# Government general degree college, Chapra.

## Study material for 1st semester Major (NEP)

## Kinetic Theory and Gaseous state

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### 1. Kinetic Theory of Gases Assumptions:

he kinetic theory of gases considers the atoms or molecules of a gas as constantly moving point masses with huge inter-particle distances and may undergo perfectly elastic collisions. Implications of these assumptions are as follows:

i) Particles

Gas is a collection of a large number of atoms or molecules.

ii) Point Masses

Atoms or molecules making up the gas are very small particles like a point (dot) on a paper with a small mass.

iii) Negligible Volume Particles

Particles are generally far apart such that their inter-particle distance is much larger than the particle size, and there is large free unoccupied space in the container. Compared to the volume of the container, the volume of the particle is negligible (zero volume).

iv) Nil Force of Interaction

Particles are independent. They do not have any (attractive or repulsive) interactions among themselves.

v) Particles in Motion

The particles are always in constant motion. Because of the lack of interactions and the free space available, the particles randomly move in all directions but in a straight line.

vi) Volume of Gas

Because of motion, gas particles occupy the total volume of the container, whether it is small or big, and hence the volume of the container is to be treated as the volume of the gases.

vi) Mean Free Path

This is the average distance a particle travels to meet another particle.

vii) Kinetic Energy of the Particle

Since the particles are always in motion, they have average kinetic energy proportional to the temperature of the gas.

viii) Constancy of Energy/Momentum

Moving particles may collide with other particles or containers. But the collisions are perfectly elastic. Collisions do not change the energy or momentum of the particle.

ix) Pressure of Gas

The collision of the particles on the walls of the container exerts a force on the walls of the container. Force per unit area is the pressure. The pressure of the gas is thus proportional to the number of particles colliding (frequency of collisions) in unit time per unit area on the wall of the container.

## 2. Molecular Velocities and Kinetic Energy:

In a gas sample, individual molecules have widely varying speeds; however, because of the vast number of molecules and collisions involved, the molecular speed distribution and average speed are constant. This molecular speed distribution is known as a Maxwell-Boltzmann distribution, and it depicts the relative numbers of molecules in a bulk sample of gas that possesses a given speed

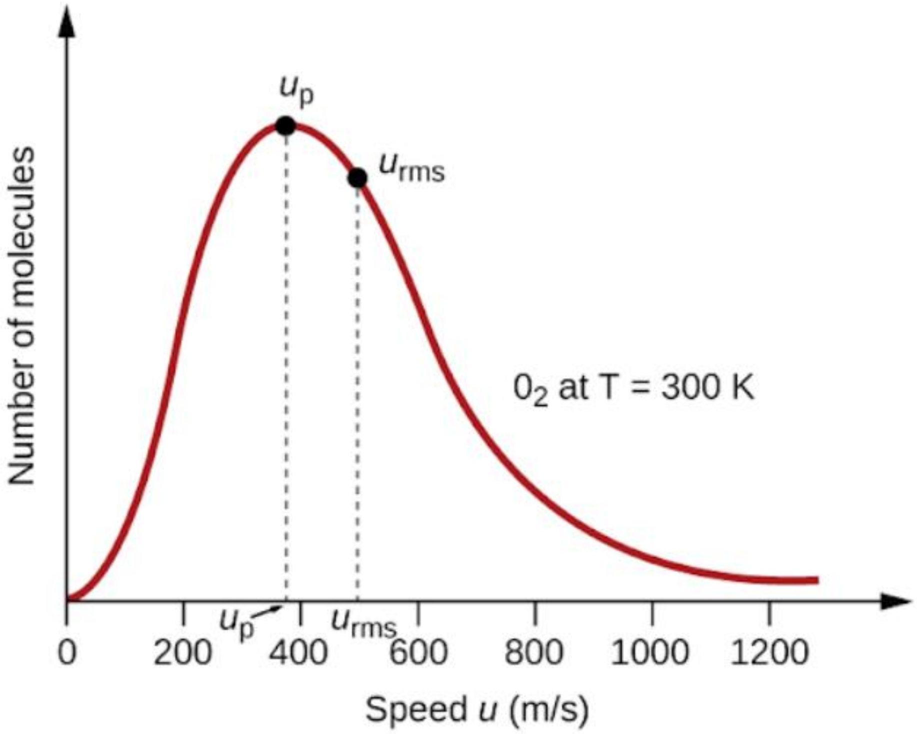

**Fig-2.1.** The molecular speed distribution for oxygen gas at 300 K is shown here. Very few molecules move at either very low or very high speeds. The number of molecules with intermediate speeds increases rapidly up to a maximum, which is the most probable speed, then drops off rapidly. Note that the most probable speed, $v_p$, is a little less than 400 m/s, while the root mean square speed, $u_{rms}$, is closer to 500 m/s.

