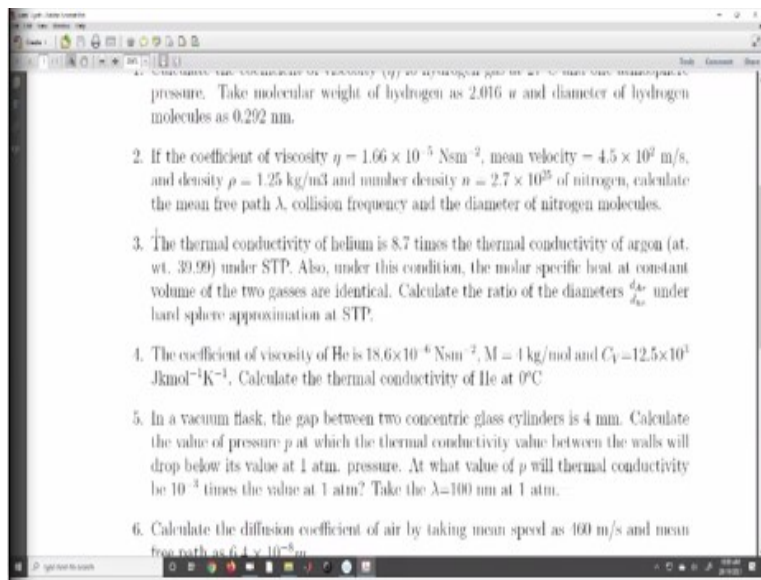


Thermal Physics
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Lecture-14
Topic-Diffusion Coefficient: Transport of Mass

Hello and welcome back to one more lecture on this NPTEL course on thermal physics. Now today is lecture number 14 and we will start from where we have left in lecture number 13.

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So, let us first look into this 2 problem sets in the classroom problem set of week 3 and we have, yeah. So, we have problem number 3 and 4 to begin with. So, the first problem is the thermal conductivity of helium is 8.7 times the thermal conductivity at argon which has an atomic weight of 39.99 under STP. Also under this condition the molar specific heat at constant volume of 2 gases are identical. Calculate the ratio of diameters under hard sphere approximation at STP.

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Classroom Problem; week-3

3) $M_{He} = 4$, $M_{Ar} = 40$
 $C_v \rightarrow$ identical

$$\frac{k_{Ar}}{k_{He}} = \frac{1}{8.7}$$

$$k \propto \frac{1}{\sqrt{m} d^2} = \frac{1}{\sqrt{m} d^2} \left(\bar{c} = \sqrt{\frac{8RT}{\pi m}} \right)$$

$$\left(\frac{d_{Ar}}{d_{He}} \right)^2 = \frac{k_{He} \sqrt{4}}{k_{Ar} \sqrt{40}} = \frac{8.7}{\sqrt{10}} \approx 2.75$$

$$\therefore \frac{d_{Ar}}{d_{He}} \approx 1.66$$

Now, in order to solve this problem we have to go back to the fundamental relation that the conductivity is actually proportional to or thermal conductivity ratio is given. Now we have to go back to this fundamental relation that k is actually proportional to 1 over root $m d$ square. Now this 1 over root $m d$ squared proportionality can might as well be written in terms of capital $M d$ square as we have discussed in one of the lectures. We just have to multiply the numerator and the denominator with a suitable constant, so that is the Avogadro number and we can write this as root over 1 by capital $M d$ square.

So, this we can use in order to compute the ratio of the 2 thermal conductivity which is in this particular form d of argon divided by d of helium whole square is equal to k of helium divided by k of Argon multiplied by the root 4 that is the atomic weight of helium and root 40 that is atomic weight of Argon. So, it will be now this ratio of k_H and k_r is already given as 8.7 in the problem. So, this ratio of diameter square is actually 8.7 divided by root over of 10 which is approximately 2.75 . Now if we take the root then we get the ratio of the diameter is approximately 1.66 .

So, it is a little tricky problem because we have to use the formula or we have to use this relation that k is proportional to 1 over $m d$ square. But once we get to that the rest calculation is extremely straightforward, right. Now for problem number 4, the coefficient of viscosity of helium is 18.6 into to the power minus 6 Newton second per meter square, capital M is 4 kg per

mole. That means basically it is another way of saying that the molecular weight of helium is 4 and C_v is equal to 12.5×10^3 joules per kilo mole inverse per Kelvin inverse.

So, from this data we need to calculate the thermal conductivity of helium at 0 degree centigrade. So, what is given? Given is the coefficient of viscosity and some other parameters and of course C_v is given. So, all we have to do is, we have to use the relation between the coefficient of viscosity and thermal conductivity in order to solve this problem.

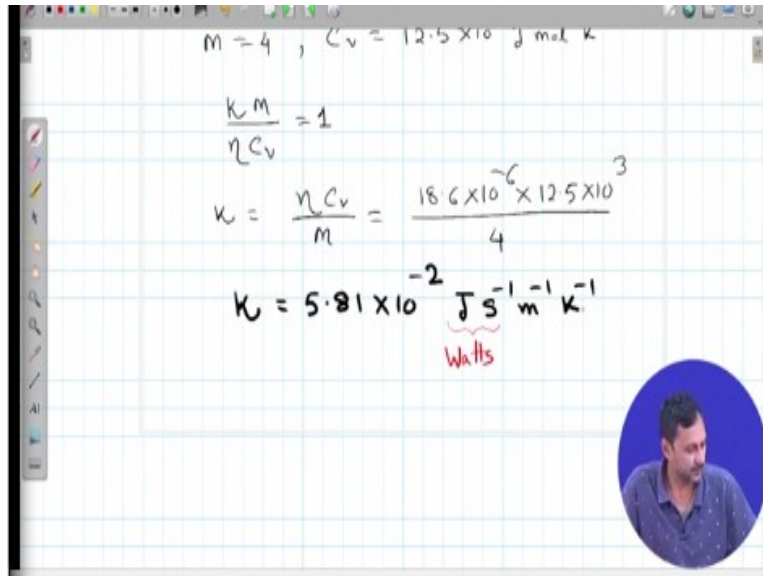
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4) For He,

