# Indian Institute of Technology Madras

# NPTEL

# National Programme on Technology Enhanced Learning

# CHEMICAL ENGINEERING THERMODYNAMICS

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## Lecture 4

## Equilibrium and Extrema in Work

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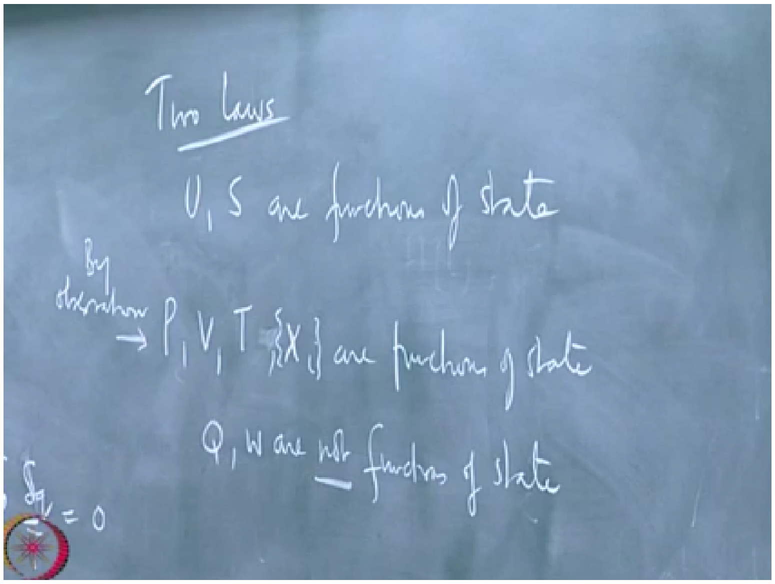

Two laws

U, S are functions of state

By observation → P, V, T $\{X_i\}$ are functions of state

Q, W are not functions of state

$\delta q_v = 0$

We just discovered the two laws are simply two statements U, S are functions of state with that you make you have all the classical derivations in essentially all of mechanical engineering all of heat work conversion devices all the results can be derived by just make the statement the natural corollary is and if you are in questionable suit is there a 3rd law is there another property that is a functional state.

So far nobody has found anything except by adding subtracting now you can do U-TS you can do U + PV – TS you can play games you already know some functions of state that is these are known to be functions of state composition are functions of state this moral fraction and say the set of composition are functions of states these this is known by observation okay by observation, these are known to be functions of state by observation you will know that Q and w are not functions of states.

Since leave the two law said these are the only observable properties and it said while Q and W are nor functions of state I can find two functions of state that are related to Q and W one was simply $\delta Q - \delta W$ which is DU or U = Q – W for a close system, in the other which is much more settled verse this entropy the second law is probably the greatest discovery of the 19th century so basically the concept here has far as an entropy is concern entropy is a very prefund concept and what you have is apart from these functions of state you have other functions of state that keep occurring again and again.

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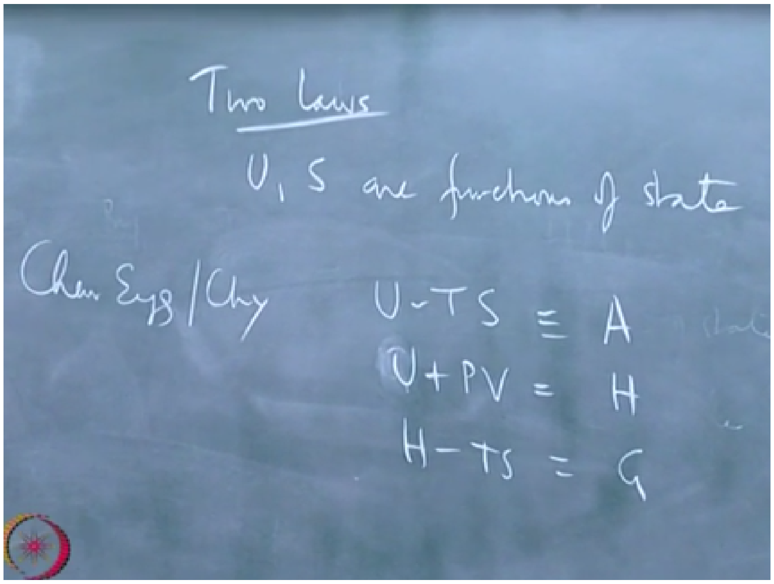

Two laws

U, S are functions of state

Chem Engg / Chy

$U - TS = A$

$U + PV = H$

$H - TS = G$

As far as chemical engineering is concerned or chemical engineering and chemistry if you like we have another additional functions the together functions of state that they have found are only combinations you have U – TS which is called A you have U + PV which is called enthalpy and then H – TS which is called the Gibbs free energy, you can generate any number of them you know if your perverse you can put $T^{1/2}$ here that is also a function of state.

Any function of a function of state is a functional state so you can combine any of number of these and produce these and only you will be interested in them I mean if sufficient number of people get interested gets a name so this is Helmholtz free energy turns out this is very important I will show that very quickly why this is of great importance similarly enthalpy is very important in some cases the free energy Gibbs free energy very important some cases specifically I will tell you result we are going to show when you are looking at equilibrium I am going to show at depending on the variables that I have able to held constant if you are looking at systems with constant T and V constant temperature constant volume.

I will show that equilibrium is attained when A is a minimum therefore A is important keeps coming again and again I am going derive this result you I am going to show you that whenever T and P are held constant pressure and temperature which is what happens in flow process and the chemical industry equilibrium is attained when G is a minima therefore A and G are very important.

