Chemical Principles

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Module 3
Lecture 14
Work Done at a Constant Temperature

Ok so now we are going to go back to today's topic of Work Done at Constant Temperature ok, so and single and multi-step work.

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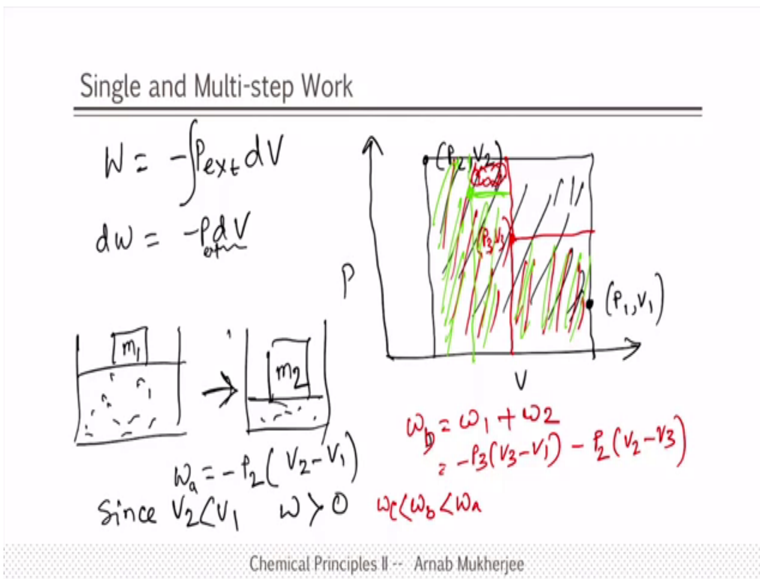

So let us talk about you know we have define we have already discussed about how to calculate the work and by definition work is minus P external d v and integration of that, why we do integration because (know) integration is typically used when we have smaller changes we have many-many changes otherwise you can also sum right. So this is a general definition W is the overall work we can if we write an (())(01:09) work then we can always write d W is equal to minus P d v this way (())(01:16) amount of change in the volume and this p even if I do not write it is always the external pressure that we are considering.

Now let us see what happens when you go from one point to another point. Let us take two points this is let us say p and v and let us say this is p1 v1 and this is p2 v2 ok. Now let us say we go from p1 v1 to p2 v2 ok. So you can imagine that process as I have a system of full of gas we have discussed that before actually and let us say I have mass m1 which is our p1 system and we are going for let us say we are going for high pressure right. So I increase the mass and my final system will be a compress system of much larger mass m2 ok.

So m1 and g will be correspond to p1 and m2, g will correspond to p2 and much smaller value. so this is the process that we are looking at and we want to go in one step if we go in one step then how much will be the work done in that case? I said that we have to pre-consider always the final pressure because that is the pressure in which the system is going to go and equilibrate to. So my external pressure actually since I changed to m2 my external pressure is p2. So now work done in this process is minus p2 v2 minus v1 right. Because that is a final state that you are going to reach p2 and v2 remember when I we are in p1 v1 we properly equilibrated state and we changed to p2 at t equal to 0 and that time we create a non-equilibrium situation thermodynamics cannot handle that situation right.

We wait for the system to equilibrate when once it gets equilibrated it reaches an equilibrium value of v2 and hen we see that how much work is done we calculate that and when we do that it is minus p2 v2 minus v1 correct. How does it look? If I plot it in the graph this is the shaded region of the (())(03:54) ok. Minus sign is due to the fact that it is the work done you know ofcourse minus and plus doesn't matter we are always considering work done on the system right. Now w since v2 is less than v1 our w is actually a positive quantity so that means we ae doing positive work on the system we are doing compression right that makes sense.

So this is the work done this is the work done that is why the region is a work done on the system that we have plotted. Now instead of one step let us break back process into two step process, let us say we don't go to from p1 to p2 directly we want to take one more step in between let us call that p3 v3 so let us say our p3 v3 somewhere here we call that p3 v3. Now in that case how much is the total work done? So now our w has to step w1 and w2 for the w1 we go from pi v1 to p3 v3, what will be the work done? Minus p3 v3 minus v1ok minus p2 v2 minus v3 ok acceptable.

