Introduction to Chemical Thermodynamics and Kinetics

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Lecture - 11

Second Law – part 1

Welcome back. So, in the last part, we discussed about first law of thermodynamics we discussed about the essence of the law that it is a law of conservation of energy and we discussed about few statements like; we discussed there in a cyclic process, the work done will be equal to the heat withdrawn, which means that first law of thermodynamics discusses about only the law of conservation of energy; however, if you ask this question that suppose; if we have, nitrogen and hydrogen in a mixture to produce ammonia at equilibrium how much nitrogen? How much hydrogen and how much ammonia is present? The first law cannot answer the only answer, it can give is through mass equilibrium we know that there will be a finite amount of nitrogen hydrogen and ammonia and we know that total amount of the mixture.

However the equilibrium concentrations cannot be predicted. So, the second law actually yields or answers give gives an answer to such questions. Now to begin with we will first use the statement of the second law; the second law, was mostly developed by a French engineer Sadie Carnot and then his work was revived by many others and then put they put it in a modern form. So, what we are going to discuss is that modified form of Sadie Carnot work. So, let us first look at the statement of the second law; these statements actually come from natural experience from the work on heat engines.

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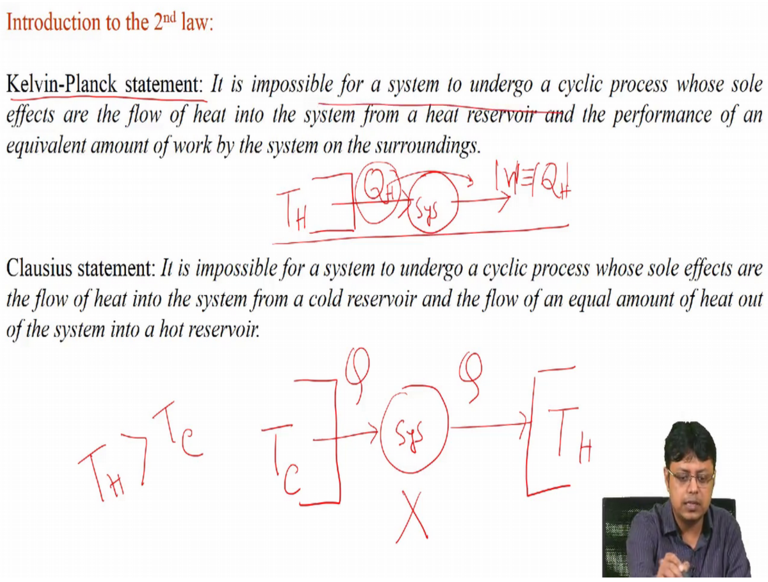

Introduction to the 2nd law:

Kelvin-Planck statement: *It is impossible for a system to undergo a cyclic process whose sole effects are the flow of heat into the system from a heat reservoir and the performance of an equivalent amount of work by the system on the surroundings.*

Clausius statement: *It is impossible for a system to undergo a cyclic process whose sole effects are the flow of heat into the system from a cold reservoir and the flow of an equal amount of heat out of the system into a hot reservoir.*

Now, there are two statements I have written here the first one is known as; kelvin Planck statement, it is based on Sadie Carnot’s work and it was a revised statement given by lord kelvin or William Thomson who is also known as William Thomson and max Planck, the statement says it is impossible for a system to undergo a cyclic process whose sole effect are the flow of heat into the system from heat reservoir and the performance of an equivalent amount of work done by the system to the surrounding. What does it mean? It means; suppose let us consider, I have heat bath at some temperature let us say I am calling this temperature as T H and then there is a engine which is our system and this system is withdrawing say some amount of heat from the surroundings which is in this case the hot path and then producing in a work in the surrounding which is equivalent to the magnitude of which is equivalent to the heat withdrawn from the surrounding, now we already discussed in the first law that for a cyclic process this is true, but the second law is saying that complete conversion of heat into work is not possible.

So, this example shows you that it does not violate first law; however, it violates second law in that here we are assuming the com complete conversion of work into heat which is not possible, now if that is not possible then how much heat or how much amount of work can be produced from a given amount of heat? That we have to work out and that is what we are going to do in today’s lecture, now another statement we often say is known as the Clausius statement how will discuss about Clausius work on particularly the irreversibility or the directionality of a process which is known as Clausius inequality sometime later, but before that we will just discuss the Clausius statement of the second law for thermodynamics and the statement says that it is impossible for a system to undergo a cyclic process whose sole effects are the flow of heat from a cold reservoir and the flow of an equivalent amount of heat out of the system into an hot reservoir.

