Chemical and Biological Thermodynamics: Principles to Applications

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Lecture - 02
Work

In the previous lecture, we discussed the basics of thermodynamics we talked about system, surrounding different type of systems. And then we also discussed that there are three fundamentals of thermodynamics work, heat and energy. We also discussed that work is the most fundamental, because we can express heat and internal energy in terms of work as we will discuss later.

In today's lectures, we will mostly discuss about work. As I described earlier work is said to be done in a process if that process can lead to change in the height of a weight somewhere in the surroundings. The processes can be of different type, for example, a very simple process can be the expansion or compression of a gas, another process can be retained in the physical state of a system for example, melting, vaporization that is also another process. Or it can be a more complex process in which the new products are formed, but let us develop some equations based upon the very first that is the work associated with the change in volume of a gas.

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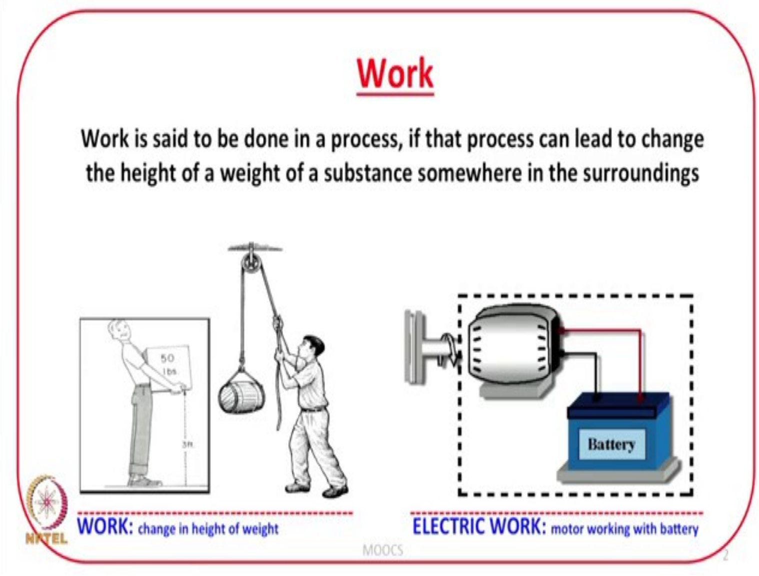

So, as we will see that whenever there is a change in height of a weight of a substance somewhere in the surrounding, we link it to the work done. This example I took in my previous lecture also that a person who is lifting the weight, we can see that the height of that weight is changing in the surroundings. Then what about the electrical work, yes, the electrical work can also be connected with the change in height of a weight somewhere in the surroundings, for example, the electrical current produced can be passed through a motor and which is connected to the fully and then fully can be connected to a weight. And we can see the height of a weight being changed in the surroundings. So, this is in terms of Layman's language.

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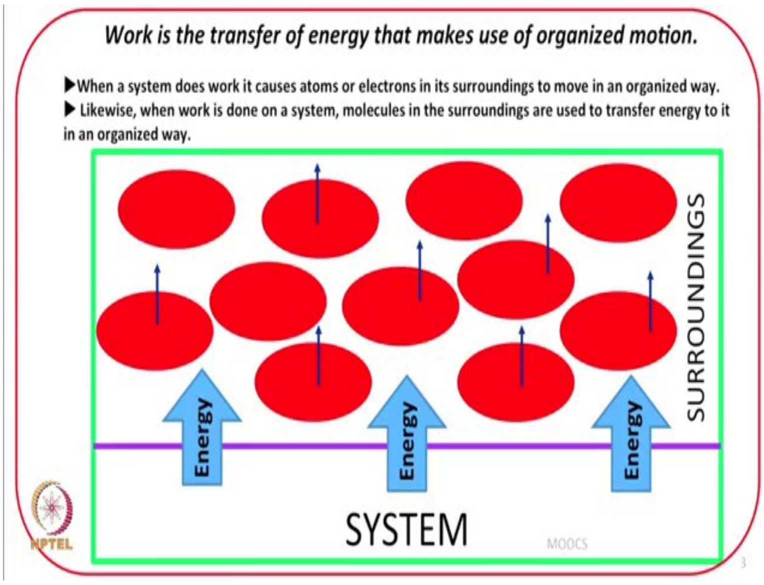

Let us discuss more about work and how we can actually calculate the work done in a process. We must realize that work is the transfer of energy that makes use of organized motion. This is how as I will describe later that we differentiate work from heat. When work is done then the transfer of energy takes place in an organized motion. Let me take an example. As we see in this figure that when energy is transferred from system to surrounding, it be form of work, it causes the atoms or electrons in the surroundings to move in an organized way. And similarly when we talk about reverse that is when the work is done on the system then the molecules in the surroundings are used to transfer energy into it in an organized way. What I am saying is the transfer of energy from the surroundings to the system occurs in an organized way when the surroundings do work on the system, but then how that energy is consumed that we will discuss later on.