Now let us draw that graphically and see what we get, we get this region and we get this region now we get the red part of that. Now let us say the first we call that as our w a and lets call that w b, now is w a bigger of w b bigger? Look at the graph which is bigger? So w a was the black shaded region, w b is the red shaded region. So w a was bigger and w b is smaller than w a ok.

So you see that instead of going in one step if I take two step the work done on the system so in order to achieve the same state the work that is require to do is smaller, is it clear?.

Because we are going again from p1 v1 to p2 v2 instead of going in one step we have now taken two steps and by raking two steps we realize that the work done is less compared to if we had taken one step right, now lets take a third step, lets call that p4 v4 which his in the green region and p4 v4 will be all the green region. Now lets call that w c, now what do you think the w c is? You see in the w c this region there is no work in that region right so w c is even smaller than w b. See we went from p1 v1 to p3 to p4 v4 I will just show that from p1 v1 to p3 v3 to p4 v4 and to p2 v2 in three steps and so as we go more and more step what will see is that work done getting less and less right.

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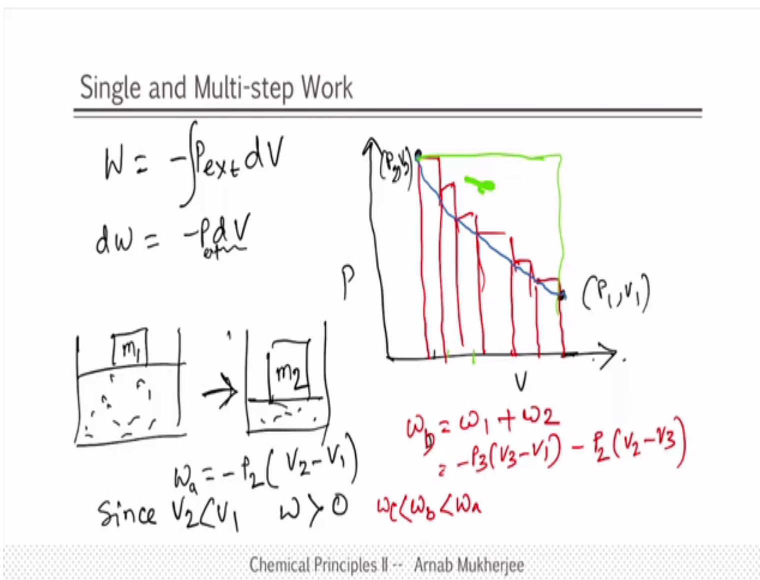

Now let us delete this particular card let us go try to take may-many more steps from p1 v1 to p2 v2. So let us take a very small amount of step will call that I will use a different color you take a very small amount of change in the pressure from p1 to let us say p1 plus delta p which will be little bit increase in the pressure which will decrease a little bit of volume so that state will be here right and we will get this much amount of work right. From there let us go to a little bit more this step. So it will be this much amount of work and like that when you go you are going to go. So you see as we are increasing more and more number of steps the work done that is there that is required to achieve the same state p2 v2 is getting less and less.

Because remember what was the first step? The first one step work was this much all under the green curve but now using many-many steps we are reducing that this amount of this place we are reducing this place work we are reducing. Now instead of taking now finite number of steps let us make infinite number of steps. What is infinite number of steps? Where you change p1 to very insignificantly small value of you know p1 plus dp, 2 dp, 3 dp once you do that you will realize this kind of graph and you can understand that, that will be the least amount of work that is required to get to the same system right. So an infinite step will require this amount of work.

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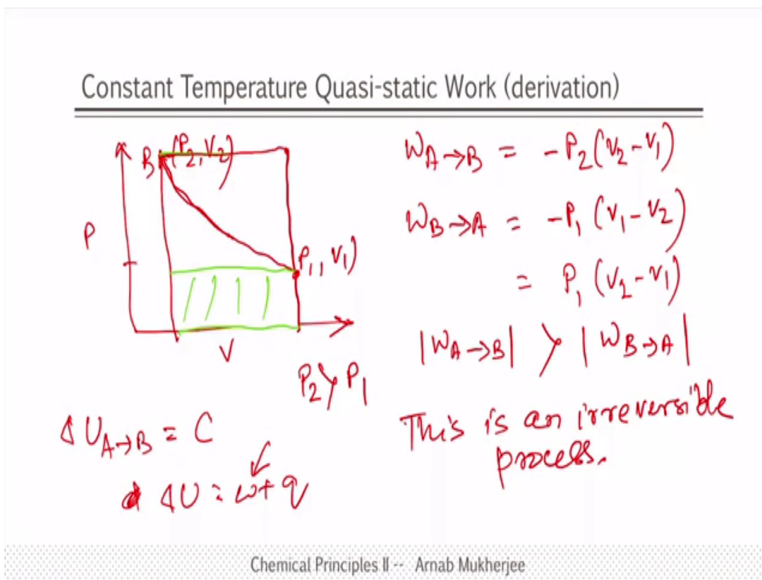

