1. Details of Module and its structure

Module Detail			
Subject Name	Chemistry		
Course Name	Chemistry 01 (Class XI, Semester - 1)		
Module Name/Title	States of Matter: Part 2		
Module Id	kech_10502		
Pre-requisites	State of matter, Intermolecular Interactions, Gaseous State		
Objectives	 After going through this module, the learner will be able to: Explain the laws governing behaviour of ideal gases. Apply gas laws in various real life situations. 		
Keywords	Gas Laws, Boyle's Law, Charles law, Gay Lussac's law, Avagadro Law, Isotherm, Isobar, Isochore, Avagadro constant, Ideal gas equation, Gas constant, Combined gas law, Equation of state.		

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- 1. **The Gas Laws:** The gas laws which we will study now are the result of research carried on for several centuries on the physical properties of gases. The first reliable measurement on properties of gases was made by Anglo-Irish scientist Robert Boyle (Fig. 1)in 1662. The law which he formulated is known as Boyle's Law. Later on attempts to fly in air with the help of hot air balloons motivated Jaccques Charles and Joseph Lewis Gay Lussac to discover additional gas laws. Contribution from Avogadro and others provided lot of information about gaseous state.



Fig. 1. Robert Boyle (1627-1691)

Source:

(https://upload.wikimedia.org/wikipedia/commons/2/28/Portrait_of_The_Honourable_Robert Boyle (1627 - 1691) Wellcome_M0006615.jpg)

2. Boyle's Law (Pressure - Volume Relationship): On the basis of his experiments, Robert Boyle reached to the conclusion that at constant temperature, the pressure of a fixed amount (i.e., number of moles n) of gas varies inversely with its volume. This is known as Boyle's law. Mathematically, it can be written as

$$p \propto \frac{1}{V}$$
 (at constant T and n)
.....(1)
 $\Rightarrow p = k_1 \frac{1}{V}$...

where k_1 is the proportionality constant. The value of constant k_1 depends upon the amount of the gas, temperature of the gas and the units in which p and V are expressed.

...(2)

On rearranging equation (2) we obtain $pV = k_1$

It means that at constant temperature, product of pressure and volume of a fixed amount of gas is constant.

If a fixed amount of gas at constant temperature *T* occupying volume V_1 at pressure p_1 undergoes expansion, so that volume becomes V_2 and pressure becomes p_2 , then according to Boyle's law :

$$p_1 V_1 = p_2 V_2 = \text{constant} \qquad \dots (4)$$
$$\Rightarrow \frac{p_1}{p_2} = \frac{V_2}{V_1} \qquad \dots (5)$$

Fig. 2 shows two conventional ways of graphically presenting Boyle's law. Fig. 2 (a) is the graph of equation (3) at different temperatures. The value of k_1 for each curve is different because for a given mass of gas, it varies only with temperature. Each curve corresponds to a different constant temperature and is known as an isotherm (constant temperature plot). Higher curves correspond to higher temperature. It should be noted that volume of the gas doubles if pressure is halved. Table 1 gives effect of pressure on volume of 0.09 mol of CO₂ at 300 K.

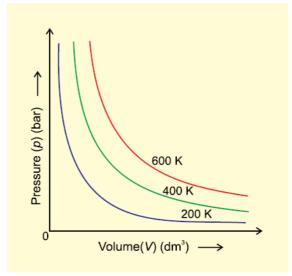


Fig. 2 (a) Graph of pressure, p vs. Volume, V of a gas at different temperatures. (Source: Fig. 5.5 (a), page no. 137, Class XI Textbook NCERT)

.....(3)

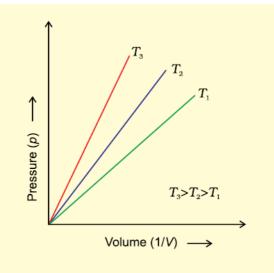


Fig. 2 (b) Graph of pressure of a gas, p vs. *1/V* (Source: Fig 5.5 (b), page no. 137, Class XI Textbook NCERT)

Fig 2 (b) represents the graph between p and 1/V. It is a straight line passing through origin. However at high pressures, gases deviate from Boyle's law and under such conditions a straight line is not obtained in the graph.

