Thermodynamics And Kinetics of Materials

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Lecture 7

Clausius inequality and entropy of transformation

Okay, so as you have seen in the previous lectures I deduced the second law in the previous lecture in two second law of thermodynamics and I told also that entropy is a, we introduced the concept of entropy and we told entropy is a state function and for that to prove that entropy is a state function we used the Carnot cycle right, we used the Carnot cycle where we have this isothermal which is a cyclic process and we told that for this cyclic process there is a quantity called delta Q is aversal by T which is nothing but equals to cyclic BS so this is a cyclic integral over the entire cyclic process which is equal to C right. So we have shown that this BS indeed is equal to 0 for a cyclic process so what that meant is basically that if you have some sort of a, if you have a cyclic process, any cyclic process say and you start at point I and then you are moving around and you go to say some point F and then again you go to I so what we are telling is if I start my initial state is I and my final state is also I then my delta S since S is a state function should depend on S it should be S is equal to Si minus Si which is equal to 0 right, this is what we have proved by using a Carnot cycle right and right so this is the, this is exactly that is what I have shown here so if you see this is delta Q reversible by T and this is integral BS again cyclic integral BS which is equal to C. So, this proved effectively that this delta Q reversible by T is a state function and the right or Q reversible by T is represents a state function and that state function is entropy and like internal energy since it is a state function for any cyclic process where my initial state and final state are the same the change in state function becomes 0. Now this we have proved for the Carnot cycle but we have considered if you remember an ideal gas but it does not matter whether I am using an ideal gas or any other substance whether it is an ideal gas or a real gas or for any other substance the cyclic integral of entropy of the differential changes in entropy the cyclic integral over this differential changes in entropy will always come out to be 0 right entropy remains a state function whatever be the substance that we are using right it is exactly as much of a state function as energy right. So however very interestingly what we also told that we talked about reversibility and irreversibility right as you remember second law is a basically gives you the definition of irreversibility gives you the definition of directionality of a process right of a natural process right and it also tells you how the entropy will change right the entropy being a property of the universe how will it change right it will always move in a particular direction irrespective of whatever process offers right so that is what we have understood so far. Now another thing if you have this Carnot cycle or heat engine that is a reversible heat engine by the way and if you look at that you can basically define efficiency to be what say for example you have a hot source from which heat is input to the engine and then there is a cold sink where some waste heat is collected and you are producing work from the engine right the work

performed by the engine so if I take the work performed by the heat absorbed by the engine as definition of efficiency then we can write efficiency equals to mod of w by 2h mod of w by because we have used a we generally use this convention means at least in this course we are using this convention that work done on the system is positive work done by the system okay but here the engine is a system is negative right so we are taking work performed the modulus of it right so whether it is negative or positive does not really matter so the modulus of work performed by the engine divided by the heat absorbed right from the hot source is what is going to define the efficiency.

CARNOT CYCLE

$$\oint dS = \frac{q_H}{T_H} + \frac{q_c}{T_c} = -\frac{q_c}{T_c} + \frac{q_c}{T_c} = 0$$

$$\frac{q_H}{q_c} = -\frac{T_H}{T_c} \Rightarrow \frac{q_H}{T_H} = -\frac{q_c}{T_c}$$

$$\oint \frac{\delta q_{rev}}{T} = \oint dS = 0$$

$$\Delta S = S_f - S_i$$

$$= 0$$

Define efficiency of a heat engine

$$\epsilon = \frac{\text{Work performed}}{\text{heat absorbed}} = \frac{|w|}{q_H}$$

$$\epsilon = \frac{|w|}{q_H}$$

Hot Source T_H

q_H

E $\rightarrow$ $|w|$ Work done by the engine

q_c

Cold Sink T_c

q_H – Heat absorbed

$|w|$ – Work done by the system

$$\frac{q_c}{q_H} = -\frac{T_c}{T_H}$$

$$\epsilon = \frac{q_H + q_c}{q_H} = 1 + \frac{q_c}{q_H} = 1 - \frac{T_c}{T_H} = \frac{T_H - T_c}{T_H}$$

All reversible engines have Same efficiency regardless of material used

When $T_c = 0\,K$, then $\epsilon = 1$

$$\epsilon = \frac{T_H - T_c}{T_H} < 1$$

Now if you see that if I use this definition of efficiency this definition of efficiency let us further understand what does this mean so if you look at this diagram you have this hot source where the temperature is TH and you have this cold sink the temperature is TC and you have the engine here right okay in this engine some cyclic process is being performed right so you have like isothermal compression then you have some adiabatic expansion the isothermal expansion adiabatic expansion followed by isothermal compression and then adiabatic compression okay so for example such as high so in such a case this is your engine right this is your engine and you have the hot source and the cold sink and you see so remember there is one reservoir here one reservoir here the reservoir that high temperature is from where the heat is being transferred to the engine so heat input from the hot source and heat rejected to the cold sink and there is also this work that is produced by the engine that is mod of W or work done by the engine. Now you can easily see that if that is so and also we know this relation that we have obtained for common fusion that is Q_C by Q_H okay that is the heat rejected by heat absorbed equals to minus T_C by T_H now epsilon is as you see mod of W which is nothing but Q_H minus Q_C because Q_H is plus right this heat input heat input is positive heat rejected by the system is negative so it is basically Q_H minus Q_C by Q_H right but we are using we are retaining a plus sign here that is not a problem because Q_C by itself is negative Q_H by itself is positive so it is like 1 plus Q_C by QH which is the same as 1 minus T_C by T_H right 1 minus T_C by T_H where T_C is the temperature of the cold the temperature of the cold sink and TH is the temperature of the hot source. Now as you can see here the efficiency depends on the temperature of the source and the sink right which is basically given by this for the expand to write it as T_H minus T_C by T_H you can immediately see that it is not the efficiency of the heat engine of this heat engine that we are talking about does not depend on the

