Chemical Principles II
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Module 04
Lecture 25
Statements of the Second Law of Thermodynamics

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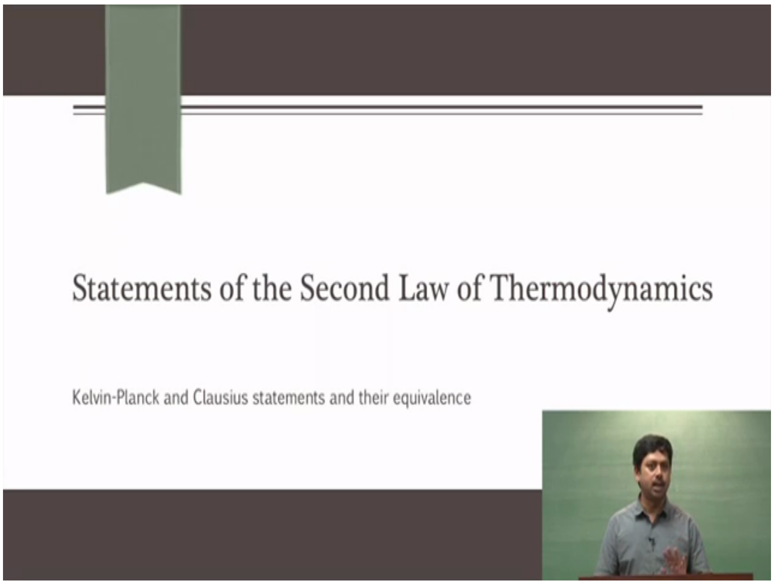

Today we are going to talk about the statements of second law of thermodynamics and mainly we will discuss two statements, one is Kelvin-Planck statement, another is Clausius statement and then we will show their equivalence. In fact, we already discussed that the second law of thermodynamics is that the definition or the statement of second law of thermodynamics is that entropy of the universe is always increasing.

At the same time we also discussed that another version of second law of thermodynamics is that efficiency of an engine cannot be equal to 1. So these two statements apparently are completely disconnected, looks like, right? But we are going to connect that. And there are many more statements of second law of thermodynamics available, so they are corollary to each other and one can show that if one is valid, the other one also will be valid. So therefore all of them will hold true or they are connected in some way. So we are going to at least connect five to six different statements of second law of thermodynamics and show that they are equivalent.

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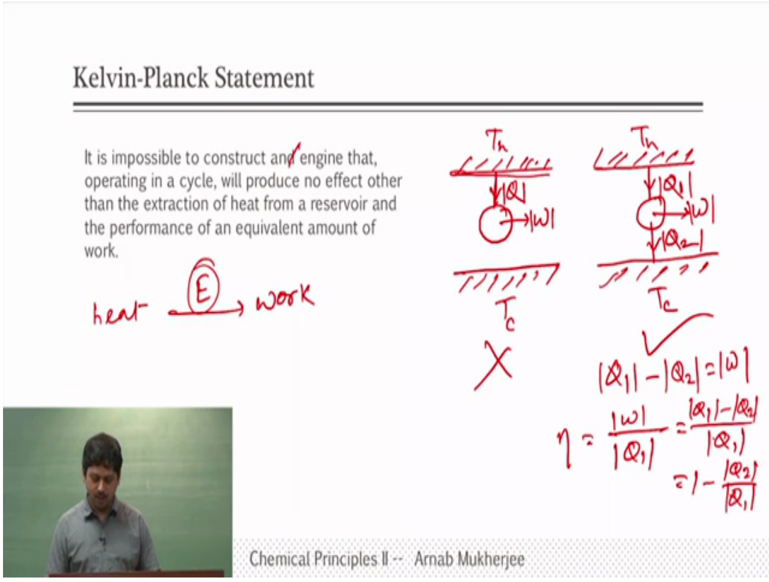

We are going to start with Kelvin-Planck statement which says that it is impossible to construct an engine that operating in a cycle will produce no effect other than extraction of heat from a reservoir and the performance of an equivalent amount of work. So what that means is that, as I said, engine is something like when you take heat and produce work, that is the purpose of an engine which I denote by E. And now how exactly the heat is converted to work that depend on the detail of construction of the engine.

First Law of Thermodynamics says that heat can be totally converted to work, there is not ambiguity in that and that is the conservation of energy. Heat and work are different kinds of energy and therefore it should be possible to convert completely heat to work. However, second law of thermodynamics add another dimension to it and it says that one cannot totally convert heat to work if the process is cyclic which means if you do it again and again, then one cannot fully convert heat to work completely.