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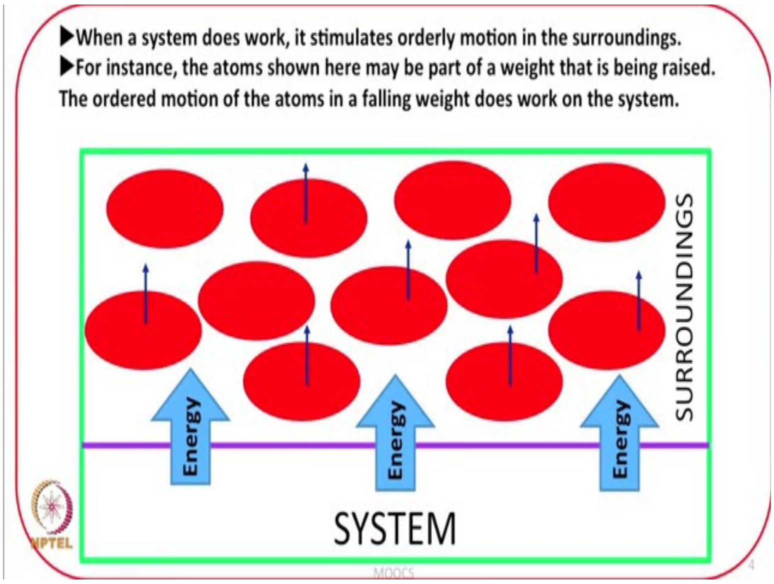

Even if I link it to the weight being raised and the work is done then the transfer of energy is again occurring in an orderly motion, and when the weight is being lowered the ordered motion of the atoms in the lowering substance does work on the system, and how we differentiate from the heat that how the energy is transferred when it is heat that we will discuss later on, but as far as work is concerned, it is the transfer of energy in an orderly fashion in an orderly motion.

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Type of work	dw	Comments
Expansion (or p-V)	$-p_{ex}dV$	p_{ex} is the external pressure dV is the change in volume
Surface expansion	$\gamma d\sigma$	γ is the surface tension $d\sigma$ is the change in area
Extension	fdl	f is the tension dl is the change of length
Electrical	ϕdq	ϕ is the electrical potential dq is the change in charge

As I said there are different types of work, the work of expansion, which is also called pressure, volume, work, and I will discuss why I am saying it as a pressure, volume, work. And we will derive expression for this a bit later which will turn out to be minus p external into dV, where p external is the external pressure and dV is the change in volume. Surface expansion that is also a type of work, which is equal to gamma times d sigma, where gamma is surface tension and d sigma is the change in area. Similarly, there is work done of extension f dl; f is tension and dl is the corresponding change of length. The electrical work can also be obtained by a multiplying electrical potential and the change in charge.

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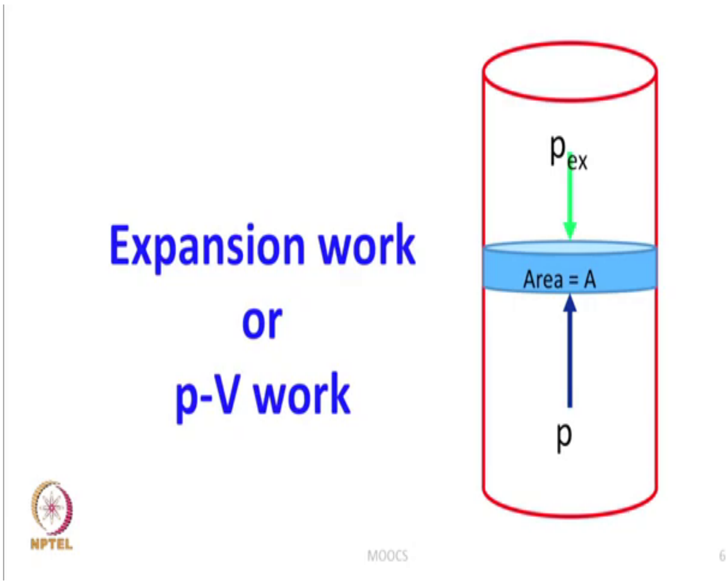

In today's lecture, we will focus on pressure volume work many books or I would say almost all the books write the work as expansion work when it is associated with the change in volume of a gas, but then if there is an expansion work then compression work is also there, so that there is no confusion. Sometimes, it is better to call it as a pressure volume one because if the volume increases then it leads to expansion; if the volume decreases then it is a compression.

Let us look at this figure. It is a cylinder in which you have a piston which is weightless, frictionless and perfectly fitting; p represents the pressure of the gas; and p ex represents the external pressure - this is due to the atmosphere. And let us consider the area of cross section as A. Now, this piston can be either a raised or it can be lowered depending upon the values of the pressure of the gas and the value of external pressure. And we will talk about the work and we will also talk about how to calculate the work done in such cases.

