Class XI (Chemistry) Notes: (States of Matter)

Intermolecular forces

The forces of attraction and repulsion between interacting particles (atoms and molecules) are known as intermolecular forces

This term does not include

a) The electrostatic forces that exist between the two oppositely charged ions and
b) The forces that hold atoms of a molecule together i.e., covalent bonds.

Dispersion Forces or London Forces

In atoms and nonpolar molecules, which are electrically symmetrical because their electronic charge cloud is symmetrically distributed, a dipole may develop momentarily. Suppose there are atoms 'A' and 'B' in the close vicinity of each other. Momentarily electronic charge distribution in one of the atoms, say 'A', becomes unsymmetrical *i.e.,* the charge cloud is more on one side than the other. This results in the development of instantaneous dipole on the atom 'A' for a very short time. This instantaneous or transient dipole distorts the electron density of the other atom 'B', which is close to it and as a consequence a dipole is induced in the atom 'B'.

The temporary dipoles of atom 'A' and 'B' attract each other. Similarly temporary dipoles are induced in molecules also. This force of attraction was first proposed by the German physicist Fritz London, and for this reason force of attraction between two temporary dipoles is known as **London force**. (or **dispersion force)** .

- These forces are always attractive
- The interaction energy is inversely proportional to the sixth power of the distance between two interacting particles $\frac{1}{r^6}$.
- These forces are important only at short distances (~500 pm)
- Their magnitude depends on the polarisability of the particle.

Dipole - Dipole Forces

They act between the molecules possessing permanent dipole. Ends of the dipoles possess "partial charges" [Always less than the unit electronic charge (1.6×10^{-19} C)]. The polar molecules interact with neighbouring Molecules resulting in dipole-dipole interaction.

- This interaction is stronger than the London forces but is weaker than ion-ion interaction because only partial charges are involved.
- The attractive force decreases with the increase of distance between the dipoles.

- Interaction energy is inversely proportional to distance between polar molecules. Dipole-dipole interaction energy between stationary polar molecules (as in solids) is proportional to $\frac{1}{r^3}$ and that between rotating polar molecules is proportional to $\frac{1}{r^6}$

A polar molecule may also have London forces between them in addition to dipole – dipole interaction, thus increasing the cumulative effect

Dipole–Induced Dipole Forces

This type of attractive forces operate between the polar molecules having permanent dipole and the molecules lacking permanent dipole. Permanent dipole of the polar molecule induces dipole on the electrically neutral molecule by deforming its electronic cloud. Thus an induced dipole is developed in the other molecule.

- Interaction energy is proportional to $\frac{1}{r^6}$
- Induced dipole moment depends upon the dipole moment present in the permanent dipole and the polarisability of the electrically neutral molecule.

Boyle's Law

At constant temperature, the pressure of a fixed amount (i.e., number of moles *n*) **of gas varies inversely with its volume**. Mathematically, it can be written as

$$p \ \alpha \frac{1}{v} \quad \Rightarrow p = k\frac{1}{v} \quad \Rightarrow pv = constant$$

$$p_1v_1 = p_2v_2$$

GRAPHS

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

$$p_1v_1 = p_2v_2 = \text{constant} \quad \Rightarrow \quad \frac{p_1}{p_2} = \frac{v_2}{v_1}$$

At high pressures, gases deviate from Boyle's law and under such conditions a straight line is not obtained in p vs 1/v 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 occupy a smaller space. This means that gases become denser at high pressure.

$$\because Density = \frac{mass}{volume}, d = \frac{m}{v} = \frac{m}{k/p} = \frac{m}{k}p = k_1 p$$

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

Charles' Law

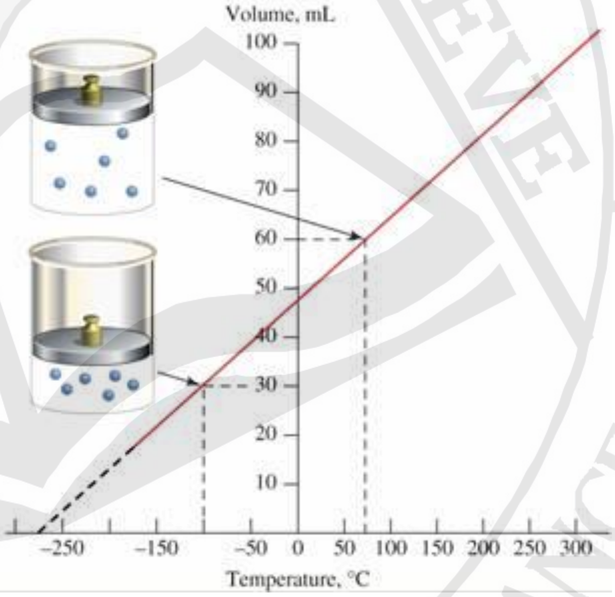
For a fixed mass of a gas at constant pressure, volume of a gas increases or decreases by $\frac{1}{273.15}$ times of the original volume for every degree rise or fall of temperature

It can also be stated as

Pressure remaining constant, the volume of a fixed mass of a gas is directly proportional to its absolute temperature.

