Chemical Engineering Thermodynamics
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Lec 8
Work and Heat

Welcome back! In this lecture we are going to talk about Work and Heat. Now, some aspect of that was covered in the first week of this lecture, this course. But using the different set of postulates, what we are going to do is we will try to little bit change the way we have treated here to provide more comprehensive illustration of the thoughts on how the work and heat concept was originated.

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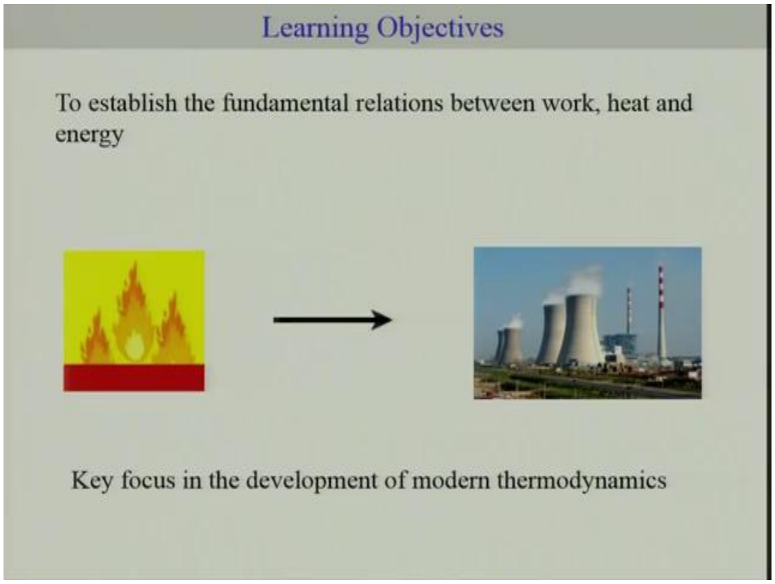

Now, so in this particular lecture what we wanted to do is we want to establish the relation between work, heat and energy. So that would, of course, will lead to the first law for the conservation of energy. But this has been a key focus for the modern thermodynamics by many scientists Sadi Carnot, James Joules and Lord Kelvin.

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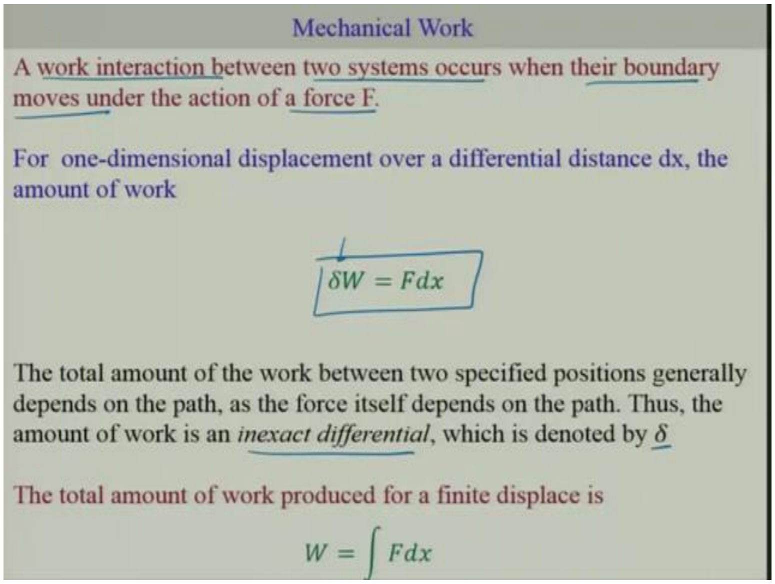

So, what we are going to do is we are going to just define first basic definition of mechanical work. So, a work, interaction between two systems which occurs when their boundary moves under the any action of the force F. So this is what we all know that there will be a work interaction between the two systems when their boundary moves under a force F. So this is basic definition of mechanical work. So for the case of one dimensional displacement over a differential distance, the amount of work is quantified as this;

$$\delta W = Fdx$$

So, the total amount of work between two specified positions essentially is going to be integral of this. The reason why putting delta here is that the force on general the amount total amount of work depends on the path along which the process has occurred. Thus the amount of work is an inexact differential and thus we represent it by delta. So for the case of final displacement which just simply take the integration of F.

$$W = \int Fdx$$

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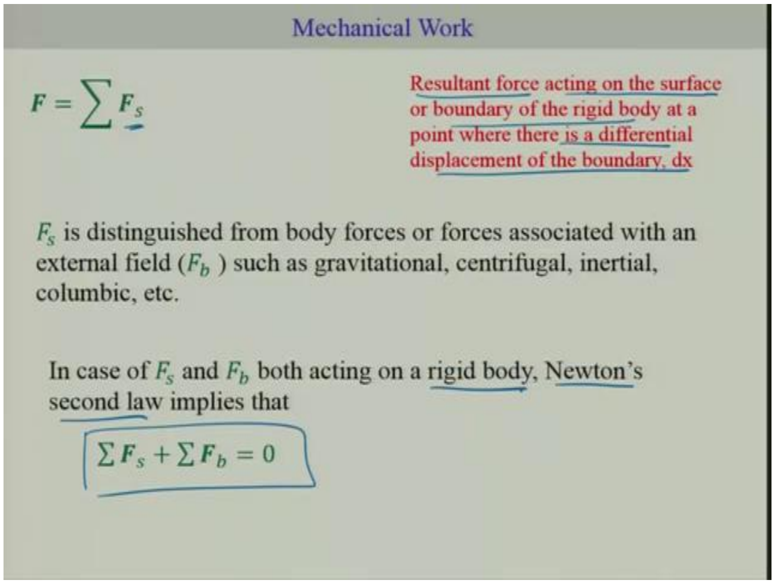

So, what is F here? F is nothing but the resultant force acting on the surface or boundary of a rigid body at a point where there is differential displacement of the boundary. Now here Fs is written here, Fs is basically distinguished from the body forces of forces associated with an external field such as gravitational, centrifugal, inertial, columbic etc.

$$F = \sum F_s$$

So, for such one you are going to write it separately. If they are Fb that means the body forces are there, then they are going to add it up or make use of Newton's second law and they are going to add all the forces, ok acting on the rigid body. So this is all we know this is the basic concept mechanics which we are well aware of.

