \frac{25 \times 50}{130} \text{ atm}$$
$$= 9.62 \text{ atm}$$

Hence, the pressure inside the cylinders is 9.62 atm.

Charles' Law

- Relation between temperature (*T*) and volume (*V*)

- Statement − At constant pressure, the volume of a fixed amount of a gas is directly proportional to its absolute temperature.
- Explanation − On the basis of kinetic theory
- Average kinetic energy of the particles of a gas is directly proportional to the absolute temperature of the gas
- When temperature is increased at constant pressure, the kinetic energy of the particles increases.
- The number and intensity of collisions with the walls of the container increase, thereby increasing the volume at constant pressure.

- Mathematically,

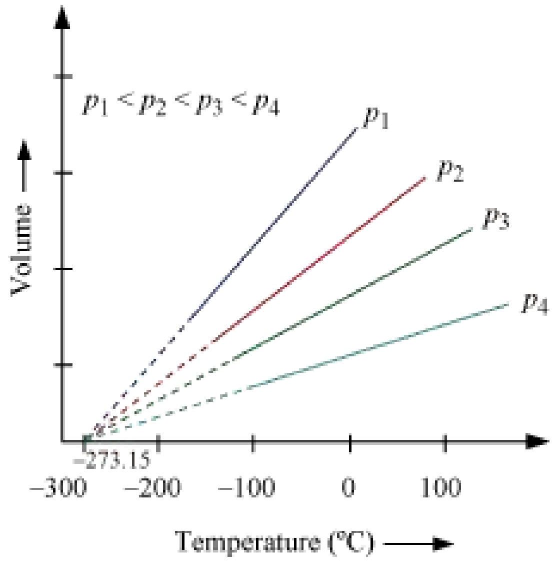
  $V \propto T$

  $\Rightarrow V = k_2 T$, where k_2 = Proportionality constant

- The value of k_2 depends upon

  - pressure of the gas
  - amount of the gas
  - unit of volume

- Graphical representation



- Straight line
- Interception on zero volume at 273.15°C
- Each line is called isobar (constant pressure plot).

- Derivation

For each degree rise in temperature, volume of a gas increases by $\frac{1}{273.15}$ of the original volume of the gas at 0°C.

Suppose, V_0 = Volume of a gas at 0°C

V_t = Volume of the same gas at t°C

Then,

$$V_t = V_0 + \frac{t}{273 \cdot 15} V_0$$
$$\Rightarrow V_t = V_0 \left(1 + \frac{t}{273 \cdot 15} \right)$$
$$\Rightarrow V_t = V_0 \left(\frac{273 \cdot 15 + t}{273 \cdot 15} \right) \qquad \text{(i)}$$

According to Kelvin temperature scale (also called absolute temperature scale or thermodynamic scale),

T = 273.15 + t

$T_0 = 273.15$

From equation (i), we obtain

$$V_t = V_0\left(\frac{T_t}{T_0}\right)$$

$$\Rightarrow \frac{V_t}{V_0} = \frac{T_t}{T_0}$$

Or, we can write

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

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

$$\Rightarrow \frac{V}{T} = \text{constant} = k_2$$

$$\Rightarrow V = k_2 T$$

- Significance of Charle's law:
- Hot air is filled in the balloons used for meteorological purposes.

Example

It is desired to increase the volume of 5 L of a gas by 40% without changing the pressure. To what temperature should the gas be heated if its initial temperature is 298 K?

Solution:

Desired increase in the volume of gas = 40% of 5 L

$$= \frac{40}{100} \times 5 \text{ L}$$

= 2 L

Therefore, final volume of the gas = (5 + 2) L = 7 L

Applying Charles' law,

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

Now, $V_1 = 5$ L

$T_1 = 298$ K

$V_2 = 7$ L

Therefore, $\frac{5\ \text{L}}{298\ \text{K}} = \frac{7\ \text{L}}{T_2}$

$$\Rightarrow T_2 = \frac{7\ \text{L} \times 298\ \text{K}}{5\ \text{L}}$$
$$= 417.2\ \text{K}$$

Standard Temperature and Pressure(STP)

The pressure and temperature of the gas keeps varying frequently. Hence, we choose a standard value for temperature and pressure to which the gas volumes can be referred.
The standard value chosen are 0°0°C or 273K for temperature and 1 atm or 760 mm of Hg for pressure and are commonly known as **S.T.P.**

Diffusion

Diffusion is defined as the random movement of gaseous molecules from regions of higher concentration to regions of lower concentration. It is a physical process and can only occur if the gases do not react with each other.

