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Lecture - 39 Clausius Inequality and Introduction to Entropy

In our previous lectures, we had a qualitative understanding of what is a reversible process, what are the factors that can make a process irreversible and we could compare irreversible process with reversible process. By understanding that their performance in terms of thermodynamic efficiency is poorer for irreversible side. The question that comes to us now is that, well in practice many processes are in fact, all processes are irreversible, but if you want to compare this irreversible processes to what extent they deviate from the ideal of the reversible one can we establish a quantitative parameter for that.

So, next we should be in a quest of establishing a quantitative parameter denoting the extent of irreversibility. So, to do that, we will first we will consider a few examples.



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So, example 1 reversible heat engine. For all this examples we will be interested to calculate the following cyclic integral of del Q which is a very important parameter for so, for as the first law consideration goes and cyclic integral of del Q over T where T is the absolute temperature. We will see later on that this happens to be a very important

parameter so far as the quantitative estimation with respect to performance in the purview of second law goes.

So, reversible heat engine. So, what is cyclic integral of del Q? This is Q H minus QL. We are interested to write an equality or inequality for this. So, can we write that this is greater than or equal to 0 greater than 0 is the most common case when you have a net work that is output which is Q H minus QL equal to 0. In the limiting case when T H and T L are very close because Q H by QL is a function of T H by function of T l. So, when T H and T L are very close the ratio of this functions is almost unity and w is equal to Q H minus QL will tend to 0.

So, if T L and T H are very close limitingly close only and then this equality should be use. So, this equality is not in a classical sense, but in a limiting sense then cyclic integral of del Q by T. So, this we are doing for irreversible heat engine. So, there are 2 heat transfers; one is Q H. So, let us assume that these are all you know both internally and externally reversible. So, this is what is the temperature here? T H minus d T H and this is T L plus d T L right.

So, this is Q H by T H minus d T H. Remember we are writing this integral not for this system plus surrounding we are writing integral only for the system which is the heat engine. So, that is why this T is the temperature of the system boundary across which the heat transfer is taking place not the temperature of the reservoir. Because of external reversibility this is as good as the temperature of the reservoir ok.

So, this other heat transfer is negative. So, given that these are tending to 0 this is Q H by T H minus QL by T L. So, this is equal to 0 as per the definition of the absolute temperature scale ok. Then we take example 2 reversible heat pump or refrigerator ok. So, what is cyclic integral of del Q? So, this is QL minus Q H this is equal to minus W in right. So, this is less than or equal to 0 just like the previous case. So, you can see that when we changed from heat engine to heat pump or refrigerator this inequality changed from greater than equal to 0 to less than equal to 0. So, in cyclic integral of del Q is not or universal parameter that maintains the same inequality across different types of devices, but whether cyclic integral of del Q by T maintains it or not let us check.

So, cyclic integral of del Q by T what is this? So, QL what is the temperature here? If this is T L this is T L minus d T L right. So, QL by T L minus d T L minus Q H by now

this is T H plus d T H d T L and d T H are all tending to 0. So, this is equal to 0. So, you can see a remarkable parameters cyclic integral of del Q by T which is equal to 0 for all reversible cycles may be refrigerator heat pump heat engine all types. Because all types of cycles can be classified into 2 categories; one is work producing another is work absorbing.

So, this is an example of work producing this is an example of work absorbing. So, in both the cases you have cyclic integral of del Q by T equal to 0. Now, let us consider example 3 and example 4, purposefully I will use the same diagrams to compare it with reversible.

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So, example 3 irreversible heat engine ok. So, cyclic integral of del Q let us say irreversible heat engine now, when there is reversible and irreversible you want to make a comparison certain things you such keep fixed. So, what you are keeping fixed? T H T L and Q H and see what is the net W because of the difference from reversibility to irreversibility.

So, with the same Q H now QL will be different. So, QL will be QL irreversible and W will be W irreversible. The manner in which we will construct the irreversible heat engine is up to us. So, the way in which we will cleverly do it is that we will consider it to be still externally reversible, but it has become internally reversible and because it is it has become internally reversible the entire reversibility is destroyed ok.

