# Introduction to Chemical Thermodynamics and Kinetics
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## Lecture – 05
## Introduction – part 2

So we just discussed what is the work of expansion and what is the work of compression and we are only discussing the work as pressure volume work which is associated with expansion or compression of a gas. Now how it will look like on an diagram if we want to diagramically represent how the pressure and volume are changing and what is the work done how will you represent it; remember that it is a multiplication of 2 terms pressure times change in volume.

Now, we said that our system is exchanging heat with a surrounding which means the temperature was kept constant which again means we are going to draw how the work done we will look like in a P V isotherm. So, we are going to show now the graphical representation for work done for compression and for expansion we will start with expansion.

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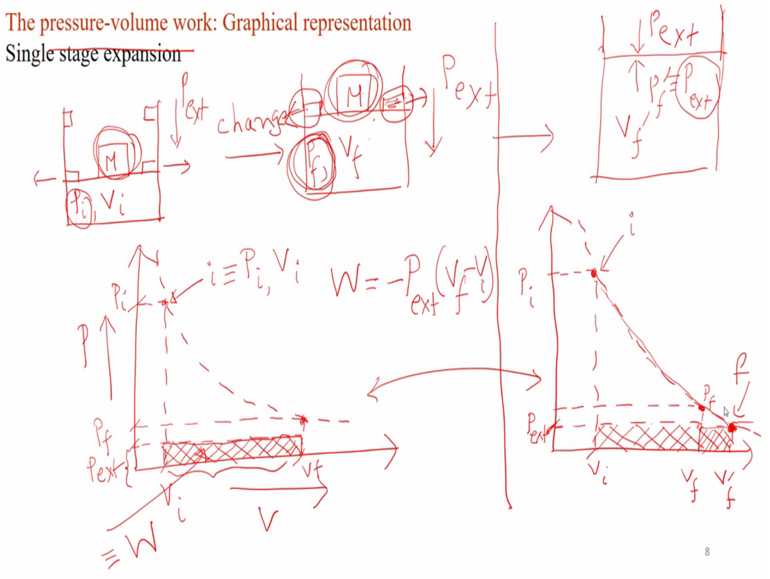

The pressure-volume work: Graphical representation

~~Single stage expansion~~

So, what we show in the previous examples is called single stage expansion and single stage compression by single stage we mean that we just put the weight and removed the pins and then the piston moves in 1 step. We so that the following changes from some initial following V i to a final following P f. However, we could have done it in the multiple stages first let us look at how the single stage expansion look like in a P V isotherm.

Now, let us once again draw it this was the expansion which means initially the following was like this and the pins were attached suppose this is the mass M and then there was another set of pins all of a sudden we remove those pins. So, that the system expands until and unless the piston touches these pins which were lying above and this is the final stage.

So, this is the change which we discussed when you are discussing the definition of terms this is the change of the system and of course, there is a associated change in the surrounding because you see that this mass has been lifted now. During the expansion work by the system; now initially suppose the system had a pressure P i and V i and then finally, we are calling it as P f and V f.

So, let us try to draw an isotherm pressure versus volume for a constant temperature and you know that if the gas behaves ideally then the state must lie on somewhere on this isotherm, because this isotherm represents the states of the ideal gas at a definite temperature. So, when we made this change we had somehow moved the system from some point to some other point in this case remember it is an expansion work that we are discussing. So, the volume should increase which means the initial volume was smaller our initial pressure was higher.

Suppose this was the initial state which were defined as P i and V i. So, P i is the corresponding pressure and V i is the corresponding volume. Now what we did is that we expanded the system to a final pressure which is P f and the following which is V f. Now this was done against an external pressure now what was that external pressure, here let us try to understand that this mass is creating a pressure which is the external pressure, here also it is creating this pressure, which is the external pressure which was constant throughout the change of this system.

Now, this P external which was exerted on the system here it may be equal to the pressure of the system itself which is P f in that case we do not need these pins because the pressure inside and pressure outside will be just equal. So, the piston will be nicely balanced, but the way we have drawn it is that we have kept the pins meaning that this P f is still slightly higher than the P external.

So, P external is somewhere here meaning if we remove these 2 pins the gas can still expand a little bit and I go to a point where this final volume, which we denote as say another V f prime this pressure of the gas will be equal to this pressure which is the external pressure remember this external pressure was constant throughout, but the pressure of the gas is changing from P i to P f to say P f prime.