So, Clausius statement says; that, suppose I have a cold reservoir and I have a hot reservoir, but the temperature of the hot reservoir is greater than that of the cold reservoir and if I thermally connect it to a system I connect both of them Clausius statement says; that it is impossible, that the system withdraws some amount of heat from this cold reservoir and flow the same amount of heat which will be same let me just denote it as Q to the hot reservoir, so this is not possible. So, we will see actually why if we what happens? If these laws are actually violated now there is an equivalence between the Clausius statement and kelvin Planck statement but we will not discuss it here, we will first proceed with the kelvin Planck statement and we will show in a minute that if we construct or if we hypothesize a system that violates the second law of thermodynamics then we can get a complete conversion of heat into work which is not possible.

Now before going into the details as I said that all these statements are actually realized in experiments on heat engines, let us first describe what is a heat engine?

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Carnot cycle:

Nicolas Léonard Sadi Carnot

Now, usually in chemistry we do not talk too much about heat engines, we usually talk about chemical systems where who are actually flow of energy into the system or out the system is associated with some chemical transformation, but here usually the heat engines are used in engineering community to understand the efficiencies of various types of engines; however, the concept built in discussing the heat engines will be utilized subsequently to describe the directionality or spontaneity of many chemical processes.

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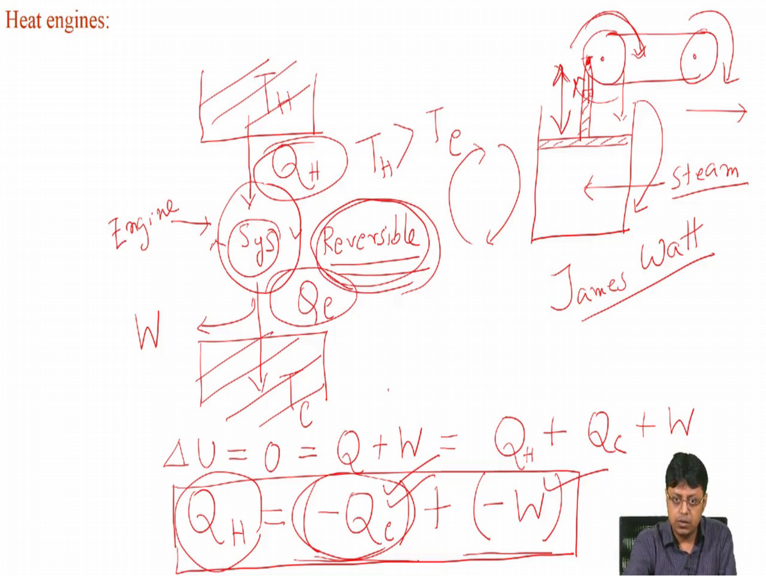
Heat engines:

Now let us understand what a heat engine is? Now, a heat engine by a heat engine we mean that there is a engine which is nothing but our system and that withdraws heat from a hot reservoir, meaning a reservoir which is at a temperature which is of course, hotter than another reservoir which we term as cold reservoir and the temperature of that we denote as T C with the condition that T H is greater than T C and in the process oh the system or the engine which is the heat engine takes the same amount of heat and it releases some amount of heat to the cold reservoir and in the process as a balance it also produces some work, now what I have drawn here is; schematically means that, if I use the first law of thermodynamics and we can actually give a formulation for this but before that let us try to understand one intra in important thing; that suppose, this system is our already familiar system which is a called ideal gas or some gas confined in a cylinder and where a piston is also act as a boundary between the system and the surrounding.

Now if the gas expands then the piston will move upward if the gas contracts then the piston will move downward, now this motion of the piston can be very cleverly connected to a axle where this motion up and down will cause a rotation of this axle and thereby you can actually get a rotational motion further which may run something; say, this may run actually a steam engine now this was actually the first design which James watt used to design his engine which was run by steam

So, the material which he used was nothing, but steam now this was again based on Sadie Carnot's work now try to understand here that if the engine if we expand the gas and if we do some work of course the wheel will rotate, but then we have to also come back because we have to keep it going otherwise there is no point of designing or devising a machine. So, what it means that? This engine or this system should work in a reversible fashion so this is very important, the reversibility of the working. Now we say that if there is a reversible process which means; actually it is a it should also work in a cyclic manner, because this system should actually come back to it is original state and again expand then contract to maintain this process and maintain the reversibility.

