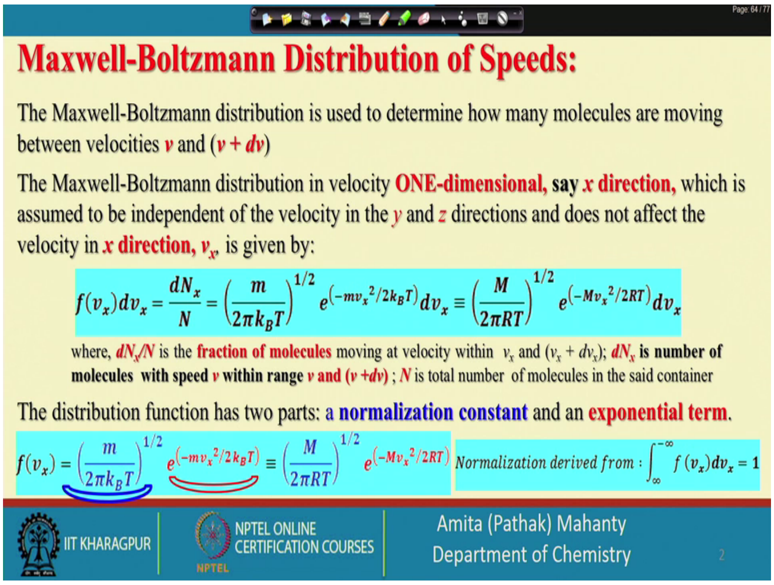
Molecules in Motion
Prof. Amita Pathak Mahanty
Department of Chemistry
Indian Institute of Technology, Kharagpur

Lecture – 08
Kinetic theory of gases (Contd.)

Welcome to the course on the Molecules in Motion. In the last class, we had talked about the kinetic energy theory in terms of the distribution, speed distribution, Maxwell's and Boltzmann speed distribution. What we are going to do today is going to, we revisit what we have done in the last class. And also to see some certain things like the average speed or the RMS speed or the most probable speed which we had just mentioned in the last class. How they can be derived because this syllabus or the course which you have taking, just mentioning the expressions for the speed of the various forms, the RMS, the most probable or the average is not sufficient; you need to know how to derive it.

It is mathematically a little bit difficult, but it is based on, once you understand that it is based on this standard integrals, then you can use the handbooks and the tables which are provided and then it does not become that difficult once you know how to proceed with it. So, today we are going to do that.

(Refer Slide Time: 01:41)



Maxwell-Boltzmann Distribution of Speeds:

The Maxwell-Boltzmann distribution is used to determine how many molecules are moving between velocities v and $(v + dv)$

The Maxwell-Boltzmann distribution in velocity **ONE-dimensional, say x direction,** which is assumed to be independent of the velocity in the y and z directions and does not affect the velocity in **x direction,** v_x, is given by:

$$f(v_x)dv_x = \frac{dN_x}{N} = \left(\frac{m}{2\pi k_B T}\right)^{1/2} e^{\left(-mv_x^2/2k_BT\right)}dv_x \equiv \left(\frac{M}{2\pi RT}\right)^{1/2} e^{\left(-Mv_x^2/2RT\right)}dv_x$$

where, dN_x/N is the **fraction of molecules** moving at velocity within v_x and $(v_x + dv_x)$; dN_x **is number of molecules with speed v within range v and $(v + dv)$**; N is total number of molecules in the said container

The distribution function has two parts: a **normalization constant** and an **exponential term**.

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

Normalization derived from : $\int_{\infty}^{-\infty} f(v_x)dv_x = 1$

So, let us see what we had done in the last class and in this if you see the Maxwell's distribution which we had talked about. I want you to understand what actually this means because we have talked about in 1 dimension the distribution of the particles in speed and velocity. We have also discussed in 3 dimension form.

So, at times what happens, you have confusion as to what we are meaning for the various terms we are using because certain books will use this as the from the distribution function or you will say the probability density, they will call it and some books will call this as a fraction of molecules with a particular ranging velocity.

So, let us first revisit and see what are the things which we are going to have and we are we will try to see and visit the same topic again, so that if there is any confusion we clarify that. So, what we have talked about? We have talked about the Maxwell Boltzmann distribution to determine how many molecules are moving between a certain range of velocity. What is that range? We have said it is, if I have talked about a velocity in a particular x in a range x direction or y direction, then the velocity, we are talking essentially of the velocity space. It is not the radial space or this space which we x, y, z represents. Here, x, y, z, whenever we are representing, we are talking about the velocity component in the 3 direction; x, y and z.

So, what we are dealing with is actually a velocity space ok. So, what we are looking here; the when we are talking about Maxwell's distribution of a particle of a molecule, it we can talk about in terms of velocity, but actually what we deal with is actually the speed of the molecule. So, in 1 dimension, what we mean that we have restricted the movement of particle or not looking into the movement of particle in y direction, in z direction; we are looking into the particles moving only in the x direction which is supposed to be independent of the velocities which is there in the, means the velocities of these particles in the y and z axis do not have any effect on the distribution of the speed of the particles where in the direction x which we are looking into.

So, what we have? We have n number of total particles now if we have total n number of particles, what we are trying to find out? See the expressions are very complicated, but you have to understand what is the basis of these expressions. So, when we are looking into the number of molecules, the total number of molecules being n, whenever we are dealing with we are trying to find out the total number of molecules were dealing with is total a total is n.

Now, what we are trying to find out? How many molecules are going to have a speed in the range this and this, v plus v plus delta v ok. And when we are talking about a movement in the x direction; we subscript it by x like we have written x here. This is how we designate it. So, what we are looking into? We are trying to find out how many molecules and; that means, we are talking about a fraction of the total molecules which is moving in a particular direction x having the velocity in the range v x plus v x plus delta v x.

So, if we are looking into that, this is how we can write if a total function total number of particles or molecules are n and what is the fraction? Fraction is the total, this is the total number of molecules in the fraction having the velocity in the total number of molecules having the velocity ranging between v x and v x plus delta v x.

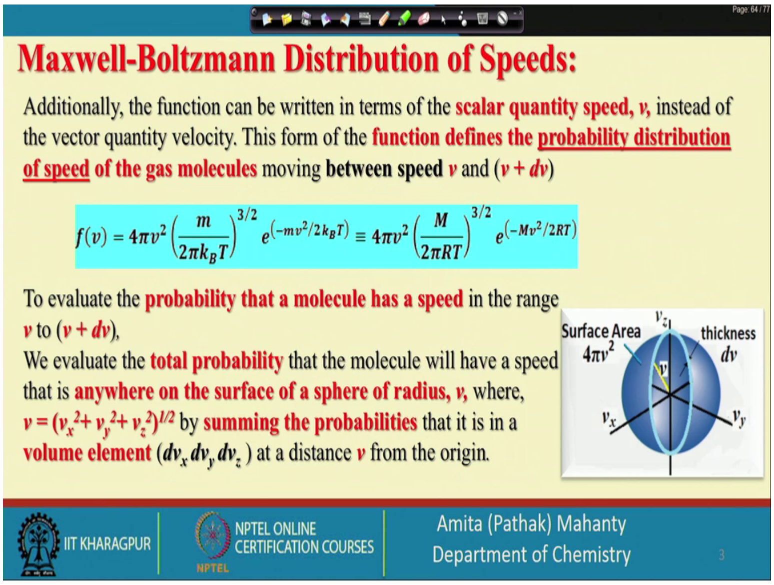
So, we can if I take the ratio of this; that means, the total molecules having the velocity in this way divided by the total number of molecules present in the system or a container, then this is going to give you a fraction. This fraction is the same when we it some books will represent this as the f x v x d d v x. This is the distribution function, this is the distribution function, this gives us the the probability of finding a molecule within the range of velocity v plus v and v plus d v x ok, when we are talking about movement in the x direction.