Another thing that you can notice in this constant temperature work is that when we go in one step lets say from p1 v1 to p2 v2 we try to go into one step so when you try to go from p1 v1 lets call that A and to B work done going from A to B was minus p2 v2 minus v1 right. Now let us go back so we go again from A to B now let us go back from B to A, what will be the work done? Minus p1 v1 minus v2 correct. Now if I rewrite this equation or lest say we just only consider the magnitude of the work then the no sign will not matter I will just write with the sign now p1 v2 minus v1. Now just let us take the magnitude of the work, so now magnitude of the work w a going to B will be p2 v2 minus v1 and this one will be p1 v2 minus v1.

Now this is p and this is v now we know that p2 is larger than p1 therefore w A to B is greater than w B to A the magnitude of the work right. Why we have to take the magnitude? Because in one case it is work done on the system it is another case work done by the system that is why we have this signs, signs only mean that but the magnitude of the work remains the same right whether environment is getting work out of the system in that case it will be negative whether we have to work on the system in that case it will be positive it is either way because we put the work in the system in order to retrieve it later on right.

We put energy into the system either oil or some other piston or a spring it compress a spring why? Because that spring later on will give us the work in terms of moving the clock right. So the directions is positive or negative just to indicate that whether we are storing the energy or taking out the energy of the system. Now you see if I go from A to B doing some work on the system when we come back from B to A by doing the same amount of work we cannot reach you understand. So when you go from A to B and do some work the same amount of work cannot bring us back from B to A. So that is why this process is called an irreversible process right.

This is an irreversible process because we have lost something actually it is very different if you calculate that so if you just plot that one work was this much another work was only this much. That is a huge amount of work that is lost just because of going in one step. Now you know that U is always same between A and B because U is a state function so delta U A B is a constant so know we know that the delta U is work plus heat and since work is so much different the difference is coming because of the heat. In both cases the heat is going out that in one case it is more and one case it less than this is great implications we will see later on.

The heat that is going out or coming in whatever the change the amount of heat that is being produced in this processes are different because of work is different in order to keep the u same, U is a state function. So U only depends on whatever pressure temperature and volume the system has and that has a fix p and fix v for one mole of gas therefore temperature is fixed and U is fixed that we discussed last time. So which means that if you do a one-step work or even a finite amount of step work you are going to be you know you are going to follow an irreversible path ok. Now let us see when you do a multi-step work what happens?

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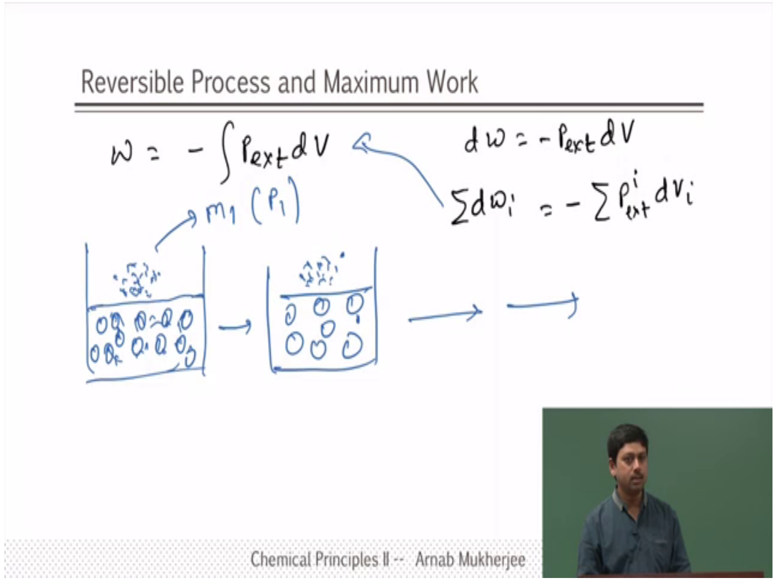

