Significance of van der Waal's constants

(i) **van der Waal's constant 'a':** Its value is a measure of the magnitude of the attractive forces among the molecules of the gas. Greater the value of 'a', larger is the intermolecular force of attraction. The unit of 'a' is $atm\ L^2 mol^{-2}$ or $bar\ dm^6 mol^{-2}$.

(ii) **van der Waal's constant 'b':** Its value is a measure of the effective size of the gas molecules. It has the unit $L\ mol^{-1}$ or $dm^3\ mol^{-1}$.

Liquefaction of gases and critical phenomena

Gases can be liquefied by lowering the temperature and increasing the pressure. The experimental observations have shown that the effect of temperature is more important in this respect than that of pressure.

The essential conditions for liquefaction of gases were put forward by Thomas Andrew by studying the pressure-volume relations of carbon dioxide at various temperatures. He observed that for every gas there is a characteristic temperature above which it cannot be liquefied, no matter how high the pressure applied be. This characteristic temperature is called the *critical temperature* (T_c) of the gas. Thus,

Critical temperature *of a gas may be defined as the temperature above which it cannot be liquefied by application of pressure.*

For example, the critical temperature (T_c) of CO_2 is 30.98°C and that of NH_3 is 132.5°C. Such gases can be easily liquified by applying pressure because their critical temperatures are above room temperature. However, the critical temperature of H_2 is –239.8°C (or 33.2K) and that of helium is –267.7°C (or 5.3K). It is difficult to liquefy such gases because they are to be cooled below these respective temperatures.

It may be noted that the higher the critical temperature of a gas the more easily can it be liquefied.

Similarly, the **critical pressure** (P_c) and **critical volume** (V_c) may be defined as follows.

The critical pressure of a gas is the minimum pressure required to liquefy the gas at its critical temperature.

Critical volume of a gas is the volume occupied by one mole of the gas at the critical temperature and pressure.

It may be noted that T_c, P_c and V_c for a gas are collectively called **critical constants**. At the critical point the densities of a substance in gaseous and liquid states are the same. Generally, gases below their critical temperatures are called vapours. Fluids above the critical temperatures are known as *super critical fluids*.

THE LIQUID STATE

The liquid state is the intermediate state between the perfectly ordered solid state and the completely disordered gaseous state. In a liquid, the molecules are quite close and attractive forces between them are stronger than those in gases. However, these forces of attraction are not strong enough as in solids to have definite shape. But they cannot be separated from one another completely and this results in definite volume for liquids.

Properties of liquids

1. **Vapour pressure:** Suppose some liquid is placed in a closed vessel. Evaporation starts and the molecules having sufficient energy to overcome the intermolecular attraction escape from the surface. As time passes, more and more molecules leave the liquid phase and come in the space above the liquid. The molecules thus present above the liquid are called vapours. These molecules, in their random motion collide with one another, with the walls of the container and with the liquid surface. Some slow moving molecules colliding with the surface of the liquid may be recaptured and get converted into liquid. This process is called condensation.

   In the beginning, the rate of evaporation is much greater than the rate of condensation because only small number of molecules are present in the gaseous state. But as molecules accumulate in the space above the liquid, the rate of condensation increases and the rate of evaporation decreases. Finally a stage is reached when the rate of evaporation becomes equal to the rate of condensation. This state in which evaporation and condensation take place at the same rate is called the state of equilibrium between the liquid and the vapour. The pressure exerted by the vapour at this stage is called the vapour pressure or saturated vapour pressure. *Hence vapour pressure of a liquid at any tempeature may be defined as the pressure exerted by the vapours in equilibrium with the liquid at that temperature.*

   The vapour pressure is a characteristic property of a liquid at a given temperature. It does not depend on the amount of the liquid. The magnitude of vapour pressure depends on the following two factors.

   (i) *Nature of liquid :* If the intermolecular forces of attraction are weak, the molecules can easily leave the liquid and come to the vapour phase and hence the vapour pressure will be high. For example, the vapour pressures of acetone, ether, alcohol etc. are higher than that of water at the same temperature.