Now, what are these per component you see you have, when you are seeing this expression, it looks very complicated, but one when you are looking in this expression, you see this is some part and then you have e to the power something and this is the interval into in which we are looking into the into the of the function distribution function n; that means, this interval is the in a velocity interval we are looking into. What is that? v x and v x plus delta v x. And we are seen since this is a probability distribution; that means, the total probability is always going to be 1. So, we need to do a normalization; normalization it gives you the term which is the constant. This is the constant term which we derive through normalization.

So, the expression has two parts. If you see look very can see into the expression, then you see it is having two parts; this one is for or what is obtained from the normalization and this one is the exponential part which is the expression for the distribution function.

So, normalization, what we do? We say that the function and the gas molecules are moving from minus infinity to plus infinity means in the x direction. So, when we normalize we put the m f of v x into d v x should be equal to 1 when integrated between infinity to minus infinity; that means, if I am talking about x minus x to infinity in the minus in the x direction, in the for the minus infinity expression.

(Refer Slide Time: 08:11)



Page: 64 / 77

Maxwell-Boltzmann Distribution of Speeds:

Additionally, the function can be written in terms of the **scalar quantity speed, v,** instead of the vector quantity velocity. This form of the **function defines the probability distribution of speed of the gas molecules** moving **between speed** v and $(v + dv)$

$$f(v) = 4\pi v^2 \left(\frac{m}{2\pi k_B T}\right)^{3/2} e^{(-mv^2/2k_BT)} \equiv 4\pi v^2 \left(\frac{M}{2\pi RT}\right)^{3/2} e^{(-Mv^2/2RT)}$$

To evaluate the **probability that a molecule has a speed** in the range v to $(v + dv)$,

We evaluate the **total probability** that the molecule will have a speed that is **anywhere on the surface of a sphere of radius, v,** where, $v = (v_x^2 + v_y^2 + v_z^2)^{1/2}$ by **summing the probabilities** that it is in a **volume element** $(dv_x dv_y dv_z)$ at a distance v from the origin.

IIT KHARAGPUR | NPTEL ONLINE CERTIFICATION COURSES | Amita (Pathak) Mahanty, Department of Chemistry

3

Now, additionally, we have written that when we were looking into the 3 dimension of the movement of the particles, what we have? The functions can be written in terms of the scalar quantity of speed v; instead of we are writing vector quantity, we always define in terms of this a scalar quantity that is the speed, the magnitude of at of the velocity part.

So, in this what we divide define that probability distribution of the speed of the gas molecules between suppose, we have the velocity v and v plus d v. Now what we are looking a when whenever we are looking at term v and not a signifying in indicating whether that it is x, y or z; that means, what we are looking is the probability that a molecule has a speed in the range this is evaluating the total is the probability which you are looking into on a surface of a sphere with the radius being that of the v, this v, what we are looking into we have derived in other classes previous classes is this is the RMS speed we always put into.

So, what we are looking is, we are evaluating the total probability that the molecules will have a speed anywhere on the surface of a sphere this is going to be the surface of the sphere and what will be the prob total probability anywhere on the surface of the sphere with having the radius, this is the radius, this is the RMS velocity when we talk in terms of speed because we are talking in terms of the magnitude only. So, this is the RMS speed which we are looking in where the RMS speed is given by something like this it is the square of the means of the velocity under root of the square of the root means velocities of each x, y, z direction by summing the probabilities that is in the volume element.

See this is the volume element we are looking into. We can specify a volume element somewhere here having very small cube x d v x d v y d v z and these v these this is a velot velocity space I has as I have already told. So, this volume element when I integrate out a sum it over, then I get a shell sort of a thing covering continuously on the surface.

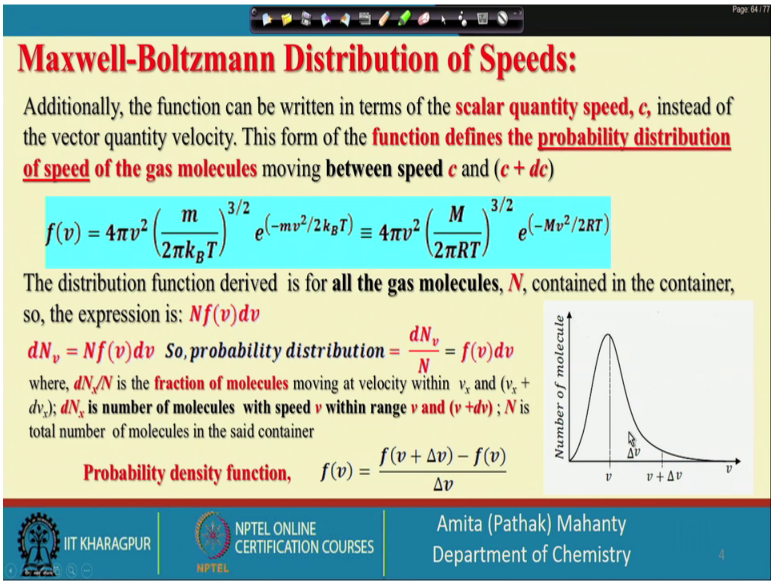
So, what we are talking about is essentially a shell thickness and from that what we have got we got this term. This is the surface which we are looking into. So, this is what we got from the term. This is not going to be there when we are talking about a one dimension movement. So, what we have added here, instead of the in addition to the additional normalization term, the exponential term, we have added this term then we are talking about the movement of particles or spinning of particles in the 3 dimension.

So, I hope you have we have done this previously. I hope we have understood what the significance is. Here we have talking about finding the total probability on a surface of a sphere of radius r, radius v this v is the RMS velocity and this surface is obtained by summing the probabilities of says small cubes which is there on this surface. If I keep summing up all the cubes, the probability in each of the cube, each of the cube has a dimension of this because x, y, z directions are there.

So, velocity in x, y, z direction in as various minute infinites my small cube; if I sum it over all the cubes which is going to be there on the surface, then I get a shell and this shell is the surface area of this is a shell is what is multiplied to find out the total probability of the finding of the molecules in the range of this v plus v plus delta v;

understood how did this come in? We have talked about in the last class, but this is what comes in and it is the additional term when we are talking about in the 3 dimension.

(Refer Slide Time: 12:28)



Maxwell-Boltzmann Distribution of Speeds:

Additionally, the function can be written in terms of the **scalar quantity speed, *c*,** instead of the vector quantity velocity. This form of the **function defines the probability distribution of speed of the gas molecules** moving **between speed *c*** and (*c* + *dc*)

$$f(v) = 4\pi v^2 \left(\frac{m}{2\pi k_B T}\right)^{3/2} e^{\left(-mv^2/2k_BT\right)} \equiv 4\pi v^2 \left(\frac{M}{2\pi RT}\right)^{3/2} e^{\left(-Mv^2/2RT\right)}$$

The distribution function derived is for **all the gas molecules**, *N*, contained in the container, so, the expression is: $Nf(v)dv$

$$dN_v = Nf(v)dv \quad So, probability\ distribution = \frac{dN_v}{N} = f(v)dv$$

where, dN_x/N is the **fraction of molecules** moving at velocity within v_x and (v_x + dv_x); dN_x **is number of molecules with speed *v* within range *v* and (*v* +*dv*)**; *N* is total number of molecules in the said container

Probability density function, $f(v) = \dfrac{f(v+\Delta v) - f(v)}{\Delta v}$

Amita (Pathak) Mahanty
Department of Chemistry

So, what we have here. So, what we, this is the distribution function; please remember, this is the distribution function. Whenever this is the function which we are having and we have if when we want to find out the probability distribution, then we multiply the distribution function with the d v, the interval, the velocity interval we will multiply. This is the function which you are getting for the if the distribution function. But when you want to find out the probability the distribution or probability of probability distribution of the particles in a particular range, then you multiply this by d v.