Graham's Law of Diffusion:

It states that the rate of diffusion of gas is inversely proportional to the square root of its density at the given temperature and pressure.

$$r \propto \frac{1}{\sqrt{d}}$$

$$r = \frac{K}{\sqrt{d}} \text{ or } K = r\sqrt{d}$$

$r =$ rate of diffusion

$d =$ density of gas

$K =$ proportionality constant

Relationship between diffusion and mass

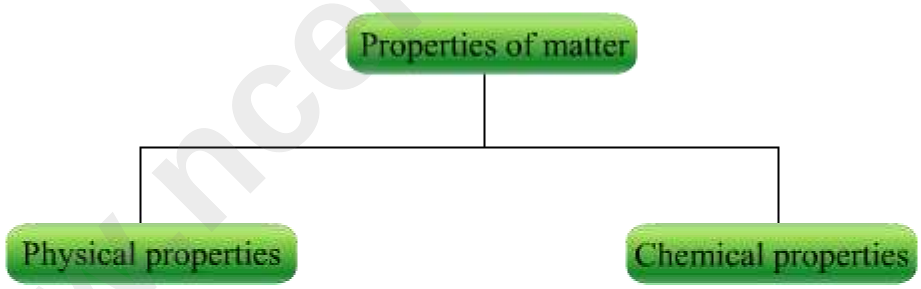
$$r = \frac{K}{\sqrt{d}}$$

$$r \propto \frac{K}{\sqrt{\frac{m}{v}}} \quad \text{as } d = \frac{m \text{ (mass)}}{v \text{ (volume)}}$$

$$\text{Hence, } r = K\sqrt{\frac{v}{m}} \quad \text{or} \quad r \propto \frac{1}{\sqrt{m}}$$

It means that the rate of diffusion is inversely proportional to the square root of mass of the gas.

Properties of Matter



- **Physical properties**
- Properties which can be measured or observed without changing the identity or composition of the substance.
- Example − Colour, odour, melting point, boiling point, density, etc.
- **Chemical Properties**
- Properties in which chemical change in the substance takes place.
- Examples − acidity, basicity, combustibility, characteristic reactions of substance with other elements and compounds

- Many properties of matter such as mass, volume, area etc are quantitative.

Measurement of properties

- **Systems of Measurement**
- English system
- Metric system
- International system of units (SI)
- **The International System of Units (SI)**
- Seven base units

Base Physical Quantity	Symbol for Quantity	Name of SI Unit	Symbol for SI Unit
Length	l	metre	m
Mass	m	kilogram	kg
Time	t	second	s
Electric current	I	ampere	A
Temperature	T	kelvin	K
Amount of substance	n	mole	mol
Luminous intensity	lv	candela	cd

- Definitions of SI base units

Unit of length	metre	The *metre* is the length of the path travelled by light in vacuum during a time interval of 1/299 792 458 of a second.
Unit of mass	kilogram	The *kilogram* is the unit of mass; it is equal to the mass of the international prototype of the kilogram.
Unit of time	second	The *second* is the duration of 9 192 631 770 periods of the radiation corresponding to the transition between the two hyperfine levels of the ground state of the caesium-133 atom.
Unit of electric current	ampere	The *ampere* is that constant current, which if maintained in two straight parallel conductors of infinite length of negligible circular cross-section and placed 1 metre apart in vacuum, would produce a force equal to 2×10^{-7} Newton per metre of length between these conductors.
Unit of thermodynamic temperature	kelvin	The *kelvin*, unit of thermodynamic temperature, is the fraction 1/273.16 of the thermodynamic temperature of the triple point of water.
Unit of amount of substance	mole	1. The *mole* is the amount of substance of a system, which contains as many elementary entities as there are atoms in 0.012 kilogram of carbon-12; its symbol is “mol.”

