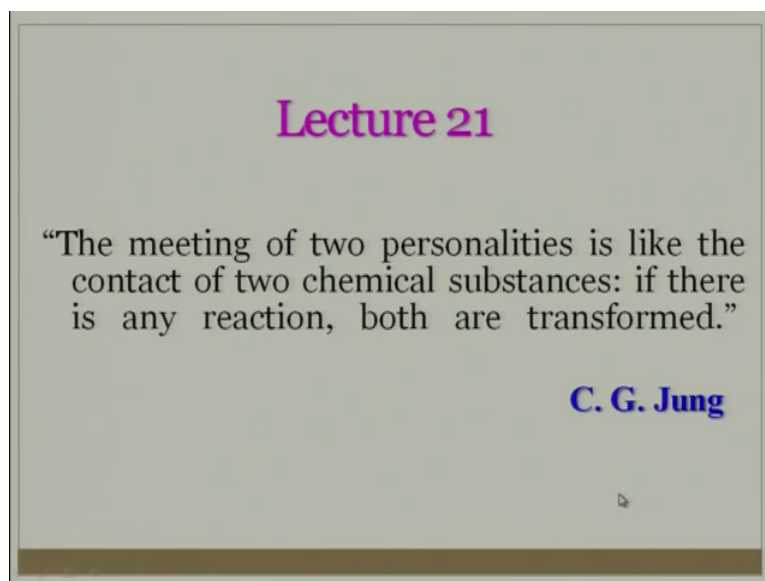


Fundamentals of Combustion (Part I)
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Lecture – 21
Collision Theory

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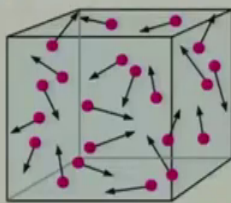
So, let us start this lecture with a thought process the meeting of two personalities is like the contact of two chemical substances. If there is any reaction both are transformed right yes or no so, that is also similar thing to what is happening it is told by the C. G. Jung and let us recall that we discuss about elementary reactions and also why the single-step chemistry is not meeting the nature right. And then we looked at basically how to write the reaction particularly for multi-step chemistry in a compact way and so also the reaction rate. And towards end I also discuss about there is a need for to find out the you know expression for the reaction rate coefficient or specific reaction rate and invoking the collision theory right.

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Collision Theory : Kinetic Theory of An Ideal Gas

Assumptions:

- It consists of a large number of molecules with spherical shape whose size and mass are identical but they vary from gas to gas.
- The total volume of all individual gas molecules is negligible as compared to the volume of the container.
- The average distance separating the gas particles is large. Force of attraction/repulsion between the molecules is negligible.
- These molecules with higher KE in random and rapid motion undergo perfectly elastic collisions among themselves and walls of container.
- The statistical treatment can be used as the number of molecules is quite large.
- The interactions among molecules are negligible except during collisions.
- The mean free path is quite large as compared to the molecule size.
- Pressure applied on the walls of the container is due to the collision of gas molecules with the container.
- The molecules of gas move with different velocities and different kinetic energies. The KE of gas molecules depends on the temperature of gas.



The diagram shows a 3D wireframe cube representing a container. Inside the cube, there are approximately 15 small red spheres, each representing a gas molecule. Black arrows of varying lengths originate from each sphere, pointing in different directions to represent the random motion of the molecules. Some arrows point towards the walls of the cube, illustrating collisions.

Collision theory means basically there will be collisions between the, what you call molecules and atoms right that. Right which will be moving randomly and when it is moving randomly then we will have to look at the kinetic theory of an ideal gas. Keep in mind that we are keeping the ideal gas in our mind why because ideal gas can be utilized very easily for combustion problem being at higher temperature and moderate pressure right. So, let us look at we will take a cube right where the, these particles are moving randomly. It is moving here and they will be colliding each other's right. And for that we will make some assumptions what is happening and that is basically assumption for the kinetic theory of gases.

