# Solar Photovoltaics: Fundamental Technology and Applications

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## Lecture - 36
## Introduction to Characterization Techniques

Welcome everyone to our solar photovoltaics course. Today, we have 8th week the first module. So far we have been discussing about the different technologies of the solar cell. In our class, we have talked about silicon solar cell, we have talked about organic solar cell, perovskite solar cell as well as quantum dot solar cell and nanoparticle-based solar cell and when we have discussed is all different kind of solar cell so the fabrication, the technology of making the solar cell.

And we have seen that most of the solar cell has one thing in common, they have a sandwiched layer between two electrodes; one is a photo anode and another is a cathode. Now, in most of this case, this cathode material is a metal electrode like platinum or like you know aluminium or some kind of like gold, silver we use as a counter electrode or metal electrode.

Now, this metal they are deposited in a special environment, they are not deposited under the ambient condition, we need a high vacuum or devoid of any gas molecule inside the chamber to deposit this metal atoms on the top of this solar cell. Now, this special environment or what we call as a vacuum environment that requires a special kind of instrument set up or special kind of chamber to create or to make that kind of condition.

In today's lecture and some subsequent lectures, will learn about this vacuum technology, what is the meaning of the vacuum, what do you mean by high vacuum, low vacuum or medium vacuum and how we can make the vacuum chamber.

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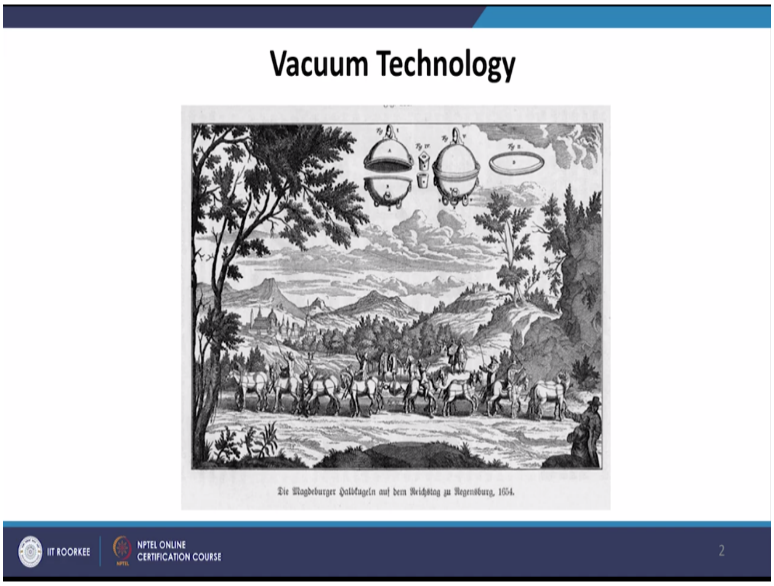

Vacuum Technology

Die Magdeburger Halbkugeln auf dem Reichstag zu Regensburg, 1654.

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So, the idea of the vacuum technology that is way back to 17th or 18th century or even before that but in the first hand we need the question like you know why we need the vacuum or what do you mean by the vacuum.

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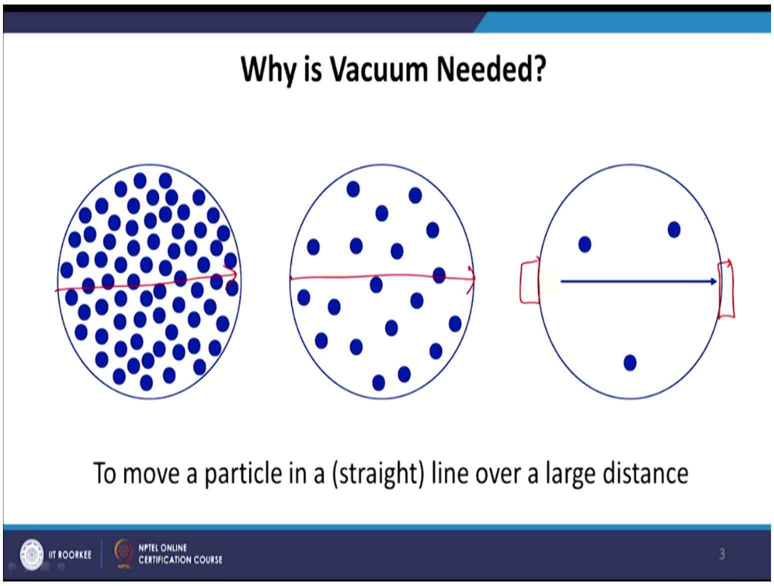

Why is Vacuum Needed?

To move a particle in a (straight) line over a large distance

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Now, let us look at this figure. Here like you know you consider an arbitrary circle like this and which has been filled with some blue color solid bubbles. So, let us consider this spherical shape is like a chamber and this blue color dots they are like the gas molecule. Now, look at the second picture here, the number of the gas molecule or number of the blue solid sphere in the second picture is less than the first picture.

Now, you look at the third picture here, here the number is much less in comparison to the first thing. So, in some system to begin with a crowded number of atoms if we start getting rid of one by one atoms or if we rarefied the systems, so finally we can achieve a system where the number or the density of the gas molecules or the density of the atoms of the gas molecules in a particular volume is much reduced in comparison to the first case.

Now, what will happen? Let us say we want to move a particle in a straight line over a large distance. So, in this case, if I have to move the particle along this distance, so this particle has to collide each and every time with this blue sphere but what happens here, you can imagine the number of collision is much reduced in comparison to the first case. Now, you come to here, the property of collision is very less in comparison to the first and the second case.

So, that means now let us consider practical case. I have a source of the atoms at this side and I have a target on the other side, now I somehow by some means I have hitted the source so that I can generate a vapour of the atoms or atoms. So, these atoms will go in a straight line. Now, while travelling along this chamber, if it is suffers multiple collisions, then its paths will be deviated and it will not be able to reach to the target substrate.

So, if I wanted to have a very uniform coating on the target substrate or our vaporized atoms, so what we require as less of the interfering atoms inside the chamber. So, to make it as a less interfering other gas molecules inside the chamber, we need to create the vacuum. So, in our atmosphere, we know that there are different layers is there and we call it as like troposphere, stratosphere, ozonosphere, ionosphere, etc.

Now, if we go above and above, so what will happen, the pressure and temperature changes and the effective density of the gas molecule also changes.

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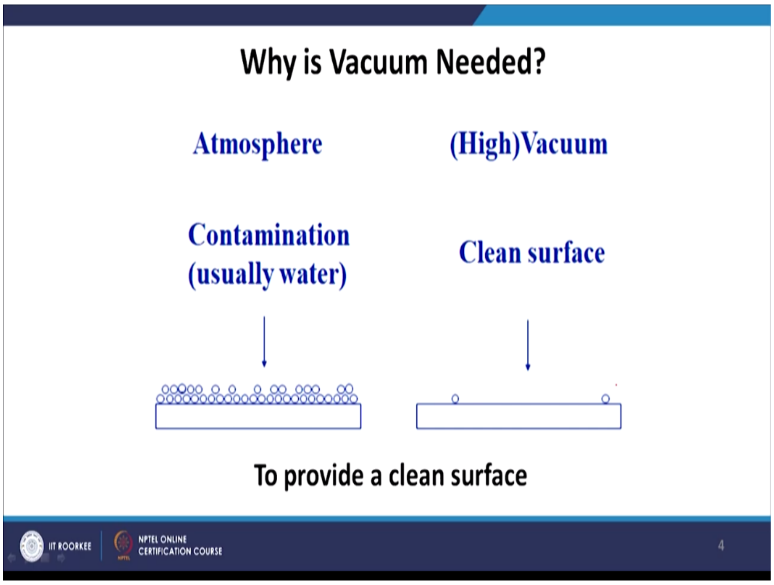

## Why is Vacuum Needed?

Atmosphere | (High)Vacuum

Contamination (usually water) | Clean surface

To provide a clean surface

For example, like you know whenever any kind of radiation has to pass through the atmosphere, we know that they have to pass through the cloud I mean which contains the condensed water and different kind of gas molecules also but if I have like you know high vacuum surface so then if I want to deposit some kind of gas molecule on that, so I do not want like lot of the other molecules to interfere with my systems.

So, I want a very clean substance and to get a clean substance or a clean surface, I do not want me interfering things inside my systems and that is why we need to create the vacuum.

