

Thermodynamics And Kinetics of Materials

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Lecture 6

Basic Concepts

Thermodynamics And Kinetics Of Materials

Hi, so in the last class I talked about Joule Thompson expansion process or Joule Thompson trucking and I told that Joule-Thompson expansion coefficient for ideal gases is 0, but there is this process called reversible adiabatic expansion that will often come across right that is something that is used in different heat engines. Although heat engines may not seem very important for non-aerosive materials, but it is very important to understand these adiabatic processes because you have adiabatic processes, isothermal processes, isochoric processes, isobaric processes and here we are talking about adiabatic processes and when a gas expands in an adiabatic process what really happens right how does the temperature relate to the volume etc. So you see you have reversible adiabatic expansion, reversible means that it is the processes is approximately slow and basically you can plot it on a PV curve say for example, if you have a PV curve then I can so say for example, this is pressure, volume then you have a pressure, volume and basically, sorry what curve is like this right it is represented this curve basically tells me that some something is like say for example, this curve is like PV to the power gamma constant, now what is this gamma right so and how to determine this gamma so for that so say for example, this is the equation of an adiabatic process or a reversible adiabatic expansion of an ideal gas. So of let us consider first an ideal gas, of an ideal gas, as soon as I tell ideal gas what comes in my constitutive state relation, a relation between the states an equation of state that is called an equation of state whether it is an ideal gas or a real gas for example, if I have a equation of state you will see in one of the assignments I have talked about Van der Waals equation of state. So equations of state basically relate the in general it relates the intensive variables say for example, for ideal gas the simplest equation of state that we know for some time is PV equals to nRT where n is the number of moles, P is the pressure, V is volume, R is universal gas constant and T is temperature. Now when I talk about adiabatic process or adiabatic expansion the first thing that comes in mind is that delta Q has to be equal to 0 as you can see here that I have noted here that delta Q is going to be 0 for an adiabatic because the process is adiabatic because it does not allow any heat exchange between the system and the surroundings.

Now delta Q equal to 0, delta W equals to minus PV and this is something that this is delta again this is reversible mechanical work which is minus PV whether work is done by the system or work is done on the system based on our convention of work done on the system is positive delta W so whether it is by the system or on the system delta W is always minus PV. So in one case for

example, if it is on the system P basically is the external pressure denotes the external pressure and dV denotes the decrease in volume so that is negative so that is why I put a negative sign. On the other hand when you tell that work is done by the system the gas is expanding against some pressure so if it is against some pressure again the internal pressure is like minus P and minus P into dV where dV is positive. So in both cases the equation is minus PV like it is force displacement relation and then you have also change in internal energy of the gas that is expanding which you can write as C_v, C_v is the heat capacity across the volume dV right this is heat capacity across the volume remember this is not the molar heat capacity but it is the total heat capacity across the volume for some n moles.

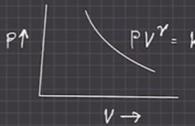
Reversible Adiabatic Expansion of An Ideal Gas

$$\delta W = -p dV \text{ where } p \text{ is the pressure applied}$$

$$\delta q = 0$$

$$dU = C_v dT$$

Equation of state

$$pV = nRT$$


$$\delta q = 0 \quad \delta W = -p dV$$

$$dU = C_v dT$$

First Law

$$dU = \delta q_{rev} + \delta W_{rev}$$

$$C_v dT = 0 - p dV$$

$$C_v dT = -nRT \frac{dV}{V}$$

$$C_v \int_{T_i}^{T_f} \frac{dT}{T} = -nR \int_{V_i}^{V_f} \frac{dV}{V}$$

$$C_v \ln \frac{T_f}{T_i} = -nR \ln \frac{V_f}{V_i} = nR \ln \frac{V_i}{V_f}$$

$pV = nRT$
 $\therefore p = \frac{nRT}{V}$

Now if it is so according to first law, first law, first law, then we can directly write dU equals to delta Q plus delta W again by delta, delta is cost path function and this is all reversal delta Q rare, delta W rare and this is C_v dE equal to 0 minus PV. Now the equation of state is PV equals to nRT. Now therefore P we can write as nRT by V and see P is not so instead of P I am substituting as nRT by V and P is the pressure or the internal pressure which is then we can write C_v dT equals to minus nRT dV by V or we can also write for the C_v dT by T and if we decide I am taking this and so C_v dT by T equals to minus nR dV by V. Now I can integrate, I am integrating and say I tell that initial temperature was T_i, final temperature is T_f and similarly it is V_i and V_f then what do I get, I get C_v ln T_f by V_i equals to minus nR ln V_f by V_i or I can write as nR ln I have put the minus sign so V_f V_i by V_i to the power minus 1 right so this is basically ln V_i by V_i. Now we will continue with this relation so C_v now we can write nR by C_v so basically what we can write is ln T_f by T_i equals to let us put some number nR minus nR or nR by C_v okay nR by C_v so here this is nR by C_v ln V_i by V_i.

So now this nR by C_v as you can see n is the number of moles constant let us assume it to be constant does not change say and R is gas constant and C_v is the entomological capacity obviously it can be a function of temperature C_v can be a function of temperature but it can also assume it to be a constant. Now in such a case what you have, you have this right you got this C_v ln T_f by V_i plus minus nR ln V_i by V_i which is basically nR ln V_i by V_i. Now what you are writing is chi see I can also write it as gamma from some text books use gamma I prefer to use the word chi right