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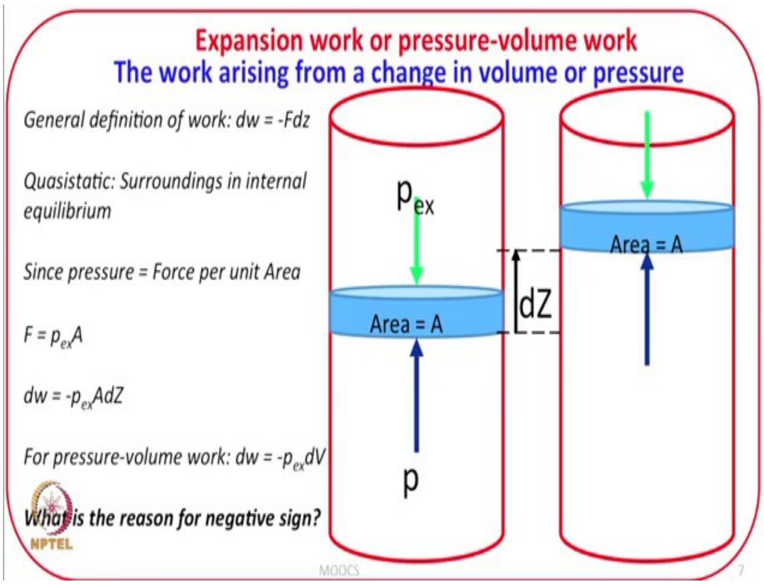

Let us with first talk about expansion work or pressure volume work as I just discussed that the work, which is arising from a change in volume or a change in pressure. Now, let us consider that this piston moves by a distance dZ. And we know that A is the area of cross section of this container or area of cross section of the piston. How do we calculate the work? Let us now recall the definition in physics, how do we calculate the work, work is force times distance, and how do we calculate force the force can be calculated from the pressure. Pressure is force per unit area. Therefore, the force on the piston will be equal to pressure into area. And it is this force p external times A, which forms the weight, which forms the weight of the substance which is either being lowered or it is being raised depending upon whether it is compression of the gas or it is expansion of the gas.

So, let us discuss the expansion work or pressure volume work, which is the work arising from a change in volume or pressure. Let us once again consider this cylinder which is having an area of cross section A, which is also the area of cross section of the piston. p is the pressure of the gas, p external is the external pressure, and let the piston moves by a distance dZ. The piston has moved up and the work has been done by the gas in driving back the surroundings. And our aim is to calculate this work. Derive an expression for calculating this work. How do we calculate this work?

Let us recall the definition from physics that work is equal to force times distance. If we know the force acting on the piston, and if we know how much distance the piston has moved, then we can calculate work. Then how do you calculate force? Force from pressure it can be calculated, because pressure is force per unit area. Therefore, force is equal to pressure times area pressure here is p external and area is A. Why do we use p ex, because it is the external pressure which constitutes the weight of the piston which is acting on the piston, therefore we have to use the p external.

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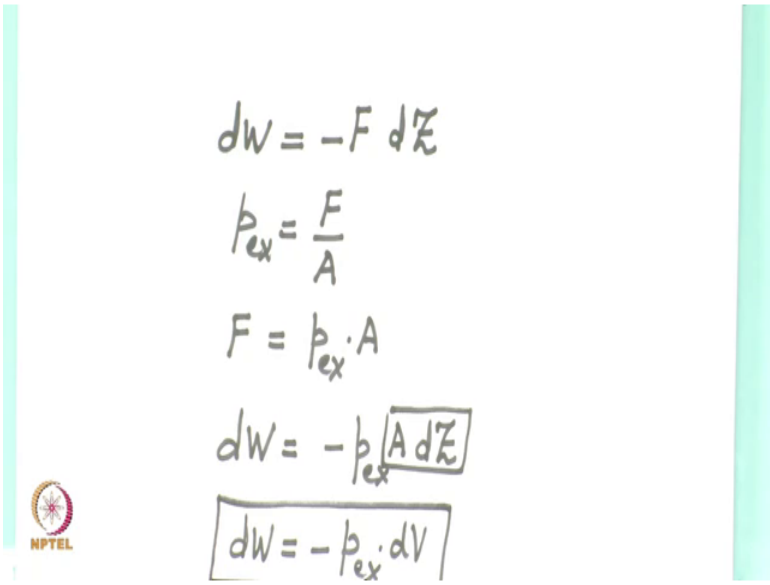

From the definition of physics work, how do we calculate work? Let us say if the piston moves by infinitesimally small distance then the work done in doing that is minus force times the distance moved. It should be very clear that why we are using the negative sign, it is because the word is being done against an opposing force that is why the negative sign will come. And p external is equal to force per unit area, therefore instead of force I will write p external into area. And now when I substitute into this, the infinitesimally small amount of work done in moving the piston by the infinitesimally small amount of length dZ will be equal to minus p external into A into dZ.

And now area into the lengths moved, this is the change in volume. Therefore, what we have is work done is minus p external times dV. This is a very important relation. This is the relation that we will be using in deriving many more equations from this. According to this equation the work done when the piston moves by a small distance dZ, which leads to change in volume of dV against an external pressure p x is given by d w is equal to minus p external time dV. The reason for negative sign I have already discussed because the work is done against an opposing force, whether it is the work of expansion that is expansion means dV is positive, compression means dV is negative.

You lower the piston that is the p external is higher than the pressure of the gas, it will lead to compression. If p external is external is lower than the pressure of the gas then it is expansion. In both the cases, the same formula we apply that is dw is equal to minus t external time dV. The sign does not get changed when the expansion changes to compression no it is always minus p external times dV, because the weight is constituted by the external pressure. In the case of expansion, the weight is height of the weight is increased in the surrounding; and in the case of a compression, the weight is getting lowered in the surrounding. So, it is always the work is being done against that weight that is why we will have to use negative sign and the same formula will be used whether it is the compression or it is expansion of the gas.

