Molecules in Motion

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Lecture - 10
Kinetic theory of gases (Contd.)

Welcome to this next session, this is going to be the more or less the last lecture on Kinetic theory of gases, which will be extension of whatever we have done previously; that means, we had talked about the collision frequency, we are going to extend that today to effusion and to understand how are they going to be used when we are having a practical application.

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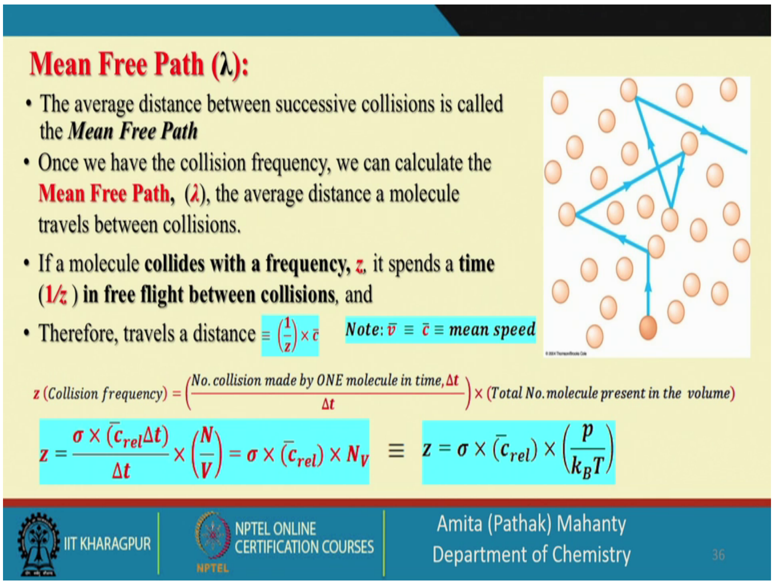

Mean Free Path (λ):

- The average distance between successive collisions is called the ***Mean Free Path***
- Once we have the collision frequency, we can calculate the **Mean Free Path**, (λ), the average distance a molecule travels between collisions.
- If a molecule **collides with a frequency**, z, it spends a **time** (**$1/z$**) **in free flight between collisions**, and
- Therefore, travels a distance $\equiv \left(\frac{1}{z}\right) \times \bar{c}$

$Note: \bar{v} \equiv \bar{c} \equiv mean\ speed$

$$z\ (Collision\ frequency) = \left(\frac{No.\ collision\ made\ by\ ONE\ molecule\ in\ time, \Delta t}{\Delta t}\right) \times (Total\ No.\ molecule\ present\ in\ the\ volume)$$

$$z = \frac{\sigma \times (\bar{c}_{rel} \Delta t)}{\Delta t} \times \left(\frac{N}{V}\right) = \sigma \times (\bar{c}_{rel}) \times N_V \equiv z = \sigma \times (\bar{c}_{rel}) \times \left(\frac{p}{k_B T}\right)$$

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So, what we are looking into we have talked about the collision previously, but what we need to understand that, if we are having a collision then there is another term which is associated with collision that is the mean free path. What is this mean free path defined as? You see the molecules are randomly moving in all the three directions and they are their direction is in all xyz direction possible.

So, this random movement of the particles they are all colliding randomly, that we have already discussed in the last class what is the collision frequency; that means, the rate of collision of a particle per unit time. So, the collision frequency also was discussed as was derived in the last class as something like this ok. So, what we have after collision what happens? When you have 2 molecules collide with each other, the average distance they travel between the successive collision is called another very important term which is a parameter which determines lot of glass properties is a mean free path.

So, the average distance a molecule travels between successive collision is called at the mean free path and usually represented by a lambda. Once we have a collision in a frequency, we can calculate the mean free path the average distance a molecule travels between collision. So, if we know the collision frequency we can relate that. If a molecule collides with the same frequency with a frequency z. That means, that is the rate at which they are colliding that is the frequency number z the collision frequency if the number of collisions molecules is colliding is z, it spends the time in the free flight between collision can be they given as 1 by z. Did you understand what I meant? A molecule collides with the suppose the molecule collides with the frequency z means they are colliding with each other at the frequency means at the rate how many times it is occurring.

So, then if the number of times the collision are occurring is z, then it spends what is the amount of time it spends? That it spends 1 by z time in the free flight between the collision did you understand. So, the time spent in the free flight is 1 by z ok. So, if time spent in the free flight is taken to be 1 by z, then what is going to be the distance traveled? If they are moving with a mean velocity c or v bar then time is 1 by z then the travel distance should be velocity by time.

So, velocity by time it is going to be z m into 1 by z into the average velocity or you can look at this otherwise the collision frequency z is equal to the collision made by one molecule in time t, divided by unit time that is the rate of collision into the total number of molecules present in the volume, which is considered. So, this is what we had derived in the last class, this is the total volume which is associated with the total number of volume in the; sorry total number of collisions will be the number of molecules within that volume per unit time, per unit time into the total number of molecules present in that total volume or container.

So, this is the volume which is going to be swept, this is the cross sectional diameter collision cross section area that is usually given by pi by d square into this is going to be the length of the tube through which it is going to sweep. So, a a molecule with diameter d will sweep a volume corresponding to this, this is the pi d square and this is the distance of the since they have traveling with the relative speed mean relative speed of crl. So, it should be crl into delta t is the total length of the tube.

See now the tube which we had taken is imagine is going to be a straight line, but in reality this shape of the tube is going to change because the collisions are happening continuously and whenever we are doing a calculation, we are imagining the tube is a fixed point with us fixed cross section area of sigma which is equal to pi d square, where d is the diameter of a molecule which is sweeping the volume of a tube ok.

So, we have to imagine that the few tube is fixed, but actually it is going to be always changing and not having a definite orientation because the collisions are happening randomly. So, what we had derived in the last class? We had derived the expression for collision frequency which is given by this sigma is the collision cross section area into the average speed of approach or mean speed of relative mean speed of approach of one molecule with the other, towards the other and this is the number density ok. And the number density we had further simplified into number of moles into Avogadro number divided by volume and this volume, we had replaced by the ideal gas law equation pv equal to nrt.