because I do not want to confuse gamma with something else so later so I use our chi, the symbol chi and sometimes people do use gamma it is like nu I am very sorry for this let us call it gamma okay and equal to $C_v nR$ so in our in here we would call it as chi. Let us call it chi if you see that so C_v by nR nR by C_v so I just write C_v by nR $\ln T_f$ by P_i equals to $\ln V_i$ by V_f now see this can be written as C_v by P_i equal to V_i by V_f whole to the power C_v by nR now this C_v by nR I am replacing by C_v by nR that is there in the superscript it is there in the superscript here C_v by nR I am replacing it by gamma the symbol gamma or the symbol chi all of them so I am using here chi for example you can see your chi and then what happens T_f by T_i so am I correct this is not correct this has to be T_f by T_i whole to the power T_f by T_i whole to the power C_v by nR equals to V_i by V_f or you can write as T_f by P_i equals to V_i by V_f whole to the power the ultra-peak that is nR by C right this is also possible so both ways you can write so this is C_v by nR the way I have taken is nR by C_v by 2 here so this one this branch here from this and this one is following from T's way of V_i right so both ways we can write so let us follow one of the ways and see so you have chi and T_f by T_i C_v by nR so basically here you have C_v by nR and here you have V_i by V_i so T_f by T_i to the power chi right where chi equal to C_v by nR is equal to V_i by 2 or T_f by T_i because V_i by V_i is equal to 1 by chi right it is 1 by pi because if you see this is C_v by nR if it is on the left hand side if it is on the right hand side it is nR by C_v right it has to be nR by C_v because what I will do here I will use this expression when I put nR by C_v on the right hand side then nR by C_v so V_i by V_i equal to power nR by C_v and if I put it on the left hand side then it becomes C_v by nR right so both are possible and as you can see here T_f by T_f equal to chi equal to V_i by T_f you can also write as T_f by T_i equal to V_i by V_i equal to power nR by chi is something that you have all done and now you see T_i by T_f is V_i by T_i now this is one interesting so if I now read a reciprocal of both terms on the both on both sides then this is T_f , T_i by T_f is 1 by T_f by T_f so and this also becomes 1 by V_i by V_i equal to power nR by chi so it becomes V_f by V_i what you call it right now.

$$\dots C_v \ln \frac{T_f}{T_i} = -nR \ln \frac{V_f}{V_i} = nR \ln \left(\frac{V_i}{V_f} \right)$$

Let $\chi = \frac{C_v}{nR} = \gamma$

$$\chi \ln \left(\frac{T_f}{T_i} \right) = \ln \left(\frac{V_i}{V_f} \right)$$

or,

$$\left(\frac{T_f}{T_i} \right)^\chi = \frac{V_i}{V_f} \Rightarrow \frac{T_f}{T_i} = \left(\frac{V_i}{V_f} \right)^{1/\chi}$$

$$\frac{P_i V_i}{P_f V_f} = \frac{T_i}{T_f} \Rightarrow \frac{T_i}{T_f} = \left(\frac{V_f}{V_i} \right)^{1/\chi}$$

$$\gamma = \frac{C_p}{C_v} \quad C_p - C_v = nR$$

$$\ln \frac{T_f}{T_i} = \frac{nR}{C_v} \ln \frac{V_i}{V_f}$$

$$\frac{C_v}{nR} \ln \frac{T_f}{T_i} = \ln \frac{V_i}{V_f} \quad \frac{C_v}{nR}$$

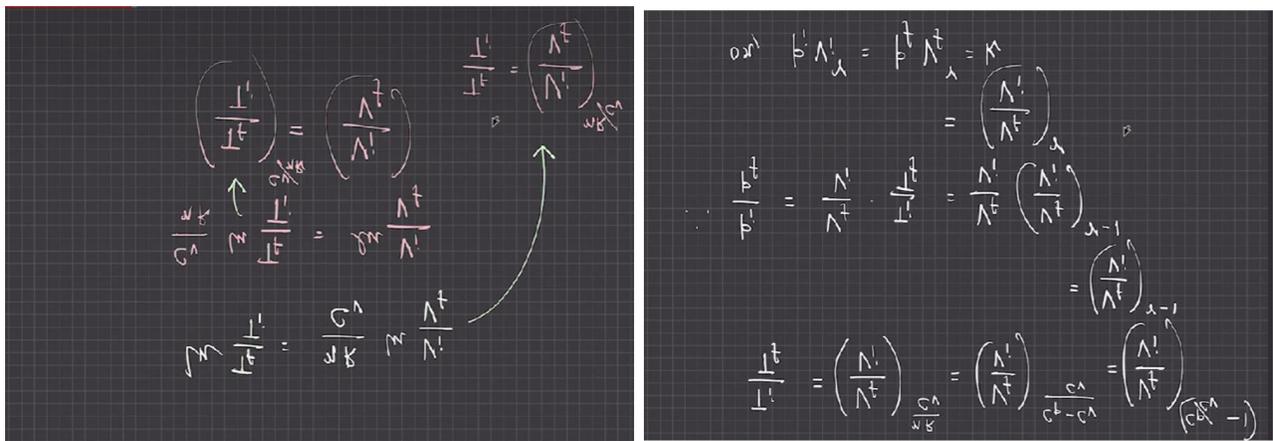
$$\frac{T_f}{T_i} = \left(\frac{V_i}{V_f} \right)^{\frac{C_v}{nR}}$$

So I will not call this gamma I will call gamma as so here we will call gamma as C_p by C_v chi as C_v by nR now you see C_p minus C_v equal to nR this is for ideal gas this we have already shown for ideal gas C_p minus C_v equal to n this is something that we have already proved and then we are writing gamma equal to C_p by C_v now this is C T_i by T_f equals to V_f by V_i to the power nR by C_v nR by C_v you have nR here and you can see you are substituting nR you substitute nR by C_p minus