$$\sum F_s + \sum F_b = 0$$

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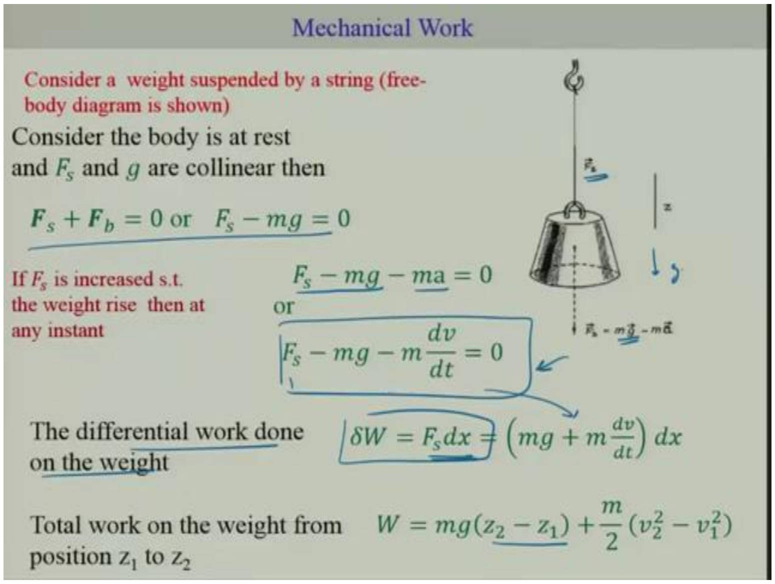

Now, let us make use of this understanding and consider a weight which is suspended by a string and a free body diagram is given here. So you have a hook, from the string and the force here is F_s and this is the body force this is this gravitational force which is mg and if it is moving then basically we are saying mg - ma. So this assuming this is basically collinear that means Fs and Fg is collinear.

Then we can consider for the case of if the object or the body is not moving then essentially you have this scenario which is $F_s - mg - ma = 0$.

$$F_s - mg - m\frac{dv}{dt} = 0$$

$$\delta W = F_s dx = (mg + m\left(\frac{dv}{dt}\right))dx$$

$$W = mg(z_2 - z_1) + \frac{m}{2}(v_2^2 - v_1^2)$$

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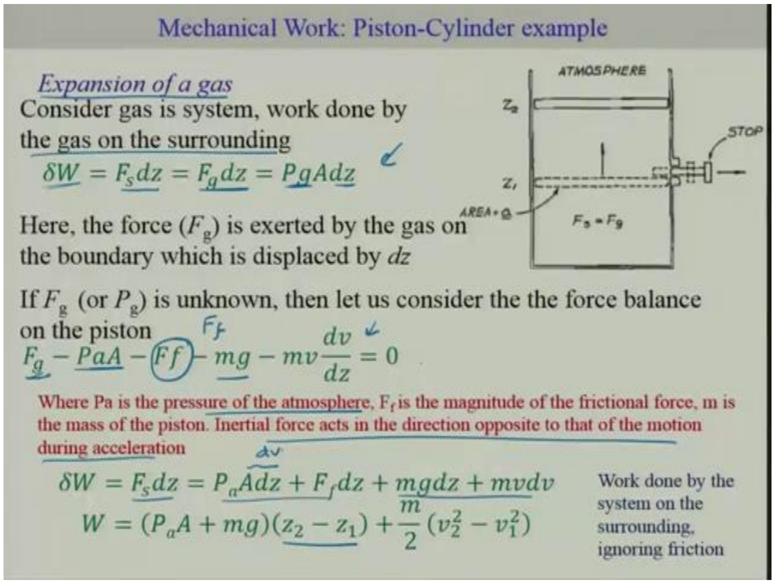

What is interesting is we will be making use of this understanding or this basic mechanics for the case of system which are of interest of thermodynamics. So, let us consider the extension of this for the system which is common interest in thermodynamics. So, example will be expansion of a gas. Now this is a rigid let us say a cylinder. You have a piston, ok and you have to stop here so now consider that the pressure inside the system is more, so that once you take off the stop, it is going to expand.

So the work done by the gas on the surrounding be the this will be given by delta W, that is equal to Fs that is the force which is exerted by the gas on the boundary which is displaced and this is you can write it as a Pg which is again the pressure on the boundary that is dismissed and multiply it by the area, multiply it by the results. So, if Fg or Pg which is at here, is unknown then you can do a simple force balance on the system.

So this will be your Fg at the piston here minus the pa. Pa stands for your pressure of the atmosphere ok minus Ff which is nothing but the magnitude of the friction force which should be this, minus your gravitational force and if there is a acceleration of the system, that v minus mv, dv by dz so this something is similar as your ma, so we write in this form, then you can get this expression. Now you know that inertial force acts in the direction opposite to the motion of the motion during the acceleration so you can rewrite this and make use of Fg from this expression and plug it in this expression you get this Fsdz is equal to nothing but this term.

So this will be the work done by the system on the surrounding ok, so if you ignore friction then you will have w is equal to Pa plus mg z2 minus z1 plus the difference in the kinetic energy. So this will be your kinetic energy plus potential energy and this is the work done by the piston on the atmosphere for displacing the air and increasing the volume by dv. So, this will be your dv. So, this is a typical example of piston cylinder.

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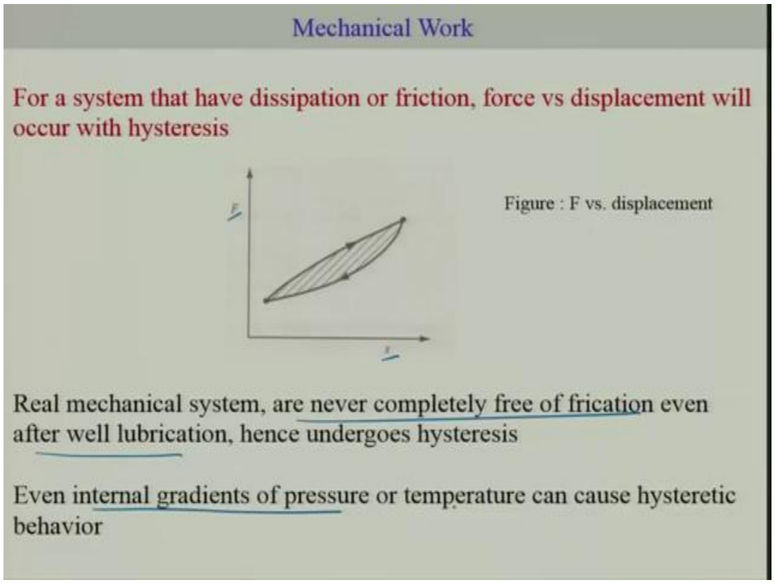

Now we know that there is a friction there will be some dissipation, so for the case of system with dissipation or friction, so the real mechanical system are never completely free of friction and even after well lubrication, hence usually you see this kind of hysteresis. Even internal gradient of pressure or temperature can cause hysteresis behavior. That is something which is in the reality.