		2. When the mole is used, the elementary entities must be specified and these may be atoms, molecules, ions, electrons, other particles, or specified groups of such particles.
Unit of luminous intensity	candela	The *candela* is the luminous intensity (in a given direction) of a source that emits monochromatic radiation of frequency 540×10^{12} hertz and that has a radiant intensity in that direction of 1/683 watt per steradian.

- Prefixes used to indicate the multiples or submultiples of a unit.

Multiple	**Prefix**	**Symbol**
10^{-24}	yocto	y
10^{-21}	Zepto	z
10^{-18}	atto	a
10^{-15}	femto	f
10^{-12}	pico	p
10^{-9}	nano	n

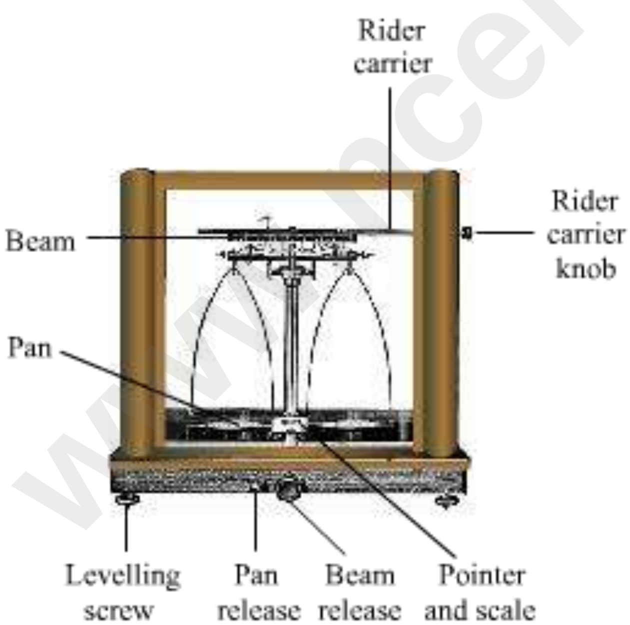
10^{-6}	micro	μ
10^{-3}	milli	m
10^{-2}	centi	c
10^{-1}	deci	d
10	deca	da
10^{2}	hecto	h
10^{3}	kilo	k
10^{6}	mega	M
10^{9}	giga	G
10^{12}	tera	T
10^{15}	peta	P

10^{18}	exa	E
10^{21}	zeta	Z
10^{24}	yotta	Y

- **Mass and Weight**

Mass	Weight
Amount of matter present in an object	Force exerted on an object by gravity
Constant, irrespective of the place	Varies from place to place due to change in gravity

- Mass can be determined accurately by using an analytical balance.



- SI unit of mass = Kilogram (kg)