C_v so it becomes V_f by V_i to the power C_p minus C_v by C_v which is V_f by V_i C_p by C_v minus 1 which is basically V_f by V_i to the power γ minus 1 right so it becomes V_f by V_i γ minus 1 now what is the relation between χ and this χ equal to χ equal to χ equal to C_v by nR right C_v by C_p minus C_v and which is basically C_p minus C_v by C_v whole to the power minus 1 which is equal to C_p by C_v which is γ minus 1 whole to the power minus 1 or which is equal to 1 by γ minus 1 right so if that is so now another thing V_i by P_f equals to V_f by V_i that is something that you can also use right V_i by so if that is so what did I do I have written here it has become clumsy so let us look at this yeah so you have say PV equals to $nR\theta$ so if I write this as $P_i V_i$ equals to n say if I keep the cost on P_i and $P_f V_f$ equals to $n P_i$ so $P_i V_i$ therefore you can write $P_i V_i$ by $P_f V_f$ equals to P_i by P_f or you can write P_i by P_f equals to V_f by V_i into P_i by P_f which is basically again we have found that V_i by P_f is nothing but V_f by V_i equal to γ minus 1 right V_f by V_i equal to γ minus 1 now you have V_f and V_f equal to γ minus 1 which gives you V_f equal to γ and V_i equal to γ so that means it basically tells you P_i by P_i equals to V_f by V_i equal to γ so now if you do that so it becomes $P_i V_i$ to the power γ see if you rearrange now it is $P_i V_i$ to the power γ because V_f to the power γ so this is a constant this is for so basically if I write such a process this is a process that I will use if I write if I use such a process this process that you are seeing here that come a little back and show you that this process that I have represented here on the pb is a reversal by the way if it is reversible it is not possible to put this path in a pb diagonal because at each point in this path cell at each point in this path the system can traverse this path both ways means it can go this way it can go also the other way and the way it is happening right at each point the increment I come here allow it to incorporate from here so it is an infinitesimal process but as you can see here that for reversible adiabatic expansion the work done is $p \, dV$ right so basically not work done the work done is $\int p \, dV$ but what you get is $p \, dV$ or γ is equal to constant so for a reversible adiabatic expansion of an ideal gas is represented by an equation of state of the form pV^γ to the power γ equals to constant where γ equals to C_p by C_v remember γ I am using here as C_p by C_v at C_p minus C_v by C_v is where I am or nR by C_v is what I am using as path ok so now we know adiabatic process we know also isothermal process we know isothermal process for isothermal process temperature is fixed isothermal temperature does not change p is same so there will be $P_i V_i$ equals to $V_f V_a$ equals to so in one case k_1 so k isothermal process so k_1 is same so k_2 is same so k_3 is same so k_4 is same so k_5 is same so we know that two equations of two equations representing isothermal and adiabatic process right isothermal for a given temperature p and adiabatic for in case of adiabatic what am I keeping fixed I am keeping nothing fixed right temperature is changing your pressure can change your volume can change right so basically you can however keep the pressure so pressure so you have PV by T right so the relation so pressure volume temperature all constant.

So you can write in one case PV to the power γ where γ is C_p by C_v in other case γ there is no γ ok now I come to a very important law it is called the second law of thermodynamics second law of thermodynamics is very fundamental because it is not the principle of conservation of energy second law of thermodynamics does not teach you the principle of

conservation of energy it teaches you directionally it tells you that there exists a property of the universe where universe is composed of system and surroundings that will change in a certain way or in a certain direction irrespective of whatever process takes place irrespective of whatever process is taking place in the universe the this property called entropy will change in a certain way so now as you can see there are two types of processes right one is called a natural process or a spontaneous process that does not require work to be done on the system right the spontaneous process does not require any work to be done on the system so that is called a spontaneous process think of a spontaneous process here for example free expansion of a gas so you have kept a gas in a chamber so in one side of the chamber you have kept a gas in the other side you have to take a vacuum or you have created a vacuum and the chambers are separated by say by valve and the valve is closed so that the gas cannot basically come flow from the left chamber to the right chamber so in such a case now in such a case if open the valve what will happen can be a free expansion of gas there is no valve so gas will automatically go and fill the chamber that was having initial effect right so and it will go on filling and and you will see surprisingly that at one point of time where it has completed off



So it will see you will see that the filling has happened spontaneously right it has happened spontaneously because there was no work that has to be done for this gas to flow through the open valve into the chamber that contains that this is an example of also this free expansion so example here if I give then I can tell one major example that I am giving is free expansion of a gas okay so because there is no work required to be done for this free expansion of the gas then there are also non-spontaneous or artificial processes for example in a hot summer day when you run your AC the AC is cooling you but AC is also releasing a lot of hot air outside and and the work done to cool the room is non-spontaneous or artificial right so there are such processes one is a natural process natural process another example of natural process I have a hot body and I have a cold body I put them and say for example I put them together you will see that there will be heat flow unless till there is an equilibrium that is all the thermal equilibrium means there will be some intermediate temperature at which both bodies will settle right so and this heat flow that will happen is again from hot body to cold body you will see later that it's a natural or a spontaneous process non-spontaneous is if the heat had to be made means if we could use a mechanism to make

the heat flow from the cold body to the hot body for example when I am talking about air conditioning see you have a very hot summer think of that so you have the surroundings say you are sitting in the room and the surroundings is really really hot inside if you do not have any air conditioning your temperature also has to go towards say for example it's like the surroundings is everywhere it's got a huge volume surrounding so ultimately your room temperature should also settle to something like 40°C right so in contact with the surroundings however when AC is running there is some work that is done so that the cold room can reject heat and to the surrounding which is already hot right the cold room can reject heat and the room remains cold because of the pressure right so is if a cooler room you can maintain a cooler room by doing some work and that is where so there is some work done and therefore this process of air conditioning is a non-spontaneous or an artificial process now all these natural and spontaneous processes have some or spontaneous process has a direction non-spontaneous process artificial processes are direction now all these processes follow second law of thermodynamics second law of thermodynamics again to recap is the property of the universe and that property the universe changes in a given direction respective a process that is taking place then it is now this is very interesting.

