Introduction to Chemical Thermodynamics and Kinetics
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Lecture - 06
First law - part 1

Hello everyone. So, in the last lecture we discussed about the pressure volume work; we took an example of an ideal gas confined in a cylinder and we said that how work can be done by the system or work can be done on the system and we took some examples of these work done how we can quantify this work done by taking into account of the pressure associated with the following change. So, in this class or in today's lecture we will discuss something more on that, and we will first introduce you to the first law of thermodynamics.

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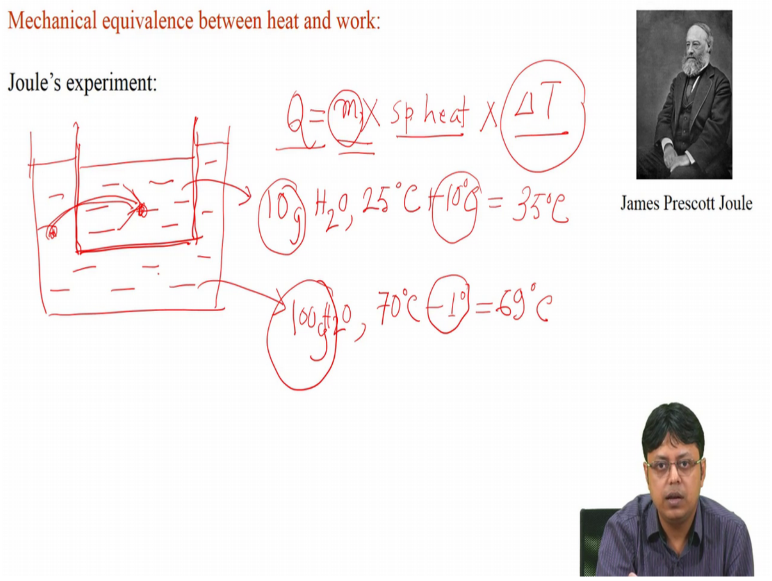

Now, let us first begin with the relation between heat and work, which is known as mechanical equivalence between heat and work. Because as you know both heat and work are 2 forms of energy, but they can be interconvertible. Let us first take an example and then we will discuss what is known as joules experiment which was demonstrated by James Prescott joule. Now before we discuss joules experiment let us conceptually try to understand how we can increase the energy of a system. Now suppose we have a system which is 10 gram of water initially kept at say 25 degree centigrade, and now we keep this system which is 10 gram of water inside another bath of water which is at higher temperature.

Let us say the temperature here is 70 degree centigrade, and the mass of the water in this bigger bucket is 100 gram. And suppose after some time of course, heat will flow from the surrounding; surrounding means here the immediate surrounding is the water which is outside and the water which is inside the smaller container is our system. So, from surrounding heat will flow freely and raise the temperature of the system, which is the smaller bucket of water. Now suppose that the surrounding loses the temperature by 1 degree which means the final temperature of the surrounding goes to 69 degree centigrade; which means since the mass of the water in the bigger bucket is 10 times than the mass of the water in the smaller bucket or smaller container.

So, equivalently you can say that the rise in temperature will be 10 degree centigrade for the system. This comes from the equation for heat change which we know already, that heat change will be mass into specific heat into change in temperature. Now since the specific heat is same in this case that both are water. So, the amount of heat change will be only proportional to the mass. So, if the heat change is fixed. So, the same amount of heat is going from outside to inside. So, the surrounding lose heat by an amount of Q and the system gains heat by and the amount of Q. So, Q is also fixed. So, delta t should depend on the ratio of masses.

So, in this case if the surrounding loses the temperature by 1 degree, the system will gain the temperature by 10 degrees. So, the final temperature will be 35 degree centigrade. Now this is an example when the surrounding loses heat and the system gains the heat and in the process the temperature of the surrounding drops by one degree and the temperature of the system is raised by 10 degree. Now joule asked a question he asked can we do the similar change for the system meaning starting from say the system at 25 degree centigrade, we are going to a final state which is the system at 35 degree centigrade.