So, what we are assuming that this container or any cube or something we are considering which may be any set, but we are taking a cuboid. It contains a large number of molecules with spherical shape whose size and mass are identical right. But they vary from gas to gas. Keep in mind these are assumptions right need not be same right spherical size because you have seen the molecules you know are various shapes and depending on what it is.

But we are considering for the simplicity. And total volume of all individual gas molecule is negligibly small as compared to the volume of the container. These assumption we have discussed earlier for an ideal gas. And when this is moving you know like there will be some separation distance between the gas right because not that

all are compact like a solid or in a liquid right. So, these are moving. So, there is a separation distance the average separation separating distance between thus particles is quite large. That means, you know one particle is here another particle in the somewhere else right. So, as a result the force of attraction and the repulsion between molecules is negligible right. There is not much distance. And these molecules with higher kinetic energy right will be moving around right and colliding with others right and it will be moving with a very high velocity right.

And whenever there is a collision taking place that will be elastic in nature what does it mean? Either they are colliding each other or they are colliding with a wall that will be elastic in nature; that means, there would not be any change in the kinetic energy or the velocity with which it will be colliding it will be not reduced, but that is not the case you know it will be reduced right we have seen. And as it is moving in the randomly it is very difficult to handle.

Why? Because if I will talk one of the one molecule is talk about velocity and then about momentum, about the all the forces acting and then doing solving you know even it will be small volume of one centimeter cube if I will consider it is very difficult to you know handle that even using the best super computer available in the world at this moment. Are you getting? So, therefore we will have to do that thing in a statistical way; that means, average way right.

And treatment can be possible only when the large number of molecules is you know like numbers number of molecules involve is quite large these kind of thing. And interaction I cannot take few molecules and consider this is the statistical. Then statistics have no meaning you know right. Therefore, large number of molecules will be there. But whereas if I go to the other one actual stimulation less are the number of molecules better it will be. Where I can my situation or handling will be easier. The interaction among the molecules are negligible, they small except during the collision. When there is colliding because there is no in forces of attractions and repulsion. Therefore, when it is not colliding you do not have much thing in that.

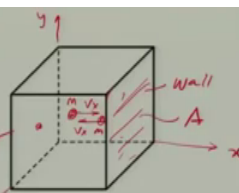
And mean free path is quite large as compared to the molecular size right. Mean free path means the distance between two collision basically is the mean free path. And pressure is applied on the walls of a container is due to collision of gas molecule with the

container not any other effect ok. The molecules of gas moves with a different velocities right and different kinetic energies and of course, you can consider that it will be different molecular weight. Mass will be also different, but we would not be considering that thing as we go along we will see we will be considering a single mass you know mass remains you know mass is same for all molecule we will start then we will have to do that.

Kinetic energy of gas molecules depends on the temperature of the gas right. Because the higher the temperature the kinetic energy will be high because the molecule will be moving at a faster velocity or the speed. So, what we will do? We will now basically invoke this kinetic theory of gases from the very simple things what you might have studied in your classroom. But you might have forgotten by this time. So, we will recall it and then do that ok.

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Pressure of an Ideal Gas:



Change in momentum of this molecule in x-direction
 $= m(v_{\text{final}} - v_{\text{initial}}) = m(-v_x - v_x) = -2mv_x$

Change in momentum imparted to the wall
 $= 2mv_x$

Let N be number of identical gas particles per unit volume
 $N = \text{Number density} = \frac{N_0}{V}$; $N_0 = \text{Number of particles (molecules)}$
 $V = \text{Volume}$

During Δt , No. of collisions or of molecules with $v_x = \frac{NV}{2}$

$V = v_x \Delta t A$

Total momentum transferred to the wall $= \mu m v_x \cdot \frac{NV \Delta t A}{2} = Nm v_x^2 \Delta t A$