$$\frac{T_i}{T_f} = \left(\frac{V_f}{V_i}\right)^{\frac{C_p - C_v}{C_v}} = \left(\frac{V_f}{V_i}\right)^{\frac{C_p - C_v}{C_v}} = \left(\frac{V_f}{V_i}\right)^{\gamma}$$

$$\gamma = \frac{C_p}{C_p - C_v} = \frac{C_p - C_v + C_v}{C_p - C_v} = \frac{1}{\gamma - 1}$$

$$\frac{P_i}{P_f} = \frac{V_f}{V_i} \frac{T_i}{T_f} = \frac{V_f}{V_i} \left(\frac{V_f}{V_i}\right)^{\gamma} = \left(\frac{V_f}{V_i}\right)^{\gamma}$$

$$P_i V_i^\gamma = P_f V_f^\gamma = k$$

Reversible Adiabatic Expansion of An Ideal Gas
 $\delta W = -PdV$ where P is the pressure applied
 $\delta q = 0$
 $dU = C_v dT$
 Equation of state
 $PV = nRT$
 $\delta q = 0$ $\delta W = -P dV$
 $dU = C_v dT$

So the way I want to define it is like that in second law you get a state function you define a state function called entropy now note that in second law you are not the first law you define something called energy and you told energy is conserved now you are defining some sort of entropy but you are not talking about anything about the conservation of entropy what you are telling is that S universe or S total always increases in the direction of spontaneous change you are telling what we are telling is S universe or S total always increases in the direction of continuous change right so in the direction of spontaneous change S universe or total entropy of the universe should always change in the direction of spontaneous change so delta S universe has to be greater than 0 for any spontaneous change now as you can see if I look at delta S it is like a macroscopic change a change that is measurable and S is an infinite symmetry so often as you have seen previously delta will be used for a macro change and means a measurable change and T for infinite simple changes in the interval now think of this there is as I told you that there is a delta S universe there is a delta S and it is always greater than 0 for a natural process right and we are telling now that this delta S universe or delta S universe is a sum of delta S system right there is delta S universe you can write

as ΔS system plus ΔS surroundings right so it is ΔS system plus ΔS surroundings let us call it ΔS surroundings so it is like I just write S_{UR} so S_{UR} basically denotes surroundings however for each case what we are telling for each part of the universe that is system part of the universe that is the system is the part that we are focusing on all the surroundings for the universe can be divided into two further terms one is called entropy transfer between the system surroundings because of the heat transfer that happens in the surroundings there is something called an entropy or a state function entropy that transfers between the surroundings and we call it ΔS_t small t ΔS with a subscript of small t basically denotes the entropy transferred to the system surroundings because of exchange of heat between the system surroundings however there is another term which is called ΔS_P which is our delta entropy production term and this entropy production term is always going to be greater than 0 as long as the process is spontaneous or natural the ΔS_P production can go to is always going to be positive or it can also be equal to 0 but it cannot be negative there have ΔS transfer can have any sign ΔS_P production is always going to be either positive or natural or something as processes or it can be also 0 so now we have to understand what does entropy production mean see here we are happening a very nice understanding and a physical phenomenon and the understanding of physical phenomena is what led to this definition of entropy once you can define entropy you find that it becomes very useful this property called entropy because very useful to understand the directionality of a process and to qualify the process as continuous or non-continuous right and so that is very very important that was very clever way to define entropy in addition to energy now think of this think of an example so continuous process means it's a natural process now what I am trying to say a natural process is irreversible for example let us think of a very simple process of a growth of a plant.

Second law of thermodynamics
 There are two types of processes
 - Natural or Spontaneous processes that does not require work to be done on the system
 - Non-Spontaneous or artificial process that requires work to be done on the system

Second law defines a state function called entropy (S)
 $S_{universe}$ or S_{total} always increases in the direction of Spontaneous change.
 $\Delta S_{universe} > 0$ for a Spontaneous change
 Note: dS or ΔS measures the change in entropy

So a plant grows into a tree so you first plant a seed and if you water and nutrition from sunlight and all comes and then the seed starts so it's called germination process and you have the seed and then the seeds suddenly gives rise to a very small plant and then the small plant has some leaves and the plant continues to grow and finally it becomes a full grown tree and but the tree itself now if I think of the process in reverse that there is a big tree and the tree is shrinking shrinking shrinking down to the seed that is not going to happen however the seed going becoming bigger in

the form of very big tree say for example is a natural process but if I have to take that big tree and convert it to a seed then it has to be an unnatural process and how much of the energy or work that I have to put in I really do not know but we can measure it we can definitely measure it but what I am trying to say that in case of spontaneous processes or natural processes or irreversible processes you we do not have to supply any work we do not have to do work in a system for a spontaneous process right so that's why for example water kept at 150 degree Celsius in the oven will vaporize so it is it will continue to vaporize unless the surroundings are changed if you change the surroundings in such a way that water starts condensing again that is different issue however unless you change the surroundings the process of evaporation of water that is kept at 150 Celsius at one of the first effervices states inside a oven right the oven temperature is 150 Celsius so if you do not change the surroundings enough water is not going to condense at all and water is continuously going to vaporize so again think of another case balloon you feel the balloon and then keep it in the refrigerator now if you are keeping it in the refrigerator you will start seeing you are kept in the refrigerator what happens the temperature of the balloon and temperature of air inside the both are going down right so the temperatures have decreased now I take the balloon and keep it outside so as soon as I take it outside the balloon expands now it expands again you bring it back to the refrigerator it collapses so you change the if you do not change the surroundings it will not going it is not going to collapse so you can't tell that it's a reversible process it's an irreversible process based on the surroundings that you have put in so for example if you are putting the balloon in the refrigerator and then you are taking it out it will expand now that's actually that expansion is inevitable it has to happen now you again change surroundings then it can contract right or collapse right so that is so you can't say that since the balloon based on the surrounding the balloon has contracted or the balloon has expanded therefore it might be a reversible process no the balloon the process is still irreversible only thing that you are doing is changing the surroundings so for us