Experiments of Boyle, in a quantitative manner prove that gases are highly compressible because when a given mass of a gas is compressed, the same number of molecules occupies a smaller space. This means that gases become denser at high pressure. A relationship can be obtained between density and pressure of a gas by using Boyle's law:

By definition, density '*d*' is related to the mass '*m*' and the volume '*V*' by the relation:

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

If we put value of *V* in this equation from Boyle's law equation, we obtain the relationship:

$$d = \left(\frac{m}{k_1}\right) p = k' p$$

This shows that at a constant temperature, pressure is directly proportional to the density of a fixed mass of the gas.

Pressure / 10 ⁴ Pa	Volume / 10⁻³ m³	(1/V) / m ⁻³	$pV / 10^2 Pa m^3$
2.0	112.0	8.90	22.40
2.5	89.2	11.2	22.30
3.5	64.2	15.6	22.47
4.0	56.3	17.7	22.50
6.0	37.4	26.7	22.44
8.0	28.1	35.6	22.48
10.0	22.4	44.6	22.40

Table 1. Effect of Pressure on the Volume of 0.09 mol CO₂ Gas at 300 K.

Problem 1: A balloon is filled with hydrogen at room temperature. It will burst if pressure exceeds 0.2 bar. If at 1 bar pressure the gas occupies 2.27 L volume, upto what volume can the balloon be expanded?

Solution: According to Boyle's Law, $p_1V_1 = p_2V_2$ If p_1 is 1 bar, V_1 will be 2.27 L If $p_2 = 0.2$ bar, then

$$V_2 = \frac{p_1 V_1}{p_2}$$
$$\Rightarrow V_2 = \frac{1 \operatorname{bar} \times 2.27 \operatorname{L}}{0.2 \operatorname{bar}}$$

= 11.35 L

Since balloon bursts at 0.2 bar pressure, the volume of balloon should be less than 11.35 L. Problem 2: A vessel of 115 ml capacity contains a certain mass of a gas at 20 °C and 780 mm pressure. The gas is then transferred to a vessel whose volume is 180 ml. Calculate the pressure of the gas at 20 °C.

Solution: According to Boyle's Law, $p_1V_1 = p_2V_2$

for V_1 = 115 ml, p_1 = 780 mm

for V_2 = 180 ml, then

$$p_{2} = \frac{p_{1}V_{1}}{V_{2}}$$
$$p_{2} = \frac{780 \times 115}{180}$$

= 498.3 mm

Therefore, the pressure of the gas is 498.3 mm.

3. **Charles' Law (Temperature - Volume Relationship):** Charles and Gay Lussac performed several experiments on gases independently to improve upon hot air balloon technology. Their investigations showed that for a fixed mass of a gas at constant pressure, volume of a gas increases on increasing temperature and decreases on cooling. They found that 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. Thus if volumes of the gas at 0 °C and at t °C are V_0 and V_t respectively, then

$$V_{t} = V_{0} + \frac{t}{273.15} V_{0}$$

$$\Rightarrow V_{t} = V_{0} \left(1 + \frac{t}{273.15} \right)$$

$$\Rightarrow V_{t} = V_{0} \left(\frac{273.15 + t}{273.15} \right)(6)$$

At this stage, we define a new scale of temperature such that t $^{\circ}$ C on new scale is given by *T* = 273.15 + t and 0 $^{\circ}$ C will be given by *T*₀ = 273.15. This new temperature scale is called the Kelvin temperature scale or Absolute temperature scale.

Thus 0°C on the celsius scale is equal to 273.15 K at the absolute scale. Note that degree sign is not used while writing the temperature in absolute temperature scale, i.e., Kelvin scale. Kelvin scale of temperature is also called Thermodynamic scale of temperature and is used in all scientific works.

