STATES OF MATTER

GASEOUS STATE

Generally four parameters are used to characterise gases : They are

1. The volume

The volume of the container is the volume of gas molecules. It is expressed in litre (L), millilitres (ml) or cubic centimeter (cm^3) or cubic meter (m^3).

$1 L = 1000 ml$ or $1 ml = 10^{-3} L$

$1 L = 1 dm^3$ or $1 dm^3 = 10^3 cm^3$

$1 m^3 = 10^3 = 10^6 cm^3 = 10^6 ml = 10^3 L$

2. The Pressure

It is the force exerted by the gas per unit area of the wall of the container. Pressure is measured by manometer (open end manometer or closed end manometer) It is expressed in atm, torr, or mm of Hg.

Units : 1 atm. = 760 mm of Hg = 76 cm of Hg = 760 torr

In S.I. unit, pressure is expressed in pascal (Pa) which is defined as the pressure exerted when a force of one newton acts on $1m^2$ area

Note : $1 atm = 101.325 \times 10^5 Nm^{-2} = 101.325$ Kpa.

It is also expressed in 'bar' $1 bar = 10^5 Pa$.

3. The temperature

The temperature is measured either in degree centigrade (°C) or in kelvin (K) with the help of thermometer. In S.I. unit Temp is expressed in Kelvin (K) $\boxed{K = {}^\circ C + 273}$

4. The Mass

Mass of gas is expressed in gm or kg or in moles.

$1 kg = 10^3 gm$.

GAS LAWS

(A) Boyle's Law

At constant temperature the volume of the given mass of gas is inversely proportional to its pressure. Mathematically,

$$V \propto \frac{1}{P} \text{ if temperature is constant}$$

$$\Rightarrow \quad V = \frac{k}{P} \quad \Rightarrow \quad PV = K$$

$\because$ log p + log V = constant

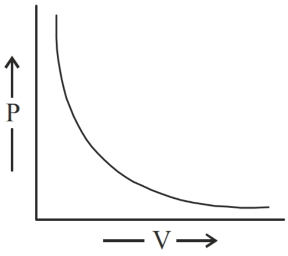
$\because$ log P = –log V + constant

Thus, Boyle's law can also be expressed as the product of pressure and volume of a given mass of gas at constant temperature is constant, i.e.,

$$P_1V_1 = P_2V_2 = P_3V_3 = \ldots\ldots\ldots\ldots.$$

Graphical Representation

(i)



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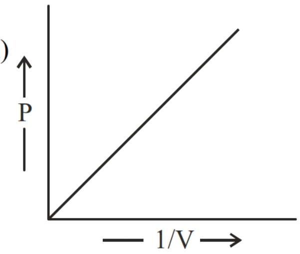

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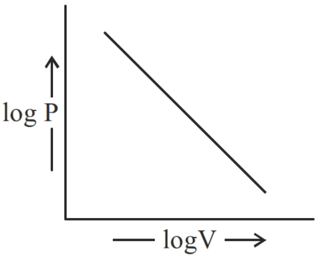

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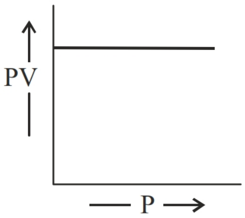

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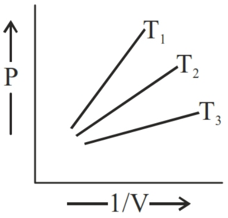

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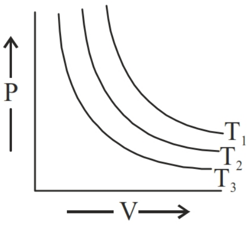

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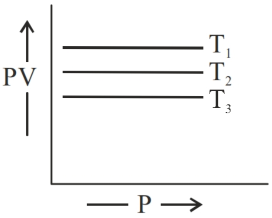


(B) Charle's law

This law is based on the observation that for each degree change in temperature, the volume of the gas is changed by 1/273rd times the initial volume of gas at 0°C. Let volume of the given amount of gas be V_0 at 0°C. If temperature is increased by t°C the new volume becomes, V_t. Thus,

$$V_t = V_0 + \frac{V_2}{273}t = V_0\left(1+\frac{t}{273}\right)$$

$$\Rightarrow \qquad V_t = V_0\left(\frac{273+t}{273}\right)$$

$$= \qquad V_0\frac{T}{273} \text{ where } [273 + t°C = T \text{ (in K)}]$$

$$\Rightarrow \qquad V \propto T$$

Hence Charle's law is stated as

The volume of a given amount of gas at constant pressure varies directly as its absolute temperature.”