The image contains two panels of handwritten text. The left panel features a diagram of a 'SYSTEM' inside 'SURROUNDINGS' with an arrow labeled ΔS_t pointing from the system to the surroundings. Below the diagram are the following equations and definitions:

- $\Delta S_{universe} > 0$ for a natural process
- $\Delta S_{universe} = \Delta S_{system} + \Delta S_{surroundings}$
- ΔS_t - Entropy transfer between the system and the surroundings
- ΔS_p - Entropy production term

The right panel is titled 'What is entropy production?' and contains the following text:

- Spontaneous processes - natural, irreversible
- Water kept at 150°C in a oven will vaporize - unless the surroundings are changed cannot be reversed
- Balloon - fill with air - keep in a refrigerator
- Balloon will expand when taken outside refrigerator. Bring it back to the refrigerator - it will collapse

So if I look at the second laws alternative statement then one very good statement that comes in is for a given system and surroundings there is a natural direction for any process there is a natural direction for any process whether the process is curdling of milk cooking of rice aging of humans

whatever it is you will have a natural direction for any process right given a system in the surroundings or whether it is heat flow or whether it is mass flow so the spontaneity of the process if you want to define we keep the system it is fixed surrounding is fixed for that system and surrounding there is a natural direction for any process and as you can see one of the very important or very famous quotes is that entropy is specific time set right now what does spontaneous process mean so I will talk about again we have given several several examples so I will give another you get another example so if why is this that one of the process in one direction is continuous in the other direction is not because there is something called precipitation of it say for example when you bounce a ball the ball bounces on the floor on a hard floor the ball bounces again bounces but every time it is bouncing it is bouncing well lesser extent and finally at one point of time the ball stops and each bounce the ball is losing its energy and it is losing energy or dissipating its energy as it bounces right so that is one very very important thing that we have to understand about entropy.

For a given system and surrounding, there is a natural direction for any process

"Entropy is time's arrow"

Spontaneous process - Dissipation of energy

Throw a stone in a pond. K.E. of stone is dispersed in the form of water waves upon impact

Surroundings: $\Delta S_t^{surr} + \Delta S_p^{surr} = \Delta S^{surr}$

System: $\Delta S_t^{sys} + \Delta S_p^{sys} = \Delta S^{sys}$

$\Delta S_t^{sys} = -\Delta S_t^{surr}$

$\Delta S_{universe} = \Delta S^{sys} + \Delta S^{surr}$

$\Delta S_p^{sys} = 0$ (Reversible) = $\Delta S_p^{sys} + \Delta S_t^{surr} \gg 0$

$\Delta S_p^{surr} = 0$ (Reversible) $\gg 0$

Entropy basically is a manifestation of the dissipation of energy for example another example if we throw a stone in a pond so there is a so when I am throwing a stone I am imparting kinetic energy to the stone now the stone comes in contact with the pond which is like a steel water is still there immediately as soon as the pond the stone is striking the pond surface you will see that the kinetic energy of the stone basically is getting dispersed in the form of waterways right it will form and you will see this ripples that you will see for example here you can see the ripples that are happening so you have a stone you have thrown it here and then you can see the ripples now think of the reverse process all these ripples come together somehow and it concentrates all the energy here and the stone comes back to you now that is a mighty difficult process means not difficult it's an impossibility right it is naturally impossible that direction you can throw the stone and the stone's kinetic energy dissipates in the form of these waterways that form okay initially the water was still and then you have water waves but these waterways coming back in so waterways are coming going out right they are going out in the this direction now think of these these these guys are coming in that seems not possible and that is not possible why because that is not a natural process unless you do some stuff you do a lot of work these ripples are not going to come in and

concentrate see that point that I am trying to make is that they will concentrate at the center now this concentrated the center to create enough energy that your ball comes back to me or your stone comes back to me that is not something that is going to happen right so it is impossible however dissipation is like your energy is in some sense getting dispersed into various possible states so instead of remaining concentrated is getting dispersed so it is spreading all over so that basically leads to this dissipation leads to a positive entropy production and this dissipation is the one that basically tells whether the process is reversible or irreversible process is spontaneous or artificial so this is something remember entropy is a very interesting subject it is also called material scientists because of the advent of this new class of materials which are high entropy materials again there is a renewed interest in understanding entropy but entropy is something that has always confused us and we have looked at it from very philosophical points of view but I am not going to discuss philosophical points of view here.

For a reversible process
 $\Delta S_{p} = 0$
 $\delta q_{rev} = \delta q_{reversible}$
 δq_{rev} is the heat absorbed during an infinitesimal step in the reversible process
 Let the temperature of the system be T

δq_{rev} is a path function (Not an exact differential)
 Entropy - Dispersion of energy in the form of heat
 T is a state function
 $dS = \frac{\delta q_{rev}}{T}$
 $\Delta S = \int_i^f \frac{\delta q_{rev}}{T} = \int_i^f dS$
 (Note: $\int_i^f \delta q_{rev}$ is marked as 'Wrong' with a red 'X')

I am going to discuss if I know this definition of entropy is it possible to use it in my scheme of things like understanding all these how many principles in the context of understanding the properties of man and that is what I am going to do so now it continues so we have system we have system here we have surroundings here and as you can see entropy transfer how does it happen it happens because there is a heat exchange or energy exchange in the system and you see there is a delta s transfer that is happening towards the system and there is a delta s transfer that is happening towards the surroundings right so you have now look at surrounds now if I just think of surroundings alone and again for whether it is system or whether it is surrounding in all cases what we can do we can divide the change in two parts right one is the entropy transfer part another is the entropy production part that together so these two terms together is giving me delta s surroundings similarly for system I can write this is delta s transfer for the system and this is delta s production for the system which gives you delta s now one thing you have to understand is transfer business so basically heat is exchanged say for example heat is input to the system from the surroundings or it is carried out from the system to the surroundings in both cases what is happening is entropy is transferred because of all this energy exchange and as a result delta s transfer system that is why I wrote this arrow that the delta s transfer system is negative of the delta s transfer in suppose so that means there is transfer system plus delta s transfer surroundings is equal to 0 so delta s universe

