Molecules in Motion
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Lecture - 09
Kinetic theory of gases (Contd.)

Welcome to the lecture 9 of Kinetic Theory of Gases. In the last class if you remember we had talked about the various we had done the derivations for the various types of speed like the average speed, the RMS speed, the most probable speed. We are going to look up into another form of the speed, when we talk about two molecules approaching each other. We will do the derivation today. And before that what we are going to discuss is what is the parameters, what we look into when the two molecules approach each other ok.

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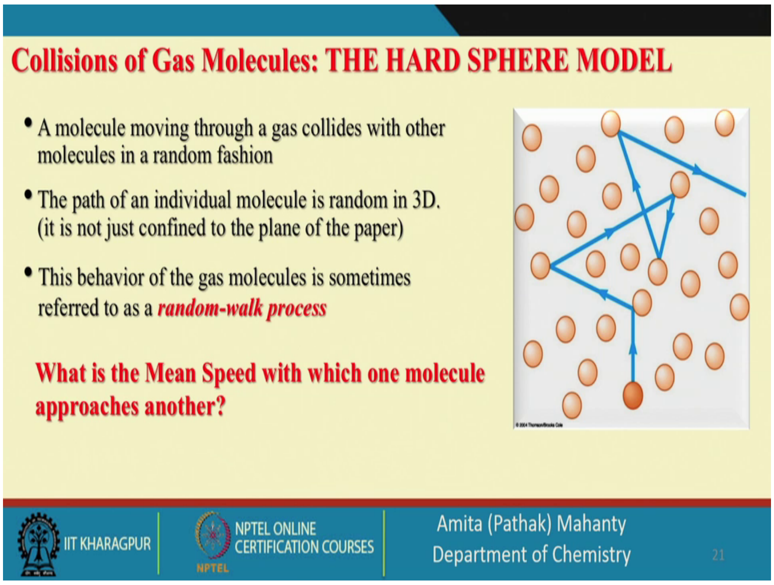

Collisions of Gas Molecules: THE HARD SPHERE MODEL

- A molecule moving through a gas collides with other molecules in a random fashion
- The path of an individual molecule is random in 3D. (it is not just confined to the plane of the paper)
- This behavior of the gas molecules is sometimes referred to as a ***random-walk process***

What is the Mean Speed with which one molecule approaches another?

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So, when we talk about 2 molecules approaching each other, we visualize the gas model, it is random movement of a large number of particles small molecules are moving randomly and they are colliding with each other in a random fashion. And the path of an individual molecule is random not only in 1 D, but actually should be visualized in 3D like not only on the paper, which we have which is depicted in this diagram this is actually extended to 3 D means the 3 dimension xyz coordinates like if you are having a molecule in a cubic container.

Similar to something like that and motion of the molecules are so random, and the movement they are undergoing is. So, random and based on whatever assumptions we had for the kinetic theory model can is extend into this gas model. So, in the whole process what we are looking into is the behavior of gas molecules in a random manner, and this sort of behavior atoms are called random walk process.

So, when they are all molecules are moving randomly, what we like to know is how is going to meet the behavior of the particles, when they come into contact with each other or when they interact in other words we say when they collide. So, that is what which we are looking into today is the collisions of the gas molecules. Now when 2 gas molecules are approaching each other, then what we should be looking into; what is the mean speed with which they are approaching each other. Whether the mean speed which we had calculated previously is the same or something different is what we are going to look into.

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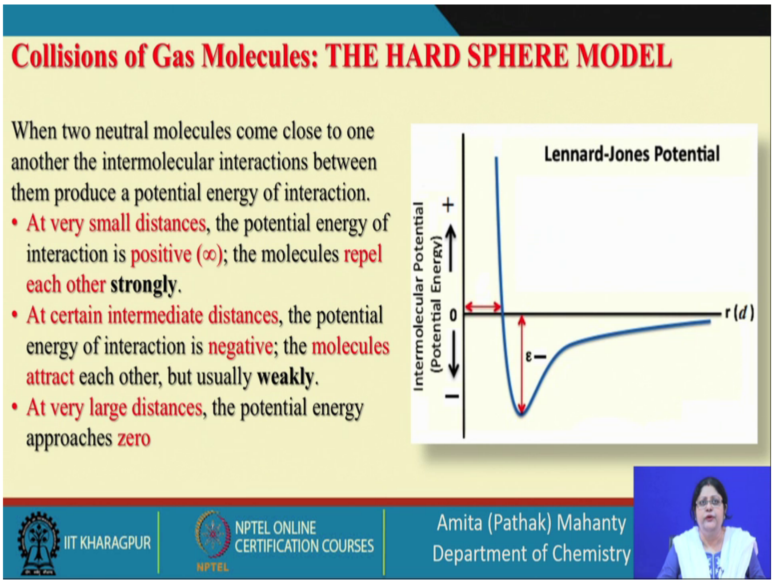

Collisions of Gas Molecules: THE HARD SPHERE MODEL

When two neutral molecules come close to one another the intermolecular interactions between them produce a potential energy of interaction.

- At very small distances, the potential energy of interaction is positive (∞); the molecules repel each other **strongly**.
- At certain intermediate distances, the potential energy of interaction is negative; the molecules attract each other, but usually **weakly**.
- At very large distances, the potential energy approaches zero

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But before that let us look into the Lennard Jones potential of any 2 molecules when they are neutral molecules, when they are interacting what happens. You have seen this potential energy curve in your books. So, what is this potential energy curve arising from? When you have 2 neutral molecules they come together or to approach each other, what happens the nucleus is a positively charged and the electrons are surrounding it.

So, there is a repulsion between the 2 electron cloud when they come closer or if they have sufficiently apart, then they have a attract attraction from the electron to the nucleus of the other. So, these sorts of interactions between the nucleus and the electron of one with the nucleus and electron of the other molecule is what we are going to look into, when we are looking into a Lennard Jones potential.

