Gaseous State

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Postulates of kinetic theory of gases

Kinetic theory of gases considers the atoms or molecules of a gas as a constantly moving point masses, with huge inter-particle distance and may undergo perfectly elastic collisions. Implications of these assumptions are –

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 them.

v) Particles in Motion

The particles are always in constant motion. Because of 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 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 particle or container. But the collisions are perfectly elastic. Collisions do not change the energy or momentum of the particle.

ix) Pressure of Gas

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.

Kinetic gas equation:-
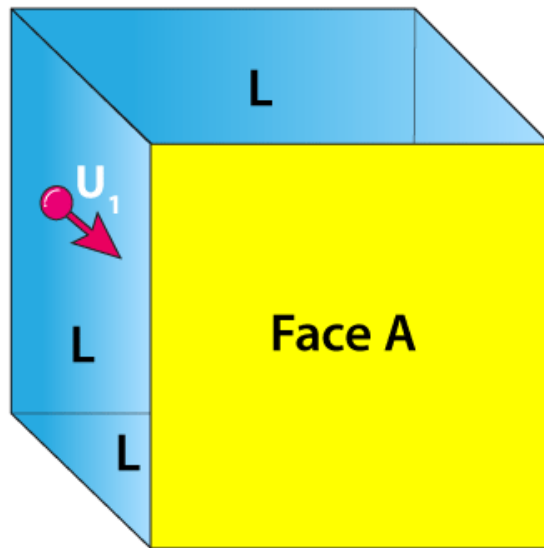
Consider a cubical container of length 'l' filled with gas molecules each having mass 'm' and let N be the total number of gas molecules in the container. Due to the influence of temperature, the gas molecules move in random directions with a velocity 'v.'

The pressure of the gas molecules is the force exerted by the gas molecule per unit area of the wall of the container and is given by the equation

$P = F.A$

Let us consider a gas molecule moving in the x-direction towards face A. The molecule hits the wall with a velocity V_x and rebounds back with the same velocity V_x, and will experience a change of momentum which is equal to $\Delta p = -2mVx$.

For a total of N number of gas molecules in the container, all such change in momentum is given by

$\Delta p = -2NmVx$

The force is given by the equation

$F = \Delta p/t$

Therefore,

$F = -2NmVx/t$

Gas molecules will hit the wall A and will travel back across the box, collide with the opposite face and hit face A again after a time t which is given by the equation

$t = 2l/Vx$

Substituting the value of t in the force equation, we get the force on the molecules as

$F = -2NmVx/2l/Vx$ F molecules $= -2NmVx/2l/Vx = -NmV^2x/l$

Therefore, the force exerted on the wall is Fwall $= NmV^2x/l$.

Now, the pressure P is given by the equation,

$P = $ Force on the wall $/Area = NmV^2xl/l^2 = NmV^2x/l^3$

Hence, $PV = NmV^2x$ ………………………(1)

Since V_x, V_y and V_Z are independent speed in three directions and if we consider the gas molecules in bulk, then

$V^2x = V^2y = V^2z$

Hence, $V^2 = 3V^2x$

Substituting the above condition in eq. (1), we get

$PV = NmV^2/3$

Therefore, **$PV = 1/3mNV^2$**   this equation above is known as the kinetic theory equation.

The velocity V in the kinetic gas equation is known as the root mean square velocity and is given by the equation

Vrms= $\sqrt{V^21+V^22+V^23}$……..$+V^2n/N$

We use this equation to calculate the root mean square velocity of gas molecules at any given temperature and pressure.

Deduction of gas laws: A) Boyles law:- Boyle's law states the relation between volume and pressure at constant temperature and mass, **It states that under a constant temperature when the pressure on a gas increases its volume decreases**. In other words according to Boyle's law **volume is inversely proportional to pressure when the temperature and the number of molecules are constant.**

$$V \propto 1/P \text{ at constant temp.}$$

The K.E.of n molecules are equal to $\frac{1}{2}$ mnu^2.we knows that kinetic gas postulates K.E. is directly proportional to the temp. Therefore $\frac{1}{2}$ mnu$^2 \propto T$

$\frac{1}{2}$ mnu^2=KT--------- (1) where K is proportionality constant. Rewriting kinetic gas equation we get,PV= 2/3 (1/2) mnu^2

Therefore ,**PV= 2/3KT**-------(2) Therefore PV= constant, which is representation of Boyles law.

B) Charles law:- Rearranging equation (2) we get, PV= 2/3 KT

Therefore V= 2/3 K/P.T at constant pressure, V=K'T----------------(3) where K'=2/3 K/P

Therefore, **Vα T** which is the representation of Charles law.

C) Avogadro's hypothesis:- Let us consider two different gases.The kinetic gaequation can be written as,P_1V_1= $1/3m_1n_1u_1^2$........(4)   and P_2V_2= $1/3m_2n_2u_2^2$ ---------(5) at constant temp.P_1V_1=P_2V_2

Therefore, $1/3 m_1n_1u_1^2$=$1/3m_2n_2u_2^2$ ----------(6)

If these two gases are at same temp., the kinetic energies of the molecules will be the same, that is,$1/3 m_1u_1^2$=$1/3 m_2u_2^2$ --------------(7) ,substituting in equation (6) we get; **n_1=n_2** Hence Avogadro's law has been deduced.

