Subject code : 05305CHE22

(PHYSICAL CHEMISTRY)

Unit-1 States of Matter

[The Gaseous State]

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Introduction -:

- There are three common state of matter, the gaseous state being the simplest state . There are certain laws of Gaseous Behavior on experimentall observations. These laws are Boyle‘s Law, Charle’s law, Dalton‘s law and Avogadro’s Law. Kronig, ClausIs, Maxwell and Boltzmann developed a theory of gases is known as Kinetic Molecular Theory of Gases, which gave sound theoratical basis of The Gase Laws.

The Kinetic Theory of Gases:-

- The main postulates for kinetic theory are as under :

1. All gases consists of a very large number of minutes particles called ‘Molecules’.
2. Molecules saperated by large distance. The volume of molecule is very small, such that it can be neglected in comparison of total volume of Gas.
3. Molecules are constantly in rapid motion, in all possible directions. During their motion they collide with one another and also with the walls of container (vessel).
4. The molecular collisions are perfectly elastic. Thus there is no net loss of energy during collisions with one another or with the walls of cantainer. But the energy is redistributed during collisions. The kinetic energy pf molecules may be transferred from one molecule to another molecule but it is not converted into any other form of energy such as heat.
5. Pressure exerted by a gas on the walls of container is due to the bombardment of gas molecules on the walls.

6. The average kinetic energy of molecules is directly proportional to the absolute temperature .

7. The distance between the gas molecules is so large that there are no attractive or repulsive forces between them. The molecules move completely in dependent of one another .

EQUATION OF STATE AND DEVIATION FROM IDEAL BEHAVIOR :-

- The equation, PV = nRT known as an ideal gas equation was derived from the postulates of the kinetic theory. It is valid for ideal gas only. Real gases obey this equation only approximately at low pressure and high temperature. The lower the pressure and the higher the temperature, the less is the deviation from an ideal behaviour. The deviation from ideal behavior is best represented in terms of the compressibility factor (also known as compression factor) Z.

  PV Compressibility factor Z= nRT

- Thus the value of Z is measure of deviation from ideal behaviour. Under all the conditions of temperature and pressure.

- • If Z = 1, then gas is an ideal gas.
- • If the value of Z is away from I (unity) the deviation is large from ideal behaviour.
- • If the value of Z is near to I (unity) the deviation is less from ideal behaviour .

The deviations of real gases from ideal behaviour can be obscrved by plotine a eranh of the compressibility factor, Z against the gas pressure P at a constant temperature. Such graphs for NH3, CH4, He and H, are shown below.

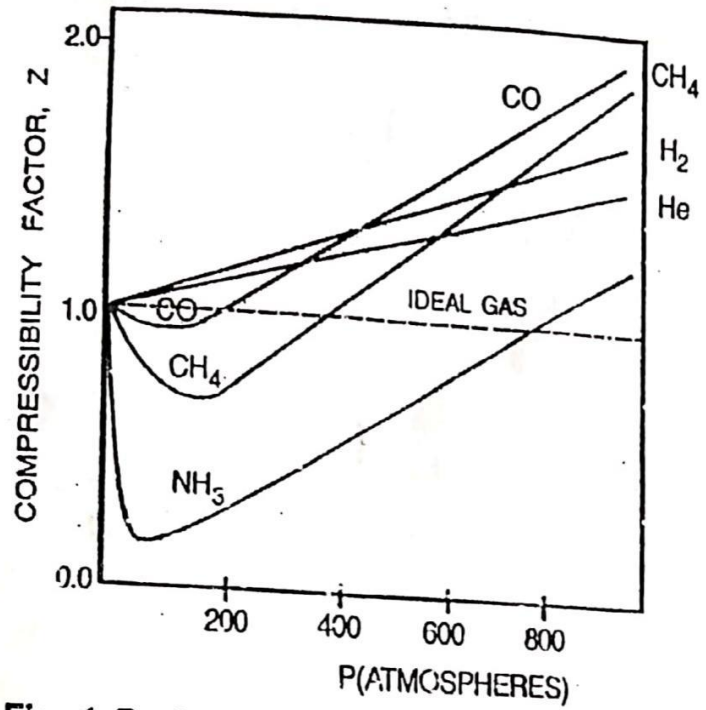

Fig. 1 Deviations of real gases from ideal behaviour

It can be seen from the graph that:

- • At extremely low pressure , all the gases have Z close to unity (1) indicating that gases behave almost ideally .
- • At very high pressures , all the gases have 2 more than unity (Z > 1) indicating that gases are less compressible than an ideal gas .
- • The value of Z is always greater than one (Z > 1) for H , and He as they are less compressible than ideal gases at all pressures .
- • For CO , CH , and NH3 , Z is less than one (Z < 1) at low pressure as they are more compressible than ideal gases and greater than one (Z > 1) at high pressure as they are less compressible than ideal gases. Thus gases having high solubility and easily liquefiable (condensable) show larger deviations .