Actually you could use U and H you can show that U is a minimum when V and entropy are held constant but you do not have an entropy meter so in a way you can stick meter and say this process as entropy constant you can talk about adiabatic process, that is the same thing as isotropic process similarly you can use enthalpy if it is S and P that are held constant so we will show these results.

But the useful results are those in which the constrains are meaningful T and V being constant very meaningful for close systems T and P being constant are very meaningful for open systems the other result that you will get is that in a isothermal system the maximum work you can get out of a close system is the change in the Helmholtz free energy that is of great interest what is the maximum work you get out of a system or what is the minimum work you can get away with.

It is not has student phenomena alone even the most per found scientist are looking for what is the minimum work they can get away with but they are asking much more deeper question then just questions of laziness but actually it is a not a bad idea to do the minimum work and get maximum results but you have to do it you have to integrate it over a 50 year period if you are looking \it very short term gains then you play the penalty later that is all.

$\delta$G again is the maximum work you can get out of a system actually – $\delta$ is there be sign changes but the change in the Gibbs free energy is the maximum work you can get out of an isothermal flow system, so these are the only important results in thermodynamics almost all results are derived out of this,.

But you are dealing with multi components systems and composition dependence is where there is ambiguity in thermodynamics, so we will get started and discuss U and S as functions of state and discuss the differential relations and you can do calculus only wit functions of state you cannot write calico equations of calculus with Q and W because they are not functions of state.

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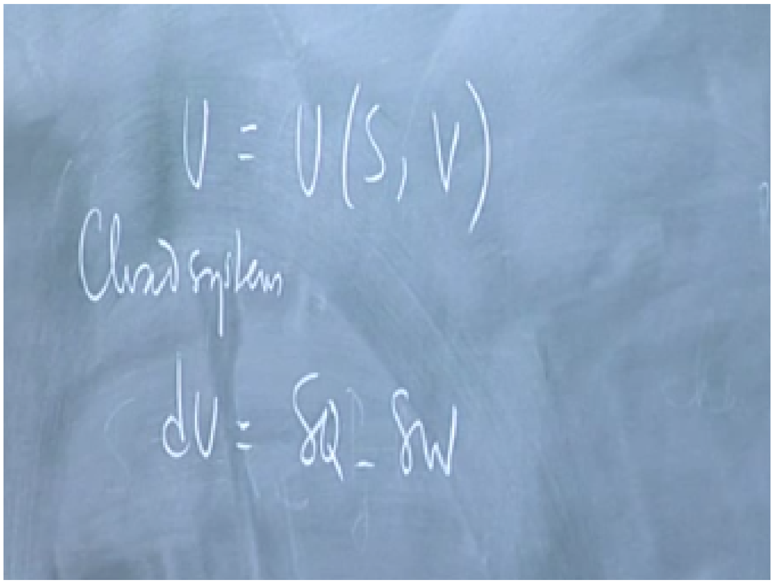

$$U = U(S, V)$$

Closed system

$$dU = \delta Q - \delta W$$

So the first point is U is a function of S and V, V is a natural variables or let me start of the first law tell you DU = $\delta$Q – $\delta$W I am going to deal with close systems Then depending on the system that you are dealing with.

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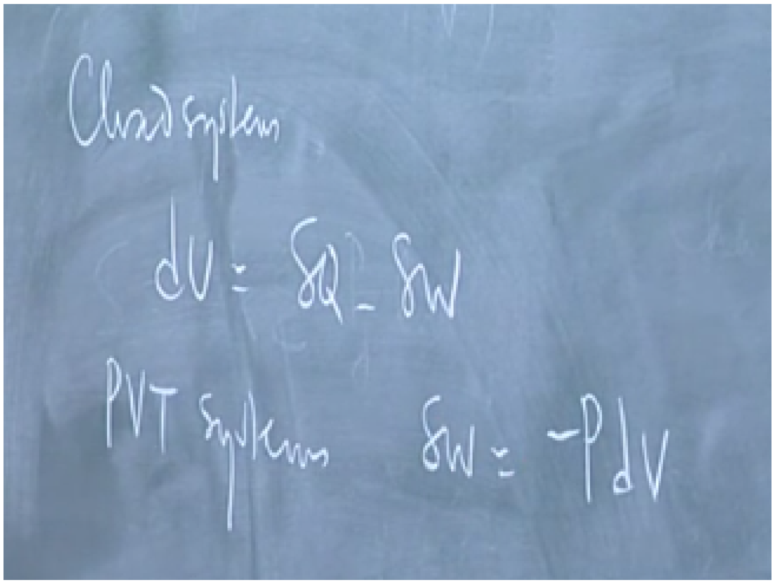

Closed system

$dU = \delta Q - \delta W$

PVT systems $\delta W = -PdV$

Which is PVT so called PVT systems which is what you deal with very often $\delta$W = -PdV or $\delta$W = PdV sorry I will leave it I will come back to the chain conversion PdV is the work down by the system $\delta$W is PdV so this becomes.