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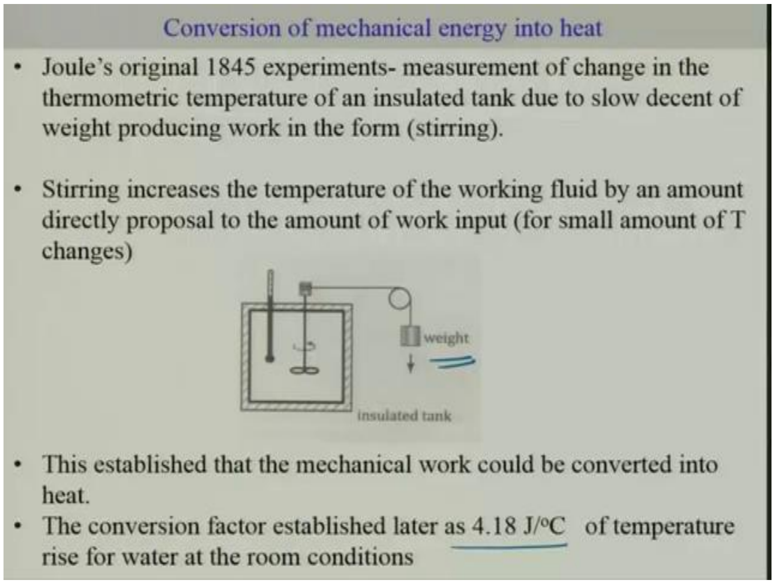

Now while we are talking about mechanical energy or mechanical work this was start of course much idea by Joule's. I am trying to particularly convert the work into heat and vice versa. So in the case of Joule's original 1845 experiments, the major amount of change in the thermometer was one of the experiment was done, so what they did was they slowly decanted this weight, this weight is connected to stirrer and once you slowly decants, it rotates leading to the increase of the temperature of the working fluid.

And they found that the increase for a small change in the temperature that increase in temperature is directly proportional to the work which is been supplied to the system. So this basic simple experiment established that the mechanical work could be converted into heat and the conversion factor was established later as 4.18 Joules per degree Celsius of temperature rise for water at the room condition. So this illustrates the first how to convert mechanical work into heat, and that was devised in the form of that was formed in the form of temperature wise.

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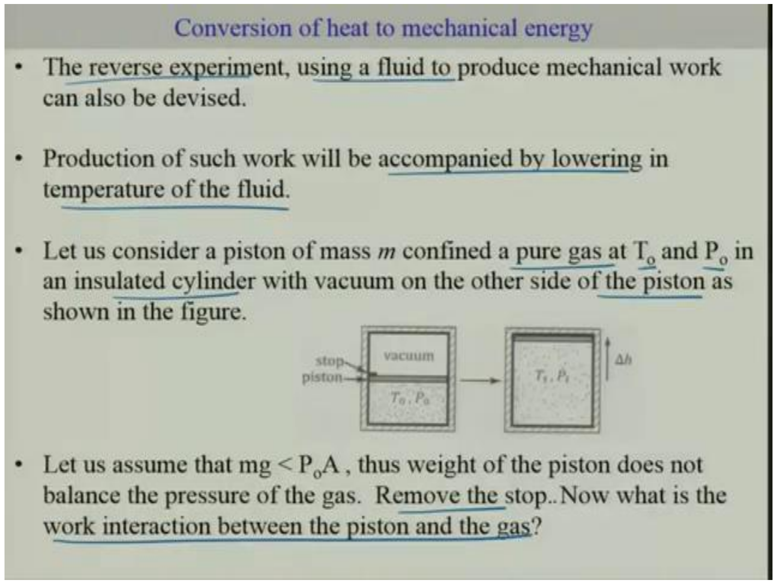

The reverse experiment also can be considered where basically using a fluid produce mechanical work, ok so instead of an object moving we are trying to use fluid to produce the mechanical work. Now when you are doing work on this, temperature rise but when the fluid does sort of work the temperature usually is going to be lower so production of such work will be accompanied by lowering the temperature of the fluid.

The example could be something like this, where we have considered a piston of mass m confined a pure gas let us say T_0 and P_0 in an insulated cylinder with the vacuum on the other side of the piston. Now, assume that the mg mass that is weight of this piston is less than P_0A, in other word if you know the stop it is going to expand thus the weight of the piston does not balance the pressure of the gas. So remember to stop and now what is the wok interaction between the piston and the gas? So basically it does the sound from work. What is the work interaction between the piston and the gas?

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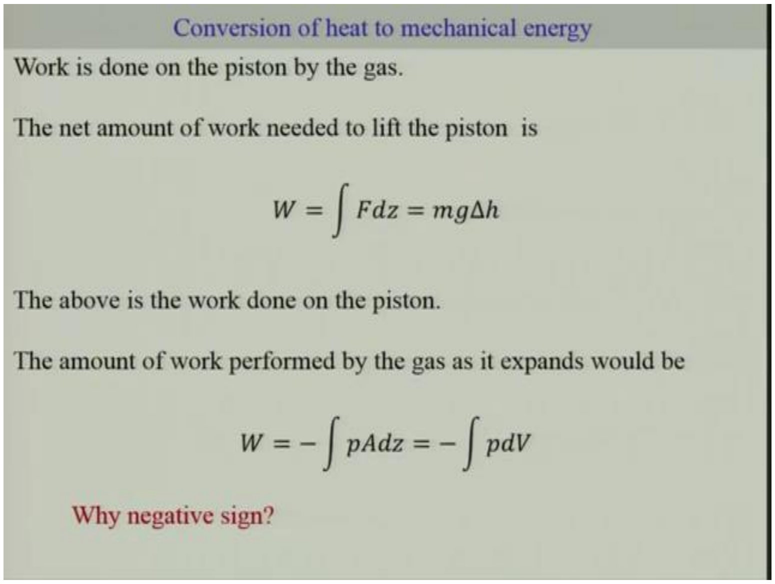

Now work is done by on this piston by the gas, so if you ask a very simple question that what is the net amount of work needed to lift the piston that would be very straight forward, that would be: $W = \int Fdz = mg\Delta h$

So this is the work done on the piston but what about the amount of work performed by the gas as it expands, so that would be:

$$W = -\int pAdz = -\int pdV$$

Now this is by definition we are putting it as a negative sign because it is the work done by the gas and by nomenclature we are using that to be negative. Any work done on the system that will be positive.

