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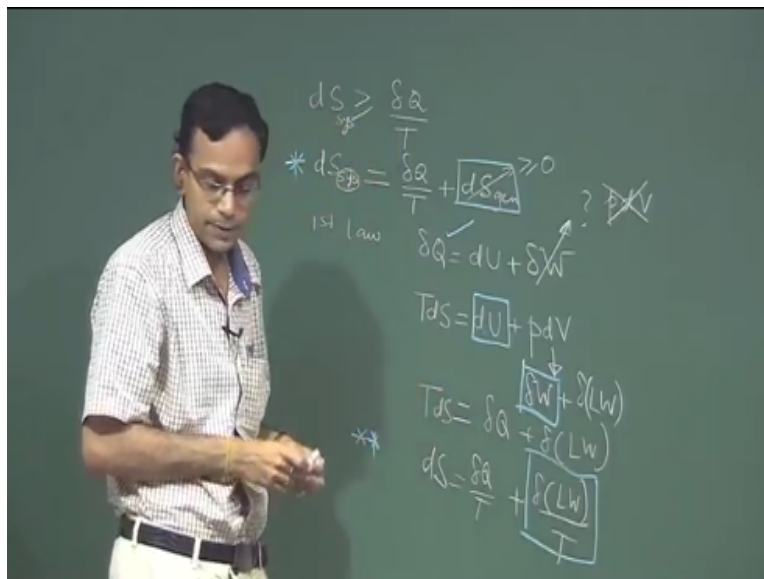
**Course  
on  
Laws of Thermodynamics**

**by  
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**Lecture 18: Entropy And its Transport**

So far we have discussed various phases of entropy transport and we will continue with that and the specific agenda of today's discussion we will to mathematically discuss the various aspects that come with the derivation of change in entropy of a system for a control mass system as well as for a flow process so to begin with I will try to draw your attention on the following inequality.

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$ds_{system} \geq \delta Q / T$  so this is something which is I think the most important inequality that we talk about when we discuss about the change in entropy so what is this  $T$  something which is very important and we will go through that through various teasing questions and exercises in the

subsequent two three modules but this T conceptually is the temperature of the system bounded here across which this  $\Delta$  heat transfer is taking place, so it is not any orbiter T it is the temperature of that system bounded here across which the heat transfer is taking place for which you're calculating this ds system.

So now you can also write this or convert this inequality in the form of an equality so you can write ds system is equal to  $\partial Q / T +$  entropy generation which is  $\geq 0$  this is for a system now of course the mathematical objective is satisfied here that we all understand that this terminology is introduced to convert the inequality to an equality but what is the physical significance of this in the context of heat and work we have to understand that entropy generation is a general conceptual paradigm it should not always be associated with heat transfer.

It could be associated with flow of information in an information system and so but here we are considering the heat transfer as an example, so now we can write so let us do let us do a different exercise let us write the 1<sup>st</sup> law for a system as  $\partial Q$  again we are not considering the change in kinetic energy and potential energy because we are considering that the thermal effects are more important.

So now in place of  $\partial Q$  can we write TDS the answer is we can write TDS only for reversible process if it is not reversible process we cannot write  $\partial Q = TDS$  now what is  $\partial W$  so in place of  $\partial W$  we can write the following the first question that let me ask me you that can be written this  $Pdv$ , okay so can we write as  $Pdv$  what is your answer, so let think about it let us say that we are instead of this we are writing  $\partial Q = TDS$  so if we do that then in place of  $\partial W$  we can write  $Pdv$  with an understanding that we are talking about a simple complex substance.

So that the work is only  $Pdv$  work but the  $Pdv$  work is not the work that you can get as output when that you get as output when the process is irreversible so the question is when the process is irreversible what is the work that you get when the process is irreversible the work that you get as an output should be less than  $Pdv$  that means because of irreversibility the irreversibility may be associated with friction free expansion whatever you are losing an opportunity of doing work so you can write  $Pdv$  your actual  $\partial W +$  some  $\delta LW$  which is something positive so the last work is 0 when it is reversible process.