What it does it and essentially say that when 2 molecules come close to one another, the intermolecular interactions between them produce a potential energy interaction. This is the potential energy and which is going to be arising out of the interactions of the electron and the nucleus of one molecule with that of the other. When the 2 molecules are very close to each other, this is what the distance is. When they are very close to each other what you see the potential energy is very high.

So, they in this potential energy curve that this is a positive side. So, this is a very high positive interaction which we are looking into, and these positive interaction in the molecules are associated with repulsive forces. And since it is a very strong value of the potential energy we say this is a strong repulsive force existing between the 2 molecules. Suppose they are the 2 molecules are in a intermediate distance from each other, what when you see the potential energy of interaction is negative this is the intermediate distance and this is the potential energy is negative where the value is small.

So, we say and the negative is associated with attraction of the molecules of the molecules, 2 molecules have attraction towards each other, but these are weak attractions. But what happens when the distance of is very large somewhere like this, then the potential energy is supposed to be approaching 0. So, this is what we are going to look into when we are talking about a gas molecule colliding, and what is the basis on which we are going to derive their collision frequency and other stuff other parameters.

So, the model which we are looking into is known as the hard sphere model.

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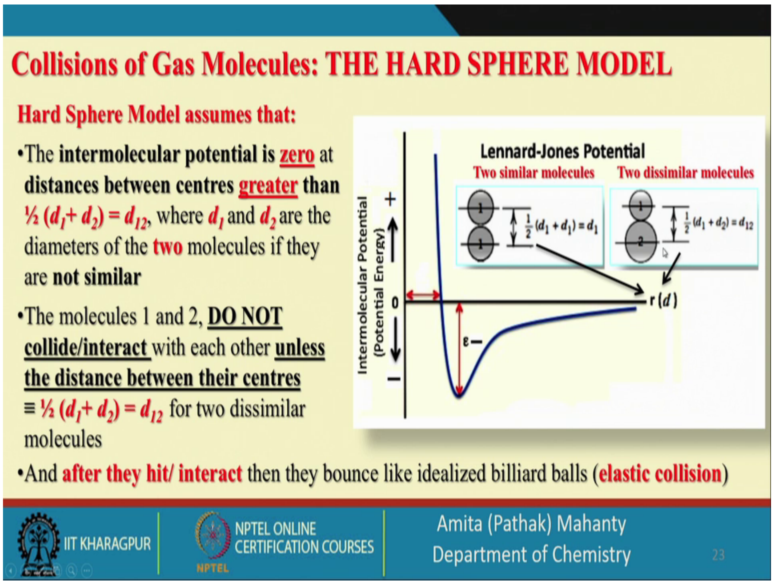

Collisions of Gas Molecules: THE HARD SPHERE MODEL

Hard Sphere Model assumes that:

- The **intermolecular potential is** **zero** at **distances between centres** **greater** **than** $\frac{1}{2}(d_1 + d_2) = d_{12}$, where d_1 and d_2 are the diameters of the **two** molecules if they are **not similar**
- The molecules 1 and 2, **DO NOT collide/interact** with each other **unless the distance between their centres** $\equiv \frac{1}{2}(d_1 + d_2) = d_{12}$ for two dissimilar molecules
- And **after they hit/ interact** then they bounce like idealized billiard balls (**elastic collision**)

And this hard fear sphere model assumes certain things what we have, when we have 2 molecules see these are 2 molecules we are looking into, and 2 molecules are of the same dimension or they are similar molecules, they can be dissimilar molecules and each of them have a certain diameter this has a diameter d 1 this has a diameter d 1 here the diameter is d 2 this is the diameter d 1.

So, what happens when you are talking about hard sphere model, the inter the intermolecular potential is supposed to be 0 at distance when the centers is between these 2 like this is one center this is another center, when the centers of the 2 molecules differ by d 1 for a similar molecule or by half d 1 by d 2, for 2 d 2 molecules which are dissimilar these are the 2 diagrams you should understand, this is becoming d 1, because both the diameters are equal.

So, d 1 plus d 1 equals to 2 d 1 and divided by 2 we are taking the half of the distance. So, it is the distance between the 2 nucleus or new centers of the molecules is d. Similarly if this is the one this is the diameter for this is the diameter for this, half of this diameter half of this diameter if I add them and then the distance is actually half of the d 1, and the diameter of half of the diameter of second molecule.

So, the intermolecular potential is 0 at distance is what? When the distance is greater than that of the value half d 1 plus d 2 did you understand? So, we are looking into a model something like this. So, this is the potential energy approaching 0, this will happen only when the centers of the 2 molecules. If the similar molecules is at a distance greater than d 1 and if their distance are at that they are dissimilar molecules, then their distances are half the diameters of the one of the diameters plus a another diameter added to together and half of that.

So, this is for a 2, 2 dissimilar molecules and this is for the similar molecules the molecules1 and 2 do not collide when will this molecules collide and when will they not. These 2 molecules do not collide or interact 1 and 2 or 2 2 we can we can consider to one the type of molecule similar kind of molecules, unless the distance between the centers is equal to this. So, what we have at greater than this distance? The separation distance between the 2 nuclei is greater than the values for half of d 1 by d 2 or d 1 for similar molecules and it is equal and it will collide and do not collide, if they are the distances are unless the distances are in the approach nearest approach distance of the diameters separation of between the 2 similar molecules or half the diameters of the separation of the 2 nucleis of the 2 dissimilar molecules.

So, we are clear now. So, what we have assumed the potential energy to be 0 at a condition, where the distances between the 2 nuclei of the molecules are greater than the value of the half of the diameters of the 2 molecules or it will be and it will collide only if their value is equal to the diameter of the half of the diameters of the 2 molecules. So, after they collide what happens? As they are going to follow the kinetic model, the after they collide or interact they bounce back and they behave like a billiard ball and this is like what you call as a elastic collision.