Rate of change of momentum $= \frac{Nm v_x^2 \Delta t A}{\Delta t} = Nm v_x^2 A$

$P = \frac{\text{Rate of change of momentum}}{A} = \frac{Nm v_x^2 A}{A} = Nm \bar{v}_x^2$ — (1)

$V = v_x i + v_y j + v_z k$ For isotropic situation, $v_x = v_y = v_z = V$

$\bar{v}_x^2 = \text{Average velocity along x-axis}$ — $\bar{v}_x^2 = \bar{v}_y^2 = \bar{v}_z^2 = \frac{1}{3} [\bar{v}_x^2 + \bar{v}_y^2 + \bar{v}_z^2] = \frac{1}{3} \bar{v}^2$

Eq (1) becomes $P = \frac{1}{3} Nm \bar{v}^2$

So, let us consider a cube here right and let us say this is having x direction and this is having y direction, this is having z direction ok. Let us say there is a I mean we are considering starting with a one particle right kind of things and then we will move into that other one. Let us say there is a particle here right, which is moving with a velocity V x and it will move what will happen? It will go and hit the wall. This is your wall right. And it will go and hit and then it will come hit this thing what will happen? Elastic collision; that means it will be coming and this is having mass M , this particle having

mass m . So, therefore what happens this will becoming with the velocity V_x mass is same M right because of elastic collision.

Now I want to find out what will be the pressure of an ideal gas because we are considering ideal gas right. Now as collision is perfectly elastic therefore, V_x in the, what you call positive x direction is same as when it will be just returning back with the same velocity right. So, therefore change in momentum of this molecule right, in x direction what it would be? Mass is not changing mass is same ok.

Student: (Refer Time: 09:19).

M final minus initial right? What it is final? Final is what it would be?

Student: Minus V_x .

Minus V_x minus initial will be minus V_x . That is $2 M V_x$ right. But that is a conservation of momentum. So therefore, the momentum change in momentum you know imported to the wall right, is equal to $2 M V_x$ just negative sign like will go away. Now if you look at I want to find out you know let us say total number of collision which will be taking place on this wall right because my interest is to find out pressure right. Pressure is basically force upon area.

So, for force I want to find out I will have to find out rate of change of change of momentum right. And by the all the particles and if it is all the particles let us take that you know there are. Let N be the number of identical gas particles I can say molecules particles per unit volume. What is this N that means, N is basically number density right is not it. It will be number density.

That is nothing, but N naught by V . What is N naught number of particles or molecules whatever you call right. I can say molecules because I will be using molecules later on and V is the volume. Now I want to find out and keep in mind that this is occurring in a very small interval of time Δt ok. Because this one is colliding the time is very very small is go on collide where you (Refer Time: 12:12) very small time scale right during this small time right. During Δt right number of collision right with velocity V_x right collisions of molecules right I am using particle molecules you know in a interchangeable with V_x right.

What it would be? What it would be? How many part you know number of collision is taking place. If you look at what it would be? Number of collision means number of particles will be there right? That many collision will be taking place? Is it so? That means, can I write down here number of collision means basically N into V is it right? That is not right because we are consider it is go and again go back and hit and come back. So, this will be half yes or no? It will hit. It will come back and hit this wall. This is also wall. If I am considering along with x direction only that means, it will come and heat other wall also. Yes or no? That means this will be divided by 2. Is that clear? No because the particle is going and coming and then is going and hit here and again, it will come back so therefore half right.

So now, what is this volume then because I need to calculate this volume? What will be this volume? Volume will be $V \times$ right with a velocity is moving into area if I consider this is my area right. Ok into Δt into area because $V \times$ is meter per second this Δt during that Δt it is occurring. So, this is the v . So therefore, total momentum transfer to the wall by all the molecules what it would be? We know the momentum transfer to the wall right by the single particle for single molecule what is that $2 M V \times$ into what? Into will be number of particles right. Is not it? Yes or no? That means, NV by 2 N and V is $V \times \Delta t$ area divided by 2 2 2 cancel it out. So, I will get $N M V \times$ square right Δt into A right. Yes or no?.