substance that is used in the engine right does not depend on the nature of the gas that is used in the engine right it only depends on the temperature of the hot source and temperature of the cold sink. Now that one very important thing I want to tell as a corollary is that all reversible engines will have the same efficiency regardless of the material used regardless of the material used it will have the same efficiency another very interesting thing here you can see if I put T_C equal to 0 kelvin then my efficiency goes to 1 efficiency becomes 1 when T_C is 0 kelvin right you cannot have efficiency more than 1 right so when T_C is 0 kelvin you can immediately see here right that if T_C is say immediately see here that if T_C is equal to 0 then this is T_H minus 0 by T_H which is T_H by T_H is equal to 1 right in other cases when T_C is not 0 kelvin you will always have efficiency which is less than 1 right ah ok.
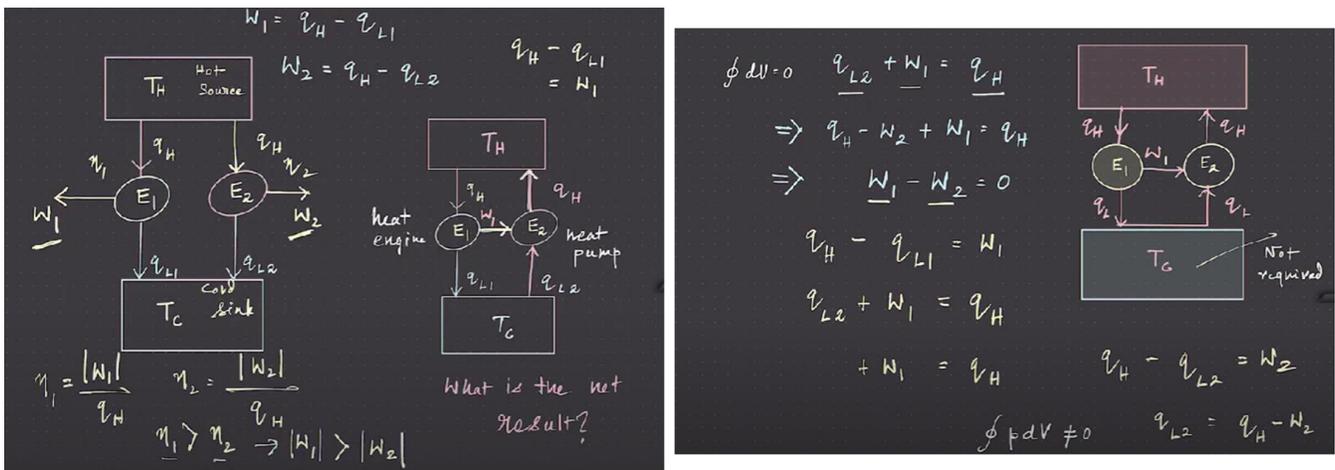
 Now think of this what we told is all reversible engines for operating at the same temperature means operating at the same temperatures of the cold hot source means for a given temperature of hot source and for a given temperature of the cold sink ok all reversible engines that have the same hot source temperature and cold sink temperature should have the same efficiency regardless of the material used right. So for example think of this as this particular configuration you have TH and you have this TL or PC is the cold sink temperature and T_H is the hot source temperature so in this case let us call it PC instead of T_L let us call it P_C I am using P_C as the cold sink temperature ok. Now you see I have just hypothetically thought that once we have thought that there are 2 engines here one is E_1 another is E_2 and we have also assumed that E_1 is more efficient let us suppose that E_1 is more efficient than E_2 now if it is so, so if say let us suppose that the efficiency of E_1 is eta 1 which is mod of W_1 by Q_H and eta 2 which is the efficiency of E_2 and that efficiency is slightly less than that of eta 1 means slightly or some way less right it is less so what we are talking about is eta 1 is greater than eta 2 right so we are talking about eta 1 is greater than eta 2 and what is eta 1? Eta 1 is so it is extracting a work W1 so it is extracting the E_1 is extracting a work W_1 so mod of W_1 by Q_H is basically eta 1 and eta 2 is mod of W_2 by Q_H now if eta 1 is greater than eta 2 obviously mod of W_1 is greater than mod of eta W_2 now if you look at this what you are talking about if you look at it more precisely you are actually absorbing heat QH from the hot source then you are transferring some Q_{L1} is rejected to the cold sink now this QL1 so but from the cold sink now there is a Q_{L2} that is coming so what I have done is instead of using two separate things I have made one of these a heat pump so E_1 is acting like a heat pump to E_2 so what is

happening from so if you look at E1 so E1 so E2 is your heat pump so if you look at this here E2 is your heat pump and E1 is your heat engine in this case I have just reversed the process in E2 so it becomes a heat pump and this is your heat engine now what is happening the work produced by heat engine E1 is now directly taken to E2 so work is done on E2 now and there is also QL2 that is entering from the cold sink now cold sink has now become a source for E2 and you are basically now rejecting a heat QH alright or you are producing a heat QH to the hot preserver which is maintained at QH now you can see here QH comes in and there is a W1 done and this W1 is overcome by E1 and it rejects QL1 and say and now from the cold sink QL2 is coming into E2 right because E2 is now acting as a heat pump and it is taking also W1 and then it is producing this heat QH which is coming to hot reservoir now if that is the condition then there is one very interesting thing that comes in because see W1 we told is the work done by E1 right and by E2 it is W2 now if I now just look at the balance you have if you look at this QL2 is coming in right so QL2 is coming in and then QL2 and W1 produces QH right so QL2 plus W1 is QH right now this implies what this implies QH minus W2 plus W1 equal to QH why is that so why is QL2 QH minus W2 because if you look at this QH if I look at E2 as a heat engine then QH is the heat input right QH is the heat input and W2 is the work done and then QL2 is the heat rejected.