$$\eta = 18.6 \times 10^{-6} \text{ N s m}^{-2}$$
$$M = 4, \quad C_v = 12.5 \times 10^3 \text{ J mol}^{-1} \text{ K}^{-1}$$
$$\frac{k M}{\eta C_v} = 1$$
$$k = \frac{\eta C_v}{M} = \frac{18.6 \times 10^{-6} \times 12.5 \times 10^3}{4}$$
$$k = 5.81 \times 10^{-2} \text{ J s}^{-1} \text{ m}^{-1} \text{ K}^{-1}$$

So, let us have a look at it. See, once again what are the data given η is equal to this M is equal to 4, C_v is given and we recall that $k M$ by ηC_v is equal to 1. So, this is the relation that we have derived in the class and we are just going to use this relation. Now from this relation all we have to do is, we have to write k is equal to ηC_v by M , we have to put the numbers and we get k is equal to 5.8×10^{-2} joules second inverse meter inverse Kelvin inverse.

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$$M = 4, \quad C_v = 12.5 \times 10^3 \text{ J mol}^{-1} \text{ K}^{-1}$$

$$\frac{\kappa M}{\eta C_v} = 1$$

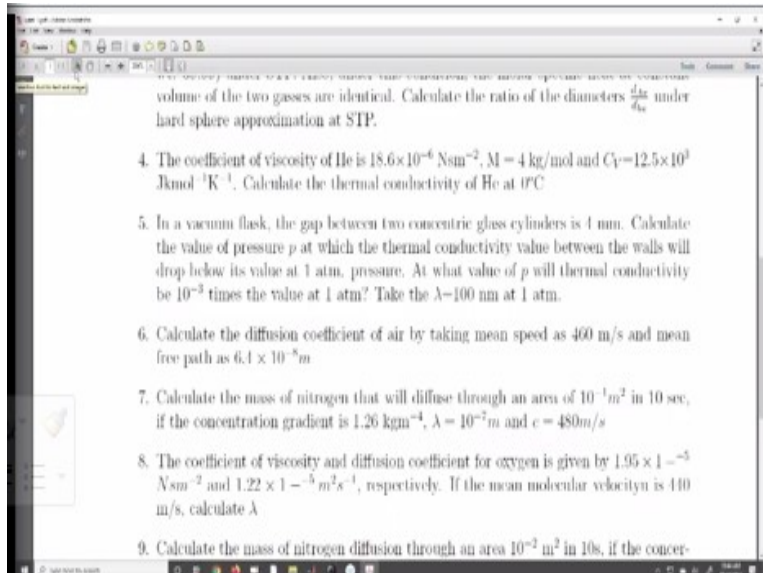
$$\kappa = \frac{\eta C_v}{M} = \frac{18.6 \times 10^{-6} \times 12.5 \times 10^3}{4}$$

$$\kappa = 5.81 \times 10^{-2} \text{ J s}^{-1} \text{ m}^{-1} \text{ K}^{-1}$$

Watts

And if you recall this is nothing but your Watts. So, this unit is same as Watts per meter per Kelvin. And then there is a third problem which I will not do it for you, so let us look at problem number 5.

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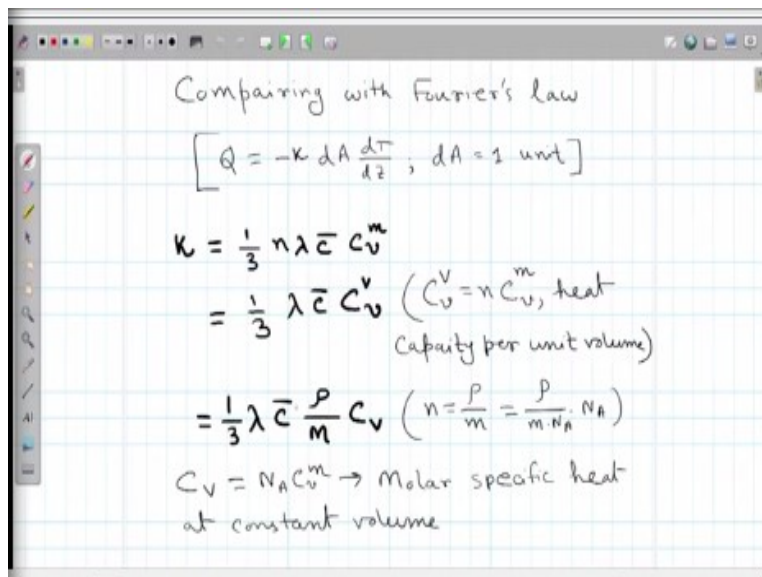
...volume of the two gases are identical. Calculate the ratio of the diameters $\frac{d_{He}}{d_{N_2}}$ under hard sphere approximation at STP.