However not by directly heating the system just like the example we said, but by doing some mechanical work. So, joule came up with a very nice setup what he did let me first draw the apparatus which in joule designed.

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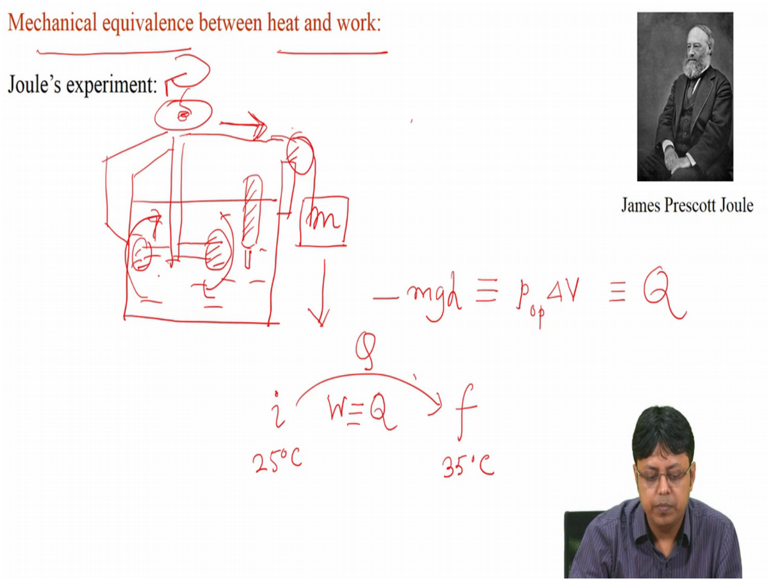

So here he took a similar bucket of water, and this bucket is now connected to a well and the part of the well is immersed in the liquid water, which is our system and there is a paddle which can rotate. And this rotation of the paddle will increase the temperature of the system by some amount which we can measure with a thermometer which is dipped inside this water.

So, connected to this well is a mass of say m if the mass falls down from a height that will create a pool in the a tension in this work, and that will make the will rotate and that will eventually make this paddle also rotate in some direction let us say in this direction and that will eventually increase the temperature of water. From that joule concluded that the work done which we wrote as minus mgh or which was equivalent to a pressure volume work in our example of the gas inside a cylinder is also equivalent to some heat change associated with the process. In this case work is done by the surrounding because mass is falling and then that work done is being converted into some amount of heat which is increasing the temperature of the system by some finite amount.

So, this is known as mechanical equivalence between work and heat; now the interesting thing with this example is that we went from the same initial state to the same final state in these 2 examples, the initial state was 25 degrees centigrade and the final state of the system was 35 degrees centigrade, but we showed that we can either do it by supplying heat directly just as we discussed in the example with the hot water bath by immersing the system in the hot water bath, or we could have done it which we are showing here is by supplying some amount of work, which is being converted into the heat.

Now, in the earlier class we discussed about the 2 stage cyclic process, where we said suppose we are going from some initial stage to a final stage by single step expansion and then we are coming back with single step compression.

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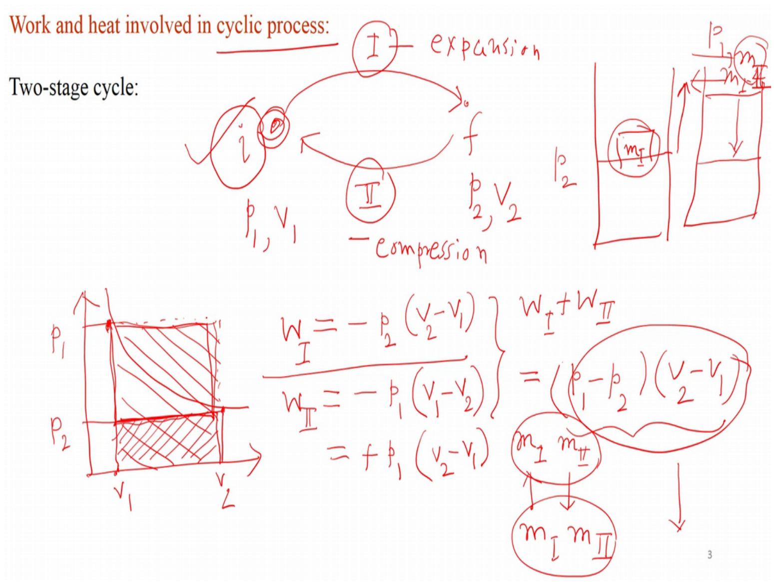