So QL2 is QH minus W2 right QH minus W2 is QL2 that is what I have substituted here and you have also this W1 and you have again here QH so basically what it tells is W1 minus W2 is equal to 0 so definitely W1 has to be equal to W2 right because as you can see here so W1 equal to W2 remember this is a cyclic process so even here please try to understand this is very very important to understand that for any state function for any cyclic process the du is also going to be 0 right however can you tell means whether this is something that you have to think about so you have a cyclic process and you have PdV is this equal to 0 you will see that it is not equal to 0 you look at the Carnot cycle for example you look at the isobaric isothermal isobaric isotropic process cycle for example that we looked at in the second class you will always see that the cyclic integral of PdV is not equal to 0 but however because see p is a state function v is also a state function right but it is a integral PdV right so this need not be equal to 0 right and in general it is the area under the PV curve right so if it is area under the PV curve you have often seen even for Carnot cycle and all that it is not really equal to 0 so please have a look at it and think about it now but you can see that now in this case W1 and W2 cannot be different they should be equal now in such a case what if W if it is so now you see there is a very important

violation that is occurring when the efficiencies are different see from pH it is coming in to E1 E1 is producing what W1 and then there is this QL and this QL is directly entering the engine E2 and there is W1 and it gives you pH so you don't require if the cold reservoir is no longer required not required the cold reservoir the cold sink is not required in this process now if that is so the entire heat is basically getting converted to what that's what it basically boils down to in some sense and if you do not have a reservoir means you should have Kelvin's technique was that you should have a hot source you should have a cold sink and there should be some heat rejected to the cold sink right if there is some work done by the by a heating right so that means that you cannot really have in the case in this case the statement is not valid so that means all reversible heat engines that means for example you want and we do they should have the same efficiency regardless of the materials so this is something that becomes very very important another thing that we told that see it is independent of the substance used why because efficiency ultimately depends on TH and TC right this is the hot source temperatures and cold sink temperatures so this is something that you should so efficiency as I told you is a function of TH and TC right now remember that if you fix TC if you want to increase efficiency by fixing a TC which is not really this if you take fix TC to 0 Kelvin then you get epsilon equal to 1 that is one thing and second thing if you fix TC to some other temperature you have you want to if you want to increase the efficiency of the engine you want to make TH as large as possible right now so again as I told you that note that when we proved that this del Q ref by T that is delta Q reversible by normalized by temperature or which is definition of dS equal to 0 for a cyclic process we have used an ideal gas right we have used an ideal gas so but again from the definition of efficiency and for any cyclic process specifically by the way if you look at this you will see that any cyclic any arbitrary cyclic process can be presented can be basically presented the series of Carnot cycles right.

Image 1 (left board):

First law

$$dU = \delta q - p\,dV \quad - \text{①}$$

$$\oint dU = 0$$

But $\oint P\,dV \neq 0$

(Check P-V diagram of the Carnot cycle, for example)

$$\therefore \oint \delta q \neq 0$$

Divide ① by T

$$\oint \delta q \rightarrow \text{path depend}$$

$$\oint \frac{\delta q}{T} \rightarrow \text{path independ.}$$

Image 2 (right board):

$$\oint C_v\,d[\ln T] = 0$$

Also, $\oint R\,d\ln V = 0$

$$\therefore \oint \frac{\delta q_{rev}}{T} = 0 = \oint dS$$

Question

Show that $\oint \frac{\delta q_{rev}}{P}$ is not a

path - independent function

So this is something that you can do by yourself but I will have some more elegant proofs soon that I will show where we can basically look at whether it is ideal gas whether it is any other substance the idea of state function does not change that is something that I will show in the next few slides so as you can see here in the next so if you go to this next idea that I want to show here so if you start with first law as you have seen in first law is a law of conservation of energy that dU equals to Q minus dT now this Q basically again we can think that it is reversible Q so but we will tell it like delta Q minus dT this is delta Q and delta because it is a path function delta Q by itself is path function but delta Q by T is a

state function remember so integral delta Q depends on the path of the process the path that is taken in the process however integral delta Q by T does not depend the path but it depends on the initial state and the final state note that right this is path dependent but this becomes path independent it only depends on the initial and the final states now as I told you that U is a state function so cyclic integral of dU is equal to 0 right this is correct this is correct however PdV is a which is P is here one state function V is one state function but integral of PdV is not equal to 0 right if you look at the thermal cycle also this is a curve here also say for example you have a say for example this process where you start with pressure of say P1 and at this constant pressure P1 so this is an isobaric process you have a have an expansion right you have an expansion in volume for this P1 so it goes to P0 and then you have an isochoric process where I just increase the pressure and then I go to again we maintain the pressure P2 and I compress it to the state 4 and then again I come back to again I have an isobaric process by which my pressure is reduced to PdV right so this entire process if you see immediately you can understand from this process that I have drawn in the PV curve that this process definitely Pdv is not going to be equal to 0 right it is not going to be equal to 0 so here or even if you can check that Carnot cycle that I have drawn so you can easily understand that this integral PdV is not going to be 0 again integral delta Q cyclic integral delta Q is also not equal to 0 because it is a path function now what I am doing is I have this equation v equals to delta Q minus PdV I divided it by P so what I get is dU by T because delta Q by T minus P by T dU okay now again I use for one mole of gas I use the ideal gas law so I have du by T minus delta Q by T equals to because this is P by T P by T is nothing but so here you can see here P by T equals to R by v where R is constant so because R by V dV now integral delta du by T is going to be equal to 0 okay this is something that even proved right.