Thus we add 273 (more precisely 273.15) to the celsius temperature to obtain temperature at Kelvin scale.

If we write $T_t = 273.15 + t$ and $T_0 = 273.15$ in the equation (6) we obtain the relationship

$$V_{t} = V_{0} \left(\frac{T_{t}}{T_{0}}\right)$$
$$\Rightarrow \frac{V_{t}}{V_{0}} = \frac{T_{t}}{T_{0}}$$
....(7)

Thus we can write a general equation as follows.

$$\frac{V_2}{V_1} = \frac{T_2}{T_1}$$
.....(8)

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

$$\Rightarrow \frac{V}{T} = \text{constant} = k_2$$
.....(9)
Thus $V = k_2 T$
.....(10)

The value of constant k_2 is determined by the pressure of the gas, its amount and the units in which volume *V* is expressed.

Equation (10) is the mathematical expression for Charles' law, which states that pressure remaining constant, the volume of a fixed mass of a gas is directly proportional to its absolute temperature. Charles found that for all gases, at any given pressure, graph of volume vs temperature (in celsius) is a straight line and on extending to zero volume, each line intercepts the temperature axis at – 273.15 °C. Slopes of lines obtained at different pressure are different but at zero volume all the lines meet the temperature axis at – 273.15 °C (Fig. 3).

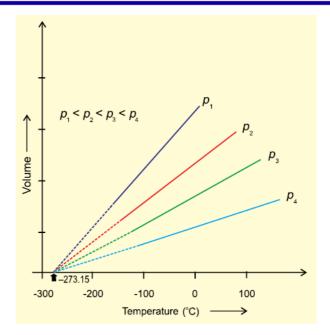


Fig. 3 Volume vs Temperature (°C) graph

(Source: Fig. 5.6, page no. 139, Class XI Textbook NCERT)

Each line of the volume vs temperature graph is called isobar.

Observations of Charles can be interpreted if we put the value of t in equation (2) as -273.15 °C. We can see that the volume of the gas at -273.15 °C will be zero. This means that gas will not exist. In fact all the gases get liquified before this temperature is reached. The lowest hypothetical or imaginary temperature at which gases are supposed to occupy zero volume is called Absolute zero.

All gases obey Charles' law at very low pressures and high temperatures.

Problem 3: On a ship sailing in pacific ocean where temperature is 23.4 °C, a balloon is filled with 2 L air. What will be the volume of the balloon when the ship reaches Indian ocean, where temperature is 26.1 °C?

Solution: $V_1 = 2 L$

 $T_2 = 26.1 + 273 = 299.1 \text{ K}$

 $T_1 = 23.4 + 273 = 296.4 \text{ K}$

From Charles Law,

$$\frac{V_2}{V_1} = \frac{T_2}{T_1}$$
$$\Rightarrow V_2 = \frac{V_1 T_2}{T_1}$$
$$\Rightarrow V_2 = \frac{2 L \times 299.1 K}{296.4 K}$$
$$= 2 L \times 1.009$$
$$= 2.018 L$$

Problem 4: The measured volume of Helium gas at 15 ^oC is 30 ml. What will be its new volume if heated at 35 ^oC at same pressure?

Solution: Given Conditions are as follows:

V1 = 30 mlT1 = 15 + 273 = 288 KV2 = ?T2 = 35 + 273 = 308 K

From Charles Law we have,

$$\frac{V_2}{V_1} = \frac{T_2}{T_1}$$
$$\Rightarrow V_2 = \frac{V_1 T_2}{T_1}$$
$$= V2 = \frac{30 \times 308}{288} = 32.08 \text{ ml}$$

Therefore, the new volume of helium gas at 35 °C is 32.08 ml.