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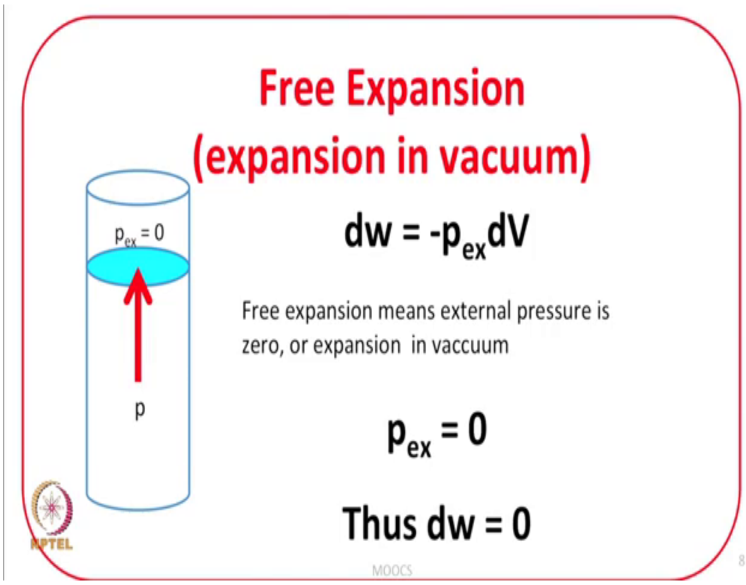

So, now let us discuss different cases. First let us discuss free expansion. What is free expansion? As the name suggests free, free means there is no opposing force that means, the external pressure is set to 0 which in other words is vacuum U let the gas expand vacuum. If p external is equal to 0 and then we use that expression the dw is equal to minus p external times dV; if p external is 0 therefore, the work done is 0. So, therefore, no work is done by the gas when it expands against vacuum, when it expands in vacuum or when it expands vacuum an external pressure of 0.

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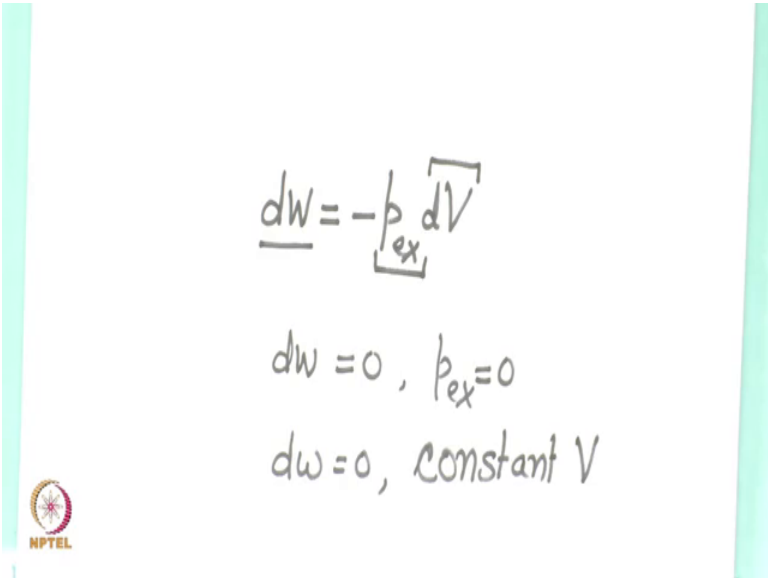

So, under what conditions, there is no work done, dw is minus p external times dV, dw will be 0, case one when p external is equal to 0 or it can also be 0 when dV equal to 0. That means, it is in vacuum when the gas expands in vacuum dw will be 0, if p external is equal to 0. And dw will be 0, if the process is done under constant volume conditions, there is no change in part.

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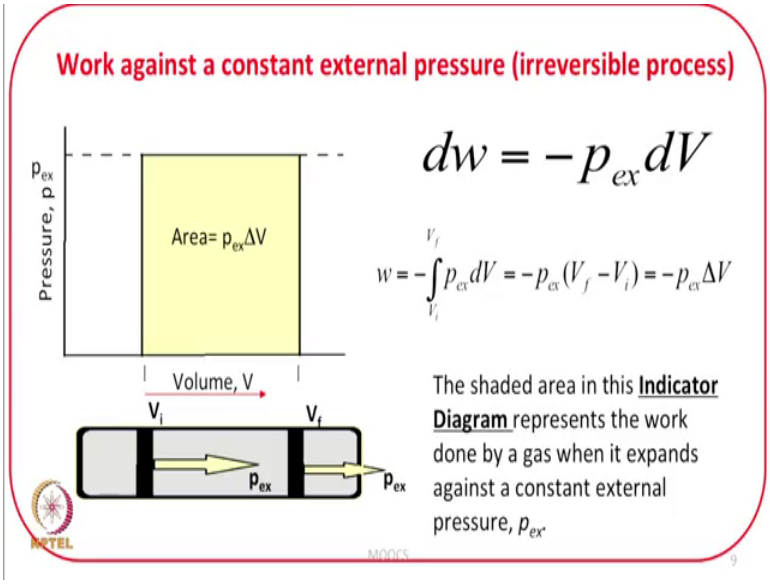

Now let us discuss the case when the external pressure is nonzero, and you fix it. When you fix the external pressure then the process becomes irreversible. And I will discuss a bit later that why it is called irreversible, and what is a reversible process.