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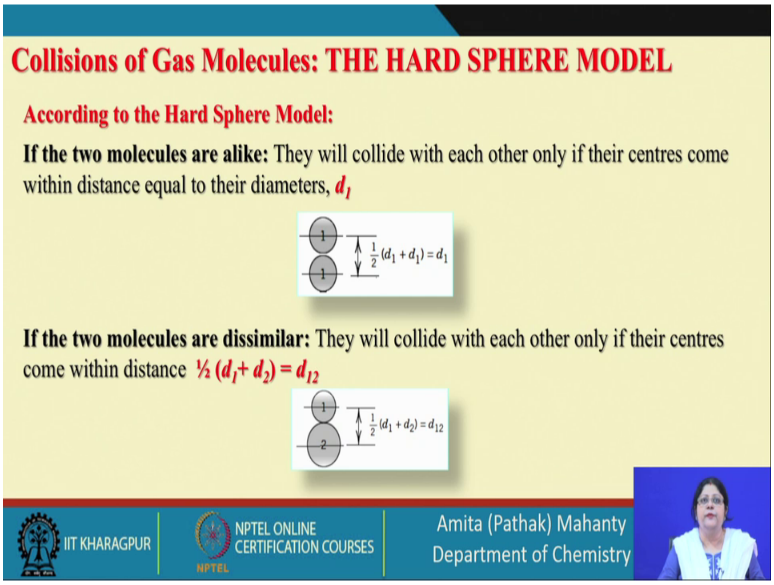

Collisions of Gas Molecules: THE HARD SPHERE MODEL

According to the Hard Sphere Model:

If the two molecules are alike: They will collide with each other only if their centres come within distance equal to their diameters, d_1

If the two molecules are dissimilar: They will collide with each other only if their centres come within distance ½ $(d_1+d_2)=d_{12}$

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So, now, we summarize what we have just now said, if 2 molecules are alike they are similar means diameters are similar, they will collide with each other only if their centers come within a distance equal to d 1. D 1 is the diameter of 1 plus the diameter of 2 divided by 2. So, that you inter nucleus inters difference between the distances from one center to the other centre of the molecule is the diameter d 1 the diameter of 1 molecule.

But if these molecules are same dissimilar they will collide with each other only if their centers come within the distance of half of d 1 by d 2 d d 1 plus d 2 this is this distance ok.

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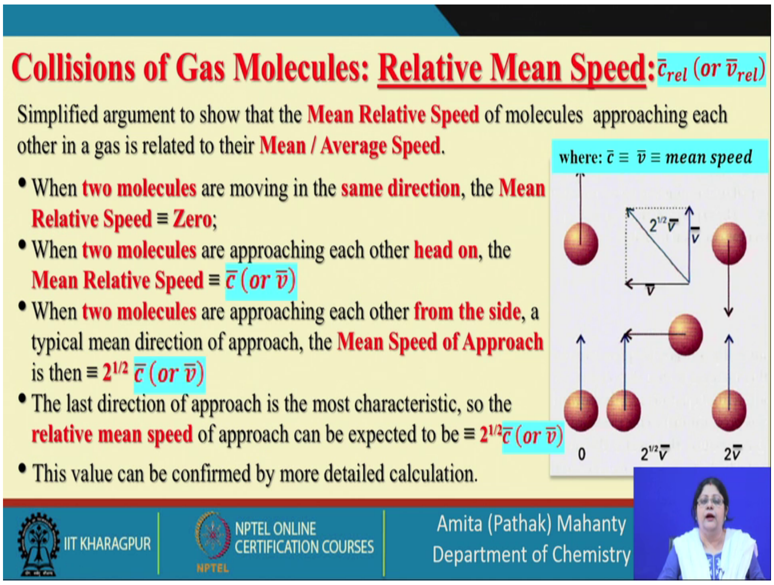

Collisions of Gas Molecules: Relative Mean Speed: $\bar{c}_{rel}$ (or $\bar{v}_{rel}$)

Simplified argument to show that the **Mean Relative Speed** of molecules approaching each other in a gas is related to their **Mean / Average Speed**.

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

- When **two molecules** are moving in the **same direction**, the **Mean Relative Speed ≡ Zero**;
- When **two molecules** are approaching each other **head on**, the **Mean Relative Speed** ≡ $\bar{c}$ (or $\bar{v}$)
- When **two molecules** are approaching each other **from the side**, a typical mean direction of approach, the **Mean Speed of Approach** is then ≡ $2^{1/2}\,\bar{c}$ (or $\bar{v}$)
- The last direction of approach is the most characteristic, so the **relative mean speed** of approach can be expected to be ≡ $2^{1/2}\bar{c}$ (or $\bar{v}$)
- This value can be confirmed by more detailed calculation.

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So, now when we talk about how they are what is the distance, where they should come in contact. So, only then we can consider they have to they will undergo a collision. Before that we should also see what is the speed through which they are approaching each other. This is not a as simple as it is depicted or I am going to as the way I am going to discuss right now.

But let us assume what we are a simplistic approach or argument to understand the velocity of approach of the molecules. We call this as a mean relative speed of approach of molecules, when one is approaching the other and this we will see is related to the average or the mean speed, which we have calculated before. So, if you have 2 molecules like you have here if you have 2 molecules and they are moving in this see here this is the its not visible, they are moving in the same direction; that means, they are going to be keep moving and they will not collide.

So, their mean the relatives velocity can be taken to be 0. So, this arrow there is a arrow which is going towards this side ok. So, that 2 molecules having the same direction, when they are moving with a relative then relative mean speed of that molecules, when they approach each other will be always 0. That means, both of them are moving at a particular velocity.

So, their approach is not likely. So, it is going to be 0. When 2 molecules are approaching each other head on like you have here one directly approaching the other what do you expect? When 2 molecules are approaching each other head on the mean relative speed should be the relative speed of the 2 molecules, it should be 2 the mean when the mean velocity of approach. So, this I think this needs to be a correction this should be 2 the average velocity of the each of the particles ok.