Now let us try to understand how this pressure volume work, which we already calculated for this process is related to the heat changes in the surrounding. Now before we discuss remember that when we are discussing the properties of heat and work, we said these change in heat and work during a process or during some transformation is across the boundary, and we always measure it we always measure this change by some effect in the surrounding. So, we are going to now discuss what is this effect in the surrounding.

Now, let us consider a cyclic process, where the we start from the initial state of say pressure pone and volume v 1 to a state which is pressure p 2 and volume v 2, but then again we come back in the second step. So, the first step we can think of if the pressure p 2 is less than p 1. So, the first step is nothing, but an expansion step and the second step is nothing, but a compression step. So, this is a cyclic process and at the end of the cyclic process the system should come back to its initial state. But we already know that the surrounding does not come back to its initial state and we described why this is so. By drawing the pressure volume work in the pv diagram, where we showed that if we start with an initial pressure p 1 and volume v 1, and then change the pressure final pressure to p 2 and volume v 2 then the opposite pressure associated with the first step should be equal to p 2 and the change in volume in this cases v 2 minus v 1.

So, the work done by the system because the system in this case was expanding, I I was the area under this curve; however, if we go back or want to restore the system in its original state we have to now set the opposing pressure to be equal to p 1, and now the associated volume change will be final volume minus initial volume which is v 1 minus v 2. Now this will be area under this entire region. So, the difference or the extra work done by the surrounding is this area which mathematically we can write as w 1 plus w 2 will be nothing, but if we write it in this way p 1 minus p 2 into v 2 minus p 1. So, we just wrote this second equation as plus p 1 into v 2 minus v 1 and then add it with our first equation.

So, this is the total work done by the surrounding on the system, and you can see that or this is basically the net work done by the surrounding on the system and you can see this is a positive quantity because v 2 minus v 1 is positive, and also p 1 minus p 2 was positive. So, the surrounding does some work. Now the system is restored to its initial condition, but the surrounding was not restored to its initial condition because we spent some work on net. Now the question is what happened to this work? Because this work must be utilized by in something in some process.

Now, since the system has been restored in the initial state, then we must conclude from here that the temperature of the surrounding must be increased. Now you can have a filling of this process how the temperature of the surrounding has been increased. So, in the initial step we suppose had a mass m 1 and this m 1was chosen in such a way that it creates a opposing pressure which was p 2. Because remember that initially the expansion was done against the opposing pressure p 2 and this was the work done. Then this mass was lifted and then what we did we took out this mass m 1, but put another mass which is m 2, which must be a heavier mass than m 1 and which is equivalent to some opposing pressure p 1, since p 1 is greater than p 2 m 2 must be heavier than m 1 and that caused a depression and the piston came back and the system was restored in its original condition.

So, in this process what we saw that a lighter mass m 1, I am using 1 and 2 notation to understand to describe the process the first step and the second step. So, it was lifted to higher altitude and then a mass which was already in the higher altitude actually was fallen to a lower altitude; which means since m 2 is greater than m 1 and net amount of mass m 2 minus m 1 actually has fallen in the surrounding, that must be converted into the temperature of the surrounding. Remember that it cannot increase the temperature of the system because we have come back to the same initial state of the system.