So, we can think about 2 different situations, but let us first confined this situation where the pins were intact and the pressure of the gas were slightly higher than the external pressure. So, the external pressure is somewhere here now what is the expression for work the expression for work says it is negative of external pressure into V final minus V initial what is V final minus V initial this is this length and if we multiply by P external which is this we are basically talking about a area which is this.

So, the work done in this case is nothing, but the area under this region which I have shaded. So, this area is nothing, but equivalent to the work done in the process. Now imagine another case which we just said that will let the system evolve until and unless the pressure becomes equal to the external pressure. So, the external pressure where somewhere here let us just draw the isotherm.

So, the external pressure is somewhere here which we denote as Pext and this was our P initial this is the initial state and this was the corresponding volume for the initial state which was P i. And now see that the final state which we denoted as V f prime is slightly shifted as you can see from here, because if you compare the picture on your left in the earlier case V f was here and the work done was something like that; however, the corresponding pressure P external was less than the actual pressure of the system which was P f in the earlier case.

So, we assert here that we are also removing these 2 pistons sorry these 2 pins and what happens then the piston moves and until and unless this external pressure and the final pressure gets adjusted the piston moves and when the final pressure drops to the external pressure there is a equilibrium. So, the piston does not move. So, the gas again expands a little bit more and the work done in this case will be this shaded area.

So, frequently we will be using this convention where the final state will denote as if the pressure of the gas itself equilibrates with the pressure with the external pressure. So, just try to remember these 2 differences in the first case the external pressure was slightly lower than the final pressure and this we did because there are 2 pins adjusted.

So, the piston could not be moved further although the pressure of the gas was higher it was forcing the piston to move, but it could not move because the pins were there and if you remove it then the gas will further expand and it will expand up to a point when the pressure drops to the external pressure. And remember at every stage we have to maintain this since the gas is expanding under isothermal condition the pressure is dropping along this line which is the P V isotherm which we got according to the Boyles law.

Now, let us consider a case where the gas is compressed or where we are discussing the work done associated for a single stage compression.

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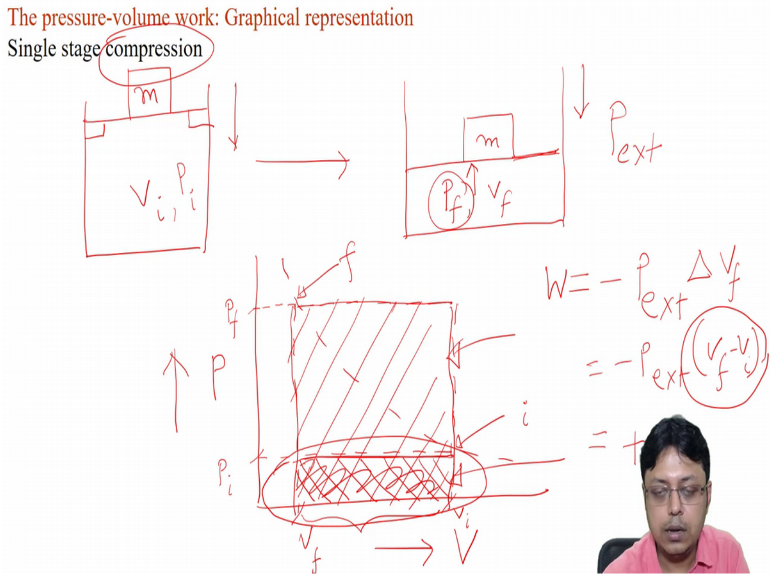

The pressure-volume work: Graphical representation

Single stage compression

So, as before we have a piston, but in this case it is a compression. So, we have a mass and the initial following is suppose V 1 and then we let the piston fall until and unless the pressure exerted by this mass is equal to the final pressure of the gas which we denote as V f associated following we denote as P f.

Now, how will you represent this entire situation on a P V isotherm? So, just as before let us consider this isotherm that the gas follows because the gas we chose is an ideal gas this is a pressure versus volume curve for a fixed temperature now. Here think about it initial volume was higher because we are talking about compression.

So, V i will be somewhere here and what about V f V f will be somewhere here because the final following is smaller than the initial following the corresponding pressures are P f and here the pressure the initial pressure was P i. So, this is the initial state in this case this is the final state because it is a compression. So, the volume is go in the other direction it is shrinking.