And that is what the statements of, Kelvin-Planck statement that, if you take heat, let us say this is high temperature reservoir, so we have discussed about what is the reservoir, right? Reservoir is a system which is large enough such that if you take away heat little bit from that, it is not going to change its temperature. So for example, or the change of the temperature will be so little that it can be negligible. We know that heat is proportional to temperature but then if we are taking from extremely large system, then a little bit amount of change of heat is not going to change the temperature.

And that is called reservoir which can supply heat without changing its temperature. So here we are denoting the temperature of the, high temperature reservoir as T h and if you take heat Q from that, and going to perform a work in a cyclic manner, W, so here we are going to use the notations such that we are going to put absolute values of that. Remember I discussed during the first law of thermodynamics lectures that work done on the system is positive, work done by the system is negative.

Similarly, we can say positive and negative in terms of whether we take heat or give away heat and things like that. However, here we are going to use the arrows to indicate whether it is positive or negative. So the arrows indicate here that heat, Q amount of heat is taken from the high temperature reservoir and W amount of work is produced without letting any heat go to the low temperature reservoir. And that violates the second law of thermodynamics according to the Kelvin-Planck statement.

So what is the correct one which does not violate? That is, if you take the Q amount of heat, do W amount of work and throw away let us say Q1 amount of heat you take in, W amount of work you do and Q2 amount of heat you leave away or throw away to the low temperature reservoir. Tc is basically indicates that the reservoir as lower temperature or cold reservoir, that is why that c is denoted for and h denotes the hot reservoir. So this is perfectly all right according to Kelvin-Planck statement.

And you can immediately see that, again we can use first law of thermodynamics and we can say that the total energy of internal energy of the system is conserved, therefore heat will be equal to minus w. So since we are not going to use the signs anymore and we can use the arrows to find out that Q1 minus Q2 is equal to W. So that is just first law of thermodynamics. So in that case an efficiency of an engine will be work done which is W divided by heat input.

Remember we are going to consider what is we are going to throw out because we did not want to throw out. It is the fact that we have to throw out is the constraint given by second law of thermodynamics. So what is our input? Our input is Q1, what is our output? It is W. So the efficiency is W by Q which is, as you can see, Q1 minus Q2 divided by Q1, giving you 1 minus Q2 by Q1, which means if the value of Q2, then only we will get efficiency 1. However, that is validated by second law of thermodynamics.

So therefore you can immediately see that Kelvin-Planck statement says that efficiency of an engine cannot be equal to 1, that is the media coming from that. So already two versions of second law of thermodynamics we know. Third version also we know, the entropy of the universe is increasing, we have to connect more and more versions.

Yeah, okay, so if I understand your question is that, we know from first law of thermodynamics that we can convert one form of energy to the other form of energy. And energy is actually anyway conserved. So what prevents this full conversion of heat to work? We will address this question later part, you will understand that what prevents it. So basically the second law of thermodynamics dictates that it is not possible. What prevents it, is actually the question that we are going to deal with in the second law of thermodynamics. But we are not going to come right away, we are going to come through different examples and then we will understand that why that happens.

For example, if we, if I tell you that what prevents it, I can also ask you one question is that, have you ever seen that heat transfers from low temperature to high temperature spontaneously? What prevents it? What prevents heat transfer from low temperature to high temperature? Whatever it is, whatever it prevents, it will prevent same way a complete conversion of heat to work. Do you understand? So whatever prevents heat transfer, spontaneous heat transfer from low temperature to high temperature will prevent complete conversion of heat to work in a cyclic process.

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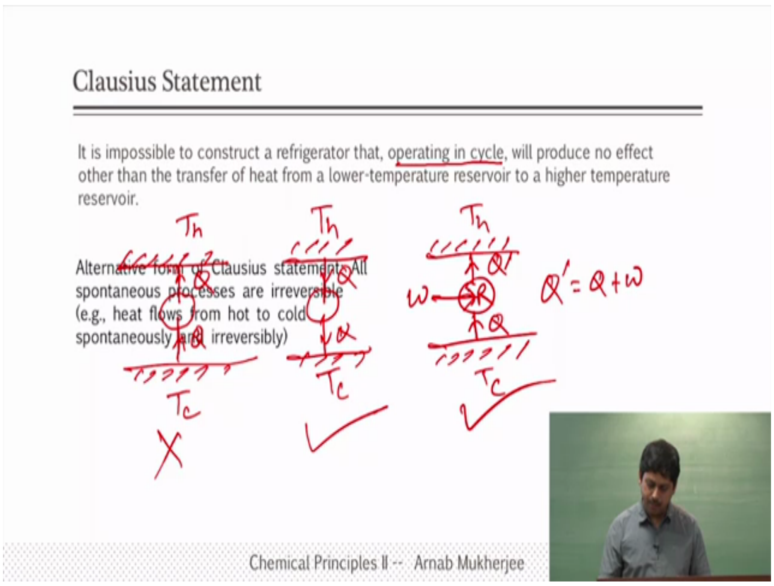