So that it will be  $pdV$  but if it is not a reversible process then you have last work, so technically speaking you cannot write  $LW = pdV$  always so when you write this  $TdS = dU + \delta W + \delta LW$  let me show let me try to use here so  $dU + \delta W$  this together from here you can write  $\delta Q$  so  $TdS = \delta Q + \delta LW$ , so that means  $dS$  so when we write  $dS$  we mean  $dS$  system not always we are writing the sub secrete  $dS$  system so  $dS = \delta Q \text{ over } T + \delta LW \text{ over } T$ .

So now compare this \* with \*\* okay compare the \* with \*\* okay so we can write if you compare the \* with the \*\* we can clearly write that this entropy generation is nothing but this  $LW/T$  that means entropy generation is always associated with the last opportunity of doing one that can be taken as a physical interpretation of entropy generation in a system where you are trying to use some heat transfer to convert that into work so if you are using some heat transfer to convert that into work there is a maximum potential of that heat to be converted to work, but you may not be able to utilize that maximum potential.

Because of entropy generation or irreversibility in the system, so physically you may have last opportunity of doing work for last work, so this is the first physical interpretation that I want to give and then using the same inequality let me try to give you a different prospect let us give an example.

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Ex  $P = P_0, T = T_0$

$$dS \geq \frac{\delta Q}{T}$$

$$\delta Q \leq T dS \Rightarrow d(T_0 S)$$

$\leq 0$   
1st Law

$$dU + \delta W$$

$$d(U + P_0 V) - T_0 dS \leq 0$$

$\Rightarrow d(H - T_0 S) \leq 0$

$\delta dV$  (quasiequilibrium / internally reversible)

Where you have process with  $P = P_0$  and  $T = T_0$  that is pressure and temperature they are kept as constant but still there is a change within the system how is it possible, remember that for system to be in equilibrium it has to be mechanically equilibrium thermal equilibrium and phase and chemical equilibrium, so these two indicate mechanical and thermal equilibrium but it does not guarantee in phase and chemical equilibrium, so they are put still be a change within the system even if you keep.

These two same and let us consider certain such a change so we can write again for such a system  $dS \geq \frac{\delta Q}{T}$  and again this  $T$  is absolute temperature by this time you know very well that in when you are considering something in the context of second law that  $T$  is absolute temperature, so now you can write  $\delta Q \leq T dS$  if you apply the first law in place of  $\delta Q$  you can write  $dU + \delta W$  neglecting changes in kinetic energy and potential energy when can you write this  $\delta W$  as  $p dV$ .

When it is a internally reversible process or pass equilibrium process so pass equilibrium or internally reversible these two terms are equivalent or internally reversible, so now this is a process where  $T$  is kept as constant so you can write  $T dS$  or rather sorry I have written  $\delta U$  by mistake, so  $dU + p dV$  you can write  $d(U + P_0 V)$  because  $P_0$  is a constant you can take it within the difference here, so  $d(U + P_0 V)$  similarly this you can write as  $d(T_0 S)$  so  $d(U + P_0 V - T_0 S) \leq 0$  this means  $d$  of what is  $u + p v$ ,  $U + PV$  is the enthalpy  $H$  so  $d(H)$  with reference

to pressure  $P_0 - T_0 S \leq 0$ , so here we come up with another mathematical function which is a combination of properties this we call as Gibb's function or Gibb's free energy of the system.

So  $dG$  so that means we can say that any spontaneous process will take place if at a constant temperature and pressure the Gibb's function or Gibb's free energy is decreasing so a spontaneous process cannot take place if the Gibb's free energy is increasing and it comes to equilibrium when it is a minimum that there is no further change in the Gibb's free energy.

So why I am telling you this because in this particular course we do not have a lot of scope of discussing about the Gibb's function and its interpretation in the context of phase and chemical equilibrium but I want to give you a very basic elementary physical picture on the Gibb's function its physical interpretation so you can see that these  $G$  therefore is the driving force for a chemical change to take place or driving force for a phase change to take place.

And we have already discussed that for a phase or chemical equilibrium the chemical potential concept with the picture and that chemical potential is linked with the partial molar Gibb's function. Now in the two examples that we have consider in this today's lecture so far we have considered the cases of irreversible situations but let us consider an example where we consider reversible adiabatic process of an ideal gas.

