

## STATES OF MATTER

Prepared by  
Shreemoyee Phukan  
Silapathar College

### **Intermolecular Forces:**

The forces of attraction between molecules which keep molecules together are called intermolecular forces. These forces are classified as Vander waals' forces. They are:

- (i) Dispersion forces or London forces.
- (ii) Dipole-dipole forces
- (iii) Dipole-induced dipole forces

**London Forces:** This type of forces are observed in non-polar molecules such as  $H_2, O_2, N_2, Cl_2$  and in noble gases.

**Dipole-dipole forces:** This forces occur between molecules having permanent electric dipoles e.g., HCl molecules.

**Dipole-induced dipole forces :** These forces are operative between dipole already present and the dipole induced by the first dipole.

**Hydrogen bonding:** The electrostatic forces of attraction between covalently bonded hydrogen of one molecule and most electronegative element of the same or different substance is called hydrogen bonding. It exists mainly between molecules which have OH, NH, FH groups. The H – Bond energy varies between 10 to 100  $KJmol^{-1}$ .

**Thermal Energy:** The energy which moves the molecules apart is called thermal energy. It is defined as energy possessed by matter by virtue of its temperature and is also measure of thermal motion or movement of molecules.

**Change in State.** It involves competition between ordering molecular interaction energy and disordering thermal energy.

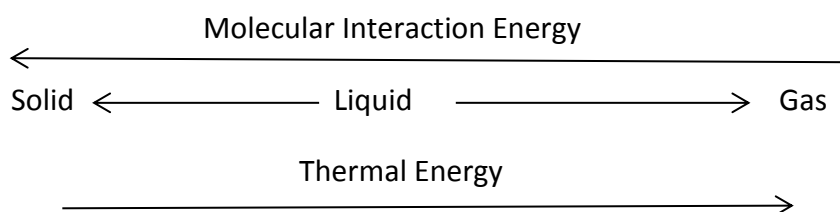


Fig. Change of state involves competition between ordering molecular interaction energy and disordering thermal energy.

**Gas laws:** The gases show uniformity in their behavior. These are governed by certain laws known as gas laws.

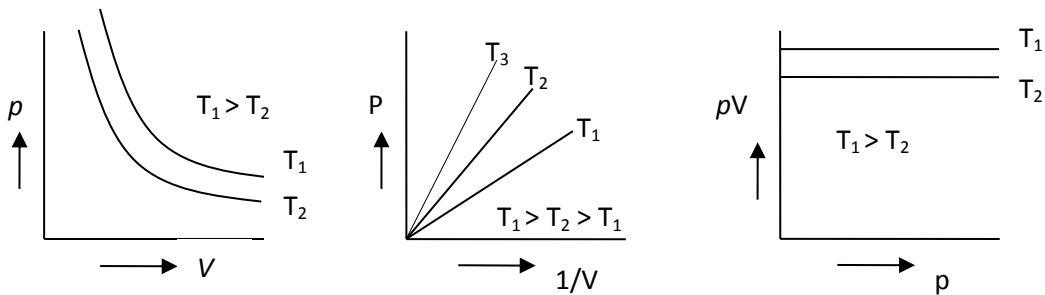
**Boyle's law (Pressure Volume Relationship):**

It states that at constant temperature (T), the pressure (p) of given mass (or n moles) of any gas is inversely proportional to its volume (V).

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

$$pV = \text{constant} , \quad p_1V_1 = p_2V_2 = \text{Constant}$$

**Isotherm:** When we plot pressure volume curve at a constant temperature, it is called isotherm. 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.

**Charles' Law (Temperature-Volume relationship):**

It states that at constant pressure (p) for the given mass (or n moles) of any gas, the temperature (T) is directly proportional to its volume (V).

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

$$V/T = \text{constant}$$

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

According to Jacques Charles, at constant pressure, the volume of the given mass of a gas increases or decreases by  $\frac{1}{273}$  of its volume at  $0^\circ\text{C}$  for each  $1^\circ$  rise or fall in temperature.

If given mass of a gas has volume  $V_0$  at  $0^\circ\text{C}$  then at

$$1^\circ\text{C} \quad V_1 = V_0 \left(1 + \frac{1}{273}\right)$$

$$-1^\circ\text{C} \quad V_{-1} = V_0 \left(1 - \frac{1}{273}\right)$$

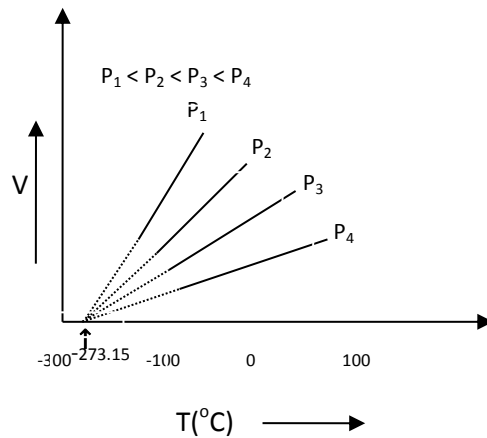
$$\pm t^\circ\text{C} \quad V_t = V_0 \left(1 \pm \frac{t}{273}\right)$$