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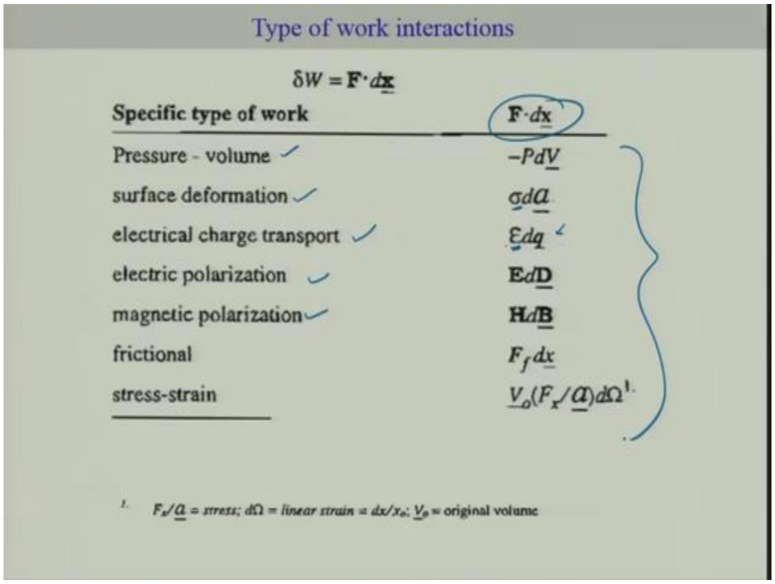

In general there main type of the work interaction you can consider, so I will come back to this example once more. But let me just summarize the typical work interaction so we have already talked about pressure and volume. So PdV, this is the surface deformation where sigma is basically related to stress and a is the area, then you have this electrical charge transport, here this electrical charge, this electric field, electrical polarizability, this is your double moment magnetic polarization, frictional stresses.

So all will have some kind of a Fdx relation which would be something of this expressions. So I just wanted to summarize before I go for back forward to the example.

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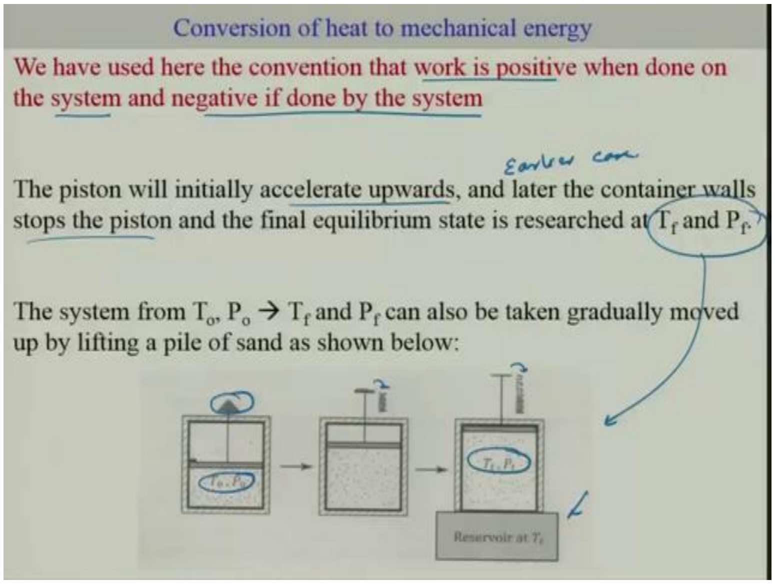

So as I mentioned in here earlier that usual convention is going to work as positive when done on the system and negative if done by the system. Now, let us consider the example again, where we have this here the system with T0, P0 and now what we have done is we can replace this let us say piston, we can consider this piston which holds a sand as well. Now, we can consider this process to be slow, the earlier process was irreversible, very fast; this was spontaneous because the pressure was much-much larger immediately it expands once you take.

Now you consider this process little slow which you can slowly remove the sand and by slowly removing the sand gradually moves by lifting a pile of sand and slowly it would come to this point. So from T0, P0 it will change to Tf, Pf. So, this piston will initially accelerate 1upward, and later the container walls stops the piston in final equilibrium state is reached. So what this was our earlier case, earlier case, earlier example.

Now here what we have done is now we put the sand here now, slowly sand is also getting out, while this process is occurring. So what we are trying to do is that in order to maintain the same temperature and pressure as we obtained here we at the end, when the processes occur slowly keeping a reservoir Tf at the end so that the temperature is also maintained.

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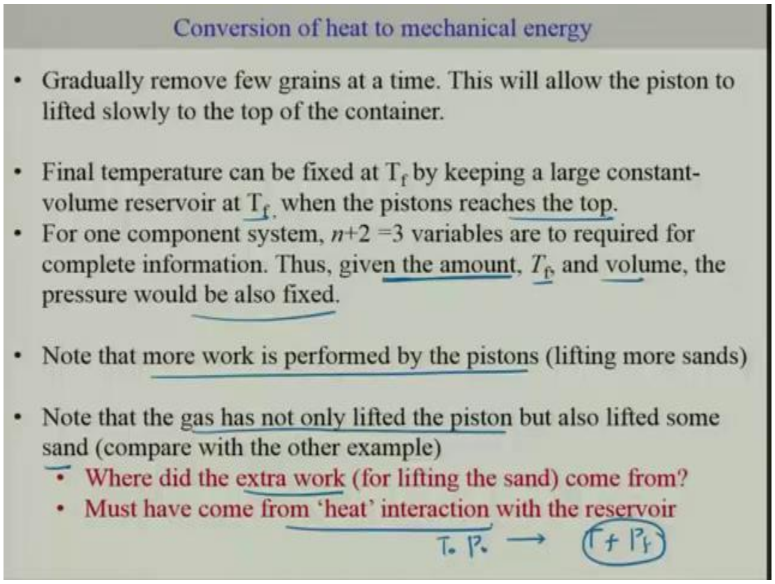

So, the idea of this was to come with the slow process, so gradually removing few grains at a time. This will allow the piston to lift slowly to the top of the container. Final temperature can be fixed at Tf by keeping a large constant volume reservoir Tf when the piston reaches the top. Now since is the pure component we are considering three variables are required for complete information thus given the amount, Tf and volume, the pressure would be also fixed.

Now the important thing is that what we are trying to asset is a note that more work is performed by the piston by lifting more size. So, the thing is that once you put this here, by that time we put this and try to maintain the temperature, some further, some more sands are being lifted; this is compared to the other example. So the gas has not only lifted the piston but also lifted some sand that is what we are trying to make statement here.