Now, when suppose the molecules are approaching from any particular direction. Because we know they are randomly distributed and they are moving randomly. So, to find out we use more or less the pythagoras theorem to find out the mean relative speed or mean relative speed of approach what we see? This is this side is approaching with velocity v, this side is also approaching with velocity v. So, what we say we take the Pythagoras theorem and see the velocity of approach is becoming the relative mean speed of approach becoming, under root 2 into the average speed.

So, this is the average speed which you are having, this is going to be twice the average speed and this is going to be 0. This is twice the average speed is when they are coming head on ok. And the last one what we are going to see since we have not put any direction or any we have not we have taken a very simplified model we have not put any angle, because all the molecules are moving in the velocity space and they are all vector quantities, velocities are vector quantities we are not associating any angle we are saying they are randomly moving.

So, if they are randomly moving then we have assumed, and this is the most simplistic approach we have assumed that it is under root 2 into the mean speed, which we have calculated previously.

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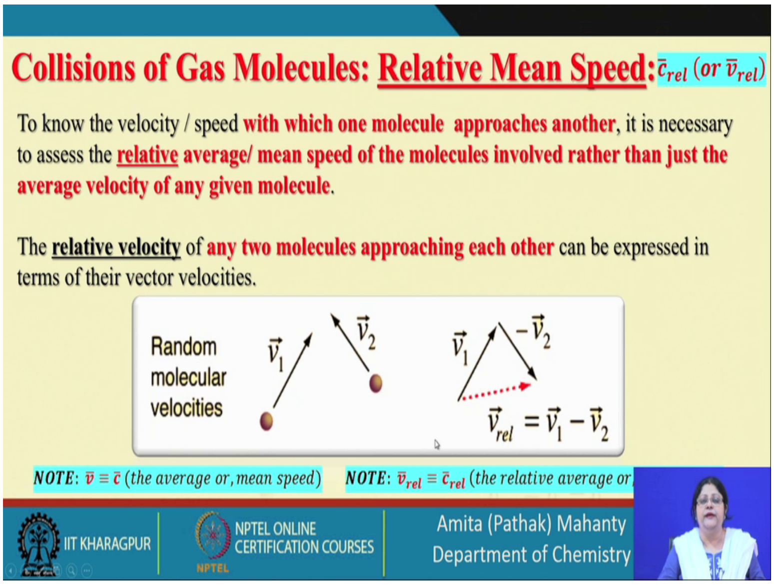

Collisions of Gas Molecules: Relative Mean Speed: $\bar{c}_{rel}$ (or $\bar{v}_{rel}$)

To know the velocity / speed **with which one molecule approaches another**, it is necessary to assess the **relative average/ mean speed of the molecules involved rather than just the average velocity of any given molecule**.

The **relative velocity** of **any two molecules approaching each other** can be expressed in terms of their vector velocities.

$\vec{v}_{rel} = \vec{v}_1 - \vec{v}_2$

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

NOTE: $\bar{v}_{rel} \equiv \bar{c}_{rel}$ *(the relative average or*

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This can be this calculation can be taken up a little more detailed, if you are understanding what is a vector a parameter. To understand the velocity and speed with which molecules approach one another, it is necessary to assess the relative average mean speed of the molecules involved rather than that is just the average velocities ok, because they are randomly moving.

So, if they are move moving in random manner they are moving at any particular direction. So, we cannot take it to be 0, we cannot take it to be two twice the average speed, we just have to take a fine out a term which is can be applied or can be related to them average and mean speed, but we call that as a relative mean speed. And this is the speed which where this molecules approach one another.

So, the relatives velocity or mean speed which we are going to be looking into is what we are going to down now discuss. The relative velocity of 2 molecules approaching each other can be expressed in terms of their vector velocities. So, this is one vector velocity and this is another, they are random molecular velocities, they are randomly moving in from xyz any direction.

So, what we can see if we have a say velocity 1 associated with one molecule, another velocity 2 that is associated with the other molecule and this is since this is I am taking if I am taking this as a positive I just take this as negative. So, this is having a negative velocity; that means, in it is a moving in the opposite direction. So, the relative velocity which of approach we can say will be the v 1 minus the velocity vector v 2 ok.

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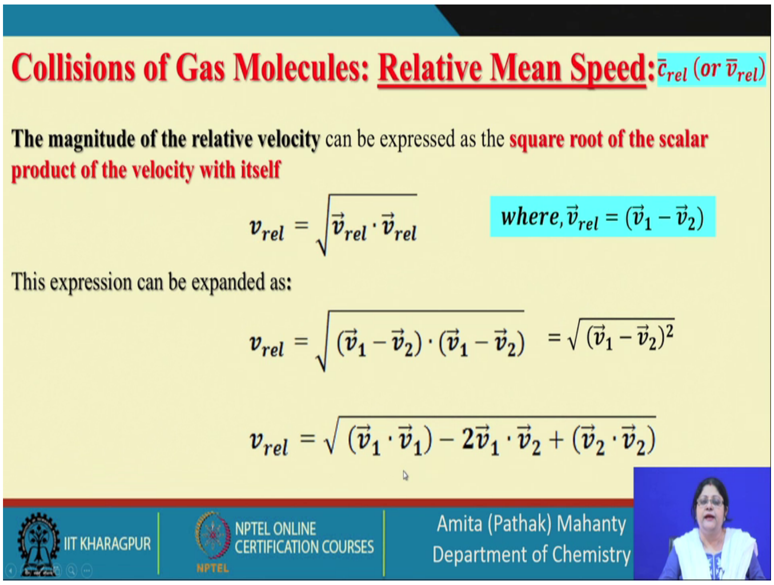

Collisions of Gas Molecules: Relative Mean Speed: $\bar{c}_{rel}$ (or $\bar{v}_{rel}$)

The magnitude of the relative velocity can be expressed as the **square root of the scalar product of the velocity with itself**

$$v_{rel} = \sqrt{\vec{v}_{rel} \cdot \vec{v}_{rel}} \qquad where, \vec{v}_{rel} = (\vec{v}_1 - \vec{v}_2)$$

This expression can be expanded as:

$$v_{rel} = \sqrt{(\vec{v}_1 - \vec{v}_2) \cdot (\vec{v}_1 - \vec{v}_2)} = \sqrt{(\vec{v}_1 - \vec{v}_2)^2}$$

$$v_{rel} = \sqrt{(\vec{v}_1 \cdot \vec{v}_1) - 2\vec{v}_1 \cdot \vec{v}_2 + (\vec{v}_2 \cdot \vec{v}_2)}$$

So, the magnitude of the relative velocity; how do you find out the magnitude of the relative velocity we have already defined what is the relative velocity, the magnitude of relative velocity can be expressed as the square root of the scalar product of the vector itself. So, what is the vector? Vector is this one. So, we take the square root of the a scalar product of the velocity with itself. So, then we multiply and they take the product of the square root of the scalar product of this velocity into what the vector itself.

