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# Lecture-15 Topic-Molecular Effusion: Theory and Applications

Hello and welcome back to another lecture on this NPTEL course of thermal physics. Now in today's class we will be discussing about effusion. So, far we have discussed about transport properties like diffusion, thermal conductivity and viscosity. And we have seen that their results of molecular collision actually that leads to the exchange of velocity and leads to the exchange of energy, leads to the exchange of particle between different parts of the gas assembly.

So, whenever there is a gradient of some sort whether let it be a temperature gradient or a velocity gradient or density gradient we have one of this properties coming into action in order to equilibrate the system. Now during the discussion of these properties we have always considered the closed system; when I say closed system I mean that we have a vessel of gas which is enclosed from all sides and whatever is happening is happening inside that vessel.

Now for today's lecture we will be talking about effusion which is a property or which is a phenomena that occurs when there is a small hole in that container. Now when we say small it has to be referred whether I mean it has to have some kind of a reference size to compare with. Now it so happens that this is the reference size in this case is the mean free path of the assembly.

Now effusion is the process which leads sometimes to let us say let us assume that you have a bicycle I hope most of you have a bicycle. Now this bicycle sometimes we have to pump, maybe once in few weeks or maybe once in month 1 month or sometimes even 2 months if the tire and tube condition is new we have to put some air into the tire. So, that the right pressure is maintained.

So, it is we considered that to be normal when I mean it is supposed to be a closed system a tire or tube system it should not have any leak but still over a span of few weeks to few months and sometimes even in few days time we see the pressure is leaking, how many times

you have a situation that your cycle pressure is lost in 4 or 5 days or sometime within a week your time you are losing pressure on one of your wheels and when you take it to the shop they cannot detect the leak.

They call it the hidden leak, now it so happens these leaks are so small that these are not detectable by the standard bubble test they do in a bicycle repair shop, they just inflate the tube put it inside a container full of water and look for the bubble. Now when there is bubble let us say there is a one bubble every few seconds it is absolutely detectable, sometimes the leaks are even so big that even without doing this bubble test we can realize where the leak is?

But let us assume a situation where there is one bubble every 10 minutes, there is a very tiny leak and one bubble every 10 minutes or let us say not even 10 minutes, one bubble in every 1 minute is coming up. So, by the time that particular portion of the tube is dipped inside water maybe it has released a bubble, maybe it has not even released a single bubble.

But still it is a leak and you will realize that only after few days when let us say of course there are two tires in your bicycle, you inflate them at the same time in approximately the same pressure, one remains intact I mean hard even after 5 days the other becomes soft then you know there is a hidden leak, most of the time. So, these cases are the cases of effusion. Now let us try to understand it in a more systematic manner.

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So, molecular effusion is typically taking place through a small hole, now when I say small that means the diameter of the whole D is much, much less compared to the mean free path. Now what is the difference of so in the last class in end of lecture 14 we have solved a problem from the classroom problem set in which the diffuse gas was leaking out of a hole across I mean and there was a pressure gradient that has been mentioned. Now in case of effusion what happens is this pressure gradient is not developing at any moment.

So, first of all there is a hole which is the typical diameter of the hole is much less compared to the mean free path and molecule leaks out without any push back that means whatever goes out, goes out nothing goes in from the other end. That is one of the primary assumptions of effusion and finally there is no pressure or density gradient that should be developed around this hole.

What I mean by this is let us say so if there is a density gradient that has been generated that means the molecules from different parts will be pushed towards this hole because of the density gradient, but in effusion what happens is the dimension of the hole is so small, so tiny that only the molecules that will fall upon this hole by chance only those will go outside, go through this hole. A molecule which is slightly further away from the hole has no knowledge that there is a opening somewhere close by, because there is no finite pressure or density gradient that is generated in the vicinity of this opening.