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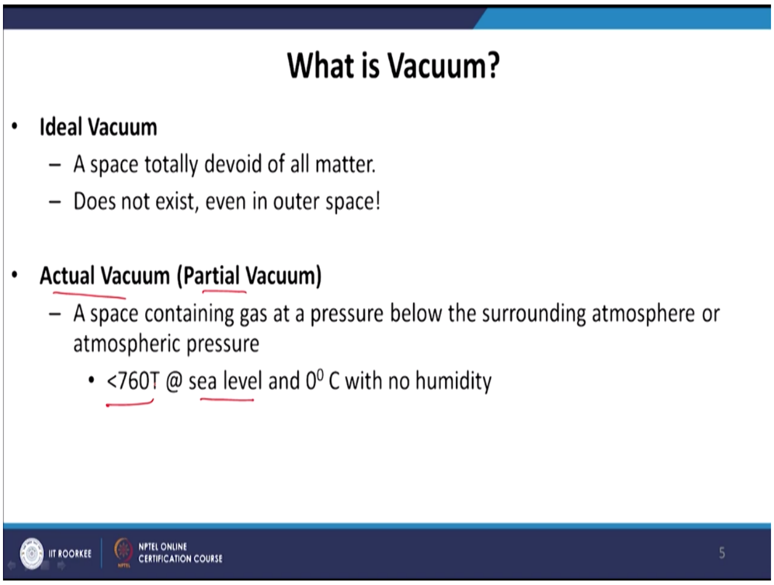

## What is Vacuum?

- Ideal Vacuum
  - A space totally devoid of all matter.
  - Does not exist, even in outer space!
- Actual Vacuum (Partial Vacuum)
  - A space containing gas at a pressure below the surrounding atmosphere or atmospheric pressure
    - <760T @ sea level and $0^0$ C with no humidity

So by definition an ideal vacuum is a space devoid of all matter, does not exist even in outer space. So, it is not possible to have a space completely devoid of any matter. So, it is a very ideal hypothesis. So, in real case, what you talk about is the partial vacuum, so the actual vacuum is actually partial vacuum. A space containing gas at a pressure below the surrounding atmosphere or atmospheric pressure.

So, we know that at sea level, the atmospheric pressure is 760 Torr, so if I wanted to clear the vacuum inside some chamber, so the pressure if the atmospheric pressure is 760 Torr then the resultant pressure should be less than 760 Torr.

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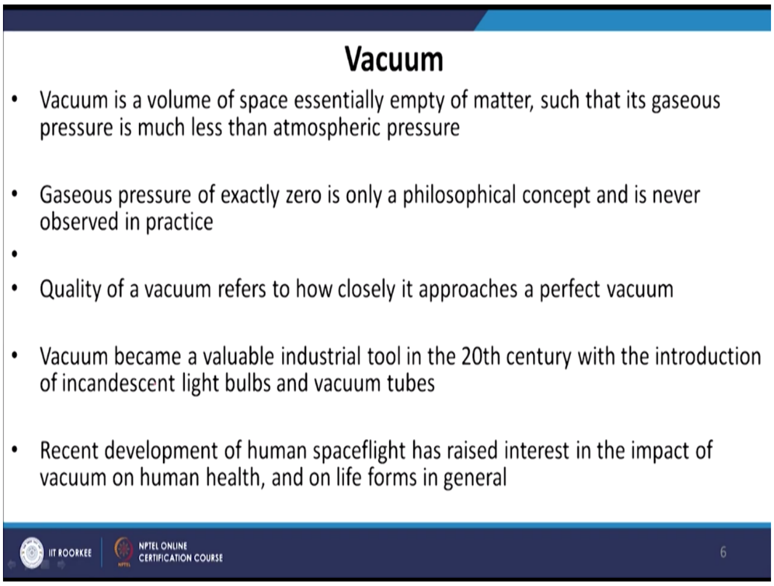

Vacuum

- Vacuum is a volume of space essentially empty of matter, such that its gaseous pressure is much less than atmospheric pressure
- Gaseous pressure of exactly zero is only a philosophical concept and is never observed in practice
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- Quality of a vacuum refers to how closely it approaches a perfect vacuum
- Vacuum became a valuable industrial tool in the 20th century with the introduction of incandescent light bulbs and vacuum tubes
- Recent development of human spaceflight has raised interest in the impact of vacuum on human health, and on life forms in general

So, vacuum is the volume of space essentially empty of matter, such that its gaseous pressure is much less than atmospheric pressure. Gaseous pressure of exactly zero is only a philosophical concept and is never observed in practice. Quality of vacuum refers to how closely it approaches a perfect vacuum. So, when we say that it is a perfect vacuum that means we consider that the effective density of gas molecule is almost zero.

And how good is our experimental systems will be how good it will be close to a perfect vacuum. Vacuum became a valuable industrial tool in the 20th century with the introduction of incandescent light bulbs and vacuum tubes. Recent development of human spaceflight has raised interest in the impact of vacuum on human health and on the life forms in general. So, as you know that in the outer atmosphere when we go to the space environment in the spacecraft, the pressure inside is different from the earth's atmospheric pressure.

So, what is the effect of this change of the pressure, so that needs to be understood before sending some astronaut in the space? So that is why the effect of the vacuum or low pressure on the human health is also another interesting area of the subject apart from the material science.

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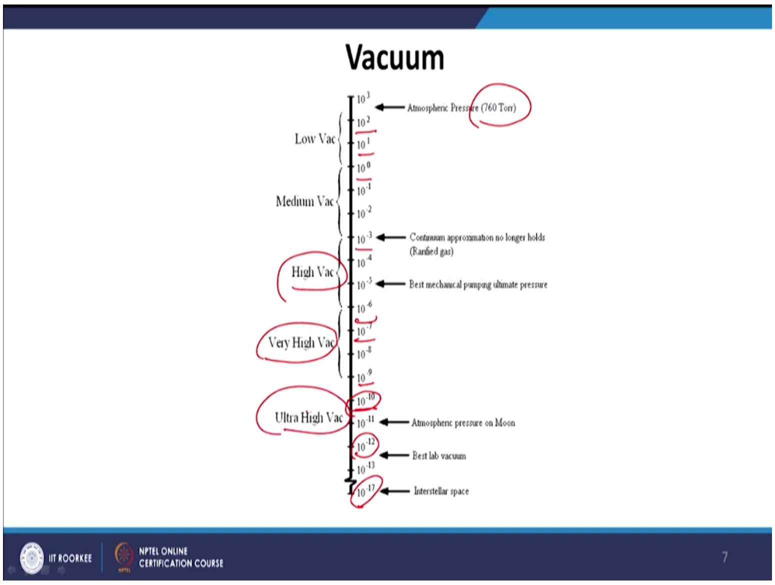

Vacuum

Now, if you look at this diagram here, so here we are showing the different level of the vacuum as you can see that when I say that the atmospheric pressure it is something like 760 Torr okay so 760 Torr. Now, when I say about the lower vacuum? So that means in a range of 10 to the power 2 or 10 to the power 1 like something like 10 Torr.

Medium vacuums that goes from 10 to the power 0 to 10 to the power -3, 10 to the power -3 to 10 to the power -6 that is the high vacuum, 10 to the power -7 to 10 to the power -10 or even 10 to the power -9 that is very high vacuum and anything beyond that something like 10 to the power -10 to 10 to the power -17, 10 to the power -17 usually exist in the interstellar space, for the best lab vacuum we make 10 to the power -12.

So, these kind of and even like 10 to the power -11 that is the atmospheric pressure on Moon. So, these are examples of the ultra-high vacuum. So, in our solar cell devices to make the metal electrode, we usually needs medium to the high vacuum and one thing is obvious from the chart that since the different level of the vacuum, the pressure is different so we need different instruments to create that vacuum.

And obviously, as we go to the high vacuum to very high to ultra high vacuum, we need more and more sophisticated instrument to create that kind of low pressure inside the system. So, let us learn about some common vacuum units we use in the system.

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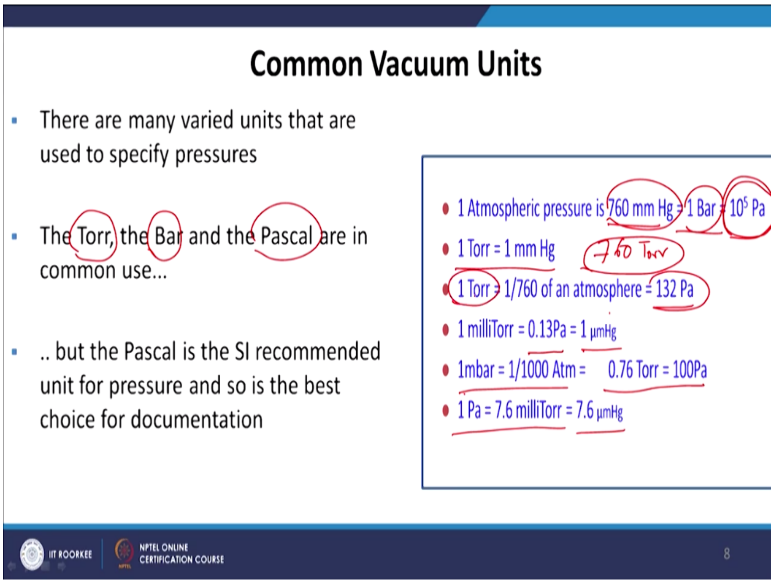

## Common Vacuum Units

- There are many varied units that are used to specify pressures
- The Torr, the Bar and the Pascal are in common use…
- .. but the Pascal is the SI recommended unit for pressure and so is the best choice for documentation

- 1 Atmospheric pressure is 760 mm Hg = 1 Bar = $10^5$ Pa
- 1 Torr = 1 mm Hg
- 1 Torr = 1/760 of an atmosphere = 132 Pa
- 1 milliTorr = 0.13Pa = 1 µmHg
- 1mbar = 1/1000 Atm = 0.76 Torr = 100Pa
- 1 Pa = 7.6 milliTorr = 7.6 µmHg

760 Torr

There are many varied units that are used to specify pressure. The Torr, the bar and the pascal are commonly used. So, the most 3 commonly used unit for pressure is one is Torr, another is bar and another is the pascal. Now, we learn about what is the relation between them but pascal is the SI recommended unit for pressure and so it is the best choice for the documentation.