Student: Sir (Refer Time: 15:40).

So, now I will have to find out total momentum then what will be the rate? Rate of change of momentum will be divided by Δt and what will be pressure I will write down. Pressure will be rate of change of momentum right. That is right. Ok let me write down rate of change of momentum divided by area. So, that will be this is your total momentum change. That means, what is the rate of momentum rate of change of momentum that is let me write down here because rate of change of momentum is nothing but $N M V \times$ square Δt A divided by Δt right because this is change in momentum right. This will cancel it out I will get $N M V \times$ square area right. And this is then I will write down and $N M V \times$ square divided by area cancel it out and there will be also what you call.

Student: $V \times$ square.

Nm.

Student: V_x square.

V_x square right. And keep in mind that this is about only one single thing right. There might be that particle or the molecule will go and hit the wall in the x direction right. Is it possible? It is not possible. So, the total velocity if I take in I write down vectorial form will be V_x . If I say this is i and then $V_y j$ plus $V_z k$. Because all three direction it can happen. But if I consider this to be isotropic; that means for isotropic case situation like V_x is equal to V_y is equal to V_z right ok. Are you getting? Now keep in mind that we are looking at statistically.

Therefore there will be some average also right. So, I can write the on V_x average square is equal to a V_y average. Because several number of particles are there. It is not a single particle. There will be number of particles. So, therefore you need to look at average velocity right average velocity right and is equal to V_z average square. This is average velocity right along x direction that is V_x square and is equal to I can write down as $\frac{1}{3} V_x^2$ average velocity, V_y^2 average velocity, V_z^2 average right. I can say is equal to $\frac{1}{3} V^2$ average I am just representing it right. $\frac{1}{3}$ by 3 I can write down because if I say this is v . That means, keep in mind that this is basically average over the things right.

This I can say right because of fact that this there are several number of molecules are there. Therefore we need to consider average velocity. So, therefore I can write down P if I say this is equation 1, then equation 1 for becomes P I can say this is what you call P is equal to $\frac{1}{3} N M \overline{V^2}$ average square right is for the all the molecules what we are considering. That might be thousands of molecules but that average velocity we are talking about right. Now, you might be wondering why we are doing that why we will be looking at pressure when you talk about what you call collision theory and other things. But we will see that we will be more interested to look at the pressure is also important and also the, we will have to look at what will be the average velocity rights of the molecules or the average speed of the molecules.

(Refer Slide Time: 20:53)

Handwritten notes on a chalkboard showing the derivation of the ideal gas law and the root mean square velocity.

Top left: $P = \frac{1}{3} N m \bar{v}^2$

Top middle: $N_0 = N V$

Top right: \therefore Internal Energy due to translational motion

Middle left: $P V = \frac{1}{3} N m \bar{v}^2 = \frac{2}{3} \left(N_0 \frac{m \bar{v}^2}{2} \right) = \frac{2}{3} U \Rightarrow P V = \frac{2}{3} U$

Middle left (circled): $N_0 \frac{m \bar{v}^2}{2} = \frac{2}{3} U$

Middle left: For ideal gas law $\Rightarrow P V = \frac{2}{3} U = n R_u T$

Middle left: $\Rightarrow U = \frac{3}{2} n R_u T$

Middle left: $N_0 \frac{m \bar{v}^2}{2} = \frac{3}{2} n R_u T \Rightarrow \bar{v}^2 = \frac{3 n R_u T}{N_0 m}$

Middle left: For a molecule \therefore

Middle right: $n = \frac{N_0}{A_v} = \frac{M}{M W}$

Middle right: Avogadro's Number

Middle right: $m A_v = M W$

Middle right: $\bar{v}_{rms} = \sqrt{\bar{v}^2} = \sqrt{\frac{3 n R_u T}{A_v n_0 m}} = \sqrt{\frac{3 R_u T}{M W}}$