So, when the volume was replaced by nrt by v ip. So, this is how we got this expression ok. So, this was the last class which we had discussed.

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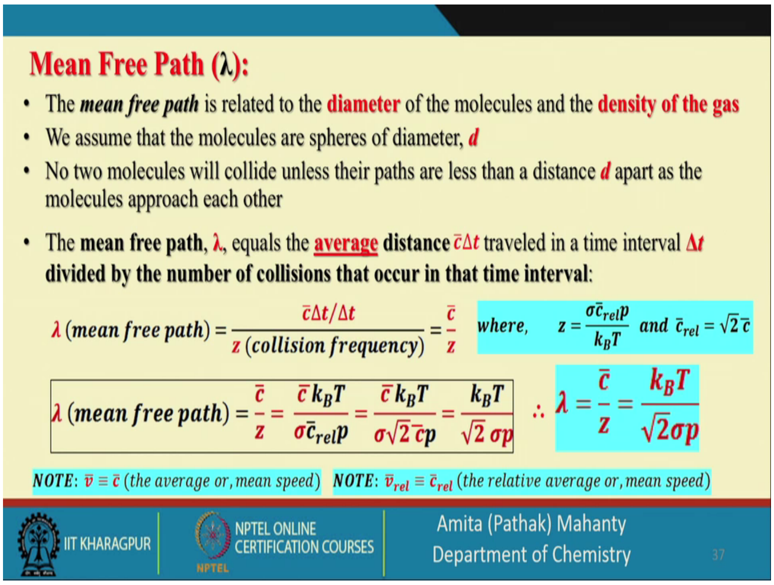

Mean Free Path (λ):

- The ***mean free path*** is related to the **diameter** of the molecules and the **density of the gas**
- We assume that the molecules are spheres of diameter, ***d***
- No two molecules will collide unless their paths are less than a distance ***d*** apart as the molecules approach each other
- The **mean free path**, λ, equals the **average distance** $\bar{c}\Delta t$ traveled in a time interval Δt **divided by the number of collisions that occur in that time interval**:

$$\lambda\,(mean\ free\ path) = \frac{\bar{c}\Delta t/\Delta t}{z\,(collision\ frequency)} = \frac{\bar{c}}{z} \quad where, \quad z = \frac{\sigma\bar{c}_{rel}p}{k_BT} \ \ and\ \ \bar{c}_{rel} = \sqrt{2}\,\bar{c}$$

$$\boxed{\lambda\,(mean\ free\ path) = \frac{\bar{c}}{z} = \frac{\bar{c}\,k_BT}{\sigma\bar{c}_{rel}p} = \frac{\bar{c}\,k_BT}{\sigma\sqrt{2}\,\bar{c}p} = \frac{k_BT}{\sqrt{2}\,\sigma p}} \quad \therefore \lambda = \frac{\bar{c}}{z} = \frac{k_BT}{\sqrt{2}\sigma p}$$

$NOTE: \bar{v} \equiv \bar{c}\ (the\ average\ or,mean\ speed)$ $NOTE: \bar{v}_{rel} \equiv \bar{c}_{rel}\ (the\ relative\ average\ or,mean\ speed)$

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Now, what we are going to see how to derive the expression for mean free path. So, mean free path is related to the diameter of the molecules and the density of the gas ok. Now we have to derived and see how it is going to happen. We assume the molecules are of a spherical shape with diameter d, 2 molecules will collide only collide when their diameters are in particular distance between the centers of the 2 molecules. That means, 2 know 2 molecules will collide unless their path are less than a distance d apart, as the molecules approach each other when that if we are assuming here all the molecules are having the same diameter of d. And the minimum approach distance becomes the diameter the centers from one diameter one molecule to the other becomes the d d distance apart the. So, they should be less than d, only then you have undergoing collisions.

And the mean free path lambda is equal to the average distance average distance mean free path is equal to the average distance travel in the unit time, divided by the total number of collisions that occurred in that time interval ok. Please understand this I am going to read it again, the mean free path lambda is defined as the number average distance average distance is going to be what? Velocity into time is always going to give you the distance.

So, the average distance is going to be the average velocity into time interval travel that is the equal to that and in time delta t. So, the average distance traveled in time interval delta t, divided by the total number of collision occurring in that particular time interval ok. So, this is what we can write? The average distance traveled this is the average velocity into the delta t is going to give you the distance in per unit time, that is by delta t divided by the collision occurring in frequency of that particular collision number of collision occurring in that particular time interval, it which is nothing but the collision frequency ok.

So, if you remember the collision frequency expression, we had something like this sigma the relative mean speed into pressure divided by kt, this the k is the Boltzmann constant t is the absolute temperature ok. So, again if we rewrite from the expression we know, from the previous page if you see we have defined this as the distance traveled in between consecutive collision, which is the mean speed divided by the collision frequency.

So, if we if we do that we redefine this we have defined collision mean free path some way I like this, and that is coming to be from here also you will see its coming to be the mean speed divided by the collision frequency. The mean speed keep it as it is and then I say z is what, I replace the expression for z whatever I had derived in the last class I put it here, here sigma rl into the relative speed of the approach of the molecules into pressure, and in the numerator goes the kBT kBT is the Boltzmann constant.

Now, you see what is the expression we had derived for the? Relative mean speed relative mean speed is defined as under root 2 into the mean speed. So, I replace and the relative mean speed of approach by the mean speed and I get a under root here. So, this is going to cancel off and then what you are left with is a expression in terms of kT by under root 2 sigma pi what is sigma? Is a collision cross section area, that is equal to pi d square where d is the diameter of the molecule or we can say if there are identical molecules, it is a diameter of the molecules or we can say it is the distance between the 2 centers of the molecules. And within this center only if their molecules are going to fall they will undergo collision.

Please always remember and each of the slide I am writing in many various times, I have used v or c. The v and c whenever they are without any subscript are meaning the same when we say that v rel or v say mean that is; that means, I am also meaning that is the c term sometimes it is not actually write that we use different types of terms, but it happens that some books write something, some books write v some book write c.