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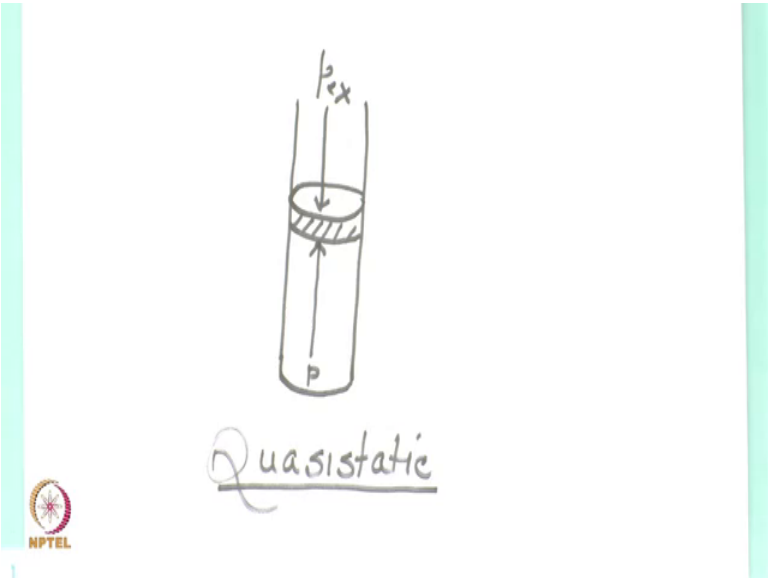

One thing that we must remember that when I am discussing this case of this cylinder and talking about this piston, and this is p external, this is pressure of the gas, then the movement of this piston is quasi-static. The discussion applies a quasi-static process. What is a quasi-static process? A quasi-static process is the one in which the surroundings remain in internal equilibrium that is there is no formation of non-uniform region of temperature or pressure. So, our present discussion applies to quasi-static processes. Now, let us talk about the work against a constant external pressure that is an irreversible process. The same formula for the work done will apply dw is equal to minus p external times dV, but here the external pressure represented by the dotted line is fixed is constant, but the volume is changed from V i to V f as can be seen in this figure.

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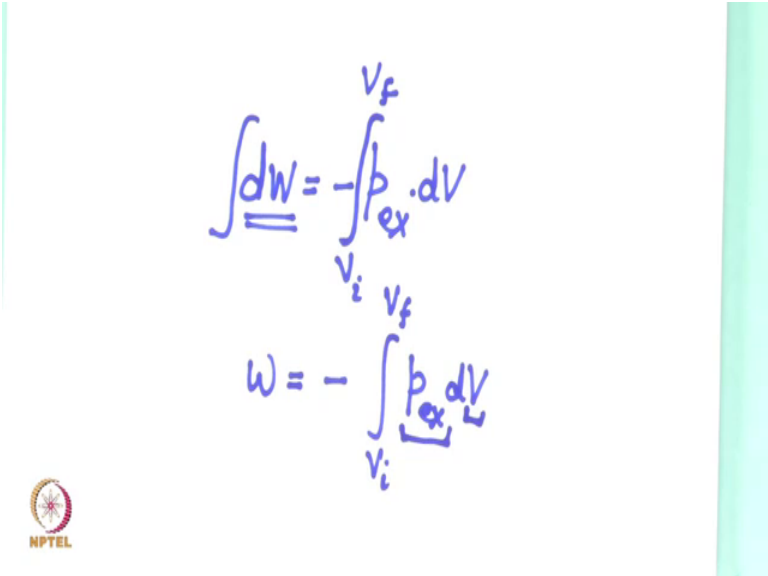

Now, let us write again dw is equal to minus p external time dV. And this is for an infinitesimally small change, but for a finite change, I need to integrate from V i to V f. What will be of now, you know the work is a path function. Therefore, I will write w is minus integration V i to V f p external times dV. There are two ways of evaluating this integral one is numerical integration and the other is a graphical method. How do you evaluate the integral, you plot p against V, and the area under the curve or line whatever it generates within the limits V i to V f will give you the value of the integral.

So, that is what let us take a look at this figure p external is constants represented by the dotted line and the limits are V i to V f, the value of the integral will be given by the area under that line within the limits. This is how we can calculate the work done against a constant external pressure, p external will come out of the integral and the resulting equation is w is equal to minus p external into V f minus V i or it is equal to minus p external into delta V. We can use this expression. And this diagram the shaded area, this is called an indicator diagram. And this indicator diagram can be used to calculate the work done by the gas, when it expands against a constant external pressure p ex. And of course, the same equation can be used when the gas is compressed against a constant external pressure from some initial volume to some final point.