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Ex: Reversible adiabatic process of an ideal gas

1st Law:  $\delta Q = dU + \delta W$  (rev)  $\Rightarrow \delta Q = 0$

$$0 = C_v \frac{p dv + v dp}{p} + p dv$$

$$0 = \frac{C_v + R}{p} p dv + C_v v dp$$

$$0 = \gamma p dv + v dp$$

$$0 = \gamma \frac{dv}{v} + \frac{dp}{p} \Rightarrow \gamma \ln v + \ln p = \ln c$$

$$\Rightarrow p v^\gamma = c$$

Eq. of state:  $pV = RT \Rightarrow p v = RT$

$$p dv + v dp = R dT$$

$$dT = \frac{p dv + v dp}{R}$$

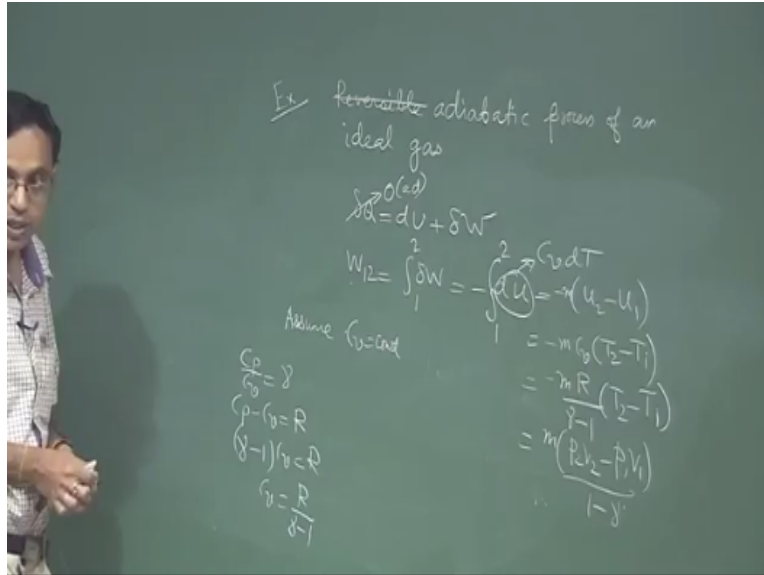
So let us apply the first law and second law for this, so let us apply the first law.  $\delta Q = DU + \delta W$  now because it is reversible you can write this PDV Ideal gas we consider it to be a simple compressible substance with the pressure volume temperature changes are more important than other changes and because it is adiabatic this is 0 so you can say so this PDV is for reversible and this is for adiabatic.

So we have used both the considerations of reversible and adiabatic now for an ideal gas DU is CVDT this we already discussed in one of our previous lectures and we know for an ideal gas the equation of state is  $PV = RT$  so let us apply it for a unit mass so if you so this will be M CVDT if it is total mass so if you apply per unit mass it will be  $CV0 = CVDT + P \times d$  of specific volume, right.

So for an ideal gas you can write  $P \times$  specific volume  $= RT$  so if you take the differential of both sides you have  $PDV + VDP$  is  $RDT$ . So you can write  $DT$  is  $PDV + VDP/R$ , let us substitute this here so if you substitute this here then you get  $0 = CV PDV + VDP/R + PDV$ . So you can write  $0 = CV + R PDV + CV VDP$ ,  $CV + R$  is  $CP$  and if you divide both sides by  $CV$  then you have  $CP/CV = \gamma$ . So  $0 = \gamma PDV + VDP$  so you can divide both sides by  $PV$  and what you get is  $0 = \gamma dv/v + dp/p$  so you can divide both sides by  $pv$  and what you get is  $0 = \gamma dv/v + dp/p$  so if you integrate now you will get  $\gamma \ln v + \ln p = \ln c$  or this means  $p v^\gamma = \text{constant}$ , so this shows that for a reversible adiabatic process of an ideal gas the pressure volume will essentially shows that  $p v^\gamma = \text{constant}$ .

With this back ground now let me give you a teaser, so let me relax the condition that it is a reversible process, this is the next example it is an adiabatic process of an ideal gas but need not be reversible that is the next example, so what happens here.