So, earlier case you are going from T0, P0 to Tf, Pf but here T0,P0 to Tf, Pf in this process you have also done some other additional work while doing the process lifting. So your final state, is still the same but additional work is been done in this process. So, where does this additional extra work comes from? So in order to get this point, remember that we say that we use we had to put some reservoir, thermal reservoir to obtain the temperature. So, what we are saying that it must have come from heat interaction with reservoir in order to get that final state.

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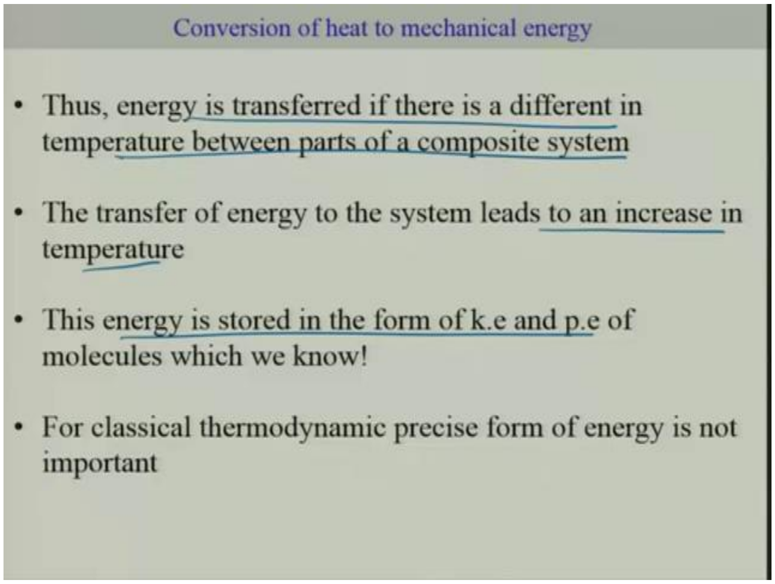

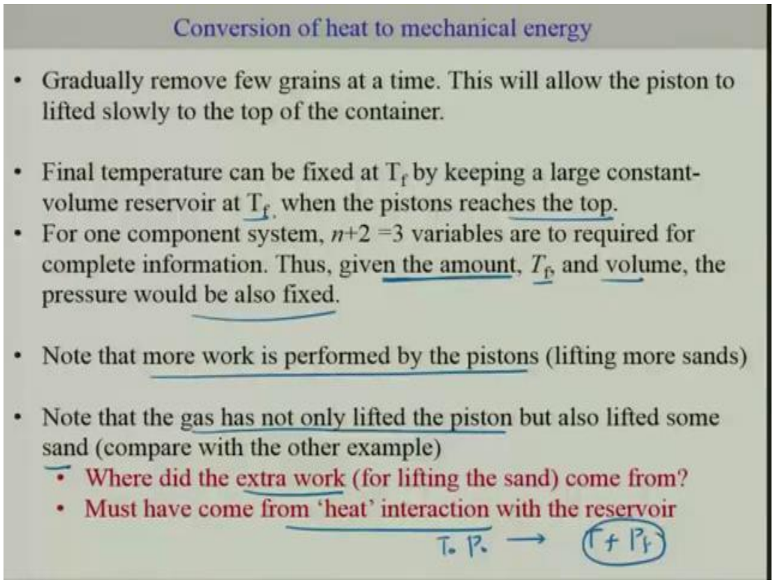

Thus, energy is transferred if there is a difference in temperature between parts to a composite system. This is what we are making, because remember that the temperature here finally will not be the same. If you have just put this sand there, final temperature would be different and that is why if you put a temperature initial temperature if have known that this is my final temperature in reservoir, if we have put the final temperature in reservoir.

So, what we are saying is that energy must be transferred and that mean the temperature was lower than Tf. So transfer of energy to the system leads to an increase in the temperature. This energy is stored in the form of kinetic energy and potential energy which we know. Now for classical thermodynamic precise form of energy is not important this we know. So this leads to basically the equilibrium states here.

So this example which I wanted to talk about, illustrates that basically the energy in this case is transferred and of course some work is being done by that particular trans of energy. But the trans of energy was possible because there is a difference in the temperature between the parts of the composite system. And we are setting that this would also lead to increase in temperature. So this was a simple example of of piston and cylinder.

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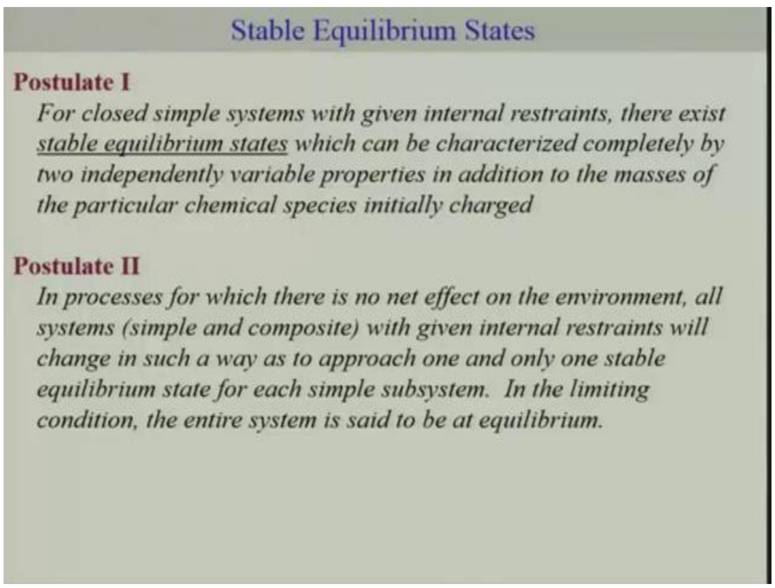

Now let us go to the next stage where basically we are reasserting the equilibrium states here. Now what we are trying to say is that in the first week of lectures we also mentioned about the equilibrium state. We are redefining this equilibrium state in the terms of different postulates. So for the case of let us say a closed system with the given internal restraints there exist a stable equilibrium state which can be categorized completely by two independent variable properties in addition to the masses of a particular chemical spaces initially charged.

So this is something which we already have talked in earlier class. Postulate that in processes for which there is no net effect on the environment, all system whether it is simple or composite with given internal restraint will change in a way as to approach one and only one stable equilibrium state for given simple subsystem. So, essentially was there is no effect of on the environment for given interval restraint the system will approach toward an equilibrium state.

And in the limiting condition the entire system is said to be at equilibrium. So this is something which we have asserted also earlier but I am trying to re-emphasize this and this will lead to something called adiabatic work interaction which becomes an interesting way to look at the conservation of energy.