So, as we know that we have CGS system and SI system in addition to the FPS system. In SI unit, the pascal is the pressure unit. So, very often we use pascal as unit for the pressure and it is the best method for the documentation of any kind of pressure. Now, atmospheric pressure that is 760 mmHg, that means if I take mercury in a some kind of beaker to 760 millimeter of the mercury the amount of pressure it will exert that is equal to the 1 atmospheric pressure, 760 mmHg that is also called 1 Bar and 1 Bar=10 to the power 5 Pascal.

So, the atmospheric pressure is 1 Bar or 10 to the power 5 Pascal. Now, another unit is Torr, 1 Torr is 1 mmHg so the atmospheric pressure is 760 mmHg so that means atmospheric pressure is 760 Torr, 760 Torr that equal to 1 Bar that equal to 10 to the power 5 Pascal, 1 Torr=1/760 of an atmosphere and that is equal to 132 Pascal, 1 millitorr is 1 micro milligram weight of the mercury and that is 0.13 Pascal.

So, obviously 1 Torr is 1 mmHg or unit 760 Torr to make 1 Bar or that is equal to the 10 power 5 Pascal or 1 Torr is 132 Pascal, so 760 Torr=760*132 Pascal so that is equal to 10 to the power 5 Pascal. One millibar is 1/1000 atmosphere, 0.76 Torr=100 Pascal and 1 Pascal is 7.6 millitorr=7.6 micro milli pressure of the mercury.

So, some of this important thing to remember is the atmospheric pressure which is 760 mmHg or 760 Torr which is equal to 1 Bar which is equal to 10 to the power 5 Pascal. One Torr is 132 Pascal, these two numbers is important to remember okay.

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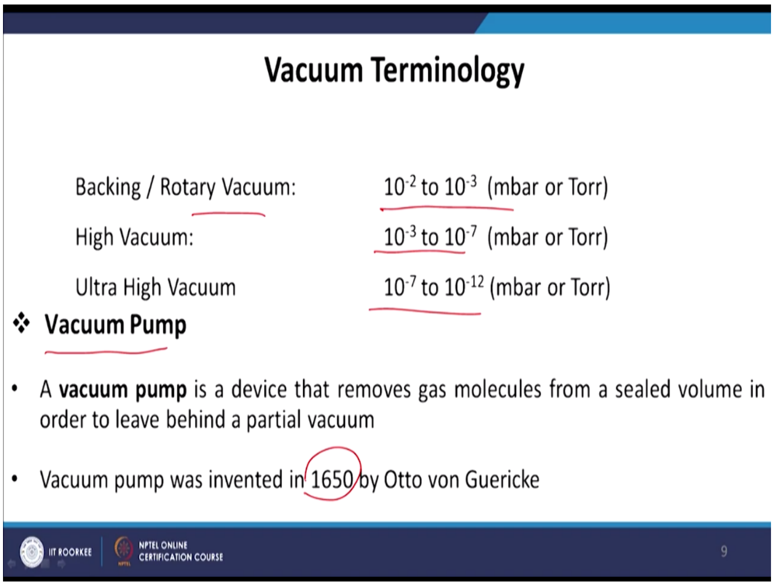

## Vacuum Terminology

| | |
|---|---|
| Backing / Rotary Vacuum: | $10^{-2}$ to $10^{-3}$ (mbar or Torr) |
| High Vacuum: | $10^{-3}$ to $10^{-7}$ (mbar or Torr) |
| Ultra High Vacuum | $10^{-7}$ to $10^{-12}$ (mbar or Torr) |

❖ **Vacuum Pump**

- A **vacuum pump** is a device that removes gas molecules from a sealed volume in order to leave behind a partial vacuum
- Vacuum pump was invented in 1650 by Otto von Guericke

Now, stop the like standard vacuum and how much vacuum that corresponds that we will see it here. Backing or rotary vacuum that correspond to 10 to the power -2 to 10 to the power -3 millibar or Torr so, 10 to the power -2 to 10 to the power -3 millibar that is the vacuum created by the rotary vacuum or rough pump. So, whatever the pump we use as a turbo pump in our daily life that is also called rough pump or the rotary vacuum pump.

That kind of vacuum pump can create a pressure of 10 to the power -2 to 10 to the power -3 millibar or 10 to the power -2 to 10 to the power -3 Torr. High vacuum is 10 to the power -3 to 10 to the power -7, so 10 to the power -3 to 10 to the power -7 millibar that corresponds to the high vacuum. The rotary pump or the rough pump will not be able to create that kind of vacuum. We need some another sophisticated vacuum pump to create that kind of vacuum.

And then ultra-high vacuum 10 to the power -7 to 10 to the power -12 millibar or Torr that is the ultra-high vacuum and we need more sophisticated pumping instruments to create that kind of vacuum. So, we have classified the vacuum into 3 different categories, one is the rotary vacuum that is 10 to the power -2 to 10 to the power -3 millibar, another is the high vacuum that is 10 to the power -3 to 10 to the power -7 millibar and another is the ultra-high vacuum that is 10 to the power -7 to 10 to the power -12 millibar okay.

So, now what do we mean by the vacuum and why we need the vacuum but next question is how can we create the vacuum or how can we create an environment where the pressure is much less than the atmospheric pressure. So that is done by the instrument called vacuum pump. Now, in everyday life we all of us have seen some kind of vacuum pump like you know when we use for sending the water from the ground floor to the first floor.

Or like you know when we use for the cultivation of agriculture the pump, so that is also an example of a vacuum pump but apart from that pump there are also some other sophisticated pump which is required like you know to for running instruments like STM, ACM, FM all these things, so we will learn those things also. So, a vacuum pump is a device that removes gas molecules from a sealed volume in order to leave behind a partial vacuum. Vacuum pump was invented in 1650 by Otto von Guericke. So, it was invented long back 1650.

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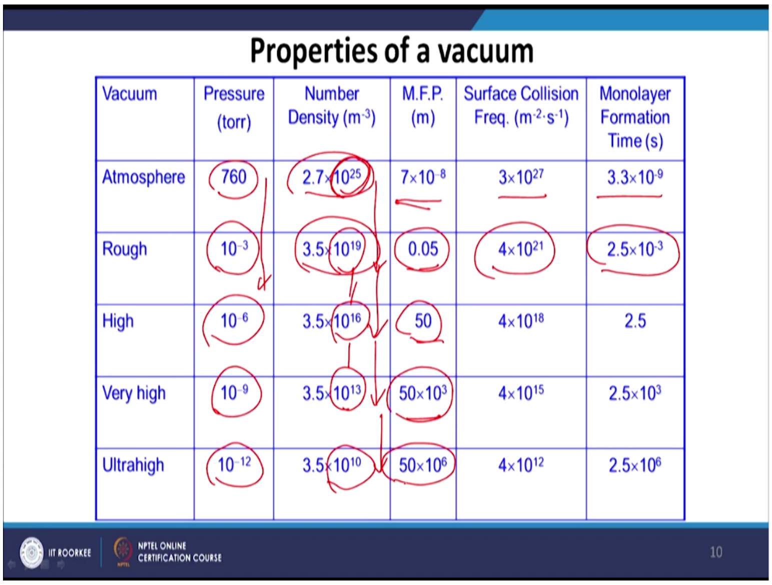

## Properties of a vacuum

| Vacuum | Pressure (torr) | Number Density ($m^{-3}$) | M.F.P. (m) | Surface Collision Freq. ($m^{-2}\cdot s^{-1}$) | Monolayer Formation Time (s) |
|---|---|---|---|---|---|
| Atmosphere | 760 | $2.7\times10^{25}$ | $7\times10^{-8}$ | $3\times10^{27}$ | $3.3\times10^{-9}$ |
| Rough | $10^{-3}$ | $3.5\times10^{19}$ | 0.05 | $4\times10^{21}$ | $2.5\times10^{-3}$ |
| High | $10^{-6}$ | $3.5\times10^{16}$ | 50 | $4\times10^{18}$ | 2.5 |
| Very high | $10^{-9}$ | $3.5\times10^{13}$ | $50\times10^{3}$ | $4\times10^{15}$ | $2.5\times10^{3}$ |
| Ultrahigh | $10^{-12}$ | $3.5\times10^{10}$ | $50\times10^{6}$ | $4\times10^{12}$ | $2.5\times10^{6}$ |

Now, we look for all the properties in a reduced pressure. So, for example like if I take an atmospheric pressure which is 760 Torr or 760 millibar, there the number density of the gas molecule is 2.7*10 to the power 25. Look at this number 10 to the power 25 and then the surface collision rate frequency is 3*10 to the power 27, so the frequency between these two molecules is very high.