So du is going to be 0 and normalized by T also integral du by P also is going to be 0 right so that has to be 0 because the cyclic integral of du itself is 0 cyclic integral of du by T is also going to be 0 you can actually show this if you look at this if you just consider any cycle you can see the change in u and you can normalize with T and you can see the cyclic integral that comes out to be 0 and another thing why it is 0 that it is 0 definitely for an ideal gas right because u for an ideal gas is only a function of temperature then I can write du equals to C_v dV right du so why is this 0 for an ideal gas at least for an ideal gas I can immediately show you this is because du equals to C_v dV right and because U is only a

function of T it is not a function of V right U dU del V for an ideal gas goes to 0 right so now if I have that so I have du by P which is Cv dT so this is basically integral so integral dU by T is nothing but integral C_v dT by T this I can write as C_v dl and T right so dl and T right and this l and T so you can think of this as some state function of y so you can see C_v dU_y and this Cv dl and T is definitely going to be 0 right for the cyclic process so because for the cyclic process you are starting with the state I and you are coming back to the state I and you are only looking at the at state I what is the change so you will basically see that Cv dl and T in this case is going to be equal to 0 similarly r dl and v right r by v dv I can write this as integral of r dl and v which is equal to 0 so as a result delta Q reversible by T has to be equal to 0 is basically the cyclic integral of ds now if I can ask you this question please try to solve this this is I think that that will be interesting because you can by yourself realize that delta Q rev by T reversible by T although that is a state function the cyclic integral goes to 0 delta Q reversible by P on the other hand is not a path in the common function T is definitely a path dependent function so two things have to be understood one is the integral Pd cyclic integral Pd v does not go to 0 another thing I have here delta Q rev by T which comes down to be 0 here but delta Q rev by P the cyclic integral is not going to be 0 right so that means it is not a path independent function so if I look at other substance right when we want to say that okay when we want to prove that okay if it is true for ideal gas it has to be also true for other substance and we have tried to tell that we showed that definitely from the definition of efficiency you can immediately understand that since efficiency depends only on the hot source and the cold sink in general you can immediately understand that it really does not depend on the substance.
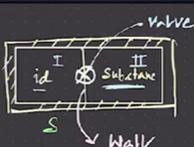
So that's a real gas or an ideal gas the cyclic integral remains 0 but you can also prove that how when you want to prove that you take a system which is isolated means it has if I take an isolated system the overall isolated system then there is no exchange of heat or the heat or matter between the system and the surroundings right and there is no exchange of heat and matter and moreover the isolated system is covered with a we separated from the surroundings by a rigid adiabatic wall which is also impermeable to any type of mass transfer so if it is rigid you can also not apply any stress over the overall system you cannot apply pressure or anything so now in this system we consider subsystems so this concept of subsystems becomes very important and then we will discuss equilibrium so you have a subsystem so

your wall you have a wall fitted with a valve okay there is a valve here so valve I think the symbol will say that there is a surface start to a stop and we go for this okay so this represents a valve see for us it represents a valve this is the valve okay now this valve is closed initially so that we are not allowing beside the substance to mix right so there is a this some so this substance can be a real gas or whatever so you have an ideal gas and you have another substance that is in the other chamber right and they are fit that they are basically separated by a valve now what we know is that the delta Q reversible by T for the ideal gas is equal to 0 that means for this system so this is subsystem denoted as 1 I know this but for this system is denoted as 2 and which has a real substance or real gas whether this is true or not we do not know right so instead of writing the substance this substance is basically we can write this some substance is 0 okay now if I have that now if you see we have this isolated system and 1 and 2 are there and the point is you have this ideal gas real substance and 1 and 2 can exchange so the idea is that it is you cannot exchange matter but you can exchange heat so we are assuming this valve the internal valve to be diaphragm that means 1 and 2 can exchange heat reversal now if that is so see for example in 1 I am telling the amount of heat that is there or absorb this or the amount of heat associated with subsystem 1 is delta Q 1 okay that is the heat absorbed okay or heat input to the system the subsystem 1 and delta Q 2 is a heat input in subsystem 2 so then definitely that this is a nice overall it is an isolated system so heat cannot be exchanged to surroundings right so delta Q 1 plus delta Q 2 have to be equal to 0 okay and we are telling 1 and 2 are in equilibrium right so 1 and 2 are in equilibrium isolated system nothing no heat can transfer

So you have delta Q1 plus delta Q2 that has to be equal to 0 now we are telling that the equilibrium means we are talking about an equilibrium thermal equilibrium say for example both have the same temperature okay so the temperature so at thermal equilibrium this is also T this is also T now you are telling you divide both by T so you have delta Q1 by T and delta Q2 by T that also has to be 0 now but this one we know is 0 this is equal to 0 for the ideal gas delta Qf by T is 0 that we have already proved if this is 0 if this part is 0 and the overall is 0 then this part which is basically considering a real substance the del Qf by T also has to be 0 so therefore this del Qf by T whether you are using a different substance than ideal gas is going to be 0 right this is one way of again the same ideal now comes a very interesting part of the second law and that is called Clausius inequality right where the

Clausius inequality states that there is this dS which is greater than or equal to delta Q by T already we know now from the second law definition and for the reverse of the reversible process that dS equals to delta Q reversible that means the inequality case that dS has to be greater than delta Q irreversible so beta Q IRR is delta Q reversible right now how do you prove that now as you see the first law is also varying that is conservation of energy so the change in internal energy to you can you learn to do you equals to delta Q plus delta W now I can tell that this delta Q is some arbitrary say for some universal process and this is also for some okay I can tell but delta Q IRR plus delta W IRR but dU is equals to also if I think of this as a reversible so you have dU equals to delta Q reversible plus delta W reversible right so both are correct right the change if I replace delta Q reversal by delta Q reversible and delta W reversal by delta W irreversible then the point is that the point is that the dU in both cases we can always have this equality right dU equals to delta Q delta W for any type of process whether it is a reversal or universal it does not matter but delta Q plus delta W for any process should be having the same dV right because of the first law so this equality holds we assume that this equality holds we want to show that the Clausius inequality statement is correct what does this mean see is that dS is equal to delta Q reversible by T however dS is greater than delta Q reversible now think of this what we want to tell here is more in terms of what so the what term by the system during a reversal process it is minus delta W there or you can write mod of delta W there is always greater than for an universal process so delta W there is greater than or we can write see what we are telling is this is what done by the system is negative