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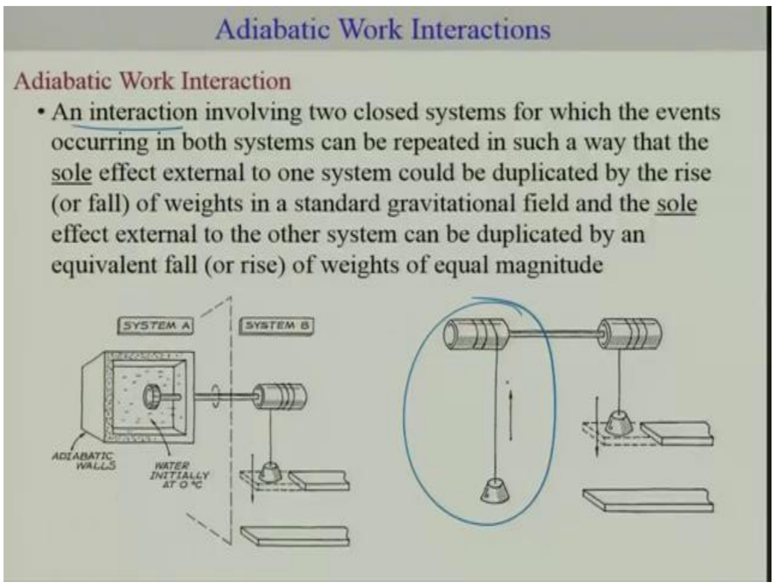

So this is the case of adiabatic work interaction, so what we are trying to do is we have consider this system A and B here. So we have, a pulley attached with a weight, and there is shaft and there is a drum. So essentially if it rotates, if it moves down this will rotate the shaft leading to essential age doing some work on this system A. So this particular is under this particular system has adiabatic walls and what we are trying to emphasize is something called adiabatic work interaction.

So this is an interaction involved between two closed system for which the event occurring in both system can be repeated in a way that the sole effect external to one system could be duplicated by the rise or fall of weight in a standard gravitational field and the sole effect external to the other system can be duplicated fall or rise of weights of equal magnitude. So if you consider this, so what this particular statement says that the effect of this on this can be replaced by this and the effect of this is nothing but the basically this.

So this is what a typical adiabatic why because there is no energy the heat exchange here. So Adiabatic means there is insulated completely, there is no exchange of heat. So, the work whatever is done can be replaced by these expert’s. So, if it is moving downward it will move upward, ok.

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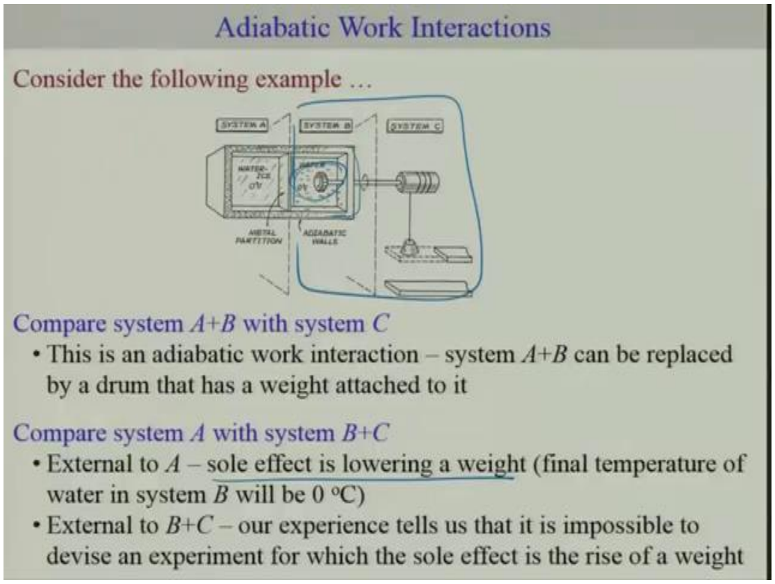

Now consider a different example where you have now system A and B, and A and B are separated by this metal partition. So, if you compare a system A plus B together ok with system C, now this system A plus C are all adiabatic, these are all adiabatic wall, then essentially you can replace this whole system by a drum with a weight attached to it.

But if you consider system A, ok only system A the sole effect is can be considered as loading a weight because essentially this system do not change any temperature because this is a metal partition they essentially it will remain as you degree. But if you consider external B plus C here you cannot replace the system A by a drum and a weight, you can no way you can come off with an experimental replacement of such a things. So it is impossible to devise any experiment for which B and C's effect sole effect will be devise of a weight, in this case.

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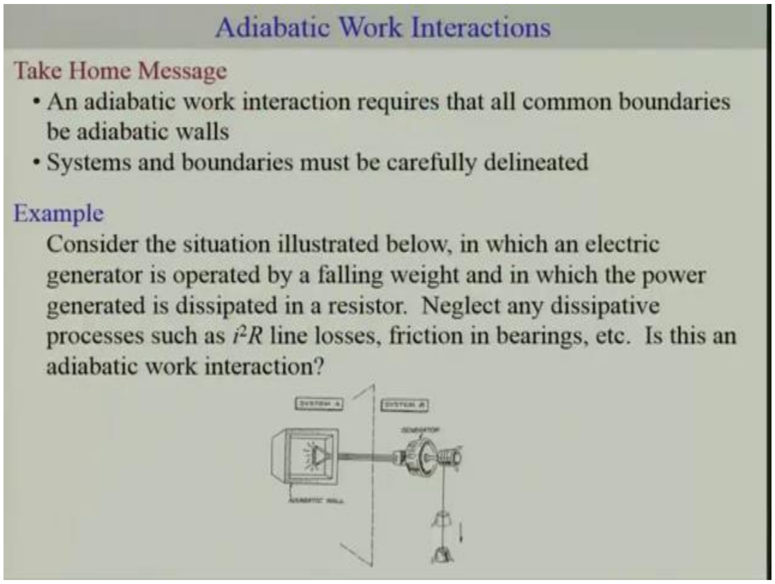