Kelvin Scale

Charles law suggests an interesting question: If a gas were cooled to 273.15° below zero, would its volume drop to zero? Would it just disappear? The answer is no, because most gases will condense to liquids long before such a low temperature is reached, and liquids behave quite differently from gases.



Lord Kelvin, suggested that it was not the volume, but the molecular translational energy that would become zero at about -273.15°C, and that this temperature was therefore the lowest possible temperature. He set the temperature units as identical in size to the Celsius degrees.

The Kelvin temperature scale (K) was developed by Lord Kelvin in the mid 1800s. The zero point of this scale is equivalent to -273.15 °C on the Celsius scale. This zero point is considered the lowest possible temperature of anything in the universe. Therefore, the Kelvin scale is also known as the "absolute temperature scale". At the freezing point of water, the temperature of the Kelvin scale reads 273 K. At the boiling point of water, it reads 373 K

Gay Lussac's Law

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

$$p \;\alpha\; T \quad \Rightarrow \frac{p}{T} = constant$$

Avogadro Law

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

$$v \;\alpha\; n \quad \Rightarrow v = kn$$

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**.

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. Standard temperature and pressure means 273.15 K (0°C) temperature and 1 bar (i.e., exactly 10^5 pascal) pressure. These values approximate freezing temperature of water and atmospheric pressure at sea level. At STP molar volume of an ideal gas or a combination of ideal gases is 22.71098 L mol^{-1}.

Combined Gas Equation

The **combined gas law** is a gas law which combines Charles's law, Boyle's law, and Gay-Lussac's law. These laws each relate one thermodynamic variable to another mathematically while holding everything else constant. Charles's law states that volume and temperature are directly proportional to each other as long as pressure is held constant. Boyle's law asserts that pressure and volume are inversely proportional to each other at fixed temperature. Finally, Gay-Lussac's law introduces a direct proportionality between temperature and pressure as long as it is at a constant volume. The inter-dependence of these variables is shown in the combined gas law, which clearly states that:

> " The ratio between the pressure-volume product and the temperature of a system remains constant. "

This can be stated mathematically as

$$\frac{pV}{T} = k$$

where:

p is the pressure

V is the volume

T is the temperature measured in kelvin *k* is a constant (with units of energy divided by temperature).

For comparing the same substance under two different sets of conditions, the law can be written as:

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

The addition of Avogadro's law to the combined gas law yields the ideal gas law.

Question: Relate density to pressure at constant temperature

Answer: We know that $density = d = \frac{mass}{volume} = \frac{m}{v}$

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

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

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

Ideal Gas Equation

The three gas laws that we covered above describe the effect of pressure, temperature and the number of moles of a gas on volume. The three independent gas laws are:

- ***Boyle's law:*** $p \; \alpha \frac{1}{v} \quad \Rightarrow p = k\frac{1}{v} \quad \Rightarrow pv = cons\tan t$
- ***Charles's law:*** $p \;\; \alpha \;\; T \quad \Rightarrow \frac{p}{T} = cons\tan t$
- ***Avogadro's law:*** $v \;\; \alpha \;\; n \quad \Rightarrow v = kn$

If volume ***(V)*** is proportional to each of these variables, it must also be proportional to their product:

$$v\alpha\left(\frac{nT}{p}\right)$$

$$v = R\left(\frac{nT}{p}\right) \Rightarrow pv = nRT$$

Where R is the universal gas constant

$$R = \frac{\left(10^5 Pa\right)\left(22.71\times10^{-3}m^3\right)}{\left(1mol\right)\left(273.15K\right)}$$

$$R = 8.314Pam^3K^{-1}mol^{-1} = 8.314\times10^{-2}barLK^{-1}mol^{-1} = 8.314JK^{-1}mol^{-1}$$

At STP conditions used earlier (0 °C and 1 atm pressure), value of R is

$$R = 8.20578 \times 10^{-2} \text{ L atm K}^{-1} \text{ mol}^{-1}.$$

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

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** i.e., the pressures which these gases would exert if they were enclosed separately in the same volume and under the same conditions of temperature.

In a mixture of gases, the pressure exerted by the individual gas is called **partial pressure**. Mathematically,

$$p_{Total} = p_1 + p_2 + p_3 + \ldots\ldots(\text{at constant } T, V)$$

Partial pressure in terms of mole fraction

- 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.**
- **Standard temperature and pressure means 273.15 K (0°C) temperature and 1 bar (i.e., exactly 10^5 pascal) pressure. These values approximate freezing temperature of water and atmospheric pressure at sea level.**
- **At STP molar volume of an ideal gas or a combination of ideal gases is 22.71098 L mol–1.**
- **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 10^5 Pa). At SATP (1 bar and 298.15 K), the molar volume of an ideal gas is 24.789 L mol^{-1}

KINETIC MOLECULAR THEORY OF GASES

It is a theory that enables us to better elucidate the behaviour of gases. Following are its postulates. These postulates are related to atoms and molecules which cannot be seen, hence it is said to provide a microscopic model of gases.