So, this example is externally reversible, but internally irreversible that makes it in totality irreversible side. So, now, Q H minus QL irreversible. So, can we say that it is greater than equal to 0 greater than of course, equality is also possible when it has become so, irreversible that because of friction all the energy is dissipated and there is no net work output. So, see here very interesting thing. For reversible also this equality can hold for irreversible also this equality can hold, but the reasons are different for reversible the equality could hold if T H and T L are very close for irreversibility the additional reasons for which this equality could hold is because of extreme reversibility.

Now, the more interesting del Q by T. So, QL this is now QL irreversible same Q H. So, QL for same Q H which QL is more reversible or irreversible? Irreversible is more because for same Q H e reversible is more and QL is the difference between Q H and W. So, if work done is more heat rejection is less right. So, here work done is less because of irreversibility. So, heat rejection is more. So, QL irreversible this is greater than QL reversible. So, Q H by T H minus QL reversible by T L was equal to 0 now you are subtracting a quantity which is greater than QL irreversible. So, it will now become less than 0 ok.

Then let us take example 4 irreversible heat pump or refrigerator. So, here what we do is that we fix up T H T L and QL Q L, but because of different work input necessary for reversible and irreversible, this Q H will now become Q H irreversible which is different from Q H reversible. So, cyclic integral of del Q which is QL minus Q H irreversible which is equal to minus W in. Now this equality will not be there. The reason is to run a refrigerator or a heat pump you require a work input you may get almost 0 work output from a heat engine, but with almost 0 heat work input you cannot run a refrigerator or a heat pump ok.

So, this is less than we know equality these are you know very settle things and these things more and more you discuss more and more you know you go to in depth concepts of the second law, then cyclic integral of del Q over T. So, this is QL by T L minus Q H by T H, but Q H is Q H irreversible.

So, for irreversible refrigerator or heat pump for the same QL you will require more work input. So, if you require more work input Q H will be more. So, Q H irreversible this is greater than Q H reversible ok. So, because Q H irreversible is greater than Q H

reversible for the same QL with Q H reversible it was equal to 0 with a number greater than that subtract it will become less than 0. So, this will become now less than 0.

So, remarkably you can see that cyclic integral of del Q by T, its strength does not depend on whether its a work producing or a work absorbing device and therefore, it can be thought of as a universal parameter describing the performance. Not only that it is equal to 0 for reversible and less than 0 for irreversible. So, more and more it is less than 0 greater and greater it should be; it should be reversible so; that means, its extent of irreversibility depends on how much lower it is from 0.

So, we are now graduating from a qualitative description of irreversibility to a quantitative description of irreversibility. So, combining all these let me now clean everything up.

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We can make a very generalized statement that for all cycles cyclic integral of del Q over T is less than equal to 0 ok. Remember from our derivation it is clear that this T is the temperature of the system boundary across which this del Q is taking place not temperature or source or sink ok. So, this is called as Clausius inequality one of the most classical inequalities deployed in thermodynamics.

So, you can replace this inequality with a sort of you know equality by writing this as say minus sigma where sigma is positive. So, greater the value of sigma more

irreversibilities. So, we are coming to slowly towards quantification of irreversibility. Now there are cases when this sigma is 0 and then it is a reversible cycle. So, when you have a reversible cycle, the reversible cycle will comprise reversible processes. So, now, let us try to evaluate this integral of del Q over T for reversible processes. The difference between these two is this is for a cycle and this is for individual process at least 2 such processes are needed to complete a cycle.

So, let us say that we have an arbitrary plane whatever may be pressure volume or whatever in which you have one reversible cycle from 1 to 2 via path A and 2 to 1 via path B ok. In another case from 1 to 2 via path A and then from 2 to 1 via path C all are reversible paths ok.

So, cycle there are 2 cycles one cycle A plus B this is reversible because both the processes are reversible. So, the cycle is reversible and cycle A plus C that is also reversible ok. So, for cycle A plus B cyclic integral of del Q by T equal to 0; that means, line integral of del Q by T from 1 to 2 via path A plus line integral of del Q by T from 2 to 1 via path B this is 0. Similarly, cycle A to C. So, from these two if we compare then we can conclude that definitely, but B and C are arbitrary paths.

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That means, integral del Q by T reversible, I am putting here reversible in a sense that without reversible these kind of expressions will not work the equality will not work, this integral del Q by T for reversible between 2 point. So, 2 to 1 is path independent ok.

