

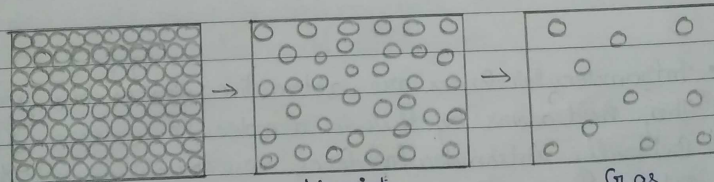
UNIT - 5

STATES OF MATTER

Three States of Matter

Some characteristics of Gases, Liquids & Solids and the Microscopic Explanation for the behaviour.

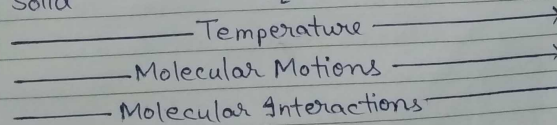
	Gas	Liquids	Solids
1.	Assumes the shape & volume of its container (particles can move past one another)	Assumes the shape of the part of the container which it occupies. (particles can move/slide past one another)	Retains a fixed volume & shape (rigid-particles locked into the place)
2.	Compressible (lots of free space between particles)	Not easily compressible (little free space b/w particles.)	Not easily compressible (little free space b/w particles.)
3.	Flows easily (particles can move past one another)	Flows easily (particles can move/slide past one another)	does not flow easily (rigid-particles can't move/slide past one another)

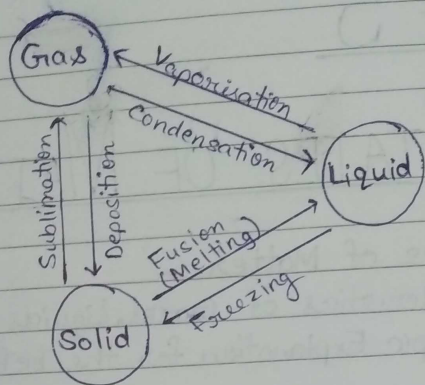


Solid

Liquid

Gas





ENTHALPY OF STATE

Intermolecular Forces

- Intermolecular forces are the forces of attraction & repulsion b/w interacting particles.
- Attractive intermolecular forces are known as van der Waals forces.
- Only a few elements can participate in hydrogen bond formation.
- Intermolecular forces are further subdivided into 3 forces:-
 - (i) Dispersion or London forces
 - (ii) Dipole-dipole forces
 - (iii) Dipole-induced dipole forces
- Intramolecular forces are attractive forces b/w molecules. They hold atoms together in a molecule.
- Generally intermolecular forces are much weaker than intramolecular forces.

Intermolecular Vs Intramolecular

- 41 KJ to vaporise 1 mole of water (Inter)
- 930 KJ to break all O-H bonds in 1 mole of water (intra)

Measures of Intermolecular Force

- Boiling Point
- Melting Point
- ΔH_{vap}
- ΔH_{sub}
- ΔH_{fus}

Types of Intermolecular Forces

Dispersion Forces or London Forces

The London or dispersion force is the weakest intermolecular force. The London or dispersion force is a temporary attractive force that results when the electrons in two adjacent atoms occupy positions that make the atoms form temporary dipoles.

This force is sometimes called an induced dipole-induced dipole attraction. London forces are the attractive forces that cause nonpolar substances to condense to liquids and to freeze into solids when the temperature is lowered sufficiently.

Characteristics of Dispersion or London Forces

- London forces are exhibited by non-polar molecules because of temporary correlated movements of electrons in interacting molecules.

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- This force is a temporary force.
 - These forces are always attractive.
 - The interaction energy is inversely proportional to the sixth power of the distance b/w 2 interacting particles.
 - These forces are important at only very short distances.
 - Their magnitude depends upon the polarisability of the particle.

Dipole - Dipole Forces

Dipole-dipole forces are attractive forces between the +ve end of one polar molecule and the -ve end of another polar molecule. Dipole-dipole forces have strengths that range from 5 kJ to 20 kJ per mole. They are much weaker than ionic or covalent bonds and have a significant effect only when the molecules are close together (touching or almost touching).

Characteristics of Dipole-Dipole Forces

- Dipole-dipole forces act b/w the molecules possessing permanent dipole.
- Ends of dipole possess "partial charges."
- Partial charges are always less than the unit electronic charge.
- This interaction is stronger than London forces but is weaker than ion-ion interaction only because partial charges are involved.
- The attractive forces decrease with the increase of distance b/w the dipoles.
- Interaction energy b/w stationary polar molecules is

proportional to $1/r^3$, interaction energy b/w rotating polar molecules is double of stationary polar molecules where r is the distance b/w the polar molecules.