- Gases consist of large number of identical particles (atoms or molecules) that are so small and so far apart on the average that **the actual volume of the molecules is negligible in comparison to the empty space between them**.
  This assumption explains the great compressibility of gases.
- **There is no force of attraction between the particles of a gas at ordinary temperature and pressure**.
  This assumption explains the fact that gases expand and occupy all the space available to them.
- **Particles of a gas are always in constant and random motion**.
  This assumption explains that if the particles were at rest and occupied fixed positions, then a gas would have had a fixed shape which is not observed.
- During their random motion particles of a gas collide with each other and with the walls of the container. **Pressure is exerted by**

the gas as a result of collision of the particles with the walls of the container.

- **Collisions of gas molecules are perfectly elastic**. This means that total energy of molecules before and after the collision remains same.
  Explanation: If there were loss of kinetic energy, the motion of molecules will stop and gases will settle down. This is contrary to what is actually observed.
- **Average kinetic energy of the gas molecules is directly proportional to the absolute temperature**. It is seen that on heating a gas at constant volume, the pressure increases. On heating the gas, kinetic energy of the particles increases and these strike the walls of the container more frequently thus exerting more pressure.

BEHAVIOUR OF REAL GASES: DEVIATION FROM IDEAL GAS BEHAVIOUR

To test how far the relation $pV = nRT$ reproduce actual pressure-volume-temperature relationship of gases, we plot pV *vs* p plo of gases because at constant temperature, pV will be constant (Boyle's law) and pV *vs* p graph at all pressures will be a straight line parallel to x-axis.

It is found that at constant temperature pV *vs* p plot for real gases is not a straight line. There is a significant deviation from ideal behaviour.

Two types of curves are seen.

a) In the curves for dihydrogen and helium, as the pressure increases the value of pV also increases.

b) In the case of other gases like carbon monoxide and methane, first there is a negative deviation from ideal behaviour, the pV value decreases with increase in pressure and reaches to a minimum value characteristic of a gas. After that pV value starts inceasing. The curve then crosses the line for ideal gas and after that shows positive deviation continuously.

It is thus, found that real gases do not follow ideal gas equation perfectly under all conditions. Deviation from ideal behaviour

Deviation from ideal behaviour is also seen 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) does not coincide.

a) At very high pressure the measured volume is more than the calculated volume.
b) At low pressures, measured and calculated volumes approach each other.

Cause of deciation from Ideal behavior

We find that two assumptions of the kinetic theory do not hold good. These are

a) There is no force of attraction between the molecules of a gas.
b) Volume of the molecules of a gas is negligibly small in comparison to the space occupied by the gas.

If assumption (a) is correct, the gas will never liquify. However, we know that gases do liquify when cooled and compressed. Also, liquids formed are very difficult to compress. This means that forces of repulsion are powerful enough and prevent squashing of molecules in tiny volume.

If assumption (b) is correct, the pressure *vs* volume graph of experimental data (real gas) and that theoretically calculated from Boyles law (ideal gas) should coincide.

VAN- DER WALLS EQUATION OF STATE

Real gases show deviations from ideal gas law because molecules interact with each other. **At high pressures molecules of gases are very close to each other. Molecular interactions start operating**.

At high pressure, molecules do not strike the walls of the container with full impact because these are dragged back by other molecules due to molecular attractive forces. This affects the pressure exerted by the molecules on the walls of the container. Thus, the pressure exerted by the gas is lower than the pressure exerted by the ideal gas.

$$P_{real} = \left(P_{ideal} + \frac{an^2}{V^2}\right)$$

The first term is the observed term and the second is the correction term

Repulsive forces also become significant.

Repulsive interactions are short-range interactions and are significant when molecules are almost in contact. This is the situation at high pressure. The repulsive forces cause the molecules to behave as small but impenetrable spheres. The volume occupied by the molecules also becomes significant because instead of moving in volume *V*, these are now restricted to

$$V_{real} = \left(V_{ideal} - nb\right)$$

where nb is approximately the total volume occupied by the molecules themselves. Here, b is a constant.

We can now rewrite ideal gas equation as

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

This equation is known as **van der Waals equation**.

In this equation *n* is number of moles of the gas. Constants a and b are called van der Waals constants and their value depends on the characteristic of a gas.

- Value of 'a' is measure of magnitude of intermolecular attractive forces within the gas and is independent of temperature and pressure.
- Value of 'b' is the measure of the effective size of the gas molecules. Hence it signifies the volume of gas effectively taken out per molecule by intermolecular repulsive interactions

Also, at very low temperature, intermolecular forces become significant. As the molecules travel with low average speed, these can be captured by one another due to attractive forces.

Real gases show ideal behaviour when conditions of temperature and pressure are such that the intermolecular forces are practically negligible. The real gases show ideal behaviour at **high temperature and low pressure**