Kinetic Theory of Gases

Kinetic theory of gases attempts to develop a model of the molecular behaviour which should result in the observed behaviour an ideal gas.

Assumptions of kinetic theory of gases

1. All gases are made of molecules moving randomly in all directions

2. The size of molecule is much smaller than the average separation between the molecules.

3. The molecules exert no force on each other or on the walls of the container except during collision (no atraction force or repulsion force).

4. All collisions between two molecules or between a molecule and a wall are perfectly elastic. Also the time spent during a collision is negligibly small.

5. the molecules obey Newton's laws of motion.

6. When a gas is left for sufficient time in a closed container, it comes to a steady state. The density and the distribution of molecules with different velocities are independent of position, direction and time.

The assumptions are close to the real situations at low densities.

The molecular size is roughly 100 times smaller than the average separation between the molecules at 0.1 atm and room temperature.

The real molecules do exert electric forces on each other but these forces can be neglected as the average separation between molecules is large as compared to their size.

Pressure of an ideal gas

$p = (1/3)\rho * \mathrm{Avg}(v^2)$ .... (1)

where

ρ = density of gas = mass per unit area

$\mathrm{Avg}(v^2)$ = average of the speeds of molecules squared

$pV = (1/3)M*Avg(v^2)$ .... (2)

M = Mass of gas in the closed container

$pV = (1/3)nm*Avg(v^2)$ .... (3)

n = number of molecules of gas in the container

m = mass of each molecule

RMS Speed: The square root of mean square speed is called root-mean-square speed or rms speed.

It is denoted by the symbol vrms

$Avg(v^2) = (vrms)^2$

The equation (1) can be written as

$p = (1/3)\rho*(vrms)^2$

Thenvrms) = $\sqrt{[3p/\rho]} = \sqrt{[3pV/M]}$

Total translational kinetic energy of all the molecules of the gas is

$K = \Sigma\ (1/2mv^2 = (1/2)M(vrms)^2$ ... (4)

The average kinetic energy of a molecule = $(1/2)m(vrms)^2$

Then from equation (2)

$K = (3/2)pV$

according to the kinetic theory of gases, the internal energy of an ideal gas is the same as the total translational kinetic energy of its molecules.

For different kinds of gases, it is not the rms speed but average kinetic energy of individual molecules that has a fixed value at a given temperature.

The heavier molecules move with smaller rms speed and the lighter molecules move with larger rms speed.

Kinetic Theory of Gases

All gas laws can be deduced from kinetic theory of gases.Ideal gas equation

$pV = nRT$

R = universal gas constant = 8.314 J/mol-L

The average speed of molecules is somewhat less than the rms speed.

Average speed = $(\Sigma v)/n = \sqrt{[8kT/\pi m]} = \sqrt{[8RT/\pi M0]}$

Due to the random motion of molecules of gas, the centre of mass of the gas does not change.

Maxwell's speed distribution law

The rms speed of an oxygen molecule in a sample at 300 K is about 480 m/s. As it is a square root of average of squared values of the individual velocities of various molecules, many molecules will have speed more than 480 m/s and many will have speed less than 480 m/s. Maxwell derived an equation giving the speed distribution of molecules. If dN represents the number of molecules with speeds between v and v + dv then

$dN = {}_4 \pi N[m/2\pi kT]^{3/2} v^2 e-(mv^2/2kT)dv$

The speed vp at which dN/Dv is maximum is called the most probable speed.

vp = SQRT(2kT/m)

Thermodynamic State

A thermodynamic state of a given sample of an ideal gas is completely described if its pressure and its volume are given.

Equation of state

An equation describing the relation between pressure, volume and temperature of a given sample of a substance is called the equation of state for that substance

For an ideal gas it is $pV = nRT$

For a real gas the equation is $[p + a/V^2][V-b] = nRT$Where a and b are small positive constants. a is related to the average force of attraction between the molecules. b is related to the total volume of the molecules. This equation is given by van der Waals.

Brownian motion

Brownian motion was random motion of molecules in liquid observed by Robert Brown. It is similar to random motion of molecules in gases. To observe the Brownian motion in liquid we need light suspended particles. The motion increases at higher temperatures. Liquids with smaller viscosity and smaller density will show more intense Brownian motion.