So, if I wanted to deposit some let us say aluminium metal atoms on my solar cell, so the aluminium vaporized atom has to suffer these many collision per unit length square per unit time before reaching to the target substrate, so that is not a good case, so that is why we need to rarefied the system and the monolayer formation time is 3.3*10 to the power -9 second and mean free path is 7*10 to the power -8 meter.

Now, what is mean free path? It is the distance the atom can travel before it undergoes a collision. We will discuss that in details in the next few slides. Now, come to about the rough pump which is 10 to the power -3 Torr or 10 to the power -3 millibar. There the number density drastically reduced to 3.5*10 to the power 19. So, look here it was 10 to the power 25, here it is 10 to the power 19 so almost it is 5, 6, 7 order of magnitude difference.

So, just by changing from the atmospheric pressure to the rough vacuum which is 10 to the power -3 millibar, so we change the number density of the molecule to 7 order of magnitude, 10 to the power 25 to 10 to the power 19, what will be the consequence? The collision rate is now 4*10 to the power 21 per meter square per second, so it is reduced and mean free path is 0.05 meter there and monolayer formation time is 2.5*10 to the power -3 second.

So, it takes less time now. Now, you come to the high vacuum which is 10 to the power -6 millibar where the number density reduced further 10 to the power 16, 10 to the power 19 to 10 to the power 16 okay and mean free path is 50 meter and you come about the very high vacuum which is 10 to the power -9 millibar, there the number density further reduced to 10 to the power 13.

So, every case it is reducing by 3 order of magnitude from here to here, from here to here okay and mean free path is 50*10 to the power 3 and now ultra-high vacuum which is 10 to the power -12 which is absorbed in the interstellar space or in the moon surface. There the number effective density of the gas molecule per unit volume per meter cube is 10 to the power 10 and the mean free path is 50*10 to the power 6.

So, you look that as we come down with the pressure along this line from 760 to 10 to the power -3 to 10 to the power -6 to 10 to the power -9 to 10 to the power -12 the number density reduced from atmosphere 10 to the power 25 to 10 to the power 19 7 order of magnitude, from 19 to 16 3 order of magnitude, from 16 to 13 again 3 order of magnitude, from 13 to 10 again 3 order of magnitude.

So, here any difference of the 3 order of pressure is also reflected as a 3 order of number density reduction, you can remember like this and the similar effect we can absorb in the mean free path. If the number density reduced, then the molecules can travel more and more distance before undergo a collision so that is why you see the mean free path is increasing from 10 to the power -8 to 0.05 to 50 to 50*10 to the power 3 to 50*10 to the power 6.

So, the lesson is that starting from the atmospheric pressure as we go from the rough vacuum to medium vacuum to high vacuum, the effective number density of the gas molecule reduced and mean free path increased. So, the probability of collision also reduced and the number or the number of the gas molecule which stays in the systems, the residual number of the gas molecule which stays in the system that also reduced drastically.

So, this slide actually explains why we need a vacuum more better way because what you have learn that when you start form the atmosphere to go to more and more high vacuum, so the two benefits we achieved one is that the effective density of the gas molecule or the number of gas molecules per unit volume that reduce drastically and consequently the mean free path increased drastically and third thing is that the collision probability also decreased.

So, it enhances the probability of reaching the vaporized atom to the target substrate in a much better and much efficient way. So, that is the ultimate objective of going to the like in a atmospheric pressure to the low vapor, low pressure okay. So, now whenever we talk about any pump or whenever you will buy any pump you will see that the manufacture will provide you a graph like this which is called a pump down curve.

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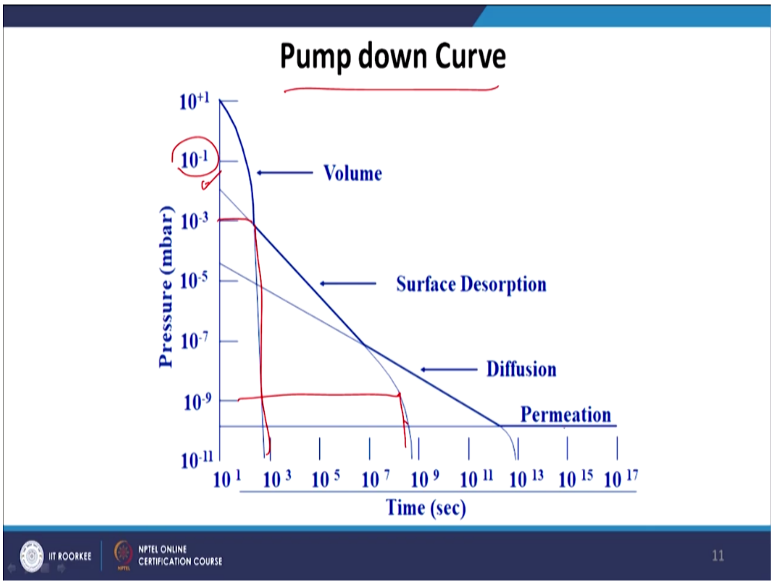

Pump down Curve

So, this pump down curve is actually a curve of pressure versus time where in y-axis we have plotted pressure in millibar and in x-axis we have plotted time in second. It tells you what is the time scale required to reduce the pressure from a particular value to another certain value. So, whenever we like let us say I have a chamber, so of course it will depend on the volume of the chamber but if the volume of the chamber is standard and if I have a pump.

So, the capacity of the pump will depend upon how much time it will take to reduce a number density of the gas molecule to a particular value and that is called the pump down curve for that particular pump okay. So, in the case of the volume depositions so you can see that the pump down curves like you know the time required is 10 to the power 1 but as we go like you know things like surface diffusions.

So, like you know coming from something like 10 to the power -1 let us say or even less than that 10 to the power -2 let us say, from this pressure to come down to 10 to the power something like you know 10 to the power -9 if I consider about like you know the surface depositions and if this is 10 to the power -9 and if this is 10 to the power -3. So, I go from a time scale of 10 to the power 3 to 10 to the power somewhat around 8.

But the volume depositions that is very rapid, very fast. If you go to the diffusion, this kinetics is much slower; if you go to the permeation, it is almost saturated. So the meaning of this curve is that if you go from a volume deposition to a surface deposition to the diffusion to the permeation, kinetics becomes much slower and that is expected. So, it is much easier to deposit on the volume rather than depositing on the inner surface.

So, that is why kinetically one process is much favourable than the other provided other constants of the parameters remains constant and that gives you an idea like you know if I have a pump, I know this much amount of time it will take to deposit a particular material and if that is not deposited by the particular time, so we know that there is a problem in the pump okay.

The classical kinetic theory is known to many of us but if we just want to revisit that in the context of the low pressure, then we can understand the idea behind this mean free path.

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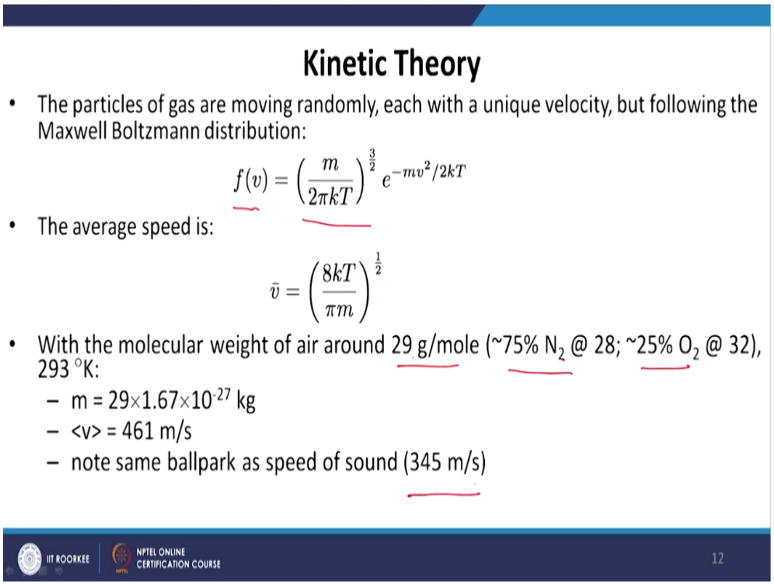

## Kinetic Theory

- The particles of gas are moving randomly, each with a unique velocity, but following the Maxwell Boltzmann distribution:

$$f(v) = \left(\frac{m}{2\pi kT}\right)^{\frac{3}{2}} e^{-mv^2/2kT}$$

- The average speed is:

$$\bar{v} = \left(\frac{8kT}{\pi m}\right)^{\frac{1}{2}}$$

- With the molecular weight of air around 29 g/mole (~75% $N_2$ @ 28; ~25% $O_2$ @ 32), 293 °K:
  - $m = 29 \times 1.67 \times 10^{-27}$ kg
  - <v> = 461 m/s
  - note same ballpark as speed of sound (345 m/s)

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The particles of gas molecules are moving randomly each with a unique velocity but following the Maxwell-Boltzmann distributions and what is Maxwell-Boltzmann distribution? We know that there are 3 different distributions; one is the classical distribution Maxwell-Boltzmann distribution and another two is the quantum distribution, one is Fermi-Dirac statistics and other is the Bose-Einstein distributions.