4. The coefficient of viscosity of He is $18.6 \times 10^{-6} \text{ N s m}^{-2}$, $M = 4 \text{ kg/mol}$ and $C_v = 12.5 \times 10^3 \text{ J kmol}^{-1} \text{ K}^{-1}$. Calculate the thermal conductivity of He at 0°C .
5. In a vacuum flask, the gap between two concentric glass cylinders is 4 mm. Calculate the value of pressure p at which the thermal conductivity value between the walls will drop below its value at 1 atm. pressure. At what value of p will thermal conductivity be 10^{-3} times the value at 1 atm? Take the $\lambda = 100 \text{ nm}$ at 1 atm.
6. Calculate the diffusion coefficient of air by taking mean speed as 460 m/s and mean free path as $6.1 \times 10^{-8} \text{ m}$.
7. Calculate the mass of nitrogen that will diffuse through an area of 10^{-1} m^2 in 10 sec, if the concentration gradient is 1.26 kg m^{-4} , $\lambda = 10^{-2} \text{ m}$ and $c = 480 \text{ m/s}$.
8. The coefficient of viscosity and diffusion coefficient for oxygen is given by $1.95 \times 10^{-5} \text{ N s m}^{-2}$ and $1.22 \times 10^{-5} \text{ m}^2 \text{ s}^{-1}$, respectively. If the mean molecular velocity is 440 m/s , calculate λ .
9. Calculate the mass of nitrogen diffusion through an area 10^{-2} m^2 in 10s, if the con-

I will just leave it to you, we will have a discussion on this problem in the forum but I am not going to solve it for you. After the; discussion in a combined manner if we cannot come to a conclusion then only I will solve it for you maybe in one of the live sessions. So, in a vacuum flask the gap between two concentric glass cylinder is 4 mm. We all know that the in there is a vacuum jacket in a vacuum flask and the gap between these two is given.

Calculate the value of pressure p at which the thermal conductivity value between the wall will drop below it is value at 1 atmosphere. At what value of p will thermal conductivity be 10 to the power -3 times the value at 1 atmosphere 10 to the minus 3 times? Take λ is equal to 100 nanometers at 1 atmosphere. Now we go back to the expression for thermal conductivity once again where is it? I am not going to solve it but I will just give you a we will just discuss it anyway.

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Comparing with Fourier's law

$$[Q = -k dA \frac{dT}{dz}, dA = 1 \text{ unit}]$$

$$k = \frac{1}{3} n \lambda \bar{c} C_v^m$$

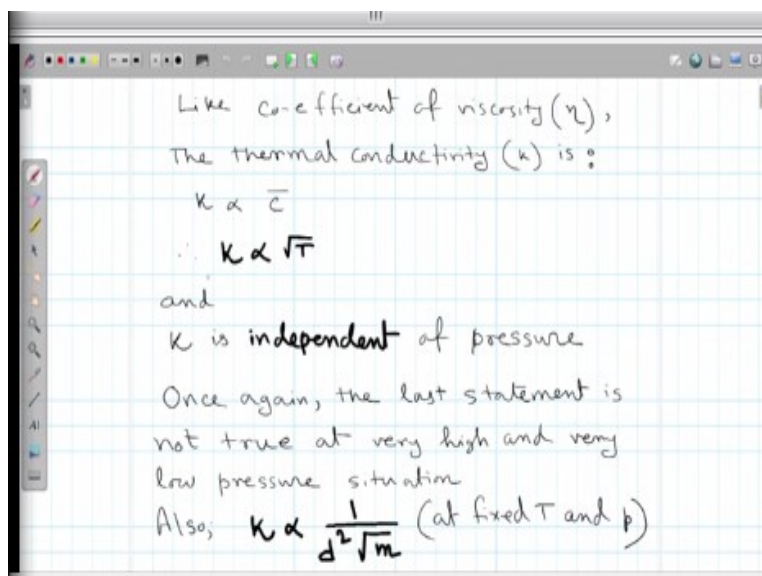
$$= \frac{1}{3} \lambda \bar{c} C_v^v \quad (C_v^v = n C_v^m, \text{ heat capacity per unit volume})$$

$$= \frac{1}{3} \lambda \bar{c} \frac{\rho}{m} C_v \quad (n = \frac{\rho}{m} = \frac{\rho}{m \cdot N_A} \cdot N_A)$$

$C_v = N_A C_v^m \rightarrow$ Molar specific heat at constant volume

So, this is the expression for thermal conductivity from the last lecture. And what do we see here?

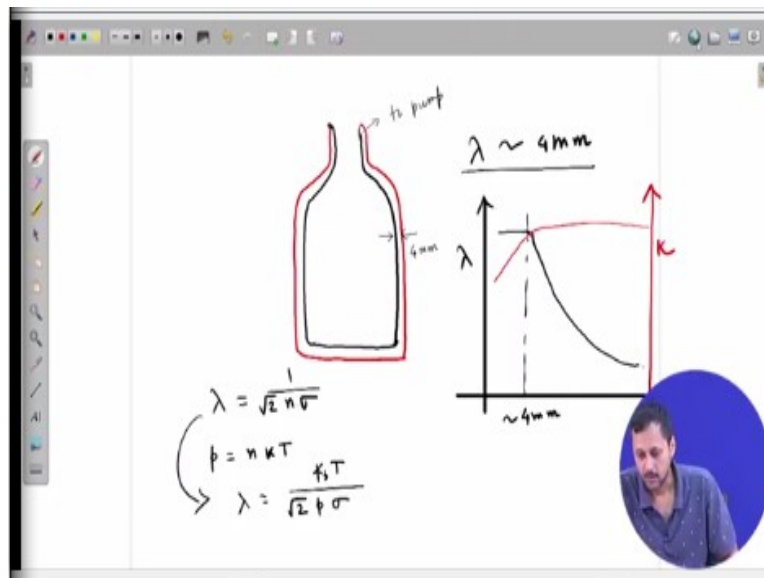
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Like co-efficient of viscosity (η),
 The thermal conductivity (k) is :
 $k \propto \bar{c}$
 $\therefore k \propto \sqrt{T}$
 and
 k is independent of pressure
 Once again, the last statement is not true at very high and very low pressure situation
 Also, $k \propto \frac{1}{d^2 \sqrt{m}}$ (at fixed T and p)

We have determined the dependences that we see that case independent of pressure. And if you recall once again I have mentioned many times that had very high and very low P this independence does not hold. Now this is the case in this problem what we are going to discuss is the case where the pressure becomes really, really low. So, what happens? So, let us I will just discuss the phenomena, you have to solve it yourself.

