

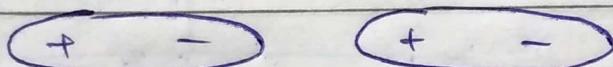
## Unit - 3

Intermolecular forces\* Vanderwaals forces:

It is now fully established that forces of attraction exist b/w non polar molecules as well. These intermolecular forces are known as cohesive forces or ~~vanderwall~~ vanderwall forces.

These forces originate from three main types of interactions, namely

- 1) dipole-dipole interaction



In the case for polar molecules which though neutral, have permanent dipoles, the vanderwaals forces are mainly due to electrical interaction b/w the dipoles known as dipole-dipole interaction.

For ex: gases such as ammonia, sulphur dioxide, HF, HCl, etc. have permanent dipoles as a result of which there is appreciable dipole-dipole interaction b/w the molecules of these gases.

The magnitude of this type of interaction depends upon the dipole moment of the molecules concerned. The greater the dipole moment the greater is the

dipole-dipole interaction. Because of the attractive interaction, these gases can be easily liquified.

### (2) Dipole-induced dipole interaction:

A polar molecule may sometimes polarise a neutral molecule which lies in the vicinity and thereby induced dipolarity  $\mu^*$  in that molecule just as a magnet induces magnetic dipolarity in the neutral piece of iron lying close by. The induced dipole then interact with the dipole moment of the first molecule and thereby the two molecules are attracted together.

- The magnitude of this interaction would considerably depend upon the magnitude of the dipole moment of the polar molecules and polarisability of the neutral molecules.

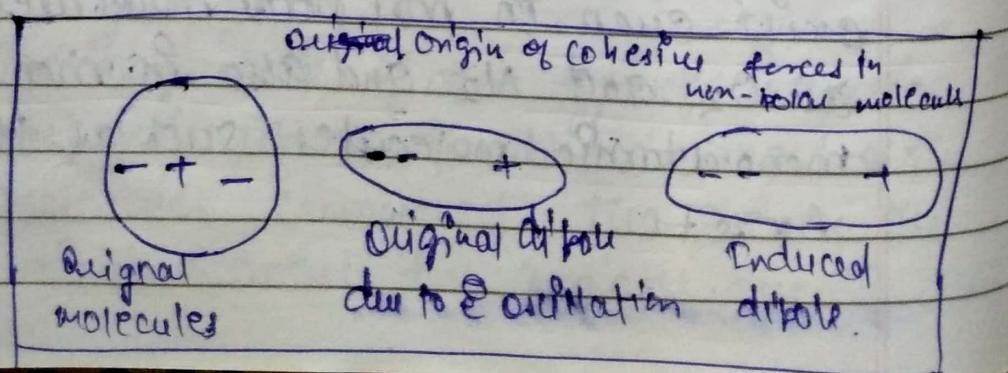
### (3) Induced dipole-induced dipole Interaction:

London forces = dispersive forces.

As we know, the van der waals forces exist even in non polar molecules such as  $O_2$  and  $N_2$  and also in non polar mono atomic molecules such as He, Ne, Ar etc.

This attraction is evident from the condensation of these gases into liquids at sufficiently high pressure and low temp this could not be understood for several years.

In 1930, F. London provided a satisfactory explanation for the existence of forces of attraction b/w non-polar molecules based on quantum mechanics. acc. to this view, electrons of neutral molecules keep on oscillating w.r.t the nuclei of atoms. As a result of this, at a given instant, positive charges may be concentrated in one region and negative charge by another region of the same molecule. therefore a non polar molecules may become momentarily self polarised. this polarised molecule may include a dipole moment in neighbouring molecules with anti-parallel orientation.



#### (4) Ion-dipole forces:

We know that ions have great tendency to attract polar molecules. The positive ion attracts the negative pole and negative ion attracts the positive pole of the polar molecule. Such an interaction is known as ion-dipole interaction and the forces causing these attractions are known as ion-dipole forces.

#### \* Critical phenomenon:-

##### Critical Constants of a Gas:

The most characteristic properties of gases are that their molecules lie far apart from one another and are in continuous rapid motion. Each molecule therefore leads almost an independent existence. This particularly so when temp. is high and pressure is low. However as the temp. of gas is decreased, the volume of occupied by the gas decreases. At a sufficiently low temp., some of slow moving molecules can not resist the force of attraction and they come closer and closer and ultimately the gas changes into the liquid state.

Therefore liquification of gas results from decrease of temperature.

Increase of pressure has also the effect of bringing the gaseous molecules closer and closer to one another (due to decrease in volume).

This is an additional helpful factor in converting the gas into liquid.

- thus increase of pressure and decrease of temperature both tend to liquification of gases. For instance, Sulphur dioxide can be liquified at  $-8^{\circ}\text{C}$  if the pressure is 1 atm. but it can be liquified even at a high temp. of  $20^{\circ}\text{C}$  if the pressure is increased to 3.24 atm. the effect of temp. however is more important than that of the pressure because for each gas there is certain temp. above which it can not be liquified, no matter how high pressure may be applied. This temp. is known as critical temp. Therefore the critical temp. of the gas may be defined as that temp. above which it can not be liquified how so ever high the pressure may be.

