# Unit

# States of Matter : Gases and Liquids

# STATES OF MATTER

Properties	Solid $rac{H}{C}$	eat ool ↓ Liqnid	leat Gas
Shape	Definite shape	No definite shape	No definite shape
Volume	Definite volume	Definite volume	No definite volume
Order	Ordered	Disordered	Highly disordered
Density	High	Intermediate	Low
Motion	Vibrational metion only	Random motion, kinetic energy is low	Random motion due to high kinetic energy
Compressibility	Nearly incompressible	Slightly compressible	Highly compressible
Intermolecular interaction Very high		Considerable	Very small
	$\begin{array}{c} & & \\$	$\begin{array}{ccc} & & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ \end{array} \xrightarrow{\text{Heat}} \xrightarrow{\text{Heat}}$	

## **INTERMOLECULAR FORCES**

• Intermolecular forces are the forces of attraction or repulsion between atoms and molecules and these forces influence physical properties and sometimes chemical properties.

	London forces	Dipole-dipole forces	Dipole-induced dipole forces
1.	Positive and negative centres overlap	Between molecules having permanent dipole	Between polar and non-polar molecules
2.	No polarity in the system	Polarity in the system	Induced polarity in non-polar molecules
3.	Very weak attractive forces	Weaker than the coulombic forces	Depends upon polarisability and size
4.	Responsible for condensation of gases $\overrightarrow{A}$ $\overrightarrow{\oplus}$ $\overrightarrow{B}$	(ð+) (ð+)	Electron cloud gets deformed due to influence of dipole
5.	Example : Non-polar molecules $H_2$ , $N_2$ , $O_2$ , $Cl_2$ , He, Ne	Example : H <sub>2</sub> O	Example : HCl

#### Hydrogen Bond

• If a hydrogen atom is bonded to a highly electronegative element such as fluorine, oxygen, nitrogen, then the shared pair of electrons lies more towards the electronegative element. This leads to a polarity in the bond in such a way that a slight positive charge gets developed on H-atom, viz,

$$H^{\delta_+}: O^{\delta_-}$$
  $H^{\delta_+}: F^{\delta_-}$   $H^{\delta_+}: N^{\delta_-}$ 

- The bond between the hydrogen atom of one molecule and the more electronegative atom of the same or another molecule is called hydrogen bond.
- Strength of hydrogen bond : Hydrogen bond is a weak bond having bond energy ranging between 10 and 45 kJ mol<sup>-1</sup>. The hydrogen bond energy depends upon the electronegativity and size of the atom linked to hydrogen. For example, for

 $H^{\delta^+}$  .....  $F^{\delta^-}$  bond, the bond energy is 45 kJ mol<sup>-1</sup>  $H^{\delta^+}$  .....  $\Phi^{\delta^-}$  bond, the bond energy is 25 kJ mol<sup>-1</sup>  $H^{\delta^+}$  .....  $N^{\delta^-}$  bond, the bond energy is 13 kJ mol<sup>-1</sup>

#### IN ERMOLECULAR FORCES vs HERMAL ENERGY

- Intermolecular forces tend to keep the particles (atoms or molecules) together. Thermal energy of a substance tends to keep its particles away from each other. Thus the two compete with each other. The three states of matter, are the result of competition between intermolecular forces and thermal energy.
- The particles in solids have very strong intermolecular forces and very little kinetic energy or thermal energy.
- The particles in any liquid have more kinetic energy or thermal energy than in solids.
- The particles in gases have very large kinetic energy or thermal energy and negligible intermolecular forces.



Intermolecular interaction become stronger  $\longrightarrow$ 



Thermal energy increases

- Melting point : The melting point of a solid substance depends on the nature of bonding in it. A solid having ionic interactions has high melting point. Thus, ionic solids have higher melting point. Molecular solids have lower melting point.
- **Beiling points :** Boiling point depends upon the strength of the cohesive forces in any liquid. Liquids having stronger intermolecular interactions, in general, will have higher boiling point. Hydrogen bonding raises the boiling point of a liquid.