So, the temperature of the surrounding has increased and this is according to joules law, which we just described. So, according to joules experiment the temperature of the surrounding in this case must have been increased.

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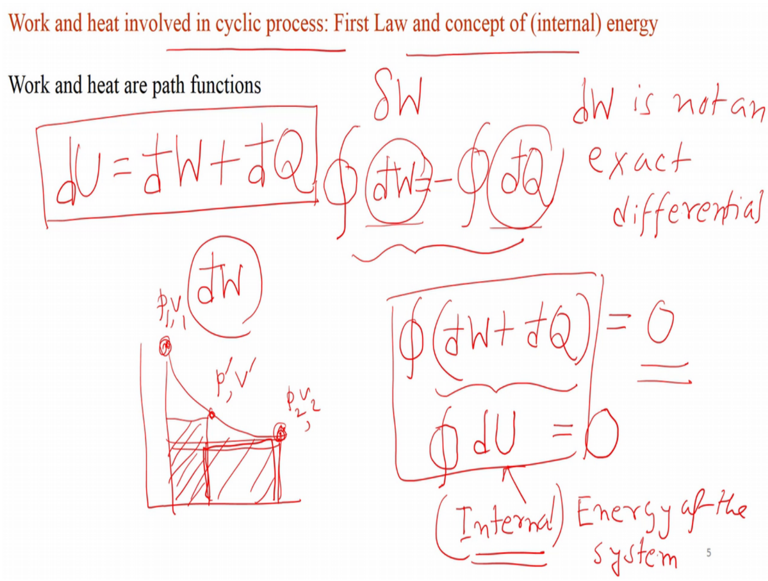

Now let us try to understand what we just discussed and based on that we will build up the concept of the first law as well as the concept of energy. So, what we discussed is that this work which we just did a net work was destroyed completely, and we got an equivalent amount of heat. Now in any cyclic process; that means, the work done will always be equivalent to the heat withdrawn in the cyclic process.

Now, cyclic process means this is with respect to the system because everything we are working on is the system. So, cyclic process means the system is under system is undergoing some initial change, but it comes back to its original state pressure, which are designated by some pressure some volume some temperature. Now in this cyclic process we can write it as cyclic integral of the work done now remember that work done now what is dW? dW is the differential work done in every step. Now remember that it depends on the path of the transformation what does it mean? If we do the work done in different way for example, we already discussed that we can go from state p 1 v 1 to a state p 2 v 2 by single step in that case the work done will be nothing, but the area under the curve.

Or if we had gone through up another path where there was an intermediate step where the system first goes from p 1 v 1 to p prime v prime and then to p 2 v 2, then in the first step the work done will be the area under this curve and in the second step the work done will be the area under this curve. So, the 2 areas will look like this in the single step it will look like this in the 2 stage case it will look like this. This already we discussed in the earlier class; however, the point here is the amount of work depends always on the path of the transformation.

So, it does not depend on the what is the initial state and what is the final state. So, work is not a state function of the system, work is a path function. The amount of work done by the system or amount of work done by the surrounding on the system depends on the particular path of transformation, and in this way we already and along this way we already discussed that if we do it by single step or 2 step the amount of work done is different. Mathematically it means that dW is not an exact differential. By exact differential we mean that a differential which depends which does not depend on the path

However since dW depended on path it must not be an exact differential or sometimes we call it as inexact differential. To denote a difference between exact and inexact differential we will write this instead of dW we will write it as d cross W, some textbook write it as del W. So, these whenever we write this cross; that means, actually that this differential is not an exact differential. Similarly the heat withdrawn will also be an inexact differential because work is just converted into heat. So, if work depends on path the heat will also depend on path.

Now, we have a problem here in the sign convention since we are saying that the work done by the surrounding should have a positive sign; that means, equivalent to that will be temperature increase or decrease in the surrounding, if work is done by the surrounding there will be a temperature increase for in the surrounding either in the surrounding or in the system. So, we will maintain a negative sign here just to make consistency in our earlier definition that, work done on the system is always positive and work done by the system is always negative.