So, that is why in each of the slide are mentioned, whenever you are seeing a v without any subscript is actually the same term as we. And they are all meaning they are movement of the particles in the three dimension. Unless we have a subscript xyz where they do not mean the velocity along any particular axis whenever we are talking about vc. That means, we are always talking about the velocity, which is supposed to be the result of a radius which we have drawn on a spherical surface with radius v in a three dimension when we were calculating what do you call distribution in speed ok. Please remember this, the v and u v and c are always identical and I have also mentioned them in each of the slides.

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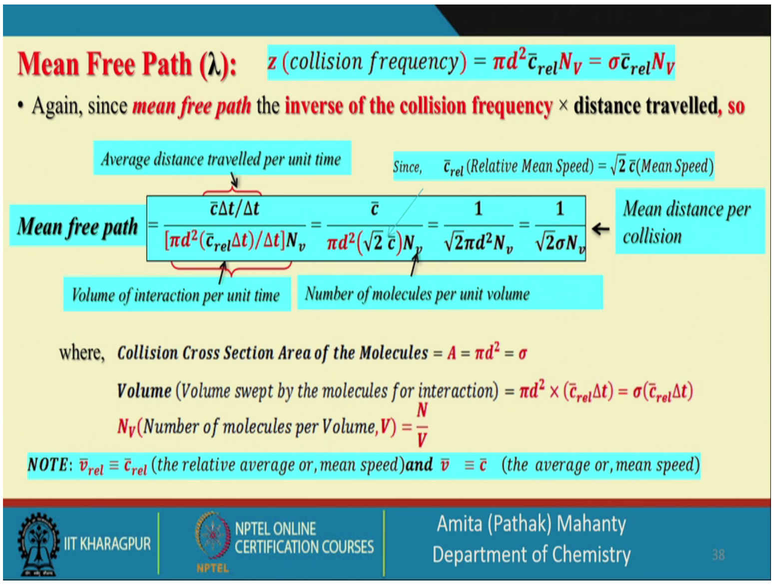

Mean Free Path (λ): $z\,(collision\ frequency) = \pi d^2 \bar{c}_{rel} N_V = \sigma \bar{c}_{rel} N_V$

- Again, since ***mean free path*** the **inverse of the collision frequency** × **distance travelled, so**

Average distance travelled per unit time

Since, $\bar{c}_{rel}$ *(Relative Mean Speed)* $= \sqrt{2}\,\bar{c}$ *(Mean Speed)*

$$\textbf{Mean free path} = \frac{\overbrace{\bar{c}\Delta t/\Delta t}}{\underbrace{[\pi d^2(\bar{c}_{rel}\Delta t)/\Delta t]}N_v} = \frac{\bar{c}}{\pi d^2(\sqrt{2}\,\bar{c})N_v} = \frac{1}{\sqrt{2}\pi d^2 N_v} = \frac{1}{\sqrt{2}\sigma N_v} \leftarrow$$

Mean distance per collision

Volume of interaction per unit time

Number of molecules per unit volume

where, ***Collision Cross Section Area of the Molecules*** $= A = \pi d^2 = \sigma$

Volume *(Volume swept by the molecules for interaction)* $= \pi d^2 \times (\bar{c}_{rel}\Delta t) = \sigma(\bar{c}_{rel}\Delta t)$

N_V *(Number of molecules per Volume,* V*)* $= \frac{N}{V}$

NOTE: $\bar{v}_{rel} \equiv \bar{c}_{rel}$ *(the relative average or, mean speed)* ***and*** $\bar{v} \equiv \bar{c}$ *(the average or, mean speed)*

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Another alternate way of deriving the mean free path, if you have understood one that is sufficient, but you can just look at it mean free path is the inverse of the collision frequency again the same thing, which I am writing. Inverse of the condition frequency means 1 by z into the distance traveled again what is distance traveled? Distance traveled is c them where they are moving with the velocity average speed. So, c is the c bar is the speed or v bar is the speed into delta t is the distance ok.

The mean free path is the average distance travelled per unit time, volume of interaction when the volume swept by the molecules in unit time into the number density. If you are putting that this is the distance travelled per unit time this is the interactions occurring per unit time into the number density, here this is the number density this is the number density. That means, the total number of molecules involved, this is the collision per molecule v multiply that by with the total number of molecules present, that gives us number density. Now we represent replace the crel with the expression for the mean speed. The relative mean speed is going to be equal to under root 2 under root the under root 2the mean speed.

So, if you replace that you again get a expression, another very interesting expression if you keep breaking and reforming the expressions you get, they are the same terms you remember, but you are writing in different from 1 by under root 2 sigma and this is the number density. Number density is number of molecules per the per the unit volume of the container and see this is pi and the sigma is the collision cross section area that is pi d square.

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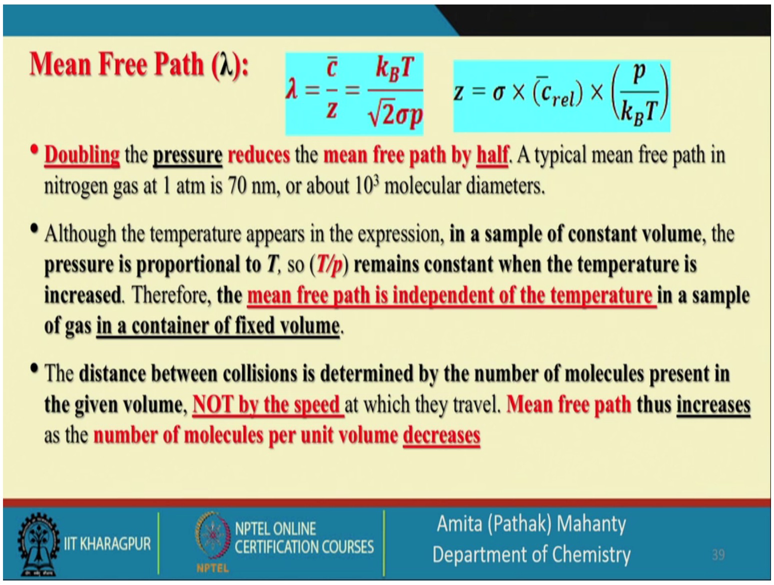