   (ii) *Temperature of the liquid :* The vapour pressure of a liquid increases with increase in temperature. As the temperature increases, the number of molecules with higher kinetic energy increases. Therefore, more molecules escape from the surface of the liquid and the vapour pressure increases.

2. **Boiling:** When a liquid is heated, the temperature of the liquid rises and its vapour pressure increases. If the temperature is increased until the vapour pressure becomes equal to the atmospheric pressure, the vapours formed within the liquid can freely rise through the liquid in the form of bubbles and escape into air. This phenomenon is known as boiling and the temperature at which this occurs is known as boiling point. Thus *boiling point of a liquid is the temperature at which vapour pressure of the liquid becomes equal to the atmospheric pressure.*

   From the above discussion it is clear that boiling point depends upon the atmospheric pressure. The boiling point of the liquid at one atmospheric pressure is called **normal boiling point.** The boiling point of the liquid at 1 bar pressure is called **standard boiling point** of the liquid. The normal boiling point of water is 100°C whereas its standard boiling point is 99.6°C. The boiling point changes with change in pressure above the liquid. Obviously, if the external pressure is high the boiling point will also be higher. Similarly, if the external pressure is decreased the boiling point is lowered. This is the reason why a liquid boils at a lower temperature on the top of a mountain where pressure is low.

3. **Surface tension:** Surface tension is another important property of liquids related to the intermolecular forces. A molecule in the interior of a liquid is attracted equally in all directions by the neighbouring molecules. Hence the net attractive pull acting on the molecule is zero. However a molecule on the surface of the liquid is attracted mainly by molecules below and beside it. The attraction to the sides cancel each other. There is no force of attraction to balance the attractive force tending to pull the molecule to the interior. Same is the case with all other molecules on the surface. Thus molecules at the surface experience a net inward attraction. As a result of this inward pull on all molecules lying at the surface, the surface behaves as if it were under tension (like a stretched membrane). This effect is called surface tension. As a result of this, the molecules at the surface are pulled inwards and tend to make the surface area of the liquid as small as possible. *Surface tension of a liquid may be defined as the force acting per unit length on the surface perpendicular to the surface of the liquid.* It is expressed in newton per metre (Nm^{-1}). *Surface tension of a liquid decreases with increase in temperature.*

Consequences of surface tension

Spherical shape of liquid drops and capillary rise are two important consequences of surface tension.

Due to surface tension, liquid surface tries to have minimum area. Liquid drops assume spherical shape because a sphere has the minimum surface area for a given volume.

Rise and fall of liquids in a capillary tube: In the case of liquids which wet glass (eg: water) the liquid rises into the capillary tube and in the case of liquids which do not wet glass (eg: mercury), there will be a fall of liquid level in the capillary tube.

4. **Viscosity:** It is a common observation that certain liquids flow faster than others. For example, liquids like water, ether etc. flow rapidly while liquids like glycerine, castor oil, honey etc. flow slowly. These differences in flow rates result from a property known as viscosity. Every liquid has some internal resistance to flow. *This internal resistance to flow possessed by a liquid is called its viscosity.* Liquids which flow slowly have high internal resistance and are said to have high viscosity. On the other hand, liquids which flow rapidly have low internal resistance and are said to have low viscosity.

   Viscosity is also related to intermolecular forces in liquids. If the intermolecular forces are large, the viscosity will be high. *Viscosity of a liquid decreases with rise in temperature.* This is because at higher temperature the attractive forces between molecules are overcome by the increased kinetic energies of the molecules.

Coefficient of viscosity (η)

The force per unit area required to maintain unit velocity difference between two layers of a liquid at unit distance apart is called coefficient of viscosity.

In CGS system, the unit of coefficient of viscosity is poise.