So delta W rev so this basically means minus delta W reversal right that is the work done by the reversible process this is work done by the irreversible process let us call it delta W IRR now what we are telling is delta W reversible will be greater than delta W reversible but it will be equal to so that is why I do not want to put the subscript IRR right we do not want to put the subscript IRR that when delta W reversible equal to delta W in such cases that delta for this particular arbitrary process also it is a reversal it has to be a reversal the equality sign only holds for reversible processes however for irreversible processes delta W reversal that is the amount of what extracted from a reversal process is always greater than the amount of what extracted from any other process right so if we have this inequality we can also write this as delta W when we take delta W on the left hand side so you can

write this as delta W minus delta W there is delta W equal to 0 right again equality holds only for when both delta W and delta W rev are reversible represent reversible processes now what is delta W minus delta W rev if you see delta Q so if I write this so if I just remove this thing so we have delta Q plus delta W is delta Q rev plus delta W rev so that is what we have right we have written delta Q plus delta W equals to delta Q reversal plus delta W reversal therefore we can tell from this relation that delta W minus delta W reversible right if I take delta W reversal this side and I take delta Q the other side so then equality delta Q reversal minus delta Q now this has to be greater than equal to 0 so delta Q reversible is greater than equal to delta Q so delta Q reversible by T is greater than equal to delta Q by T where delta Q by T is for a mini arbitrary process the equality holds again for the reversal process now delta Q reversible by T what is the definition of delta Q reversible by T that is nothing but Ts and Bs that means is greater than equal to delta Q by T that means that is the Clausius inequality so Bs again just to recap Bs is delta Q reversible by T for any other process other than reversible by Bs is greater than delta Q by T any other process means which is not reversible so that means reversible I can write this of this subscript of IRR which is universal process and we can tell that this is what is Clausius inequality now what is the what is the what meaning of Clausius inequality Clausius inequality basically tells you the directionality of a process for example heat will always flow from a hot body to a cold body not vice versa means from a heat will not be and unless you have connected an engine or fitted an engine or you are making a heat pump where you have something where work is being done work is being done on the system you cannot have spontaneous flow of heat from cold body to hot body but you can have it from hot to cold right how do you prove that using Clausius inequality as we know that Bs is greater than equal to delta Q by T and this now if you have hot body so you have say delta QH that is coming out of the hot body and delta QC which is entering the cold body so I can hot body is at temperature TH so what we are telling TH is greater than TC and delta QH is the heat transfer from the hot body and delta QC is the heat transferred into the cold body so you have Bs is greater than equal to delta QH by TH plus delta QC by TC and delta QH is basically leaving right it is leaving so delta QH has to be negative right it is leaving the system it is not heat input but it is heat output and delta QH is entering means it is positive right so delta QC is minus of delta QH that is the one so now ds equal to delta QH by QH minus delta QH by TC or if I take delta QH common which is negative remember this is negative you have 1 by TH minus 1 by TH now 1 by now if delta QH is negative and ds has to be greater than right ds has to be greater than delta QH T then if ds has to be greater than or equal to so delta QH is negative so 1 by TH minus 1 by TC also has to be negative right now 1 by TH minus 1 by TC have to be negative means it has to be less than 0 or equal to 0 is the equal to this now if that is so since TC is less than equal to TH since TC so if 1 minus 1 by T minus 1 by TC is less than equal to 0 you can immediately see 1 by TH minus 1 by TC is equal to TH TC this is TC minus TH now TC is less than TH therefore 1 by TH minus 1 by TC has to be less than C right only when TC equal to 2 then only it is equal to 0 so 1 minus 1 by TH minus 1 by TC in general will be less than C or TC has to be less than T so what that ds to be greater than equal to C that means heat will always flow out of the hot body into the cold body right so this is the reactionality we have assumed and this reaction is correct if you would have done the other way ds should have been less than 0 which is not possible ds has to be greater than 0 according to Clausius inequality which again comes from the

second law ok second law basically defines the reaction of the natural process now you will tell me ok what happens in an isolated system for completely isolated system you can have subsystems but we have already shown that delta Q in an isolated system the delta Q right the amount of heat input or output is going to be equal to 0 right because it is in a robotic system it has a ducted walls right it cannot exchange heat with the surrounding so delta Q is going to be 0 but depending on whether the processes so if the process is a reversible process that is happening in the isolated system then ds equal to 0 this is for reversal processes but if it is a natural process and universal process then ds has to be greater than 0 or continuous this is for this is basically for isolated system so remember for an isolated system your outside basically your wall that separates the system surroundings is adaption now if it is adaption delta Q is 0 but ds is greater than 0 so entropy does not decrease so this is the most important part entropy does not decrease in an isolated system but it increases in an isolated system when there is a spontaneous change if there is a spontaneous change that means a spontaneous process on a reversible process then ds does not increase but it increases right in an isolated system however ds can be equal to 0 for processes that are not spontaneous and reversible. Now let us think of this example that we are talking about 100 degree Celsius and one atmosphere pressure and we are talking about this particular process water liquid goes to water vapor at 100 degree Celsius now remember water vapor and water liquid are at equilibrium at 100 degree Celsius because if you look at say for example you take a pot with water and you put it on a burner and you raise the temperature to 100 degrees you will see at 100 degrees you will see these bubbles that are coming out right inside the water and this water is started boiling right but you will see that water is still remaining right you are not if you remain exactly at 100 degree Celsius you see there is an equilibrium between liquid water and water vapor right because that is the transition temperature at one atmosphere pressure again if I change the pressure then water can boil at a different temperature right so either we can depending on the pressure that the system experiences water can boil at a lower temperature at a higher temperature right so it depends on that. So this is our phase so basically if you look at that this is a transition temperature, transition temperature is a temperature at which water in two states the liquid state as well as the vapor state are in equilibrium right so in this at this transition temperature any transfer of heat right if I want to transfer heat so that water goes water liquid goes to water vapor okay this heat that this heat transfers reversible in this way that I can also think of extracting heat in such a way reversibly in such a way that water vapor condenses to liquid right so at this temperature right so basically it is a transition temperature so at this transition temperature since both are possible all the transfer of heat is going to be reversible

At 100°C and 1 atm. pressure,

$\delta q_P = dH$

Water (l) $\underset{100°C}{\rightleftharpoons}$ Water (vapour) $q_{P,rev} = \Delta H$

Transition temperature

$q + W = \Delta U$

Any transfer of heat is reversible at the transition temperature

$q_{P,vw} - P\Delta V = \Delta U$

$q_{P,rev} = \Delta U + P\Delta V = \Delta H = T\Delta S^{tr}$

$q_{rev} = \Delta H^{tr} = T\Delta S^{tr}$

$\therefore \Delta S^{tr} = \dfrac{\Delta H^{tr}}{T^{tr}}$

Calculate the change in entropy when an ideal monoatomic gas at 30°C and 1 atm. pressure is allowed to expand from 0.5 L to 1 L and is heated to 100°C at the same time.