Mean Free Path (λ): $\lambda = \frac{\bar{c}}{z} = \frac{k_BT}{\sqrt{2}\sigma p}$ $z = \sigma \times (\bar{c}_{rel}) \times \left(\frac{p}{k_BT}\right)$

- **Doubling** the **pressure** **reduces** the **mean free path by half**. A typical mean free path in nitrogen gas at 1 atm is 70 nm, or about 10^3 molecular diameters.
- Although the temperature appears in the expression, **in a sample of constant volume**, the **pressure is proportional to** ***T***, so (***T/p***) **remains constant when the temperature is increased**. Therefore, **the mean free path is independent of the temperature in a sample of gas in a container of fixed volume**.
- The **distance between collisions is determined by the number of molecules present in the given volume**, **NOT by the speed** at which they travel. **Mean free path thus increases** as the **number of molecules per unit volume decreases**

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So, the mean free path if you see the expression here, what is the expression for Z, what is the expression for C and what is the C means the mean speed not relative that its the mean speed of approach or mean a speed with where they are traveling, it is not the rel speed here not relative mean speed, but it is this mean speed, which we are talking about. So, if we are talking about the expression for lambda, just have a look please keep remembering only this expression. So, that you can substitute for each of the term and understand, what happens in this you have having pressure in the denominator.

So, if you are doubling the pressure what will happen? The mean free path should be reduced by half they are inversely proportional. So, if you are double the pressure then the mean free path should be um becoming half. If you are looking into the typical mean free path of nitrogen molecule at one atmosphere, it is going to be around 70 nanometers around say 10 to the power 3 molecular diameters. All the temperature appears in the expression if you see in a sample of constant volume, suppose the total container is may fixed the pressure is going to be directly proportional to t do you have the ideal gas laws, when temperature in the volume is constant then the pressure is directly proportional to T ok.

So, if the pressure is if the volume is constant ok. So, if the volume is constant, though the temperature is appearing in the numerator. So, if the increase in pressure should increase the mean free path, but since for a constant volume if you have a constant volume, pressure increase is going to be proportional to the temperature increase; that means, T by P will remain a constant, when the temperature is increased the p will also increase.

So, if this is the condition then you see this will have no effect on the lambda. Both are if we are both are going to if you are having p proportional to T; that means, change of p by T will not be affecting they will be remaining a constant. So, the mean free path is independent of the temperature for a fixed volume of a container, because in spite of the fact that temperature is appearing directly in the numerator. The distance between the collision is determined by the number of molecules present ok.

So, if there are number of molecules are more, they are going to be colliding with each other more frequently and the distance they need to travel is going to be less ok. So, the number of molecules in the distance between collisions is determined by the number of molecules present in the given volume, and not necessarily by the speed; so in spite of the fact that speed is there in the expression. So, it is not that the speed is going to be the determining factor, it is the number of molecules which is present in the system is going to determine whether the lambda, the mean free path is going to increase or decrease.

So, in mean free path does increases with the number of molecules per unit volume with increases as the number of molecules per unit volume decreases that the number of molecules are less, they have to travel a longer distance to encounter each other obviously; that means, you have to have a lambda which is going to be will get bigger and bigger ok. So, it is not dependent on the speed, but on the number of molecules and it is independent of the temperature for a constant volume system, and for a if you pressure if the pressure is doubled, then the mean free path is going to be halfed ok.

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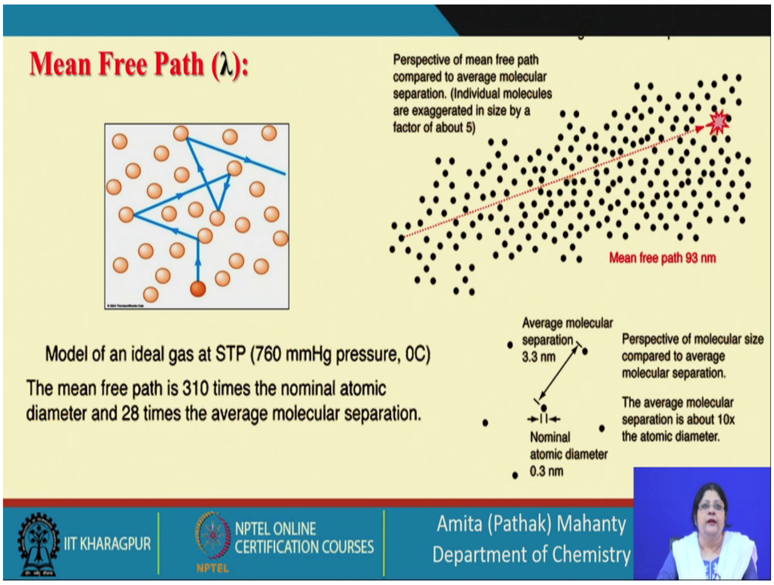

Mean Free Path (λ):

Model of an ideal gas at STP (760 mmHg pressure, 0C)

The mean free path is 310 times the nominal atomic diameter and 28 times the average molecular separation.

Now,. So, if you take a look at the nature of dimensions of what we are talking into. If you see the perspectives of molecular mean free path compared to the average molecules of you have the average distance between 2 molecules and the diameter of a single molecule. If you are comparing in that is order, then you see these are actually not to scale, but you can see the mean free path is this is a collision this is another collision ok. But if you are looking at this the mean free path is almost around 10 times a 310 times the atomic diameter and 28 times the average molecular separation. That means, if you are seeing the ratio in which we are looking into you have the molecular size compare compared to the average molecular separation what is the molecular size? The atomic diameter is around this and the molecular separation is point 3.3.