Now, the Maxwell-Boltzmann distribution which is obeyed by most of these macro systems that is given by the fv or the probability with the velocity v that=m/2 pi kT to the power whole 3/2*e to the power –mv square/2kT. That we have learnt from the Maxwell-Boltzmann theory okay. This is the particle of a gas when it is moving randomly with the probability of having each with the velocity v.

So, from this one if we intricate it and we get the average speed v bar=8kT/pi m to the power whole half okay. So, where k is the Boltzmann constant, t is the temperature and m is the mass of the gas molecule. Now with the molecular weight of the air around 29 gram per mole considering that the air has 75% nitrogen and 25% oxygen where the molecular weight of the nitrogen is 14*2=28 and that for oxygen is 16*2=32.

If we consider that and if we consider the weight percentage of that what it will comes out the weight of the air is 29 gram per mole, so that means 1 mole of air weigh 29 gram at the room temperature. So, if we consider that the value of m comes out to be 29*1.67*10 to the power -27 kg. So, if you substitute the value of m like that and the temperature 293 Kelvin and value of the Boltzmann constant then the average speed comes out like 461 meter per second.

Note, same ballpark as speed of sound, what is the speed of sound, 345 meter per second, so this is little bit higher than the speed of sound. So, the average speed of the gas, average speed of any gas in the normal air considering the room temperature and the average molecular weight of the air as 29 gram per mole is very close to that for the speed of the sound in the air.

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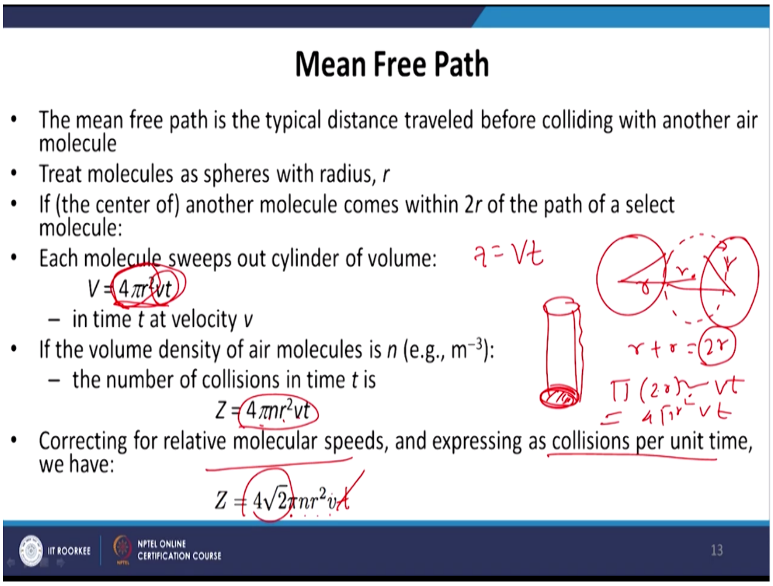

## Mean Free Path

- The mean free path is the typical distance traveled before colliding with another air molecule
- Treat molecules as spheres with radius, $r$
- If (the center of) another molecule comes within $2r$ of the path of a select molecule:
- Each molecule sweeps out cylinder of volume:
  $V = 4\pi r^2 vt$
  - in time $t$ at velocity $v$
- If the volume density of air molecules is $n$ (e.g., m$^{-3}$):
  - the number of collisions in time $t$ is
    $Z = 4\pi n r^2 vt$
- Correcting for relative molecular speeds, and expressing as collisions per unit time, we have:
  $Z = 4\sqrt{2}\pi n r^2 v\cancel{t}$

So, the mean free path is the typical distance travelled before colliding with another air molecule. So, as we have defined earlier also is the distance the molecule can travel before it suffers collision with another neighboring molecule? Treat molecular sphere with radius r, so consider that every molecule is now a sphere which has a radius of r.

If the center of another molecule comes within 2r of the path of the select molecule, now if I have to collide, this molecule with another gas molecule which is also has a radius of r, so when they have to collide then basically both of them has to come face to face. So, that means this sphere has to come now like this. So, in that case, the effective radius then will be r+r that is 2r and that is why when the center of the another molecules comes within a distance scale of 2r then a molecule can undergoes the collision with the another molecule.

So, now whenever considering it as a 2r as effective the distance between the two centers, so then each molecule sweeps out a cylinder of volume 4 pi r square vt right. So, now you can consider that there is a cylinder like that the cylinder of volume. What will be the cylinder of the volume? This is the of this circle times this distance. Now what is the area? Pi * 2 r square, because now this is the effective distance for the collision to happen.

Now, 2r square is 4r square so this is 4 pi r square that is the area of the base. Now, if the area of the base that is the two molecules has to come close together, so that we got this area. Now to get a cylinder volume I have to multiply the base area along with the height. Now, what is the height? Now, this gas molecule which is we have considered as a sphere, they are moving with the velocity v.

So, at time t if they come close to each other, then the distance they can travel is v into t, so that the length scale this z length that is equal to v into t. So, that is why the volume v is pi into 2 r square into v into t, so that is what this is 4 pi r square v into t that is what it is written here 4 pi r square into v into t the volume of the sphere. So, each molecule sweeps the cylinder of volume 4 pi r square vt in time t at velocity v.

Now, if the volume density of the air molecule is n, the number of collision in time t, how many collisions it will do if there are n number of molecules in unit volume. So, obviously it will be 4 pi r square vt into n because now each molecule will sweep out a cylinder of volume 4 pi r square vt and there are n number of molecules per each volume. So, the collision probability in time t, it will be the volume of the cylinder times the number of the molecules available in that cylinder.

So, that is 4 pi nr square vt so that is the volume times the number of molecules per unit volume. So, now we have considered so far the average speed, now correcting for the relative molecular speed because now both of the molecules is moving each other, so we have to consider the relative molecular speed. So, we can express the collision per unit time, we have now Z=4 root 2 pi n r square v.

So, basically if we consider the relative motion between the two gas molecules, the 4 factor will be replaced by 4 root 2 so that is what instead of 4 we have written 4 root 2 and the pi is like pi and n is n, r square is r square and v comes like v and then we have the t also but if we consider the unit time, then t goes out. So, per unit time the collision probability or the collision per unit time, it will be 4 root 2 pi n r square v.

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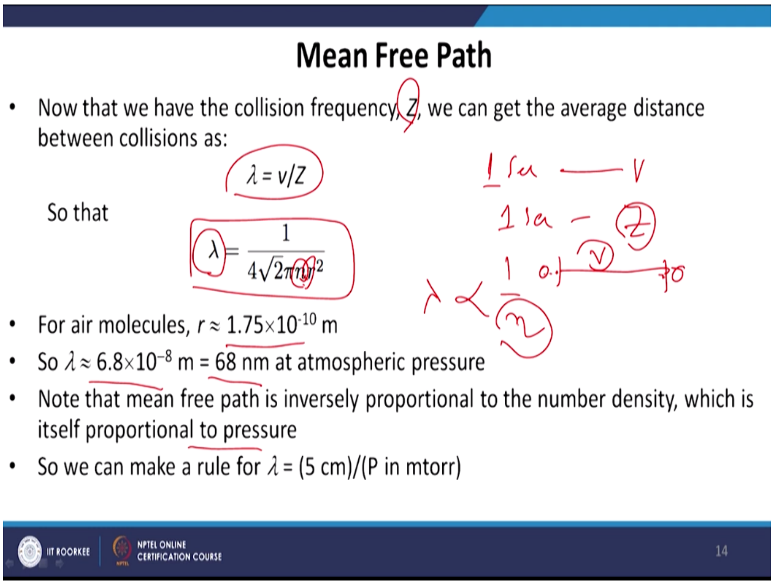

Mean Free Path

- Now that we have the collision frequency, Z, we can get the average distance between collisions as:

$$\lambda = v/Z$$

So that

$$\lambda = \frac{1}{4\sqrt{2}\pi n r^2}$$

- For air molecules, $r \approx 1.75\times10^{-10}$ m
- So $\lambda \approx 6.8\times10^{-8}$ m = 68 nm at atmospheric pressure
- Note that mean free path is inversely proportional to the number density, which is itself proportional to pressure
- So we can make a rule for $\lambda$ = (5 cm)/(P in mtorr)

Now, that we have the collision frequency, there is number of collisions per unit time, what is that, that is the collision frequency, so that is Z. So, now we can have the collision frequency, so we can get the average distance between the collisions. So, average distance between the two collisions is lambda, if you define as lambda that is v/Z. Why v/Z? Because at unit time let us say at unit second at 1 second the molecule can travel this much distance.