Now, let us try to understand what will be the work done in this case think about it what is P external as I said that P external is making this compression and the piston will fall until and unless this pressure of the gas balances the P external. So, P external in this case is nothing, but the final pressure. So, the work done by definition is negative of P external into change in volume which is in this case V f minus V i. So, V f minus V i the magnitude is still similar like the example we talked about; however, the external pressure here is higher.

So, the work done will be area under this curve if you now compare what was the work done in the earlier case let us go back. So, the in the earlier case this was the work done we went for a final state to an initial state and in this case the work done as you can see is this. So, work done for the compression is higher by the work done for expansion which is this region.

So, we had a very interesting situation here we said that we are going from the same initial stage of the system during the expansion, we started from some initial state of the system to some final state and during the compression we did a reverse of this process we went back, but what we saw that in that entire process when we are expanding the work the system worked as denoted by the shaded area this is the work done by the system; however, when the compression was happening the work done on the system by the surrounding was greater.

So, work of compression is always greater in magnitude than the work of expansion in magnitude at least you see here that here V f minus V i is a negative quantity. So, this entire thing should be a positive quantity according to our convention now what we just said is a interesting situation.

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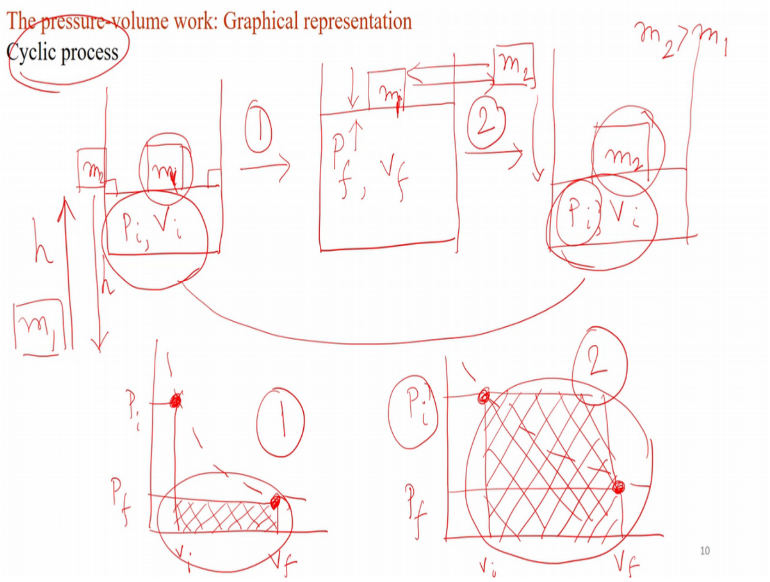

The pressure-volume work: Graphical representation

Cyclic process

We said that we started from an expansion say we put some mass here where the initial volume was V i and suppose then we expanded the system until and unless these thing expands and nicely balances this mass. So, that the final pressure is equivalent to the external pressure which is created by this mass and the associated volume suppose is V f.

Now, we are saying let us do the reverse process where we put a mass. So, that in this case a heavier mass. So, that the system actually comes back to it is original position which is P i vi for this mass of course, in this case the masses should be different this was a lighter mass that is why the system expanded and these was a heavier mass let us call it as m 1 and m 2.

So, here what we did is that we just took out the m 1 mass and put the m 2 mass here. So, since m 2 was higher than m 1 we created again more external pressure. So, the piston moved down and we come came back to the same initial state. Now this process is known as a cyclic process why because we started with a initial state and quick came back to the same initial state for the system.

So, on the P V isotherm what we are saying is during the expansion we started from P initial V initial this state to P final V final to this state and the work done by the system which is a negative work was equivalent to this; however, when you did the opposite process where we started from our initial state remember was this P f. So, this is process number 1. So, this is work done in the process number 1 which is an expansion work this is process number 2. So, it is work done in the compression.

So, our initial pressure was P f note it down and the following was here and our final pressure was P i according to our notation and the corresponding following was V i. So, the work done was the opposing pressure into the changing volume in this case the opposite pressure must be P i because as you see that P i balanced the external pressure. So, the area under the curve is this.

So, this is what I meant by work of compression is always greater than work of expansion for a single stage process which means the system did not produce much work, but we have to we had to spend lot of work in order to bring back the system. Now there is a fallacy the fallacy is think about it we started from this point for the system and reached here in the process in the change 1 and then we started from this point and we went back to the same position.