4. **Gay Lussac's Law (Pressure- Temperature Relationship):** Pressure in well inflated tyres of automobiles is almost constant, but on a hot summer day this increases considerably and tyre may burst if pressure is not adjusted properly. During winters, on a cold morning one may find the pressure in the tyres of a vehicle decreased considerably. The mathematical relationship between pressure and temperature was given by Joseph Gay Lussac and is known as Gay Lussac's law. It states that at constant volume, pressure of a fixed amount of a gas varies directly with the temperature.Mathematically,

$$p \propto T$$

 $\Rightarrow \frac{p}{T} = \text{constant} = \mathbf{k}_3$

This relationship can be derived from Boyle's law and Charles' Law. Pressure vs temperature (Kelvin) graph at constant molar volume is shown in Fig. 4. Each line of this graph is called isochore.

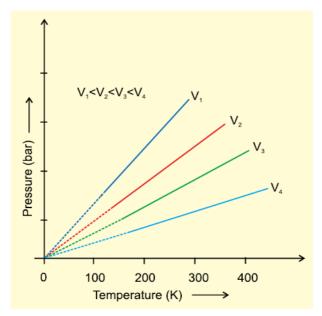


Fig. 4. Pressure vs temperature (K) graph (Isochores) of a gas.

(Source: Fig 5.7, page no. 140, Class XI Textbook NCERT)

Problem 5: A 20 liter container is filled with a gas to a pressure of 2.5 atm at 273 K. If the pressure of the gas gets reduced to 2.0 atm, what will be its final temperature? Solution: The volume of the container remains constant.

Given,

P1 = 2.5 atm, P2 = 2.0 atm T1 = 273 K, T2 = ?

Applying Gay Lussac's Law we have,

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

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

$$= T2 = \frac{2.0 \times 273}{2.5} = 218.4 \text{ K}$$

Therefore, on reducing the pressure of the gas, the temperature will get reduced to 218.4 K.

5. Avogadro Law (Volume - Amount Relationship): In 1811, Italian scientist Amedeo Avogadro tried to combine conclusions of Dalton's atomic theory and Gay Lussac's law of combining volumes (Unit 1) which is now known as Avogadro law. It states that equal volumes of all gases under the same conditions of temperature and pressure contain equal number of molecules. This means that as long as the temperature and pressure remain constant, the volume depends upon number of molecules of the gas or in other words amount of the gas. Mathematically we can write

$$V \propto n$$
 where *n* is the number of moles of the gas.
 $\Rightarrow V = k_4 n$ (11)

The number of molecules in one mole of a gas has been determined to be 6.022×10^{23} and is known as Avogadro constant. You will find that this is the same number which we came across while discussing definition of a 'mole' in Unit 1(Basic concepts of Chemistry).

Since volume of a gas is directly proportional to the number of moles; one mole of each gas at standard temperature and pressure (STP) will have same volume. The previous standard is still often used, and applies to all chemistry data more than decade old. In this definition STP denotes the same temperature of freezing temperature of water i.e. 0 °C (273.15 K), but a slightly higher pressure of 1 atm (101.325 kPa). One mole of any gas of a combination of gases occupies 22.413996 L of volume at STP.

Standard ambient temperature and pressure (SATP), conditions are also used in some scientific works. SATP conditions means 298.15 K and 1 bar (i.e., exactly 105 Pa). At SATP (1 bar and 298.15 K), the molar volume of an ideal gas is 24.789 L mol⁻¹.

Molar volume of some gases is given in (Table 2).

Table 2. Molar volume in litres per mole of some gases at 273.15 K and 1 bar (STP).

Gases	Molar Volume / L mol ⁻¹
Argon (Ar)	22.37
Carbon dioxide (CO ₂)	22.54
Dinitrogen (N ₂)	22.69
Dioxygen (O ₂)	22.69
Dihydrogen (H ₂)	22.72
Ideal gas	22.71

Number of moles of a gas can be calculated as follows

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

.....(12)

where m = mass of the gas under investigation and M = molar mass

Thus,

$$V = k_4 \quad \frac{m}{M} \qquad \dots \dots (13)$$

Equation (13) can be rearranged as follows :

$$M = k_4 \quad \frac{m}{V} = k_4 d \qquad \dots \dots (14)$$

Here, 'd' is the density of the gas. We can conclude from equation (14) that the density of a gas is directly proportional to its molar mass.