Now what prevents it, we are going to understand. So that is precisely the Clausius Statement which says that it is impossible to construct a refrigerator that operating in cycle, will produce no effect other than the transfer of heat from low temperature to, low temperature reservoir to a high temperature reservoir. So operating in a cycle is very important, do not forget that. And no effect other than transfer, which means there is nothing else that is happening other than transfer of heat to low temperature to high temperature.

If I graphically show you that one, then again I am drawing a high temperature reservoir. High temperature means again the temperature is constant in that, that is no doubt because anything that you left it will have an equilibrium temperature, T h. And then you have a low temperature reservoir and we are drawing like Q amount of heat and transferring the same. Okay, I am not giving you the mod sign but let us take everything as under the mod sign. So we are considering everything as positive quantity. Arrows will tell us whether it is positive or negative.

Now this says that we are transferring heat to low temperature, same amount of heat without doing anything else, produced no other effect. It is producing nothing else but transferring heat from low temperature to high temperature. It is not doing anything else and that is a violation of second law of thermodynamics. However the other way around, it is not violation. Transfer of heat from high to low spontaneously is not a violation. You see there we are already kind of bringing a symmetry.

If you see forces and physical laws, they are all symmetric. If it forces, it will have an equal and opposite force back and all but here absolutely we are saying that this is but however this is okay, and this is also okay. That, if I want to transfer from low temperature to high temperature, I have to put I some work W and let us say Q amount of heat I am taking in from low temperature, W amount of work I am doing, so therefore Q plus W let us call it Q prime, will be transferred to high temperature.

So Q prime is, Q plus W. Assume mod sign for everything. This is okay, this does not violate second law of thermodynamics. And therefore refrigerator works, right? Wherever you throw away heat from low temperature to high temperature, remember temperature of the refrigerator is 4 degree centigrade, the normal one and outside temperature may be 37 degree or 30 degree, still it works. It works why? Because something else goes in, otherwise it would not have worked.

So these typical constructions where you transfer heat from low temperature to high temperature called refrigerator R and engines are the opposite which takes heat from high temperature and does the work. However complicated that may look like but inside, if you look at a car engine, it is very complicated inside. But all that it does is that it takes heat and converts to work. The design has to be done in such a way that you try to get as much efficiency as possible or to make it work in a certain way.

That is all design or engineering, how you do that but basic principle is that. And this particular thing in Clausius Statement that heat cannot spontaneously transfers, our everyday observation, is not it? So every day observation is that it never happens. So second law of thermodynamics again is not that we can derive somewhere, it is from our observation we see that. And it is never being violated. So these two statements that we talked about, they are actually equivalent statements.

As I said exactly that whatever prevents heat transfer from low temperature to high temperature spontaneously does prevent the transfer of heat to work completely. So let us see that that happens. So there is an alternate statement, it is this.

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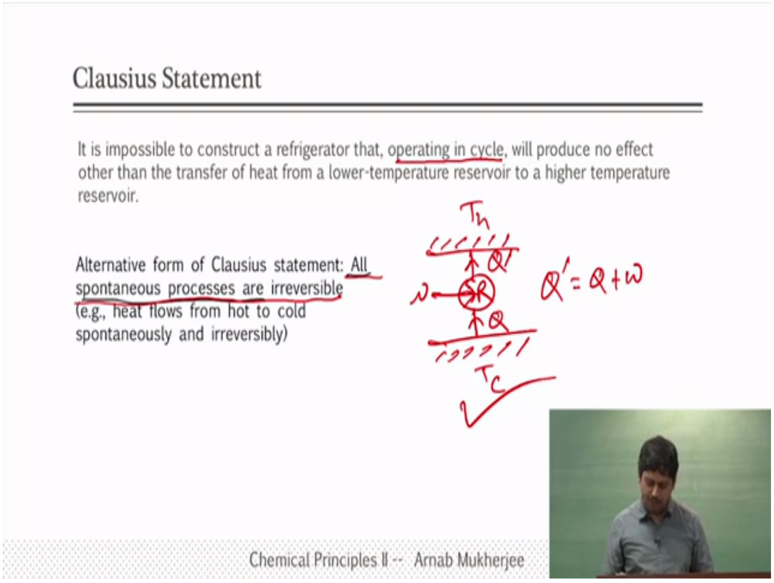