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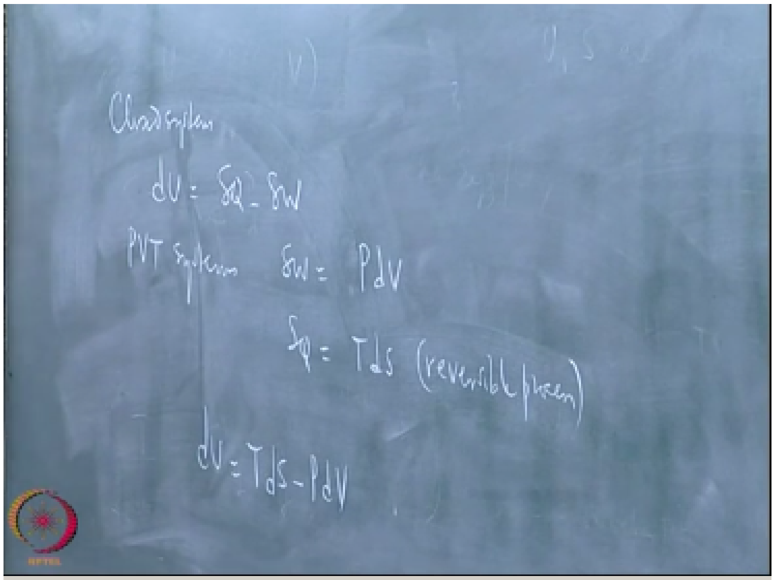

And $\delta$Q = TdS for a revisable system I will come to this because $\delta$Q/ T was defined as DS so you get this result TU – dU = Tds – PdV is actually combine form of the two laws the second law itself the laws can be stated very simply while I said you in lesser function so state the laws are simply stated like this.

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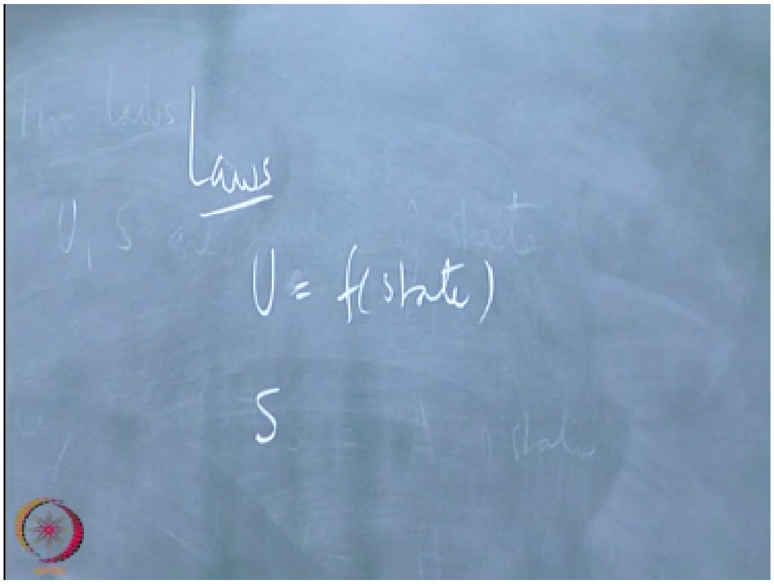

Laws

U = f(state)

S

You say U is the function of state that is all then you saying S = maximum and I should rewrite the S.

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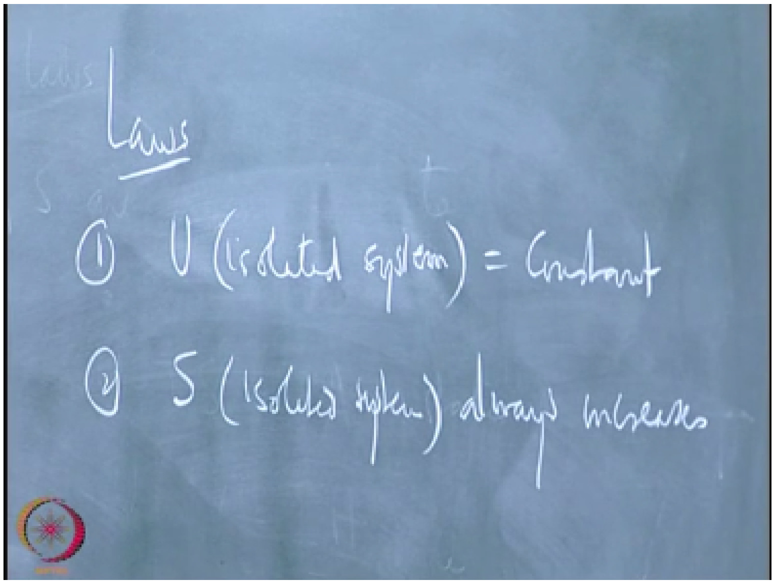

Laws

① U (isolated system) = Constant

② S (isolated system) always increases

Sorry I should say U of the of an isolated system = constant and S for an isolated system always increases these are actually the statement of the two laws for as we concern going a bit dark and forth but partly because you know the these some of these results this is one way of stating it as far as calculus is concerned is far as equilibrium systems are concerned all unit to know is that U and function of state, to derive maximum minima you have to make the statements in terms of the laws itself.

And once we have said this let me rewrite this and slightly different fashion this is alright, then we have to rewrite this.

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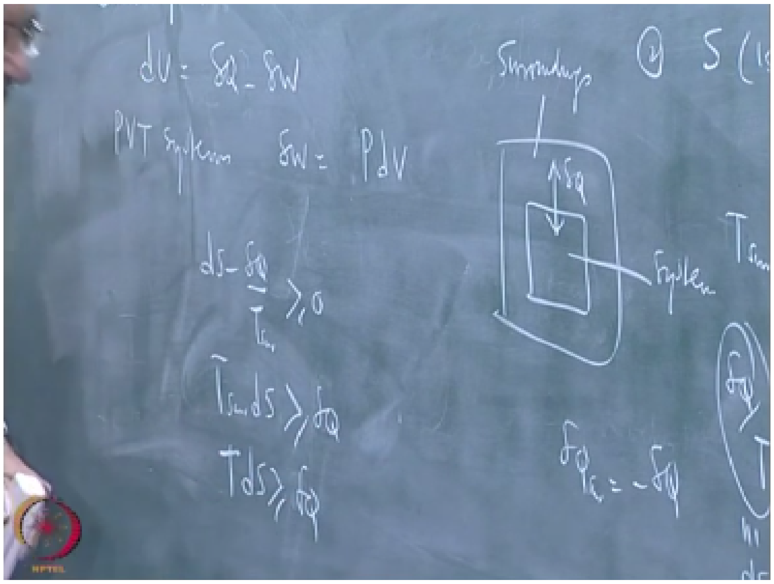