So, in this cyclic process we did not change the state of the system; however, the state of the surrounding must have changed because we got some little work from the system, but we expanded more work on the system. Now where is the fallacy this cannot happen which means the system has come back to it is original state as if system has done nothing; however, the surrounding has spent more work because the net work gained and the work spent are unequal. So, the net work produced by the surrounding to bring back the system is more.

Now, the fallacy can be resolved as following remember that there are 2 different masses m 1 and m 2. So, in this entire cyclic process what we did we lifted this mass m 1 to a height say h and kept it there and instead we brought back mass which is m 2 by the same height. So, the masses or the different masses of the altitude of different masses are now altered in the surrounding.

So, the lighter mass has gone up at the heavier mass has gone down and that is the reason why we spent more work on the system to bring it back. So, this is a very interesting example where we showed that we talked about a cyclic process initially, we let the system expand then it expanded and then we compressed it where it came back where we started from. So, the system has done nothing, but the surrounding has used the system to perform some work some additional work and what is that work that work is basically lifting masses in the surrounding in this case we lifted a lighter mass and dropped a heavier mass which means actually the surrounding has spent some work in this entire process.

So, these typical processes are known as cyclic process will also consider other cyclic process in in in this course.

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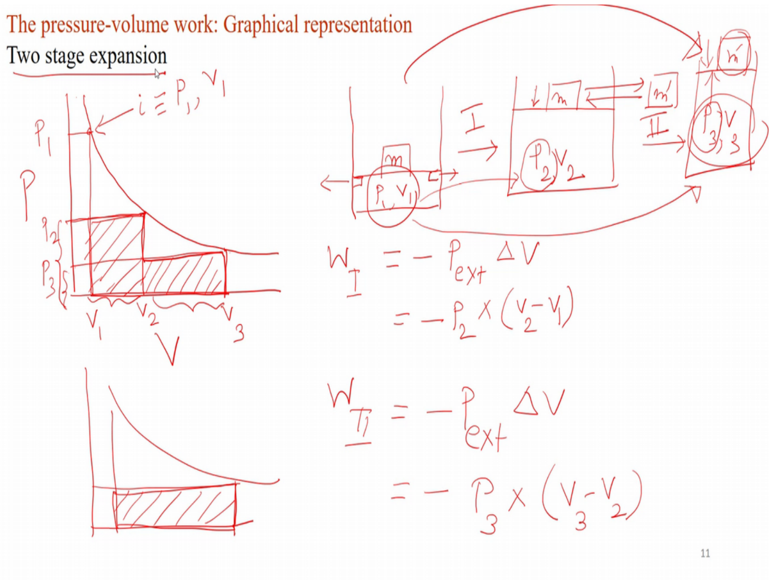

The pressure-volume work: Graphical representation

Two stage expansion

$$W_{I} = -P_{ext}\,\Delta V = -P_2 \times (V_2 - V_1)$$

$$W_{II} = -P_{ext}\,\Delta V = -P_3 \times (V_3 - V_2)$$

Now, let us move on and discuss how will represent the pressure volume work for a 2 stage expansion process by 2 stages I mean here that we will do the compression in 2 steps which are in sequence to each other now as before let us start. So, we have a pressure volume curve and then we are considering the expansion work this is the isotherm and suppose initially remember that this is an expansion work this is the initial stage.

Let us denote it as the first stage as the state of the system for the initial state as P 1 V 1 and then we go to a state where the pressure is P 2 and the associated volume is V 2 and then you will eventually go to a state where the pressure is P 3 and the associated following is V 3. Now what is it mean; that means, we had put a piston here with some mass say m and we let the system expand to certain stage.

So, in the first stage we remove these pins and what happens here is that as soon as we remove the pins the gas expands from an initial state P 1 V 1 to an intermediate state P 2 V 2 and then again we change the mass by some other mass. So, that the gas further expands and the final volume is P 3 sorry final pressure is P 3 and the final volume is P 3.

Now, in this case in the first stage first step number 1 what we did is the external pressure was nothing, but P 2 because remember that the pressure was reduced to P 2 and that is exactly balanced this external pressure created by the first mass m. So, the work done will be P opposing which is P 2 into P 1 minus P 2. So, work done in stage 1 is minus P external into delta V and minus P external in this case is P 2 and delta V is nothing, but V 2 minus V 1. So, this is represented by area under this curve.