The alternate statement of Clausius is that alternate form of Clausius Statement is that all spontaneous processes are irreversible, that means if heat transfers from high to low, it cannot go from low to high. See, reversible means what? It could have transferred both ways, right? Which I said symmetric and in rough way, in a very crude manner. So it is irreversible. It just goes one way, all spontaneous processes.

And we gave examples yesterday about some spontaneous processes happening. And you can understand a spontaneous process by running a movie backward. If you take, again just to remind that we are dropping a ball from some height and we see that it is just falling to the ground and getting, stopping and it is never coming back to the hand. So it is an irreversible process that starts from my hand and goes to the ground. We have never seen a process that come from like ball comes directly to hand. Now how do we understand that?

If we run, if you take that movie which happens like and then run it backward, and we see that is impossible, that ball never comes to hand. Then we will know that, that is an irreversible process that has happened. Whereas somebody in the swing, by running the movie backward will not be able to know whether the movie is running backward or forward, which means in that case the process is not irreversible. And we said that in one case the entropy is increasing, another case entropy is not increasing, we just gave very brief example of that.

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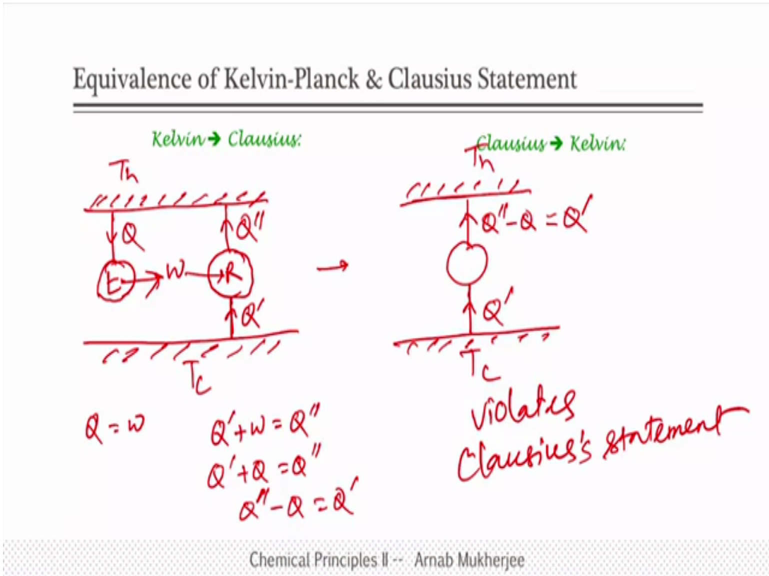

Anyway, so now we have to show that these two, apparently two very different statements are equivalent and for that what we will do is that we will first start with Kelvin Statement and say that if Kelvin Statement is violated, what happens? So let us say we take heat from high temperature Q, do a work W, do not throw any heat to the low temperature, do not throw, okay. Let us say that this is allowed. What will happen in that case? Here I am going to draw another engine, another process where, or you can say I am going to attach a refrigerator.

Let us say this is an engine which is perfectly all right. With this engine I am going to attach a refrigerator. Refrigerator runs backward, right? So I am going to take heat Q from this, let us say Q prime and since I need some work, I will take the work that is output of this particular engine W into this and I am going to throw away some Q prime heat to the high temperature. So is it clear? This particular part for everybody? So what will happen in that case?

This combined system together how does it look? So this process is not, this process is allowed, the second part is allowed, okay. I am not violating Clausius Statement by that because I am taking work from there. Now let us do some calculation. Q equal to W we get from the left hand side and Q prime plus W is equal to Q prime prime from the right hand side. Now which means that I can write Q prime plus equal to Q prime prime, okay. So now I write the combined system.

I the combined system I am taking Q prime heat because nothing is going in this side. I am only taking Q prime heat, right? And how much amount of heat is going there? Q, I am taking in Q and giving Q prime prime, so it is Q prime prime minus Q. What is Q prime prime minus Q? Q prime. So what you see here that the heat Q prime transfer spontaneously from low temperature to high temperature, which violates Clausius Statement.