Suppose I have system and then I have surrounding then I have an exchange of heat between the system and the surroundings, now if the heat is coming into the system the surrounding temperature has to be higher than the system temperature so let me say T surroundings < T system then $\delta Q$ is < 0 everything all the science refried to the system of interest not the surroundings, so when I say $\delta Q < 0$ that means the system observed heat the convention I use is that if heat is observed it is positive.

If work is done by the system which positive the new books have an opposite convention work done on the system is taken as positive but in terms of these variables so mine would be $\delta w = PdV$ according to the new a U pattern I mentions not only new more than 20 years old but lots of books use either convection the convention is that anything that increases the energy of a system is positive, so a work is done by the system it louses energy so work done on the system is concerned positive.

So you will find a – sign here but those that have a – here will have a + here, so in terms of measurable variables the equations will be the same we just use any convention you want but we consist and I am not going to take Q by asking those by or on you will that you can figure that out by common sense, so if this is two if $\delta Q$ is the $\delta Q$ / T, T system will be just defined as T $\delta Q/T$ is the energy observed by the system and if I take the surroundings $\delta Q$ surroundings by T surroundings.

Is greater than equal to 0 because I surrounding plus system constitute and isolated system and the laws is valid only for an isolated system, this $\delta$Q surroundings = - $\delta$Q is a far s surrounding is concerned the heated that it receives is the heat lost by the system so and dQ / T $\delta$Q /T is defined as dS and the for initial change in differential quaniitity heat being transferred therefore I do not have to worry about that it actual process is reversible that is reversible, so I have dS – $\delta$Q / T surroundings is < = 0.

Or you get T surroundings times dS is < = 0 you have to find the smallest value of T surrounding for which it is valid for you to generalize the result, this smallest value of T surroundings for heat absorbed by a system would be = T itself, right this most general cases pd is < = 0 if TdS < = 0 then P surroundings the S is automatically < = 0 sorry TdS is < $\delta$Q not 0, so the real law of the close systems for all kinds of process.

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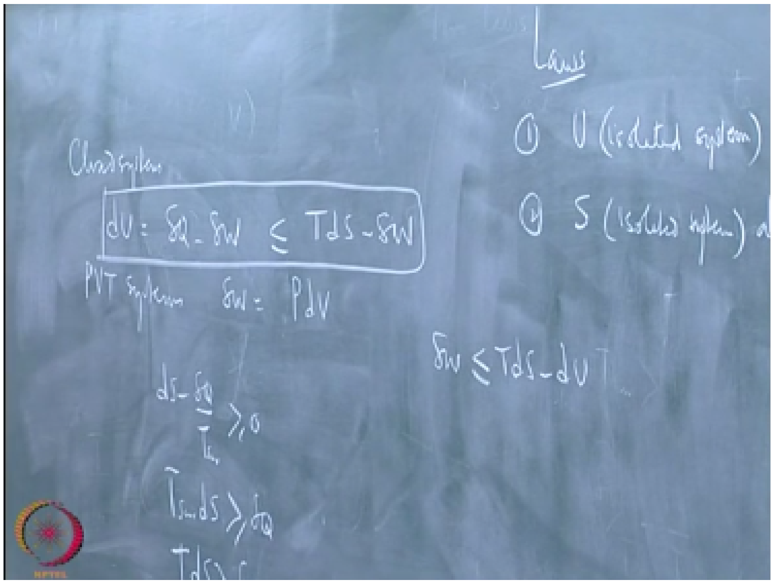

This is equal to this is > = TdS – $\delta$dV this is the combined form of the two dot in since your first quantity of interest is work to rewrite this and ask what is $\delta$W > = TdS – So δw itself at constant it is suppose I held S constant in a process δw has to be less than or equal to –du, so the maximum value of δw can be equal to –du, so absolutely trivial result. But if I know a system goes from state 1 to state 2 and I know the difference in the internal energy minus of that is the maximum work I can get out of the system at constant entropy. But this is not the most useful way of writing it you rewrite this as, you write Tds-d(u-TS) sorry, Tds-STd sorry I will rewrite this way.

This gives you du-Tds I put a minus sign here this gives you –du+Tds and then I have +SdT so I will subtract –STd and because this enamel u-ds is going to appear again and again and write this as –dA-SdT. So I have this profound conclusion δW at constant temperature maximum value is –dA, instead it is the most process are correct and raiser thermal conditions in the sense that you have a close system you start at room temperature you may heat, cool do whatever finally you come back to room temperature.

So if I take the whole process the change maximum work I can get out of the system is minus the change in Helmholtz free energy. Therefore it is a great interest to know how the Helmholtz free energy varies with the state else system. In the case of open systems the derivation is not a simple but let me stated in any case. There are two more results that you can easily see I can write d(u+pv-dfpv) so instead of this I can rewrite this equation in terms of h enthalpy, I can also rewrite it in terms of Gibbs free energy which is h-TS, but it is not useful in close system, in close systems these are the two useful results. I am now going to look at open systems.