Similarly, if we further consider that in the second step which is step number 2 the gas further expanded until and unless the pressure is P 3, which balanced this opposite pressure created by the mass m prime then the work done in step 2 is nothing, but where using the same formula P external into delta v in this case P external is P 3 times change in following was V 3 minus V 2. So, this is V 3 minus V 2 and this is P 3 and this is P 2. So, the area under the curve is nothing, but this which is the work done.

So, the net work done you can see is this shaded area is entire area. So, what you will learnt we see that if we had done in a single stage expansion meaning, if we had skipped this step 1 and 2 and directly gone from a situation where P 1 V 1 state is going into us the gas is going from an initial state with pressure P 1 and volume V 1 to a final state with pressure P 3 and volume v 3 then the external pressure would happen P 3 and then the work done will be simply the area under this curve which we just discussed.

So, we see here that for a 2 stage expansion we get more work than a single stage expansion, which is great which means that we can increase the number of steps now to get more and more work now let us see how much work we can get maximum or what is the maximum amount of work that the system can produce in this case of course, the hint is we will make this number of steps as large as possible.

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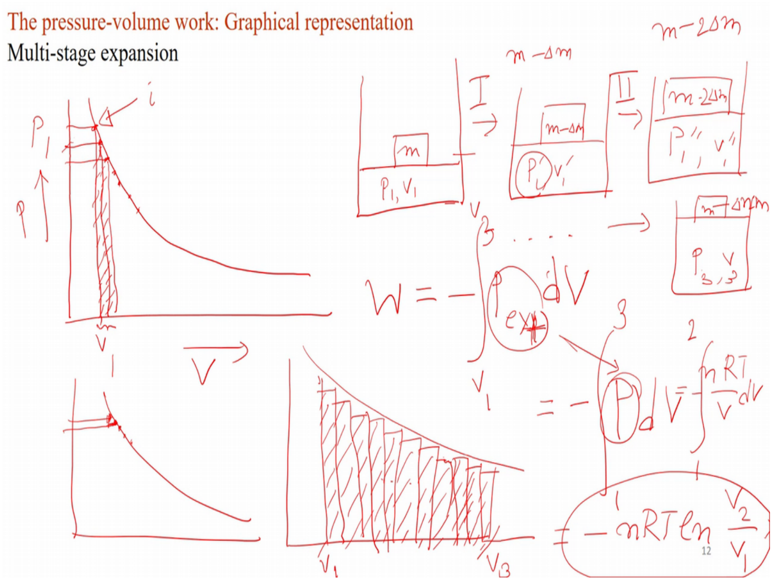

The pressure-volume work: Graphical representation

Multi-stage expansion

Now, let us see what we mean by that. So, this is called a multi stage expansion where we are having the same situation we have a piston with the initial mass that is holding this gas at P 1 and V 1 and this is the P V isotherm and then what we are saying is that will reduce the mass by small amount say first we reduce the mass by very small amount by say delta m let us assume that there is no pin here.

So, if I reduce the mass by delta m what will happen the external pressure will reduce a little bit? So, the gas will expand to a point where the a pressure of the gas is P 1 prime V 1 prime. So, this is nothing, but m minus delta m in the second case will again reduce the mass by another delta m amount. So, that mass is now m minus 2 delta m something like that.

So, the pressure will be even less. So, the gas will further expand in this way if we proceed this is known as multi stage expansion to the same final thing, which we just discussed, which is say something like b 3 or V 3 whatever with this mass which nicely balances that by say n number of reduction in the mass. So, what will be the work done in this n step process.

So, what we are saying here is that this was the initial state which was denoted by a pressure P 1 and the corresponding volume V 1 then we reduced the external pressure by little bit such that the external pressure is now this pressure suppose which is P 1 prime. So, the gas will expand little bit which is this much amount. So, the work done will be the area under the curve in step number 2 this was step number 1 in the step number 2 what we are doing we are again reducing the pressure a little bit the external pressure. So, the gas will again expand and do some work.

So, you can see overall I do not see a curve for the work done by the gas like this. So, this is the same initial volumes a V 1 and this is the same final volume V 3, but the now the area under the curve is very very interesting. So, this will be the area under the curve which means now we have increased the number of steps and got much more work done by the system which is great.