So, because this is the path independent integral the differential del Q by T reversible we can write this as differential of a property S. So, why so, this is an exact differential because this integral of this does not depend on the path. If integral of this does not depend on the path, then this represents differential exact differential of a function which is called as point function this we have earlier discussed.

And this point function we call as entropy. Remember this is not the definition of entropy, because this just talks about the change in entropy. It does not talk about what is entropy itself physically and it does not talk about what is entropy in a quantitative absolute sense right what is the value of entropy.

It say it just says that it is a difference in entropy. So, we will later on understand through you know from discussions from now on words that what is the physical meaning of this entropy and then how we can relate that physical meaning a more absolute definition of entropy which comes through the third law of thermodynamics. So, now the question is that a special example. So, the entropy definition comes through this.

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Now, a special example special case reversible plus adiabatic process. Why this case process is so, important you have seen that in the Carnot cycle this appears as one of the processes.

So, reversible adiabatic process is a process, where you know what happens? In the reversible adiabatic process because it is reversibly you can use this and because it is adiabatic del Q is 0. So, reversible plus adiabatic process means d S equal to 0 between all state points that successively change during the process, this is called as isentropic process because the entropy remains constant this is also called as isentropic process. That means, in the Carnot cycle we have 2 processes as reversible adiabatic and 2 processes as reversible isothermal.

So, 2 processes are isentropic that is entropy remains constant and 2 processes are temperature remaining constant. So, it is very convenient if we can draw the Carnot cycle in a temperature entropy diagram or T S diagram and that is how because we want to compare all the cycles with the Carnot cycle, the drawing of the cycle diagrams in temperature entropy plane or T S plane as become so, popular. So, I am just giving you the genesis why do we draw T S diagrams. So, we will just try to draw the T S diagram of a Carnot cycle. So, T S diagram for Carnot cycle. So, the we will just summarize the processes 1 to 2 the first process is reversible plus adiabatic compression right.

Then 2 to 3 reversible plus isothermal heat addition, 3 to 4 reversible plus adiabatic expansion and 4 to 1 reversible plus isothermal heat rejection. Heat addition takes place at temperature T H and heat rejection takes place at temperature T L. So, we will draw the T S diagram. Numerous times from now on wards in this course we will be drawing T S diagram this is the first T S diagram that we are drawing.

So, reversible adiabatic compression it starts with state point 1, reversible adiabatic means entropy remains constant. So, it will be a vertical line up or down. See if you compress then you impart energy to the fluid and you do not allow any heat transfer to dissipate that energy. So, the internal energy of the system will increase so, that will increase the temperature. So, it will go from 1 to 2. So, never try to memorize any process in a cycle just use your common sense to figure out whether temperature will increase decrease or entropy will increase decrease. 2 to 3 you have reversible isothermal heat addition.

So, remember d S reversible is del Q by T. So, d S sorry d S is equal to del Q by T reversible. So, if del Q is positive, then d S is positive because this T is absolute temperature always positive. So, entropy increases at constant temperature this is T H.

Then reversible adiabatic expansion is just opposite to compression. So, it will be like this where entropy remains constant and heat rejection is just opposite to heat addition and this takes place at T L. Now how do you find out the efficiency of this cycle? So, first of all there is a very interesting thing. So, what is the net work output of this cycle? The net work output is same as the net heat transfer right.

Cyclic integral of heat equal to cyclic integral of work. So, what is the heat transfer this is this area under the T S diagram right because why? The heat transfer Q H is the area under this and heat transfer QL is the area under this. So, Q H minus QL is the pink color area that we consider and that is the work done. So, efficiency let me write it here is equal to 1 minus QL by Q H what is QL? Q L is you know this 1 4 let us put some name here A B. So, 1 minus area 14 A B divided by area 2 3 A B all right.

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So, essentially 1 minus 1 4 A B is what? 1 4 let us write this as delta S. So, delta S 1 4 A B is delta S into T H sorry delta S into T L right and 2 3 A B is delta S into T H. So, this is 1 minus T L by T H and it satisfies our definition of absolute temperature scale because for reversible cycle QL by Q H is equal to T L by T H ok. So, to summarize today we have learnt how to quantify reversibility and irreversibility and how to describe the del Q over T for a reversible cycle and for a reversible process and how to apply that concept to a Carnot cycle. We will continue with discussions on this line in the next lecture.

Thank you very much.