In SI system the unit is $N\,s\,m^{-2}$ (newton second per square metre)

Keep in Memory

- Attractive intermolecular forces due to dipole-dipole, dipole-induced dipole and dispersion forces are collectively called van der Waals forces.
- Dipole-dipole interactions occur in polar molecules such as HCl
- Dipole -induced dipole interactions are found in mixtures containing polar and nonpolar molecules. e.g., $HF + O_2$, $HCl + N_2$
- Dispersion or London forces are found in nonpolar molecules and in noble gases.
- **Boyle's law** states that at constant temperature, the volume of a given mass of gas is inversely proportional to its pressure. i.e; $PV = \text{constant}$ or $P_1 V_1 = P_2 V_2$
- **Charle's law** states that at constant pressure, volume of a given mass of gas is directly proportional to the temperature on Kelvin scale. i.e., $\frac{V}{T} = \text{constant}$ or $\frac{V_1}{T_1} = \frac{V_2}{T_2}$

- The lowest hypothetical temperature of -273.15°C at which all gases are supposed to have zero volume is called absolute zero. The scale of temperature taking -273.15°C as zero (i.e., absolute zero) is called Kelvin scale or Thermodynamic scale of temperature.
- **Gay Lussac's law** (or pressure-temperature law) states that the pressure of a given mass of gas is directly proportional to the Kelvin temperature at constant volume.

  i.e., $\frac{P}{T}$ = constant or $\frac{P_1}{T_1} = \frac{P_2}{T_2}$
- **Avogadro's law** states that equal volumes of all gases under similar conditions of temperature and pressure contain equal number of molecules
- Ideal gas equation: $PV = nRT$, $PV = \frac{wRT}{M,}$ $P = \frac{dRT}{M}$
- Values of R in different units: 8.314 $J\,K^{-1}\,mol^{-1}$, 8.314×10^{-2} or 0.08314 $bar\ K^{-1}\ mol^{-1}$, 0.0821 $litre\ atm\ K^{-1}\ mol^{-1}$, 1.987 $calorie\ K^{-1}\ mol^{-1}$
- **Combined gas law equation:** $\frac{P_1V_1}{T_1} = \frac{P_2V_2}{T_2}$
- A gas at 273 K and 1 bar pressure is said to be at Standard Temperature and Pressure (STP)
- **Daltons law of partial pressures** states that the total pressure exerted by a mixture of two or more non-reacting gases is equal to the sum of the partial pressures of the individual gases.

  i.e., $p_{total} = p_1 + p_2 + p_3 + \ldots\ldots$
- The partial pressure of a component gas is the pressure the gas would exert if present alone in the vessel at the same temperature as that of the mixture.
- Partial pressure of a gas = Mole fraction of the gas × Total pressure.
- Dalton's law is used to calculate the pressure of a gas from the measured pressure of it when collected over water.
- In order to explain the general behaviour of gases, Maxwell, Boltzmann and others put forward the kinetic molecular theory of gases.
- A gas which obeys the general gas equation $PV = nRT$ (or Boyle's law and Charle's law) at all temperatures and pressures is called an **ideal gas.**
- **Actual gases show ideal behaviour only at low pressures and high temperatures.**
- The cause of deviation of real gases from ideal behaviour is due to two faulty assumptions of the kinetic theory of gases. They are (i) The volume of the gas molecules is negligible as compared to the total volume of the gas (ii) The forces of attraction among molecules are negligible

- **van der Waal's equation:** $\left(P+\frac{an^2}{V^2}\right)(V-nb) = nRT$
- van der Waals constant '*a*' is a measure of the magnitude of attraction among molecules of the gas while '*b*' is a measure of the effective size of the gas molecules.
- **Critical temperature(*Tc*)** of a gas is the temperature above which it cannot be liquefied by applying pressure
- Higher the value of *Tc* of a gas the more easily can if be liquefied.
- **The critical pressure (Pc)** of a gas is the minimum pressure required to liquefy the gas at its critical temperature.
- **Critical volume** (*Vc*) of a gas is the volume occupied by one mole of the gas at the critical temperature and pressure.
- The temperature at which a real gas behaves like an ideal gas over an appreciable pressure range is called **Boyle temperature**
- **Vapour pressure** of a liquid at a temperature is the pressure exerted by the vapours in equilibrium with the liquid at that temperature.
- Vapour pressure increases with increase in temperature.
- Boiling point of a liquid is the temperature at which the vapour pressure of the liquid becomes equal to the atmospheric pressure.
- Surface tension and viscosity of liquids decrease with increase in temperature.
- Spherical shape of liquid drops and rise and fall of liquid in capillary tubes are due to surface tension.