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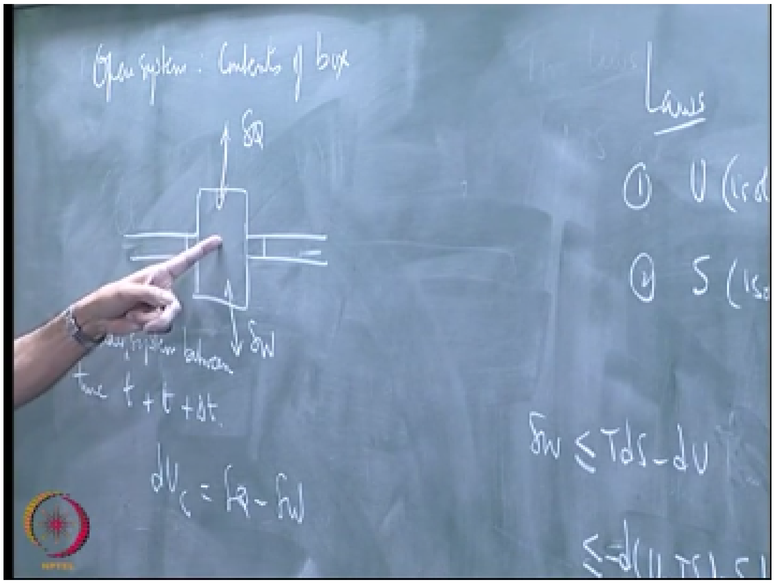

In an open system I have something coming in and something coming out again thermodynamics only however complex this maybe all I need is one box and one line in and line out. So if I have a system that exchanges heat again and I changes work with the surroundings you do not I mean you do not quite realize how liberated you are, you do not want have to draw one more arrow because all exchanges the surroundings can only be in terms of heat or work. Let us say Joule liberated you, you did not have to look for one more way of exchanging energy.

We have mass coming in and mass going out what I do in this case very simple I think I will draw a more complicate picture I means two lines okay, what do I mark here is the amount of mass suppose I am considering a system between t and t+δt this is time, I am going to consider an open system between t and t+δt. The open system actually consists to the following, my open system is simply contains of box, the box could be a whole factory could be anything.

This is my system I have a system into which mass comes in and mass goes out, now I consider this open system between time t and t+δt I will write time here. this is du what I want to do is to calculate, I want to calculate du I know du close system is equal to δQ-δW, now write C here it is close system this I already know. I want to relate this close system dU to the open system it is very easy for a close system I just have to concentrate on the same mass elements. So at time t I take everything that is in the box plus the mass that would have come in and then a time t+δt this is already come in but mass has gone out.

So I take the contents of the box plus the mass that went out, so my close system this is the following which is why in den B for incident it does not bothered to deal with open systems and great detail because he can always derive results for open systems in terms of close systems.

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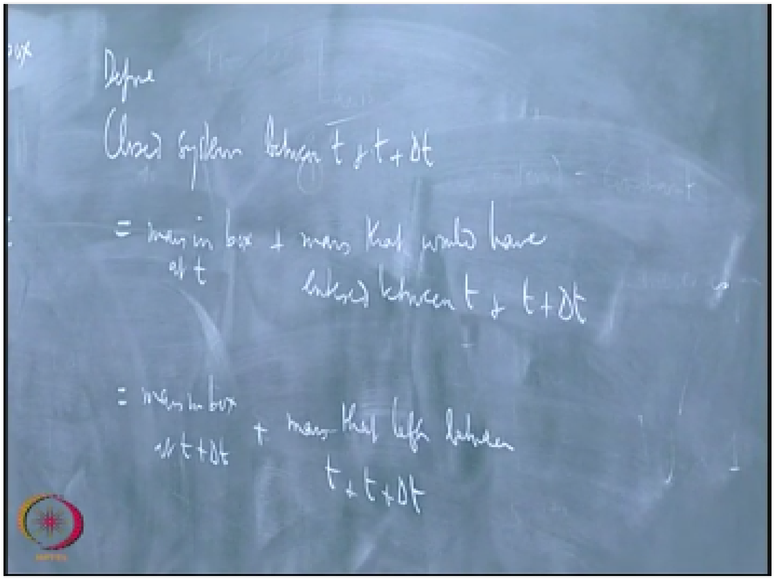

Define

Closed system between $t$ & $t+\delta t$

= mass in box at $t$ + mass that would have entered between $t$ & $t+\delta t$

= mass in box at $t+\delta t$ + mass that left between $t$ & $t+\delta t$

So I am going to define a close system, a close system does not exchange mass or the surroundings I need a close system only between t and t+δt some small interval of time, this is equal to mass in box plus mass that would have entered between t and t+δt, mass in box at t this is also equal to mass in box at t+δt plus mass that left between t and  t + Δ.

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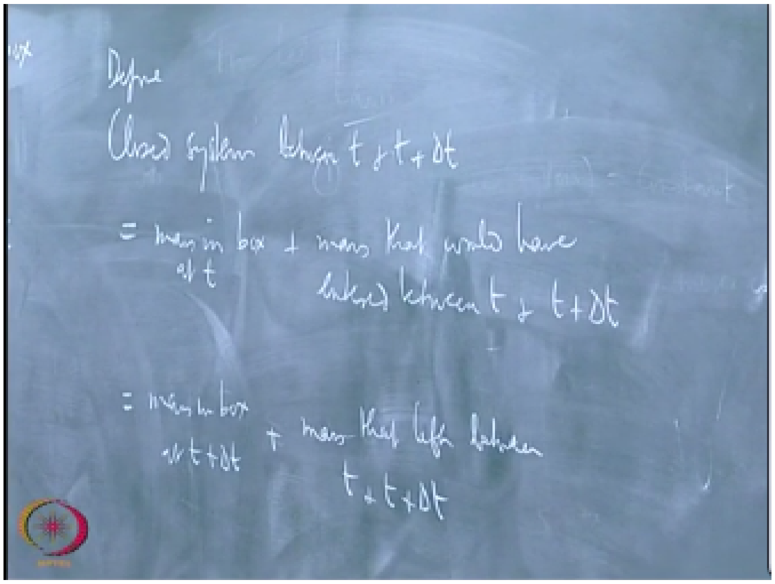