EFFECT OF TEMPERATURE ON DEVIATIONS FROM IDEAL BEHAVIOR :-

- The graphs of compressibility factor , Z against pressure P for nitrogen at different temperatures are shown below.

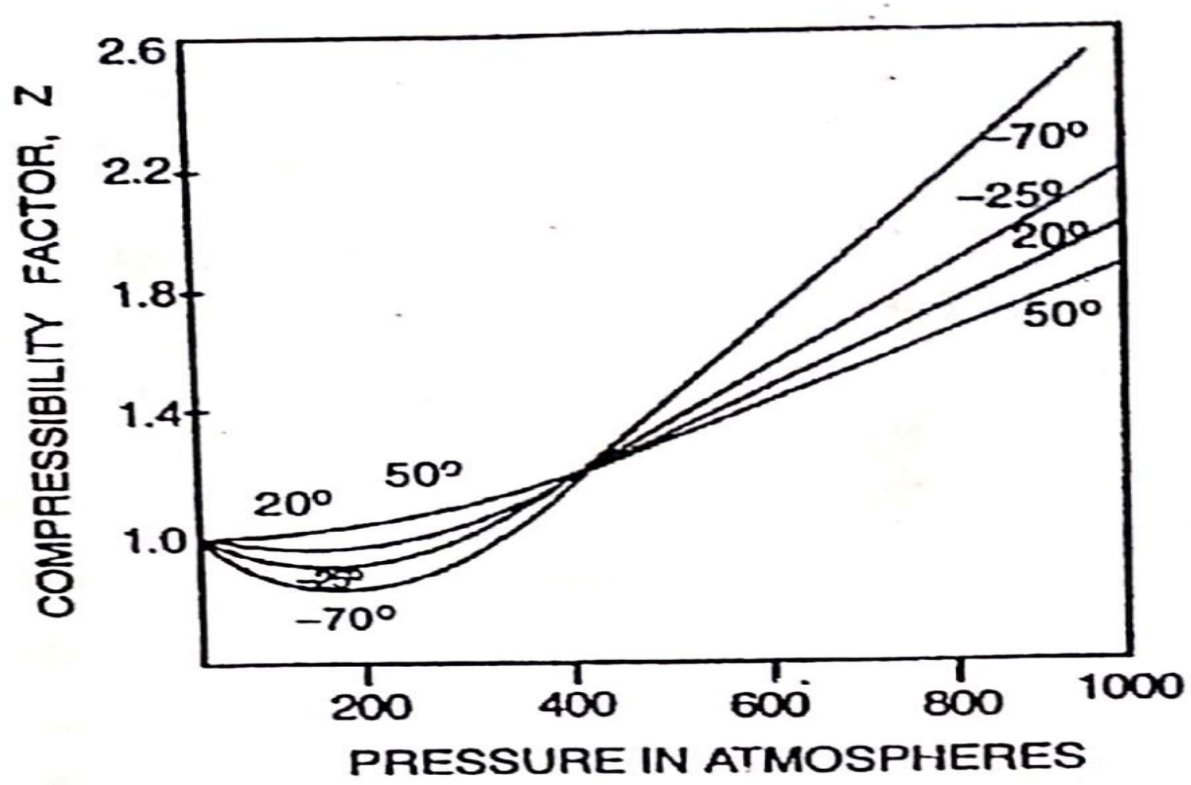

Fig. 2

- Fig . 2 Effect of temperature on deviation of nitrogen gas from ideal behaviour It can be seen from the graphs that :
- • The dip in the curves becomes smaller and smaller as the temperature is raised .
- • At 50 ° C the curve is almost horizontal (no dip) in a range of pressure between 0 and about 100 atmospheres indicating that the compressibility factor , Z becomes almost one under these conditions . Thus the product PV remains constant and hence Boyle's law is obeyed within this range of pressure at 50 ° C . This temperature is called the Boyle temperature.
- • Below Boyle temperature , the value of Z at first decreases approaches a minimum and then increases as pressure is increased continuously .
- •Above 50 ° C the value of Z continuously increases with increase in pressure .

- Boyle Temperature (TB) : Temperature at which a real gas obeys Boyle's law is known as the Boyle temperature .
- The Boyle temperature is different for different gases . For Hydrogen it is -165 ° C and for Helium is -240 °C . Thus at - °C, Hydrogen gas obeys Boyle's law and at -240 °C Helium gas obey Boyle's Law .

EXPLAINATION FOR THE DERIVATIONS :-

- (1) According to the postulate of the above Kinetic Theory of gases , " The distance between the gas molecules is so large than there are no attractive or repulsive forces between them " . This is also not true under all conditions of temperature and pressure . This postulate is valid only at low pressure or at high temperature because at low pressure and high temperature the distance between gas molecules is large (because volume is large) . But at high pressure and low temperature , the volume of gas is so small that the gas molecules are very close to one another . The distance between gas molecules is small and hence attractive and repulsive forces cannot be neglected . Because of the above two reasons it is necessary to make suitable corrections to the ideal gas equation to make it applicable to real gases .

