

## Vanderwaal's Interactions:

A Dutch scientist in 1873, pointed out that particles (atoms, molecules or ions) of substances exert attractive forces on each other, when they are brought near to each other. These are physical forces (electrostatic in character) and much weaker than chemical forces (i.e. ionic & covalent bonds). These are named as Vanderwaals forces. He used the concept of these forces to explain the deviation of behaviour of gases at low temp. from that of the ideal gases. He proposed that particles of substances interact even if outer shells of the atoms have acquired the noble gas configurations. Vanderwaals forces can be defined as follows:

Vanderwaals forces are very short lived intermolecular attractive forces which are believed to exist between all kinds of atoms, molecules and ions when they are sufficiently close to each other.

Ex!:

The atoms of the molecules like  $N_2$ ,  $O_2$ ,  $Cl_2$  etc in which the valence ~~as~~ orbitals are either used in

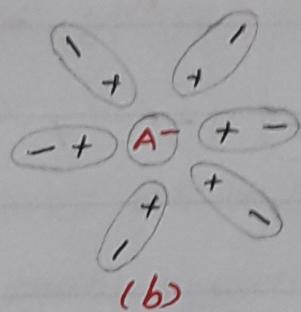
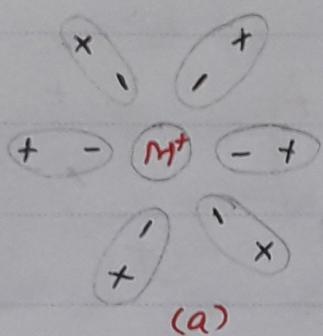
normal bonding or occupied by non-bonding  $e^-$ s, are neither firmly attached in the liquid nor solid states by Vanderwaals bonds or forces. These forces are almost absent when the molecules of a gas are far apart and are in rapid kinetic motion.

But those atoms or molecules of the gase are brought nearer to each other by increasing the pressure and kinetic energy is withdrawn by cooling, Vanderwaals forces are capable of holding the molecules together to form the liquid or the solid state.

### Ion-dipole interactions:

Polar molecules are attracted towards ions. The negative end of dipole is attracted towards the cation while the positive end, towards the anion.

This type of interaction is called ion-dipole interaction. Ion-dipole interactions have been used to explain the dissolution of NaCl in  $H_2O$ . When NaCl is put in  $H_2O$ , it dissolves in it since the negative ends of water molecule dipoles aggregate around  $Na^+$  ions and the positive ends around  $Cl^-$  ions.

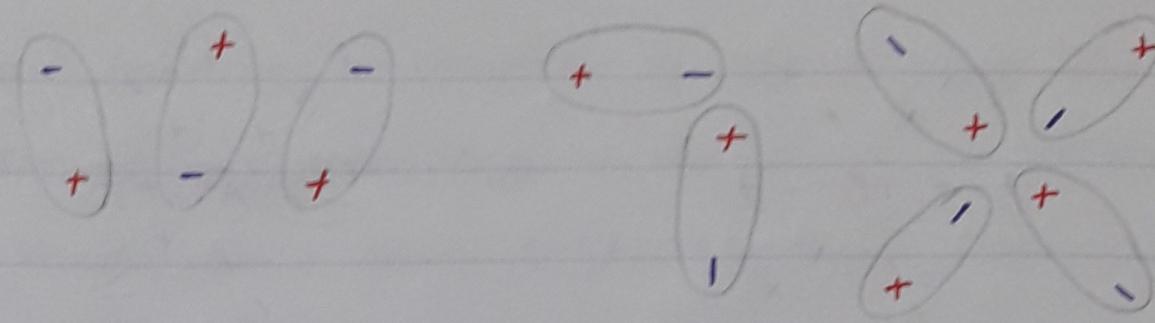


### Ion-dipole interaction.

- Cation ( $M^+$ ) attracts the negative end of the dipole.
- Anion ( $A^-$ ) attracts the positive end.

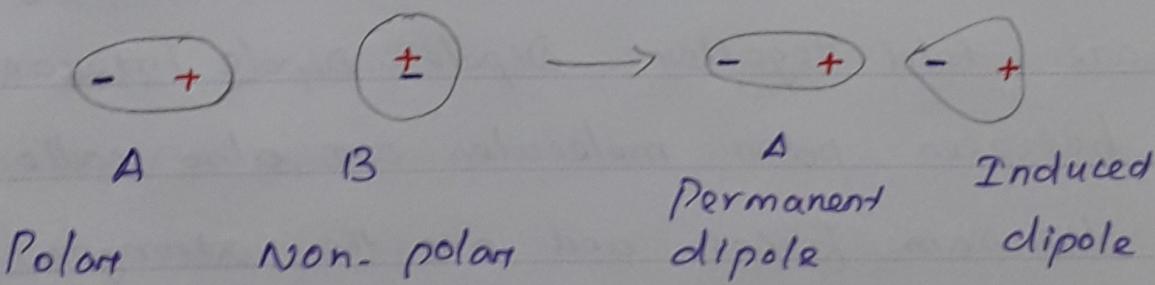
### Dipole-Dipole Interactions:

These forces are found in polar molecules having permanent polarity in them. We know that a polar molecule has separate centres of positive and negative charge and possess permanent dipole moment. When polar molecules are brought nearer to each other, they orient themselves in such a way that the positive end of one dipole (polar molecule) attracts the negative end of another dipole and vice-versa. Due to this interactions many molecules are held together. Dipole-Dipole interactions between polar molecules are also called Keesam forces and are the strongest of all other types of Vanderwaals forces.



### Dipole- Induced dipole interactions:

This type of force is found in a mixture containing polar & non-polar molecules. When a non-polar molecule is brought near to a polar molecule, the positive end of the polar molecule attracts the mobile e<sup>-</sup>s of non-polar molecule and thus polarity is induced in non-polar molecule. Now both the molecules become dipoles and hence the positive end of the polar molecule attracts the displaced e-cloud of non-polar molecule. Thus the two types of molecules are held together by forces which are also called Debye forces.



## 5

## Equations of state of real gases:

### Introduction:

A gas is termed as an ideal gas, if it obeys gas laws or the gas equation  $PV = nRT$  under all conditions of temp. & pressl.. However, no gas is 'ideal': almost all gases show significant deviations from ideal behaviour. The ideal behaviour with such gases is observed only under certain conditions of Temp. & Pressl.. These gases are thus termed as real or non-ideal gases.

### Modified Vanderwaal's Equation:

It is known that gases show significant deviations from the ideal behaviour at high Pressl.. & low Temp.. The extent of deviation depends on the nature of the gas, Pressl.. & Temp.. at which the behaviour is studied. These results are contrary to those predicted by the kinetic theory of gases where it was postulated that the behaviour of gases were alike under all conditions of Temp. & Pressl.. Hence, the model suggested by the kinetic theory of gases must be modified in order to study the

behaviour of real gases. The deviations of gases from ideal behaviour are due to two faulty assumptions made in the kinetic theory.

1) The volume of the molecules is negligible

In comparison to the total volume of the gas

2) There are no forces of attraction between the molecules.

The fact that molecules have appreciable collision diameters means that they possess an effective volume. Under normal conditions, the volume of the molecules is very small. However, at

high pressures, the volume occupied by the gas molecules is appreciable and hence cannot be neglected. Furthermore, the volume of a gas can be decreased by lowering the temp. and increasing the press. until the gas liquifies and finally solidifies. Solids can not be further compressed.

This conforms that the molecules of a gas do occupy some definite volume.

Vanderwaals in 1873 introduced two correction terms to the ideal gas equation  $PV = nRT$  and obtained an equation of state for a real gas.

The first correction is made for the volume occupied by the molecules themselves and the second one is for the forces of attraction between the molecules.

### (i) Correction due to volume:

When  $n$  moles of a gas are placed in a container of volume  $V$ , the space in which the molecules are free to move is equal to  $V$ , if the volume occupied by the molecules themselves is negligible. Since the molecules have a finite size, the actual volume available to them for their movement would not be  $V$  but less than  $V$ . If ' $b$ ' is the effective volume per mole of the gas then this volume must be subtracted from the total volume in order to get the actual volume for their movement.

$$\therefore V_{\text{ideal}} = V - nb.$$

For ' $n$ ' moles of gas,

$$V_{\text{ideal}} = (V - nb)$$

$b$  is also sometimes called excluded volume and is usually treated as a constant and characteristic for each gas.

### b) Correction due to molecular attraction:

Consider a molecule in the interior

of a gas. It is surrounded

uniformly by other molecules so that  
there is no resultant attractive

force on this molecule. However, as  
it approaches the wall of the vessel, the

uniform distribution of molecules around it is disturbed  
and it is now attracted by molecules from one side

only. The molecule will thus experience a net inward  
pull. Hence, it will strike the wall of the vessel  
with lower velocity and will exert a lower pressure.

~~The measured pressure  $P$  will thus be less than  
the ideal pressure. It is therefore necessary to  
add a correction term ( $P_a$ ) to the observed pressure  
in order to obtain the ideal press..~~

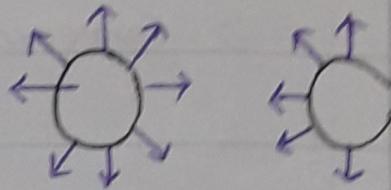
∴ Corrected (ideal) pressure  $P_{\text{ideal}} = P + P_a$ .