So, in order to maintain the reversibility we can say from the first law; that, for any reversible cycle as we know that the associated change in internal energy should be 0 and from first law; it is nothing but, related to the heat withdrawn and work done. Now look at it here actually we have two types of heat one heat is actually withdrawn from the surrounding and one heat is released to the surrounding, but there are two different surroundings here one surrounding is; the hot bath or hot reservoir and then hot surrounding is the cold bath or cold reservoir, so the system or the engine takes up the heat from the hot reservoir and releases it to the cold reservoir.

So, we can write it in this way and perform some work of course, so this Q is nothing, but a combination of Q H and Q C, now note that; usually we use a convention, that for Q H we use a positive convention because it is a heat withdrawn from the surrounding to the system and for Q C has to be a negative quantity, because it is released into the surrounding which is the cold bath here or in other words we can say it slightly differently; that the, heat withdrawn from the hot reservoir is nothing but the heat released in the cold reservoir plus the work done by the system now the negative sign here in the first term which is Q C here indicates that heat is released to the surrounding which is the cold reservoir here and the negative sign associated with the W or the work done indicates that the system performs work, because we took a convention that if the work is done on the system that is a positive work and if the work is done by the system that is a negative work.

So, in some sense the total amount of heat is partitioned into some amount of heat and some amount of work, that is the essence of second law. What we just said in the previous slide a statement that complete conversion of heat into work is not possible, I cannot take Q H and completely convert it into a work which is equivalent to Q H, always whenever I am withdrawing some heat some amount of heat will be always lost which is Q C and then the rest will be produced rest will be utilized to produce work; which means, if we can make the Q C to be 0 then we can approach the limit which is Q H is equivalent to the negative of work done negative in the sense that it is work done by the system but that is not possible, we will always have some finite amount of Q C and that will reduce the efficiency of the heat engine. Now how will you calculate the efficiency? Keeping in mind that, this efficiency of the system or the heat engine has to be in such a way that the system or the engine runs in a cyclic fashion and in a reversible cyclic fashion.

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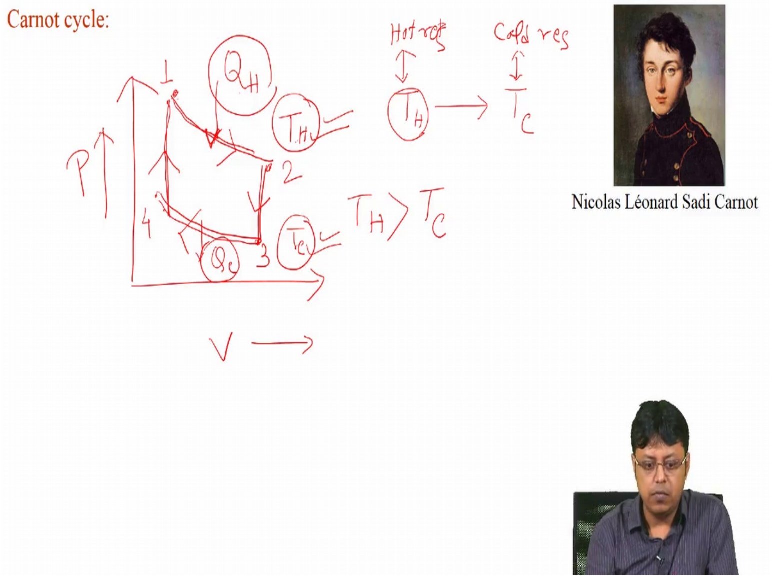

Carnot cycle:

Nicolas Léonard Sadi Carnot

Now the first answer to this problem was given by French engineer as we already told Sadie Carnot and then Carnot proposed a hypothesized mechanical cycle, by who which one can withdraw heat from a hot body and release it to a cold body and simultaneously perform some work using a system. So, we will first try to understand it in our already familiar pressure volume diagram, because that will tell us how much work has been done or has been performed in a cyclic process where the cycle is initiated by something like; withdrawal of the heat, now suppose the we have some change in state of the system say from state 1 to state 2 and in this process the heat is first withdrawn, now this is an arbitrary line which I have drawn going from arbitrary path.