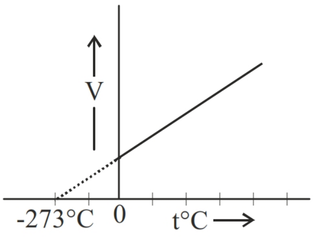
Mathematically

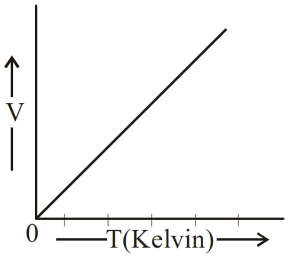
$$V \propto T \quad \text{(if P and ‘n’ are constants)}$$

or $\frac{V}{T}$ = constant if pressure and ‘n’ are constants.

Thus, $\boxed{\frac{V_1}{T_1} = \frac{V_2}{T_2} = K}$ (constant) at constant pressure

Graphical representation





(C) Pressure-Temperature Law

The pressure of a given mass of a gas increases or decreases by $\frac{1}{273}$ of its pressure at 0°C per degree change of temperature. $p_t = p_0 + \frac{p_0 \times t}{273}$

$$\Rightarrow \qquad p_t = p_0 \times \left(1+\frac{t}{273}\right)$$

$$\Rightarrow \qquad p_t = p_0 \times \left(\frac{273+t}{273}\right) = p_0 \cdot \frac{T}{273} \qquad \Rightarrow \qquad \text{where } 273 + t = T$$

or $\qquad P \propto T.$

i.e. at constant volume, the pressure of the given mass of gas is directly proportional to its absolute temperature.

$$\therefore \quad \boxed{\frac{P_1}{T_1} = \frac{P_2}{T_2}}$$

(D) Avogadro's Law

The volume of same number of moles of all gases measured at constant temperature and pressure are the same. That is, at the same temperature and pressure equal volume of all gases contain equal number of moles or molecules.

Mathematically $V \propto n$ at constant T and p

$$\Rightarrow \quad V = k.n$$

For the same value of number of moles at constant temperature and pressure the proportionality constant ‘k’ will be a universal constant. At 0°C and 1 atm the value of k for 1 mole of gas is 22.4 litres.

Ideal Gas Law Equation of State

Combination of Boyle’s law, Charle’s law and Avogadro’s law gives the ideal gas equation.

Boyle’s law $V \propto \frac{1}{p}$ if T is constant.

Charle’s law → $V \propto T$ if P is constant.

and Avogadro’s law → $V \propto n$ if P and T are constant.

Thus, $V \propto \frac{nT}{P}$ i.e. $PV \propto nT$ → or $\boxed{PV = nRT}$

Where R is molar gas constant

or $\boxed{PV = RT}$ for 1 mole of gas

Numerical values of R

(i) $R = \frac{PV}{T}$ (For one mole of gas)

Since one mole of a gas at one atm pressure and 0°C (273 K) occupies a volume of 22.4 litre.

$$\text{Then } R = \frac{1 \times 22.4}{273} = 0.0821 \text{ litre atm. mol}^{-1}\,\text{k}^{-1}.$$

(ii) If pressure is taken in dyne/cm^2 and volume in ml.

$$R = \frac{76 \times 13.67 \times 981 \times 22400}{273} = 8.314 \times 10' \text{ erg k}^{-1}\text{ mol}^{-1} \text{ (CGS units)}$$

(iii) Since $1\text{J} = 10^7$ erg

Thus $R = 8.314$ J mole^{-1} k^{-1}. (SI units)

(iv) Again, Since 1 calorie = 4.184×10^7 erg.

$$R = \frac{8.314 \times 10^7}{4.184 \times 10^7} = 1.987 \approx 2 \text{ calorie mol}^{-1}\,\text{k}^{-1}$$

(v) If pressure is taken in bar so that volume is 22.7 dm^3

$$k = \frac{1 \times 22.7}{1\,\text{mole} \times 273\text{k}} = 0.083 \text{ bar m}^3\text{k}^{-1}\text{mol}^{-1}$$

Dalton’s Law of Partial Pressure

At a given temperature the total pressure exerted by two or more non reacting gases occupying a definite volume is equal to the sum of the partial pressure of the component gases,

Mathematically,

$$P = P_A + P_B + P_C + P_D + \ldots\ldots\ldots\ldots$$

where P is the total pressure and P_A, P_B, P_C ……… are the partial pressures of the gases A, B, C, ……….. respectively.