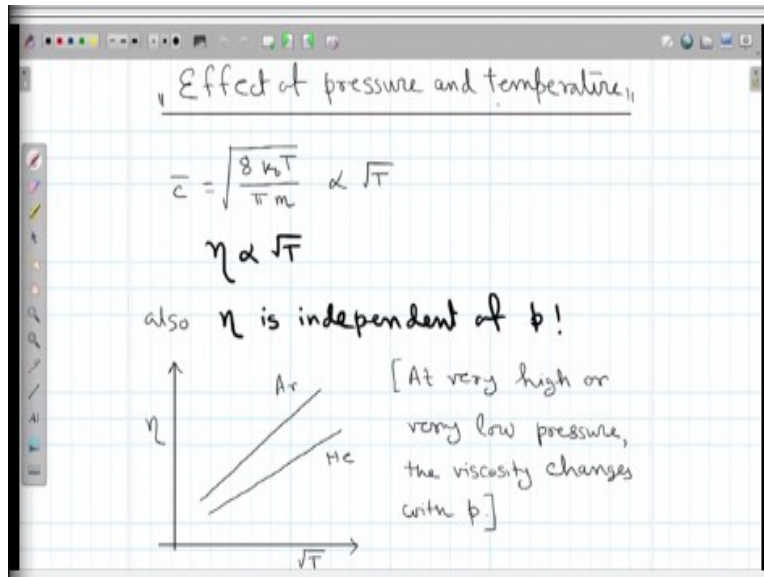
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So, we have a flask, vacuum flask. So, let us say this is my flask, so this is the outer wall and we also have an inner wall, I hope this drawing you can understand what I am trying to draw, it is not very accurate drawing but you can at least understand. So, the problem is, so this is a vacuum sealed wall. So, between the inner wall and the outer wall we have a distance of 4 mm. Now, so basically at the beginning let us assume that one of these sides are open and this is that 1 atmosphere. Now in 1 atmosphere what is given?

It is given that the mean free path is 100 nanometers and so this is what is given. Now what happens is let us, assume that we close this surface and basically we start evacuating from here. So, we start we connect it to some pump, yeah, and we start reducing the pressure. Now thermal conductivity does not change up to a point when λ is comparable to 4 millimeters not nanometer, 4 millimeter. So, if we simply plot just to give you an idea what happens is, if we have pressure versus λ what was the dependence, if you recall? We have to go back to lecture 12 for that, we have to go back to lecture 12.

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So, once again this is oh! sorry, sorry not lecture 12 my mistake. We do not need actually. We remembered that λ is equal to $1/\sqrt{2} n \sigma$ and p is equal to $n kT$. So, actually this can be written as λ is equal to $1/\sqrt{2} p \sigma$ and they will be $k B T$ here. So, if we keep the temperature constant, so λ and p they are inversely proportional. So, as the pressure decreases λ increases when we have discussed it many times.

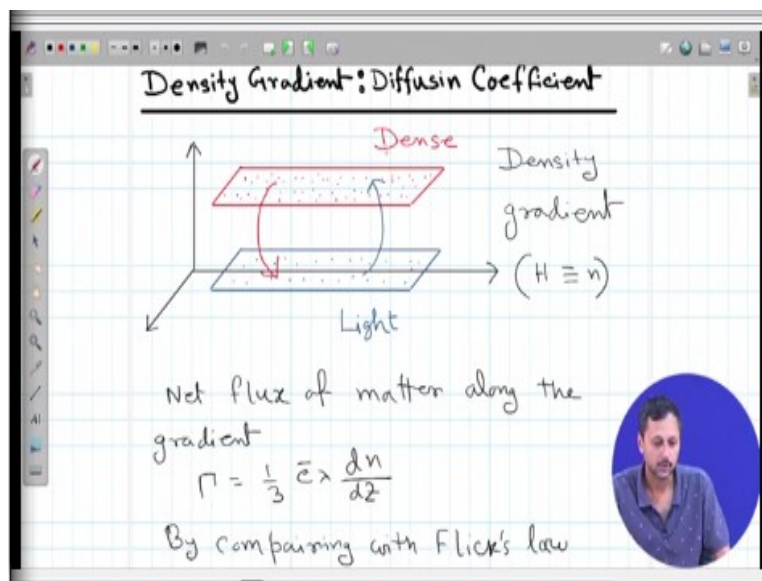
So, it will keep decreasing up or as the pressure decreases λ will increase and it can increase only up to a value of 4 nanometers beyond that your curve will be flat, why? Because the maximum distance or maximum mean free path is once again I have repeated it many times, I am repeating it once again. The maximum allowed mean free path is equal to the dimension of the container.

So, this is where λ is approximately equal to 4 millimeter which is the dimension of the container in this particular case and beyond that λ becomes flat then the thermal conductivity starts reducing with pressure because in the expression of thermal conductivity also there is an n dependence. So, what is the expression for thermal conductivity? You see this is one third $\lambda c \bar{v} n C_v m$.

So, as long as the λ and n both are varying with pressure this n dependence cancels out. But when λ becomes constant here when the λ becomes constant k depends on n , reducing n the number density reducing pressure will reduce the number density and it will start decreasing. So, using this concept, so you can find out a pressure at which k will start decreasing as a function of pressure.

So, on the same plot if I add another axis which discusses the k dependence, dependence of k with pressure, right. So, what happens is, for that particular axis I mean for the same range k remains constant up to this value and then it will start decreasing? So, that is where the flux is actually insulating. A flux is insulating if and only if the thermal conductivity of this, of the thermal jacket insulating jacket is much less as compared to the one in 1 atmosphere pressure. So, I think you have got enough hint and now you can solve this problem, please keep the discussion alive in forum, if you cannot solve this problem even after this I will provide a solution.