Vapour

In general a gas can be liquefied either by increasing the pressure or by decreasing the temperature. However, it the temperature is sufficiently high, no amount of pressure can liquefy the gas. The temperature above which this behavior occurs is called the critical temperature of the substance. A gas below its critical temperature is called vapour.

Critical temperature of a substance: Above this temperature, the substance cannot be converted into liquid by increasing the pressure i.e., by compressing.

Vapour: Vapour is gas below the critical temperature of the substance.

Water cannot be liquefied at a temperature greater than374.1°C by increasing the pressure. 374.1°C is the critical temperature of water. Hence below 374.1° water in gas form is called water vapour and above 374.1° it is called water gas.

Vapours obey Dalton’s law of partial pressure.

Evaporation

Evaporation is a process in which molecules escape slowly from the surface of a liquid. Only those molecules whose kinetic energy is more than the average escape from the surface. Because of this, as more and more molecules evaporate, kinetic energy of the remaining liquid decreases and temperature goes down. This effect is observed in water in pots.

Saturated vapour pressure

When we place an open flask with a liquid in a closed jar, after sufficient time, volume of the liquid becomes constant. We know that liquid evaporates, but at this point in time, when volume of liquid is constant, we have to interpret that rate of transformation from liquid to vapour equals the rate of transformation from vapour to liquid.

If some vapour from outside is injected into the space above the liquid in the jar, we observe that the volume of liquid will increase. That means more vapour is getting transformed into liquid.

When a space actually contains the maximum possible amount of vapour, the vapour is said to be saturated or it is called saturated vapour. If the amount of vapour in a space is less than the maximum possible, the vapour is called unsaturated vapour.

Saturated vapour increases with temperature. At higher temperature, the space contains more vapour. This is because more liquid molecules escape from liquid surface at higher temperatures.

The pressure exerted by a saturated vapour is called saturated vapour pressure. As a higher temperature more amount of vapour is there of a liquid, saturated vapour pressure is also higher at higher temperatures for a substance. Even into an empty jar, as vapour increases more and more, and pressure increases above the SVP, vapour starts condensing and liquid forms. This is as per definition of vapour. A vapour can be transformed into a liquid at a constant temperature by increasing pressure.

In the atmosphere around us air which is mixture of nitrogen and oxygen and water vapour are mixed with each other. If a given volume air contains maximum amount of vapour possible, the air called saturated with water vapour.

Kinetic Theory of Gases

Boiling

As we heat a liquid, the kinetic energy of the entire liquid increases, energy of many molecules in various places becomes sufficient to break the molecular attraction. Hence vapour bubbles form, float to the surface and escape from the liquid surface. This phenomenon is called boiling and the temperature at which it occurs is called boiling point.

Boiling point of a liquid depends on the external pressure over its surface. Boiling occurs at a temperature where the SVP equals the external pressure. Hence in a pressure cooker boiling of water occurs at a higher temperature. At a higher temperature only SVP of water vapour equals the higher pressure in the cooker.

Dew point

The temperature at which the saturation vapour pressure is equal to the present vapour pressure is called the dew point.

Example: Air at temperature 15°C has a pressure of 8.94 mm Hg. This air unsaturated at SVP of air at 15°C is 12.67 Hg mm. At 10°C, SVP of air is 8.94 mm. Therefore, dew point of this air is 10°C.

If the temperature is of an unsaturated air is decreased below dew point, some vapour will condense.

Humidity

The amount of water vapour present in a unit volume of air is called the absolute humility. Its general units are g/m^3

The ratio of amount of water vapour present in a given volume to the amount of water vapour required to saturate the volume at the same temperature is called the relative humidity.

Relative humidity = RH =

Amount of water vapour present in a given volume of air at a given temperature

Amount of water vapour required to saturate the same volume of air at the same temperature

RH may also be defined as

Vapour pressure of air/SVP at the same temperature

SVP = Saturation vapour pressure: The pressure exerted by a saturated vapour is called saturation vapour pressure.