And while travelling this distance in this time scale this 1 second, it can undergo Z number of collisions. So, what is the average distance then they can travel before they suffer the collision. So, let us say so 1 molecule and this distance is v, there is 1 molecule here, another molecule is here, so one molecule travels from here to here and the distance between the two molecules is v and between these two distance the number of collision that can happen is Z.

So, what is the probability or what is the average distance between the two collisions? Obviously, that is v/Z so that is what it is defined here the lambda or the average distance between the collisions is v/Z. Now, we have already found out an expression of the Z, so if we plug in the value of Z as 4 root 2 pi n r square v so v and v cancels out giving that lambda=1/4 root 2 pi n r square.

So, for air molecules the value of this r radius is 1.75*10 to the power -10 meter that you have learnt. So, if we consider the value of r like that, so the value of lambda comes out as 6.8*10 to the power -8 meter or 68 nanometer at atmospheric pressure and this lambda is called the mean free path because it is the average distance the molecule can travel before it undergoes a collision.

And you note that this average distance the molecule can travel before it undergoes a collision or like you know I mean the mean free path that is inversely proportional to the number density n. So, lambda is inversely proportional to the number density n which is itself proportional to the pressure. So, the mean free path is inversely proportional to the number density as you have learnt from this equation.

Now, number density or the number of gas molecule in a particular volume that will depends upon the pressure. Now, we have learnt that from one of our earlier chart if we go back okay, so you have seen here if we go back to the pressure from 25 to 19 to 10 to the power 16 to 10 to the power 13 to 10 to the power 10, so as the pressure is reducing the number density is reducing. So, number density is depending on the pressure.

So, since the mean free path is inversely proportional to the number density, that means the number density will be lower, mean free path will be higher. Now, if I go to the low and low pressure or if I go from the low to high vacuum, the number density reduced that is why the mean free path increased. Now, when I read about this that we have talked about that there are 3 important parameters to note.

When we reduce the atmospheric pressure to the high vacuum to very high vacuum to ultra-high vacuum what you have observed, the number density of the gas molecule is reduced but consequently the mean free path increase and this explains the reason because the mean free path is inversely proportional to the number density. Now, when we reduce the pressure since the pressure reduction leads to the reduction of the number density that is why it leads to the increase of the mean free path okay.

So, we can make a rule that the lambda=5 cm/P in millitorr. So, if we put the values of the lambda in terms of the P, we can also get an expression the lambda=5 cm/P in millitorr but what is important is that here the mean free path expression starting from the Maxwell-Boltzmann statistics, we can derive an expression for the mean free path which is inversely proportional to the number density of the gas molecule which is again dependent upon the pressure of the gas molecular which is proportional to the pressure of the gas molecule.

And that is why mean free path is inversely proportion to the pressure as you reduce the pressure, mean free path will increase and vice versa. If you wanted to put in terms of the pressure, so lambda is inversely proportional to the pressure or by doing some putting some numbers arbitrary numbers for the air molecule at the normal standard atmospheric pressure we can get a value lambda=5 cm/P in millitorr.

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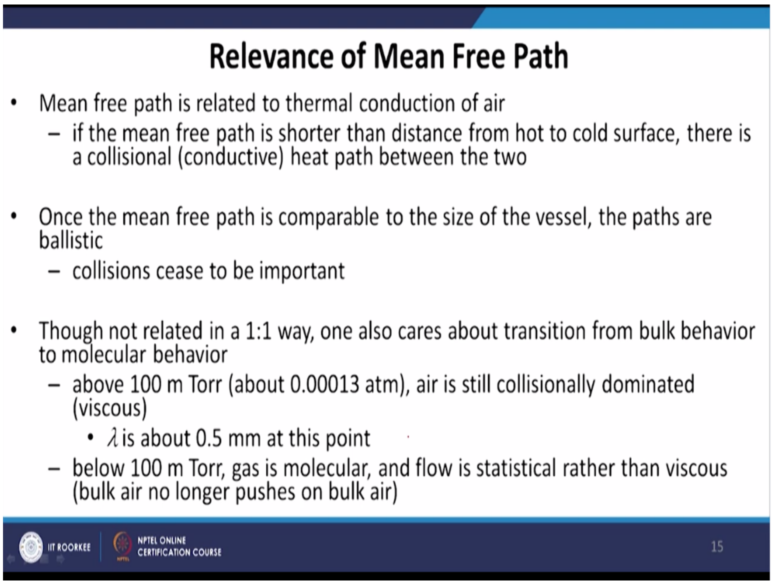

## Relevance of Mean Free Path

- Mean free path is related to thermal conduction of air
  - if the mean free path is shorter than distance from hot to cold surface, there is a collisional (conductive) heat path between the two
- Once the mean free path is comparable to the size of the vessel, the paths are ballistic
  - collisions cease to be important
- Though not related in a 1:1 way, one also cares about transition from bulk behavior to molecular behavior
  - above 100 m Torr (about 0.00013 atm), air is still collisionally dominated (viscous)
    - $\lambda$ is about 0.5 mm at this point
  - below 100 m Torr, gas is molecular, and flow is statistical rather than viscous (bulk air no longer pushes on bulk air)

So, then what is the relevance of the mean free path? Mean free path is related to the thermal conduction of the air. If the mean free path is shorter than distance from hot to cold surface, there is a collisional conductive heat path between the two. Once the mean free path is comparable to the size of the vessel, the paths are ballistic, collisions cease to be important. Though not related in a 1:1 way, one can also cares about transition from the bulk behaviour to molecular behaviour.

Above 100 meter Torr so which is equivalent to 0.3013 atmosphere, air is still collisionally dominated that is viscous and lambda is about 0.5 millimeter at this point. Below 100 millitorr gas is molecular and flow is statistical rather than viscous bulk is no longer pushes on bulk air. So, basically what it gives rise like you know the mean free path idea that leads to the concept of the molecular conductions in the air.

So, based on the molecular conduction, we can define the conduction either as a viscous flow or as a molecular flow.

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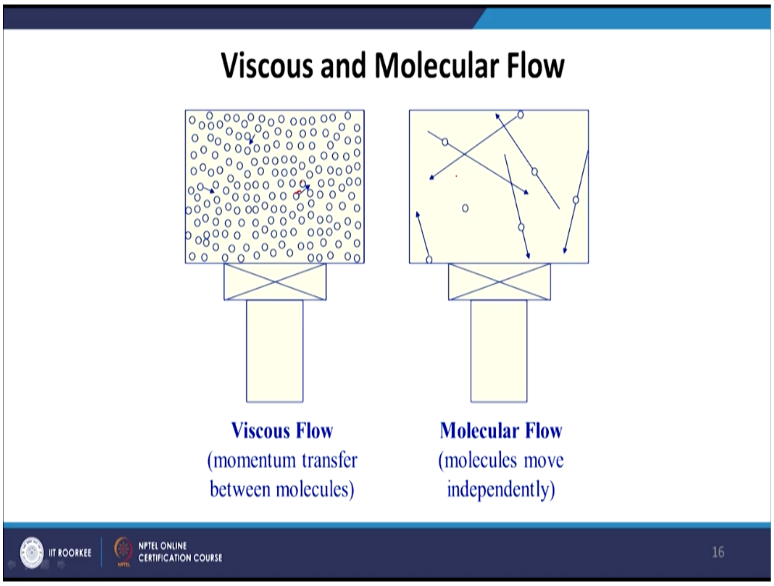

Viscous and Molecular Flow

**Viscous Flow**
(momentum transfer between molecules)

**Molecular Flow**
(molecules move independently)

In a viscous flow like which is shown in this block, a momentum transfer happens between molecules whereas in a molecular flow molecules moves independently okay. So, in a viscous flow, so the collision properties much higher, as you can see here the number of molecules is higher. So, when one molecule collides with another, there will be a momentum transfer between molecules.

But here the molecules move independently, there will be no momentum transfer between this molecular flow.