The mathematical representation of Charles' law

$$V_t = V_0 + \frac{V_0 t}{273.15}$$

$$V_t = V_0 \left(1 + \frac{t}{273.15}\right)$$

**Isobar :** A graph of volume vs temperature at constant pressure is known as isobar. Graphical representation of Charles law as shown below:



**Absolute Zero:** The zero value of thermodynamic temperature equal to 0 Kelvin on  $-273.15^{\circ}\text{C}$ . It is the lowest possible temperature. The gases should occupy zero volume at 0 Kelvin. Relationship between Kelvin scale and Celsius scale is  $T = (t + 273)$  K.

**Gaylussac's Law: (Amanton's Law/Pressure temperature relationship):**

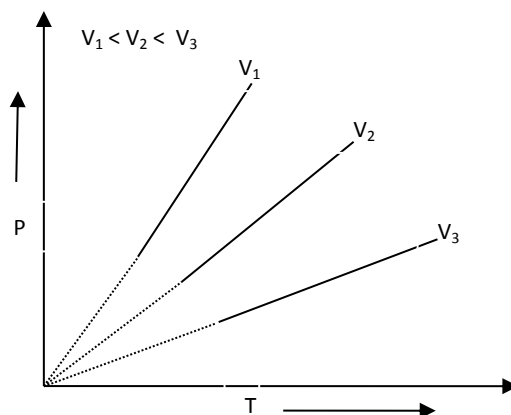
The pressure of a given mass of a gas at constant volume is directly proportional to absolute temperature. Mathematically,

$$P \propto T \text{ or } P = kT \text{ or } \frac{P}{T} = k \text{ at constant } V \text{ and } n$$

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

**Isochores:** A graph of P vs T at constant volume is known as Isochores.

Graphical representation of Gay Lussac's Law as follows:



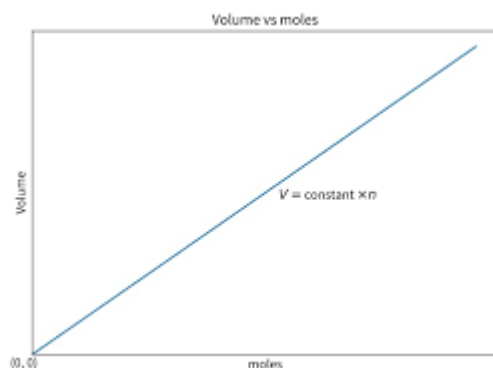
**Avogadro Law (Volume – Amount Relationship):** It states that equal volumes of all gases under the same conditions of temperature and pressure contain equal number of molecules.

Mathematically,

$V \propto n$  at constant T and P where n is the number of moles of the gas.

$$\frac{V}{n} = K \text{ or } \frac{V_1}{n_1} = \frac{V_2}{n_2} \quad \text{at constant T and P.}$$

Graphical representation of Avogadro's Law:



At STP molar volume of an ideal gas or a combination of ideal gas is 22.71098 L

$$\text{moles } (n) = \frac{\text{mass of the gas under investigation } (m)}{\text{molar mass of the gas } (M)}$$

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

$$\therefore V \propto n$$

$$V = K n$$

$$V = K \frac{m}{M}$$

$$M = K \frac{m}{V} \quad \therefore M = Kd$$

It concludes that the density of a gas is directly proportional to its molar mass.

- The vapour density of gas and density of gas are two distinct properties.
- Vapour density is the ratio of a mass of certain volume of gas or vapour to the mass of an equal volume of hydrogen under same conditions of T and p. While density is defined as mass per unit volume of a gas.
- Vapour density has no unit while density of gases are usually expressed in  $\frac{g}{L}$ .

**Ideal Gas:** A gas that follows Boyle's law, Charles' law and Avogadro law strictly is called an ideal gas. Such a gas is hypothetical.

**Ideal Gas Equation (Equation of states):** if we represent three gas laws i.e, Boyle's, Charle's and Avogadro's laws together in a single equation are called ideal gas equation.

$$V \propto \frac{1}{P}, T \text{ and } n \text{ constant (Boyle's law)}$$

$$V \propto T, P \text{ and } n \text{ constant (Charle's law)}$$

$$V \propto n, P \text{ and } T \text{ constant (Avogadro's law)}$$

$$V \propto \frac{nT}{P} \text{ or } PV \propto nT \text{ or } PV = nRT$$

This is known as ideal gas equation. R is known as universal gas constant ( $R = 8.314 \text{ JKmol}^{-1}$ ). 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.