Because remember that the amount of heat withdrawn will be dependent on the path, because heat is a form of energy and it is a path function. Now think about it like if we have to withdraw heat from a source and then if this process going from 1 to 2 is not an isothermal process meaning that is the temperature of the system actually gets increased in the process, then the we can say that this transformation or the transfer of the heat from the outside must be irreversible, because if it is happening at a increase in the temperature then such flow of heat has to be irreversible, in order to maintain reversibility because we have to maintain it remember because the system has to be restored in it is original condition, then we assure one thing that this path has to be an isotherm so this cannot be an wavy line that as we have drawn here the first part has to be some isotherm, where the system actually withdraws heat from the surrounding which is the hot reservoir keeping at the same temperature of the surrounding or the hot reservoir.

Similarly by the same token when the system releases it remember it will release it to a cold reservoir and which is at a temperature T C and since T H is greater than T C, then we can say that; by the same token, the system must be brought in contact with the resolver, but before that the systems temperature has to be equal to the cold reservoirs temperature, so means these two are 2 isotherms has to be in the steps at which the system is withdrawing heat from the hot reservoir or the system is releasing heat to the cold reservoir, now since T H and T C are different these two of course, these two isotherms are different isotherms and I have drawn the isotherm for releasing the heat Q C to the colder body at a position which is lower than that earlier isotherm the reason is T H is less than T C.

Now this is basically a reverse process, but we have to connect it remember in the first process we said the system is withdrawing heat from the reservoir keeping at a temperature T H it is an isothermal process, then we said that there is another process what the system is releasing the heat Q C to the cold reservoir keeping at a temperature T C, now in order to achieve these two things in between the system must make a transition where the temperature of the system goes from T H to T C.

So, what i said is that earlier the system was in thermal equilibrium with the hot reservoir and then we have to cool down the system, so that it comes in thermal equilibrium with the cold reservoir, so that we can do some isothermal expansion in this case and then again an isothermal compression. So, we need actually two adiabats to connect these two isotherms and the real meaning here is that; the adiabats, are required to change the temperature of the system from T H to T C and then from T H, T C to T H. So, we have considered a cyclic process in this case. Now this is the actual formalism which Carnot came up with now let us try to understand how much work is done for each step of the process so that we can calculate the total work done in the process?

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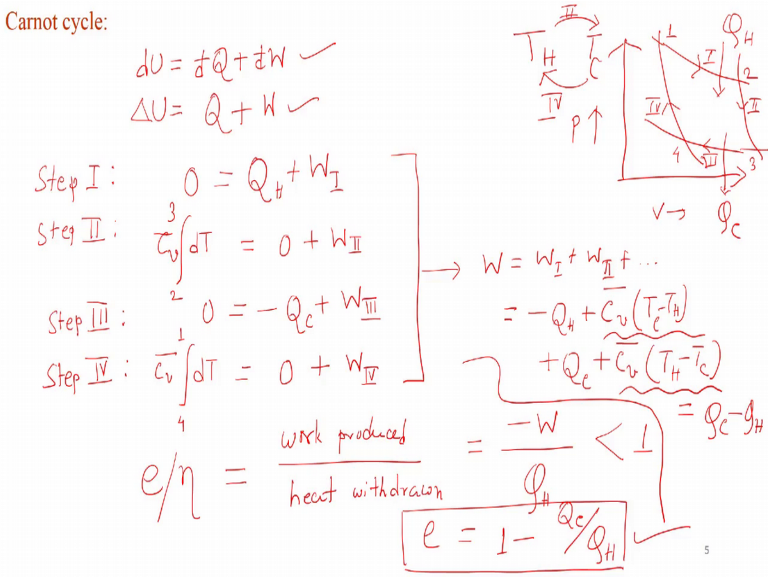

Carnot cycle:

$dU = \text{đ}Q + \text{đ}W$ ✓

$\Delta U = Q + W$ ✓

Step I: $0 = Q_H + W_{I}$

Step II: $C_v \int_2^3 dT = 0 + W_{II}$

Step III: $0 = -Q_c + W_{III}$

Step IV: $C_v \int_4^1 dT = 0 + W_{IV}$

$$\longrightarrow W = W_I + W_{II} + \dots$$
$$= -Q_H + C_v(T_c - T_H) + Q_c + C_v(T_H - T_c)$$
$$= Q_c - Q_H$$

$$e/\eta = \frac{\text{work produced}}{\text{heat withdrawn}} = \frac{-W}{Q_H} < 1$$

$$\boxed{e = 1 - Q_c/Q_H}$$ ✓

Now, let us also designate that we will call this as step one this as step 2 this as step 3 and this as step 4 and we can just quickly redraw it once again, so that we can always refer. So, this is basically the Carnot known as Carnot cycle, so it is going from state 1 to 2 by isothermal expansion; then 2 to 3 by adiabatic expansion, then 3 to 4 by isothermal compression, then 4 to 1 again by adiabatic compression. Now; this is step 1, this is step 2, this is step 3 and this is step 4 and this cycle is continued and the system or the heat engine continuously take for 8 in each cycle Q H amount of heat and releases Q C amount of heat.