Suppose the distribution function is derived for all gases of containing N molecules, then the expression becomes n the total number of molecules present into the function, this is the distribution function and into the interval. So, this gives you the distribution of the total molecules present probability of probability distribution or probability density of n number of molecules in the system.

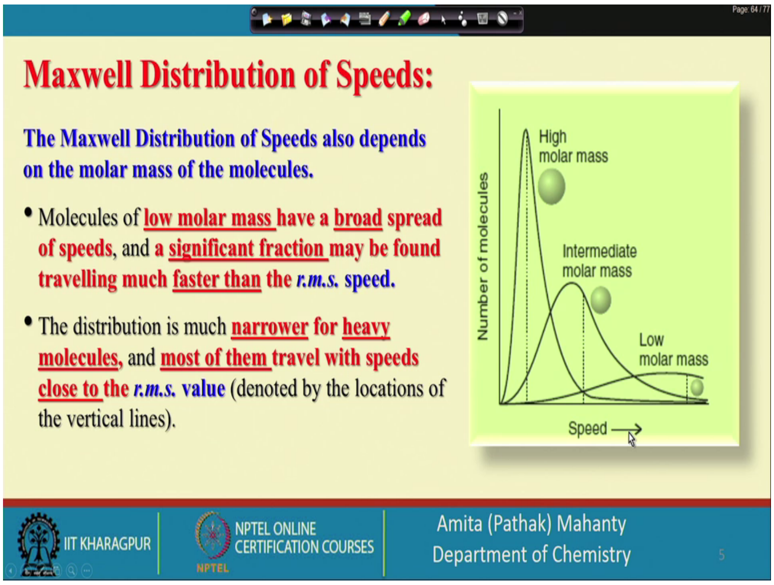
So, now if you want to find out what is the fraction of molecules which fraction also gives you the equivalent information to finding out what is the probability of finding a particular and section of molecules having a particular range of velocity? So, here is what we have written in the, just now we have we have just discussed what is this going to be this is going to be the number of molecules which is going to have the velocity in the range v plus v plus delta v.

See some books they write v as the RMS speed, v as the radius of the surface we are looking into, some books will say it is c. So, whenever we are writing c or v RMS or v, please try to remember at various sections I have written different forms, but c as long as we are writing c, it is the RMS speed we are talking about we if we are writing v and we are writing v RMS these both are going to mean the RMS speed.

So, here what we are finding out if the total number of fraction of the molecules what will be the total fraction if the total fraction will be the same as the f x in a d v and f f v d v. This is going to be the function which we are going to have and divided by n that gives you the frac fraction and that gives you the probability of finding a molecule at a particular range of velocity ok.

So, that you can represent the probability dens density can be represented in terms of this. What we are looking into? We are looking into the function distribution function in them is range v plus delta v. This is the v plus delta v and minus the one which is at v. So, what we are finding out is the divided by the total width of the velocity, gives you the probability which is going to be there in this section, in this area ok.

(Refer Slide Time: 15:43)



Maxwell Distribution of Speeds:

The Maxwell Distribution of Speeds also depends on the molar mass of the molecules.

- Molecules of low molar mass have a broad spread of speeds, and a significant fraction may be found travelling much faster than the *r.m.s.* speed.
- The distribution is much narrower for heavy molecules, and most of them travel with speeds close to the *r.m.s.* value (denoted by the locations of the vertical lines).

In the last class, I could not show you the diagram for the molecular distribution, how it depends on the molar mass. If you see the I have got a few slides on that now in this today's lecture the; how the molecular mass if you are this is the molecule which is having higher mass, this is intermediate and low. You see how the distribution function is looking at you.

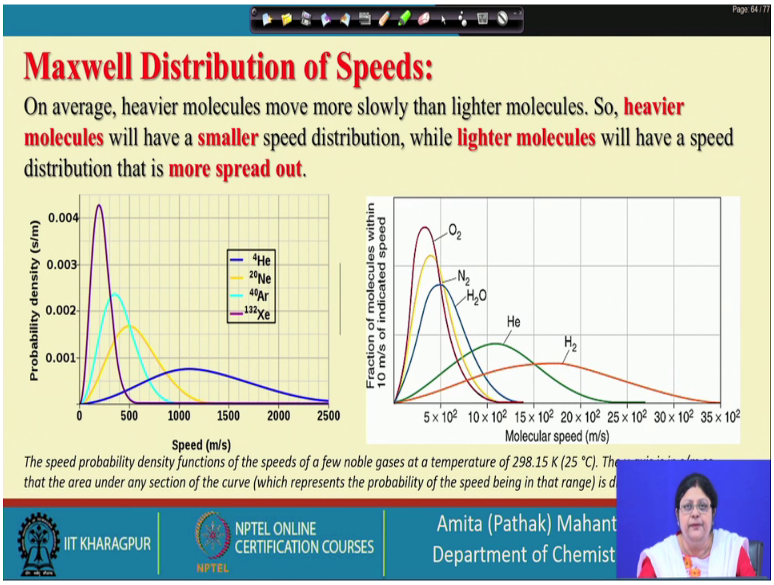
We have to remember the total distribution total area covered under the graph will always be equal because we are talking about a total same set of molecules under same conditions. So, the total area under the curves will be; obviously, higher. Now, depending on the distribution function, if you remember the distribution function, what you can see the molecular mass have when you have a low molar mass, you see the low molar mass, what you have you have a broad spread of the speed distribution.

So, and a significant fraction will be found traveling faster than the RMS speed. This points which is written get drawn, this is going to be the expression in a position for the RMS speed. So, if at RMS speed is a reference which we are looking into then we can see, that if you have a lower molecular mass, then the distribution is going to be broader. This is number of molecules in the y axis it can be the probability distribution density or it is going to be the number of a fraction of molecules in a particularly speed range, these can also be written in the y axis. This axis always remains a speed and. So, if I may indicate the dotted lines at this RMS speed, if you look at it, the broad speed has significant fraction of may be found and traveling at much faster than the RMS speed.

So, as we go towards this is going to be go a going to a higher speed. So, what we have a significant fraction may be found traveling much faster than the RMS speed. This is the RMS speed and you see significant fraction is going to fire found higher in the range.

Now the distribution is narrow, if I the distribution is narrow, for that is for the heavier molecules, then the most of the molecules will travel with the speed close to the r.m.s. This is the RMS, this is peak no it is not the peak. It is just out below the peak ok; this is; that means, this is slightly higher than what is the specified value for the speed. So, this is the RMS speed and from this we can find out then the narrower distribution for heavier molecule most of them will travel with this speeds close to the RMS value.