A gas that follows Boyle's law, Charles' law and Avogadro law strictly is called an ideal gas. Such a gas is hypothetical. It is assumed that intermolecular forces are not present between the molecules of an ideal gas. Real gases follow these laws only under certain specific conditions when forces of interaction are practically negligible. In all other situations these deviate from ideal behaviour. You will learn about the deviations later in this unit.

6. **Ideal Gas Equation:** The three laws which we have learnt till now can be combined together in a single equation which is known as ideal gas equation.

Boyle's Law:	At constant <i>T</i> and <i>n</i> ; $V \propto 1/p$	
Charles' Law:	At constant <i>p</i> and <i>n</i> ; $V \propto T$	
Avogadro Law:	At constant <i>p</i> and <i>T</i> ; $V \propto n$	
Thus,		
$V \propto \frac{nT}{p}$		(15)
$\Rightarrow V = R \frac{nT}{p}$		(16)

where, *R* is proportionality constant. On rearranging the equation (16) we obtain pV = n RT(17)

$$\Rightarrow R = \frac{pV}{nT}$$
.....(18)

R is called gas constant. It is same for all gases. Therefore it is also called Universal Gas Constant. Equation (17) is called ideal gas equation.

Equation (18) shows that the value of R depends upon units in which p, V and T are measured. If three variables in this equation are known, fourth can be calculated. From this equation we can see that at constant temperature and pressure n moles of any gas will have

the same volume because $V = \frac{nRT}{p}$ and n,R,T and p are constant. This equation will be applicable to any gas, under those conditions when behaviour of the gas approaches ideal behaviour. Volume of one mole of an ideal gas under STP conditions (273.15 K and 1 bar pressure) is 22.710981 L mol⁻¹. Value of R for one mole of an ideal gas can be calculated under these conditions as follows :

R =
$$\frac{(10^5 \text{ Pa})(22.71 \times 10^{-3} \text{m}^{\circ})}{(1 \text{ mol})(273.15 \text{ K})}$$

= $8.314 \times 10^{-2} \text{ bar L } \text{K}^{-1} \text{ mol}^{-1}$

$$= 8.314 \text{ J K}^{-1} \text{ mol}^{-1}$$

At STP conditions used earlier (0 °C and 1 atm pressure), value of R is 8.20578×10^{-2} L atm K⁻¹ mol⁻¹.

Ideal gas equation is a relation between four variables and it describes the state of any gas, therefore, it is also called equation of state.

Let us now go back to the ideal gas equation. This is the relationship for the simultaneous variation of the variables. If temperature, volume and pressure of a fixed amount of gas vary from T_1 , V_1 and p_1 to T_2 , V_2 and p_2 then we can write

$$\frac{p_1 V_1}{T_1} = n \mathbb{R} \quad \text{and} \quad \frac{p_2 V_2}{T_2} = n \mathbb{R}$$

$$\Rightarrow \quad \frac{p_1 V_1}{T_1} = \frac{p_2 V_2}{T_2} \qquad \dots \dots (19)$$

Equation (19) is a very useful equation. If out of six, values of five variables are known, the value of unknown variable can be calculated from the equation (19). This equation is also known as Combined gas law.

Problem 6: At 25 °C and 760 mm of Hg pressure a gas occupies 600 mL volume. What will be its pressure at a height where temperature is 10 °C and volume of the gas is 640 mL.