So, let us now try to understand what is the work done in this entire process, now for that we will use the first law of thermodynamics which tells that d U is nothing, but d cross Q plus d cross W or we can actually use the finite change relationship because this is for the differential change, but since one when the system is going from state 1 to state 2 it is a finite change, so we will better write it as delta U is Q plus W, now in the step 1: what it does? think about it is an isothermal expansion.

So, in the isothermal process see it is internal energy is a function of temperature only delta u for step one will be 0. So, from first law the left hand side of this equation is 0 is equal to the heat associated in this case is nothing, but Q H and associated work I am writing at writing as W suffix 1, similarly in step 2: we have an adiabatic compression, now for adiabatic compression we have there is no heat change because it is an adiabatic and then instead of delta U if it is an ideal gas we could write it as C v d T between the states 2 to 3, if it is an one mole ideal gas we can actually write it as C b bar d T assuming that C v does not depend on the range of that temperature over which the transformation was made and then there was a term del U del v T d v, but we already said that term is 0 for ideal gas.

So, that should be equal to 0 because Q H is 0 for an adiabatic process plus W 2, similarly for step 3: remember that again there is an isotherm, but now heat is released Q C amount of heat is released so I have to use a negative sign plus W 3 and then again in step 4: there is another adiabat and remember that in this case I am going from state 4 to state 1 d T and which is nothing but 0 because it is an adiabatic process, so associated heat exchange is 0 so W 4. So, the total W can be obtained by adding all the W's and let us see what is the total work done? So, it is basically W 1 plus W 2 and so on.

So, the first equation gives us in the first process it is minus Q H, the second equation gives us it is C v and integral of d T between the limits 2 and 3, let us suppose that the; what happened between 2 and 3? Think about it. Initially the system was actually at a temperature T H, so the initial temperature of the system was T H and the final temperature of the system was T C during the process 2 this has happened. So, this will be nothing, but C v T c minus T H and then for the third process again will have; plus Q

C and again in the fourth process will have; C p T H minus T C because here the final temperature is again T H for the fourth process these are the two adiabats and the initial temperature is T C.

So, we will use the molar quantity, so we are using C b bar notation. Now let us try to understand. So, what is this total energy that we total work done that we got? Now the efficiency of an heat engine is defined in the following way which is denoted as sometimes e or some textbook write it as eta, which is denoted as how much work is produced in the process and how much heat has been withdrawn in the process, now remember the work produced in this case; I will write it as, minus W because it is work produced by the system and the heat withdrawn in this case; is Q H, because it withdrew the heat only in the first step. So, in the according to the second law this efficiency cannot be equal to 1 because if it is equal to 1 then the magnitude of Q H will be equivalent to magnitude of W which is not possible, complete conversion of heat into work is not possible.

So, this efficiency should be always less than 1, now let us try to calculate what was the efficiency that we just got by this in Carnot cycle, so we already see here that these two quantities cancel with each other because they just have opposite sign, so ultimately we get something very interesting which is Q C minus Q H and then if we just plug in into this equation we will get that it is Q C minus Q H, but with a negative sign, so it will be Q H minus Q C and that is the expression for minus W. So, ultimately we will get the efficiency to be equivalent to Q C by Q H, now this is the expression for efficiency of a Carnot engine, if the engine was or the material of the engine active material of the engine was an ideal gas now think about it; that if we had Q C close to 0, meaning if we had a absolute 0 sink or heat sink where actually I am dumping the heat then the efficiency goes close to 1 or we could have met the Q H the heat source to have infinite having infinite temperature there also we will see that we can get the efficiency to be closer to 1.

So, right now we have written it in terms of the heat withdrawn, but we will write it in terms of also the temperature of the cold and the hot reservoir, let us see how we can get to that expression.