Induced-Dipole Forces

• Ion-Induced Dipole Forces

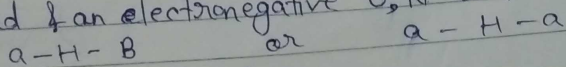
An ion-induced dipole attraction is a weak attraction that results when the approach of an ion induces a dipole in an atom or in a non polar molecule by disturbing the arrangement of electrons in the nonpolar species.

• Dipole induced dipole forces

- This type of attractive forces operate b/w polar molecules having permanent dipole & the molecules lacking permanent dipole.
- The interaction energy is inversely proportional to the sixth power of the distance b/w 2 interacting particles.
- Induced dipole moment depends upon the dipole moment present in the permanent dipole & the polarisability of the electrically neutral molecule.
- Molecules of larger size can be easily polarised.
- High polarisability increases the strength of attractive interactions.

Hydrogen Bond

The hydrogen bond is a special dipole-dipole interaction b/w the hydrogen atom in a polar N-H, O-H or F-H bond & an electronegative O, N or F atom.



a & B are O, N & F

Thermal Energy

- Thermal energy is the energy of the body arising from the motion of its atoms & molecules.
- It is directly proportional to the temp. of a substance.
- It is the measure of the average kinetic energy of the particles of matter & is thus responsible for the movement of particles.
- The movement of particles is called thermal motion.
- Intermolecular forces tend to keep the molecules together but thermal energy of the molecules tends to keep them apart.
- The three states of matter are a result of balance b/w the intermolecular forces & the thermal energy of the molecules.

Boyle's Law (Pressure - Volume Relationship)

It states that, at constant temperature, the pressure of a fixed amount of gas varies inversely with its volume.

$$P \propto \frac{1}{V} \text{ (at const. } T \& n \text{)}$$

$$\Rightarrow P = k_1 \frac{1}{V}$$

$$\Rightarrow pV = k_1$$

$$\Rightarrow P_1 V_1 = P_2 V_2 = \text{const.}$$

$$\Rightarrow \frac{P_1}{P_2} = \frac{V_2}{V_1}$$

Charles's Law (Temperature - Volume Relationship)

It states that, at constant pressure, the volume of a fixed mass of gas is directly proportional to its absolute temperature.

$$V \propto T \text{ (at const. } P \text{ \& } n)$$

$$V = k_2 T$$

$$\frac{V}{T} = k_2$$

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

Gay Lussac's Law (Pressure - Temperature Relationship)

It states that, at constant volume, pressure of a fixed amount of a gas varies directly with the temperature.

$$P \propto T$$

$$\Rightarrow P = k_3 T$$

$$\Rightarrow \frac{P}{T} = k_3$$

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

Avogadro Law (Volume - Amount Relationship)

It states the equal volumes of all gases under the same conditions of temperature and pressure contain equal number of molecules.

$$V \propto n$$

$$\Rightarrow V = k_4 n$$

$$\Rightarrow \frac{V}{n} = k_4$$

$$\Rightarrow \frac{V_1}{n_1} = \frac{V_2}{n_2}$$

We have,

$$V = k_4 n$$

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

$$\text{So, } V = k_4 \frac{m}{M}$$

$$M = k_4 \frac{m}{V}$$

$$\boxed{M = k_4 d}$$

+

Ideal Gas Equation

At const. T & n : $V \propto \frac{1}{P} \Rightarrow$ Boyle's Law

At const. P & n : $V \propto T \Rightarrow$ Charles's Law

At const. P & T : $V \propto n \Rightarrow$ Avogadro Law

Thus, $V \propto \frac{nT}{P}$

$$V = R \frac{nT}{P}$$

$$\boxed{PV = nRT}$$

$$\boxed{R = \frac{PV}{nT}}$$

The three laws combined in one single formula is called the ideal gas equation.

At STP, the value of R is 0.314 kJ/mol and this equation is called equation of state.

Now,

$$\frac{P_1 V_1}{T_1} = nR \quad \& \quad \frac{P_2 V_2}{T_2} = nR$$

$$\Rightarrow \boxed{\frac{P_1 V_1}{T_1} = \frac{P_2 V_2}{T_2}}$$

This equation is called the combined gas law.

As it is containing 5 variables & it is also known as the special equation of quartz Lussaigne's.