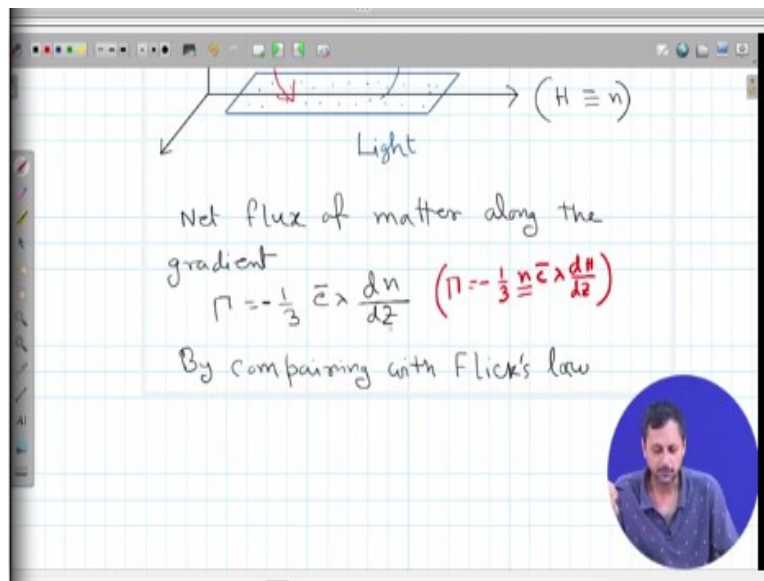
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So, now let us go back to the lecture and let us talk about the density gradient. When we have a density gradient at the system and we can compute something called the diffusion coefficient. So, once again we go back to the picture where we have two adjacent layers. Now in this case one layer is dense, the other layer is light, what do I mean by dense and light? That means the one layer actually has more packed molecules as compared to the other layer.

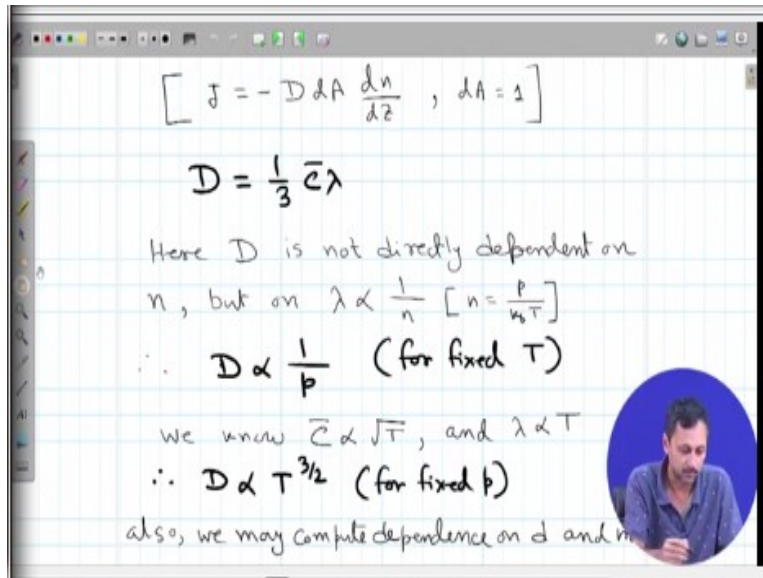
Now what happens is molecules will come from move freely between these layers, so that once again it will be driven towards equilibrium that is density equilibrium in this particular case, which in a more technical term we call the chemical equilibrium. So, in this case when we have a density gradient the quantity H is equivalent to n . So, the expression for net flux in this case along the gradient the net flux γ will be given by one third $c \bar{\lambda} dn dz$.

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As opposed to the other if you go back to the original expression it was λ is equal to of course there is a minus sign I have just omitted the minus sign, sorry. So, there should be a minus sign here as well, so it will be minus one third $n c \bar{\lambda} dH dz$, that was the original expression. But because in this case H is equivalent to n , we have not written n out explicitly here, so the expression becomes -one third $c \bar{\lambda} dn dz$.

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$$[J = -D dA \frac{dn}{dz}, dA = 1]$$

$$D = \frac{1}{3} \bar{c} \lambda$$

Here D is not directly dependent on n , but on $\lambda \propto \frac{1}{n}$ [$n = \frac{p}{k_B T}$]

$$\therefore D \propto \frac{1}{p} \quad (\text{for fixed } T)$$

We know $\bar{c} \propto \sqrt{T}$, and $\lambda \propto T$

$$\therefore D \propto T^{3/2} \quad (\text{for fixed } p)$$

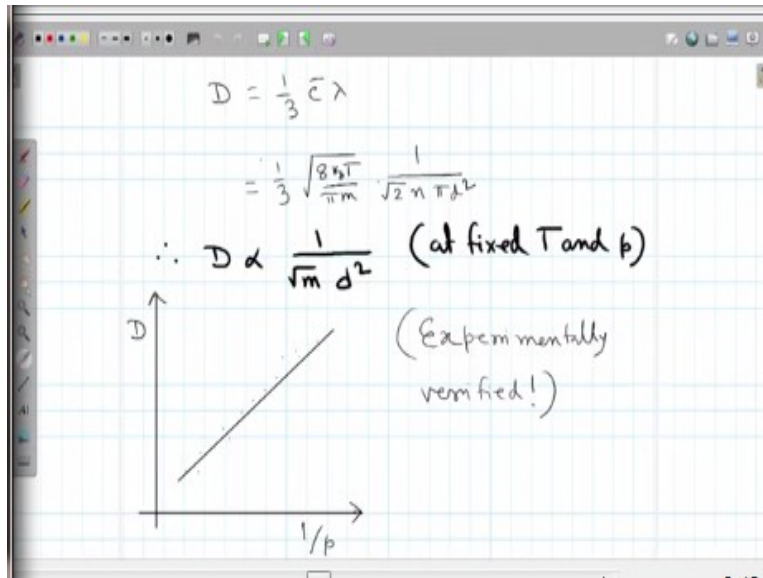
also, we may compute dependence on d and m

Now, when we compare this with the Fick's law of diffusion which is J is equal to minus $D dA \frac{dn}{dz}$ and we are working in the case when dA is equal to 1, we get D is equal to one third $\bar{c} \lambda$. Now what is this D is called? The diffusion coefficient and it is once again not directly dependent on n but if we recall that λ is proportional to $1/n$, okay. Then we see that D is also proportional to $1/n$ and n and p they are directly proportional to each other.