(Refer Slide Time: 18:38)



Maxwell Distribution of Speeds:

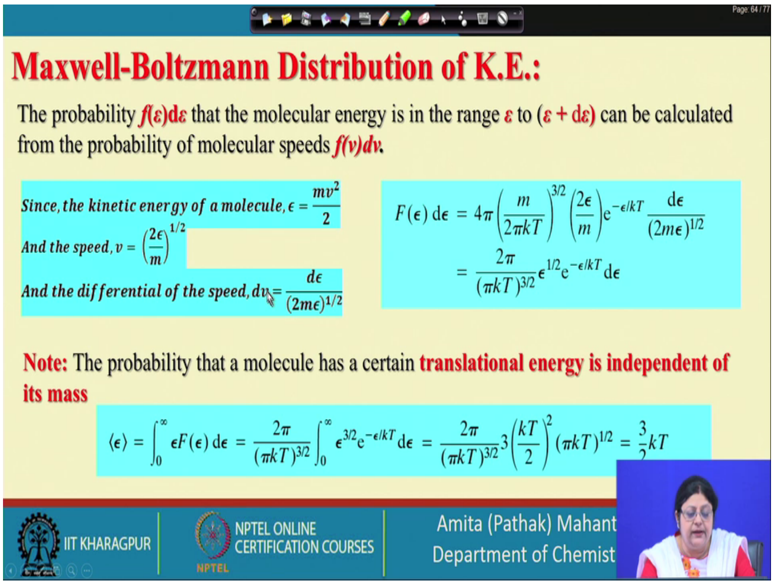
On average, heavier molecules move more slowly than lighter molecules. So, **heavier molecules** will have a **smaller** speed distribution, while **lighter molecules** will have a speed distribution that is **more spread out**.

The speed probability density functions of the speeds of a few noble gases at a temperature of 298.15 K (25 °C). The
that the area under any section of the curve (which represents the probability of the speed being in that range) is d

So, now with if you have a distribution function which we can look into, the average or values which will a probability density or probably distribution of fraction of molecules in a particular range, if we look into this, the heavier molecules will move slowly than the lighter molecules. So, heavier molecules with will have a smaller screen distribution and the lighter molecules will have a speed distribution which is very a spread widely spread.

So, if you see the molecular weights of these gases, you can see this is the gas which is helium which is much more spread out. This is lighter molecule compared to that one which is highest and molecular weight will be xenon. So, this is going to be an narrower. So, it is as we go in increase in molecular weight the distribution is going to be more widespread.

(Refer Slide Time: 19:33)



Page: 64 / 77

Maxwell-Boltzmann Distribution of K.E.:

The probability $f(\varepsilon)d\varepsilon$ that the molecular energy is in the range ε to $(\varepsilon + d\varepsilon)$ can be calculated from the probability of molecular speeds $f(v)dv$.

Since, the kinetic energy of a molecule, $\epsilon = \frac{mv^2}{2}$

And the speed, $v = \left(\frac{2\epsilon}{m}\right)^{1/2}$

And the differential of the speed, $dv = \frac{d\epsilon}{(2m\epsilon)^{1/2}}$

$$F(\epsilon)\,d\epsilon = 4\pi\left(\frac{m}{2\pi kT}\right)^{3/2}\left(\frac{2\epsilon}{m}\right)e^{-\epsilon/kT}\frac{d\epsilon}{(2m\epsilon)^{1/2}}$$
$$= \frac{2\pi}{(\pi kT)^{3/2}}\epsilon^{1/2}e^{-\epsilon/kT}\,d\epsilon$$

Note: The probability that a molecule has a certain **translational energy is independent of its mass**

$$\langle\epsilon\rangle = \int_0^\infty \epsilon F(\epsilon)\,d\epsilon = \frac{2\pi}{(\pi kT)^{3/2}}\int_0^\infty \epsilon^{3/2}e^{-\epsilon/kT}\,d\epsilon = \frac{2\pi}{(\pi kT)^{3/2}}3\left(\frac{kT}{2}\right)^2(\pi kT)^{1/2} = \frac{3}{2}kT$$

IIT KHARAGPUR | NPTEL ONLINE CERTIFICATION COURSES | Amita (Pathak) Mahant Department of Chemist

We had talked about the Max Boltzmen distribution in terms of the kinetic energy. See, when we are talking about the distribution in terms of the velocity, since velocity half m v square, it is equal to the kinetic energy. So, we can always represent the distribution function function in terms of the kinetic energy. We had represented that, but if this class also I am going to show you what is going to be that distribution of the energy. So, when I when I write speed distribution, I write f of v and then d v.

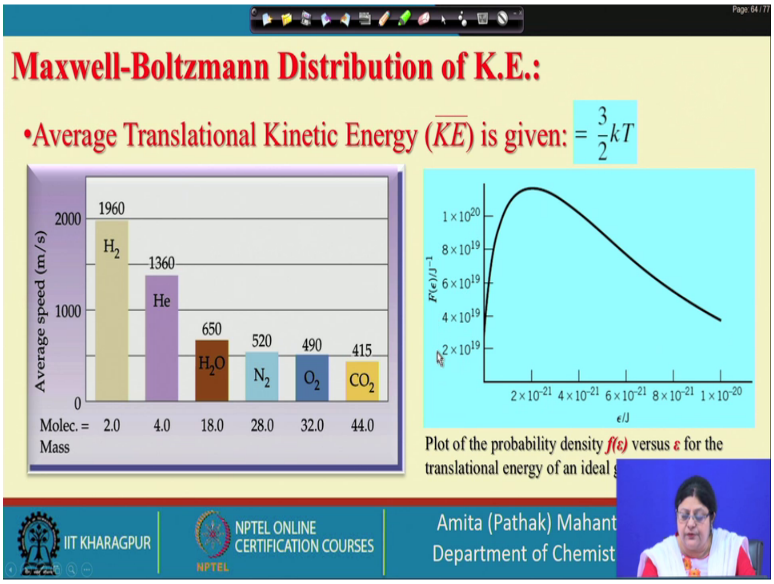
Here we were going to write f of e epsilon de which is this is going to be the probability distribution of the energy and here what we are looking into, we are going to be looking into the probability of finding a molecule having a energy ranging between epsilon and epsilon plus the epsilon. So, this is what we are look going to look into when we are looking into the calculation.

So, the kinetic energy is given by this, half m v square and the average speed; if you want to find out the speed here from this from expression, then what you get, this is the expression multiplied this divided by m to the power half, the differential of this equation because we have we have a differential in the expression for the distribution. So, what will be the d v be? Now, you differentiate this respect with respect to de. So, this is going to be the expression d e by 2 m e to the power half is what we are going to get, by differentiating this.

So, that will be equivalent to the d v. So, now, when we want to find out the function for the probability distribution and of energy, what we write? We write the same terms which we have for the velocity; instead, what we have here we have derived the normalization term. This is for the probability distribution taken to be 1. We describe the deduce the constant term and then we get the expression. I would like you to do this as an assignment and the probability of finding a molecules in this translation is independent of it is mass.

This you can do once you understand what is going to be the translation energy average translation energy, the average translation energy will be the distribution of the energy into the energy for a particular molecule. If you do that and integrate between 0 to infinity use the standard integral, you should get 3 by 2 k T.