So, the average molecular separation is 10 10 to the 10 times that of the atomic diameter ok. The separation of 2 molecules is around 10 10 10 times that of the diameter of a single molecule. But when we are comparing that with that of the mean free path, that said collision distance travel between the collision is far more compared to that of the diameter of the molecule or the distance between the 2 molecule ok.

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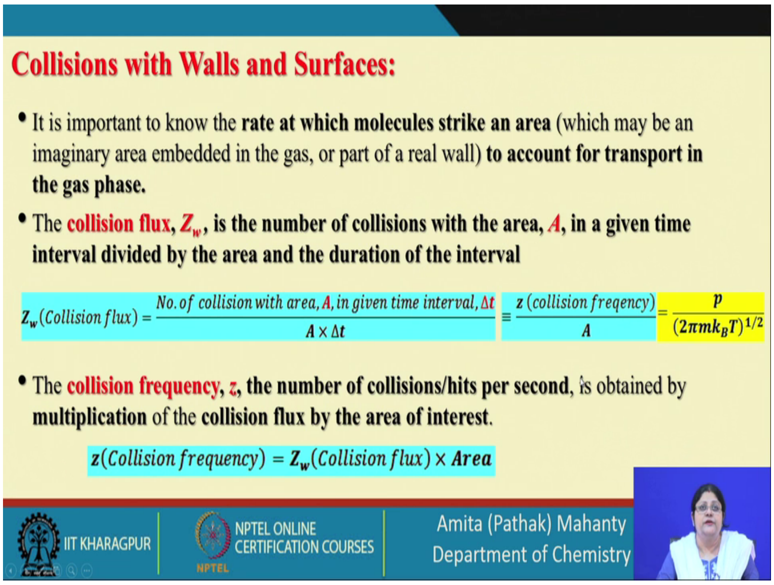

Collisions with Walls and Surfaces:

- It is important to know the **rate at which molecules strike an area** (which may be an imaginary area embedded in the gas, or part of a real wall) **to account for transport in the gas phase.**
- The **collision flux, Z_w, is the number of collisions with the area, A, in a given time interval divided by the area and the duration of the interval**

$$Z_w(Collision\,flux) = \frac{No.\,of\;collision\,with\,area, A, in\,given\,time\,interval, \Delta t}{A \times \Delta t} \equiv \frac{z\,(collision\,freqency)}{A} = \frac{p}{(2\pi m k_B T)^{1/2}}$$

- The **collision frequency, z, the number of collisions/hits per second,** is obtained by **multiplication** of the **collision flux by the area of interest**.

$$z(Collision\,frequency) = Z_w(Collision\,flux) \times Area$$

So, now the next thing should be when we are talking about collision, we have talked about mean free path the next important is, which is important in understanding the transport properties associated with the gas phase is to find out the rate at which this strike an area ok, a imaginary area which can be in a gas phase or a real wall. So, for this which we are going to be looking into, we are looking into a flux what is the flux? Flux is the number of collisions with a particular area A at a given time per the unit area, which we are looking into ok. So, the collision flux is the number of collision number of collisions with the area of interest A per unit time divided by the area into the in duration of the interval ok.

So, in other words, we can write it is the collision frequency this you can see that the number of collision occurring on area A and unit time. So, this is the collision frequency divided by the area of interest ok. And this can be a derived I am not looking into here the expression is given, but we are going to derive that ok. So, the collision frequency if we want to find out it is nothing but the collision flux multiplied by the area right.

So, the numbers of collisions are heat per second is obtained by multiplying the flux by the area of interest ok.

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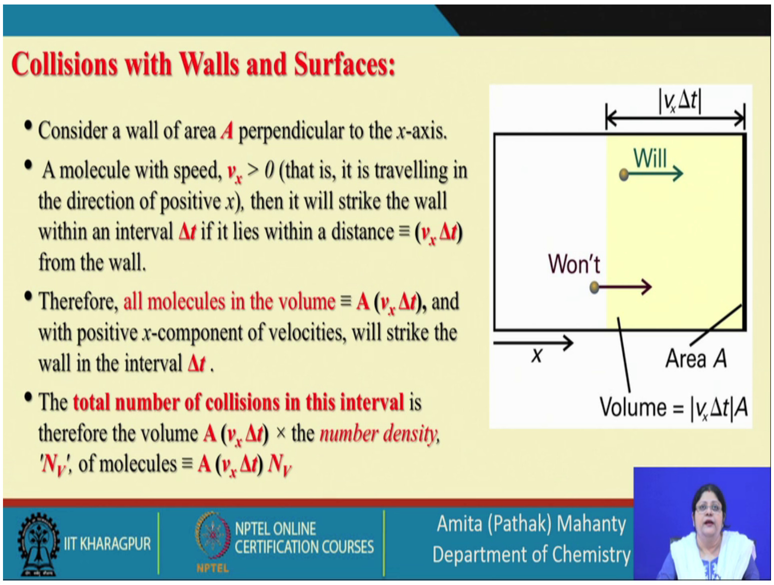

Collisions with Walls and Surfaces:

- Consider a wall of area *A* perpendicular to the *x*-axis.
- A molecule with speed, $v_x > 0$ (that is, it is travelling in the direction of positive *x*), then it will strike the wall within an interval Δt if it lies within a distance ≡ $(v_x \Delta t)$ from the wall.
- Therefore, all molecules in the volume ≡ $A\,(v_x \Delta t)$, and with positive *x*-component of velocities, will strike the wall in the interval Δt .
- The **total number of collisions in this interval** is therefore the volume $A\,(v_x \Delta t)$ × the *number density*, 'N_V', of molecules ≡ $A\,(v_x \Delta t)\,N_V$

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Now, let us look into this. This is a something which we had talked about in previous classes, now you see we are not looking into three dimension. We are looking of the molecules moving in a one particular direction in which direction we have the wall and the area of interest in that wall.

Now, let us consider a wall of area A perpendicular to x suppose this is the direction x and perpendicular to that, we have the wall. A molecule with speed traveling along the direction x is supposed to be vx is greater than 0; that means, it is traveling in the positive direction towards the wall. It will strike the wall within an interval of delta t if it lies within the distance dv v delta t ok.