Now, this indicates that if we could do it by infinitely large number of steps then we will get a maximum work what will be the mathematical expression for this work. So, what we are saying is that in this case the work done is nothing, but negative of P external into delta v in this case I have used a differential notation because I am changing the volume by little bit amount and then I have to integrate by the small small work done for each change in the delta V where the entire volume is going from V 1 to V 3 say. Now if we do that in a very small step what we are saying here is that if I reduce this external pressure by a very small amount which is delta P in this case which is associated with the mass delta m.

So, then I can approximate that this reduction in the pressure will be always equivalent to the pressure of the system itself meaning we are seeing the pressure dropping as if the system is adjusting the external pressure every time. So, this external pressure will be nothing, but the pressure of the system itself for every step. So, we see the external pressure is nothing, but the pressure of the system itself for each step in other words the system is nicely adjusting it is pressure. So, that at every step the pressure of the system gets adjusted and equals to the external pressure.

So, we replace this external pressure by the pressure of the system itself and now we can integrate because this P is nothing, but in a T by V because as long as it is following the ideal gas equation we can write that and then integrate from stage 1 to stage 2 and the result is nothing, but minus nRT actual log of V 2 by V 1. So, you see a very nice thing here. So, these denote the maximum work done by the system in an expansion work.

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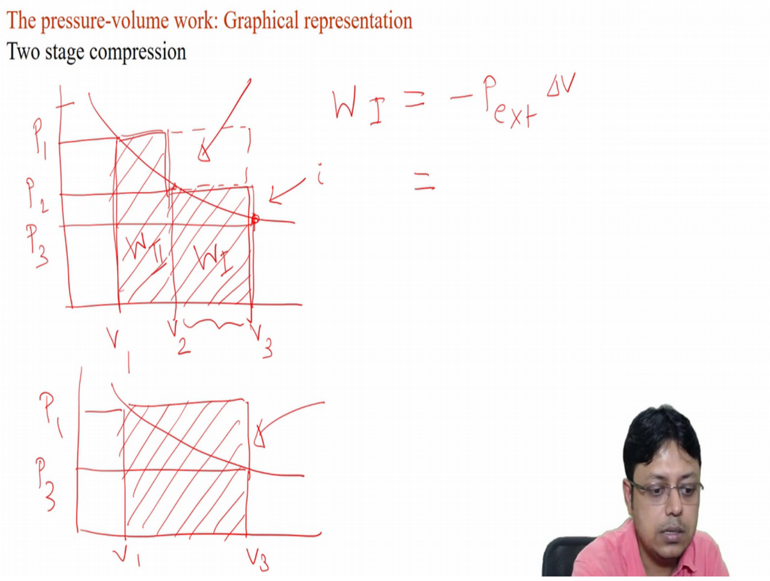

The pressure-volume work: Graphical representation

Two stage compression

Similarly, you can think of a 2 stage compression first and multi stage compression first where we have to spend less and less work as we increase the number of steps remember that in the single stage we had an initial pressure say in this case like P 3 and following V 3. So, this was my initial state and then we went to will go through an intermediate state where they volume is V 2 and the pressure is P 2 and then in the final state will go back to the pressure P 1 and following V 1.

So, during this compression the work done in stage 1 which we denote as W 1 will be nothing, but P external into delta V and what is P external here P external has to be P 2 here because remember that the gas is now compressed until and unless the pressure equals the external pressure equals the pressure of the system. So, the pressure of the system is changing until and unless it nicely balanced to the external pressure and in the second stage the external pressure has to be P 1. So, the work done will be nothing, but the addition of this 2 area.

So, this is for W 1 and this is for W 2 for the 2 stage compression note the striking difference if we had done it with a single step going from V 3 P 3 to P 1 V 1, we would have said the external pressure P 1 right away in the beginning and the work done by the surrounding on the system would have been this area under the curve.

So, we see just the opposite effect of expansion in the expansion case we are getting a minimum work in the single step and moment we increased the number of steps we saw that we are getting more and more work. In this case if we do a single step compression the work done on the system was much more and then moment to change it to a 2 step we see the area is now lessening by an amount this. So, in the same token if we keep on increasing the number of steps the work done on the system by the surrounding must be less and less.

Let us just try to draw that what will happen for the multi stage compression.