1. Reversible isothermal expansion at 30°C

$+$

2. Reversible heating at constant volume

$pV = nRT$

 Now if that is so delta Q reversible again this is a constant pressure so as you know delta Qp is a right delta Qp is nothing but delta H right so at constant pressure what you are basically telling is del R this is not correct you have to write delta Qp equals to TH right the differential so you are telling so basically I think this way Q reversible so that means Q reversible Qp reversible is equal to delta H. Now delta but Q reversible equals to T delta S transformation right we can write delta H transformation goes to T delta S transmission right so as a result delta S transformation that means change in entropy at the transition temperature is basically nothing but delta S transition by T right so this is something that is very very important so as you know Q plus W equals to delta Q right so and what I am talking about is so W so this is like Q delta yeah so Q minus T delta V equals to delta U now Q equals to delta U plus T delta P now that is a constant pressure because there is no V delta P delta U plus P delta V so as you can see here and delta U plus P delta V is nothing but delta H at constant pressure right this is U at constant pressure at constant pressure so this is equal to delta H. Now Qp is also basically the same as so because if the heat transfer is reversible right at transition temperature is reversible right heat transfer is reversible so this is Qp reversible so this is reversible so if it is reversible then it is also equal to P delta S so delta H equal to P delta S at the transition temperature P tr so basically what we are doing is delta H tr, tr is the at the transition temperature or delta H transformation is equal to P delta S transformation, delta S transformation is the entropy change associated with transmission and therefore delta S transformation can be obtained if I know the enthalpy of transmission and I divide it by the transmission temperature P t. So that is the idea so if that is so let us now so basically as you can see now that the enthalpy of transmission and entropy of transmission is related, and the relation is basically based on the it says that delta S transformation is nothing but delta H transmission by T transmission. Now think of this let us think of another problem right you can think of this problem one problem in the same line so we are talking about calculate the change in entropy when an ideal monoatomic gas at 30 degree Celsius and 1 acoustic pressure is allowed to expand right from 0 5 liters to 1 liter and is heated to 100 degree Celsius at the same time now you can think of this so it is first allowed to expand from 0.5 liters to 1 liter where you are keeping the gas at 30 degree Celsius and 1 atmospheric pressure right so reversible as thermal expansion at 30 degree Celsius is the first process you can think of this as two processes and the second process is basically heating of the gas at constant volume right you are just putting gas at constant volume and we are assuming the gas to be ideal and

monoatomic right so that means we are assuming this pressure Tv is equal to n. Now if you see this you have dS which is nothing but delta Q equal to T right this is from your second law right second law is giving you this so delta S if I know this so I can write integral dS equal to integral delta Q by T and as I told you that this is our state function so I can take I state I and then state F right that is what I have done right you can see the equation here that is what we have done. Now remember this is all so what we are talking about is reversible isothermal expansion at 30°C right so we are telling first that temperature is constant which is equal to 30°C so delta S then can be written as the integral basically is basically delta S. So integral is basically going to be delta S.

Delta S is equal to 1 by T delta Q reversible and delta Q reversible integral is nothing but Q rev by T and T says basically if I look at it it is going from I to T. Now as you can see here we told it is an ideal monotonic gas right we have this reversible isothermal expansion now in this case the change in internal energy dU right there is no change in temperature there is no change in temperature it is constant but dU for an ideal gas is Cv dT for example right so that is if there is no change in temperature or if there is no change in temperature then dU is going to be 0 right if dU is going to be 0 then delta S then Q reversible is minus W reversible right so first of all delta S equals to 1 by T I to F del Q F which is Q F by T I to F. Now comes the part where the temperature is now at 30 degrees Celsius because we are keeping isothermal expansion right or isothermal 0.5 liters to 1 liters right this is an isothermal expansion now if I am doing that temperature is constant and we have to find out what is Q rev. Now Q rev is nothing but as you can see because there is no change in internal energy and delta U equals to 0 equals to Q rev plus W rev and therefore Q rev equals to minus W rev. Rev means reversible it means reversible I am repeating the words just so that you become more and more familiar so they basically notes reversible and this is basically minus W rev because delta is 0 because of the constant temperature again delta is 0 equals to 30 degree Celsius constant. So, this is one sub process right where we are talking about reversible isothermal expansion from I to F. Now minus W rev and W rev is nothing but integral p dV right W rev is minus p dV integral minus p dV but there is a minus sign here so minus minus becomes plus so it is I to F p dV so again we are talking about ideal gas so p V so you are telling that p is nothing but nRT by V that is what I have written but t is constant R is constant n is constant so nRT dV so this is nRT ln Vf by Vn I nf upon Vn. So now if that is so then delta s is Q

rate by T so 1 by T there is a 1 by T as you can see here then nRT ln Vf by Vn right n is the number of so we are talking about 1 then an ideal monotonic flux right so we have not indicated n so that is not a problem because we know the pressure right initial pressure at the initial step we know the pressure you know the volume we know the because volume is 0.5 liters we know R we know initial temperature also it is 30 right so basically as you can see here that for the process number one sub process number one right so that is why I have given this is equal to p IVI by Ti right n equals to p IVI by Ti there is an R missing so there is an nR right so because there is a R here so n equals to p IVI by R Ti and R R R cancels out so this becomes just p IVI by Ti so yeah that just becomes p IVI by Ti then n Vf by Vn right now what we are telling in step two right this is a step two so this what we did first is step one right in step one is what we did so let us call instead of one let us call it step one okay now if you have step one now we are looking at the step two what is step two step two you keep the volume constant but you increase the temperature to 100 degrees right from when that was the half so and then heat it to 100 degree celsius at the same time right we have just divided into sub processes for convenience now here Qf is going to be so volume is constant so that is so Qf equals to delta Q so integral delta Qf which is integral of dV because we are no longer volume is constant so p dV in this sub process p dV is going to be 0 right there is no volume change right the volume is constant