which is equal to $\Delta S_{\text{system}} + \Delta S_{\text{surroundings}}$ is nothing but $\Delta S_{\text{production}}$ the system and $\Delta S_{\text{production}}$ of the surroundings of the entropy transfer term that happens between the system and the surroundings right if you interrupt is transferred from say system the surroundings there is also an entropy transfer from the surroundings to the system as a result the ΔS_{total} term goes to 0 so you have now ΔS_p over the system and the surroundings if I sum now if you have ΔS_p you have ΔS_p system and you have ΔS_p surroundings now this as I told that this ΔS_p is the production right it is an entropy production term which can either be which in for natural processes is going to be greater than 0 and for both system and surroundings but it can also be equal to 0 when the process is reversible when the process is reversible $\Delta S_{\text{universe}} = \Delta S_{\text{system}} + \Delta S_{\text{surroundings}} = 0$ for a reversible process that is occurring within the system now remember if a reversible process is occurring in the system it does not necessarily mean that there is a reversible process example in the surroundings also however what I am telling is if it is reversible then that is the only case when $\Delta S_{\text{production}}$ term is 0 otherwise $\Delta S_{\text{production}}$ terms are going to be greater than 0 and that basically dictates or that basically describes the natural direction of the process for a given system and surroundings.

Prove that entropy is a state function

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

$$\delta q_{\text{rev}} = T dS$$

For an arbitrary cyclic process, no matter the path, the integral $\oint \frac{\delta q_{\text{rev}}}{T} = S_f - S_i = 0$

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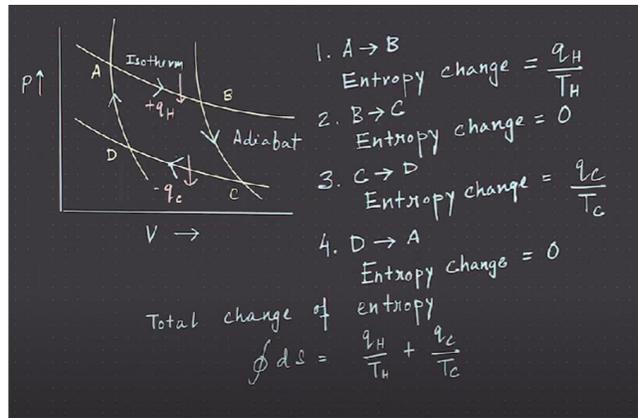
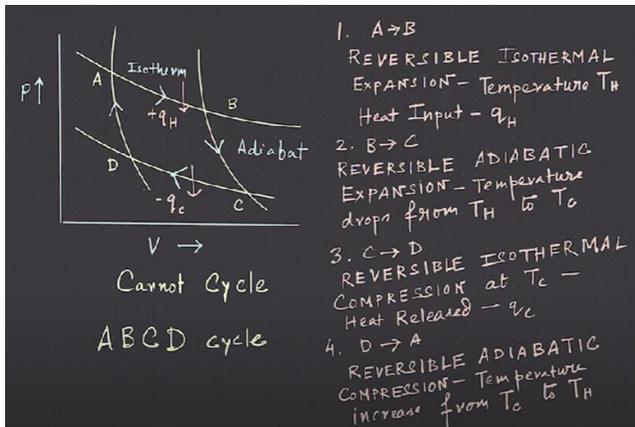
$$\delta q_{\text{rev}} = T dS$$

$S_f - S_i$	\int_i^f
$S_i - S_f$	\int_f^i

For an arbitrary cyclic process, no matter the path, the integral $\oint \frac{\delta q_{\text{rev}}}{T} = S_i - S_f + S_f - S_i = 0$

So as I told again that for a reversible process again that which can be plot and the d-diagram process that basically can be reversed and and it will just refresh the path back and at every point of this reversible process it is so slow it is so infinite every point the system is allow system and surroundings is allowed to take to come to it right now as you can see for a reversible process the system the relative surroundings $\Delta S_{\text{production}}$ is going to be 0 right so that is right now you have let us assume that ΔQ_{rev} okay so we are writing ΔQ_{rev} reversal so this is ΔQ_{rev} is nothing but $\Delta Q_{\text{reversal}}$ and that is like the reversible heat input to a system say for example or heat absorbed by a system giving an infinite similar step in a reversible process and let the temperature of the system be T now as you know as you know very well that ΔQ_{rev} is a path function right it is a it is not an exact differential unlike state functions it means the amount of Q input or amount of Q input to the system or amount of Q extracted from the system is going to be dependent on the path along which the heat was transferred right there are different ways to transfer heat to the surroundings or to the system and it will now if $\Delta Q_{\text{reversal}}$ is a path