So let us say we are following an infinite (())(15:13) processes then how do you write the W? Minus p external d v. you noticed one thing in this particular case I have put the P external so W equal to minus p external d v is a formula right that is a formula that we are using because the formula we are using because d w is minus p external d v this is the formula that we are using right and p as you can see p is not being varied p external is just the value whereas d v is the differential amount. So we are changing the v now interestingly when we changing the v very-very small p also changes extremely small way and since p is changing a little bit small way we can imagine that we are basically what we are doing is that we are writing the total work done by changing the external pressure at every step up the way, I is the step that is taking us from one point to another point.

Now we know that whenever there are discrete number of steps we do a sum whenever there are infinite number of steps we do integration. So essentially what we are doing we are changing the pressure little bit small amount and let the system equilibrate as I said the thermodynamics cannot deal with non-equilibrium system. I will give you one physical way of remembering this lets take a box of a box of gas molecules and remember earlier what I was having is a block of mass m which could be replace by another black right but imagine that instead of the block now I have instead of block I have sands a pile of sand.

So I will gas molecules I will put a cycle now just to distinguish gas molecules are circles and pile of sands as dots and that pile had a mass m1 giving rise to pressure p1 and now I am going to go to p2 higher pressure. What I am going to do is that in the next step I am going to add in this pile I am going to add one more sand ok, is very difficult for me to produce this particular picture but imagine that I had exactly the same one and I put one more sand and you know the sand is very-very small so I am changing the pressure extremely small and let the system equilibrate, system gets equilibrated it gives me a different volume.

Then I add one more sand and one more sand and that way I am taking the system extremely slowly from p1 v1 to p2 v2. If I do that then I can say that since I am doing multiple steps I can write now sum as an integration and now we are going to evaluate this integration. So w is minus p external d v that is and the p is now within the integral because p is also changing along with the v.

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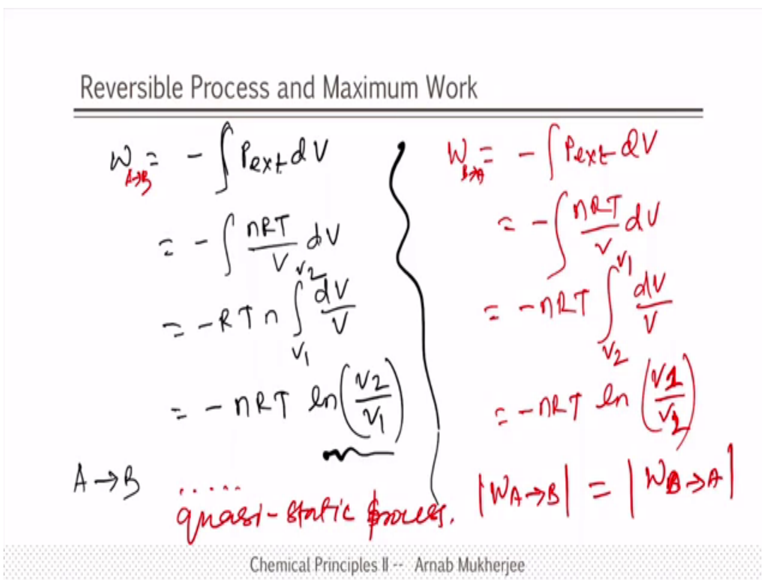

Now we know that from ideal gas system the p v equal to n R T right so our p is n R T by v. So I am going to replace that here and it is a constant temperature process I told you right it is a constant temperature process because whenever you are changing your p lets say you put one more p. What is going to happen if the volume remains constant? If the volume remains constant if we increase your p your temperature is going to increase. Now volume changes in order to adjust that so but if you do not let your system to exchange this extra heat to that you have in the system because of the pressure so ideally lets say the system is static it is an isolated system you put the more pressure what is going to happen? Temperature is going to increase because there is no way to release the heat but you know from zeroth law of thermodynamics that if two systems are in contact with each other they will become in thermal equilibrium.