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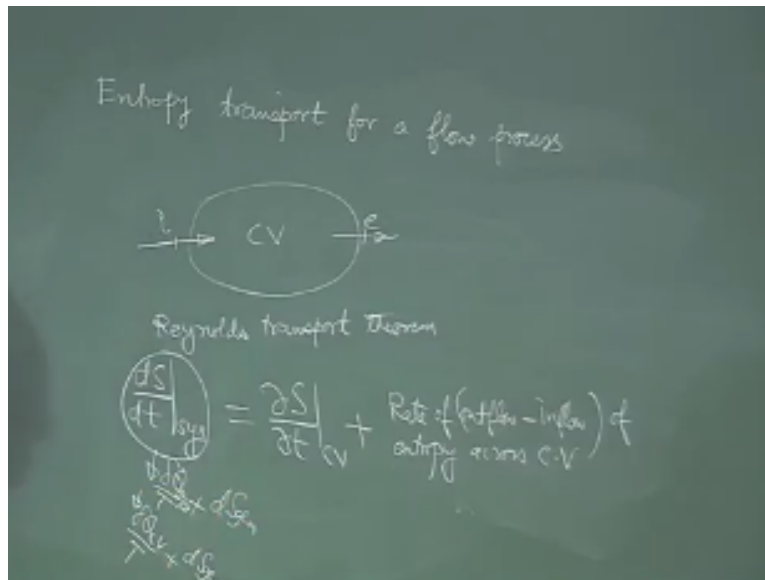
So  $\delta Q = du + W$  by the way for the reversible adiabatic process of an ideal gas if you have  $p v^\gamma =$  constant the work done we have already seen that is integral  $p dv$  so  $p_2 v_2 - p_1 v_1 / 1 - \gamma$  in the chapter of heat and watt we have derived this, we can example of a reversible polytropic process we have air we have use the index  $n$  here just use  $\gamma$  instead of  $n$ . Now we will find out the work done here, so it is a adiabatic therefore  $\delta Q$  is 0 it is not reversible.

So we cannot write  $\delta W = p dv$  so  $W_{12} = \int \delta W$  from state 1 to state 2 is equal to  $-du$  integral of this, so  $-(u_2 - u_1)$ . So as an example, assume so  $du$  is what so this is per unit mass so  $m \cdot du$  so  $m \cdot u_2 - u_1$  so assume  $C_v = \text{constant}$ , so this if you assume  $C_v = \text{constant}$  this is then becomes  $m C_v (T_2 - T_1)$ . So now you know that you can write  $C_p / C_v = \gamma$  and  $C_p - C_v = R$  so from this you can write  $C_v$  in terms of  $R$   $C_p$  you can write as  $\gamma C_v$  so  $\gamma - 1$   $C_v = R$  so  $C_v = R / (\gamma - 1)$ .

So  $-mR /$  or minus you can absorb okay,  $-mR / (\gamma - 1)$  so you can write  $R(T_{spv})$  so this you can write  $(p_2 v_2 - p_1 v_1) / 1 - \gamma$  this is something which is bound to create a confusion within you that with the reversible adiabatic process whatever answer we got as work done the same answer we have got as work done when we relax the requirement of reversible process, so the work is becoming same for reversible and irreversible process so where is the fallacy.

Actually the work done  $p_2v_2 - p_1v_1 / 1 - \gamma$  is true for a reversible process even if  $C_p$  and  $C_v$  are functions of temperature, but for an irreversible process we show that this is true only if  $C_p$ ,  $C_v$  are constants otherwise this integration cannot be done in this way. So this is true only for calorically perfect gas, but not for all ideal gases. Calorically perfect means only when  $C_p$ ,  $C_v$  is constant but if  $C_p$ ,  $C_v$  is not constant then we cannot use this, okay. The next agenda will be to discuss about.

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Entropy transport for a flow process, so let us say that there is a control volume there is some inflow boundary there is some outflow boundary, so we can write the entropy transport across the control volume in terms of the entropy transport of a control mass system, why we intend to write it in this way is because we already know how to describe the entropy transport through across a control mass system. So we want to use that to extend it to the entropy transport for a control volume so for control mass system we have already read the  $ds = \partial q / T + d$  of entropy generation.