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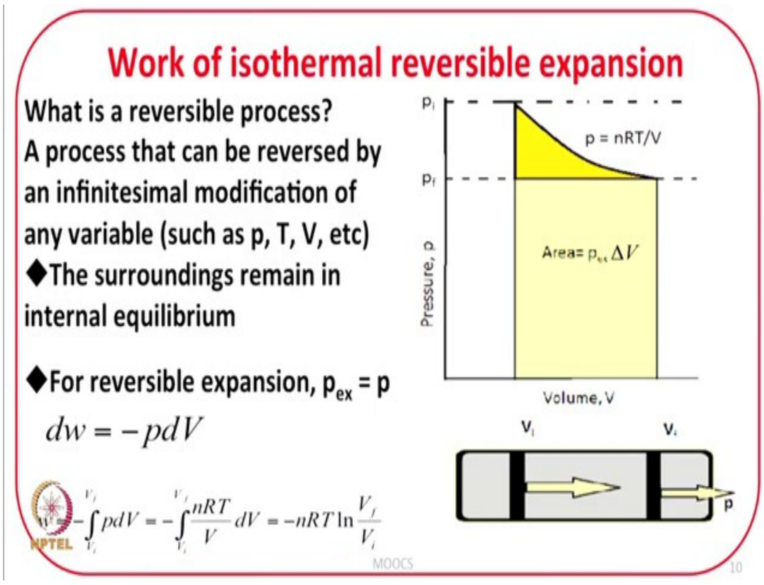

Moving ahead, let us now talk about work of isothermal reversible expansion. This is also very important. First of all let us try to understand what is a reversible process. As the name itself suggests that a process which can be reversed can be called reversible, but there is more to the definition. A process is said to be reversible, if it can be reversed by an infinitesimal small modification of any variable such as pressure, temperature, volume, what I mean is suppose if we increase the pressure of a gas by an infinitesimally small amount, it can push back the piston a little bit. And then if we increase the pressure of the surroundings that is p external by a very small amount then it can push the piston a little down that is the process can be reversed by an infinitesimally small modification of the pressures and the same can be achieved by temperature compound. The other condition is that surroundings must remain in internal equilibrium.

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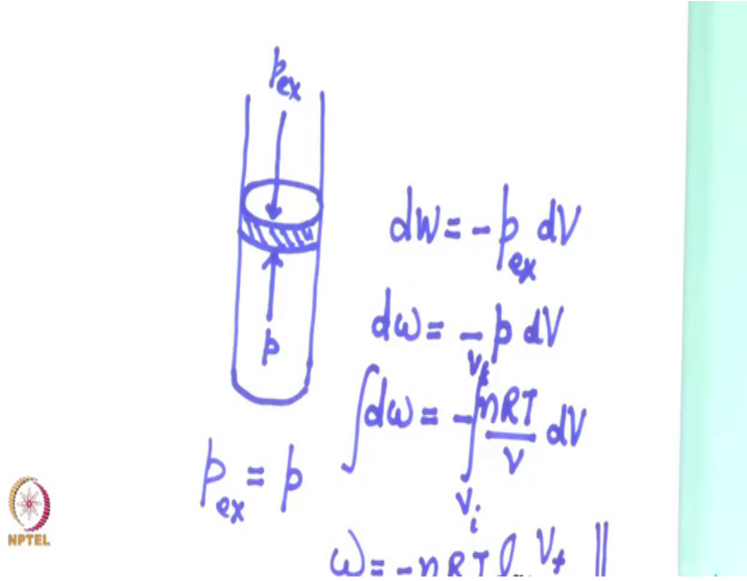

Now, how do we achieve reversibility the reversibility can be achieved if we match the external pressure and the pressure of the gas. Because then only if there is a match then let me show it here, this is pressure of the gas, this is p external, and if both are being matched being match means there is a mechanical equilibrium. In that case, if I raise, if I increase the p external by an infinitesimally small amount, it will lead to the compression of the gas. On the other hand if I increase the pressure of the gas by infinitesimally small amount, it will push back the piston and the expansion will take place. Therefore, the condition for reversibility is that let there be a mechanical equilibrium, and we set p external is equal to p.

So, in that case, what we have is we go back to the definition dw is equal to minus p external times dV. And instead of p external, I will replace it by the pressure of the gas, and let us assume the ideality then dw is equal to n R T by v into dV, I am using p V is equal to n R T. And now let us say I go from V initial to V final then w will come out to be minus n R T log V final over V initial. So, this is the expression to calculate the work of isothermal reversible expansion. And the same applies to work of isothermal reversible compression. It is only the volume, in one case it is increase and the in the other case there is a reduction in the volume.

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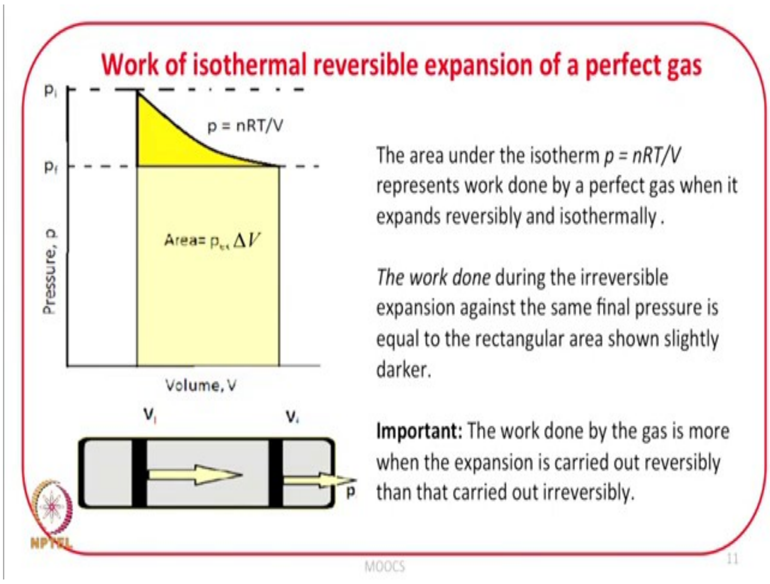

Now, let us take a look at this figure and consider the reversible expansion from V i to V f then as I described earlier that dw is equal to minus V i to V f p dV.