**Combined gas law:** 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

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

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

**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  $\frac{m}{M}$ , we get

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

$$\frac{d}{M} = \frac{p}{RT} \text{ (where } d \text{ is the density)}$$

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

**Dalton's Law of Partial Pressures:** It states that the total pressure exerted by the mixture of non-reacting gases in definite volume and constant temperature is always equal to the sum of their individual pressures which each gas would exert if it occupies the same volume at a constant temperature.

$$p_{\text{total}} = p_1 + p_2 + p_3 + \dots + p_n$$

Partial pressure  $p$  of a gas = mole fraction of the gas  $\times$  total pressure.

For a gas  $i$ ,  $p_i = x_i p_{\text{total}}$ , where  $p_i$  = Partial pressure of gas,  $i$ .

$x_i$  = Mole fraction of gas, i.

If  $n_1$ ,  $n_2$  and  $n_3$  are moles of non reaction gases filled in a vessel of volume  $V$  at temperature  $T$ .

The total pressure  $P$  is given by  $PV = (n_1 + n_2 + n_3)RT$

This is the equation of state of a gases mixture.

- The partial pressure of water vapours in moist gas is referred as aqueous tension.

$$p_{\text{moist gas}} = p_{\text{dry gas}} + p_{\text{water vapour}}$$

$$p_{\text{dry gas}} = p_{\text{moist gas}} - p_{\text{water vapour}}$$

$$= p_{\text{moist gas}} - \text{aqueous tension}$$

- Dalton's law is valid for gases which do not react chemically. For example it is not valid for a mixture of  $\text{SO}_2$  and  $\text{O}_2$ .

**Kinetic Theory of Gases:** The behavior of gases is explained on the basis of following assumptions:

- (i) Every gas comprises of large number tiny particles called as molecules. These particles are identical in shape, mass and size.
- (ii) The volume occupied by molecules is very small as compared to total volume occupied by gas. The particles of gas are in continuous state of motion and during motion they collide with each other as well as the wall of container. As a result pressure is created on the walls of container.
- (iii) The molecules of gas are perfectly elastic and spherical. Therefore, during collision energy is not lost. It is transferred from one particle to other, but the average kinetic energy of the molecules remains same.
- (iv) The attractive forces between the particles are zero (because the distance between them is large).
- (v) Average kinetic energy of gas molecule  $\propto$  absolute temperature.

**Ideal Gas and Real Gas:** The gases which follow gas laws under all the conditions of temperature and pressure are called ideal or perfect gases.

Real gases do not follow gas laws under all the conditions of temperature and pressure.

The real gases show deviations from ideal behavior because following two assumptions of kinetic molecular theory of gases not correct:

- (i) The forces of attraction between the molecules of gases are negligible.
- (ii) The volume occupied by the molecules is negligible as compared to total volume of the gas.

### Deviation of Real Gases from the Ideal Behaviour:

- As the temperature decreases and pressure increases, the deviation of real gas from the ideal gas behaviour also increases. At low pressure all the gases show ideal behaviour.

- **Compressibility factor (Z)** gives the idea about the extent of deviation of real gases from the ideal behaviour (i.e.  $\frac{pV}{nRT} = z$ ) for ideal gas  $Z = 1$

**Negative deviation:** In such case,  $Z > 1$ , gas is more compressible.

**Positive deviation:** In such case,  $Z > 1$ , gas is less compressible.

- **van der Waals' Equation** explains the behaviour of real gases. It is modified ideal gas equation.

$$\left(p + \frac{a}{V^2}\right)(V - b) = RT \text{ (for 1 mole of gas)}$$

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

Where, **a** and **b** are called van der Waals' constant.

- (i) **a** is measure of attractive forces between the molecules of gases. The units of **a** are  $\text{atmL}^2\text{mol}^{-2}$ . Gases having high value of **a** are easily liquefied.
- (ii) **b** gives idea about the effective size of gas molecule. It is also known as co-volume or excluded volume. Units of **b** are  $\text{L mol}^{-1}$ . Greater the size of **b**, larger will be the size of gas molecule and smaller will be compressible volume.

If two gases have same values of **a** but different values of **b**, the gas having smaller value of **b** will show more compressibility and will occupy lesser volume.

- (iii) If two gases have same values of **b** but different values of **a**, the gas having a larger value of **a** will occupy lesser volume due to more attraction among molecules.

**Limitations of Van der Waals' Equation:** There is specific range of temperature and pressure, to apply the equation. It deviates at too high and too low temperature.