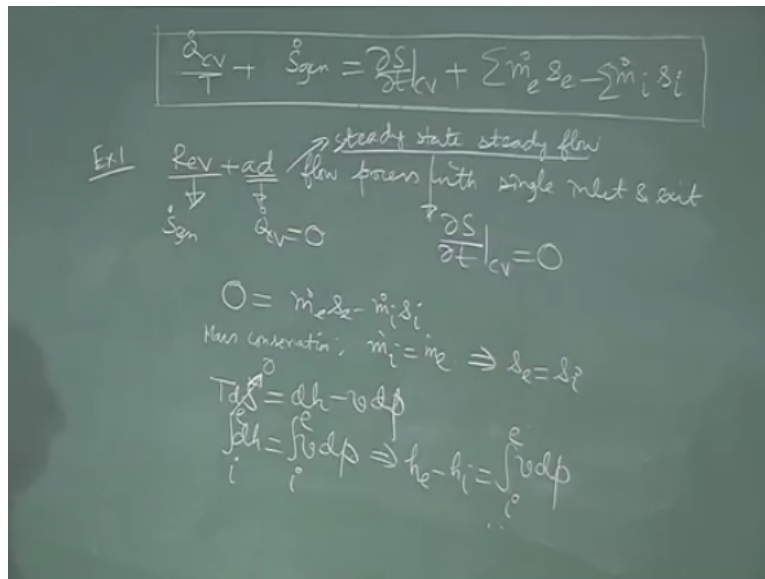
So that means we know what is  $ds$  of with respect to system so now we want to apply that to  $ds$  with respect to control volume so what we want to do is something like this let us say that we apply the Reynolds transport theorem, so I am straight away writing it for taking the property as  $s$  it could be any general extensive property so  $ds/dt$  for with respect to the system is  $\partial s / \partial t$  with



respect to the control volume plus rate of outflow minus inflow of entropy across the control volume.

So instead of entropy we could use any property but as an example we are using entropy as a property now what is  $ds/dt$  of the system this is  $\partial q/T + ds_{gen}$  this  $\partial q/T$  is the  $\partial q$  system but in the derivation of Reynolds transport theorem what is considered is that there is a control mass system which is going inside with this control volume in the limit as that time  $\partial t$  that is under consideration is  $\Delta t \rightarrow 0$ . So when the control mass system is almost coincident with this control volume that means the  $\delta q$  of the system will be same as  $\delta q$  control volume, so this will become  $\delta q_{cv}/t + ds_j$ .

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Therefore we can write  $\delta q_{cv}/t + Ds_{gen} = \partial s/\partial t|_{cv} + \text{rate of outflow} - \text{inflow of entropy}$  is  $\sum \dot{m}_e s_e - \sum \dot{m}_i s_i$  this gives what is  $\dot{m}$  is the mass flow rate this is waste on the assumption that across the inflow and the outflow boundaries this is inflow boundary this is outflow boundary there could be many inflow and many outflow boundaries across each boundary the property is

uniform so that the total property you can just simply write mass flow rate times the entropy that particular section so this can be thought of as an average specific entropy over the section across which the transport is taking place.

So this is so you can write so you can write this equation or this particular equation as an equation that commands the entropy transport during a flow process, so let me give you one example we will talk about two examples first example reversible and adiabatic flow process with single inlet and exit, so because it is adiabatic you have so one particular in this expression one particular thing which we have missed is that the right hand side is expressed on the rate equation.

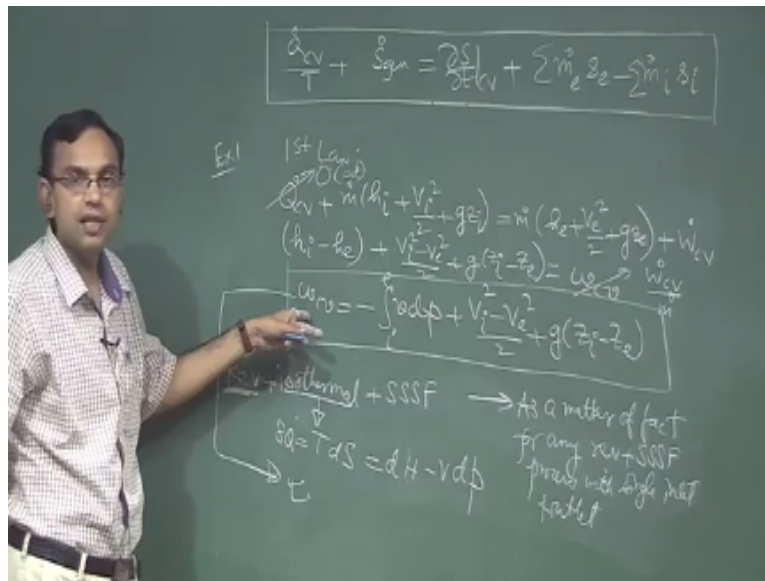
So left hand side should also be expressed as a rate equation so instead of  $ds$  this it will be  $s \cdot$  gen that is the rate of entropy generation and this will be  $Q_{CV}/t$  so the important thing that we have made important consideration we have made is that right hand side we have expressed on the rate equation in a transport theorem so that left hand side should also be expressed on the rate equation.