The RH may also be defined as

SVP at the dew point/SVP at the air temperature

As the vapour pressure of air at the actual temperature is equal to the SVP at the dew point.

Determination of relative humidity

Regnault’s hygrometer has two test tubes whose outer surfaces are silvered with thermometers. In one of the test tubes some ether is taken and there is an arrangement for sucking outside air through the ether. As the outside air is sucked through the ether, it evaporates and temperature in the test tube falls. As the temperature is decreasing at a particular temperature, vapour in the air outside the test tube starts condensing on the test tube surface and the silver surface becomes dull or hazy. This temperature, which is dew point, is noted along with the temperature of the other test tube. Then sucking of air through the test tube having ether is stopped and temperature of the tube slowly starts increasing. As the temperature crosses the dew point, the silver surface starts shining again. This temperature is noted again. The average of these two temperatures gives the dew point (average is taken to minimize experimental error). So the dew point (temperature) and air temperature outside are known. If f and F are the saturation vapour pressures of air at the dew point and the air temperature respectively, the relative humidity is f/F*100%.

Phase diagrams

It is a diagram that shows the relation between saturated vapour pressure and temperature in the case of gas, liquid and solid. The three phases solid to liquid, liquid to gas as well as solid to gas (if feasible in the case of a substance) are shown in this diagram. There is a point in this diagram where all three phases can exist simultaneously in equilibrium. It is called triple point.

For carbon dioxide, the triple point is 5.11 atm pressure and 216.55 K temperature. At atmospheric pressure, the diagram shows that carbon can be in solid state at low temperatures or in vapour state at high temperatures. Solid carbon dioxide when heated at atmospheric pressure becomes gas directly. Hence it is called dry ice.

Dew and fog

In winters, as temperature falls, surfaces of window-panes, flowers, grass etc. become still colder due to radiation. The air near to them becomes saturated and water vapour condenses and droplets are formed on them. It is known as dew. At still lower temperature entire air in the atmosphere gets saturated, water vapour condenses around or on the dust particles in the air. These dust particles floating in air with condensed water vapour on them form a thick mist, which restricts visibility. This thick mist is called fog.

Formula

1. **$p = 1/3*\rho*\text{Mean}(v^2)$**

   p = pressure of gas
   ρ = density of gas
   $\text{Mean}(v^2)$ = mean square speed of molecules of gas

2. **$pV = 1/3*M*\text{Mean}(v^2)$**

   V = Volume of gas

M = Total mass of the gas taken

3. $pV = 1/3*Nm*Mean(v^2)$

N = total number of molecules in the sample

m = mass of one molecule

4. $Mean(v^2) = \Sigma V^2/N$

Square root of $Mean(v^2)$ is also called root-mean square speed vrms

Equation 1 can be written as $p = 1/3*\rho*v^2rms$

So vrms = $SQRT(3p/\rho)$

6. In thermal equilibrium in a mixture of two gases, the average kinetic energies of all molecules are equal. If v1 an v2 are rms speeds of the molecules of A and B

$½m1v1^2 = ½m2v2^2$

7. pV = Nkt

k is known as the Boltzmann constant.

Its value is 1.3^{8}*10^(-23) J/K

R = NA*k (NA is Avogadro's number = 6.02*10^23

R = 8.314 J/mol-K

8. pV = nRT

9. RMS spped in terms of temperature

v(rms) = SQRT(3kT/m)

10. v(rms) = SQRT(3RT/M0)

11. Average kinetic energy of a molecule

$\frac{1}{2}mv(rms)^2 = (3/2)\ kT$

12. Total kinetic energy of all molecules

U = (3/2)nNA kT

or

U = 3/2nRT (R = NA*k)

n = number of moles of substance

13. maxwells speed distribution law

$dN = 4\ \pi[m/2\ \pi kT]^{3/2}v^2e-(mv^2/2kT)dv$

14. The speed at which dN/dv is maximum is called the most probable speed.

vp = SQRT(2kT/m)

15. van der Waals equation for real gases

For an ideal gas
pV = nRT
This is called the equation of state for that substance
For a real gas
$[p + a/V^2][V-b] = nRT$
where a and b are small positive constants.
a is related to the average force of all attracion between the molecules.
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