So, this is what we are going to get? This gives you the absolute value of the velocity component in terms of the magnitude. So, the absolute magnitude of the velocity which is supposed to be a vector can be found out by expressing as a square root of the scalar product of the velocity, multiply with itself. So, this is the velocity multiplied by itself and what we have defined the v velocity as? The v velocity is the relative velocity is one v 1 or for the molecule corresponding to 1, and minus the velocity 2 corresponding to the molecules moving the molecule 2 moving in the opposite direction.

So, the expression can be expanded, you can produce the further extension of this by replacing what you have defined the v relative as. The v relative velocity vector component is actually given as v 1 minus v 2 the vector components, and since its multiplication you can write it these way square it up. And if it is a square then you can see you a minus b square formula a a square minus 2 ab plus b square is how you are going to write that.

So, if you are writing that just have a look at it what we have written.

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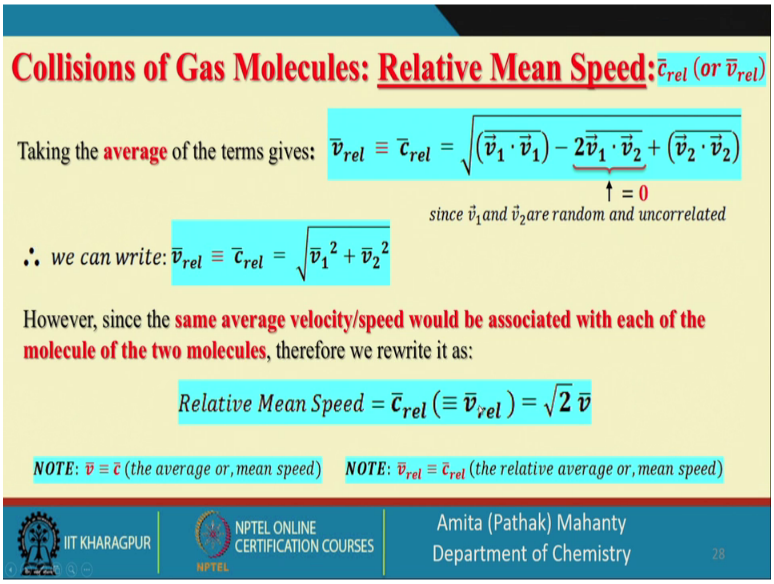

Collisions of Gas Molecules: Relative Mean Speed: $\bar{c}_{rel}$ (or $\bar{v}_{rel}$)

Taking the **average** of the terms gives: $\bar{v}_{rel} \equiv \bar{c}_{rel} = \sqrt{(\vec{v}_1 \cdot \vec{v}_1) - \underbrace{2\vec{v}_1 \cdot \vec{v}_2}_{\uparrow = 0} + (\vec{v}_2 \cdot \vec{v}_2)}$

since $\vec{v}_1$ and $\vec{v}_2$ are random and uncorrelated

$\therefore$ we can write: $\bar{v}_{rel} \equiv \bar{c}_{rel} = \sqrt{\bar{v}_1^{\,2} + \bar{v}_2^{\,2}}$

However, since the **same average velocity/speed would be associated with each of the molecule of the two molecules**, therefore we rewrite it as:

$$\text{Relative Mean Speed} = \bar{c}_{rel}\,(\equiv \bar{v}_{rel}) = \sqrt{2}\,\bar{v}$$

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)

Now, if we are going to find out the average of these terms what we do? We if we want to find out the average of we take the average of each of the velocities and if you see in this term, since this these are more or less random. So, they are not correlated, they are random not correlated maybe orthogonal. So, if they are vectors are orthogonal, their product is going to give you a 0.

So, this term becomes 0, if this term becomes 0, then what we have left with it is a multiple a square of the v 1 and square of the v 2 if we are taking the averages. So, this is the average v ones plus the average v 2 square. So, the relative velocity what we have now come to is relative velocity which can also be written as I we remember we either use v or c for the velocity component, whenever we are writing a bar over it is meaning the mean or the average value and this is how it is going to look right. It is the square of v 1 plus the square of v 2 of the mean velocities as.

However since the same velocity vectors would be associated with each of the molecules, because we are talking about most of the times we will try to simplify and take the molecules to be similar. So, they will be having the same type of same average velocity associated with them. So, each of them will be associated with the same type of velocity if, they are of the same size or similar molecule, which we will always henceforth take that they are also similar kinds of molecule.

So, if we if we do that, then you have this is a twice vy v 1 square. So, if you take v 1 square or v 2 square we just call it a v; that means the average speed. So, if it is average they are all moving in the average speed v, then that relative mean velocity is nothing, but under root into the mean velocity. What this mean velocity is what we had calculated from the kinetic model, what we are now getting what is the mean velocity of approach of one molecule towards other ok.

So, that is nothing, but the relative velocity of approach is nothing, but under root of the mean velocity calculated through the kinetic model.