Solution: Given $p_1 = 760 \text{ mm Hg}$, $V_1 = 600 \text{ mL}$ $T_1 = 25 + 273 = 298 \text{ K}$ $p_2 = ?$ $V_2 = 640 \text{ mL}$ $T_2 = 10 + 273 = 283 \text{ K}$

According to Combined gas law,

$$\frac{p_1 V_1}{T_1} = \frac{p_2 V_2}{T_2}$$

$$\Rightarrow p_2 = \frac{p_1 V_1 T_2}{T_1 V_2}$$

$$\Rightarrow p_2 = \frac{(760 \text{ mm Hg}) \times (600 \text{ mL}) \times (283 \text{ K})}{(640 \text{ mL}) \times (298 \text{ K})}$$

= 676.6 mm Hg

Problem 7: 350 liter of ammonia gas at 298 K and 20 atm pressure are allowed to expand in a space of 600 liters capacity and to a pressure of one atmosphere. What will be the drop in temperature?

Solution: Given: $p_1 = 20$ atm, $V_1 = 350$ L $T_1 = 298$ K $p_2 = 1$ atm $V_2 = 600$ L $T_2 = ?$

According to Combined gas law,

$$\frac{p_1 V_1}{T_1} = \frac{p_2 V_2}{T_2}$$

$$T_2 = \frac{p_2 V_2 T_1}{p_1 V_1}$$

$$T_2 = \frac{1 atm \times 600 L \times 298 K}{20 atm \times 350 L}$$

$$T_2 = 25.5 \text{ K}$$

Therefore, the drop in temperature is (298 - 25.5) = 272.5 K

Density and Molar Mass of a Gaseous Substance: Ideal gas equation can be rearranged as follows:

 $\frac{n}{V} = \frac{p}{RT}$

Replacing *n* by (m/M), we get

$$\frac{m}{M V} = \frac{p}{R T}$$
.....(20)
$$\frac{d}{M} = \frac{p}{R T}$$
.....(21)

where, d is the density. On rearranging equation (21) we get the relationship for calculating molar mass of a gas.

$$M = \frac{d RT}{p}$$
(22)

Problem 8: What is density of ammonia (NH₃) gas at 25 $^{\circ}$ C and 2 atmospheric pressure? (Given: atomic weight of N = 14 and H = 1, R = 0.0821 L atm K⁻¹ mol⁻¹)

Solution: We have,

$$\frac{d}{M} = \frac{p}{RT}$$

$$p = 2 \text{ atm}, T = 25 \,^{0}\text{C} = 298 \text{ K}, R = 0.0821 \text{ L atm K}^{-1} \text{ mol}^{-1}$$

$$M = 14 + (3 \times 1) = 17 \text{ g mol}^{-1}$$

$$d = \frac{2 \times 17}{0.0821 \times 298}$$

$$= 1.39 \text{ g L}^{-1}$$

Problem 9: If the density of a gas is 1.38 g L⁻¹ at 3.6 atm and 280 K, then what will be its molecular weight?

Solution: Given: d = 1.38 g L⁻¹, p = 3.6 atm, T = 280 K, R = 0.0821 L atm K⁻¹ mol⁻¹

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

$$M = \frac{1.38 \times 0.0821 \times 280}{3.6}$$
= 8.81 g mol⁻¹

7. **Summary:** This module explained the interdependence of some observable properties namely pressure, volume, temperature and mass leads to different gas laws obtained from experimental studies on gases. Boyle's law states that under isothermal condition, pressure of a fixed amount of a gas is inversely proportional to its volume. Charle's law is a relationship between volume and absolute temperature under isobaric condition. It states that volume of a fixed amount of gas is directly proportional to its absolute temperature ($V \propto T$). If state of a gas is represented by p_1 , V_1 and T_1 and it changes to state at p_2 , V_2 and T_2 , then relationship between these two states is given by combined gas law according to which

$$\frac{p_1V_1}{T_1} = \frac{p_2V_2}{T_2}$$
 . Any one of the variables of this gas can be found out if other five variables

are known. Avogadro law states that equal volumes of all gases under same conditions of temperature and pressure contain equal number of molecules.