Define

Closed system between $t$ & $t + \delta t$

= mass in box at $t$ + mass that would have entered between $t$ & $t + \delta t$

= mass in box at $t + \delta t$ + mass that left between $t$ & $t + \delta t$

So what is the du close system is equal to u close system at t + Δ t – u close system at t this Δ t will treat as eventually I am going to take a differential change in time dt if you like.

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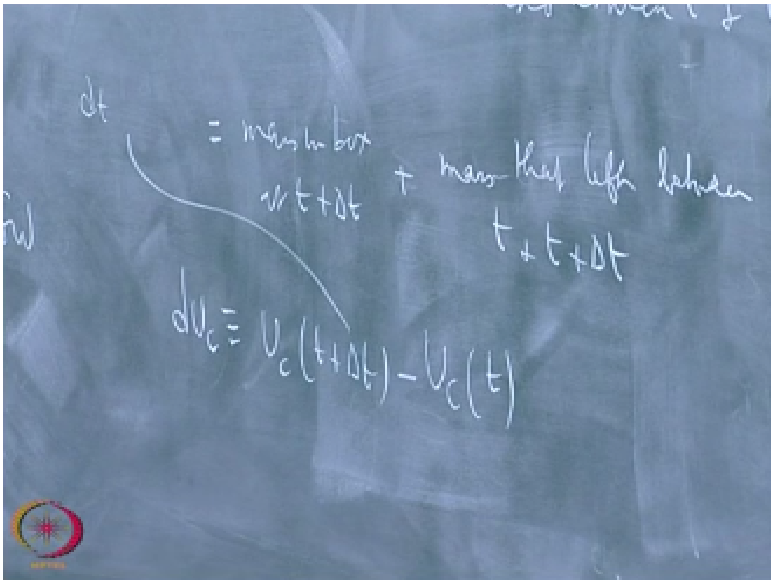

dt = mass in box at t + Δt + mass that left between t + t + Δt

$$dU_c = U_c(t+\Delta t) - U_c(t)$$

What is this equal to u close system at t + Δ t is u of the open system at t + Δ t for open system is make system I have interest so I do not put any subscript plus mass that left what is the mass that left is the rated which is mass is leaving in to Δ t or dt in to u this is small u is the specific internal energy of the mass that is leaving which means it is the internal energy per unit mass.

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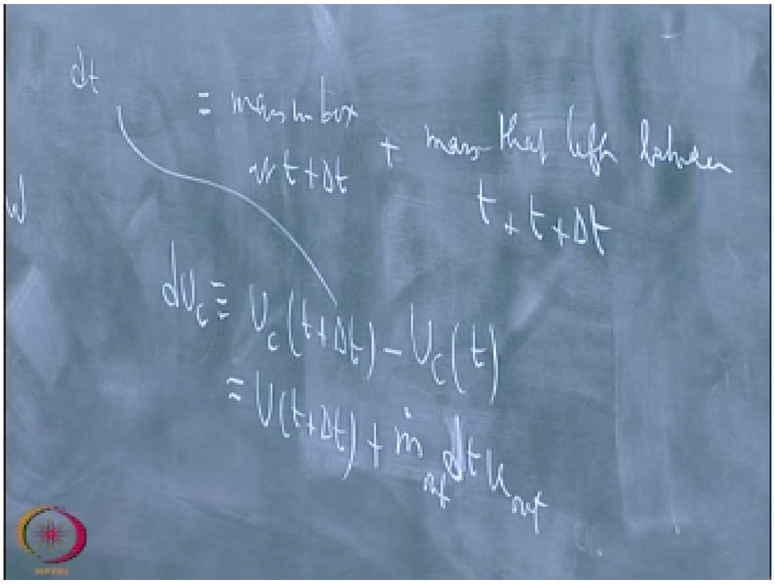

M dot is the rate times dt is the total mass that left at multiplied by internal energy per unit mass minus this is the first part what is u close system at time t it is this which is u for the open system at time t that is the internal energy total internal energy of the contents of the box at time t plus this maybe different m.n maybe different from m. okay it is not necessarily a steady system that I am talking about right now, it is the same interval of time bt time $U_{in.}$

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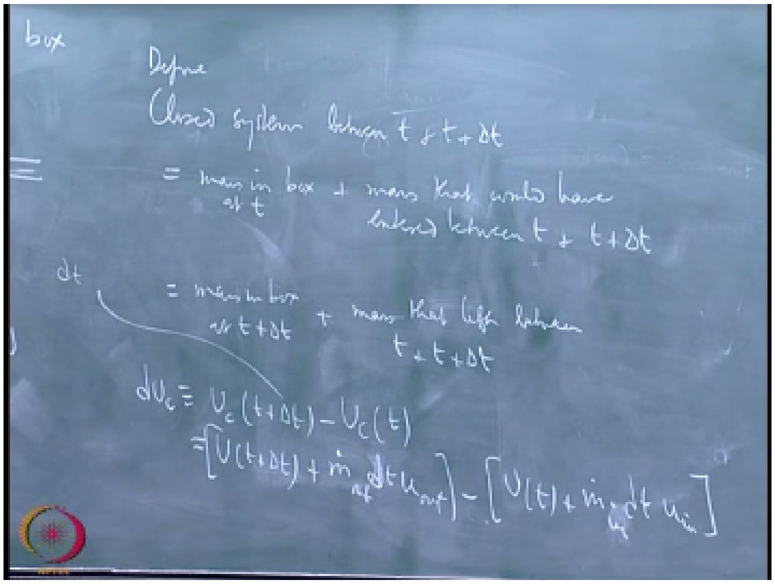