(Refer Slide Time: 22:27)



Page: 64 / 77

Maxwell-Boltzmann Distribution of K.E.:

•Average Translational Kinetic Energy ($\overline{KE}$) is given: $= \frac{3}{2}kT$

Plot of the probability density $f(\varepsilon)$ versus ε for the translational energy of an ideal

IIT KHARAGPUR

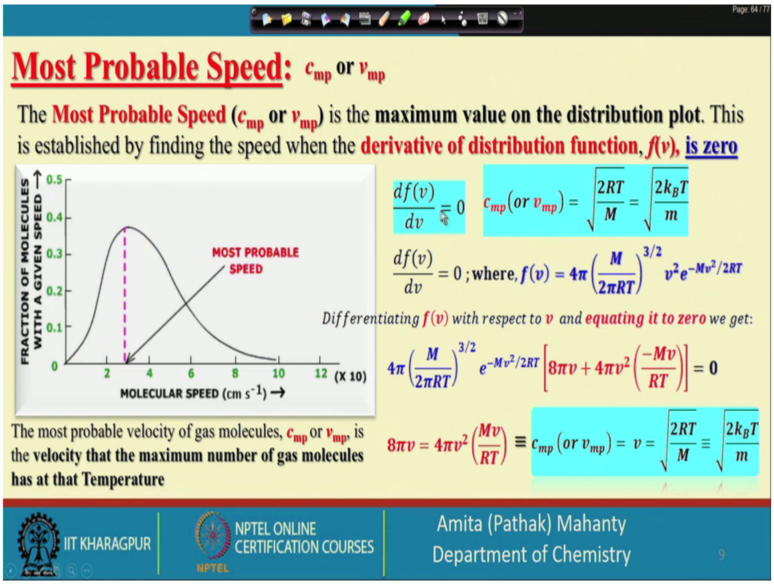
NPTEL ONLINE CERTIFICATION COURSES

Amita (Pathak) Mahant

Department of Chemist

I would like you to draw do this yourself and you see we have discussed this in the previous class, how the shape of the distribution curve for energy is going to be much steeper here then that of the molecular distribution of speed. So, this is how we have we have the distribution function in terms of the energy.

(Refer Slide Time: 22:45)



Page: 64 / 77

Most Probable Speed: c_{mp} or v_{mp}

The **Most Probable Speed** (c_{mp} or v_{mp}) is the **maximum value on the distribution plot**. This is established by finding the speed when the **derivative of distribution function, $f(v)$, is zero**

$$\frac{df(v)}{dv} = 0 \qquad c_{mp}(\text{or } v_{mp}) = \sqrt{\frac{2RT}{M}} = \sqrt{\frac{2k_BT}{m}}$$

$$\frac{df(v)}{dv} = 0\,;\text{where, } f(v) = 4\pi\left(\frac{M}{2\pi RT}\right)^{3/2} v^2 e^{-Mv^2/2RT}$$

Differentiating $f(v)$ with respect to v and equating it to zero we get:

$$4\pi\left(\frac{M}{2\pi RT}\right)^{3/2} e^{-Mv^2/2RT}\left[8\pi v + 4\pi v^2\left(\frac{-Mv}{RT}\right)\right] = 0$$

$$8\pi v = 4\pi v^2\left(\frac{Mv}{RT}\right) \equiv c_{mp}(\text{or } v_{mp}) = v = \sqrt{\frac{2RT}{M}} \equiv \sqrt{\frac{2k_BT}{m}}$$

The most probable velocity of gas molecules, c_{mp} or v_{mp}, is the **velocity that the maximum number of gas molecules has at that Temperature**

Amita (Pathak) Mahanty
Department of Chemistry

9

Now, what we are, I am going to look into is we have in the last class we have talked about the most probable speed, we have talked the RMS speed, we have talked about the average speed but we have not actually found out in the expression. I want you to do this.

The most probable speed for finding out the most probable speed the maximum value can this value is the maximum value of the distribution curve corresponding to this. So, if we want to find out the maxima of a certain thing, then what you have you have take the differentiation and put it equal to 0 is the point where you have the value estimated for the maximum point in a curve ok.

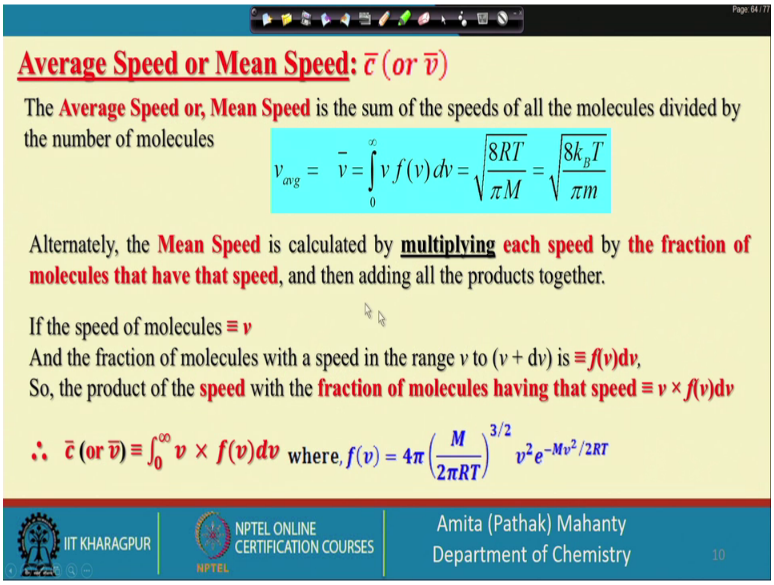
I hope you know that; when you are doing a differential calculus to find out a maxima in a particular point for a particular plot, the point which is having the maxima will have a differential value equal to 0. So, that this is established by this is going to be used to find out the most probable speed because most probable speed is the place where you have the peak of the distribution curve.

So, this is the distribution and which if we differentiate with respect to the d v, then that should be equated to 0. And if I equate to equate that to 0, if this is my probability distribution curve, I differentiate with respect to d v and then equate it to 0. So, this is what I get you just have a look at how what we have done I have differentiated this with respect to d v, so, which is the term which is going to be there.

So, this is this will not be affected this remains as it is. So, what is going to be affected? This v term and e to the power term is also going to be affected. So, what we get the first differential we are going to get is 8 pi v from this expression and then you have 4 pi v square. This is coming from this expression. So, if I now get, if I have this entire expression equal to 0, this is constant, this is does not get changed because these are does not have the variable.

So, if you can keep this equate this to 0. So, eventually what you get is 4 8 pi v equal to this one and from here, you see you can get the value in terms of the R T by M or k B T by small m. I hope you have understood how to do it you just have to differentiate the distribution function with respect to d v that the velocity in what do you call say the interval and then, you equate that to 0 is 0 and whatever velocity expression you get from here will be the most probable speed ok.

(Refer Slide Time: 25:54)



Average Speed or Mean Speed: $\bar{c}\ (or\ \bar{v})$

The **Average Speed or, Mean Speed** is the sum of the speeds of all the molecules divided by the number of molecules

$$v_{avg} = \bar{v} = \int_0^\infty v\, f(v)\, dv = \sqrt{\frac{8RT}{\pi M}} = \sqrt{\frac{8k_BT}{\pi m}}$$

Alternately, the **Mean Speed** is calculated by **multiplying** **each speed** by **the fraction of molecules that have that speed**, and then adding all the products together.