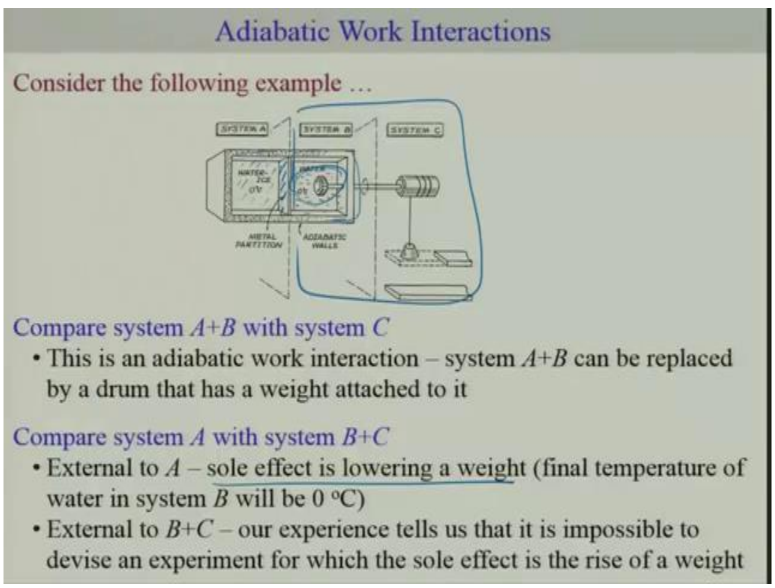

So what it means that this tells you that the adiabatic work interaction requires that all the common boundaries adiabatic wall. So here if you consider B and C this wall is not adiabatic and hence it could not replace the system A by another drum and a weight scenario, ok. So, that is a condition or conclusion based on this exercise that the adiabatic work interaction requires all common boundaries be adiabatic walls.

Thus, system and boundary must be carefully delineated. Now, consider this example which you can easily solve, that the situation here is below here. So you have a generator, you have a pulley system here and this is a generator it is operated by a falling weight in which the power is generated is dissipated in resistor. So, if we neglect any dissipative processes such as in square then will this be an adiabatic work interaction? And the answer is yes, you can convert this by the drum and weight scenario.

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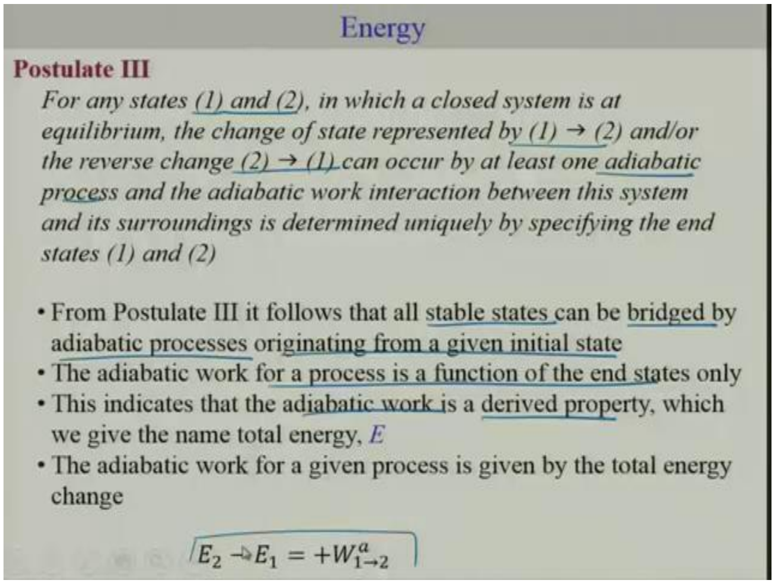

So, now I move from this adiabatic work and let us get to the energy and then we will try to connect this adiabatic work and energy and later to your first law. So, this is another postulate again we suggest to reiterate our understanding here. For any system one and two, in which a close system is at equilibrium the change of the state is represented by 1 to 2 or the reverse change can occur by at least one adiabatic process and the adiabatic work interaction between the system and the surrounding is determined uniquely by specifying the end state 1 and 2.

So, what it is saying that if 1 and 2 are in equilibrium state then basically you can always connect, you can find the change by at least one of the adiabatic process and that adiabatic process, the cause for the work interaction will be simply determined by this n state. So this is summarized here that it follows all stable states can be bridged by adiabatic processes originating from a given initial state. The adiabatic work for process is a function of n state only this indicates that the adiabatic work is a derived property.

Remember that if the property is depends only on the state so if a adiabatic work which we are saying is basically a function of n state then essentially this is a derived property, we can say this to be E, in other words we can say that the difference in this E for the case of adiabatic process would be simply Wa 1 to 2. This is a representative of adiabatic work adiabatic, adiabatic which should be difference in this derived property which because it just simply depends on the state and this E is nothing but of course total energy.

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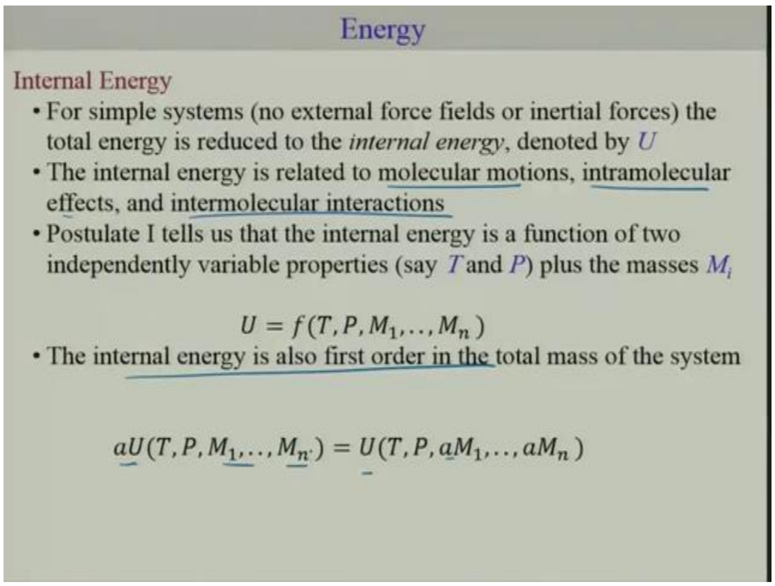

Now most of the cases we are going to ignore the external force, initial force hence the total energy can be reduced to the internal energy which is nothing but which relates to the molecular motion, intramolecular facts and intermolecular interactions which we all know. Now, earlier we have also mentioned that U could be a function of this.

$$U = f(T, P, M_1, \dots, M_n)$$

This is something which we are aware of. Earlier in our lecture, week 1 discussion we have gone through as far as we know that it is also first order total mass essentially the order is given here. If you consider U to be a times m1 times to so for, it would be simply a times U of this that we know that extensive property of the energy.