box

Define

Closed system between t & t + Δt

= mass in box at t + mass that would have entered between t & t + Δt

dt

= mass in box at t + Δt + mass that left between t & t + Δt

$dU_c = U_c(t+\Delta t) - U_c(t)$

$= \left[U(t+\Delta t) + \dot{m}_{out}\, dt\, u_{out}\right] - \left[U(t) + \dot{m}_{in}\, dt\, u_{in}\right]$

So this u t + Δ t – u of t is du + you have this is equal to Δq – Δw.

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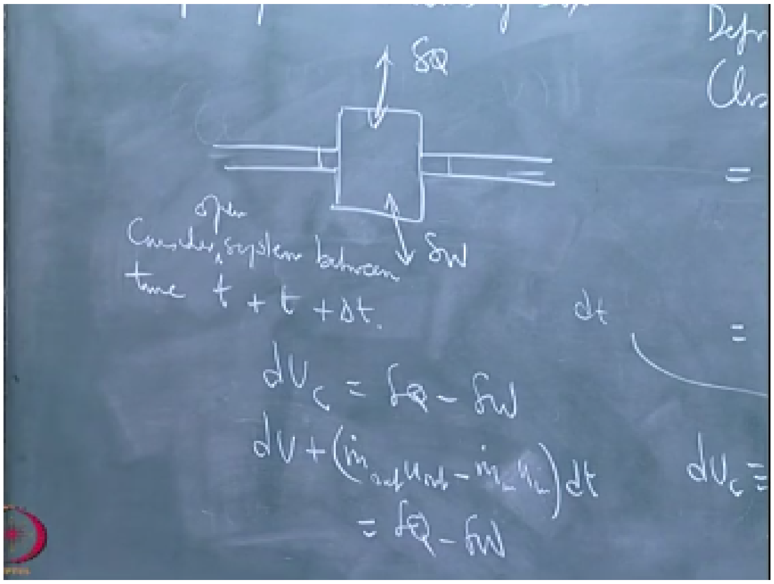

Consider open system between time t + t + Δt.

$$dU_c = \delta Q - \delta W$$

$$dU + (\dot{m}_{out} u_{out} - \dot{m}_{in} u_{in})\,dt = \delta Q - \delta W$$

dt

$dU_c =$

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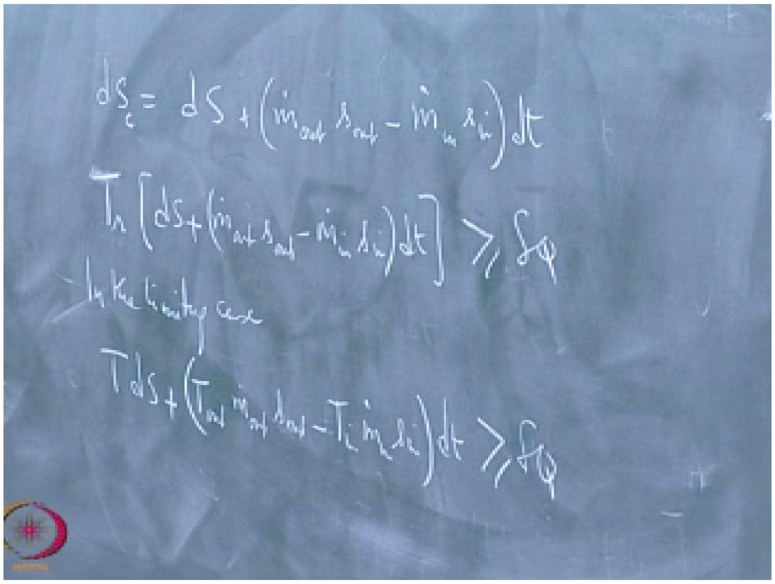

$$dS_c = dS + (\dot{m}_{out} s_{out} - \dot{m}_{in} s_{in}) dt$$

$$T_R \left[ dS + (\dot{m}_{out} s_{out} - \dot{m}_{in} s_{in}) dt \right] \geq \delta q$$

In the limiting case

$$T dS + (T_{out} \dot{m}_{out} s_{out} - T_i \dot{m}_{in} s_i) dt \geq \delta q$$

Else I have the second law which tells me the tds for close system is greater than or equal to δ q, lets us realize that the second law really tells you that t reservoir right or surroundings times ds for a close system we replace t reservoir by t and we wrote the law as a limiting case. If I have an open system I am as a low for fact that the temperature here can be different from the temperature maybe talking of a heat exchanger where the typically the fluid comes in at one temperature goes out in the other temperature.

So every time I have to take the reservoir temperature as the temperature relating to the stream the point at which I am doing this calculation in open system. So if I rewrite this for example ds for the close system would be exactly like before ds for the open system plus m. out s out – m. in s in times dt. If I am writing the second law I have to multiply this by t reservoir, so I get t reservoir times bs + m. out – m. in actually this is not in a I have written it in a this was a basically written at wrongly because I mean I am not written in wrong but t reservoir can be different for each other streams t reservoir does not mean one temperature.