So, any work done in the surrounding will be equivalent to the heat withdrawn by the system or heat produced in the surrounding, but we are maintaining this negative sign just to make consistency in our definition of work done. Now if you proceed with this equation which is cyclic integral of the differential of work done is equal to negative of cyclic integral of the heat withdrawn from the surrounding, we can combine these 2 things and write d cross W plus d cross q is 0. Now we got a very beautiful thing what we see here although d cross W individually depends path on the path of the system d cross q also depends on the path of the system.

If we take their addition that does not depend on the path of the system that will be always 0. So, 0 means whichever path we take since it is always zero; that means, their combination that some differential has to be a state function which does not depend on the path of the system. That is test function we call it as d U, we are not writing here a d cross Q because its a state function which does not depend on the path of the system and we simply write this equation that cyclic integral of d U is 0, where U is called the energy of the system or more accurately U should be called as the internal energy of the system we will discuss why we call it as a internal energy.

Now, we can combine these 2 relations what we just got we just saw that dU is nothing, but d cross W plus d cross q. So, this is the first law of thermodynamics written in its differential form.

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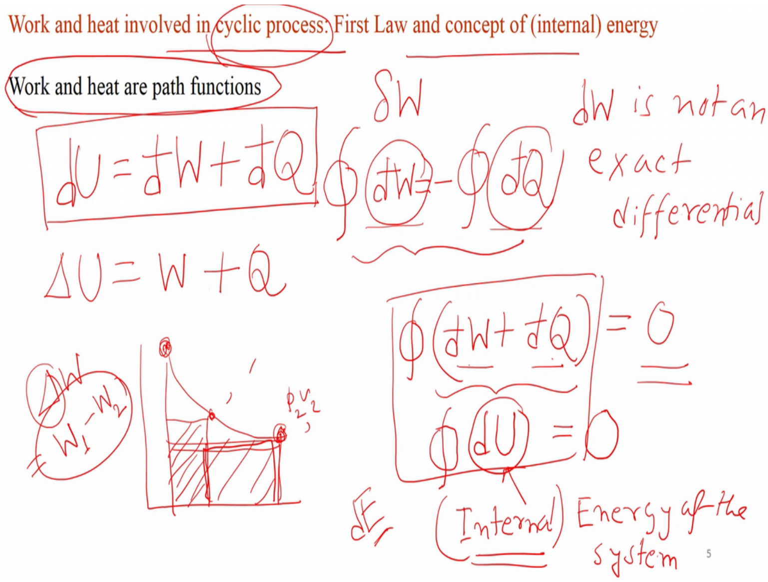

So, we started with the logic that work and heat are path functions, which depends on the path of the system; however, for a cyclic process we saw that work done must be equal to the heat withdrawn and then from that logic we figured out that when you add these 2 quantities the work done, and the heat withdrawn their addition will be always 0 and we got a new quantity which we defined as d U some textbook write it as dE E stands for the energy.

And that dU will be an exact differential because cyclic integral of that is always 0. By cyclic integral we again mean that we are going from a initial state to a final state and coming back. So, we are following a cyclic process and during this cyclic process the internal energy of the system does not change or does not follow on the path of the system, wherever you do a single step compression or a multi step compression it does not matter. Since you are starting from the same initial state and coming back to the same in his shell state it does not matter.

Now, we could write this first law in its differential form sorry in its integral form and there we write it as U is delta U is equal to w plus Q. Now we do not write anything write delta w, because delta w will mean something like w of state 1 minus w of state 2 that does not make sense because this delta transfer from some initial state to a final state. Let me explain it further.