So you have delta Qf which is basically integral du and du is nothing but n Cv and dV okay Cv m is a molar heat capacity at constant volume and which from equilibrium partition theorem we already know is nothing but 3 by 2 n k right so this is like 3 by 2 arc right so now you have delta S for sub process 2 you are basically looking at so Qf T which is integral p i to p i of du right so that is what I am looking so this is basically du by T and du is basically n Cv p and n is again p i v i v r p i with 3 by 2 r r again gets cancelled here as you can see and you have dT by T so I can write p i v i v i and then p i by T i whole to the power 3 by 2 right because this 3 by 2 r came because Cv m is basically like molar capacity Cv m denotes the molar heat capacity right so you get now delta S total which is the delta S for the sub process 1 right you just now add it and delta S equals sub process 2 so it basically becomes p i v i by p i ln so you have in the first case ln v f by p i right you have ln p f by p i this is equation 1 and you have now equation 2 now you add 1 and 2 then you have p i v i by p i you just do the simplification you get ln v f by v i p f by p i whole to the power 2 and you can also now plug in the

values and check delta S is greater than C delta S has to be greater than C now one thing this is all fine now how do you measure entropy how do you measure entropy okay so there are various ways to measure entropy so one of the ways is first we measure enthalpy and we know that enthalpy if I know the enthalpy if I know the enthalpy I can basically relate it to entropy okay so that's what I will try to do because one of the ways you can immediately you could immediately see say for at the transition temperature delta H transmission if I know the delta S transmission is nothing but delta H transmission by the temperature of transformation right now you can understand that entropy measurement again is indirect right they are directly measurable quantities but these are directly measurable quantities directly means using some instrument so you can measure C v you can measure C p that is the heat capacity constant volume heat capacity constant pressure then thermal expansion coefficient then compressed isothermal compressibility even temperature pressure volume all of these can be measured directly however if I want to measure enthalpy or you have to measure entropy then basically you use something called calminator so here for example I will give you an example of differential scanning calminator okay so it's power controlled by power.

So what we are talking about is if you look at this very simple example here you have the sample for which you require some properties right you want to be calminator and here is the reference sample okay and if you see the both the chambers right where you have sample and when you have the reference both are basically both are basically connected to a thermocouple right they both are connected to thermocouple and there are there these two fitters right there is one heater here there is one heater here right so we are telling the temperature of the sample plus the reference are increased at a constant rate okay and that is called the scanning rate okay so T0 is the initial temperature set then Sr is the scanning rate which is in Kelvin per second so at this constant rate you are increasing the so Sr is the scanning rate and so Tt at any time t t is basically T0 which is the initial temperature plus Sr times small t small t is time now as you can see here Cp itself may be a function of temperature so if I tell Cp is in general so P is what Cp itself is equals to Cp okay Cp itself can change as a function of temperature right now if at all Cp is not a function of temperature whether it is function of temperature or not it does not really matter so if it is a function of temperature it becomes slightly more complex but anyway what I want to tell we are increasing the temperature of both the sample and the reference

at the same rate right we are trying to do that and we want to maintain same temperature input how do I maintain same temperature in both if I know that there is a temperature increase in one then I want to basically just increase the power of the heater in the other so that I can maintain the same temperature everywhere so basically what I want to do the process is to transfer so what I am trying to do so you understand so say for example you have the sample and you have your reference now you are seeing that the sample is basically losing means it is trying to lose the temperature lose some temperature or lose some temperature then what you want to do is you are just using the heater here so that again the sample comes to the same temperature how do you do that you want to transfer excess energy to or from the sample undergoing a physical or tender process right so if it is undergoing the sample is undergoing a physical process by which this losing temperature you want to transfer energy to it so that the sample again is maintaining the same temperature as that of the reference right

So if there is no physical or chemical change of the sample at temperature t if we assume that there is no physical change of the sample at t then because if it is there then you have to also think of the latent heat or the heat of transmission right if there is no physical or chemical change then it becomes very easy because you have the initial temperature of t naught and Qp is basically Cp times delta t which is Cp times t minus t right and delta t is nothing but t minus t naught it is basically Sr times t now if physical and general process if this physical change is equal to true then excess heat transfer to maintain the same change in temperature in the sample as that the reference is basically Qp plus Qp excess right that is what you have to give right because if there is a physical or chemical change right if that is true so we are talking about no physical if there is a physical or chemical change is true if physical or chemical change is going to be true then the excess heat transfer to maintain the same change in temperature in the sample right to same change in temperature in the sample as in the reference basically tells you you require this Qp but there is also a Qp excess that is required right you require to have this Qp and this Qp excess we call Qp excess which is basically equals to Qp Cp delta t right Qp equal to you have seen Qp equal to Cp delta t but this Qp excess corresponds to Cp excess times delta t right so this is some excess heat capacity times delta t if there is a physical or chemical change that is basically true now Cp excess is nothing but Qp excess by delta t right or this is basically Qp excess by Sf which is basically given by joule 12 k now if it is an endothermic process or an

exothermic process so what we are trying to look at is if there is no physical chemical change then this is nothing but Cp delta t now Cp itself being a function of temperature would have complicated the process but if you assume that Cp is not a function of temperature for the temperature change that we are talking about right the temperature change if we take the temperature change to be small and we assume that Cp is not changing in these temperature range then you can write Qp equals to Cq delta t directly into Cp into T minus T naught otherwise Cp itself has to be expressed in a function of temperature and you have to find out the integral Cp dT and where Cp itself is a function of temperature so you have to calculate the integral that's all now but if there is a physical or chemical change of the sample if there is a physical or chemical change in the sample then you add this Qp excess the Qp excess is equal to Cp excess and the temperature difference delta t which is T minus T naught which is basically Sf times now that if that is so then Cp excess can be written as Qp excess by delta t or Qp excess by Sf.