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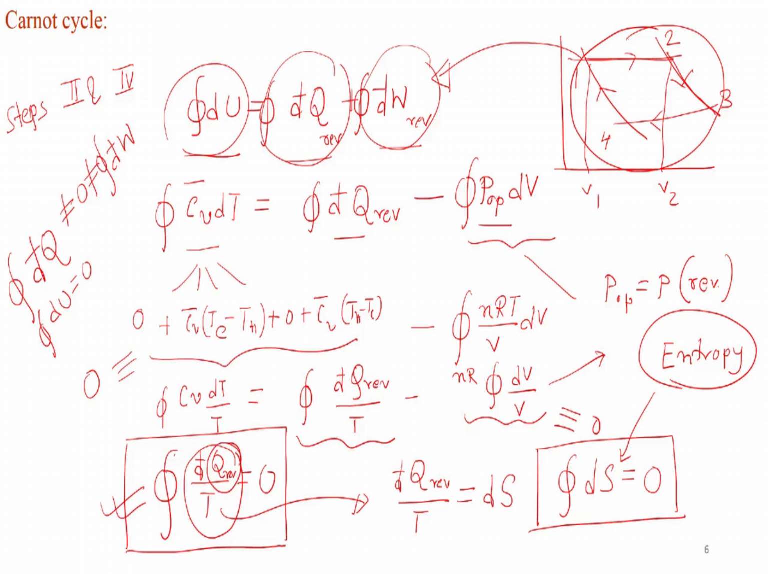

Carnot cycle:

Steps II & IV

$\oint dU = \oint đQ_{rev} + \oint đW_{rev}$

$\oint \bar{C}_v dT = \oint đQ_{rev} - \oint P_{op} dV$

$0 + \bar{C}_v(T_c - T_H) + 0 + \bar{C}_v(T_H - T_c) \quad - \oint \frac{nRT}{V} dV$

$P_{op} = P$ (rev.)

$0 \equiv \oint C_v \frac{dT}{T} = \oint \frac{đQ_{rev}}{T} - nR \oint \frac{dV}{V} \equiv 0$

$\oint \frac{đQ_{rev}}{T} = 0$

$\frac{đQ_{rev}}{T} = dS$

$\oint dS = 0$

Entropy

$\oint đQ \neq 0 \neq \oint đW$

$\oint dU = 0$

So what we just said is that; let us just focus on the step 2 and step 4 which are basically the adiabats, which are these two steps where we are going from 2 to 3 and 4 to 1, now think about it; in this case, what was the total cyclic? This is a cyclic process of course, the entire process, will mostly to get to that relationship between heat withdrawn and the temperature at which it is withdrawn we need to again consider the cyclic process, now for every cycle let us write it in this way that; I have for in the cyclic process d Q is d cross Q plus d cross W which follows from the first law, now I will just write a suffix reversible here in order to denote that it is for a reversible process and usually for a reversible process all the d Q's should add up to 0 that is well known.

Now, let us try to a for a reversible cyclic process by the way, but in this case actually reversible isothermal process it will be 0 not for any cyclic process, but in this case we will show that this term also will go to 0, now before going to that what is d U is nothing, but the C v d T and d cross Q reversible we are just keeping it as such and then I have the reversible work done that minus it is P opposing d V. Now each of this term it is basically what the way we have drawn it here, we have drawn the cycle this is the Carnot cycle and we have written an expression for the entire cycle itself, but the cycle has actually four parts now a cycle means there was a cycle for d U there is a cycle for d cross Q reversible there is a cycle for d cross W reversible that is what we have written here; however, remember each of this term actually is can be split into four terms because there are four steps.

Now for example: in the first case C v d T was 0 because it was isothermal and then we had some C v d T which is basically C v T the final temperature was T C minus T H then again it was 0 for the third step and in the fourth step it was C v T H minus T C which basically cancelled out and then let us just focus on these term; which says, that P opposing d V now usually not usually easier for any isothermal process or any adiabatic process also since it they are both reversible the P opposing can be set to be equal to the pressure of the system because actually these are all reversible, remember that this path is a reversible isothermal path and this path is a reversible adiabatic path. So, we can write it as minus P d V and using the formula we can just write for the ideal gas it is n R T by V d V, now we can divide both side by T to get a equation something like; integral C v d T by T is equal to cyclic integral of d cross Q reversible by T minus n R cyclic integral of d V by V.

Now what is the value of this? In the first case; you will have some pressure volume work and first step 1, so that will be minus n R l n say V 2 by V 1 where V 2 is this volume and V 1 is this volume and then you can actually work out for each step; however; you will figure out, that they all cancel each other why because it is a cyclic process since it is a cyclic process you can easily figure out that this term also goes to 0 and we already told that this term also goes to 0. So, what we get is? This term also should be 0, d Q reversible by T over a closed cycle path, now we have a very interesting situation here we see that d cross Q is not an exact differential, so for any cyclic process we already discussed that d cross Q is not 0 when we discussed about the first law and then we said similarly d cross W was also not 0 and then we added them and define that found out that their addition is 0 and from there who we got a quantity which is d U cyclic integral of that was 0 that is why it you called it as an exact differential.