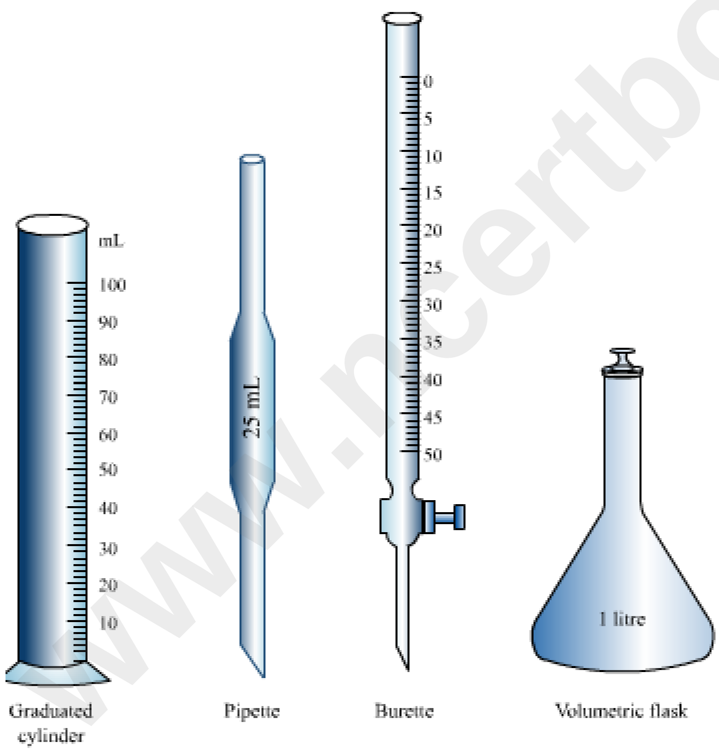
- 1 kg = 1000 g = 10^6 mg

- **Volume**
- Amount of space occupied by an object
- Has the units of $(\text{length})^3$
- SI unit = m^3
- Often used units = dm^3, L

  $1\ dm^3 = 1000\ cm^3$

  1 L = 1000 mL

- 1 Litre is equal to 1 dm^3.
- 1 Millilitre is equal to 1 cm^3.
- Measuring devices − Burette, pipette, graduated cylinder, volumetric flask



- **Density**
- Amount of mass per unit volume

  i.e. Density $= \dfrac{\text{Mass}}{\text{Volume}}$

- SI unit of density = $\frac{\text{SI unit of mass}}{\text{SI unit of volume}}$

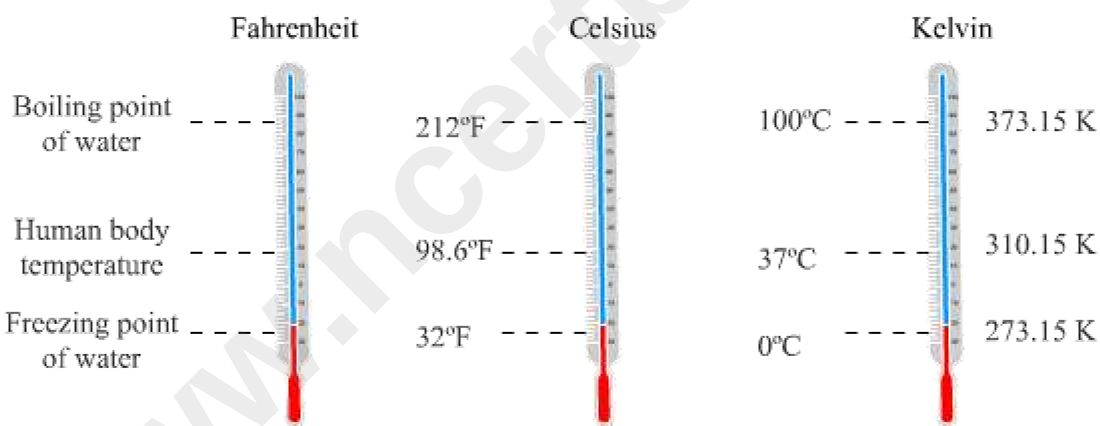
$= \frac{kg}{m^3}$ or $kg\ m^{-3}$

- Often used unit = $g\ cm^{-3}$
- **Temperature**
- Three scales − degree Celsius (°C)

degree Fahrenheit (°F)

kelvin (K)

- SI unit = Kelvin (K)
- Thermometers using different temperature scales



- Relation between °F and °C scale

$°F = \frac{9}{5}(°C) + 32$

- Relation between K and °C scale

$K = °C + 273.15$

- Negative values of temperature are possible in °C scale, but not in °F and K scale.

Example

The boiling point of water at sea level is 212 °F. What is its equivalent in Kelvin scale?

Solution:

To convert temperature from Fahrenheit scale into Kelvin scale, the following equations are used.

$°F = \frac{9}{5}(°C) + 32$

$\Rightarrow °C = (°F - 32)/1.8$

$K = °C + 273.15$

Converting °F into °C,

$°C = (212 - 32)/1.8$

$= 100$

Therefore, the boiling point of water is 100°C converting °C into K.