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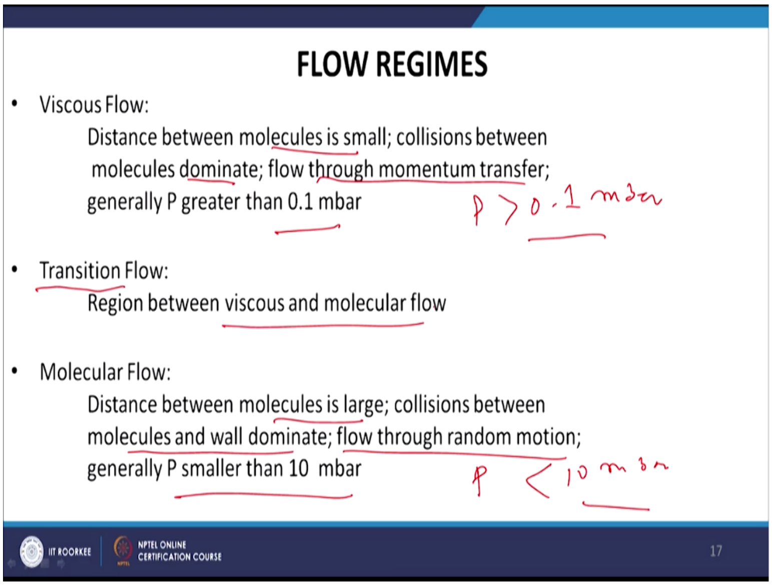

## FLOW REGIMES

- Viscous Flow:
  Distance between molecules is small; collisions between molecules dominate; flow through momentum transfer; generally P greater than 0.1 mbar

$P > 0.1$ mbar

- Transition Flow:
  Region between viscous and molecular flow
- Molecular Flow:
  Distance between molecules is large; collisions between molecules and wall dominate; flow through random motion; generally P smaller than 10 mbar

$P < 10$ mbar

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Now, we will be looking for a region where the transition happens from the viscous flow to the molecular flow. So, the viscous flow the distance between molecules is small. Collision between molecules dominates and flow through momentum transfer. So, there are 3 parts in it; first in a viscous flow the distance between the molecules is small, collision dominates and flow happens through the momentum transfer.

And in this case pressure is usually greater than 0.1 millibar. On the other hand, molecular flow, distance between molecules is large, collision between molecules and the wall dominate. So, in the previous case, you can see that the collision between the two molecules is dominating so the one molecule can transfer momentum to the another molecule but here collision between the molecule and the walls dominate.

So, the molecule does not transfer the momentum to the neighboring molecule but it rather collides with the wall. So, here the distance between the molecules is large and collision between molecules and the wall dominate and flow through random motion not through the momentum transfer and it usually happens for pressures smaller than 10 millibar. So, it is happening greater than 0.1 millibar, P>0.1 millibar and here P is smaller than 10 millibar.

So, what is the region then in between 0.1 millibar to 10 millibar, that is our transition region, transition flow where the region between the viscous flow and molecular flow. So, when the pressure is between 0.1 millibar to 10 millibar that defines the transition flow regions.

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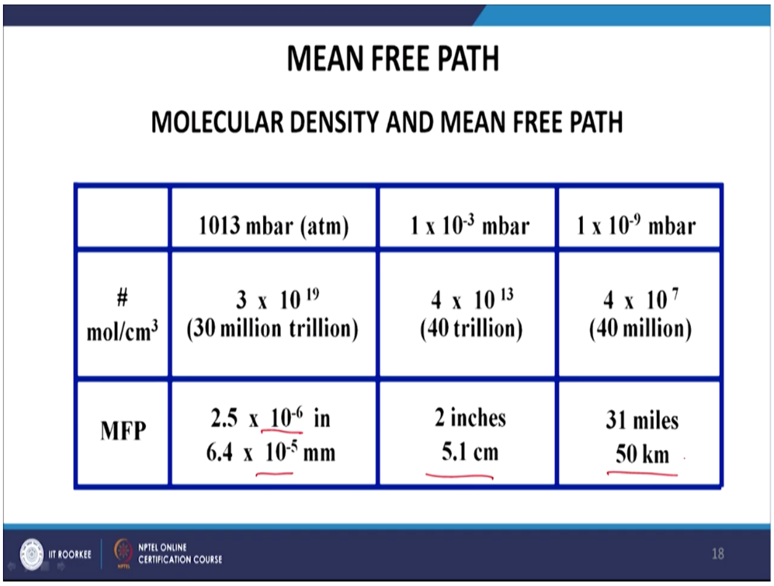

## MEAN FREE PATH

### MOLECULAR DENSITY AND MEAN FREE PATH

| | 1013 mbar (atm) | 1 x $10^{-3}$ mbar | 1 x $10^{-9}$ mbar |
|---|---|---|---|
| # mol/$cm^3$ | 3 x $10^{19}$<br>(30 million trillion) | 4 x $10^{13}$<br>(40 trillion) | 4 x $10^{7}$<br>(40 million) |
| MFP | 2.5 x $10^{-6}$ in<br>6.4 x $10^{-5}$ mm | 2 inches<br>5.1 cm | 31 miles<br>50 km |

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So, if we consider that like you know what will be the molecular density and mean free path when this pressure changes. For an atmospheric pressure like the number density of the molecular density is 3*10 to the power 19 but when you go 10 to the power -3 millibar it is 4*10 to the power 13 and when you go to 10 to the power -9 millibar it is 10 to the power 7 and mean free path as you have learnt that in the case of the atmospheric pressure it is 10 to the power -6 inch or 10 to the power -5 millimeter.

When you change the pressure 10 to the power -3 millibar, it is 5.1 centimeter increase drastically. When you reduce the pressure more 10 to the power -9 millibar it increased more and more to 50 kilometer. So, as we change the pressure or as we decrease the pressure, number density of the gas molecule decreases and consequently mean free path increases significantly.

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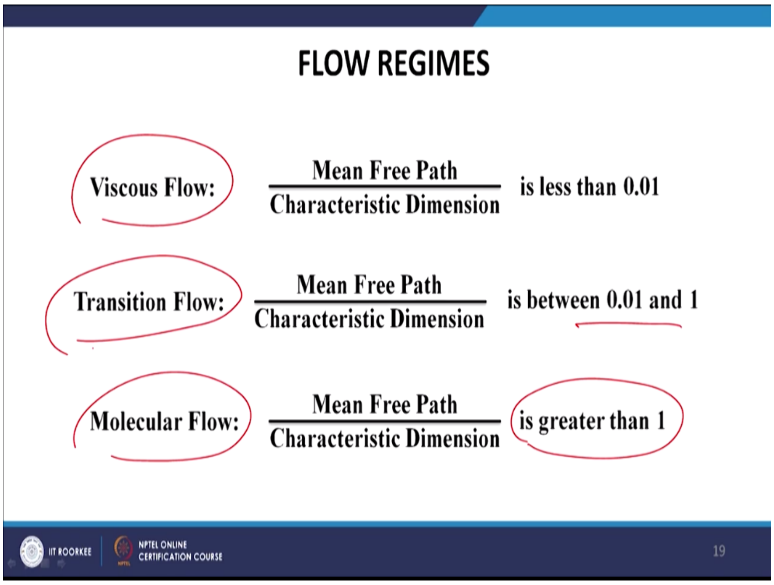

FLOW REGIMES

Viscous Flow: $\frac{\text{Mean Free Path}}{\text{Characteristic Dimension}}$ is less than 0.01

Transition Flow: $\frac{\text{Mean Free Path}}{\text{Characteristic Dimension}}$ is between 0.01 and 1

Molecular Flow: $\frac{\text{Mean Free Path}}{\text{Characteristic Dimension}}$ is greater than 1

So, we can define the flow regions also by quality factors. So, for example for the viscous flow we can define the mean free path divided by characteristic dimension is less than 0.01. So, if we take a ratio of the mean free path by the characteristic dimension, if it is less than 0.01 then it defines the viscous flow and if the value is greater than 1, then this is the molecular flow and between 0.01 and 1 that is the region for the transition flow.

So, whenever we look for whether it is a viscous flow or whether it is a molecular flow basically we need to know the mean free path of the system and we need to know the characteristic dimension and we need to take a ratio of the mean free path to the characteristic dimension. If it is less than 0.01 then it is a viscous flow, if it is greater than 1 then it is a molecular flow, if it is in between 0.01 and 1 then it is a transition flow. Now, what is conductance in viscous flow?