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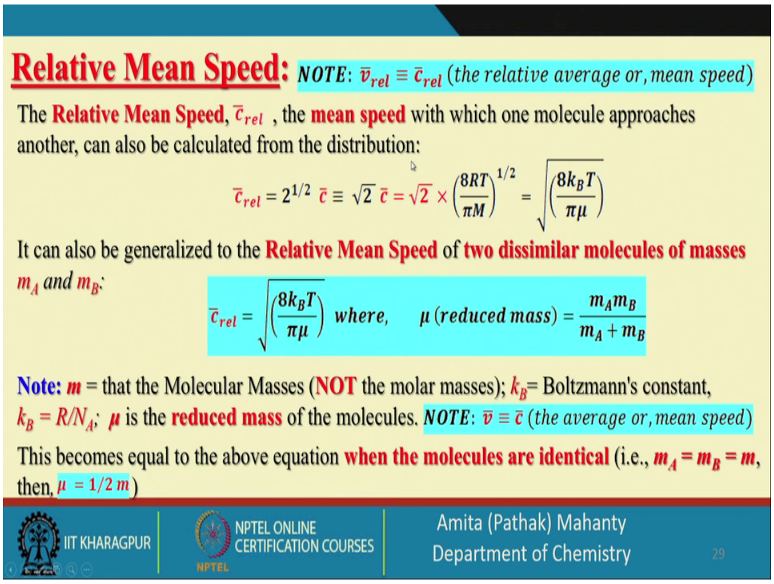

Relative Mean Speed:

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

The **Relative Mean Speed**, $\bar{c}_{rel}$, the **mean speed** with which one molecule approaches another, can also be calculated from the distribution:

$$\bar{c}_{rel} = 2^{1/2}\ \bar{c} \equiv \sqrt{2}\ \bar{c} = \sqrt{2} \times \left(\frac{8RT}{\pi M}\right)^{1/2} = \sqrt{\left(\frac{8k_BT}{\pi\mu}\right)}$$

It can also be generalized to the **Relative Mean Speed** of **two dissimilar molecules of masses** m_A *and* m_B:

$$\bar{c}_{rel} = \sqrt{\left(\frac{8k_BT}{\pi\mu}\right)}\ \ where, \quad \mu\,(reduced\ mass) = \frac{m_A m_B}{m_A + m_B}$$

Note: m = that the Molecular Masses (**NOT** the molar masses); k_B= Boltzmann's constant, $k_B = R/N_A$; μ is the **reduced mass** of the molecules. **NOTE:** $\bar{v} \equiv \bar{c}$ *(the average or, mean speed)*

This becomes equal to the above equation **when the molecules are identical** (i.e., $m_A = m_B = m$, then, $\mu = 1/2\ m$)

So, if you look at this, the relative mean speed or velocity, which we are usually relate with c will we have a bar over that this mean speed which is for which is one molecule approach into another can be given as under root 2 into the mean speed. And if we substitute the value of c here what is the value of c here? C is 8 pi RT by M pi to the power half ok.

And you can replace this by R by kkt RT by kt and mass by small mass if you are then you get the expression here like this, but remember you have a different formula here.

Here what we are knocking talking about this is not the molar mass which we had talking about in the kinetic model. Here this mass is the molecular mass this is not the molar mass which was associated in the kinetic model and this mass is the reduced mass of the 2 molecules which may be similar or dissimilar ok.

So, what is this reduced mass given by? Reduced mass is nothing, but the product of the mass means what you take is 1 by mA is plus 1 by mB what is mA and mB are the 2 molecules. If you take 1 by mA plus 1 by mB is what you get is reduce mass, you take the addition if you add them 2 what you get? It is mA mB divided by mA a mB ok. So, the m here we have replaced we can we can simplify this to if the molecules are identical suppose that A and B are same molecules, then what does it become then you have the reduced mass becoming to half m ok.

If it becomes a half m then you come back to the equation which you are dealing with. So, this becomes equal to m only when the molecules are of similar kind ok. So, you will be able to find out what is the relative velocity of approach for one molecule to the other, only remember that here the denominator in the mass in terms if you take it in terms of kt, this mass is not actually the mass of the substance, but it is the reduced mass of the substance which you are talking about. And here is m is the molecular mass which is associated with each of the molecule ok.

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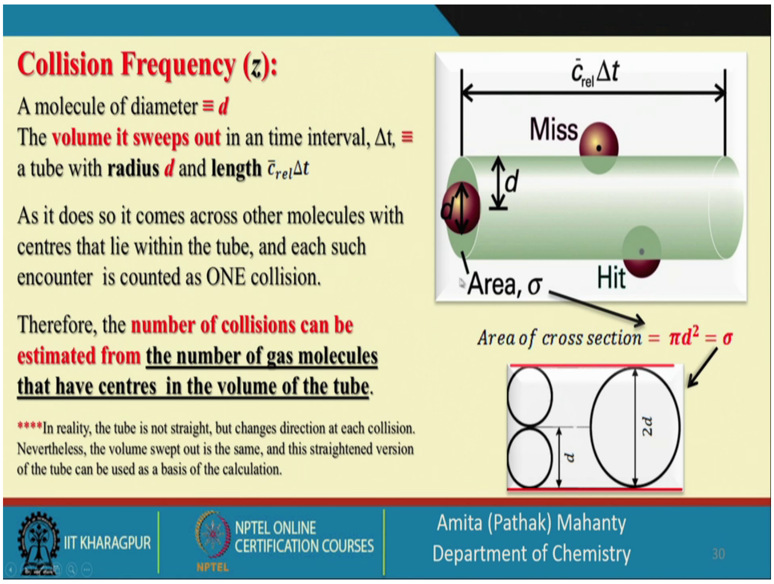

Collision Frequency (z):

A molecule of diameter ≡ d

The **volume it sweeps out** in an time interval, Δt, ≡ a tube with **radius** d and **length** $\bar{c}_{rel}\Delta t$

As it does so it comes across other molecules with centres that lie within the tube, and each such encounter is counted as ONE collision.

Therefore, the **number of collisions can be estimated from** **the number of gas molecules that have centres in the volume of the tube**.

****In reality, the tube is not straight, but changes direction at each collision. Nevertheless, the volume swept out is the same, and this straightened version of the tube can be used as a basis of the calculation.