The kinetic energy (KE) of a particle of mass (m) and speed (u) is given by:

KE =1/2mu$^2$

Expressing mass in kilograms and speed in meters per second will yield energy values in units of joules (J = kg m2 s–2). To deal with a large number of gas molecules, we use averages for both speed and kinetic energy. In the KMT, the root mean square velocity of a particle, $u_{rms}$, is defined as the square root of the average of the squares of the velocities with n = the number of particles:

$$u_{\text{rms}} = \sqrt{\overline{u^2}} = \sqrt{\frac{u_1^2 + u_2^2 + u_3^2 + u_4^2 + \ldots}{n}}$$

The average kinetic energy for a mole of particles, KEavg, is then equal to:

$$\mathrm{KE}_{\mathrm{avg}} = \frac{1}{2} M u_{\mathrm{rms}}^2$$

where M is the molar mass expressed in units of kg/mol. The KEavg of a mole of gas molecules is also directly proportional to the temperature of the gas and may be described by the equation:

$$\mathrm{KE}_{\mathrm{avg}} = \frac{3}{2} RT$$

where R is the gas constant and T is the kelvin temperature. When used in this equation, the appropriate form of the gas constant is 8.314 J/mol·K (8.314 kg $m^2$ $s^{-2}mol^{-1}K^{-1}$). These two separate equations for $KE_{avg}$ may be combined and rearranged to yield a relation between molecular speed and temperature:

$$\frac{1}{2} M u_{\mathrm{rms}}^2 = \frac{3}{2} RT$$

$$u_{\mathrm{rms}} = \sqrt{\frac{3RT}{M}}$$

If the temperature of a gas increases, its $KE_{avg}$ increases, more molecules have higher speeds and fewer molecules have lower speeds, and the distribution shifts toward higher speeds overall, that is, to the right. If temperature decreases, $KE_{avg}$ decreases, more molecules have lower speeds and fewer molecules have higher speeds, and the distribution shifts toward lower speeds overall, that is, to the left. This behaviour is illustrated for nitrogen gas in **Figure 2.2**.