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So, the opening has to be that tiny, that small, so that there is no pressure or density gradient that will generate around this. If that happens then we cannot call it an effusion anymore we

have to go back to the domain of diffusion when there is a finite pressure gradient and the molecules are coming I mean driven towards that pressure gradient from all directions and finally they are going out of that hole. So, I hope this gives you a clear idea or clear difference between the effusion and the diffusion process. In effusion process there is no pressure gradient and whatever happens just because let us say this molecule; this is the molecule of interest.

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Somehow makes its way through collision and falls upon this hole and then it goes out. Of course as there are very large number of collision and large number of particles inside even that will lead to a certain I mean considerable number of molecule loss from this gas assembly.

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So, now let us look into the mathematics of this system, mathematics of this, you see phi which is the flux, flux means number of particles that will be heating in unit time per unit area, that is called the flux and phi is equal to 1 4 n c bar. Now what we can do is we can substitute n is equal to p by K b T which is directly from the ideal gas equation and of course c bar is equal to 8 KT by pi m which is the result of the Maxwell's distribution of velocities. So, by substitution we see phi is equal to 1 4 p by K b T root 8 KT by pi m.

So, there is a root T here, there is a T here that cancels out and finally we get an expression of phi which is p divided by root over 2 pi m K b T. Also we can simply multiply you see there are two terms which are microscopic in nature. One is m, one is K b, K b is typically the measure of thermal energy per molecule and m is the mass of a molecule. So, I can multiply N A and N A with that.

Please remember that this thing is inside a root, so N S square will be N A outside, so we have to just multiply this with N A in the numerator and we can write the denominator as 2 pi m RT because small m times N A is M, k b times N A is R. so, we see that the flux phi is proportional to given that the diffusion is or effusion is so small that it is not giving rise to a noticeable change in pressure. So, we can assume that pressure is constant for a while of course pressure will change eventually it will not be a constant forever.

Because even if small number of molecules start escaping one by one, so eventually the number density will be lower. So, if we start with some known number density n, it will eventually go down. Similarly n and p they are directly linked with each other, so the pressure will also be lost. So, you see but for a short period of time or for a period of time for which the pressure will not change significantly, we can assume pressure to be a constant.

And of course temperature can be kept constant by putting this system inside on top of a heat path that can be done. So, we can readily see that the right hand side depends varies inversely proportional to M the molecular mass. And this leads to a law called the Graham's law of effusion which states at constant pressure the flux through a small hole is inversely proportional to the square root of the molecular weight of the gas.

So, if we have two gases inside similar container with similar dimension of hole punched present in both the container. And if one gas has higher molecular weight the other gas has

lower molecular weight. Of course the gas with lower molecular weight will effuse faster as compared to the gas with higher molecular weight; this is precisely the Graham's law of effusion. Now we will see an example of this law when we will be solving the problem set, not 1 but basically we will take 1 direct example and also there are other cases which will be taking up.

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if A is the cross section area of the hole then total number dN escaping in dt dN = - \$ A dt  $\frac{dN}{dE} = -\phi A$ dm = - m\$A+(m→ molecule mass) dv/dt = - \$A/(n→ number density) --- --

Now if A is the cross section of the hole in question and then the total number of particle that will be escaping in time dt, please remember phi is given in the units of number per unit area, that means a number per unit area per unit time. So, if I want to get the number for a given time interval and the whole dimension is given the cross section area of that opening is given, then dN is simply minus phi A dt.

And this negative sign over here, this is why because we are losing out molecules, so number is decreasing that is why there is a negative sign. So, eventually we can write dN dt is equal to minus phi A, will be using this to solve one of the problems. Also all we have to do is if we want to just check what is this change in mass of that container with time, so we have to compute a quantity that is dM dt which is nothing but dN dt multiplied by mass of each molecule which is minus m phi A.

And in a similar manner we can also compute the volume, so the volume change, so I mean it is not exactly the volume of the container, volume of the container remains the same. But volume of the effused gas assuming that the number density remains constant is dN dt is equal to minus phi A by n. So, it is exactly the same expression but that is divided by n in the left hand side and the right hand side.

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Because please remember n is equal to N divided by v. So, if we want to get volume, all we have to do is we have to divide N by, so we have to divide this expression by n here.