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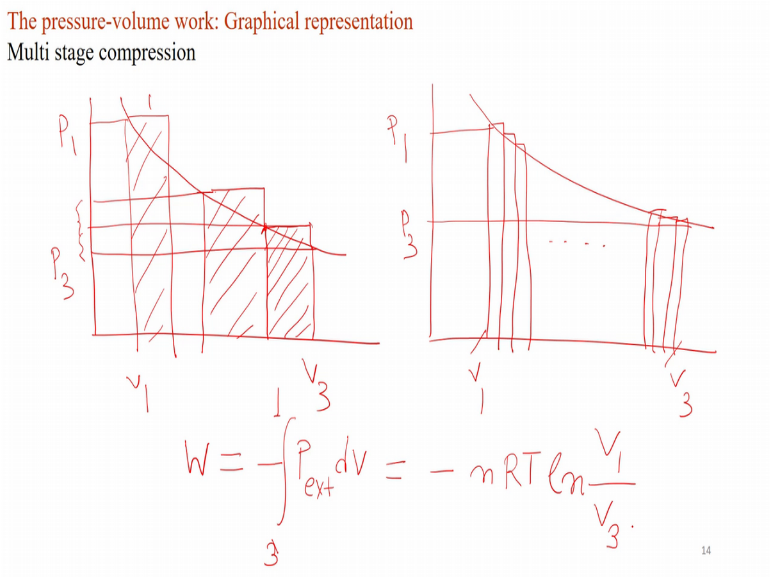

The pressure-volume work: Graphical representation

Multi stage compression

$$W = -\int_{3}^{1} P_{ext}\,dV = -nRT \ln\frac{V_1}{V_3}.$$

In this case remember that we have to increase the external pressure every time. So, just in the same token we have to increase the pressure little bit. So, that the gas is compressed. So, the gas will get compressed until and unless it reaches equilibrium which is at this point. So, the compression in the first step will be like this, compression in the second step if we increase the pressure this much in the second step will be like this.

So, the work done will be a summation over all these areas and if you reduce the number of steps it will look like something like this this was P 1 and this was P 3. So, we see that we can actually have the minimum work done on the system for the compression, if we do it in a multi stage way where the number of steps is infinite as before the expression of the work done will be similar that I will have the external pressure into little change in volume. So, I have to integrate from 3 to 1.

So, ultimately I will get the same expression nRT ln, but in this case it will be V final minus v initial. So, it is V 1 by V 3. So, what we learned is that if we do a cyclic process in this case where we first did a multi stage expansion.

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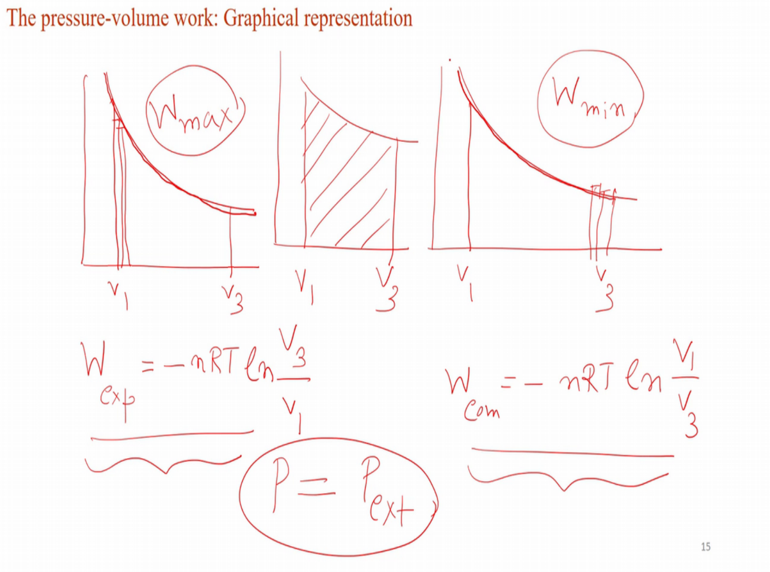
The pressure-volume work: Graphical representation

And then did a multi stage compression, the work done for the expansion is nothing, but minus nRT ln P 3 minus V 1 where this is V 1 this is P 3. So, this is the work done by the system because this is expansion and when you do the compression we do exactly the opposite thing, but the work done will be minus nRT ln P 1 by V 3.

Now, note that in the expansion case we drew it like this. So, the area is slightly less than the compression case because in the compression case we have to increase the pressure a little bit for every step; however, in the limit of very large number of steps where we approximated the external pressure or the pressure of the system to be adjusting with the external pressure for every stage, then for both compression and expansion it will be just the area under the P V isotherm for that change in volume.