Area of cross section = $\pi d^2 = \sigma$

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Now, what happens when you are 2 molecules are approaching each other? 2 molecules when they are approaching each other with a relative speed say a molecule has a diameter d that is approaching, another molecule and in the volume which is going to sweep in interval t is let us say otherwise, suppose I want to see which are the molecules which is going to be undergoing a collision.

So, for under understanding that what we see, we see we have to have maintain a minimum distance from the centers of the 2 molecule; now for that what we visualize is we take a volume which is going to be swept by a molecule of diameter d. When this is swept by a diameter molecule is swept sweeping a distance or a some distance dt, and the volume it is going to cover is going to be a say tube or cylinder. So, this tube or cylinder which can be obtained is the volume in which within this whatever molecule is going to fall into will undergo collision.

So, how I am going to define? I have to define a d molecule see d is this molecule, this is the diameter of the molecule now it is going to sweep a volume and this volume is going to be associated with the sweeping of the total volume of at time t. So, if we I have the we want to find out the total volume swept, what we have to look in time t in t interval is the tube with the radius d this is the radius d and with the length of how much? When they are moving with the velocity the molecules are moving with the velocity the relative mean velocity of c (Refer Time: 25:23), then what you when they are approaching this what is what can we say? Then the volume which is going to sweep is going to be this is the length velocity equal to distance by time ok.

So, the velocity into time is the distance which we have done number of times. So, this is going to give you the length of the tube and what is going to be the cross section? The cross section is going to be the diameter of the molecules. So, as we see what we visualize is the number of collision that can be estimated from the number of gas molecules that have centers within this volume. Whichever molecules is having a center within this volume will undergo collision, any other molecule which is not within this swept area will not be undergoing collision ok.

So, the tube which we have um swept using a molecule of diameter d is what is the a volume in which the number of molecules included, a number of molecules in this will undergo collision. So, to understand this more clearly what we usually visualize that we have only one molecule which is moving, all other molecules in this swept area. Suppose you have a molecule d and it is going to sweep a area which is the molecules are moving with a velocity relative means velocity of this, and this will sweep a volume of this.

So, I see a just visualize one molecule moving, all the rest of the molecules which have their sentence within this tube are frozen. When they are moving only one is going to move and only those particles is going to collide, which is having the center within this tube. So, from if I know the total number of molecules in the tube then I can find out how many collisions they are undergoing ok. So, I if I know the number of collisions they are undergoing that gives me the collision frequency ok.

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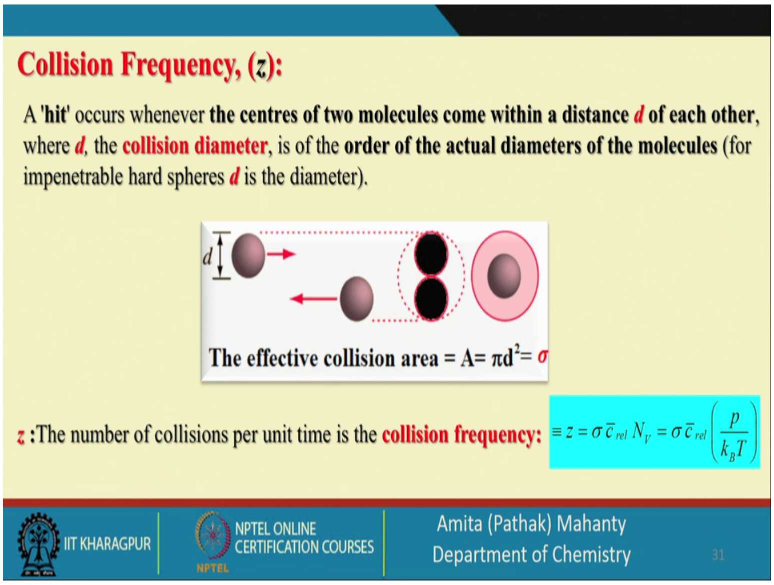

Collision Frequency, (z):

A **'hit'** occurs whenever **the centres of two molecules come within a distance *d* of each other**, where ***d***, the **collision diameter**, is of the **order of the actual diameters of the molecules** (for impenetrable hard spheres ***d*** is the diameter).

The effective collision area = A= $\pi d^2 = \sigma$

z :The number of collisions per unit time is the **collision frequency:** $\equiv z = \sigma \bar{c}_{rel} N_V = \sigma \bar{c}_{rel} \left(\frac{p}{k_B T} \right)$

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So, that is what we are going to see when a hit occurs, when the centers of 2 molecules come within the distance d with if they are similar kind of molecules. And this d is known as the collision diameter. And in order it is in the order of the actual diameter of the molecule. Now the number z the frequency can be given here. And we are going to just now derive what how did we get this.

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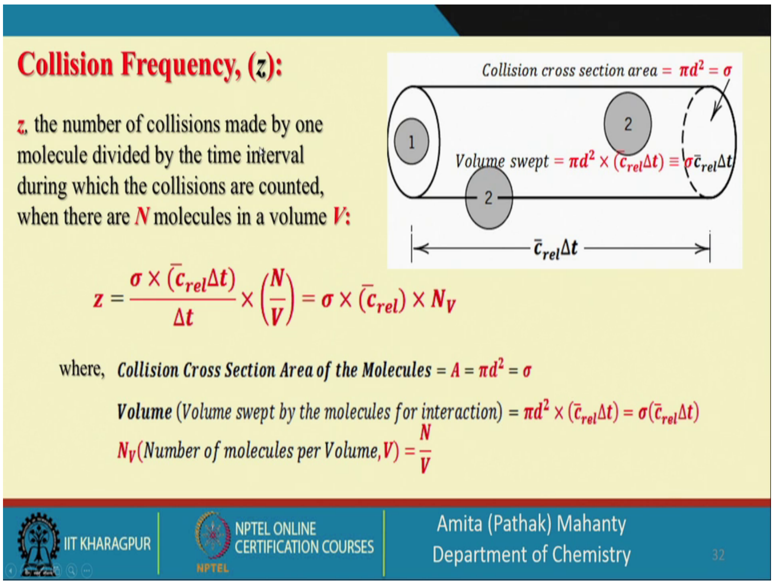

Collision Frequency, (z):

z, the number of collisions made by one molecule divided by the time interval during which the collisions are counted, when there are N molecules in a volume V:

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

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)* = $\frac{N}{V}$

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What how did we get this? Suppose the z is the number of collision made by one molecule, in time interval delta t which is during which the collision has be is counted, then we multiply with the total number of molecules the number density, then the we can get the number of collision occurring per unit time that will give you us give us the frequency.