For instance the critical temp. of  $\text{CO}_2$  is  $31.1^\circ\text{C}$  this means that it is not possible to liquify  $\text{CO}_2$  at above  $31.1^\circ\text{C}$  by any means.

At the critical temp., a certain pressure is needed to liquify the gas. This pressure is called critical pressure. For instant at  $31.1^\circ\text{C}$   $\text{CO}_2$  is liquified under a pressure of 72.9 atm. Therefore the critical pressure of this gas 72.9 atm.

The critical temp of oxygen is ~~-183~~  $-118^\circ\text{C}$  and that of Hydrogen is  $-240^\circ\text{C}$ . These gases therefore can not be liquified ordinary temp. Their critical pressure are 49.4 atm and 12.8 atm respectively.

The volume occupied by 1 mole of a gas at its critical temp and critical pressure is known as critical volume.

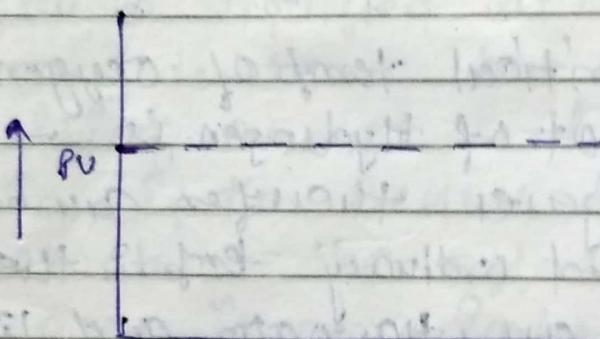
For ex. critical volume of  $\text{CO}_2$ , Oxygen and Hydrogen are 940.0, 78.2, 61.5 ml/mole respectively.

## \* Ideal and non-ideal gases:

A gas obeys gas laws completely & is known as ideal gas or perfect gas.

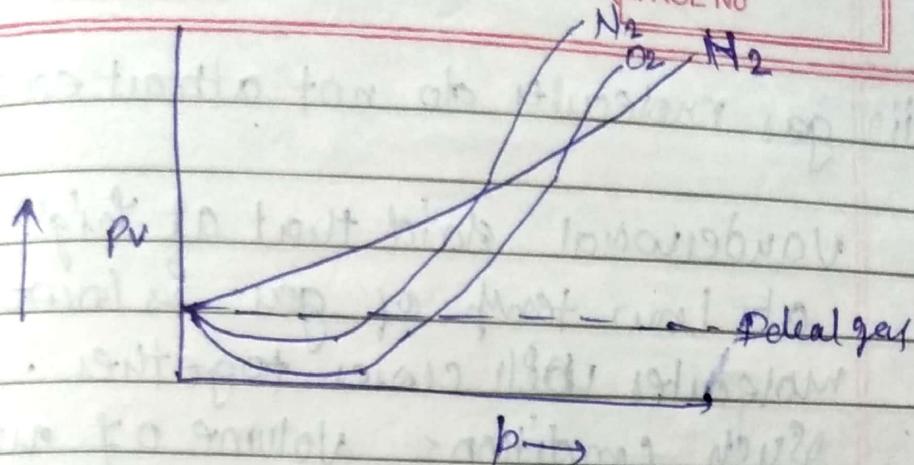
A gas which does not obey gas laws completely, is known as non-ideal gas or real gas.

When a graph obeys Boyle's law completely then following type of graph is obtained.



$\rightarrow$   
no gas is found to be ideal gas,  
all known gases are real gases and  
they show more or less deviations  
from gas laws.

The deviations by real gases from ideal behaviour may be shown as



from above curves, it is clear that real gas shows larger deviations at high pressure and low temperature.

therefore a real gas will show lesser deviation at low pressure and high temp. It means that a real gas behaves almost ideal gas at low pressure and high temp.

\* Cause of deviation and ~~vanderwaals eq~~ <sup>(v)</sup>  
Real gases show larger deviation at high pressure and low temp. from ideal gas eq ( $PV = nRT$ ), the reason of these deviation explained by Vanderwaals. He said that gas laws are based on postulates of kinetic theory of gases and two postulates are wrong.

- (1) gas molecules are so small that their volume may be neglected in comparison of total volume of gas

(iii) gas molecules do not attract each other

Vanderwaal said that at high pressure  
at low temp of gas is lower and  
molecules will closer together. In  
such conditions volume of molecule  
and attraction forces b/w them can  
not be neglected. If we neglect  
these facts, the gas will show  
Larger deviation.

In order to explain the behaviour  
of real gases, Vanderwaal  
proposed following for correcting  
ideal gas equation. ( $PV = nRT$ )

- (1) Volume correction
- (2) Pressure Correction