Partial Pressure

The pressure that a component gas of the gaseous mixture would exert if it were the only gas present in the volume under consideration at a given temperature is the partial pressure of that component.

Let n_1 and n_2 be the no. of moles of two non-reacting gas A and B filled in a vessel of volume V at temp. T.

Thus total pressure in the vessel P, may be calculated as

$$PV = (n_1 + n_2)\,RT$$

partial pressure may be calculated as

$$P_AV = n_1\,RT \text{ and } P_BV = n_2RT$$

Thus,

$$(P_A + P_B)\,V = (n_1 + n_2)\,RT$$

$$\Rightarrow \quad \frac{P_A}{P} = \frac{n_1}{n_1 + n_2} = X_A$$

$$\Rightarrow \quad P_A = X_A \cdot P$$

$$\Rightarrow \quad P_B = X_B \cdot P$$

i.e. $\boxed{\text{Partial Pressure} = \text{Mole fraction} \times \text{Total P}}$

Diffusion and Effusion of Gases

Diffusion : The ability of a gas to mix up spontaneously with the another gas to form a homogeneous mixture against the law of gravitation is called diffusion.

Effusion : A process in which gas is allowed to escape under pressure through a fine orifice or small aperture made in the vessel or wall of a closed container is called effusion.

Graham's law :

At a constant temperature and for constant pressure gradient the rates of effusion or diffusion of different gases are inversely proportional to the square root of their densities.

If r_1 and r_2 are the rates of diffusion of two gases having densities d_1 and d_2 respectively.

$$r_1 \propto \frac{1}{\sqrt{d_1}} \quad \& \quad r_2 \propto \frac{1}{\sqrt{d_2}}$$

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

Since the gas densities are directly proportional to their vapour densities and molecular weight M_1 and M_2.

$$\frac{r_1}{r_2} = \sqrt{\frac{(\text{vapour density})_2}{(\text{vapour density})_1}} = \sqrt{\frac{M_2}{M_1}}$$

Again if m_1 and m_2 are the number of moles of two gases or t_1 and t_2 are the time of flow for equal volumes of the gases, we have

$$\boxed{\frac{r_1}{r_2} = \frac{m_1}{m_2} = \frac{V_1}{V_2} = \frac{t_2}{t_1} = \sqrt{\frac{d_2}{d_1}} = \sqrt{\frac{M_2}{M_1}}}$$

When the pressure is not constant then rate of effusion may be taken proportional to pressure

$$r \propto p \quad \text{and} \quad \boxed{r \propto \frac{1}{\sqrt{M}}}$$

Then, $\quad r \propto \frac{P}{\sqrt{M}} \quad$ or $\quad \Rightarrow \quad \frac{r_1}{r_2} = \frac{p_1}{p_2}\sqrt{\frac{M_2}{M_1}} = \frac{m_1}{m_2}$

Kinetic Theory of Gases

The kinetic theory was presented by Bernoulli (in 1738) and developed by Clausius and Maxwell (in 1860). The theory based on the following postulates :

1. Gases are made up of small structural units called atoms or molecules. Volume of individual atom or molecule is considered negligible.
2. Gas molecules are always in rapid random motion colliding with each other and with the wall of the container.
3. Collision among gas molecules is perfectly elastic, i.e. there is no loss in kinetic energy and momentum during such collision.
4. Gas molecules neither attract nor repel each other.
5. Pressure exerted by gas is due to collisions of gas molecules with the wall of the container.
6. Kinetic energy of gas molecules depends only on absolute temperature.

   Kinetic energy $\propto$ absolute temperature
7. The force of gravity has no effect on the speed of gas molecules.

Kinetic Gas Equation

- On the basis of the postulates of kinetic theory of gases, it is possible to derive the mathematical expression, commonly known as kinetic gas equation, i.e.

$$\boxed{PV = \frac{1}{3}mnc^2}$$

where P = pressure of the gas, m = Mass of a molecule, n = number of molecules present in the given amount of a gas and c = Root mean square speed.