$$aU(T, P, M_1, \dots, M_n) = U(T, P, aM_1, \dots, aM_n)$$

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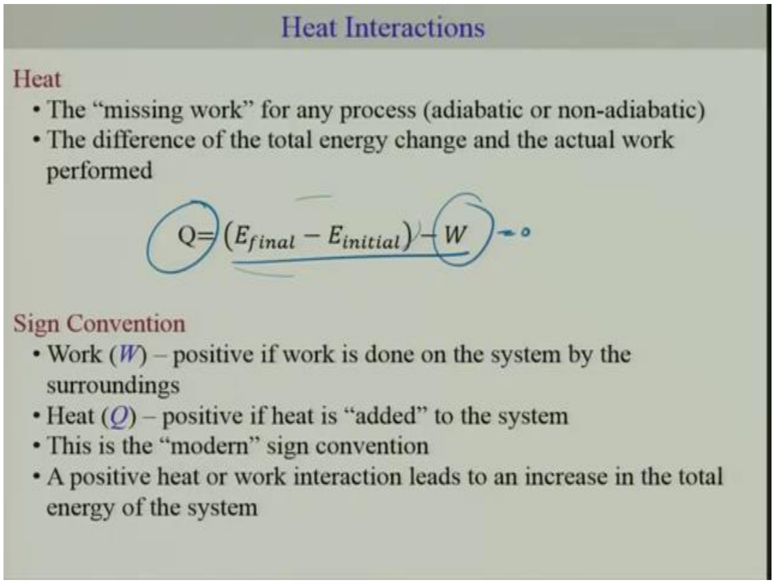

So now we connect all these things, so essentially the missing work for any process ok whether it is adiabatic or non-adiabatic would be nothing but heat. So, for the case of a adiabatic one, this is going to be 0 as we have already discussed. But it the case of non-adiabatic you are doing additional work or that would be your missing work and the difference is basically nothing but this: $Q = (E_{final} - E_{initial}) - W = 0$

So this is our sign convention which we have already discussed.

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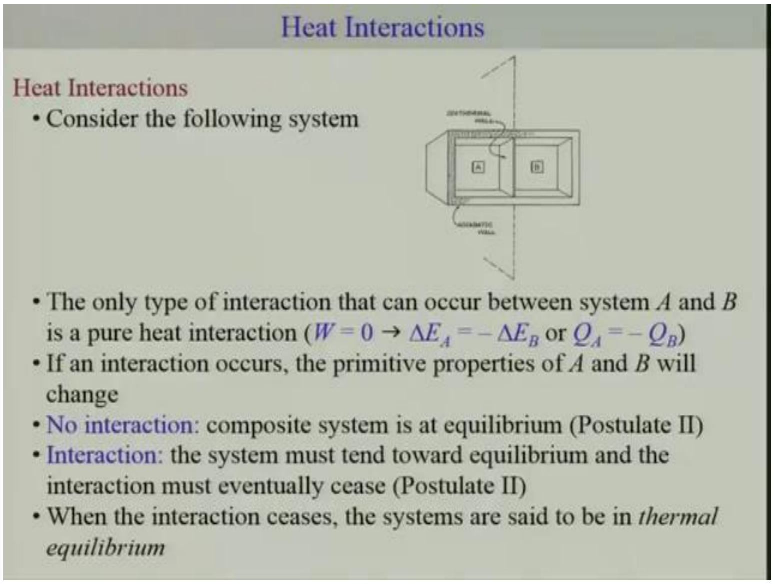

So I could quickly go through this heat interaction in this last few slides here. So this is a simple system which we are considering system composite system A and B separated by a diathermal wall. So the only type of interaction that can occur between A and B is basically heat interaction because this is a diathermal only the heat can flow and essentially there will be no work because this is rigid.

So you have delta Ea is equal to minus delta Eb based on the energy conservation which is what this is. And the corresponding Qa is basically minus Qb. Ok. So, what we are saying is that this when the interaction ceases after some time the composite system will be at equilibrium that is postulate II. And that is what we are trying to say to the system must tend towards equilibrium state and treasures machine should eventually cease. In that case the system would be considered as thermal equilibrium. So that is another way of putting things making use of this property or the postulates.

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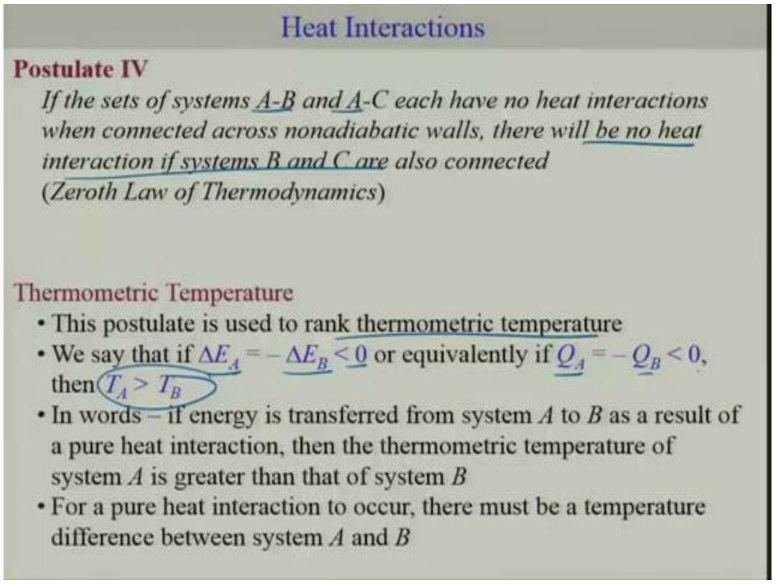

And that leads to our final postulate here that if the sets of system AB and AC each have no heat interactions when connected across non adiabatic walls, there will be no heat interaction if system B and C are also connected. So that means if A and B are at thermal equilibrium and A and C are at thermal equilibrium then D and C has to be at thermal equilibrium. This is what we know is zeroth law of Thermodynamics.

And this can also be considered in the form of thermometric temperature. So this postulate can rank the thermometric temperature. So if we say that delta Ea is equal to minus delta Eb which is less than zero, or equivalently Qa is equal to -Qb which is less than 0 then essentially the temperature of A should be greater than the temperature B. This you can consider from that composite system here.

So if there is a heat transfer from A to B, this is based on the convention if heat is transferred here the heat is going to be negative. The corresponding temperature has to be more than A will be more than that of B that is what basically the statement saying. So in other word for the pure heat interaction there must be a temperature difference between system A and B.

Believe that what this lecture we wanted to do is to re-emphasize the set of understanding which we have created in the first week, but in a different form and to illustrate that similar thing you can do in different way, a different to come to first law of thermodynamics. In the next lecture we are going to do is we are, we will focus on basic examples of the open systems and close systems and hopefully that will give you a refresher memories of engineering thermodynamics before we had to move complicated aspect of a chemical thermodynamics.