Law	Representation	Graphical representation	Applications
Boyle's law	$V \propto \frac{1}{P}$ $PV = \text{constant}$ (at constant temperature)	$V = \begin{array}{c} & & & \\ & & & & \\ & & & \\ & & & & \\$	Determining volume using equation $P_1V_1 = P_2V_2 =$
Charles' law	$\frac{V \propto T}{T} = \text{constant}$ (at constant pressure)	$\begin{array}{c} \bullet \\ T(\mathbf{K}) \longrightarrow \\ \hline \end{array} \begin{array}{c} & & \\ & & $	To calculate volume at different temperatures. $V_t = V_0 \left( 1 + \frac{t^{\circ}C}{273.15} \right)$ $V_0 = $ volume at $0^{\circ}C$
Gay-Lussac's law	$\frac{P \propto T}{\frac{P}{T}} = \text{constant}}$ (at constant volume)	$ \begin{array}{c} \uparrow\\  \\  \\  \\  \\  \\  \\  \\  \\  \\  \\  \\  \\  \\$	$\frac{P_1}{T_1} = \frac{P_2}{T_2}$

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GAS LAWS

- Avogadro's law : Equal volume of all gases under similar conditions of temperature and pressure contain equal number of molecules.
- $V \propto n$  (at constant temperature and pressure)
- n = number of moles

#### **Ideal Gas Equation**

- An ideal gas is defined to be a system in which there are no inter molecular/ interatomic forces. Such a system can only exist as a gas.
- Any real system will approach ideal gas behaviour in the limit that the pressure is extremely low and the temperature is high enough to overcome attractive intermolecular forces.
- An ideal gas is a gas to which the laws of Boyle and

Charles are strictly applicable under all conditions of temperatures and pressures.

From Boyle's law we get,  $V \propto \frac{1}{P}$  (at constant *n* and *T*) From Charles law we get,  $V \propto T$  (at constant *n* and *P*) From Avogadro's law we get,  $V \propto n$  (at constant *T* and *P*) Combining the above three equations we get

$$V \propto \frac{nT}{P}$$
 or,  $V = R \frac{nT}{P}$  [where  $R$  = ideal gas constant]  
or  $PV = nRT$ 

Ideal gas equation is a relation between four variables and it describes the state of any gas. For this reason, it is also called Equation of State. • R = 0.082 lit-atm mol<sup>-1</sup> K<sup>-1</sup> = 8.314 × 10<sup>7</sup> erg mol<sup>-1</sup> K<sup>-1</sup> (C.G.S) = 8.314 J mol<sup>-1</sup> K<sup>-1</sup> (M.K.S) = 2 calorie mol<sup>-1</sup> K<sup>-1</sup>

#### **filustration** 1

The pressure exerted by 12 g of an ideal gas at temperature t °C in a vessel of volume V litre is one atm. When the temperature is increased by 10 degrees at the same volume, the pressure increases by 10%. Calculate t and V (mol. wt. of gas = 120). **Soln.:** Given : P = 1 atm, w = 12 g; T = (t + 273) K;

if 
$$T = t + 10 + 273 = t + 283$$
 K;  $P = 1 + \frac{10}{100} = 1.1$  atm

From, gas equation,  $PV = \frac{W}{M}RT$ 

$$1 \times V = \frac{12}{M} R(t + 273) \qquad \dots (i)$$
  
$$1.1 \times V = \frac{12}{M} R(t + 283) \qquad \dots (ii)$$

By (i) and (ii) t = -173 °C or t = 10 K Also from (i), on substituting tV = 0.82 litre

• Dalton's law of partial pressures : If a mixture of two or more gases, which do not react chemically, is enclosed in a vessel, the total pressure exerted by the gases is equal to the sum of their partial pressures.

 $P_{\text{total}} = P_1 + P_2 + P_3 + \dots$ 

 $P_1$ ,  $P_2$ ,  $P_3$  = pressure of the gases 1, 2 and 3 which they would exert if present alone in a vessel i.e., partial pressure of gases 1, 2 and 3 respectively.