But  $P_a \propto \left(\frac{n}{V}\right)^2$  Measured Press  $P = P_{\text{ideal}} - P_a$

where  $n/V$  is no. of molecules per unit volume.

$$(\text{cor}) \quad P_a = \frac{an^2}{V^2}$$

where  $a$  is the ~~cons~~ proportionality constant.



Intermolecular forces  
in a gas.

$\therefore$  The corrected pressure  $P_{\text{ideal}} = P + \frac{an^2}{V^2}$ .

Hence, the product of ideal pressures/ideal volume should be included in ideal gas' eqn..

$$\therefore \text{we get } \left[ P + \frac{an^2}{V^2} \right] + (V - nb) = nRT.$$

This is known as the modified Vanderwaals eqn..

For 1 mole of a gas Vanderwaals eqn. becomes

$$\left[ \left[ P + \frac{a}{V^2} \right] (V - b) = RT \right]$$

### Berthelot equation :

Berthelot derived an empirical relation for the behaviour of real gas as

$$\left[ P + \frac{an^2}{7V^2} \right] (V - nb) = nRT$$

where  $a$  &  $b$  are Berthelot constants & the appearance of  $1/T$  terms with  $an^2/V^2$ ; taken into account the dependence of intermolecular attractions with temperature.

## Dieterici Equation:

Dieterici suggested the following equation of state

$$P(V-nb) = nRTe^{-an/VRT}$$

For 1 mole of the gas, the eqn. becomes

$$P(V-b) = RTe^{-a/VRT}$$

At low pressure, the volume of the gas will be large and hence  $b$  may be neglected in comparison to  $V$ .

Also  $a/VRT$  will have a small value and  $e^{-a/VRT}$  becomes,

$$e^{-a/VRT} = 1 - \frac{a}{VRT}.$$

$$\therefore PV = RT \left[ 1 - \frac{a}{RTV} \right]$$

$$P = \frac{RT}{V} \left[ 1 - \frac{a}{RTV} \right]$$

$$\left[ P = \frac{RT}{V} - \frac{a}{V^2} \right].$$

## Clausius Equation:

$$\left[ P_c + \frac{a}{T_c^2(V_c+b)^2} \right] (V_c-b) = RT_c$$

where  $T_c$ ,  $P_c$  &  $V_c$  are Press., Vol. & Temp. at critical point.

## Critical Phenomena:

During the early part of 19<sup>th</sup> century, a number of gases such as  $\text{CO}_2$ ,  $\text{SO}_2$ ,  $\text{NH}_3$  etc., were liquefied by subjecting the gas to decrease in Temp<sup>l</sup>. and increase in Press<sup>l</sup>. The effect of Temp<sup>l</sup> is rather more important than that of Press<sup>l</sup>.) The essential conditions for liquification of gases were discovered by Andrews in 1869 as a result of his study of P-V-T relationships for  $\text{CO}_2$ .

It was found that, above a certain Temp<sup>l</sup>. it was impossible to liquefy a gas no matter what press<sup>l</sup>. was applied. This Temp<sup>l</sup>. is called critical temp<sup>l</sup>. ( $T_c$ ).

The pressure required to liquefy a gas at this temp<sup>l</sup>. is called the critical pressure ( $P_c$ ).

The volume occupied by one mole of the substance at critical temp<sup>l</sup>. & press<sup>l</sup>. is called the critical volume ( $V_c$ ).

A gas or liquid in this condition is said to be at the critical point  $T_c$ ,  $P_c$  and  $V_c$ .

taken together are known as the critical constants for a gas. At the critical  $T_c$ ,  $P_c$  the physical properties of a gas are indistinguishable from its liquid form and no distinction can be observed between the two. The phenomenon of smooth merging of a gas with its liquid form is called the critical phenomenon. It is a reversible process.

### Ionic bond (Ionic forces)

(An ionic bond involves a complete transfer of one or more valence e<sup>-</sup>s) of atoms participating in bond formation, resulting in a positive ion and a negative ion bound together by electrostatic forces. Electrons in an ionic bond tend to be mostly found around one of the two constituent atoms due to the large electronegativity difference between the two atoms.

This is often described as one atom giving e<sup>-</sup>s to the other. This type of bond is generally formed between a metal and a non-metal such as Na & Cl in NaCl. Sodium would give one e<sup>-</sup> to chlorine forming a positively charged  $\text{Na}^+$  & negatively charged Cl<sup>-</sup>.