Here we are getting similar situation we see that d cross Q divided by T I should maintain this notation because d reversible divided by T is 0. So, for any cyclic path which means; all the, d cross Q is not a state function, d cross Q reversible by T is a state function and that we are denoting as d S, so we can write it in a compact from that cyclic integral of d S is equal to 0 where S is known as entropy of the system, now again entropy of the system does not have any meaning, we only talk about change in entropy of the system this is the differential change and we are talking about a cyclic path.

So, we see that entropy is a state function and entropy is defined as the reversible exchanged divided by the temperature at which it was changed.

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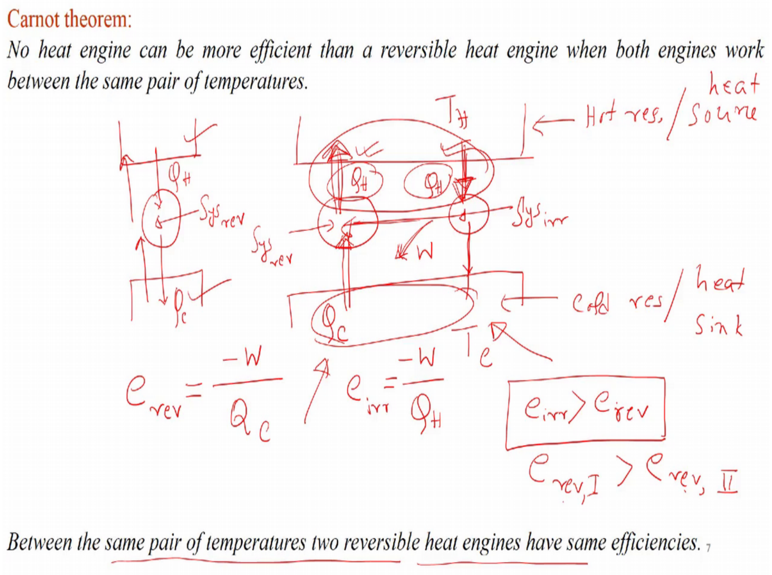

Carnot theorem:

No heat engine can be more efficient than a reversible heat engine when both engines work between the same pair of temperatures.

Between the same pair of temperatures two reversible heat engines have same efficiencies.

Now, we will proceed with the entropy in a while, but before that will first discuss something known as Carnot theorem. Now this is again based on a conceptual understanding how a heat engine works? Now the theorems tale tells you that no heat engine can be efficient than a reversible heat engine.

So, our reversible heat engines are maximal efficient engines, now why how to understand this process? Let us consider as before that there is a reversible engine, which we denote as say some system or engine which is reversible and it is withdrawing heat from the cold reservoir and it is performing some work and also it releases the heat which is say Q C to the cold reservoir, so this withdrawing heat from the hot reservoir and releasing heat to the cold reservoir, now since it is a reversible engine which what it means is that? It can also work in a reverse direction; now let us hypothesize a situation that we have a source or heat sink at temperature T H heat source sorry and a heat sink which is at temperature T C, so this is nothing, but a hot reservoir and this is nothing, but a cold reservoir or sometimes we call it as a source or heat source and this we call it as heat sink.

Let us have our irreversible engine which is withdrawing heat from this hot reservoir and transferring the heat to the cold reservoir and let us couple to it our reversible heat engine which actually is now working in a reverse direction, since it is reversible we can always reverse it direction. Now suppose the amount of heat which this reversible engine is dumping to the hot reservoir is the same amount which does other engine is withdrawing from the hot reservoir and we also couple these two reservoir, now the efficiency for the reversible engine will be nothing but 1 minus if we write it in terms of the temperature of that we are ready to prove that relationship, we can write it as temperature of the cold body minus temperature of the hot body similarly for the efficiency of the other engine for any engine actually we should in this way, now we it is not necessary this at this point so we can also bypass this relation.

So, we can write efficiency of our reversible engine with the original a definition that it is the work done divided by the heat withdrawn in this case the heat withdrawn is Q H, it will be not Q H it will be some other Q which is say Q C and then for the irreversible engine it will be the work done divided by the heat withdrawn, but the heat withdrawn in this case is Q H and since we know that we have said remember that these 2 Q H's are same meaning the heat withdrawn by the irreversible engine is similar to the heat dumped by the reversible engine and since Q C or the irreversible engine efficiency like if we assume that it is more than the reversible engine efficiency we can easily get a feeling that Q H should be greater than Q C.