function that means it cannot express as an exact differential and another thing it is not only dependent on it is not dependent on the initial states it depends on how that you find out the integral of δQ reversal to get the amount of Q absorbed or amount of Q input to the system or amount of Q absorbed by the system then basically in these cases we need to know what is the path along which this heat transfer has techniques and when I talk about this dispersion of energy in the form see one of the things is when I am throwing a stone there is kinetic energy and then there is this water waves there and the final dispersion that dispersion of energy that happens is in the form of in general it is in the form of thermal waves right not in the form of heat now see a very interesting thing δQ reversible as you have seen is a path function it is a function that depends on the path of the process but T or temperature is a state function that also we know now S we define as a state function now S is defined in a very interesting way dS equals to δQ_{rev} right so there is a greater than dS is going to be equal to exactly equal to because it is a reversible heat transfer δQ_{rev} is the infinite symbol heat transfer in a reversible process otherwise they will be an inequality right so that I have come to but see the point that dS equals to δQ_{rev} right so δS that is the macroscopic change a measurable change is equals to you just have to take an integral from I to F δQ_{rev} by T now if I would have written this so for example I to F and δQ_{rev} is equal to Q then this is completely wrong this is utterly wrong this is wrong however if I take initial and final state and I am writing δQ_{rev} by T and I am telling that this is nothing but this is nothing but I will have dS where S is supposed to be a state function now we have to understand why is it that dS equals to this one where δQ_{rev} definitely is a path function why is it that δQ_{rev} by T is going to be dS or a state function this basically this is a δQ_{rev} by T itself is a measure of a state function and that state function is nothing but entropy so we will consider a very interesting process and these processes are called cyclic processes again it's a cyclic process we are not telling whether it is a reversible process whether it is an irreversible process but it's a cyclic process what does cyclic mean I start with initial so I have you can see here clearly you have an initial process so you start with initial I and you go to F then you come back to I and that is like so from I I go to F from F I come back to I and that is basically a definition of a cyclic process now in such a cyclic process if I have to evaluate this integral this is a cyclic integral or the entire cycle from that means it goes from I it goes to F then F to I so this entire cyclic path you have got you are evaluating the integral then you will see that δQ_{rev} if it is a reversible cyclic process in the cyclic process reversible that is all paths can be present by a on the PV diagram then δQ_{rev} by T is integral of the a cyclic integral of dS and as we know that it is going to be so for example if I go from I to F the entropy change is S_F minus S_I and then from F to I it is S_I minus S_F .



So you have two changes I am borrowing one is from I to F so this is basically S_F minus S_I change and then again you go from F to I S_I minus S_F and as you can see if I add it the entropy change for this cyclic process is going to be 0 right for an arbitrary cyclic process no matter the path this is basically going to be S_I minus S_I if I add them together it is going to be S_I minus S_I right it is basically nothing but I write this way it is basically nothing but S_I minus S_F plus S_F minus S_I which is going to be equal to 0 now we have to say format why this $\Delta Q_{rev} / T$ is a state function for that we define a very interesting cycle cyclic process the thermal cyclic process which is called the Carnot cycle ok and we are telling from A to B there is an isothermal expansion of volume and from B to C there is an adiabatic expansion of volume from C to D there is isothermal contraction of volume and from D to A it is a adiabatic contraction of volume and finally you get an ABCD cycle A B C D C right that is it now as I told A to B is inversely isothermal expansion temperature T_H and at the for isothermal right it is a fixed temperature because assume the temperature is T_H ok and heat input is T_H now B to C is an isothermal adiabatic expansion if it is adiabatic then temperature can drop from T_H so here goes T_H so it is from T_H it has gone to T_C but what about Q? Q is going to be 0 there is no heat transfer right it is an adiabatic process now you go again as a compression right, reversible as a compression at T_C so there is a this temperature from C to D the temperature is T_C it is a nice term with the temperature T_C and then there is a heat released this is something very important the heat released is minus Q and finally from D to A it is a reversible adiabatic compression temperature increases again so if it is compressed adiabatically compressed the temperature increases from T_C to T_H and you have completed the cycle now if I just look at the entropy change according to the definition let us assume that it is $\Delta Q / T$ or Q / T if that is so then I will look at the entropy change so here it is Q_A / T_H here it is Q_C / T_C A to B is Q_H / T_H B to C is 0 because it is adiabatic so because it is adiabatic and remember this is isothermal with temperature T_H right hot and then the C D isotherm is a temperature T_C right again it is an isotherm in the different temperature T_C and so the entropy change in C from C to D is Q_C / T_C now if you see E to A again Q is going to be means there is no Q Q is going to be 0 and T_C has now increased to D you know but if you look at the entropy change of this entire cycle then what you find is that this is nothing but $\oint ds$ in the cyclic integral of ds is nothing but Q_H / T_H plus Q_C / T_C now as you know that for isothermal process you have $\Delta U = T \Delta V$ and since it is isothermal $C V D T$ right

ΔU is $C_V \Delta T$ but ΔT is 0 because it is an isothermal process right ΔU is equal to 0 so Q_H is equal to minus W_H now what we tell reversible isothermal expansion so we can write W_H equals to minus $\int_{V_A}^{V_B} P dV$ and now again we can assume that in the chamber that is undergoing the cyclic process means that the cycle process is undergone by the ideal gas fitted with a piston say for example and also the walls of this chamber are well for the are kept either at a fixed temperature and at T_H and there is also T_C and for the adiabatic processes we are assuming that there is we are not as you know we are enforcing that there is no heat transfer between the system and the surface right there is no heat transfer Q is equal to 0 now as you can see if I use $P = \frac{nRT}{V}$ plus nRT this is something that I have been doing for quite some time and we are putting T_H T_S is your isothermal temperature so it becomes minus $nRT_H \ln \frac{V_B}{V_A}$ okay therefore Q_H is nothing but Q_H is minus W_H which is $nRT_H \ln \frac{V_B}{V_A}$ now again B to C is a adiabatic process so $V_B T_B^\gamma = V_C T_C^\gamma$ to the power γ if remember this is one very interesting thing that you are saying $V_B T_B^\gamma = V_C T_C^\gamma$ and $V_C T_C^\gamma = V_D T_D^\gamma$ now you will tell how is this happening how do you do that so basically instead of writing details in terms of pressure if you write in terms of temperature then you will get this relation T_H by T_H to the power γ T_C by T_C which is equal to V_B by V_C now you have for B to C one isotherm sorry one adiabatic so B to C is an adiabatic process so it is an adiabatic process and what is happening in B to C again have a look at that B to C you have an adiabatic expansion on the other hand when it goes from D to A D to A it is adiabatic compression now you have adiabatic expansion in your compression and you have now here when you did this you wrote $V_B T_B^\gamma = V_C T_C^\gamma$ this is your V_B and V_B was at a temperature T_H V_C was at a temperature T_C so you get $V_B T_H^\gamma = V_C T_C^\gamma$ equal to $V_C T_C^\gamma = V_D T_D^\gamma$ as you can see $V_D T_D^\gamma = V_A T_A^\gamma$ so here it becomes $V_B T_H^\gamma = V_A T_A^\gamma$ that is what I mean now similarly from D to A the same thing happens now what I am doing is I am multiplying this way.