*D) Grahams Law of diffusion:-* Consider equation (6).......

$1/3 m_1n_1u_1^2$=$1/3m_2n_2u_2^2$

$u_1^2/u_2^2 = n_2m_2/n_1m_1$ if n_1=n_2=N then, $u_1^2/u_2^2 = Nm_2/Nm_1 = M_2/M_1$

but $M_1/V = d_1$ and $M_2/V = d$ therefore , $u_1^2/u_2^2 = d_1/d_2$ ---------(8)

Deviation from ideal behavior:- Ideal gas obeys the gas laws for all values of pressure and temp.,in reality, all gases obey the gas laws only over a range of pressure and temp. And not for all values of pressure and temp., hence real gases can be described in terms of the deviations from the gas laws.

Deviations from Boyle's law:- If we plot PV against P, for a ideal gas should be straight line parallel to the X axis .This indicates that for an idea gas PV should remain constant at constant temp.For real gas,such a straight line will not obtained. Gases like hydrogen ,nitrogen shows positive devitions.for these gases product PV increases with increase in pressure.som gases like methane and carbon dioxide shows product PV is found to be decreases. Small deviations from the Boyles law are observed only t low pressures.
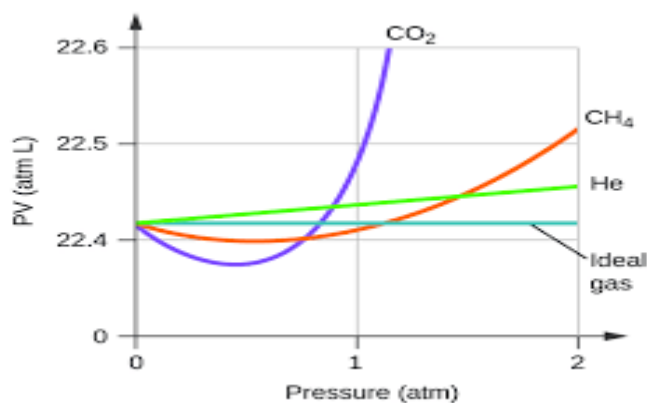
Deviations from Charles law:- for a given amount of gas at constant pressure the volume of a gas increases or decreases by 1/273 times its volume at 0oC,for every degree rise of fall in temperature.1/273 or 0.003661 is the temp.coefficient of the gas.,This remains same for all gases for all range of pressure and temp.

Reasons for the deviations from idea behavior:- There are two main faulty assumptions,these postulates are,

1) The volume of gas molecules that is the actual volume occupied by the gas molecules is negligible in comparison with the volume available to them that is the volume of the container.

2) Therefore the actual volume of gas = volume of container – Volume of the molecules

3) Molecules of the gas don't exerts any force of attraction over one another. In reality molecules of real gases exerts force of attractions with each other, as distance between two molecules increases force of attraction increases. Hence deviations from the ideal behavior are expected at high pressure.

4) K.E.of molecules increases,some of K.E.is used to overcome the intermolecular force,hence the gas behaves ideally.,but as temp.is lowered,the average K.E.of gas molecule will decreased.it may not be sufficient to overcome the force of attraction.Hence, a deviation from ideality may be observed.

Van- der Waals equation of state:- it is an equation which shows relation between all the variables at the given state is called equation of state. For gases state P,V,T and n are variables that defines the states. PV=nRT is also an equation of state, but this is not obeyed by real gases for all the values of pressure, volume and temperature .hence some parameters has to be taken into account to explain the behavior of real gas. There are two faulty assumptions of kinetic theory of gases these are,
A) The volume of gas molecules is negligible in comparison with volume occupied by them.
B) No intermolecular force of attraction are present in the gaseous state. Van- der Waals provided an equation of state, that will be obeyed by al real gases, at all values of pressure and temperature.

Critical Phenomeno: PV isotherms of real gases:- Critical phenomena. The essential condition for the liquefaction of the gas is described by the study of critical temperature, critical pressure and critical volume and their inter relationships. When a gaseous system is transformed to its liquid state, there is a tremendous decrease in the volume.

The ideal gas law assumes that a gas is composed of randomly moving, non interacting point particles. This law sufficiently approximates gas behavior in many calculations; real gases shows complex behavior that deviate from the ideal model., however as shown by graph (isotherms refers to the different curve so he graphs, which represent a gas state at different pressure and volume conditions but at constant temperature ,iso means same and therm means temperature – hence isotherm.

Real gas isotherms:- As per ideal gas equation PV=nRT, pressure and volume should have an inverse relationship. Notice that the higher isotherms on the graph, which represent the gas state at high temperature, show the typical, concave decreasing curve of an inverse relationship. As

temperature decreases, however, the isotherms on the lower portion of the graph significantly deviate from this ideal inverse relationship between P and V.