So ideally in order to keep the temperature constant what is done is that you have a reservoir of a particular temperature, reservoir meaning is like a sea in which in the sea if you put some ice lets say the sea's temperature is 20 degree centigrade, you put a ice of 1 kg, what will be the temperature? 20 degree centigrade because the amount of water that is there is very difficult to change the temperature and if you lets say put some boiling water 1 kg, what will be the temperature? 20 degree so that is called reservoir, reservoir is so big and at a particular temperature that it can supply energy and take out energy without changing its own temperature.

So what is happening is there is whenever you are changing your pressure you are increasing the temperature or heat the system that is (())(20:39) by the reservoir but the (())(20:42) or whatever is kept at that time the (())(20:45) temperature reservoir and allows the volume to change. Unless the temperature is constant (())(20:52) change right it is very important to know because how the process is going on. Now equation is very simple so we since our temperature is constant we can always write p as (())(21:03) that I have written. Now since temperature is constant and R is constant I will write R T as outside and in also outside.

Now I have d v by v going from v1 to v2 so minus n R T l n v2 by v1 so that is the isothermal work done on a system. Now you see since v2 is less than v1 in case of compression this quantity is negative and negative-negative will be your positive work. If it is an expansion the l n this term will be positive and therefore we will get a negative term. Now this is when we are going from v1 to v2 that means A to B process now let us see what is going to happen when you do the reverse one? Then you also write the same thing p external d v you write n R T by v dv minus n R T dv by v now we are going from v2 to v1 minus n R T l n v2 by v1, sorry v1 by v2.

Now this is this was work done from A to B this is work done from B to A and we can see that the magnitude of the work done going from B to A is exactly equal to magnitude of the work done going from A to B. So if I do the process extremely slowly then it is called as a reversible process which means an irreversible process will do two things if we have to compress it we will have to so minimum amount of work and correspondingly if the system does the work it will do the maximum amount of work, that is what called maximum work done and you will see later on that the maximum work is possible because the process is done in a reversible manner.

We call it reversible manner that you should know that ideally nothing is reversible because we are talking about an ideal gas that when you compress even if you put a sand and all the piston is connected to the container which has some fiction that friction will create some heat and therefore ou are going to loose something. So therefore nothing is reversible practically so that the closet to a reversible is called quasi static. So we are actually going almost as slowly as, as if it is static, how does it start static? Because we are changing it, we are changing it extremely slowly one point to the next point to the next point we are doing such a way that it looks almost reversible. So therefore it is called quasi static process so quasi static process is process when which the things are changed very-very-very slowly.

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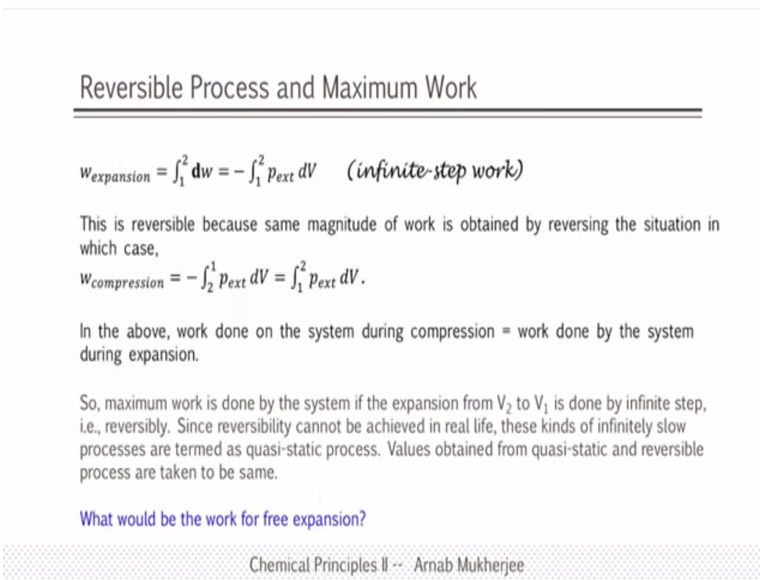

So that you can show the same thing here I have said the same thing maximum work is done by the system if the expansion from v2 to v1 is done by infinite number of steps I reversibly. Since the reversibility cannot be achieved in real life this kind of infinite slow processes are termed as quasi static process. Values obtained from quasistatic and reversible process are (())(24:34) now just for your own this thing can you tell me that what will be the work done for free expansion?

You know what is free expansion? Free expansion is where there is no external pressure therefore it will be zero, so work done for a free expansion is zero.