So, in that way D is inversely proportional to the pressure. So, as pressure decreases the diffusion coefficient increases, right. So, it is something similar to the dependence of λ because D and λ are proportional. Also we know that the quantity \bar{c} which is the mean velocity is dependent on the root over of temperature. And of course this dependence is when we have a fixed temperature. And when we have a fixed pressure with temperature the \bar{c} the mean velocity depends on root T whereas λ depends on T .

Once again if you recall when we substitute for n is equal to p by $k_B T$. In the expression of λ T goes in the numerator and λ is directly proportional to T . So, the dependence of the diffusion coefficient D on temperature is T to the power $3/2$ for a fixed T . Now once again we can compute the dependence of D on the molecular parameters like d and m , this d here being the dimension of the molecule the diameter of the molecule and m being the mass of the molecule.

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Now this dependence if we compute it carefully, we see that \bar{c} is equal to $\sqrt{8kT/\pi m}$, whereas λ is equal to $1/(\sqrt{2} n \pi d^2)$. So, when temperature and pressure both are fixed, D is proportional to $1/\sqrt{m} d^2$. So, this is the dependence of molecular dimension on the coefficient of diffusion. Also the $1/p$ dependence has been verified experimentally, just given an illustrative plot of the diffusion constant as a function of $1/p$. As you see this D is proportional to $1/p$, so D versus $1/p$ should be a straight line and experimental data also suggests that D is linearly varying with $1/p$, right.

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Handwritten derivation on a grid background, titled "Units and dimensions":

In this case, it is easy to compute dimension

$$D = \frac{1}{3} \lambda \bar{c}$$

$$[D] = [\lambda] [\bar{c}] = [L] [L] [T]^{-1}$$

$$= [L]^2 [T]^{-1}$$

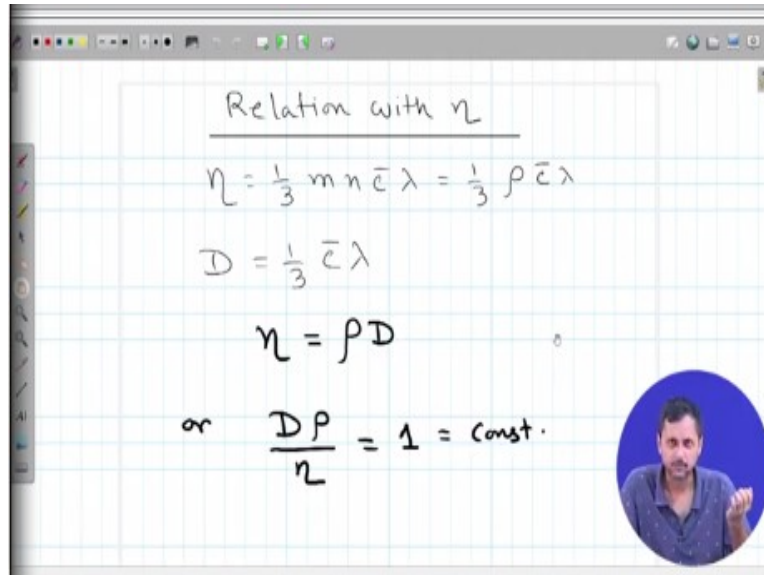
S.I. unit $\Rightarrow m^2 s^{-1}$

In the bottom right corner, there is a small circular inset video of a man speaking.

Now let us compute as before the units and dimensions. Now in this case we are not going back to the Fick's law but it is very straightforward the dimension calculation as D is given by one

third λ c the dimension of D is the dimension of λ multiplied by dimension of c bar which is simply length square per unit time. So, the SI units of diffusion coefficient will be meter square per second. So, this is exactly like I mean this is very simple unit meter square per second.