So, if they are moving with this velocity in this direction, then what this is I am done before also then in interval delta t which are the molecules which it is going to strike the wall? Only the molecules which is going to have v at a distance v delta t v delta t is the distance and what is the area? Area is this. So, the total volume which is going to be in this a zone is going to comment all the molecules within this volume will have the chance of colliding with A the wall A ok.

So, the total number is going to be volume total volume is going to be the distance into the area, distance is the velocity when through which they are traveling v into the time interval t the velocity into time interval gives you the length. So, therefore, all molecules in this area in the volume this, in the volume this with positive x component of velocity will strike the wall at interval delta t, in time delta t the total number of collision in this interval is therefore, the volume into the number density.

So, total number of collisions will be always the total number of molecules present a moving towards that at that direction, into the number density because we are always talking about one collision into the number density. The total number of collisions in that interval will be the all the molecules within this area a within this volume into the number density, and what is the number density we are represent the number density by Nv which is nothing but number of moles per unit volume of the container.

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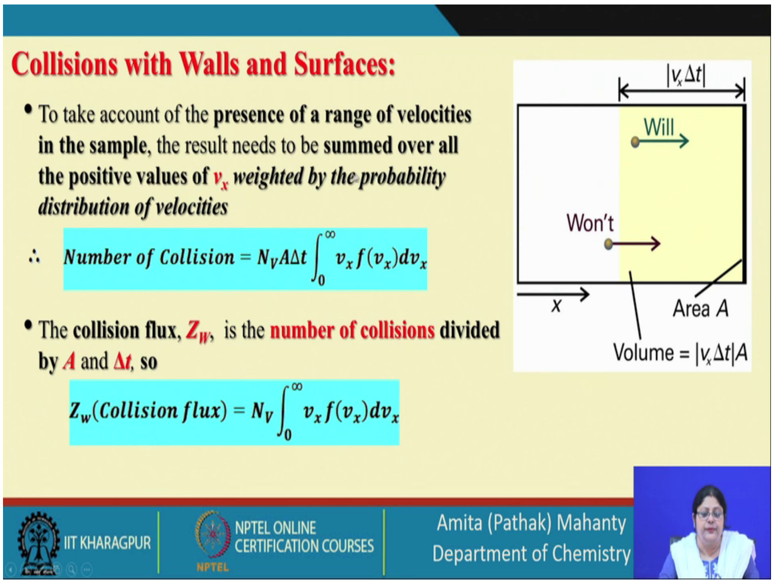

Collisions with Walls and Surfaces:

- To take account of the **presence of a range of velocities in the sample**, the result needs to be **summed over all the positive values of v_x *weighted by the probability distribution of velocities***

$$\therefore \quad Number\ of\ Collision = N_V A\Delta t \int_0^\infty v_x f(v_x) dv_x$$

- The **collision flux**, Z_W, is the **number of collisions divided by** A and Δt, **so**

$$Z_w(Collision\ flux) = N_V \int_0^\infty v_x f(v_x) dv_x$$

So, to take account of the presence of the various velocities, because velocities can the sample which you can result some will have higher velocity some because of you know that velocities are having a distribution. So, we have to take in all the ranges of velocity into account what we need to do? To take account of all the possible velocities, what in the sample we need to sum over all the positive values of the velocity, weighted by the probability distribution. That means, to find out the total number of collision what we need to do; see total number of collision we are finding out is the total number of molecules present which is going to strike in this world, into the total number density ok. That means, distance whatever molecules are present here into the number density, gives you the total number of collisions which might like its likely to occur.

So, the total number of collision is number density into area, just have a look what we are looking into total number of collision is this ok. Now we are going to look into that, we are going to sum it over all the positive values of x and into weighted by the probability distribution. When we are looking in the moving in only in the positive direction and in the x direction, we integrate the x was this side a v was this side v delta t was the term, which was a outside we have taken the v inside.

So, velocity into the distribution function gives you the weighted fraction. So, you well let us find out what is this going to be. And what is if this is the collision if a number of collision or collision frequency, then what should be the collision flux? Collision flux is going to be number of collision divided by A and delta t ok.

So, let us see what is going to be the collision flux, this is the number of collision then divided by A delta t. So, this is the of collision flux which we are getting ok.

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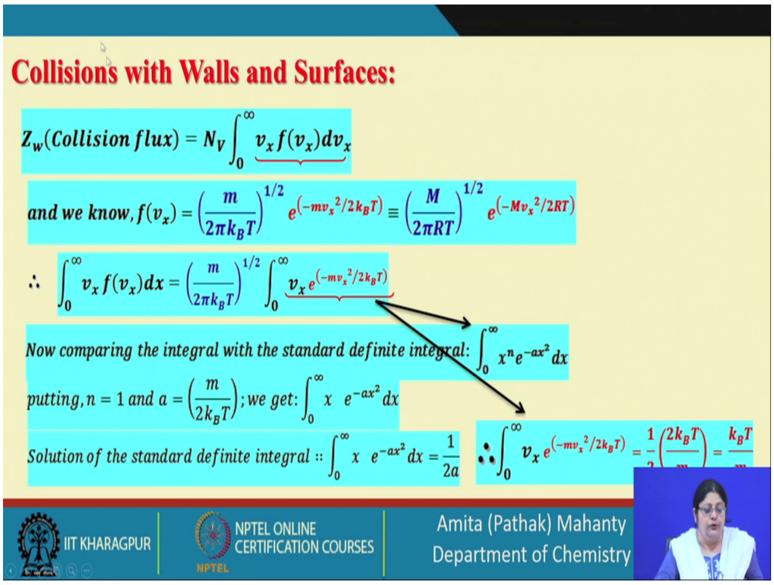