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So, now the next topic that I would like to draw your attention is the speed of the molecules that will be effusing. Now let us quickly go back to this picture of molecules effusing out of the box through a very small hole. So, let us assume that we are just focusing attention on one molecule that is present here and another molecule that is also present close by.

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Let us say these are two molecules. Now if the molecules are I mean of course there is a finite probability that both these molecules will eventually go out of this hole. And let us assume that one of the molecules has a higher velocity as compared to the second molecule. It is possible because when we talk about molecular speed distribution, we accept the fact that the molecular speed has a wide distribution, so molecules can have very low or very high speed.

And the molecule that are or the mean speed or RMS speed which we consider is actually the ensemble averages. So, when we assume that this black molecule is basically fast as compared to the blue molecule. And please remember black molecule I mean both the molecules black and the blue molecules they can go randomly anywhere in any direction.

But given the fact that the black molecule has a faster speed as compared to the blue molecule and they start of more or less I mean at the time we start the observation they are very close by, they are kind of in the same region of the box. The chance the black molecule it will eventually move it is way through the many collisions and eventually going out of this is slightly higher as compared to the blue molecule primarily because the black molecule has higher speed.

Of course the speed is subject to change but typically the one that has high speed even after an elastic collision it will retain most part of it is speed. So, that is to say the effusion process selects I should not use the word select I should use the word select with quote and unquote. It kind of it is slightly biased towards molecules which has higher speed as compared to the average speed of the gas assembly. So, that is why faster molecules has a greater probability to reach the whole from different parts. And the speed distribution function will have, it can be shown systematically that speed distribution function of the effused molecule. If we place some kind of a detector outside here, this is for the speed detector if we arrange something and measure the distribution of molecular speed. Of course there will be a distribution but the distribution it can be shown that this will have an additional velocity speed term into it.

And it will be not a c square e to the power minus b c square type of dependence but it is a c cubed e to the power minus b c square of a dependence. So, if black line is the Maxwell speed distribution law then the red line will be the effusion the speed distribution of the effused molecules. Similar, so for these exact same reason the mean kinetic energy will also be slightly higher. So, we have discussed the phenomena of effusion. Now it is time that we look into some very basic problems on this topic.

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So, question number 9, an unknown gas has a rate of effusion which is 4 times faster than oxygen gas. Determine the identity of the gas. So, this is the only information that is given that, so when the effusion rate is given, we have to assume that identical condition has been maintained. So, all we know that, so what we have to do is? We have to remember that phi is proportional to M, so 5 being the number of particles per unit time per unit area. So, if I just leave the area out of question, number of particles per unit time which is basically d phi dt will be proportional to 1 over m once again.

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And this is precisely the Graham's law of effusion, so R is proportional to 1 over m and m of oxygen is 16. So, m of the unknown gas I just marked it with or the rate of effusion for the unknown gas which I just labeled as u and the ratio of rate of oxygen effusion of oxygen is M 0 by M u whole root which is given as 4. So, the red difference or the ratio of the rate is given as 4.

So, this gives you and M 0 is 16, so this gives you M u is equal to 1 which is possible only for hydrogen gas. So, the gas is in question is the hydrogen gas. Now for the next question problem number 10. We have a closed vessel is partially filled with liquid mercury with a small hole of area 10 to the power minus 7 meter square in it. The vessel is placed in a region of high vacuum at 273 Kelvin and after 30 days it is found to be lighter by 2.4 into 10 to the power 5 kg. Find the vapour pressure of mercury at 273 Kelvin, so this is the question we have.

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Combining  $b = \sqrt{\frac{2\pi n^{T}}{m}} \frac{1}{A} \left| \frac{dm}{dt} \right| = \frac{1}{A} \sqrt{\frac{2\pi R^{T}}{m_{w}}} \frac{dm}{dt}$ Knudsen method for measurement of vapour pressure) 2.4×10-5 kg/see = 9.26 × 10 2 kg / see A = 107 m2, Mw = 200.6  $b = 10^{7} \times 9.26 \times 10^{-12} \sqrt{\frac{2 \times 17 \times 8.3}{2 \times 50.6}}$ .....