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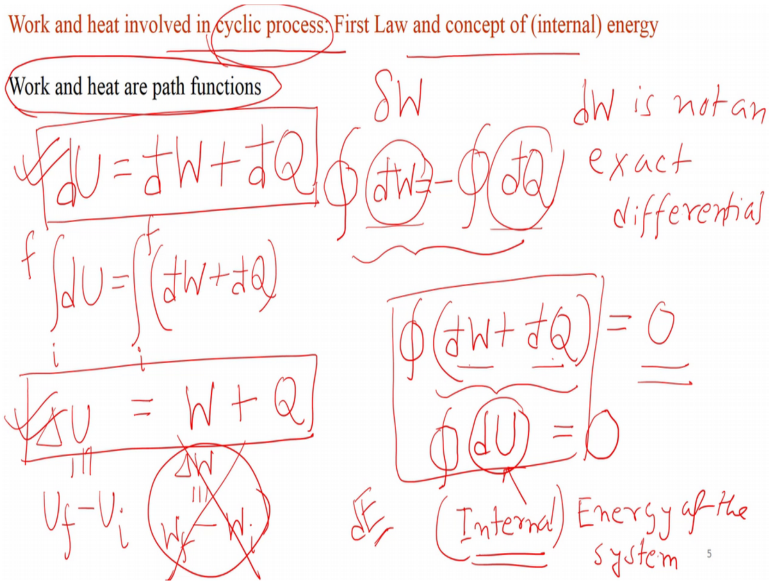

Now suppose we make a finite change from a initial state say i to a final state f. So, we will get an integral form of this equation, and dU integrated over initial state to final state will be delta U; where delta U is nothing, but energy of the system in the final state minus energy of the system in the initial state.

Now, when you write the right hand side I write here as w plus Q; because if I write it as delta w; that means, that would mean the work done in the initial state and work done in the final state which is meaningless, because work is a form of energy in transit. Same is true for Q and work and heat are path functions. So, we do not write the integrated law as delta w or delta Q, but for any exact differential we write it as delta. So, we will use this convention where we write the change in internal energy as delta U, but change in work our heat as w and Q whereas, when you talk about a differential form we write the change in internal energy as small d u, and the differential change in work and heat are always written as d cross Q and t cross w. So, this is the first law in its differential form and this is the first law in its integrated form.

Now, we have already discussed what is the mathematical form of the first law, and we also had a concept of energy which is the internal energy.

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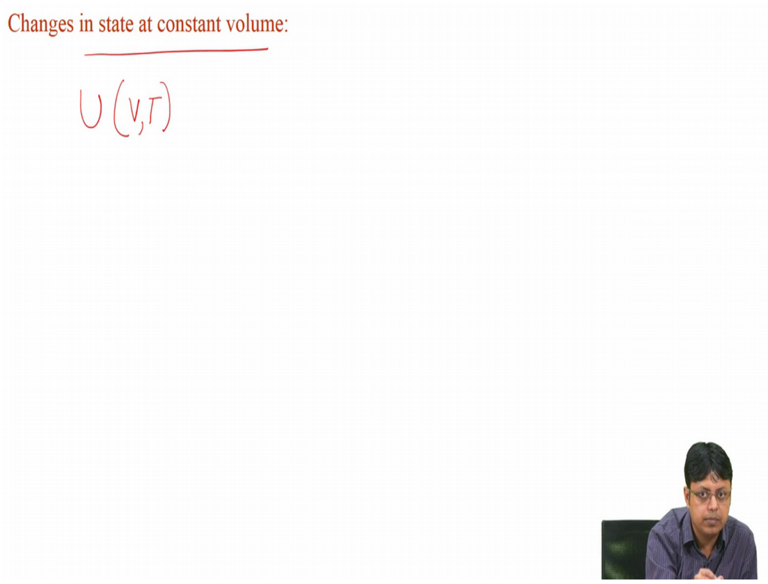

Now, let us suppose that we do some transformation keeping the volume of the system constant. Now we can write the energy which we are writing as U, as a function of say volume and temperature.