$A \rightarrow B$ $\Delta U = q + W$
 Isothermal $\Rightarrow \Delta U = 0$ $q_H = -W_H$
 $W_H = - \int_{V_A}^{V_B} P dV$ $P = nRT$
 $= - nRT_H \ln \left(\frac{V_B}{V_A} \right)$
 $q_H = nRT_H \ln \left(\frac{V_B}{V_A} \right)$
 $\left(\frac{T_f}{T_i} \right)^\gamma = \frac{V_i}{V_f}$
 $B \rightarrow C$ Adiabatic expansion $V_B T_H^\gamma = V_C T_C^\gamma$
 $D \rightarrow A$ Adiabatic compression $V_D T_C^\gamma = V_A T_H^\gamma$
 $V_A V_C T_H^\gamma T_C^\gamma = V_B V_D T_H^\gamma T_C^\gamma$

$V_A V_C = V_B V_D$
 or, $\frac{V_A}{V_B} = \frac{V_D}{V_C}$
 $C \rightarrow D$ Isothermal compression
 $q_C = -W_C = nRT_C \ln \left(\frac{V_D}{V_C} \right) = nRT_C \ln \left(\frac{V_A}{V_B} \right)$
 $= -nRT_C \ln \left(\frac{V_B}{V_A} \right)$
 $\frac{q_H}{q_C} = - \frac{nRT_H \ln \left(\frac{V_B}{V_A} \right)}{nRT_C \ln \left(\frac{V_B}{V_A} \right)} = - \frac{T_H}{T_C}$

I am multiplying this term I take this term and multiply with this term and I take this term and I multiply with this term so what we get is $V_A V_C T_H^\gamma T_C^\gamma$ and this is $V_B V_D T_H^\gamma T_C^\gamma$ to the power γ is equal to $V_A V_C T_H^\gamma T_C^\gamma$ or what you can write is $V_A V_B V_A V_C$ equals to $V_B V_D V_A V_C$ so that is what I have written $V_A V_C$ equals to $V_B V_D$ or V_A by V_B equal to V_D by V_C now if you see Q_C is equal to minus W_C that is again an isothermal

process that is an isothermal compression from V_C it has come to V_B now Q_C again the same formula if I write and you are taking ideal gas I get $n r T_C \ln V_i / V$ so Q_C is minus $n r T_C \ln V / V_A$ so Q_H by Q_C if I do so I have $n r T_H Q_H$ is $n r T_H \ln V / V_A$ and this is minus $n r T_C \ln V / V_A$ which is nothing but T_H by V_C with a minus sign see remember there is a minus sign and it becomes so V by $n r V$ by V_A gets cancelled so you have $n r n r$ gets cancelled so you have only T_H here and T_C now if you have that as I told in corner cycle the cyclic integral of dS is Q_H by T_H plus Q_C by T_C now Q_H by T_H according to this machine Q_H by T_H is minus Q_C by T_C so it is right Q_H by Q_C minus T_H by T_C so if I take this guy here and Q_H by T_H and this Q_H by T_H and this is here so this becomes Q_C by T_C and there is a minus sign and this is Q_H by T_C right so Q_C has been taken that way so basically you get you can easily see that you can do it and see that that minus Q_C by T_C plus Q_C by T_C is equal to 0 so definitely for an ideal gas we have proved that indeed the cyclic integral of $\delta Q / T$ is going to be 0 so definitely we can see that it has that means $\delta Q / T$ has to be a state function right because it will depend only on the as as we told that S_i minus S_i the cyclic integral of dS is nothing but S_i minus S_i if S is a state function because we are proving that the quantity $\delta Q / T$ remember don't write it as d let us not be confused here $\delta Q / T$ is integral the cyclic integral of dS which is 0 and we told that we insisted that S has to be a state function but we are also showing just based on the standard cycle with ideal gas but remember there is one very small and interesting point here we have proved that for a cyclic process indeed $\delta Q / T$ it is cyclic reversible cyclic process $\delta Q / T$ indeed is 0 but for that proof we used a substance which is an ideal gas however we should prove that entropy is a state function irrespective of whatever substance we are taking right and that is something we can we can look at another thing that i want to tell you that because of this cycle and recyclers are sometimes used to are basically used in heating means heating means are made of recycles i think they make use of recycles to get the sub work done so as you can see here then you can define something called an efficiency of an engine so this is an efficiency of a heat engine and that is nothing but work performed by heat engine right so it is mod of W that is the work performed by heat engine okay so in the next class we will go further into it and we will try to see whether it is true for general substances that entropy is indeed a state function that we can prove and very simple and is improved so and we will go from there in the next class so thank you so much.

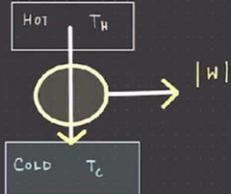
CARNOT CYCLE

$$\oint dS = \frac{q_H}{T_H} + \frac{q_C}{T_C} = -\frac{q_C}{T_C} + \frac{q_C}{T_C} = 0$$

$$\frac{q_H}{q_C} = -\frac{T_H}{T_C} \Rightarrow \frac{q_H}{T_H} = -\frac{q_C}{T_C}$$

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

Define efficiency of a heat engine $\epsilon = \frac{\text{work performed}}{\text{heat absorbed}} = \frac{|W|}{q_H}$

$$\epsilon = \frac{q_H + q_C}{q_C} = 1 + \frac{q_C}{q_H} = 1 - \frac{T_C}{T_H}$$


If T_C is fixed, we want to make T_H as large as possible