If the speed of molecules ≡ v
And the fraction of molecules with a speed in the range v to $(v + dv)$ is ≡ $f(v)dv$,
So, the product of the **speed** with the **fraction of molecules having that speed** ≡ $v \times f(v)dv$

$$\therefore\ \bar{c}\ (\text{or } \bar{v}) \equiv \int_0^\infty v \times f(v)dv \quad \text{where, } f(v) = 4\pi\left(\frac{M}{2\pi RT}\right)^{3/2} v^2 e^{-Mv^2/2RT}$$

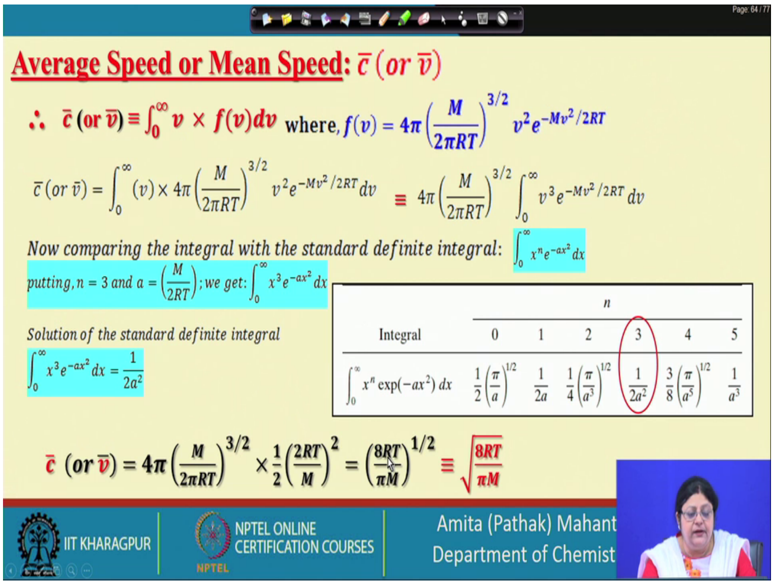
Amita (Pathak) Mahanty
Department of Chemistry

So, similarly, if you want to find out the mean or the average speed, the average mean speed is the sum of the speeds of all molecules divided by the total number of molecules. So, sum of all molecules is divided by the total number or in alternately we see, we can say the mean speed is can be calculated by multiplying each speed term by the fraction of molecules that have that particular speed.

So, then adding all these products together, we should get the mean speed. So, what we are going to multiply? Multiply each of the speed term with the fraction of the molecules in that particular speed and then add up all the products ok. So, they have the speed of the molecules is v, the velocity of the molecules in the range is going to be v a if v f d v, the product of this will be this one, right. So, I product of this and now how I sum it up. I sum it up means if I keep summing, then I can actually the discrete can be put to in a continual continuous integral.

So, I can integrate it from 0 to infinity to get the total products, a multi black replication of total products. So, this is how I am going to get.

(Refer Slide Time: 27:26)



Average Speed or Mean Speed: $\bar{c}$ (or $\bar{v}$)

$$\therefore\ \bar{c}\ (\text{or } \bar{v}) \equiv \int_0^\infty v \times f(v)dv \quad \text{where, } f(v) = 4\pi\left(\frac{M}{2\pi RT}\right)^{3/2} v^2 e^{-Mv^2/2RT}$$

$$\bar{c}\,(or\ \bar{v}) = \int_0^\infty (v)\times 4\pi\left(\frac{M}{2\pi RT}\right)^{3/2} v^2 e^{-Mv^2/2RT}dv \equiv 4\pi\left(\frac{M}{2\pi RT}\right)^{3/2}\int_0^\infty v^3 e^{-Mv^2/2RT}dv$$

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

putting, $n = 3$ *and* $a = \left(\frac{M}{2RT}\right)$*; we get:* $\int_0^\infty x^3 e^{-ax^2}dx$

Solution of the standard definite integral

$$\int_0^\infty x^3 e^{-ax^2}dx = \frac{1}{2a^2}$$

	n					
Integral	0	1	2	3	4	5
$\int_0^\infty x^n \exp(-ax^2)\,dx$	$\frac{1}{2}\left(\frac{\pi}{a}\right)^{1/2}$	$\frac{1}{2a}$	$\frac{1}{4}\left(\frac{\pi}{a^3}\right)^{1/2}$	$\frac{1}{2a^2}$	$\frac{3}{8}\left(\frac{\pi}{a^5}\right)^{1/2}$	$\frac{1}{a^3}$

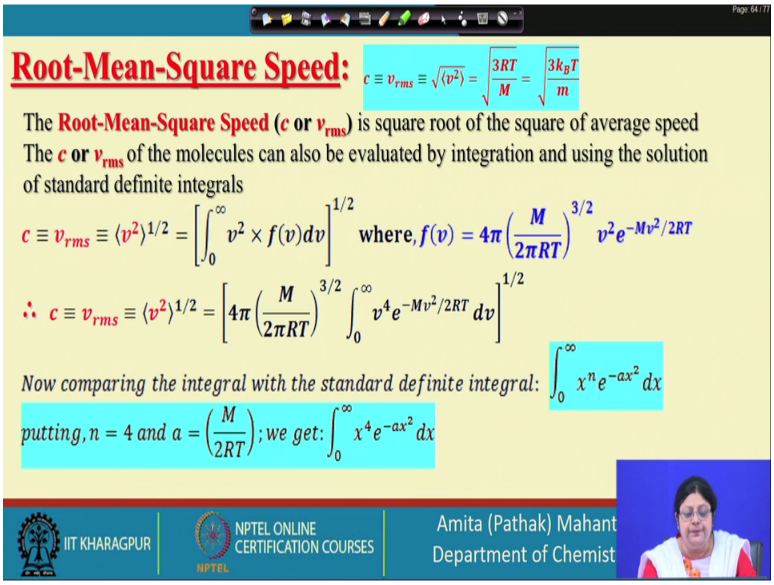
$$\bar{c}\ (or\ \bar{v}) = 4\pi\left(\frac{M}{2\pi RT}\right)^{3/2} \times \frac{1}{2}\left(\frac{2RT}{M}\right)^2 = \left(\frac{8RT}{\pi M}\right)^{1/2} \equiv \sqrt{\frac{8RT}{\pi M}}$$

So, this is the function which we I have. So, I put it here, just have a look what we have done. We have just taken this we have differentiate this d v function, we put d from the function is itself and then we have put v because the velocity at each multiplied by the fraction of the molecules in that and then summing up for all particular molecules. So, I integrate; instead of summing up, I have integrated.

Now, I have a look at to the expression which we get. This is the expression we have. Now all these terms are at constant. So, we can take it out. We are left with this expression. Now when this is a standard integral the standard integral is something like this, now compare it with this the standard integral, I am given from the handbook. So, the standard integral if you compare with this and this, here n becomes equal to 3. If n becomes equal to 3, then the product of this expression becomes 1 by 2, 2 a square and what is the a square which we have defined the a square will be M by 2 pi a R T.

From here, we are comparing this entire thing to be a minus a square a x square. So, if I take x as v, then M by 2 R T will become the a. So, if I put it there, you see the integral value becomes here. Now I put a it I just is just the simplification, what I put I find out the total the value of c or the v, the average mean value by multiplying this into whatever fraction which we have derived from this. If you multiply this, you will get a expression something like this. If you had until you do it yourself, it is difficult to understand. It is just a simplification step.