Now the experiment that has been described here is actually called the Knudsen method for measuring vapour pressure of certain liquids. So, I will very briefly discuss this one the experiment, then you will have a slightly better idea of what I am talking about. It is very simple experiment.

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So, we have a weighing balance let us say. So, we have a weighing balance which has a scale, I think you are all familiar with this. So, it has a scale, now what we do? We place a vessel on top of this, so we place a vessel on this and let us assume that there are gas particles inside, so this is the vessel fantastic, I hope you understand what I am trying to draw here. And let us say there is a small hole through which gas molecules they escape.

Now as the gas molecule escapes the reading goes down. And we see we have already derived an expression which was already there here so dM dt is equal to minus m phi A which can be slightly modified by this relation. So, you see let us go back here, so dM dt is equal to m phi A. And phi is p by root 2 pi m k b T, so combining we have p is equal to root over 2 pi k b T by m 1 over A and times dM dt.

So, after simplification we have 1 by A root over of 2 pi RT by M w which is the molecular weight of the gas, molecular weight of the gas in question and dM dt. So, this is the equation, so if we know dM dt we can calculate p. Now the question is what is the p we are talking about. We have a certain liquid, so some liquid which is filled in this. Now liquid has a tendency to evaporate, right and we have to measure the vapour pressure. So, if this is the liquid, the top of the liquid will be filled with vapour.

So, we have liquid and we have vapour. This vapour will be effused slowly through this small hole. Now as it effuses and please remember vapour pressure is a measure of the I mean characteristics of this particular substance. So, if we have a particular liquid present the vapour pressure will be p v and which is a fixed number it depends only on the temperature and this whole arrangement has to be maintained at a constant temperature T.

So, the vapour pressure which we measure by this, or so what I mean to say is p v will be a constant and it is a function of the temperature only. So, if we fix the temperature T and of course the vacuum the whole system has to be put under moderate vacuum. So, that the condition that nothing goes back inside this vessel is maintained. So, that means the effusion can be successfully performed.

So, what happens is, as the molecule loses it is as the assembly loses molecule the mass decreases we can measure the mass here. And corresponding pressure what we are talking about is maintained as the molecules are escaping this hole more and more molecules are going from the liquid to this vapour phase in order to maintain the vapour pressure. So, as I have said while deriving this expression that pressure will fall after a certain point, it will start falling noticeably after a certain time.

But in this case as long as there is liquid the pressure will remain constant, so this can be applied in order to measure the vapour pressure by using this simple relation. So, dM dt is

given here dM dt is 2.4 into 10 to the power minus 5 divided by 30 days. So, we have to convert everything in seconds and eventually we get a number 9.26 into 10 to the power minus 12 kg per second. A is given, M w is given, M w is the molecular weight of the mercury and we put everything inside here.

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And finally we get a number which I have not calculated; you can very easily calculate that. All we have to do is we have to simplify this expression but this is absolutely dual. Then we go to the last problem of this problem set and last problem of the week.

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And this is a problem in which it is basically once again the phenomena of effusion a thin walled vessel of volume V, kept at constant temperature. Please remember this is important, temperature is constant contains a gas which slowly leaks out through a small hole of area A.

The outside pressure is low enough, so that leakage back into the vessel is negligible once again the ideal condition for effusion.

And then what we have to find out is the time required for the pressure in the vessel to decrease by 1 by e times. As I have mentioned the pressure will decrease and here we have to find out the rate of decrease in terms of the quantity that is A, V and the mean molar molecular velocity c, which is once again a constant because even if the pressure is falling we are keeping the temperature intact.

Please remember what is the temperature expression root 8 kT by pi m, it depends only on the temperature. So, as long as the temperature is constant c is constant, V and A are of obviously the constant quantity. So, we have to find out the rate of effusion in terms of known parameters. So, same geometry, familiar equation that dN dt is equal to minus phi A, n is given by N by V, N being the total number of molecule.