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Relation with η

$$\eta = \frac{1}{3} m n \bar{c} \lambda = \frac{1}{3} \rho \bar{c} \lambda$$

$$D = \frac{1}{3} \bar{c} \lambda$$

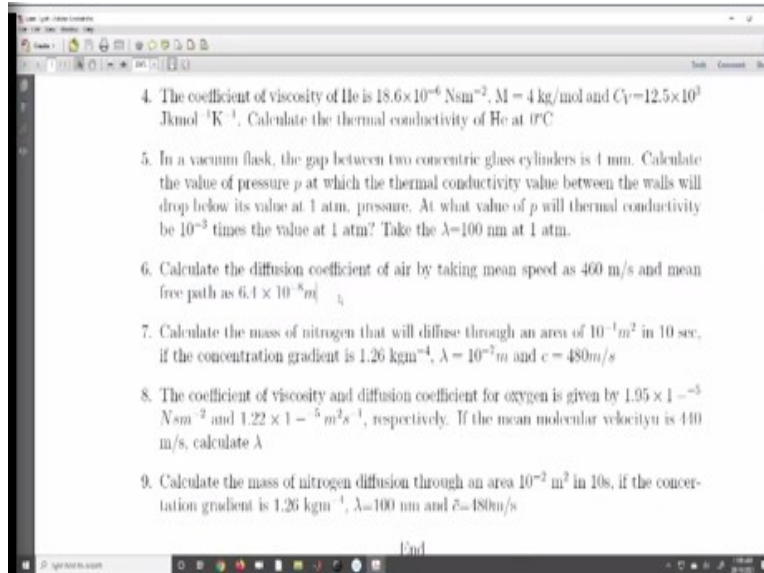
$$\eta = \rho D$$

or $\frac{D \rho}{\eta} = 1 = \text{const.}$

And also there is a relation that exists between the coefficient of viscosity and the diffusion coefficient. Of course both of them are transport properties, so there has to be a relation. So, η is equal to one third $m n \bar{c} \lambda$ is equal to one third $\rho \bar{c} \lambda$ and D simply equal to one third $\bar{c} \lambda$. So, we can see that η is equal to ρD and D times ρ by η is equal to 1 which is a constant.

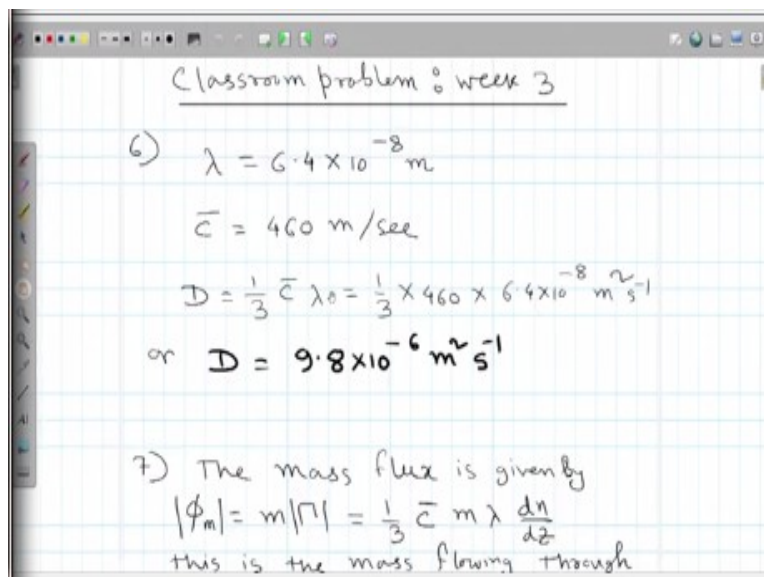
Once again when we will be discussing towards the in the next lecture we will be discussing the fundamental dependence or rather we will discuss about little more advanced theories, we will see that $D \rho$ by η , sorry, $D \rho$ by η is not exactly 1 but it is a constant nonetheless, fine. Now with this we move to the just a minute anything else. So, we will move to the classroom problem set and we have two problems to solve, that is, problem number 6 and problem number 7.

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So, this 2 rather 3 problems 6, 7 and 8, this 3 we have to solve in order to get an insight on this diffusion phenomena. So, let us focus on problem number 6. So, we calculate the diffusion coefficient of air by taking means speed of 460 meters per second and mean free path of 6.8 into 10 to the power minus 8 meters. Now, this is probably the most, easy problem that we get in the discussion of diffusion coefficients.

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Because this is simple application of the relation that $D = \frac{1}{3} \bar{c} \lambda$ times c or c times λ . So, we just have λ , we just have c and we put these values here side by side one after the other and we get $D = 9.8 \times 10^{-6} \text{ m}^2 \text{ s}^{-1}$.

square per second. So, this is more of a it is a problem, so that you get a feel for the number what are the typical range of this diffusion coefficient. So, this is why this problem is chosen.

So, you see this is almost 10^{-5} meter square per second because 9.8 is almost 10. So, we can call it 10^{-5} meter square per second. For problem number 7, we have calculate the mass of nitrogen that will diffuse through an area of 10^{-1} meter square, sorry it should be 10^{-2} actually, my mistake, I will correct this. So, it will be 10^{-2} meter square in 10 seconds, if the concentration gradient is 1.26 kg per meter to the power minus 4 and λ is 10^{-7} meters c bar is 480 meters per second.

Now what we have to compute here is the mass of nitrogen that will diffuse through and given area in given time. So far the quantity of interest has been the flux, now we have to that is basically the number of molecules that is going through an unit area in unit time. Now what we have to do? We have to calculate the mass that is going through a different area in given time and this is not very difficult as we have already realized.

All we have to do is we have to multiply the flux with the mass, yes, ϕ_m which is the mass flux which is simply m times γ , please remember that γ is the flux that is the net flux towards the gradient. Of course if there is a gradient only the relation will hold. So, m times γ , so that means one third $c \bar{m} \lambda \frac{dn}{dz}$, so this is the expression for mass flux that is going in the direction of the or rather in the opposite direction of the gradient, I have just put a mod here.

So, to avoid the negative sign, it does not matter we know that mass will flow opposite to the gradient because this is where nature comes in, nature wants to equilibrate everything. So, will be a minus sign, I have just avoided that to avoid any confusion. So, ϕ_m is simply m times γ .

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per unit area per unit time

$$|\phi_m|^0 = \frac{1}{3} \times 480 \times 10^{-7} \times 1.26$$

$$= 2.02 \times 10^{-5} \text{ kg m}^{-2} \text{ s}^{-1}$$

So, total mass diffusing out through 10^{-2} m^2 in 10 sec is

$$M = |\phi_m| \times 10 \times 10^{-2} \text{ kg}$$

$$= 2.02 \times 10^{-5} \times 10 \times 10^{-2} \text{ kg}$$

or $M = 2.02 \times 10^{-6} \text{ kg}$

So, this is basically the mass flux that means mass flowing through unit area in unit time. So, ϕ_m we can compute because \bar{c} is given which is the mean velocity and λ is given which is the mean free path and this one the gradient dn/dz is also given. So, let us go back to the problem again see dn/dz . So, dn/dz that is given in the units of kg per meter to the power 4 because n has an unit of kg per meter cube.