(Refer Slide Time: 29:18)



Root-Mean-Square Speed: $c \equiv v_{rms} \equiv \sqrt{\langle v^2 \rangle} = \sqrt{\frac{3RT}{M}} = \sqrt{\frac{3k_BT}{m}}$

The **Root-Mean-Square Speed** (*c* or v_{rms}) is square root of the square of average speed

The *c* or v_{rms} of the molecules can also be evaluated by integration and using the solution of standard definite integrals

$$c \equiv v_{rms} \equiv \langle v^2 \rangle^{1/2} = \left[\int_0^{\infty} v^2 \times f(v)dv\right]^{1/2} \quad \text{where, } f(v) = 4\pi\left(\frac{M}{2\pi RT}\right)^{3/2} v^2 e^{-Mv^2/2RT}$$

$$\therefore\ c \equiv v_{rms} \equiv \langle v^2 \rangle^{1/2} = \left[4\pi\left(\frac{M}{2\pi RT}\right)^{3/2} \int_0^{\infty} v^4 e^{-Mv^2/2RT}\, dv\right]^{1/2}$$

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

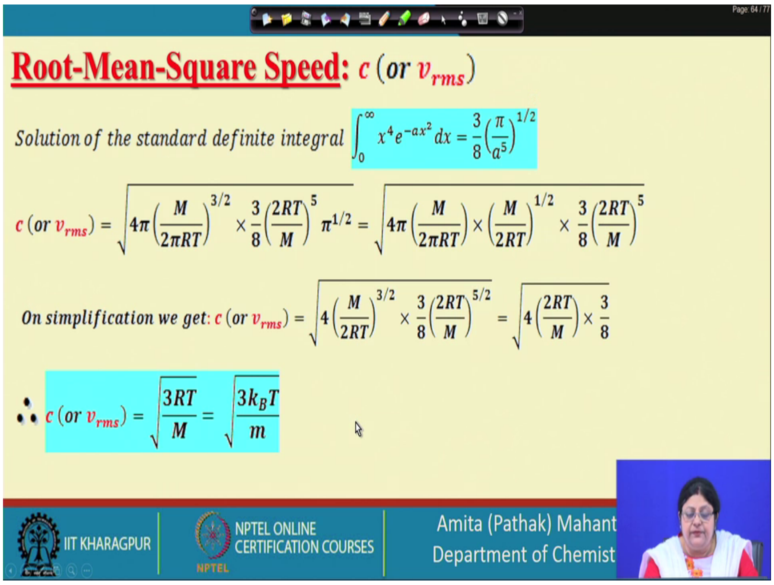
putting, $n = 4$ *and* $a = \left(\frac{M}{2RT}\right)$; *we get:* $\int_0^{\infty} x^4 e^{-ax^2} dx$

Similarly, when we want to find out Root Mean Square, what do we do? Root Mean Square means root square of the average, square of the average speeds with each of the speed which we have to take. So, and we have to take the square of it. So, the c or the RMS speed both of them are same. The molecules can be evaluated by integrating or we say the sum of all the events or we can say integration using the solution of a standard integral.

So, here what we have. Here we have, the square root of square of averages. So, average speeds which we have if we denote v, then we have square of that and under root of that. So, this is the function which we are going to get. I hope you are understanding. So, this is the function we are going to get that will be raised to the power half according to the expression. And what is the function? Function is already known to you. So, if the function already has a 3 v term. So, if you have another v squared term here then you have v to the power 4 and the whole thing is raised to the power half because that is that definition of RMS speed which we have. It is a square root of the square of average speeds.

Now, we can compute this by comparing this with the standard integral something like this, a is the constant terms other than the v 1, v term is going to be the expression equivalent to x. So, we what we have it is x cos x square and there are other a term will be M by 2 by R T, 2 R T and then what is the n here n is 4 right.

(Refer Slide Time: 31:05)



Page: 64 / 77

Root-Mean-Square Speed: $c\ (\text{or } v_{rms})$

Solution of the standard definite integral $\int_0^\infty x^4 e^{-ax^2}\,dx = \frac{3}{8}\left(\frac{\pi}{a^5}\right)^{1/2}$

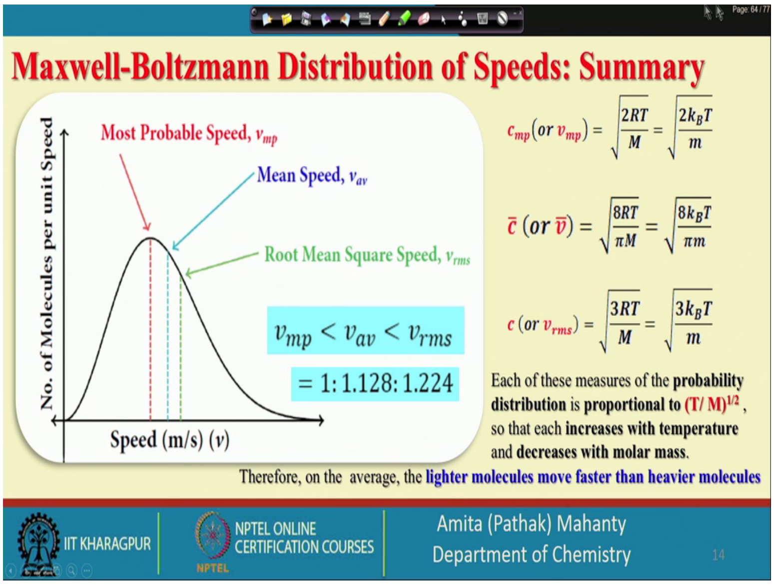
$$c\ (\text{or } v_{rms}) = \sqrt{4\pi\left(\frac{M}{2\pi RT}\right)^{3/2} \times \frac{3}{8}\left(\frac{2RT}{M}\right)^5 \pi^{1/2}} = \sqrt{4\pi\left(\frac{M}{2\pi RT}\right) \times \left(\frac{M}{2RT}\right)^{1/2} \times \frac{3}{8}\left(\frac{2RT}{M}\right)^5}$$

On simplification we get: $c\ (\text{or } v_{rms}) = \sqrt{4\left(\frac{M}{2RT}\right)^{3/2} \times \frac{3}{8}\left(\frac{2RT}{M}\right)^{5/2}} = \sqrt{4\left(\frac{2RT}{M}\right) \times \frac{3}{8}}$

$$\therefore\ c\ (\text{or } v_{rms}) = \sqrt{\frac{3RT}{M}} = \sqrt{\frac{3k_BT}{m}}$$

If you have n is 4, then you compare that with the standard integral, the expression is something like this. I have done it for you, but it is just a simplification that you put in ok.

(Refer Slide Time: 31:14)



Maxwell-Boltzmann Distribution of Speeds: Summary

$$v_{mp} < v_{av} < v_{rms}$$

$$= 1:1.128:1.224$$

$$c_{mp}(or\ v_{mp}) = \sqrt{\frac{2RT}{M}} = \sqrt{\frac{2k_BT}{m}}$$

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

$$c\ (or\ v_{rms}) = \sqrt{\frac{3RT}{M}} = \sqrt{\frac{3k_BT}{m}}$$

Each of these measures of the **probability distribution** is **proportional to** **$(T/M)^{1/2}$**, so that each **increases with temperature** and **decreases with molar mass.**

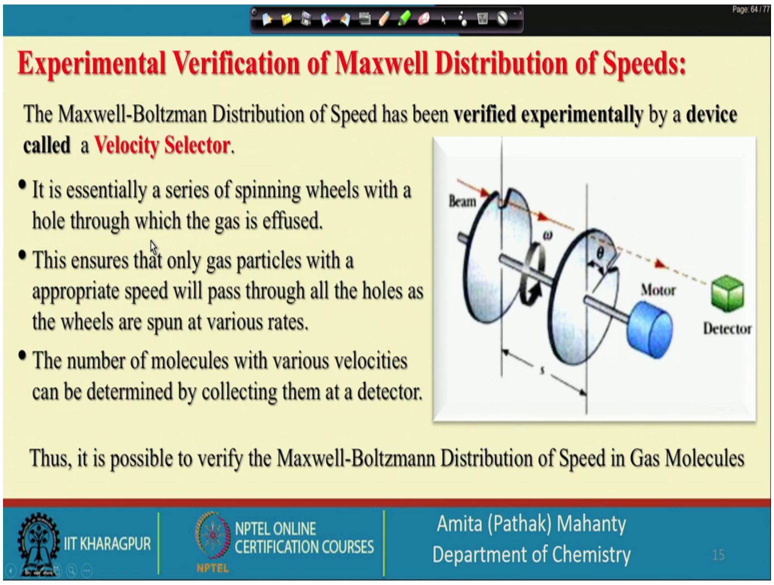
Therefore, on the average, the **lighter molecules move faster than heavier molecules**

IIT KHARAGPUR | NPTEL ONLINE CERTIFICATION COURSES | Amita (Pathak) Mahanty
Department of Chemistry

So, we have done and discussed this previously, all these expressions which you have. Each of this probability distribution is proportional to M by T by M half to the power half; that means, increase in temperature and decrease with, decreases with the molar mass. So, the lighter molecules move faster than the heavier molecules. This is what we had discussed in the last class.