So, we see that we can get the maximum work for expansion by the system or the minimum work for compression by the surrounding on the system and these 2 magnitudes nicely cancel each other. So, if you do a cyclic process like this then the work done by the system exactly cancels out the work done on the system. So, the system comes back to it is initial state the surrounding also comes back to it is initial state. So, such processes are known as reversible process where as if we have done nothing we have just moved along this isotherm when we did the expansion and we went back along this isotherm when we did compression. So, both the states of the system and the surrounding in this particular cyclic process are restored and such processes are called isothermal reversible process.

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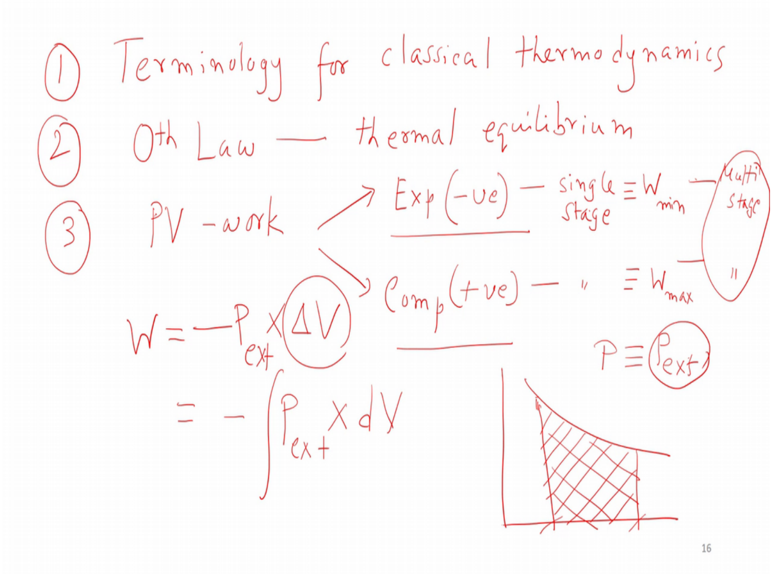

① Terminology for classical thermodynamics

② 0th Law — thermal equilibrium

③ PV-work

$\nearrow$ Exp $(-ve)$ — single stage $\equiv W_{min}$ — Multi stage

$\searrow$ Comp $(+ve)$ — " $\equiv W_{max}$ — "

$$W = -P_{ext} \times \boxed{\Delta V}$$

$$= -\int P_{ext} \times dV$$

$$P \equiv \boxed{P_{ext}}$$

So, to summarize what we discussed today we first discussed what are the terminology for classical thermodynamics, were defined many terms such as system surrounding what are open isolated and closed system we give examples to each 1 and then we moved on and first discussed the zeroth law of thermodynamics, which basically talks about the systems in thermal equilibrium and gives a concept of temperature.

So, the zeroth law is nothing, but a law of thermal equilibrium, then we focused on particular process were we talked about expansion and compression work in the expansion case all this work are known as basically pressure volume work and we talked about the expansion work and the compression work. So, the expansion work remember that here the system works.

So, by convention we call it as a negative work and for the compression work the work is done on the system, we are taking it to be positive and for that we defined the work done as P external width multiplied by the change in volume with a negative sign if this following change is finite, we use delta V if this following change is very small then we write it as in the differential notation and integrate over the entire process.

And we also discussed what is a single stage expansion we got that this corresponds to minimum work from the system, Similarly we talked about single stage compression and we showed that we have to spend maximum work by the surrounding on the system, then we talked about multi stage and we showed that in the very large number of stage if this number of steps is infinitely high.

Then the work done during the expansion by the system and a work spent during the compression by the surrounding on the system will be equal and this work will be nothing, but the area under the pressure volume isotherm. If and we in this particular case we took the example of an ideal gas. So, we asserted that at every finite step which is very very small which is infinitely small step the pressure of the system is getting adjusted to the external pressure, because in this case the external pressure is changing by infinitesimal small amount. So, that the system pressure is also adjusting to it during the expansion as well as during the compression.

So, the both work magnitude wise will be equal and for a cyclic process will come back wherever we started, for the system as well as for the surrounding for the single stage case we come back for the cyclic process we come back for the system, but the surroundings are not restored to it is initial state and we saw that it spends more work and it was explained that this more work was done because we lifted some masses in the surrounding. So, in the next lecture we will discuss more on these more on the cyclic process and we will discuss first how we can develop the concept of the first law of thermodynamics from this discussion.

Thank you.