Collisions with Walls and Surfaces:

$$Z_w(Collision\ flux) = N_V \int_0^{\infty} \underbrace{v_x f(v_x) dv_x}$$

$$\text{and we know, } f(v_x) = \left(\frac{m}{2\pi k_B T}\right)^{1/2} e^{(-mv_x^2/2k_BT)} \equiv \left(\frac{M}{2\pi RT}\right)^{1/2} e^{(-Mv_x^2/2RT)}$$

$$\therefore \int_0^{\infty} v_x f(v_x) dx = \left(\frac{m}{2\pi k_B T}\right)^{1/2} \int_0^{\infty} \underbrace{v_x e^{(-mv_x^2/2k_BT)}}$$

$$\text{Now comparing the integral with the standard definite integral: } \int_0^{\infty} x^n e^{-ax^2} dx$$

$$\text{putting, } n = 1 \text{ and } a = \left(\frac{m}{2k_B T}\right); \text{we get: } \int_0^{\infty} x\ e^{-ax^2} dx$$

$$\text{Solution of the standard definite integral :: } \int_0^{\infty} x\ e^{-ax^2} dx = \frac{1}{2a}$$

$$\therefore \int_0^{\infty} v_x e^{(-mv_x^2/2k_BT)} = \frac{1}{2}\left(\frac{2k_BT}{m}\right) = \frac{k_BT}{m}$$

Now, look into this, what we have looked into? We have taken we have we have simplified this we are not looking into this part; we are just looking into this part ok. When we are looking into this part we put this value of the one dimension velocity distribution if you remember, the four pi term is not four pi term which is supposed to v square term is not there. So, this is the term which is coming from the normalization, and this is the exponential term ok.

So, if you look into this it is v into the exponential term. So, what we are getting? We are getting this function something similar to what we are having is a standard integral; see this is what we are getting and this is the standard integral when we compare these 2 what should be n? N should be 1 right and what should be a? A should be this term that is m by 2 kT k is the Boltzmann constant. So, if I compare that this expression if I have n equal to 1 then the solution of that differential integral is 1 by 2 a.

So, if I put the 1 by 2 a what do I get? I put the values in one the expression of 0 to infinity here in terms of this, and this term I am replacing by 1 by 2 a. So, one this is my one 1 by 2 and this is my a this is my a clear. So, I get kT by m.

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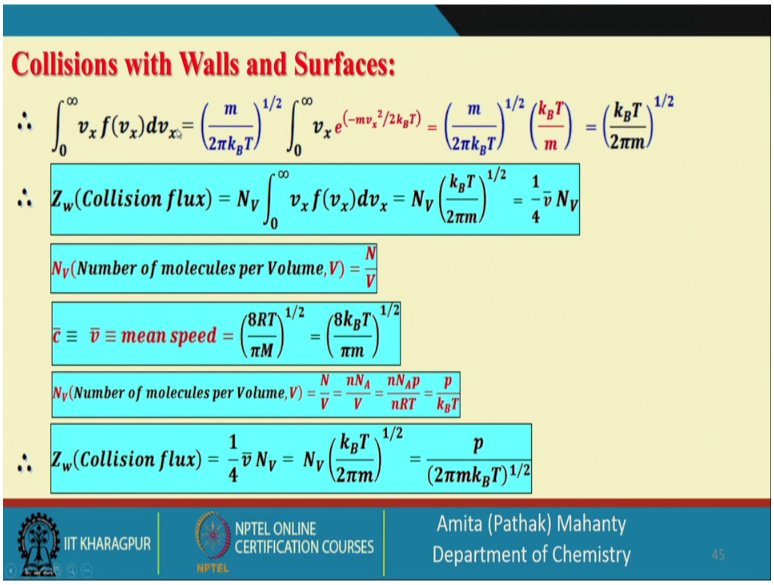

Collisions with Walls and Surfaces:

$$\therefore \int_0^\infty v_x f(v_x) dv_x = \left(\frac{m}{2\pi k_B T}\right)^{1/2} \int_0^\infty v_x e^{(-m v_x^2/2k_B T)} = \left(\frac{m}{2\pi k_B T}\right)^{1/2} \left(\frac{k_B T}{m}\right) = \left(\frac{k_B T}{2\pi m}\right)^{1/2}$$

$$\therefore Z_w(\text{Collision flux}) = N_V \int_0^\infty v_x f(v_x) dv_x = N_V \left(\frac{k_B T}{2\pi m}\right)^{1/2} = \frac{1}{4} \bar{v} N_V$$

$$N_V(\text{Number of molecules per Volume}, V) = \frac{N}{V}$$

$$\bar{c} \equiv \bar{v} \equiv \text{mean speed} = \left(\frac{8RT}{\pi M}\right)^{1/2} = \left(\frac{8k_B T}{\pi m}\right)^{1/2}$$

$$N_V(\text{Number of molecules per Volume}, V) = \frac{N}{V} = \frac{nN_A}{V} = \frac{nN_A p}{nRT} = \frac{p}{k_B T}$$

$$\therefore Z_w(\text{Collision flux}) = \frac{1}{4} \bar{v} N_V = N_V \left(\frac{k_B T}{2\pi m}\right)^{1/2} = \frac{p}{(2\pi m k_B T)^{1/2}}$$

So, if I get the whole expression, I can rewrite the number density or the collision flux as this, which we have evaluated to be this I have multiplied for this one we have multiplied by this, because this was the term which was previously there the normalization term the constant term. So, this was added multiplied by this. So, what you get it? You get here is this value you simplify this you get something like this.

Now, you can put in various forms of that. So, collision flux can be derived as this, now you substitute for the value of c velocity the mean speed and you can get some simplified to in terms of this or the number of molecules per unit volume, the number density if you are applying this you can use this. If you apply all these you get this very simplified. It is not very difficult if you understood this part others are only simplification.