So you see that violating Kelvin Statement violates Clausius Statement as well. Although initially that was not our intention, we have properly put a work here. But when we put them together, what we observe is that, that is what is happening because I our combined system work output of this left hand side engine is used in the right hand side refrigerator. So net effect is zero there. All that is happening is that Q prime heat is going from low temperature and going to the high temperature. Is it clear?

So then we can say, okay, so now when you mathematically equivalence to relation, so you say that A equivalent to B and B also equivalent to A, you have to give both. So first part is done, Kelvin to Clausius. Now we are going to do Clausius to Kelvin. So we are going to just erase this. So this is done.

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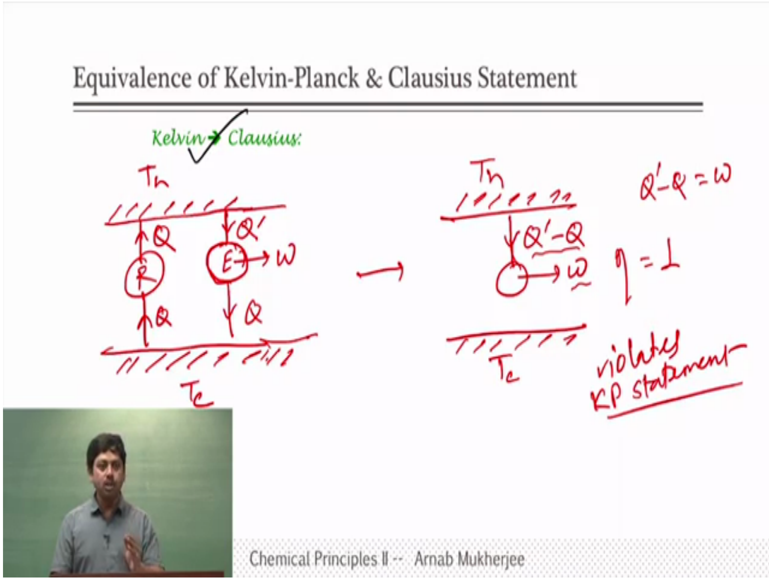

Clausius to Kelvin, we can transfer heat from low temperature to high temperature without doing any work, correct? Let us say that does not violate second law of thermodynamics. Let us say it is true that it is possible, not true but let us say it is possible to transfer heat spontaneously from low temperature to high temperature. We have to show that it violates Kelvin-Planck Statement. How do we do that? We are going to take Q prime amount of heat and throw away let us say Q prime prime and do some work W.

You see here that right hand side, I have not, I did not have the intention to violate Kelvin-Planck Statement because I have taken properly Q prime amount of heat, did some work and then threw away Q prime prime. No intention to violate anything here. One thing I would like to do is that I am going to adjust little bit my numbers. So again this is a refrigerator and this is an engine. Correct? I am going to adjust this particular engine in such a way that I can get whatever number I want to. How do I do that?

Let us say, that I say okay, instead of throwing away Q prime prime, I am going to throw Q. So my efficiency will be adjusted anyway. Efficiency is what? W by Q prime whatever I am taking. So depending on my efficiency the Q prime will be adjusted. But I can adjust my Q, I have this number, sorry, I have in my hand the number Q to adjust because if I adjust Q depending on the efficiency the Q prime will be adjusted. I am not changing the Q prime, I am only changing the Q.

Idea is that for the combined system now what is going to happen you see is that how much amount of heat is taken in now? Q prime minus Q, correct? It does W amount of work and does not throw anything. Now what is Q prime minus Q? So you can see that Q prime minus Q from here we get equal to W, which means that this is equal to this, efficiency is 1. This violates KP Statement, cannot get efficiency 1.

You see what has happened. So you can say that if my W would not be equal to Q prime minus Q, then you could say that okay, some amount of heat is going. But I am showing you here that full conversion of the heat is happening to the work if I manage a combined system in such a way that whatever amount of heat I am taking in and that much amount of heat I am throwing out, combine that with, if Clausius Statement could be violated you could have constructed that engine in such a way that we will get efficiency 1 engine.

But that is not allowed by second law of thermodynamics. So now you see that violating Kelvin-Planck Statement violates Clausius Statement, violating Clausius Statement violates Kelvin-Planck Statement. Now it again answers your question that whatever prohibits that spontaneous transfer of heat from low temperature to high temperature must be stopping it from having an efficiency 1 engine. Right? Now whatever is stopping it, we will come to know that later on, maybe few classes later. It will take some time to develop the whole thing.