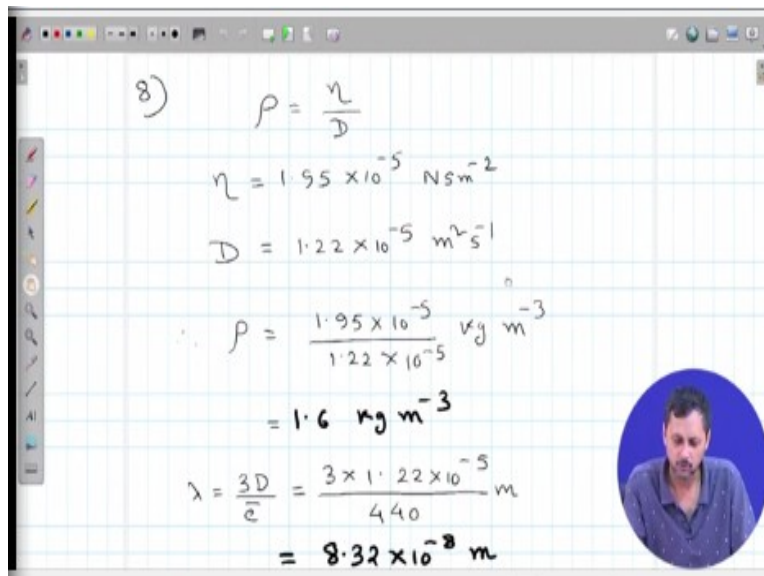
That will be divided by once again by a meter, so it will be minus kg meter to the power minus 4, λ is given, \bar{c} is given. So, we can very easily compute ϕ_m which is $2.02 \times 10^{-5} \text{ kg per meter square per second}$, so this is the proper unit. Now what we have to find out is mass that is passing through a given area in 10 seconds. So, all we have to do is, we have to multiply this quantity by the area and the time. So, M that is the total mass that is actually flowing through that area is ϕ_m multiplied by the time T that is 10 seconds multiplied by the area that is $10^{-2} \text{ meter square}$.

And the unit will be you see meter square, meter square cancels, second, second cancels, so unit will be simply kg. And after putting all these numbers we get M equilibrate $2.02 \times 10^{-6} \text{ kgs}$ that is if I express it in grams it will be 10^{-3} grams , so it will be milligrams actually. So, 2 milligram mass will be lost if we keep a small hole of the area $10^{-2} \text{ meter square}$ in a container of nitrogen for 10 seconds. So, this is a very nice problem in order to give you a real feel of how much mass we will lose in a given time.

And we will come back to more of this type of problems, so we will be discussing effusion next. So, the last problem of the class which is probably number 8, the coefficient of viscosity and diffusion coefficient of oxygen is given by 1.5×10^{-5} to the power, sorry this should be 10 to the power minus 5 N s meter square and 1.22×10^{-5} once again this is a mistake. So, it should be 10 to the power minus 5 meter square per second, respectively.

If the mean molecular velocity is 440 meters per second, calculate λ . So, what is given? Here the coefficient of viscosity η is given, diffusion coefficient D is given and the mean molecular velocity is given, oh! sorry actually it is a printing mistake here. So, basically first we have to calculate, so that there is another part I will correct that in the final version. We first have to calculate the density ρ and then we have to calculate λ .

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$$\begin{aligned}
 8) \quad \rho &= \frac{\eta}{D} \\
 \eta &= 1.95 \times 10^{-5} \text{ N s m}^{-2} \\
 D &= 1.22 \times 10^{-5} \text{ m}^2 \text{ s}^{-1} \\
 \therefore \rho &= \frac{1.95 \times 10^{-5}}{1.22 \times 10^{-5}} \text{ kg m}^{-3} \\
 &= 1.6 \text{ kg m}^{-3} \\
 \lambda &= \frac{3D}{2} = \frac{3 \times 1.22 \times 10^{-5}}{440} \text{ m} \\
 &= 8.32 \times 10^{-8} \text{ m}
 \end{aligned}$$

So, we first have to calculate density ρ and ρ is given by η by D , η is 1.95×10^{-5} to the power minus 5 , D is 1.22×10^{-5} to the power minus 5 . So, we see calculation of ρ is very straightforward, we just have to divide one by the other and 10 the power minus 5 and minus 5 nicely cancels out, leaving behind, 1.6 kg per meter cube. So, this gives you the density of oxygen, so 1.6 kgs per meter cube.

Next we have λ which can be computed from the relation that D is equal to one third λc , so λ is equal to $3D$ by c bar which is just putting these numbers will give you 8.3×10^{-8} meters. So, that is where we stopped in today's lecture and the next and the last topic for the transport properties is the effusion properties. Now, what is effusion? I will just give you a very brief idea.

See, we have so far discussed about diffusion, when the dimension of the let us say we have just discussed a problem that there is a hole in a container and there is a measurable density gradient and the molecule is diffusing out, molecule is going out of that hole. In case, when the dimension of the hole becomes so small that the gas assembly does not feel a density gradient or a pressure gradient.

So, density gradient essentially means a pressure gradient, because n and p they are directly linked. So, if the hole is really, really tiny, then the gas assembly as a whole will not experience a pressure gradient. But still because there is an opening and if the opening is anything more than the molecular diameter of course that is when we call it an opening not before that. So, some molecules will definitely escape out of the container.

So, that means the molecules are going out each, let us say what molecules are escaping the container one by one without passing the knowledge to the other molecules. So, this is a phenomena we call the effusion. In the next class or the last class for this week, we will be taking up effusion. And of course we will have some more concluding remarks in order to end the topic of transport phenomena, till then thank you.