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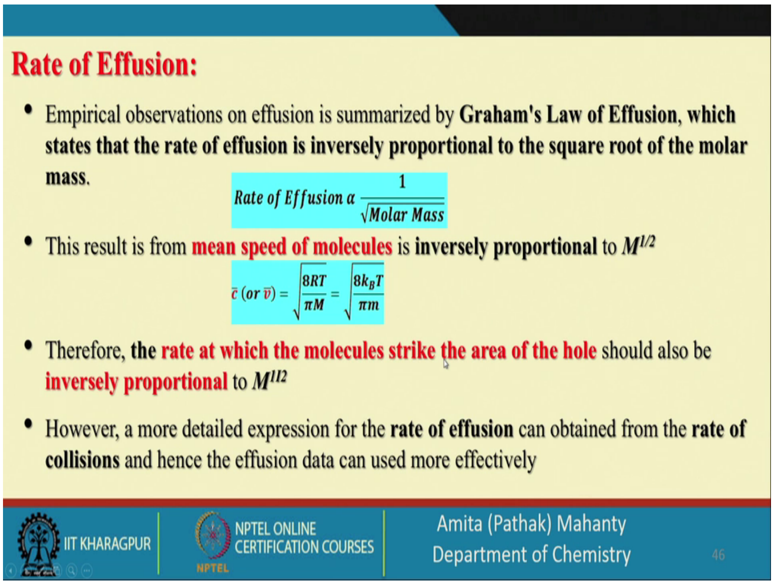

Rate of Effusion:

- Empirical observations on effusion is summarized by **Graham's Law of Effusion, which states that the rate of effusion is inversely proportional to the square root of the molar mass.**

$$Rate\ of\ Effusion\ \alpha\ \frac{1}{\sqrt{Molar\ Mass}}$$

- This result is from **mean speed of molecules** is **inversely proportional** to $M^{1/2}$

$$\bar{c}\ (or\ \bar{v}) = \sqrt{\frac{8RT}{\pi M}} = \sqrt{\frac{8k_BT}{\pi m}}$$

- Therefore, **the rate at which the molecules strike the area of the hole** should also be **inversely proportional** to $M^{1/2}$
- However, a more detailed expression for the **rate of effusion** can obtained from the **rate of collisions** and hence the effusion data can used more effectively

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Only other thing is the rate of effusion we need to understand and this is probably is going to give you the last section of the discussion. The empirical observation of on effusion is summarized by Graham's Law of Effusion, which states the rate of effusion is inversely proportional to the square root of the molar mass. What is effusion? Effusion is when you have a gas particle moving through a hole, the rate at which it is going to pass through the hole.

So, it is going to depend on the number of times it is going to strike that hole. So, the actually it is going to be related to the collision to on the wall ok. And this wall is does not have a area it has a area, but it does not strike and come back it passes through. So, the rate of effusion is inversely proportional to the molar mass was what was given by the Graham's Law of Effusion. Result this results from what we have already got the kinetic model. Now we know that it results from the term all results from the mean speed of the molecules being inversely proportional to the mass ok. The speed at which they are going to be moving is going to be related to the rate of effusion and that speed is actually related to the expressions if you remember is inversely related to the molar mass.

So, since c is inversely proportional to the molar mass, the rate at which they are going to be escaping is also going to be related to the molar mass. Therefore, rate at which the molecule strikes the area of a hole should be inversely proportional to the molar mass.

More detailed expression of rate of if you can be obtained from the rate of collision and hence the effusion that can be effectively used ok.

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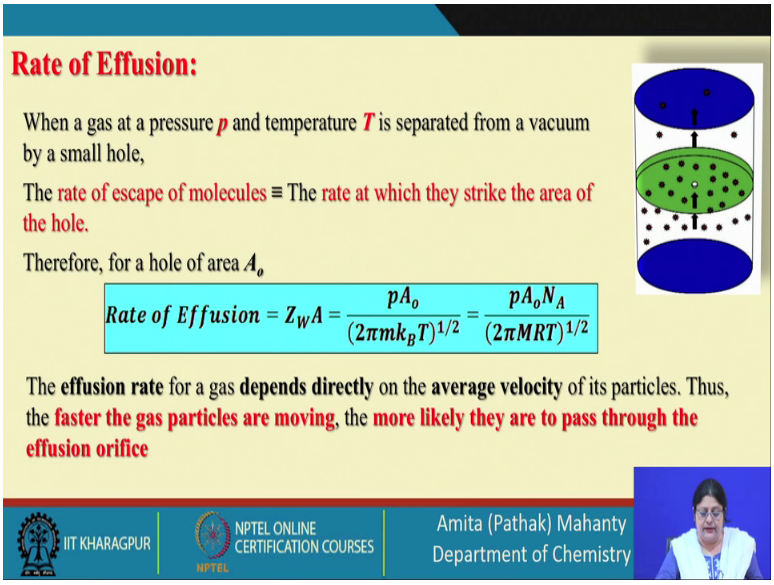

Rate of Effusion:

When a gas at a pressure p and temperature T is separated from a vacuum by a small hole,

The rate of escape of molecules ≡ The rate at which they strike the area of the hole.

Therefore, for a hole of area A_o

$$\boxed{Rate\ of\ Effusion = Z_W A = \frac{pA_o}{(2\pi m k_B T)^{1/2}} = \frac{pA_o N_A}{(2\pi MRT)^{1/2}}}$$

The **effusion rate** for a gas **depends directly** on the **average velocity** of its particles. Thus, the **faster the gas particles are moving**, the **more likely they are to pass through the effusion orifice**

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So, when the gas of say pressure p and temperature is a separated in a vacuum by a small hole. Something like what I have shown here there is one hole through which the gas can pass, rate of escape of molecules is equal to the rate at which the molecules are striking that area. So, once we know the collision flux; that means, the number of heats the particle is making on the particular area, divided by area per unit time, then we get the can we calculate the rate of effusion.

So, the rate of effusion through a whole of area A naught is going to be nothing but the flux the collision flux into the area. That means, this is the actually the rate of collision whatever is colliding rate of collision is actually equal to the rate of effusion, and which is nothing but the collision flux into the area. And collision flux we have derived is this and this is the area of interest. So, if you rewrite it you can replace the small m with the big m kT can be replaced by M and then you get a Avogadro number in the top.

So, you please remember the relations between M k and R; k means and then Boltzmann constant. The infusion rate for a gas depends directly on the average velocity or speed of the particle. Thus, faster the particle is going to move more likely they are going to escape or pass through the whole ok.

Thank you so much.