Middle right: $\bar{v}_{rms} = \sqrt{\frac{3 R_u T}{M W}}$

Bottom left: $v_{rms} \propto T^{\frac{1}{2}}; T \uparrow v_{rms} \uparrow$

Bottom left: $v_{rms} \propto \frac{1}{M W^{\frac{1}{2}}}; M W \downarrow \Rightarrow v_{rms} \uparrow$

Bottom left: $\boxed{v_{rms} = \sqrt{\frac{3 R_u T}{M W}}}$

Bottom left: Molecule speed is independent of pressure.

So, let us look at that if you look at we have seen that P we have seen that is $\frac{1}{3} N M V$ average square root. If I say this is $P V$ $P V$ means is a, what you call volume. This is a V is volume keep in mind that I am using V for velocity and V for volume is equal to $\frac{1}{3} N M V$ square into V I can write down V here. Yes or no? Now what is this $N V$? $N V$ is nothing but your.

Student: N naught.

N naught is equal to $N V$. So, I can write down $\frac{1}{3} N$ naught right. $M V$ square divided by 2 into 2 I can write down 2 here. And what is this one? This is basically translational velocity or the kinetic energy of the molecules which is due to the motion. What you call this? This we call it as a internal energy. Can you call it?.

Student: Yes sir.

Because the molecules are there it is going and hitting right. Of course, there might be molecule which will be vibration vibrating right and there will be also rotational. But you are considering the single and then this will be we call it as a internal energy due to translation ok. That means, this is basically $\frac{2}{3}$. By that I can write down that $P V$ is equal to $\frac{2}{3} U$. Can I write down? $\frac{2}{3} U$. U is the internal energy due to translation translational motion. That means, we know from for ideal gas law right for ideal gas law $P V$ is equal to $\frac{2}{3} U$ is equal to $n R_u T$ yes or no right? And I can write down this

thing is basically we know this thing right. That I can write down basically U is equal to $\frac{3}{2} n R u T$ and what is this U ? U is equal to N naught $M V$ square by 2 right. That is nothing but U is equal to $\frac{3}{2} n R u T$. So, this will cancel it out. So, therefore what will be $\frac{3}{2} n R u T$ right divided by $N M$ right.

Student: N naught sir.

N naught yes you are right N naught. Now what is N ? N we know, it will be N naught divided by $A v$. What is $A v$?

Student: Avogadro.

Avogadro's number Avogadro this is M by molecular weight. So, this is Avogadro's number. Now I will put this one here that is 3 in place of M N naught right. Keep in mind what is this velocity? Yes. What is this velocity? This is basically.

Student: (Refer Time: 25:26).

Velocity for molecule right this velocity is for a molecule average velocity square. Why because I am dividing the N number of molecules yes or no? N number is or may be some you know million molecules will be there or maybe 10000 molecules whatever it may be dividing. So, therefore in a in place of N I am now writing N naught right divided by $A v$ and this is your $R u T N$ naught M . So, this will cancel it out right V square. And what is this M and $A v$? $M A v$ is nothing but your molecular weight right. yes or no?

Student: Yes sir.

So, therefore these velocity if I take root this became $V r M s$. Root is equal to root. So, $V r M s$ is equal to root over $\frac{3}{2} R u T$ divided by molecular weight make sense? And if you look at $V r M s$ is proportional to what? Proportional to T half and $V r M s$ is inversely proportional to molecular weight or by half. That means, if temperature is higher; that means, temperature is higher $V r M s$ will be higher. If molecule that molecular weight will be lower; that means, lighter molecules will have $V r M s$ will be higher. Yes or no? And keep in mind that molecular speed is independent of what pressure ok.

So, we will stop over here and we will discuss in the next class like what will be the, I will take an example what is the you know velocity. What order velocity will be there? Will it be you know centimeter per second? Meter per second or something more? That will see taking some small example ok.

Thank you very much.