#### Illustration 2

A sample of butane gas  $C_4H_{10}$  of unknown mass is contained in a vessel of unknown volume V at 25°C and a pressure of 760 mm Hg. To this vessel 8.6787 g of neon gas is added in such a way that no butane is lost from the vessel. The final pressure in the vessel is 1920 mm Hg at the same temperature. Calculate the volume of the vessel and the mass of butane. Ans.: Partial pressure of  $C_4H_{10}(p_1) = 760$  mm Hg

By Dalton's law of partial pressure, 
$$P_{\text{total}} = p_1 + p_2$$
  
 $1920 = 760 + p_2$  or  $p_2 = 1160 \text{ mm Hg}$   
 $p_2 = x_2 \times P_{\text{total}}$   
where  $x_2 = \text{mole fraction of Ne}$   
 $x_2 = \frac{P_2}{P_{\text{total}}} = \frac{1160}{1920} = 0.60$ ; Moles of Ne  $= \frac{8.6787}{20.2} = 0.43$   
 $x_2 = \frac{n_2}{n_1 + n_2}$ ;  $0.60 = \frac{0.43}{0.43 + n_1} \implies n_1 = 0.28$   
Molecular weight of  $C_4H_{10} = n_1 \times 58 = 16.24 \text{ g}$   
Again for  $C_4H_{10}$   
 $PV = n_1 RT$ ;  $T = 273 + 25 = 298 \text{ K}$ 

$$P = \frac{760}{760}$$
 atm

$$V = \frac{n_1 RT}{P} = \frac{0.28 \times 0.0821 \times 298}{\left(\frac{760}{760}\right)} \text{ atm} = 6.85 \text{ atm}$$

 Graham's law of diffusion : The rate of diffusion of a gas is inversely proportional to the square root of its density.

Rate of diffusion (r) 
$$\propto \frac{1}{\sqrt{d}}$$
  
or  $\frac{r_1}{r_2} = \sqrt{\frac{d_2}{d_1}}$  or  $\frac{r_1}{r_2} = \sqrt{\frac{M_2}{M_1}}$ 

As we know,

molecular mass  $(M) = 2 \times \text{vapour density} (d)$ 

### Illustration 3

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The pressure in a bulb dropped from 2000 to 1500 mm of mercury in 47 minutes when the contained oxygen leaked through a small hole. The bulb was then completely evacuated. A mixture of oxygen and another gas of molecular weight 79 in the molar ratio of 1 : 1 at a total pressure of 4000 mm of mercury was introduced. Find the molar ratio of the two gases remaining in the bulb after a period of 74 minutes.

Ans.: The molar ratio of oxygen and the other gas in the evacuated bulb = 1: 1 and the total pressure of the gas mixture is 4000 mm, hence the partial pressure of each gas is 2000 mm. The drop in the pressure of oxygen after 74 minutes

$$=\frac{(2000-1500)\times74}{47}=787.2 \text{ mm of Hg}$$

- $\therefore \quad \text{After 74 minutes, the pressure of oxygen} = 2000 787.2 = 1212.8 \text{ mm of Hg}$
- Let the rate of diffusion of other gas be  $r_n$ , then

$$\frac{r_n}{r_{O_2}} = \sqrt{\frac{32}{79}}$$

... Drop in pressure for the other gas

$$= 787.2 \times \sqrt{\frac{32}{79}} = 501.01 \text{ mm of Hg}$$

:. Pressure of the other gas after 74 minutes = 2000 - 501.01 mm = 1498.99 mm of Hg

Molar ratio = 
$$\frac{\text{Moles of unknown gas}}{\text{Moles of O}_2}$$
  
=  $\frac{1498.99}{1212.8}$  = 1.236:1

Avogadro's number and ideal gas equation : Amedeo Avogadro stated that one mole of any gas at standard pressure and temperature contains the same number of molecules. The value is called Avogadro's number and represented by N,  $N_A$  or  $N_0$ .

 $N_{\bullet} = 6.023 \times 10^{23}$  molecules/mole

Ideal gas equation can be written in terms of Avogadro's number as

 $PV = N_0 kT$ ,  $k = \text{Boltzmann constant} = 1.38 \times 10^{-23} \text{ J/K}$ Thus gas constant  $R = kN_0$ .