So, we get dn dt is equal to, so if this is the relation then dn dt will be V times d N dt, phi is 1 4 in c bar. So, putting everything together we get dn dt is equal to small n, so that means the change in density is equal to minus Ac bar by 4 v times n. So, this is a differential equation which can very easily be integrated to get n is equal to n 0 e to the power minus Ac bar by 4 v times T. And keeping in mind that p is linearly proportional to n by p n p is equal to n by k b T in a similar manner and please remember temperature is constant.

So, we can simply write p is equal to p 0 e to the power minus t by t 0, where t 0 is nothing but 4 v by A c bar this factor here. So, this leads us to the final conclusion what amount of time the pressure falls to a factor of 1 by e that is when t is equal to t 0, so t 0 is my answer, it is 4 v by A c bar, this is the time in which the pressure will fall to it is value at 1 by eth of it is original value, starting value I would say.

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Correction to the expression · Presence of velocity "memory" · Effect of boundary (specially at low pressure) · Contribution of rotation and vibration in the molecular energy The expression for N, W and D are modified accordingly --- --- 🔳 🐘 🖉 🖉

So, this brings us to the last part, last 1 minute of this lecture which is the correction to the expression of the whatever transport properties we have derived so far. Now why there needs to be a correction, very briefly let me tell you there is a presence of velocity memory. So, in the basic assumption of Maxwell speed distribution function, we have assumed that all the collisions are uncorrelated.

So, 1 molecule that will collide once and it will collide the next, there will be no connection or no correlation between the velocity of the molecule before and after the collision. But this is not the case, the correlation is maintained, so these are complicated statistical theories, we are not going into the details of this but I can tell you, the correlation between molecular velocities are maintained.

So, basically as if the molecule maintains a memory of it is previous velocity I mean velocity before the collision even after this collision. And for low pressure the effect of boundary is also very important. We have always assumed that the boundaries are uniform, these are flat boundary and we have not considered the effect that what happens if the boundaries are not properly smooth or not there are certain bends and wedges in the boundary, we have ignored all these things.

And those things becomes very important especially when we are going to low pressure region. And finally we have not considered the contribution of rotation and vibrational degrees of freedom in the molecular energy expression. So, the expression of the parameters eta, k and D are to be modified accordingly. There are very detailed worked out theories which are available.





And the final corrected versions or advanced theory I mean the relations that we get from the first principles calculation that we have derived in the class, so the advanced theory which is available. We see interestingly that the basic dependence is properly captured. Basic dependence on the dimension of the molecule, basic dependence on of course there is one thing I forgot to mention that hard sphere approximation which we have assumed for the molecular collision might not be 100% correct.

Because sometimes the molecules just collides with themselves with the deformation of the shape which we have not considered. So, that hard sphere approximation also is not a very valid approximation in all possible cases. So, what we have is, so for example for eta we have two third pi d square m k b T by m whole to the power half. Here the pre factor is 5 by 16 instead of two third.

Similarly for k the pre factor is once again two third and we have a 25 by 32 pre factor rest are the similar I mean rest other parameters are the same, C v m is the specific heat per molecule. Similarly for the diffusion coefficient we have a pre factor of two third and it should be 3 by 8th. So, what we see that even with a very I mean advanced theory only the pre factors are changing not the basic dependence.

If you look at the basic dependence the basic functional forms are exactly the same. So, what we have learned although it is basic, for all practical purpose we can consider that to be good. Good enough in a sense for not only for a basic understanding but also we can be rest assured that these are you know very robust theories that we have learnt. And all the basic dependence on molecular parameters on temperature and pressure that we have derived are valid.

So, with this I bring an end to the discussion on this transport properties and transport coefficient. Not entirely because next week onwards we will be discussing Brownian motion, Einstein's theory of Brownian motion. And molecular diffusion will be also discussed from a slightly different perspective in the next week, till then thank you.