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Topic :- Gaseous state

Explanation of Deviation from ideal behaviour :-

It is necessary to modify the Kinetic theory of Gases. The following two Postulates of this theory require reassessment

(1) It was assumed in the derivation of Kinetic theory that the volume occupied by the gaseous molecules themselves is negligibly small as compared to the total volume occupied by the gas.

It has been calculated in some of the gases under ordinary Pressure that the volume occupied by the molecules is only 0.014% of the total volume. But if the Pressure is very high i.e. of 100 atmosphere, the volume of gas will decrease appreciably whereas the volume of molecules will remain almost the same because the molecules are incompressible. Hence the volume of the molecules will no longer be a

negligible fraction of the total volume.

Similarly, when the temperature is decreased to a large extent, the total volume of the gas will decrease considerably, but not the volume of the molecules themselves. In this case too, the volume occupied by the molecules will no longer be negligible.

Thus the Postulate is not valid at high Pressures and at low temperatures.

(2) Another assumption made was that the forces of attraction between gaseous molecules are negligible. It is known from experiences that the temperature of a gas falls when it expands.

In expansion, the gaseous molecules fall apart from one another. If there is no forces of attraction between the gaseous molecules then the system<sup>2</sup> will not have to do any work in expansion and

the temperature will not fall. But since the temperature does fall this indicates that there is a force of attraction between gaseous molecules and some work has to be done by the system in overcoming these forces.

At low pressure or at high temperature the volume of gas is large and therefore molecules lie far apart from one another. The attractive forces between them are accordingly very weak and may be negligible. The postulate is valid under this condition.

But when pressure is too high and temperature is too low the volume of the gas is very small and molecules lie closer to one another. The attractive forces, therefore, become appreciable and cannot be neglected. Under such conditions the assumption is no longer valid. It is necessary, therefore, to apply suitable correction to the ideal gas equation to make it applicable to real gases.