Density & Molar Mass of a Gaseous Substance

$$PV = nRT$$

$$\Rightarrow PV = \frac{m}{M} RT$$

$$\Rightarrow P = \frac{m}{M \times V} RT$$

$$\Rightarrow P = \frac{d}{M} RT$$

$$\Rightarrow PM = dRT$$

$$\Rightarrow \boxed{M = \frac{dRT}{P}}$$

$$\Rightarrow M \propto d$$

$$\Rightarrow \boxed{\frac{M_1}{M_2} = \frac{d_1}{d_2}}$$

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Dalton's Law of Partial Pressure

It states that the total pressure exerted by the mixture of non-reactive gases is equal to the sum of the partial pressures of individual gases.

→ In a mixture of gases, the pressure exerted by the individual gas is called partial pressure.
ie. $P_{total} = P_1 + P_2 + P_3 + \dots$

→ Pressure of a dry gas can be calculated by subtracting vapour pressure of water from the total pressure of the moist gas which contains water vapour too.

→ Pressure exerted by a saturated water vapour is called aqueous tension.

$$P_{dry\ gas} = P_{total} - \text{aqueous tension}$$

Partial Pressure in terms of Mole Fraction

Suppose at the temperature T , 3 gases enclosed in the volume V , exert partial pressures P_1, P_2 & P_3 respectively. Then,

$$P_1 = \frac{n_1}{V} RT$$

$$P_2 = \frac{n_2}{V} RT$$

$$P_3 = \frac{n_3}{V} RT$$

n_1, n_2 & n_3 are the no. of moles of these gases & the expression for total pressure will be:

$$P_{total} = P_1 + P_2 + P_3$$
$$= \frac{n_1}{V} RT + \frac{n_2}{V} RT + \frac{n_3}{V} RT$$
$$= \left(\frac{n_1}{V} + \frac{n_2}{V} + \frac{n_3}{V} \right) RT$$

On dividing P_1 by P_{total} , we get

$$\frac{P_1}{P_{total}} = \left(\frac{n_1}{n_1 + n_2 + n_3} \right) \frac{RTV}{RTV}$$

$$\frac{P_1}{P_{total}} = \frac{n_1}{n} \text{ where } n = n_1 + n_2 + n_3$$

$\frac{P_1}{P_{total}} = x_1$, x_1 is called the mole fraction of 1st gas

$$P_1 = x_1 P_{total}$$

Similarly,

$$P_2 = x_2 P_{total}, P_3 = x_3 P_{total} \text{ \& so on.}$$

$$P_i = x_i P_{total}$$

lume

Kinetic Molecular Theory of Matter

The Kinetic Molecular Theory of Matter is an explanation of the behaviour of matter, based on the idea that the particles that make up the matter always in motion. The particles can be atoms, molecules or ions.

1. Matter is composed of tiny particles, the size of the particles is fixed for each substance.

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2. The particles are in constant random motion & therefore possess kinetic energy (energy of motion, which can be transferred by collisions).
 3. The particles interact with each other by means of electrostatic attractions & repulsions, & therefore possess potential energy (stored energy, possessed by matter as a result of its position, condition, and/or composition).
 4. The kinetic energy (velocity) of the particles increases as temperature is increased.
 5. The particles in a system transfer energy by means of elastic collisions (collisions in which all energy transfer results in motion, not deformation).
 6. Compared to the space through which they travel, the particles that make up the gas are so small that their volume can be ignored.
 7. The individual particles are neither attracted to one another nor do they repel one another.
 8. When particles collide with one another (or the walls of the container) they bounce rather than stick. These collisions are elastic if one particle gains kinetic energy another loses kinetic energy so that the average remains constant.

9. Kinetic energy

10. Kinetic energy

11. Potential energy

- (i)
- (ii)
- (iii)

9. Kinetic energy is transformed to work and/or heat in elastic collisions.
10. Kinetic energy is a disruptive force between particles; it makes them more independent of each other.
11. Potential energy is a cohesive or attractive force between particles.

Ideal Gas	Real Gas
(i) It obeys gas laws under all conditions of temperature & pressure	(i) It obeys gas laws only under low pressure & high temp.
(ii) No gas is ideal.	(ii) All gas are real.
(iii) Volume occupied by the molecule is negligible as compared to the total volume occupied by the gas.	(iii) Volume occupied by the molecules is not negligible as compared to the total volume occupied by the gas.
(iv) The forces of attraction among the molecules of gas are negligible.	(iv) The force of attraction among the molecules can't be neglected at high pressure & low temperature.
(v) It obeys the ideal gas equation, $PV = nRT$	(v) It obeys van der Waals equation $\left(\frac{P + \frac{an^2}{V^2}}{V - nb}\right) = nRT$

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Behaviour of Real Gases: Deviation from ideal gas behaviour