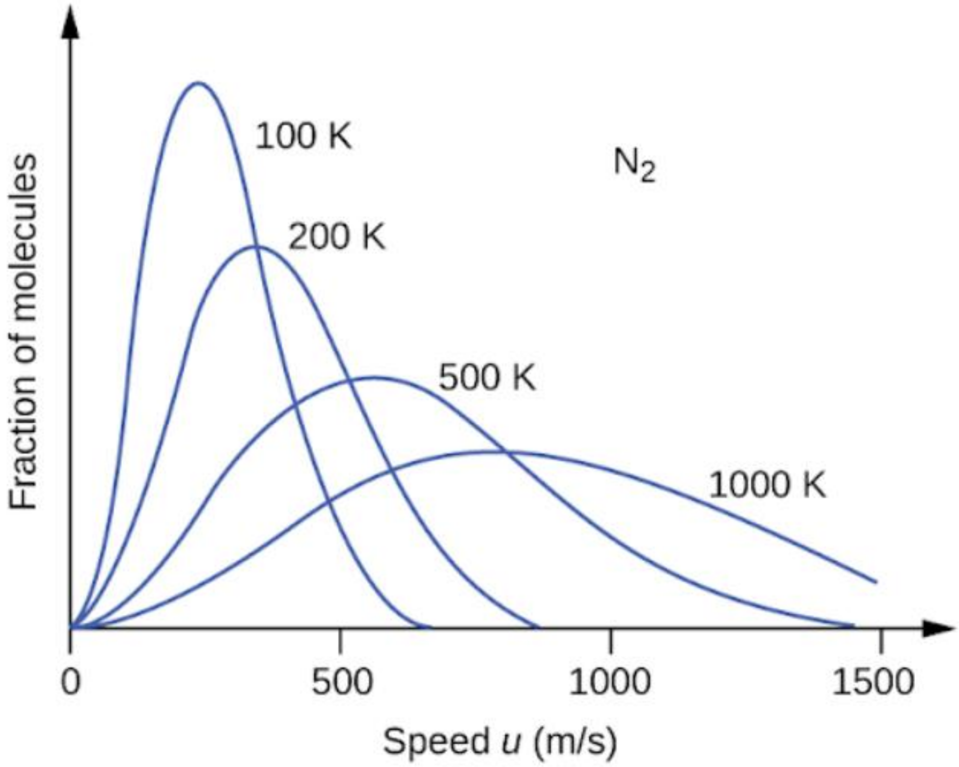

**Figure 2.2.** The molecular speed distribution for nitrogen gas (N2) shifts to the right and flattens as the temperature increases; it shifts to the left and heightens as the temperature decreases.

At a given temperature, all gases have the same $KE_{avg}$ for their molecules. Gases composed of lighter molecules have more high-speed particles and a higher $u_{rms}$, with a speed distribution that peaks at relatively higher velocities. Gases consisting of heavier molecules have more low-speed particles, a lower urms, and a speed distribution that peaks at relatively lower velocities. This trend is demonstrated by the data for a series of noble gases shown in **Figure 2.3**.

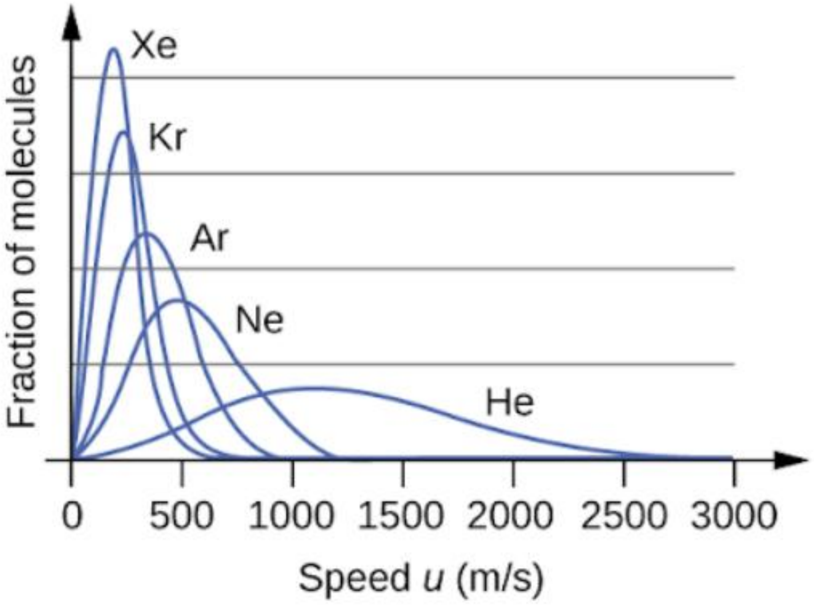

**Figure-2.3.** Molecular velocity is directly related to molecular mass. At a given temperature, lighter molecules move faster on average than heavier molecules.

### 3. Real gas and virial equation:

It is often useful to fit accurate pressure-volume-temperature data to polynomial equations. The experimental data can be used to compute a quantity called the compressibility factor, Z, which is defined as the pressure–volume product for the real gas divided by the pressure-volume product for an ideal gas at the same temperature.

We know,

$$(PV)_{\text{ideal gas}} = nRT$$

Letting P and V represent the pressure and volume of the real gas, and introducing the molar volume, $V^{/} = V/n$,

we have

$$Z=(PV)_{\text{real gas}} /(PV^{/})_{\text{ideal gas}} = PV/nRT= PV^{/}/RT$$

Since $Z=1$, if the real gas behaves exactly like an ideal gas, experimental values of Z will tend toward unity under conditions in which the density of the real gas becomes low and its behaviour approaches that of an ideal gas. At a given temperature, we can conveniently ensure that this condition is met by fitting the Z values to a polynomial in P or a polynomial in $V^{/-1}$.The coefficients are functions of temperature. If the data are fit to a polynomial in the pressure, the equation is