$K = °C + 273.15$

$= 100 + 273.15$

$= 373.15$

Hence, 212°F is equivalent to 373.15 K.

Ideal Gas Equation, Dalton's Law of Partial Pressure

Ideal Gas

- The gas which strictly follows Boyle's law, Charles' law and Avogadro law
- The intermolecular forces are assumed to be absent between the molecules of an ideal gas.

- Under a certain specific condition (when the intermolecular forces are negligible), real gases follow the above laws.

Ideal Gas Equation

- Equation obtained by the combination of Boyle's law, Charles' law and Avogadro law

Boyle's law: $V \propto \frac{1}{p}$ …(At constant T and n)

Charles' law: $V \propto T$ …(At constant p and n)

Avogadro law: $V \propto n$ …(At constant p and T)

By combining the above three laws, we have

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

$$\Rightarrow V = \mathrm{R}\frac{nT}{p}$$

$\Rightarrow pV = n\mathrm{R}T$…….(i)

R = Proportionality constant, known as Universal Gas Constant

Equation (i) is called ideal gas equation.

- At STP, for one mole of a gas, R = 8.314 $\mathrm{JK^{-1}\ mol^{-1}}$

Or, R = 8.20578×10^{-2} L atm $\mathrm{K^{-1}\ mol^{-1}}$

- It is also called the equation of state
- Reason: It relates between four variables and describes the state of a gas.
- **Combined gas law:**

If the temperature, volume and pressure of a fixed amount of a gas vary from T_1, V_1 and p_1 to T_2, V_2 and p_2, then we have

$$\frac{p_1V_1}{T_1} = nR \qquad \text{(ii)}$$

$$\frac{p_2V_2}{T_2} = nR \qquad \text{(iii)}$$

From equations (ii) and (iii), we have

$$\frac{p_1V_1}{T_1} = \frac{p_2V_2}{T_2} \qquad \text{(iv)}$$

Equation (iv) is called combined gas law.

Examples

1. A vessel of 200 mL capacity contains a certain amount of gas at 27°C and 0.9 bar pressure. The gas is then transferred into another vessel of capacity 150 mL at 27°C. What would be the pressure of the gas in the vessel of capacity 150 mL?

Solution:

According to combined gas law,

$$\frac{p_1V_1}{T_1} = \frac{p_2V_2}{T_2}$$

Here, initial pressure of the gas, p_1 = 0.9 bar

Final pressure of the gas, p_2 = ?

Initial volume of the gas, V_1 = 200 mL

Final volume of the gas, V_2 = 150 mL

Initial temperature of the gas, T_1 = (27 + 273) K = 300 K

Final temperature of the gas, T_2 = (27 + 273) K = 300 K

Now, $\frac{p_1V_1}{T_1} = \frac{p_2V_2}{T_2}$

$$\Rightarrow \frac{0.9 \times 200}{300} = \frac{p_2 \times 150}{300}$$

$$\Rightarrow p_2 = \frac{0.9 \times 200 \times 300}{150 \times 300}$$

= 1.2 bar

Hence, the pressure of the gas in the vessel of capacity 150 mL would be 1.2 bar.

2. How many grams of nitrogen are present in an 8.21 L sample of a gas at 5 atm and −23°C?

Solution:

It is given that,

V = 8.21 L

p = 5 atm

T = (−23 + 273)K = 250 K

Here, R = 0.0821 L atm K^{-1} mol^{-1}

From the ideal gas equation, we have

$pV = n\text{R}T$

$$\Rightarrow n = \frac{pV}{\text{R}T}$$

$$= \frac{5 \text{ atm} \times 8.21 \text{ L}}{0.0821 \text{ L atm K}^{-1} \text{ mol}^{-1} \times 250 \text{ K}}$$

= 2 mol

Molar mass of nitrogen gas= 28 g

This means that 1 mole of nitrogen gas weighs 28 g.

Therefore, 2 moles of nitrogen gas will weigh 2 × 28 g, i.e., 56 g.

Thus, at 5 atm and −23°C, 56 g of nitrogen gas are present in an 8.21 L sample of the gas.