CORRECTIONS FOR DEVIATIONS : VAN DER WAALS EQUATION :

- Vander Waal proposed the equation for state for non ideal gas by considering the gas molecules as rigid sphere having certain diameter and also having intermolecular forces of attraction between them . Vander Waal introduced two correction terms in the ideal gas equation.
- (1) **Correction for Volume** : As the volume of gas molecules cannot be neglected at high pressure and low temperature , the entire (whole) volume of container is not available for the free movement of molecules . Vander Waals introduced the term b . The term b represents the volume occupied by all molecules in one mole of gas . This volume is known as **Excluded volume or Co - volume .** The volume in an ideal gas equation should be replaced by free volume (available for free movement) . If the volume of one mole of gas is V , the free volume is

$$V_{free} = V - b$$

- For n mole of the gas free volume (compressible volume) is

$$V_{free} = V - nb$$

- Thus V is replaced by V - nb from ideal gas equation . For free volume or compressible volume , the actual volume of gas molecules must be excluded from the volume of gas . The excluded volume can be calculated as shown below . Consider two gas molecules as umpenetrable and incompressible spheres , each having diameter d (or 2r) and volume 4/3 πr3.
- Due to intermolecular attractive forces amongst the gaseous molecules their velocity (speed) decreases . As velocity decrease , molecules collides (strikes) with the walls of container slowly . Thus they exert lower pressure than they would have exerted in absence of attractive forces . Because of this reason the term of pressure P in an ideal gas equation is to be corrected . The certain quantity ' p should be added to P to correct it .The correct pressure ,therefore , should be P +p.

Calculation for Correction Factor (P) :-

- The force of attraction exerted on single molecule dependes upon the number of molecules around it . If the numbers of molecules are more , the attraction exerted on single molecule will be more . Because of more attraction the number of molecules colliding with the wall also will be small . Thus the pressure will be low . Thus the correction factor p depends upon the number of molecules of gas in a given volume . This means that correction factor , p depends upon the density of gas . The correction factor p is proportional to the square of the density (ρ) of the gas .

$$p \propto \rho^2 \qquad \ldots\ \ldots\ \ldots (2)$$

- But density (ρ) is inversely proportional to the volume of the gas .
- If V is the volume of the one mole of a gas , the correction factor p becomes
- $p \propto 1/V^2 = a/V^2$
- where a is a constant depending upon the nature of gas .

- This is the value of a correction factor p for one mole of gas in a volume V. The kinetic gas equation for one mole of a real gas is

$$[P + a/V^2m](Vm - b) = RT \quad \ldots\ldots\ldots (3)$$

- where V stands for the molar volume of the gas . This equation is the van der Waals equation , a and b in equation (4) are known as van der Waals constant . Their values depend upon the nature of the gas . If there are n moles of gas in a volume , V , the correction factor p will be proportional to n2 92 according to equation (2) . Thus the correction factor p becomes,

- $p \propto n^2\rho^2 \propto n^2/V^2$

$\therefore P \propto n^2/V^2 = an^2/V^2$

$\therefore (P + an^2/V^2)(V - nb) = nRT$

THE CRITICAL PHENOMENA CRITICAL CONSTANTS OF A GAS :

- (1) The Critical Temperature : Tc When the temperature is high and the pressure is low , the gas molecules lie far apart from one another and are in continuous rapid motion leading an independent existence . However , as the temperature of a gas is lowered , the velocities of molecules and hence kinetic energy decreases . The volume occupied by gas also decreases . At sufficiently low temperature , the force of attraction increases and the molecules come closer to one another and ultimately the gas is converted into liquid (liquefied) . Thus , liquefaction of gases results from decrease of temperature .
- Increase of pressure also brings the gaseous molecules closer to one another and hence is helpful in converting gas into liquid . Thus increase of pressure and decrease of temperature cause liquefaction of gases . For example SO , can be liquified at - 8 ° C if pressure is 1 atm .

- All the gases have temperature above which it cannot be liquified even if the pressure is high .
- **The temperature above which the gas cannot be liquefied even if the pressure is very high is called Critical Temperature Tc.**
- For example the critical temperature of carbon dioxide is 31.1 ° C.This means that carbon dioxide cannot be liquefied above 31.01 ° C by any means.
- (2) The Critical Pressure : (Pc) At the critical temperature , a certain pressure is needed to liquefy the pressure is called the critical pressure .
- **A certain pressure needed to liquefy the gas at the critical temperature is called the Critical Pressure .**
- The critical temperature of carbon dioxide is 31.1 ° C . At this temperature of 31.1 ° C , carbon dioxide can be liquefied under a pressure 72.9 atm . Thus the critical pressure of carbon dioxide is 72.9 atm The critical temperature of Oz is -118 ° C and that of H is -240 ° C and their critical pressures are 49.7 and 12.8 atm .

- (3) The Critical Volume : Vc The volume occupied by one mole of a gas at its critical temperature and critical pressure is called the Critical Volume . The critical volume of CO2 , O2 and H , are 94.0 , 78.2 and 65.5 ml per mole .

Thank You