$Z=1+B^{*}(T)P+C^{*}(T)P^{2}+D^{*}(T)P^{3}+\ldots$

For a polynomial in $V^{/-1}$, the equation is

$Z=1+B(T)/ V^{/}+C(T)/V^{/2}+D(T) / V^{/3}+\ldots$

These empirical equations are called virial equations. As indicated, the parameters are functions of temperature. The values of $B^{*}(T)$, $C^{*}(T)$, $D^{*}(T)$ , …, and $B(T)$, $C(T)$, $D(T)$,…, must be determined for each real gas at every temperature. (Note also that $B^{*}(T)\neq B(T)$, $C^{*}(T)\neq C(T)$, $D^{*}(T)\neq D(T)$, etc. However, it is true that $B^{*} = B/RT$.) Values for these parameters are tabulated in various compilations of physical data. In these tabulations, $B(T)$ and $C(T)$ are called the second virial coefficient and third virial coefficient, respectively.

## 4. Deviation of gases from ideal behaviour:-

An ideal gas is composed of randomly moving minute particles, which undergo elastic collisions. Real gases are the ones which do not follow the ideal relations of gas law. The deviation of real gas from ideal gas behaviour occurs due to the assumption that if pressure increases the volume decreases. The volume will approach a smaller number but will not be zero because the molecules will occupy some space that cannot be compressed further.

The experimental observation of gases correctly corresponds to its theoretical model. The difficulty arises when we test the extent to which the relationship, $pV = nRT$, the ideal gas equation, is followed to depict the actual pressure-volume-temperature relation of gases. To check on this point, let us plot pV versus V graph. At constant temperature, the pV relation will be constant. The pV versus p graph will be a straight line parallel to x-axis. Know more about Ideal Gas Formula.

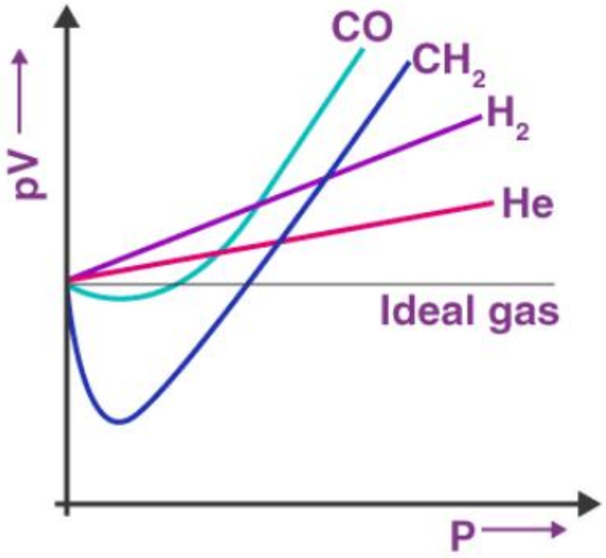

**Figure-4.1.** The above figure shows the graph constructed from actual data for some gases at 273 K.

Looking at the graph, it is seen that at constant temperature the pV vs p plot is not a straight line for real gases. There is a significant deviation from the ideal behaviour. In the case of hydrogen and helium, if the value of p increases then pV also increases. In other cases for example methane and carbon dioxide, initially there is a negative deviation from the ideal behaviour, the increase in pressure decreases the value of pV and reaches a minimum value. After it reaches the minimum point, pV value starts increasing and crosses the line for the ideal gas and then shows positive deviation continuously.

So it can be said that the real gases do not follow the ideal gas equation at all temperatures and pressure.