We had only talked about how it is you have to look into the thing that the value of the speed and RMS speed is going to be the highest. The mean is going to be somewhere in between the most probable and the RMS and the mean the most probable is always going to be representation of the peak; that means, this most probable means this is the fraction of the molecules, maximum fraction of the molecules are having this particular speed not the highest speed maximum probable fraction of the molecules are having this particular speed is known as the most probable.

(Refer Slide Time: 32:19)



Experimental Verification of Maxwell Distribution of Speeds:

The Maxwell-Boltzman Distribution of Speed has been **verified experimentally** by a **device called** a **Velocity Selector**.

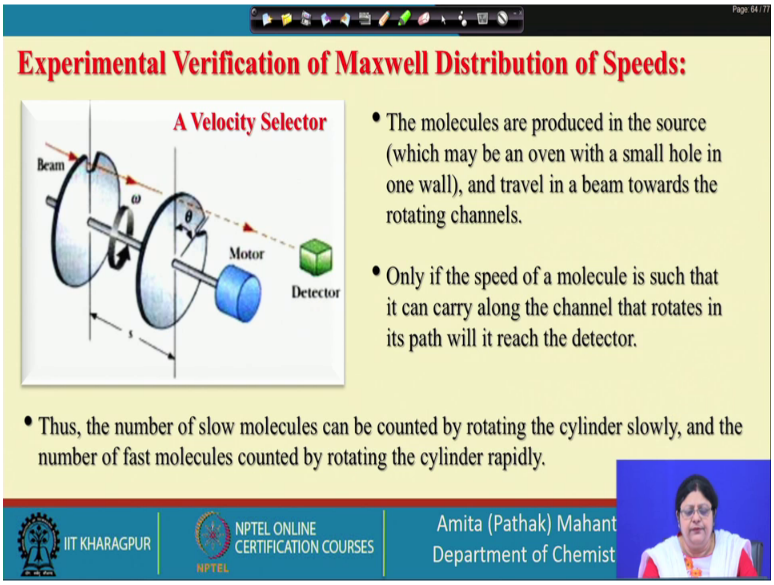
- It is essentially a series of spinning wheels with a hole through which the gas is effused.
- This ensures that only gas particles with a appropriate speed will pass through all the holes as the wheels are spun at various rates.
- The number of molecules with various velocities can be determined by collecting them at a detector.

Thus, it is possible to verify the Maxwell-Boltzmann Distribution of Speed in Gas Molecules

So, we can verify this with the distribution function by using velocity. See, we have done the Maxwell's distribution, now we need to know whether the distribution which whichever we have derived is going to be followed. So, for that we need to do some experiments and this experiment is done by a device using a device called the velocity selected. What is it? It is a series of spinning wheels with a hole through which the gas can pass or refuse. This ensures that only a gas particular particularly particle with particular appropriate speed will pass through all their holes, as the spins and then wheels are also moving the wheels are moving, the wheel has a speed of their own the there are holes in the wheel.

So, if the particular molecule is passing, then they have to have a appropriate speed to pass through the hole; the number of molecules for the various velocity can be determining, by collecting the samples in the detector.

(Refer Slide Time: 33:30)



Experimental Verification of Maxwell Distribution of Speeds:

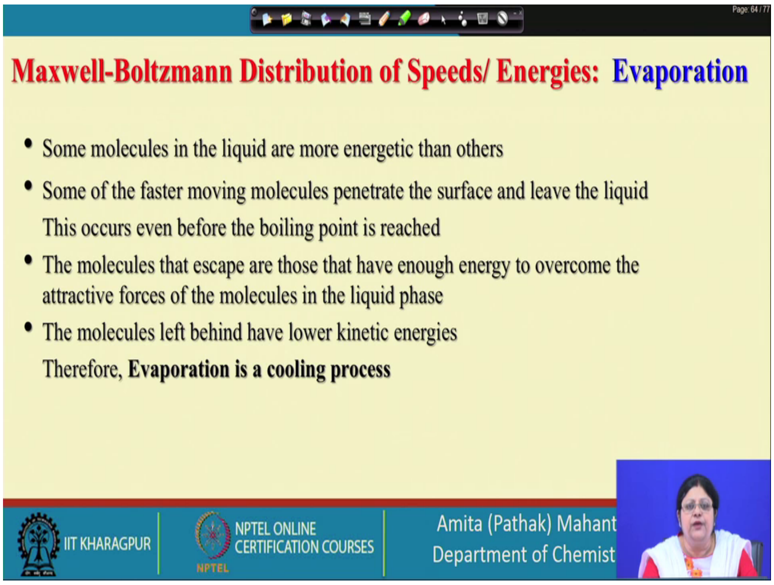
A Velocity Selector

- The molecules are produced in the source (which may be an oven with a small hole in one wall), and travel in a beam towards the rotating channels.
- Only if the speed of a molecule is such that it can carry along the channel that rotates in its path will it reach the detector.
- Thus, the number of slow molecules can be counted by rotating the cylinder slowly, and the number of fast molecules counted by rotating the cylinder rapidly.

And we can verify that the molecules are produced in the source from here, only if this molecules in such a is such that it carries along with the channel through passing through the hole which is a put on mounted on the wheel which is also having a speed is going to pass through.

The number of slow moving molecules can be calculated by rotating the cylinder slowly and the number of fast moving can be found out by increasing the speed of the wheels which we are looking into. So, this gives you that if you see the detector, you can find out the number of particles which you are having a particular speed.

(Refer Slide Time: 34:15)



Maxwell-Boltzmann Distribution of Speeds/ Energies: Evaporation

- Some molecules in the liquid are more energetic than others
- Some of the faster moving molecules penetrate the surface and leave the liquid
  This occurs even before the boiling point is reached
- The molecules that escape are those that have enough energy to overcome the attractive forces of the molecules in the liquid phase
- The molecules left behind have lower kinetic energies
  Therefore, **Evaporation is a cooling process**

If you collect it over a sample, then you will see that they are following the distribution law which we have already discussed.

Now, we can extend the distribution law to a certain concept which is everyday experience for us. Suppose we are talking about evaporation, what is evaporation and if you have noticed the evaporation is always a cooling process, what happens; some molecules are in the little liquid or which is highly energetic there on the surface, they leave. They are having sufficient energy to intercom overcome the intramolecular forces which is existing with them or within the liquid.

So, as soon as these molecules which are of higher energy, higher speed; higher energy is associated with higher temperature. So, whenever the molecules which is having higher energy, it tends to escape from the surface; what happens the molecules of the fraction of molecules with high energy is now gradually leaving the surface. So, higher energy associated is essentially meaning that the in a system is going to have higher temperature.

So, if the higher energy molecules are escaping because they are having sufficient energy to overcome the intermolecular forces there is existing in the liquid, then the fraction of the higher high energy molecules is reduced, so that if fraction of molecules having higher temperature is reduced. So, evaporation should be a cooling process ok.

Thank you. We will discuss the next class.