So, number of collision made by one molecule, per unit time into the number density will give you the total number of collision occurring in that area volume a which we have swept. So, what is the number of collision number of collisions will be actually going to be the total number of molecules which will be occupying in the swept area what is the swept area? This is the diameter, pi this is the area of cross section area of cross section where the diameter is supposed to be d square.

So, pi d square is also known as sigma, sigma is known as the collision cross section area into the distance what was the distance, that was the velocity into time was giving you the distance of this length of this tube. So, this is the volume which we accept which is swept by the molecule at unit time that is dt into the total number of molecule present that is a number density, that is number of molecules per unit volume of the container ok.

So, we can write down the number density in terms of Nv.

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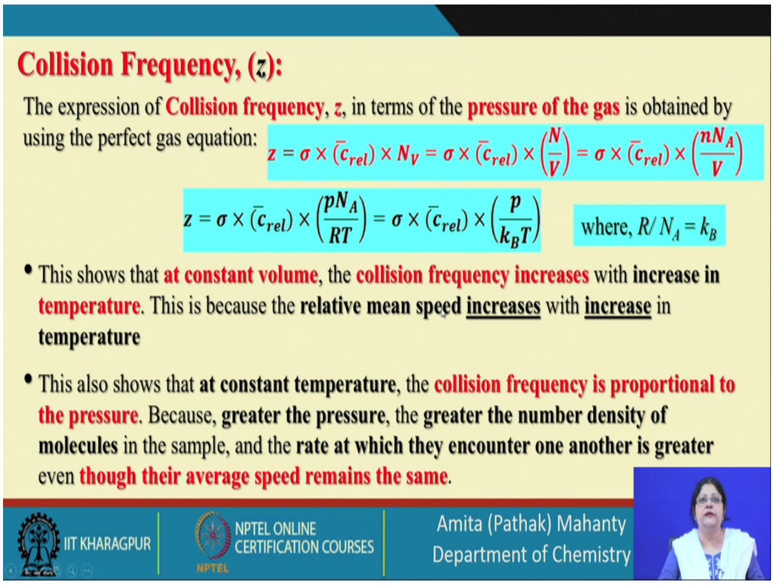

Collision Frequency, (z):

The expression of **Collision frequency**, *z*, in terms of the **pressure of the gas** is obtained by using the perfect gas equation: $z = \sigma \times (\bar{c}_{rel}) \times N_V = \sigma \times (\bar{c}_{rel}) \times \left(\frac{N}{V}\right) = \sigma \times (\bar{c}_{rel}) \times \left(\frac{nN_A}{V}\right)$

$$z = \sigma \times (\bar{c}_{rel}) \times \left(\frac{pN_A}{RT}\right) = \sigma \times (\bar{c}_{rel}) \times \left(\frac{p}{k_BT}\right)$$

where, $R/N_A = k_B$

- This shows that **at constant volume**, the **collision frequency increases** with **increase in temperature**. This is because the **relative mean speed** **increases** with **increase** in **temperature**
- This also shows that **at constant temperature**, the **collision frequency is proportional to the pressure**. Because, **greater the pressure**, the **greater the number density of molecules** in the sample, and the **rate at which they encounter one another is greater** even **though their average speed remains the same**.

And if we look into this in a more detail, Nv can be replaced by a Nv number of molecules per unit volume can be replaced by in the number of moles into Avogadro number gives you the total number of moles a molecules divided by the total volume, and this total volume we are since we are dealing with we can apply the ideal gas law v pv equal to nrt. So, we can find out what v is v is going to be nrt by p ok.

So, you replace nrt by p here what you get you get a expression in terms of the pressure ok. So, what we have let us have a look at this the collision frequency at constant volume what is going to happen? At constant volume called collision frequency is going to increase with increase in temperature. See the expression does not have a directly proportional temperature factor. But when we increase their collision frequency increases only when there is a increase in temperature if the volume is held constant.

Why is this? So, because if you are increasing the speed the relative mean speed of approach increases; so, since temperature increases the relative mean speed, because in the relative mean speed has a term in which is related to the speed. So, what we should remember is this expression of the frequency. In this expression we do not really have the temperature, but when you have a constant volume that when you have constant volume increase in temperature will increase the relative speed, and hence the total collision frequency supposed to increase.

Now, what happens? We can also see that at constant temperature the collision frequency is proportional to the pressure ok. If we are taking temperature as a constant, then the collision frequency is proportional to the pressure; greater the pressure greater than because if what is going to be how is pressure calculated. Pressure is the number of molecules which is exerted exerting force on the wall that is the if the number of particles are going to be increasing; that means, the number density or number of particles is increasing, then the pressure is going to increase.

So, pressure if you are having at constant temperature, temperature is held constant the collision frequency is going to be increased if you increase the pressure because if you are increasing the pressure mean directly means, that you are increasing the number density of the gas particles and if the gas number density increases, the pressure will all increase and that will if number is increasing they are more likely to collide. So, the frequency of collision will increase.

So, the rate at which they encounter one another it is going to be greater if we are increasing the pressure. And that means the number density though their average speed remains the same, because we have held temperature constant. So, the average speed of approach remains the same, but the rate at which the encounter or strike each other. That means the collision frequency increases if you are increasing the pressure.

Thank you.