- pV value decreases after an increase in pressure & reaches to a min. value characteristic of gas. After the pV value starts increasing. The curve then crosses the line for ideal gas and after that shows +ve deviation continuously. It is thus found that real gases do not follow ideal gas equation perfectly under all the conditions.
- A gas which obeys the gas laws & gas equation $PV = nRT$ strictly at all temperatures & pressures is said to be an ideal gas. The molecules of ideal gases are assumed to be volume less points with no attractive forces b/w one another. But no real gas strictly obeys the gas equation at all temperatures & pressures. Deviations from ideal behaviour are observed particularly at high pressure or low temperatures. The deviation from ideal behaviour is expressed by introducing a factor Z known as compressibility factor in the ideal gas equation. Z may be expressed $Z = PV/nRT$.
 - In case of ideal gas, $PV = nRT$ so, $Z = 1$
 - In case of real gases $PV \neq nRT$ so, $Z \neq 1$Thus in case of real gases Z can be < 1 or > 1
 - (i) When $Z < 1$, it is a -ve deviation. It shows that the gas is more compressible than expected from ideal behaviour.
 - (ii) When $Z > 1$, it is a +ve deviation. It shows that the gas is less compressible than expected from ideal behaviour.

Causes of deviation from ideal behaviour

The causes of deviations from ideal behaviour may be due to the following two assumptions of kinetic theory of gases. These are:

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

- Deviation from ideal behaviour also becomes apparent when pressure vs. volume plot is drawn. The pressure vs volume plot of experimental data (real gas) and that theoretically calculated from Boyle's law (ideal gas) should coincide. It is apparent that at a very high pressure the measured volume is more than the calculated volume. At low pressures, measured & calculated volumes approach each other.

- Real gases show deviations from ideal gas law because molecules interact with each other. At very high pressures molecules of gases are very close to each other. Molecular interactions start operating. At high pressures molecules do not strike the walls of the container with full impact because these are dragged back by the other molecules due to molecular attractive forces.

Thus the pressure exerted by the gas is lower than the pressure exerted by the ideal gas.

$$P_{\text{ideal}} = P_{\text{real}} + \frac{an^2}{V^2}$$

↑
↑
 observed pressure correction term

Here 'a' is a constant term.

- Repulsive forces also become significant. The volume occupied by the molecules ~~because~~ also become significant because instead of moving in volume 'V' these are now restricted to (V-nb) where 'nb' is approximately the total volume occupied by the molecules themselves. Here 'b' is a constant term. Having taken into account the corrections for pressure & volume, we can rewrite the equation as:

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

This equation is called as the van der Waals equation. Where 'n' is no. of moles of the gas. Constants a & b are called van der Waals constants & their value depends upon the characteristic of the individual gas.

The value of 'a' is a measure of magnitude of intermolecular attractive forces within the gas & is independent of temperature & pressure.

Van Der Waals Equation

Atoms & molecules are never truly ideal because they all interact with other gas particles; weak attractions b/w separate gas particles are known as intermolecular attractions or van der Waals forces after the chemist who proposed a correction to the ideal gas law to calculate pressure of a real gas. Van der Waals proposed

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that the ideal gas equation could be corrected for real gas behaviour by subtracting the effective gas particle volume from the volume of the container & by correcting for intermolecular attractions.

$$PV = nRT$$

$$(P + \text{attractions})(V - \text{gas volume}) = nRT$$

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

- The deviation from ideal behaviour can be measured in terms of compressibility factor 'Z', which is the ratio of the ideal gas that is:-

$$Z = \frac{pV}{nRT}$$

- For an ideal gas $Z=1$ at all temperatures & pressures because of ideal gas relationship, the graph Z vs p will be a straight line parallel to the pressure axis. For gases which deviate from ideality, value of Z deviates from unity.
- At very low pressures all gases have $Z=1$ & behave as an ideal gas. At high pressure $Z>1$, these gases are difficult to compress, where $Z<1$ at intermediate pressures.

Thus gases show ideal behaviour when the volume occupied is large so that the volume of the molecules can be neglected in comparison to it.

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- The temp. at which a real gas obeys all ideal gas laws over an appreciable range of pressure is called Boyle temperature or Boyle's point.

Ans-1

Boyle's point depends upon its nature, above Boyle's point real gases +ve deviation from their ideality & Z values are greater than 1. The forces of attraction b/w the molecules are very feeble. Below Boyle temperature real gases first show decrease in Z value with increasing pressure, which reaches a min. value. On further increase in pressure, the value of Z increase continuously.

$$Z = \frac{pV_{\text{ideal}}}{nRT}$$

Ans-2

If the gas shows ideal behaviour then, $V_{\text{ideal}} = nRT/p$,
On putting this value of nRT/p in the equation we get an equation:-

$$Z = \frac{V_{\text{real}}}{V_{\text{ideal}}}$$

Ans-