- Relation between density and molar mass of a gaseous substance:

$pV = n\mathrm{R}T$

$\Rightarrow pV = \frac{m}{M}RT$ ($n = \frac{m}{M}$ Where, m = Mass of the gas, M = Molar mass of the gas)

$\Rightarrow \frac{m}{MV} = \frac{p}{RT}$

$\Rightarrow \frac{d}{M} = \frac{p}{RT}$ (Where, Density, $d = \frac{m}{V}$)

$\Rightarrow M = \frac{dRT}{p}$

Dalton's Law of Partial Pressures

- Partial pressure: Pressure exerted by the individual gases in a mixture
- Statement: At constant temperature, the total pressure exerted by a mixture of two or more non-reacting gases, enclosed in a definite volume, is equal to the sum of the partial pressures of the individual gases.
- Mathematically,

$P_{\text{total}} = p_1 + p_2 + p_3 + \ldots\ldots\ldots$.. (At constant T and V)

Where, p_{total} = Total pressure exerted by the mixture

$p_1 + p_2 + p_3$, ... = Partial pressures of the individual gases

- $p_{\text{dry gas}} = p_{\text{total}}$ − Aqueous tension

Where, $p_{\text{dry gas}}$ = Pressure of dry gas

p_{total} = Total pressure

- Aqueous tension: Pressure exerted by saturated water vapour

- Partial pressure in terms of mole fraction:

  Suppose three gases are enclosed in a vessel of volume, V at temperature, T and exert partial pressures, p_1, p_2 and p_3 respectively.

  Then, we have

$$p_1 = \frac{n_1 RT}{V}$$
$$p_2 = \frac{n_2 RT}{V}$$
$$p_3 = \frac{n_3 RT}{V}$$

  Where, n_1, n_2, n_3 = Number of moles of the gases

  Now, $p_{total} = p_1 + p_2 + p_3$

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

  By dividing p_1 by p_{total}, we have

$$\frac{p_1}{p_{total}} = \left(\frac{n_1}{n_1 + n_2 + n_3}\right) \frac{RTV}{RTV}$$
$$\Rightarrow \frac{p_1}{p_{total}} = \frac{n_1}{n_1 + n_2 + n_3}$$
$$\Rightarrow \frac{p_1}{p_{total}} = \frac{n_1}{n} \quad (n = n_1 + n_2 + n_3)$$
$$\Rightarrow \frac{p_1}{p_{total}} = x_1$$
$$\Rightarrow p_1 = x_1 p_{total}$$

- x_1 is called the mole fraction of the first gas

- General equation

$p_i = x_i\, p_{total}$

p_i = Partial pressure of *i*th gas

x_i = Mole fraction of *i*th gas

Example

A gaseous mixture of oxygen and nitrogen contains 22.4 g of oxygen and 145.6 g of nitrogen. The pressure of the mixture is 700 Nm^{-2}. What are the respective partial pressures of oxygen and nitrogen in the mixture?

Solution:

Molar mass of O_2 = 32 g mol^{-1}

Molar mass of N_2 = 28 g mol^{-1}

Therefore, number of moles of O_2 in the mixture $= \dfrac{22.4\,g}{32\ g\ mol^{-1}} = 0.7\ mol$

Number of moles of N_2 in the mixture $= \dfrac{145.6\ g}{28\ g\ mol^{-1}}$

= 5.2 mol

Hence, mole fraction of O_2, $x_{O_2} = \dfrac{0.7}{0.7 + 5.2}$

$= \dfrac{0.7}{5.9}$

= 0.119

Mole fraction of N_2, x_{N_2} = 1 − 0.119

= 0.881

Given, total pressure, p_{total} = 700 Nm^{-2}

Therefore, partial pressure of O_2, $p_{O_2} = x_{O_2}\ p_{total}$

$= 0.119 \times 700\ Nm^{-2}$

$= 83.3\ Nm^{-2}$

And, partial pressure of N_2, $p_{N_2} = x_{N_2}\ p_{total}$

$= 0.881 \times 700\ Nm^{-2}$

$= 616.7\ Nm^{-2}$