The root mean square speed (RMS speeds) may be defined as the square root of the mean of squares of the individual speed of all the molecules.

$$\text{RMS speed} = \sqrt{\frac{c_1^2 + c_2^2 + c_3^2 + \ldots.. + c_n^2}{n}}$$

- Kinetic Energy the K.E. (E_K) of a gas is given by the following relations

$$E_k = \frac{3}{2}RT \quad \text{(For one mole of gas)}$$

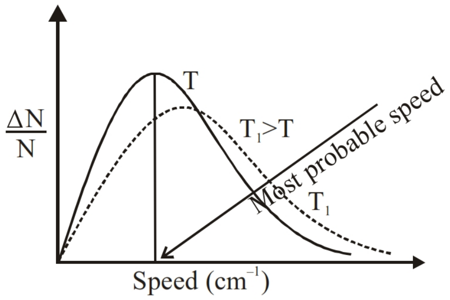
$$E_k = \frac{3}{2}nRT \quad \text{(For n moles of gas)}$$

MAXWELL'S DISTRIBUTION OF SPEEDS

The gas molecules move randomly in all the directions with every changing speeds. It may not be possible to find the speeds of individual molecules but from probability considerations it has become possible to work out the distribution of molecule between different speeds. This is known as Maxwell Boltzman distribution.

⇒ The distribution of speeds remain constant at a given temperature although individual speeds of molecules may go on changing.

⇒ The plot of fraction of molecules $(\Delta N/N)$ having different speeds vs the speed at a given temperature is shown in figure,



⇒ The maximum fraction of molecules possesses a velocity (or speed) corresponding to the peak in the curve. This speed corresponding to the speak in the curve is referred to as most probable speed (α).

⇒ The area under the curve represents total number of molecules.

⇒ As the temperature is increased, the molecules possessing higher speeds increase. Therefore, the maxima, in the curve gets flattened and shifts to the right side (shown, by dotted curve). This is because of the increase in the value of most probable speed (α). In fact, there will be separate distribution curve for every temperature. However, area under the curve will remain the same.

⇒ In brief it may be concluded that with the increase in temperature, the value of most probable speed increases but fraction of molecules possessing this speed decreases.

DIFFERENT TYPES OF MOLECULAR SPEEDS

1. Most Probable Speed (α). It is the speed possessed by maximum fraction of molecules at particular temperature.

$$\alpha = \sqrt{\frac{2RT}{M}} = \sqrt{\frac{2RT}{M}}$$

Here, R = Gas constant; M = Molecular mass;
m = Mass of molecule

2. Average Speed $(\bar{v})$. It is average of the speeds possessed by different molecules at particular temperature. It is given by following expressions

$$\bar{v} = \frac{v_1 + v_2 + v_3.....}{N} = \sqrt{\frac{8RT}{\pi M}}$$

3. Root Mean Square Speed (u or u_{rms}). It is the square root of the mean of squares of speeds of individual molecules at particular temperature. It is given by following expressions

$$u_{rms} = \sqrt{\frac{v_1^2 + v_2^2 + v_3^2.....}{N}} = \sqrt{\frac{3RT}{M}} = \sqrt{\frac{3PV}{M}} = \sqrt{\frac{3P}{d}}$$

VANDER WALL EQUATION (EQUATION OF STATE FOR REAL GAS)

⇒ Real gases deviate from ideal behaviour and do not obey ideal gas laws at all temperatures and pressures. The deviation is observed at low temperatures and high pressures.

⇒ Deviations of real gas from ideal behaviour is expressed in terms of Compressibility factor (z), which is mathematically expressed by relation (PV/nRT).

⇒ If Z = 1, i.e., PV = nRT It refers to ideal behaviour

If $Z > 1$ i.e., $PV > nRT$

Positive deviation, i.e., the gas is less compressible than expected from ideal behaviour.

⇒ If $Z = 1$, i.e., $PV < nRT$

Negative deviation, i.e., the gas is more compressible than expected from ideal behaviour.

⇒ At low temperature and high pressure, neither the volume of molecules is negligible nor the attractive forces among the molecules.

⇒ Vander waal applied volume correction and pressure correction to the ideal gas equation $PV = nRt$ and developed the equation of state for real gas as:

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

Significance of van der Wall constant 'a' and 'b' :

(i) Significance of 'a'. The value of constant 'a' gives the idea of the magnitude of attractive forces between the molecules of the gas. Its units are atm $L^2 mol^{-2}$. Larger the value of a, larger will be the intermolecular attraction among the gas molecules.

(ii) Significance of constant 'b' The constant 'b' is called co-volume or excluded volume per mol of a gas. Its units are L mol^{-1}. It is a measure of effective size of gas molecules. The value of b is four times the actual volume of the molecules.