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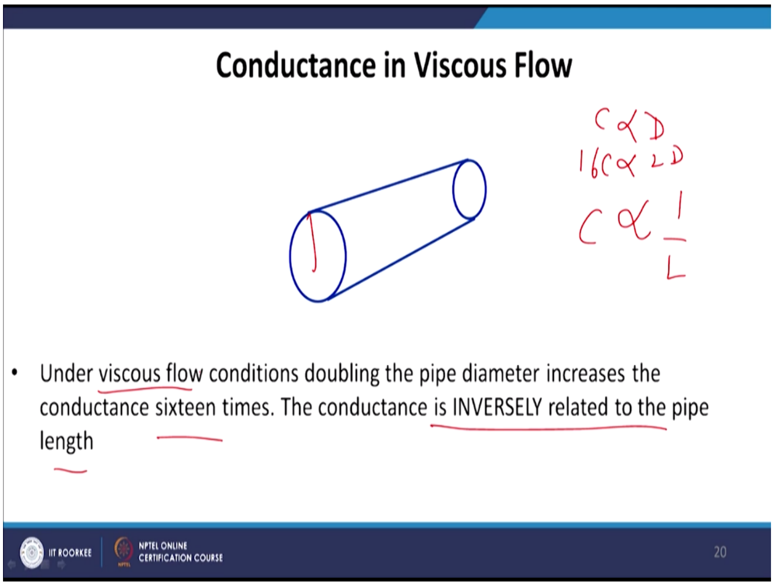

## Conductance in Viscous Flow

$C \propto D$

$16C \propto 2D$

$C \propto \frac{1}{L}$

- Under viscous flow conditions doubling the pipe diameter increases the conductance sixteen times. The conductance is INVERSELY related to the pipe length

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Under viscous flow conditions, doubling the pipe diameter increase the conductance 16 times. Well I mean one important thing to know here that why we are talking about the mean free path, is it only that it is lessen with the pressure. No, actually the mean free path changes whether the flow is viscous flow or a molecular flow but what is the important for that, this viscous flow of the molecular flow is directly related to the conductance and that is we are all interested about.

Under viscous flow, condition doubling the pipe diameter, so this is the diameter right, so if you double the diameter of the pipe that increase the conductance 16 times. So, the conductance is inversely related to the pipe length. So, if you increase the diameter D to 2D so the conductance if it is D now it is 16C and the conductance is inversely proportional to the length of the pipe.

So, this is the condition under the viscous flow but the molecular flow it will be different. Actually, these all things we required in consent to the vacuum gadgets when you talk about the vacuum gadgets and the piping and all these things, so these concepts will be very important. Now there is an equation, we are not deriving it here, we can write the conductance or what will be the flow of the gas molecule per unit time or how good the flow is, that we define in terms with the conductance.

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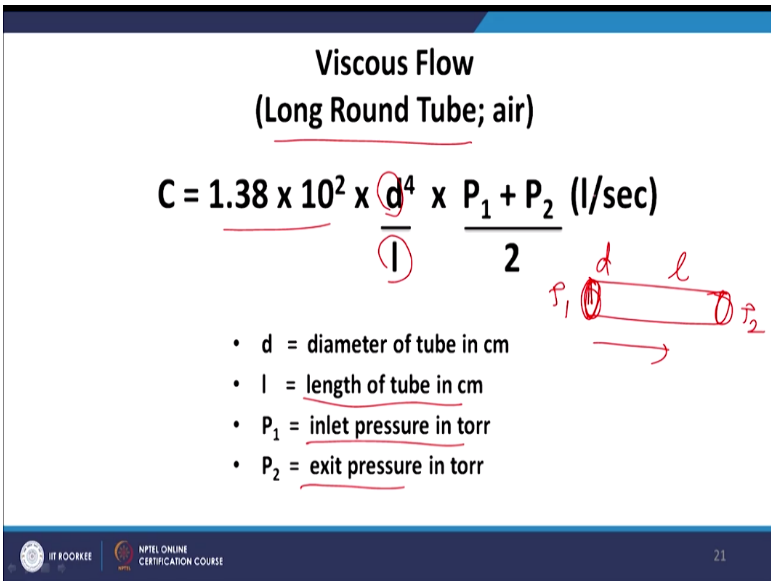

Viscous Flow

(Long Round Tube; air)

$$C = 1.38 \times 10^2 \times \frac{d^4}{l} \times \frac{P_1 + P_2}{2} \ (\text{l/sec})$$

- d = diameter of tube in cm
- l = length of tube in cm
- $P_1$ = inlet pressure in torr
- $P_2$ = exit pressure in torr

Under the viscous flow, if we consider a long round tube so the conductance is given by 1.38*10 to the power 2*d to the power 4/l*P1+P2/2 liter per second okay. Here d is the diameter of the tube in centimeter, l is the length of the tube in centimeter, l is the length of the tube, P1 is the inlet pressure and P2 is the exit pressure. So, basically if I have a long round tube like this okay and the diameter here is d and the length is l.

So, the conductance inside this tube is proportional to the d to the power 4 inversely proportional to the length and it depends upon the pressure P1 at the inlet and pressure P2 at the outlet. So, P1+P2/2 so it is d to the power 4/l*P1+P2/2, this amount of centimeter per second.

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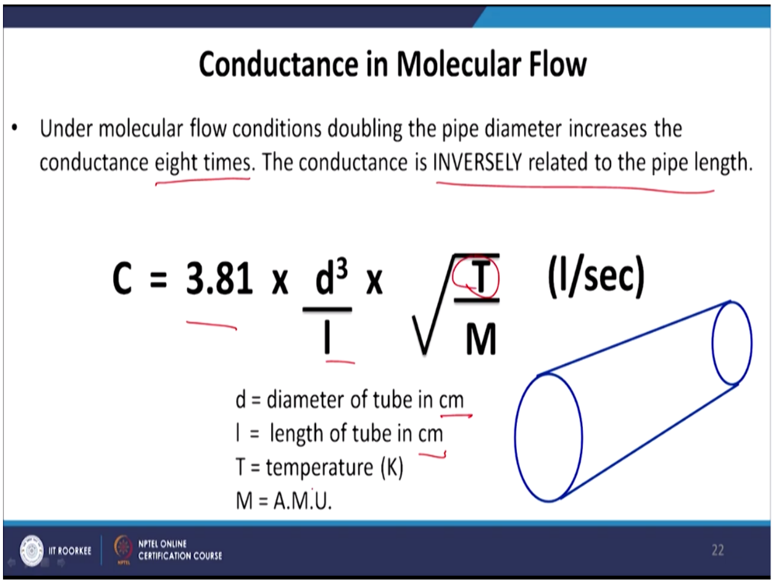

Conductance in Molecular Flow

- Under molecular flow conditions doubling the pipe diameter increases the conductance eight times. The conductance is INVERSELY related to the pipe length.

$$C = 3.81 \times \frac{d^3}{l} \times \sqrt{\frac{T}{M}} \ (\text{l/sec})$$

d = diameter of tube in cm
l = length of tube in cm
T = temperature (K)
M = A.M.U.

And if you go to the molecular flow it will be different. Conductance in a molecular flow, it is given by 3.81*d cube/l*square root of T/M. So, under molecular flow condition doubling the pipe diameter increase the conductance 8 times not the 16 times under viscous flow and the conductance is inversely related to the pipe length. So, one thing is common both in viscous flow and molecular flow.

So, it is if we increase the diameter of the pipe conductance increase significantly, so that is expected right. So, if we have a smaller diameter pipe and let us say if I have a larger, very larger diameter pipe and if I passing the water through both of these pipes, a narrow pipe and a very large pipe, so in which case you expect to have a more amount of water to pass, of course in a large diameter pipe.

So, that is why the conductance in a large diameter pipe is higher than a narrower diameter pipe and the dependence on the diameter is 16 times or d to the 4 in the case of the viscous flow and it is d cube in the case of the molecular flow and in both of these cases, it is inversely proportional to the length and that is also expected. Let us say I wanted to pass the water through a pipe, through water pipe.

Now, I have a 10 centimeter pipe and I have a 10 meter pipe. Now, in which case I will expect that the flow is more favourable? Of course, in a smaller length pipe, the flow will be more uniform and more favourable than a longer length pipe. So, that is why it is inversely proportional, conductance is inversely proportional to the length, you can remember like that but in the case of the molecular flow, it also depends upon the temperature and the mass, atomic mass unit.

So, in addition to d cube/l, it also depends here d is the diameter of the tube in centimeter, l is the length of the tube in centimeter and T that is the temperature in Kelvin and M is atomic mass unit is the molecular mass which is expressed in atomic mass unit. So, basically what we have learnt that if we go from the atmospheric pressure to the lower pressure.

Like if we go to the roughing pump, if we use the rough pump, if we go to the rotary vacuum, something like 10 to the power -2 millibar or if we go to medium vacuum or like high vacuum or ultra-high vacuum so the number density of the gas molecular reduce drastically, mean free path increase. We have derived an expression for the mean free path and we have seen that mean free path is inversely proportional to the pressure.

And as the mean free path changes considering the characteristic dimension, we can define a quality factor which gives the flow is viscous or molecular or in a transition region right and if the flow is viscous of the molecular, conductance will be different and now the conductance in a viscous flow and the molecular flow, it depends upon the diameter and the length of the pipe and that all actually is important to understand when we are talking about the vacuum gadget subsequently.

So, in today's lecture, we have learnt about like you know why we need to create the vacuum and what are the different concepts related to the vacuum but what is important to know right now, how we can create the vacuum. So, we know that we need a pump to create the vacuum but in the next lecture, we will learn about the different kind of pumps and the different kind of pumps how they can create the vacuum okay. Thank you so much.