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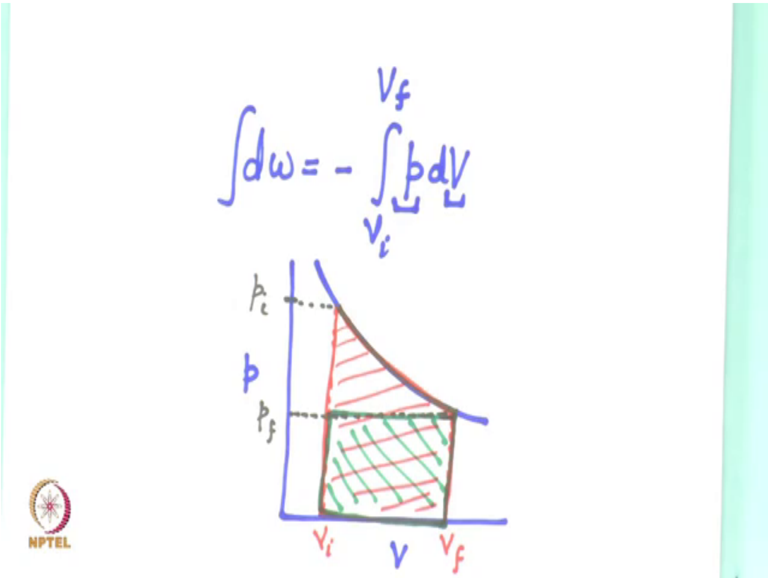

So, I need to plot pressure against the volume. If we plot pressure against volume this is what you get under isothermal conditions. And now if I choose the initial and final volume, this is V i this is V f, then according to this, the value of the integration will be area under this curve, this represents the work done. However, if the expansion is carried out, this is your p i and this is your p f. Now, if you carry of the expansion against the final pressure constant then as I discussed earlier that this indicator diagram, this one this will give the work done, because the area under minus p external d. In that case you have to plot a graph of p, you have to keep p f you have to keep constant and the volume change is V i to V f the area is this. So, therefore, we can clearly see that this area total area which is representing the work done under reversible expansion is more than the other area this area which represents the work done under irreversible expansion.

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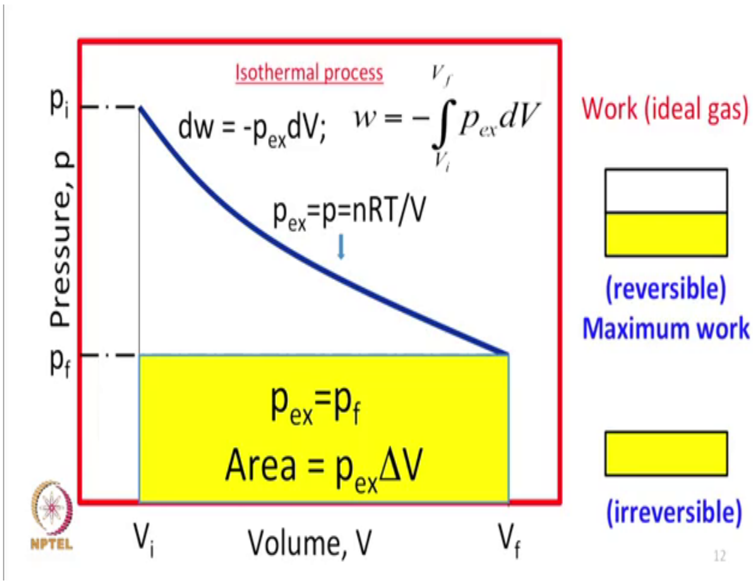

So, therefore, this figure compares the work of reversible expansion as well as of the irreversible expansion, which is more clearly shown here. This is just the same thing which I discussed on the paper that if you look at the right hand side of this figure the yellow and white areas together represents the work done by the gas assumed ideal. When it expands from v i to v f and the yellow portion only represents the work done by the gas when it expands against the constant external pressure that is the p f.

Another important point to note is that maximum work is obtainable from the system when it operates under reversible conditions. This statement which I am saying is not just applicable to the expansion of the gases as we will prove later that it applies to all the processes. But especially in the case of expansion of a gas, if we keep the reversible condition, we are matching p external and the pressure of the gas. And therefore, if we are matching then this is the curve that we are obtaining and by an infinitesimally small modification of the pressure, we can either you know lead to compression or expansion, but since we are talking about the work or to be obtained from the system that means, we have to talk about expansion.

So, expansion means you have to lower the pressure outside pressure external pressure from by an infinitesimally small amount then the pressure of the gas. Because if you try to increase the pressure - external pressure a little bit that will lead to compression of the gas the pushing power will be reduced. And therefore, the maximum work is obtained from the system when it operates under reversible condition or the maximum work is done by the gas particularly when we talk about the current case, the maximum work is done by the gas when it is expending under reversible conditions.