The expression for the second law that we have used  $S_2 - S_1 = Q/t +$  entropy generation that is not the rate that is the total change so we divide that by time  $\Delta t$  and take the Kelvin as  $\Delta t$  is used so  $Q_{CV} / \Delta t$  is 0 reversible means entropy generation is here let us consider that in addition to this reversible adiabatic steady state steady flow process this is very important.

A reversible adiabatic steady state steady flow process so if you considering this steady state steady flow process what is essentially means that there is no change of property within the control volume so steady state steady flow process there is no change in the property within the control volume and single inlet and single outlet means this  $\dot{E}$  will be replaced by just you can write 0 is equal to  $m_e s_e - m_i s_i$ .

And the mass conservation is  $m_e$  is equal to  $m_i$  so you can write  $s_e$  is equal to  $s_i$  so this is true for reversible and adiabatic process so this kind of process is also called as isentropic process because the entropy remains constant throughout the process now let us applied the  $Tds$  relationship you can apply the  $Tds$  relationship for any process so you can write  $Tds$  equal to  $D_H - Tdp$  so now you apply this there is no change in the entropy during the process, so this is 0 so  $D_H$  is equal to  $Tdp$  so  $i$  to  $e$  this is  $I$  to  $e$  so  $H_e - H_i$  is equal to integral of  $Tdp$  from  $i$  to  $e$

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Now let us apply the first law so  $\dot{Q}_{cv} + \dot{m} \cdot (h_i + V_i^2/2 + gz_i) = \dot{m} \cdot (h_e + V_e^2/2 + gz_e) + \dot{W}_{cv}$  what is  $\dot{W}_{cv}$  is  $\dot{W}_{cv} / \dot{m}$  dot okay. Now look at this equation  $h_i - h_e = - \int v dp$  so you can write  $\dot{W}_{cv}$  integral of  $V dp$  from I to e +  $V_i^2 - V_e^2 / 2 + g z_i - z_e$ , this is true for reversible adiabatic process. If you consider the isothermal process reversible + isothermal + steady state steady flow, so for the isothermal process so we are replacing the adiabatic process by isothermal process, so isothermal process because it is reversible isothermal process you can write  $\dot{Q} =$  or  $\Delta Q = T ds$ .

And  $T ds$  you can write as  $dh - v dp$ , so this you can always write okay, so in place of the heat transfer now you could, now you cannot write 0 but you can write  $T ds$  in place of  $T ds$  you can write  $dh - v dp$ . So if you write  $dh - v dp$  then you will see that the work done expression comes out to be the same. You just substitute this  $\Delta Q$  as  $T ds$  and  $dh - v dp$  and put it in the expression for the first law. So instead of it will come out to be  $\dot{m} \cdot (h_2 - h_1 - \int v dp)$ , where small  $v$  is the specific volume.

So you will see that you will get the same expression for the work done, so we are consider two limiting cases one reversible adiabatic and one is reversible infact any reversible process it does not need to be isothermal because here we are not consider any where the  $t$  is constant, we have just used  $Tds$  this  $t$  itself could be a variable therefore we have not committed the  $t$  is the constant so reversible isothermal is a special case but it could be any general process.

So for any reversible process, so as a matter of fact for any reversible steady state steady flow process with single inlet and outlet, this is the expression that we get for the work done per unit mass, it is very important expression and we will take up with this expression and go further for our next lecture thank you very much.