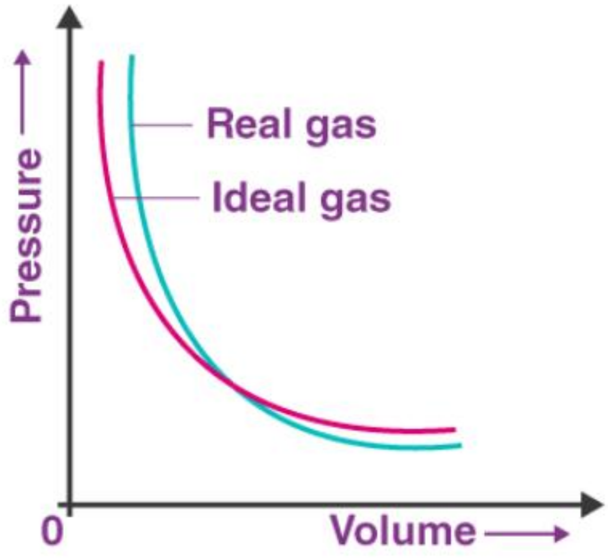

**Figure-4.2.**

The deviation of real gas from ideal gas behaviour is also seen when the pressure versus volume graph is plotted. The graph of pressure versus volume should coincide with the experimental data that is the real gas, and the theoretical data that is calculated according to Boyle's law.

5. **Boyle temperature($T_B$):-**

The temperature at which a real gas obeys the ideal gas law over an appreciable range of pressure is called Boyle temperature.

**N.B.**

- For a given gas, this temperature is dependent upon the nature of the gas.
- Boyle temperature ($T_B$) is related to the Van der Waal's constant a, b as given below. At this temperature, the attractive and repulsive forces acting on the gas particles arrive at a balance for a real gas.
- At higher Boyle's temperature, gases can easily be liquefied.
- At lower Boyle's temperature, gases are difficult to liquefy.

  $T_B = a/ (Rb)$

where "a" is the Van der Waals constant representing intermolecular attractive forces, "R" is the ideal gas constant, and "b" is the Van der Waals constant.

### 6. Van der Waals Equation:-

The Van der Waals equation is an equation relating the relationship between the pressure, volume, temperature, and amount of real gases. For a real gas containing ‘n’ moles, the equation is written as; Where P, V, T, and n are the pressure, volume, temperature and moles of the gas, respectively, and ‘a’ and ‘b’ constants specific to each gas.

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

Where,

P = pressure, V = volume, a = constant that measures the attractive force between the molecules, b = volume correction factor, nb = volume occupied by the gas molecules and T = Absolute Temperature.

- Unit of “a” and is atm lit$^2$ mol$^{-2}$
- Unit of “b” litre mol$^{-1}$

The van der Waals constant 'a' represents the magnitude of intermolecular forces of attraction and the Van der Waals constant 'b' represents the effective size of the molecules.

### Volume Correction in Van der Waals Equation:

The 'nb' term in the equation represents the volume correction. The term 'n' multiplied by 'b' accounts for the volume occupied by the gas molecules themselves. This correction adjusts the available volume by subtracting the volume occupied by the molecules, leading to a reduction in the overall volume available for the gas to expand. By using this correction term, the Van der Waals equation provides a better estimation of real gas behavior, especially when compared to the ideal gas law, which assumes negligible molecular volume and no intermolecular interactions.

Pressure Correction in Van der Waals Equation:

The $an^2/V^2$ term in the Van der Waals equation represents the pressure correction. The term 'n/V' represents the molar density of the gas, and 'a' is a constant that accounts for the strength of the intermolecular attractive forces. The correction term $an^2/V^2$ adds an extra term to the pressure to consider the decrease in pressure due to attractive forces between the gas molecules.

## Problems

**I**. Explain the deviation of real gases from Boyle's law.

**II**. Explain critical phenomena with Andrews's experiment on $CO_2$.

**III**. What corrections are made by van der Waal in the assumptions of the kinetic theory of gases? How did he deduce a new equation in the light of these?

**IV**. Using van der Waal's equation, explain the deviations of gases from Boyle's law.

**V**. Explain in Brief, exceptional behaviour of hydrogen and helium.

**VI**. What is isotherm and critical isotherm?

**VII.** What is Boyle point? Explain with respect to ideal and real gases.

**VIII**. What are the causes of deviations of gases from ideal behaviour? How are they accounted for in van der Wall's equation?

**IX**. What do you mean by the degree of freedom (n)?

**X.** What is the degree of freedom of the monoatomic gas molecule?

## SUGGESTED READINGS/ REFERENCE BOOKS:

**A.** Rakshit, P.C., Physical Chemistry Sarat Book House.

**B.** Levine, I. N. Physical Chemistry, Tata McGraw-Hill

**C.** Atkins, P. W. & Paula, J. de Atkins' Physical Chemistry, Oxford University Press.

**D.** Castellan, G. W. Physical Chemistry, Narosa.