Now, what does it mean? That means, it is actually taking the net effect of this composite system is that as if it is withdrawing some heat from the cold reservoir and then the second engine does some work part of it is transferred to the first engine because it has to balance this Q C and Q H because Q H is greater than Q C, so part of this work is converted to balance to add up with this Q C to give Q H which is being transferred to the hot reservoir and again from the hot reservoir this engine is taking up Q H heat. So, from the hot reservoir we see that there is nothing withdrawn or gained because the heat deposited at by the reversible engine is the heat which is withdrawn by the irreversible engine. So, everything is happening with respect to the cold reservoir and what we see here is that the net effect is withdrawing the heat somehow from the cold reservoir and performing some work, so which violates the kelvin Planck statement.

So, this cannot be possible which we conjectured or the reversible engine cannot be less efficient than the irreversible engine now you can similarly argue that if I had two reversible engines and you can similarly show that if I have a reversible engine 1; which is more efficient that than the reversible engine 2 you can make an analogy, but then one can easily switch this in the position you can put the irreversible reversible engine 1 here and 2 here and then you can get another relation which is basically irreversible 2 is greater than a irreversible 1; which means, these are contradictory statement and this leads to the another way of looking at the Carnot theorem, that between two same temperatures a reversible engine must be more efficient than an irreversible engine.

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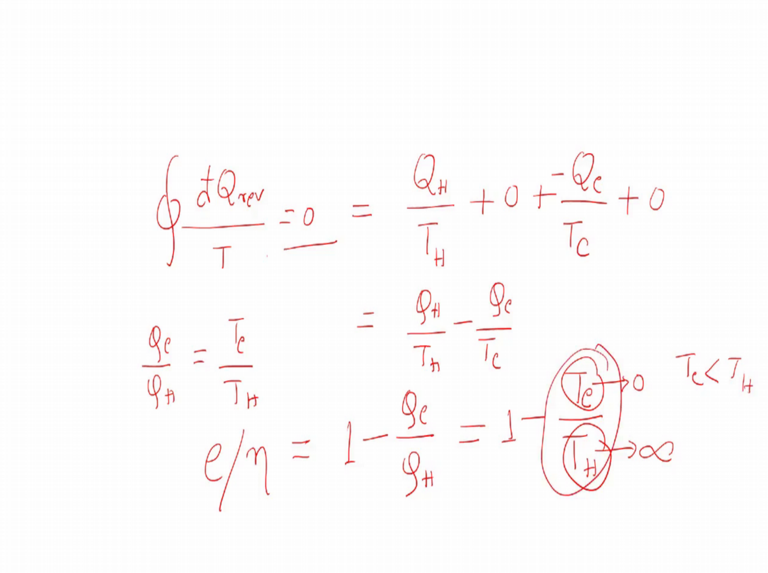

$$\oint \frac{\text{đ}Q_{rev}}{T} = 0 = \frac{Q_H}{T_H} + 0 + \frac{-Q_C}{T_C} + 0$$

$$= \frac{Q_H}{T_H} - \frac{Q_C}{T_C}$$

$$\frac{Q_C}{Q_H} = \frac{T_C}{T_H}$$

$$e/\eta = 1 - \frac{Q_C}{Q_H} = 1 - \frac{T_C \rightarrow 0}{T_H \rightarrow \infty} \qquad T_C < T_H$$

So, before we conclude we will just quickly discuss one particular relation. So, we had already discussed that cyclic integral of d cross Q reversible by T is 0 now from the Carnot cycle we know that for the first step what is the value of this; for the first step it is Q H drawn at a temperature T H, in the second step it was adiabat no heat was drawn withdrawn and then in the third step again it was minus Q C because the heat was released at a temperature T C and in the fourth step it was again 0. So, overall what we are getting is; Q H by T H minus Q C by T C and then since the entire thing is equal to 0 we can write; Q C by Q H is nothing, but T C by T H. So, the equation for efficiency e or eta we could write 1 minus Q C by Q H which is equivalent to writing 1 minus T C by T H.

Now you can see that if T C approaches close to 0 the efficiency goes close to 1 or if T H approaches close to infinity then also the efficiency goes to 1; however, for finite cases since T C is less than T H will have some fractional value for this and the efficiency will be always less than 1.