Qp is excess we can tell or this is excess one so this is basically in joule per Kelvin so now if you see it is an endothermic process then as you know in that endothermic process heat is absorbed so basically you will see a peak like this it is a positive and the exothermic process you will see it is this so you will see basically a negative in the current exothermic process. Now if you look at this delta H is Cp excess times delta t the delta H is Cp excess dT integral T1 to T2 right so T1 to between T1 and T2 is what we are doing between two temperatures T1 and T2 is what we are basically looking at right T1 is your say for example the reference the initial temperature and T2 is your final temperature so if I now integrate Cp excess Tp then what I get is basically the delta H associated with the physical or chemical change in the sun that is how we measure delta H. Now if I measure delta H now you will tell okay you have measured delta H so what how do you measure delta S that is very interesting. Now if I want to measure entropy we know delta Q is TdS right if it is reversible delta Q is irreversible. So what we know from second law second law tells you delta Qp reversible equals to TdS but delta Qp reversible is nothing but P means constant pressure so it is nothing but dH which is equal to Cp dT.

So dS equals to Cp by TdT now Cp is now you can now think of this as like it is a functional temperature so A plus Bt plus C by T square plus dT square something like that right we have some values representing values for nickel okay in different forms again there is a temperature range that you

have to give if you have such an empirical or experimentally determined expression then you have to also give the temperature range for which A B C D these positions are valid. Now once you know this once you know this you already know delta H right you already know delta H so basically delta S is basically I can tell very easily now from this expression itself it is clear that from these two from E's relation you can write dS equals to write dS equals to Cp by TdT and you can just do now the delta S is integral Cp by TdT for a temperature range Ti equals to F that is it then basically get delta S. Now the delta S basically you can directly get from the delta H by T also okay if I know delta H delta H by T will give me delta S for the transformation right this is how we can measure entropy. Now if you see there is one very interesting point here I want to tell that is Cp as you have seen from the Debye's theory that Cp tends to 0 right but the heat capacity tends to 0 as T tends to 0 right. Now we can also think of that from Debye's theory that Cp equals to At cubed is valid at low temperature till 0 Kelvin at low temperature means temperatures below the room temperature
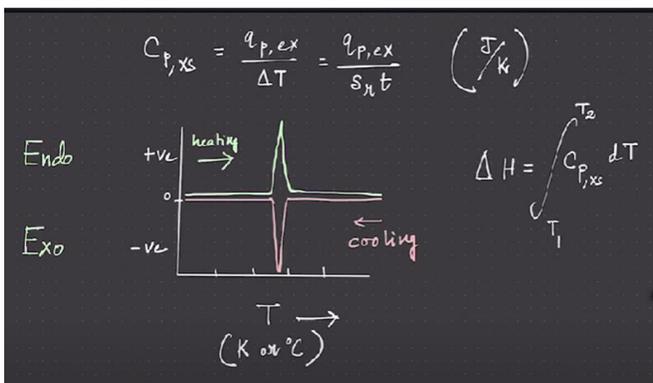
Now if you see that Cp by T if I plot it as T and there are these phase changes so basically this is my solid region this is my liquid and this is my gas as you can see Cp by T extrapolated at 0 it is 0 Cp is going to be 0 at as T tends to 0. Now Cp is going to be 0 so as T tends to 0 but T is not exactly equal to 0 so we are basically looking at some extrapolation that we want to do with the extrapolation is done with this relation Cp equals to At cubed right this blue curve is going to give me that extrapolation curve right so we use that but you see typically for a solid the Cp is increasing with temperature right it increases increases till the melting point right this is your melting point this is your melting point so if I have gone up to melting point now you see Cp by T is discontinuous right it is discontinuous now at the liquid again there is this is your Cp by T and at the solid this is your Cp by T and at Tm this is discontinuous right there is a jump and then from this Cp by T again you come down come down and then again there is a boiling point now at the boiling point again there is a jump and then you get what is called gas right so basically the Cp by T is going increasing now it goes and then from solid when it goes to liquid there is a jump at that melting point and again from liquid to gas when it is going there is a jump at the boiling point you can easily understand this basically if you Cp by T again remember ds equals to Cp by T dT that's what we have done right we have written this Cp by T dT now that means s equals to integral Cp by T right integral of this terms if I do that you can see s basically if you look at

the part s again you have the solid, you have solid here, you have liquid here and you have gas and as you can see the entropy goes starts from zero at zero Kelvin goes up then there is a delta s melt and then this delta s melt there is a transformation here right so there is at melting point there is a transformation right this is the melting transformation solid is transformed to liquid in this case you have seen a you are seeing a jump in delta s right there is a jump and why is there a jump because you see you are adding heat you are adding heat to solid and then at some point the solid has changed to liquid you just go above Tm the solid has changed to liquid right so now the liquid again there is a this entropy change right the entropy change is higher than that in solid right the entropy itself is higher than that in solid and then again at boiling point where the liquid has to transform to gas again you see there is a jump in the entropy and that is the entropy of transformation right there is this delta s transformation here so this corresponds to delta s boil and this is the delta s melt right and this is delta s boil you can see that and again for the gas phase definitely entropy is much higher than the solid phase you can immediately see that and you can appreciate that the dispersion will be much more or the number of energy states that will be accessible for gas will be much more than in the solid, solid is much more compact than gas right so as a result the entropy of solid is in general the lowest then comes liquid and gas has the highest right and remember this jumps in the entropy of transformation or heats of transformation these jumps basically tell you that there is a tangential density phase I will also define later the order of transition so I will end here today and we will try to continue this topic further in the next few classes.