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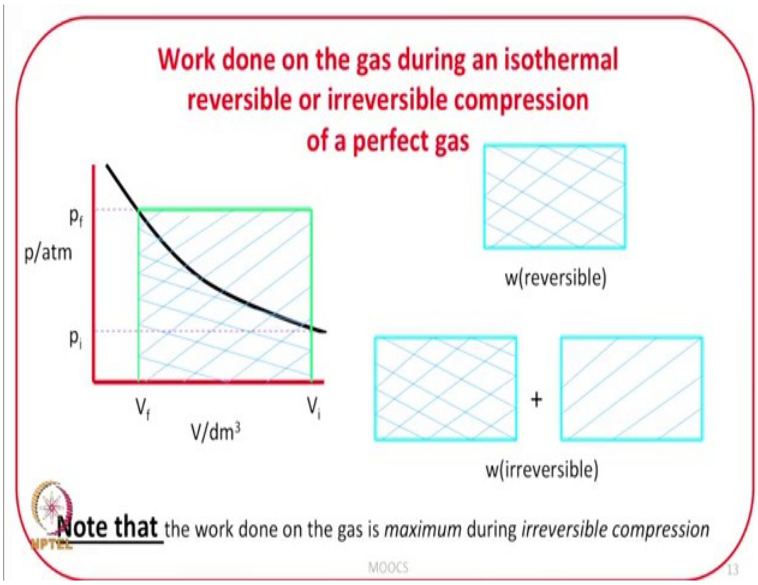

Now, what about the compression, this figure describes the work done on the gas you know when you talk about compression. So, let me put back the previous discussion. Compression means now you have to apply more pressure, this external pressure should be more than the pressure of the gas then it will lead to compression. If I say that the maximum work is done by the gas when it is expending under reversible condition then what about the work done on the gas, will it be maximum when the conditions are reversible or will it be more when the conditions are irreversible.

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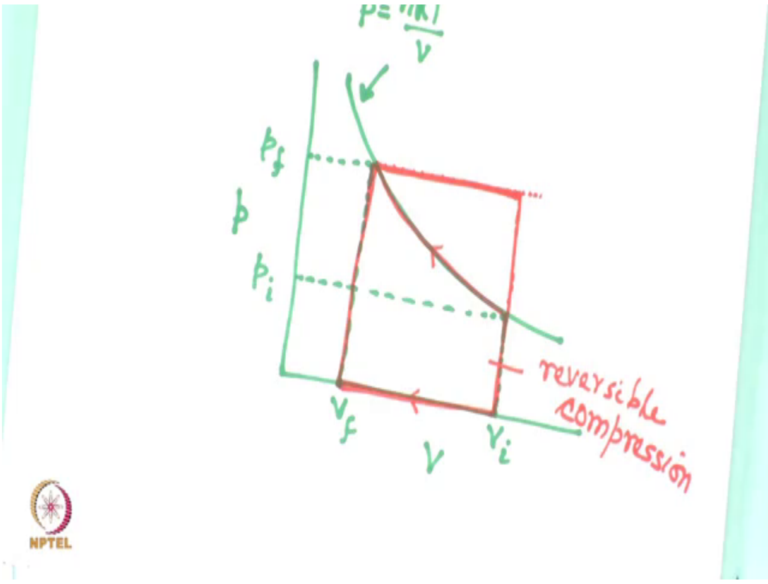

Let us take a look at this figure. In this picture, this is pressure, this is volume and this is your p v isotherm, you know this is equal to p is equal to n R T by V; this is according to that. Now, let us say I choose these limits, I am talking about compression that means, this is my V i, this is my V f and correspondingly this is my p i and this is going to be my p f. When the compression is done reversible, we are moving this way, reversible means we are talking about this area reversible compression. And if I increase the pressure on the gas all of a sudden to a final pressure that is make the process irreversible. In that case, according to the indicator diagram, the total area that I must talk about is this, this one, total, this is for an irreversible case.

So, obviously, in irreversible compression under isothermal conditions, the work done on the gas is more than the work done on the gas under reversible compression. And it is clearly shown in this slide also that the work done under reversible condition is the area represented by the cross lines and irreversible is the total area within that green and closure that is the cross line plus the state lines. So, work done on the gas under irreversible condition is more compared to reversible condition. So, the conclusion of this slide is that the work done on the gas is maximum during irreversible compression.

So, in today's lecture, we talked about work, what is work, how to obtain the value of the work under different condition; and specifically we focused on the expansion or compression of a perfect gas. And we also talked about what is the work done when the gas expands in vacuum or there is a change at constant volume, there is no work done if the volume is highly fixed. Then we also talked about how to calculate the value of work done when a perfect gas expands under reversible isothermal conditions and irreversible isothermal conditions. So, we have talked about one of the fundamentals of thermodynamics the work the most important.

And in the next lecture, we will connect internal energy with heat and work, and formulate the first law of thermodynamics. And there I will demonstrate that we can connect work with both heat and internal energy that means, we can express work both in terms of heat as well as internal energy that is why I said earlier that amongst all the three basic fundamental properties work is most fundamental.

Thank you.