- (a) **Critical temperature ( $T_c$ ):** It is the temperature above which a gas cannot be liquefied by applying any amount of pressure.

$$T_c = \frac{8a}{27Rb}$$

- (b) **Critical pressure ( $P_c$ ):** It is the minimum pressure required to liquefy the gas at its critical temperature.

$$P_c = \frac{a}{27b^2}$$

(c) **Critical volume ( $V_c$ ):** It is the volume occupied by the gas at its critical pressure and temperature.

$$V_c = 3b$$

(d) **Relation between critical pressure, critical temperature and critical volume**

$$p_c V_c = \frac{3}{8} RT_c$$

(e) **Important of Critical Temperature and its relation with the Van der Waals' constant 'a':-**

The van der Waals' constant 'a' and critical temperature ' $T_c$ ' and the ease of liquefaction of a few gases are in the order.

<b>Gases:</b>	He	<	H <sub>2</sub>	<	O <sub>2</sub>	<	N <sub>2</sub>	<	CO <sub>2</sub>	<	HCl	<	NH <sub>3</sub>	<	SO <sub>2</sub> .
<b><math>a(\text{atm L}^2 \text{mol}^{-2})</math></b>	0.034		0.244		1.36		1.39		3.59		3.8		4.17		6.71
<b><math>T_c</math> (K)</b>	5.2		33.2		154.3		126.2		304.2		324.7		405.5		

(f) **Inversion temperature:** It is the temperature at which a gas does neither shows cooling or heating. It means Joule Thomson effect at this temperature is zero but below and above this temperature, the gas on subjecting for Joule Thomson effect shows cooling and heating respectively.

(g) **Boyle's temperature:** It is the temperature at which real gas behave as ideal gas. For nitrogen Boyle's temperature is 50°C.

(h) **Triple point:** It is the temperature at which a substance exists in all three states. The triple point of water is at 4.58 pressure and 0.0098°C.

## LIQUID STATE

**Evaporation:** This is spontaneous phenomenon taking place at all temperatures. It is the process in which the liquid changes into vapour and leaves the surface. It results in cooling.

- (i) Rate of evaporation  $\propto$  Temperature
- (ii) Rate of evaporation  $\propto$  Surface area
- (iii) Rate of evaporation  $\propto$  1/Strength of inter molecular forces.

**Vapour Pressure:** It is the pressure exerted by vapours in atmosphere in equilibrium with liquid at a given temperature.

- It increases with increase in temperature.
- It is not affected by volume of liquid taken.
- Higher the vapour pressure of liquid more will be its volatility.
- Boiling point is the temperature at which vapour pressure of liquid is equal to the atmospheric.

**Heat of Vaporisation ( or Evaporation):** It is the amount of heat required to evaporate 1 mole of a given liquid at constant temperature. Its value decreases with increase in temperature. At critical temperature it becomes zero.



**Surface Tension:** It is the force per unit area acting on perpendicular to the length of liquid. The units of surface tension are Newton/meter and dynes/cm. It can also be expressed in terms of surface energy per unit area, as  $\text{Jm}^{-2}$ .

**Effect of temperature and pressure:** Surface tension decreases with increase in temperature because force acting per unit length decreases due to increase in kinetic energy of molecules. Surface tension increases with increases in external pressure because force attraction will increase.

- Surface Tension  $\propto 1/\text{temperature}$  (because the kinetic energy of molecules increases)
- It is measured by instrument called as **stalagmometer**.
- The drops of liquid are spherical due to surface tension.
- Surface active agents decrease the surface tension.

**Viscosity:** It is internal resistance to the flow of liquids which one layer offers to other layer trying to pass over it. The CGS units of viscosity are poise ( $\text{g cm}^{-1}\text{s}^{-1}$ ). It is measured by Ostwald's method. ( $\eta$ ) is known as coefficient of viscosity.

- Fluidity ( $\Theta$ ) is reverse of coefficient of viscosity ( $\eta$ ).

Force is proportional to area of contact and velocity gradient.

$$F \propto A \text{ (area)}$$

$$\propto \frac{dV}{dx} \text{ (velocity gradient)}$$

$$F = \eta A \frac{dV}{dx}$$

Where ' $\eta$ ' is called the coefficient of viscosity and it has the unit of poise,  $\text{g cm}^{-1}\text{s}^{-1}$  in S.I system it is  $\text{Pa s}$  or  $\text{N m}^{-2} \text{s}$  or  $\text{kg m}^{-1}\text{s}^{-1}$ . Poise is  $\frac{1}{10}$ th of S.I. unit.

**Effect of Temperature and Pressure:** Viscosity of liquid decreases with increase in temperature because rise in temperature increases the kinetic energy of molecules, this results in decrease in inter layer friction. It increases with increase in pressure because force required maintaining the flow increases due to decrease in velocity gradient and increasing in area of contact.

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