For example if I had a heat exchanger the surrounding should be if I had a shell normal two tube heat exchanger I have one tube inside one tube outside if it is counter current the temperature exchange would happen from two streams at different temperatures. So t reservoir for the system could be the temperature as a system but this could be t out this could be t in that is describe the temperature at the outlet it is could be the temperature at the inlet.

So I should actually write tr for every term here, so in the limiting case which is what you are looking at you will get tds + t out m. out s out – t in for an open system.

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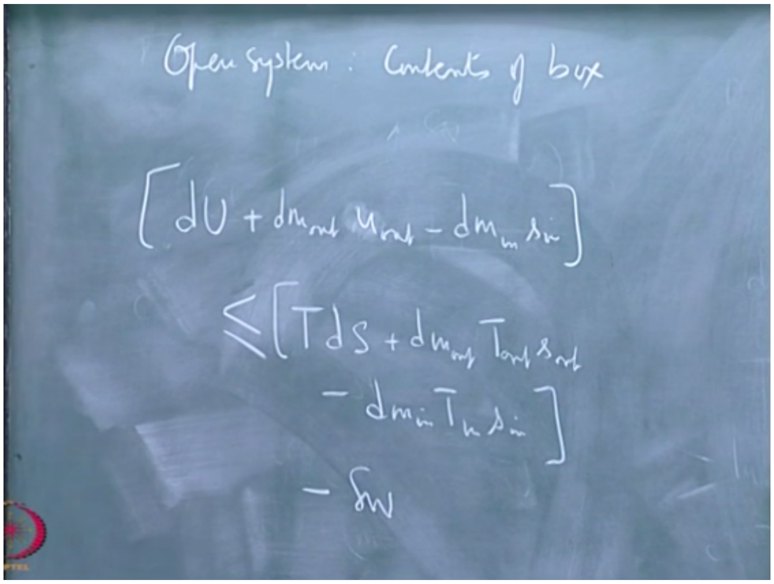

Open system : Contents of box

$$\left[dU + dm_{out}\,u_{out} - dm_{in}\,s_{in}\right] \leq \left[T\,dS + dm_{out}\,T_{out}\,s_{out} - dm_{in}\,T_{in}\,s_{in}\right] - \delta W$$

So the combine form of the law for would be dU+I will write m.*dt will be dm so I will write the simply dm out s out u out-dm sin $S_n$ this whole thing is du for the close system is less than or equal to Tds which is this one here, Tds +dm out*T out S out-dm $_{in}$ *$T_{in}$ $S_{in}$ this whole thing is Tds for a close system – $\delta$w.

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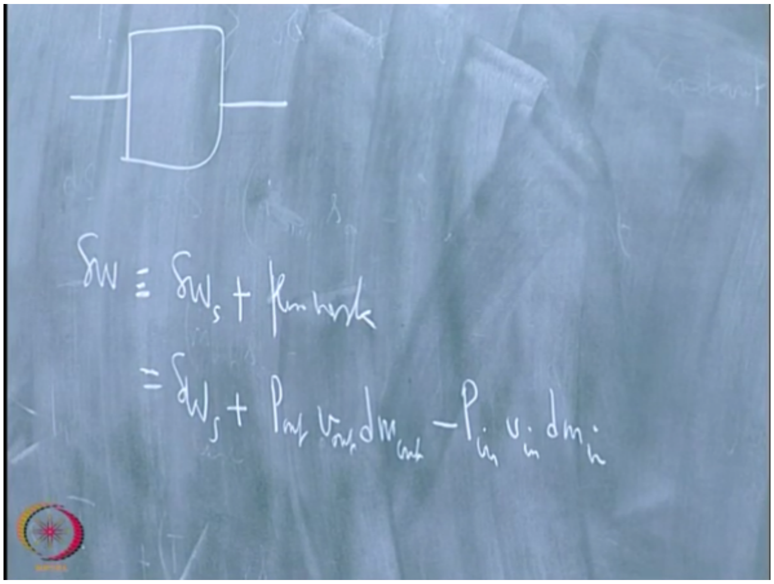

And one last step to do if you have a open system there has to be work done on the system by something this surroundings that pushes the fluid in that is compulsory similarly there is work done by the system and pushing the fluid out so that is called flow work and flow work is a compulsory part it is not useful work that you get out of the system.

So it is convenient to redefine $\delta$w in terms of network+ flow work so for example we define this as $\delta$w= $\delta w_s$ s is usually use for shaft work in mechanical engineering it could be a turbine with the fluid flowing in fluid flowing out and turbulent relates rotating sometimes it written as assume usual work all these are same $\delta w_s$+ flow work and flow work is easily calculated flow work is simply the work at the work done by the system would be pressure at the outlet V at the outlet this is specific volume times Dm out, Dm out times V out is the total volume of the fluid that pushed out.

It pushed out at a pressure P out so the work done as P*dv- of course work done on the system $P_{in}$ $V_{in}$ Dm$_{in}$ this is a definition okay so it is not $\delta w_s$ is not a conceptually new quantity it simply a useful quantity that is defined by subtracting from the total work done by the system the work done due to flow network done due to flow very often, these two are equal so in most chemical assumption does not make a difference.

A shaft work and total work will be the same but sometimes occasionally those two terms can be very important so what we do is instead of this $\delta$w I write the $\delta$ws +$P_{out}V_{out}$ dm$_{out}$-$P_{in}$ $V_{in}$Dm$_{in}$, so this is your law a open system can be written as little more allgiantly will do that in a minute.

Actually I think I will stop here let you ask questions we will I will start from this and show that at steady state basically in any processing chemical industry are only interested in what happens is steady state because if you are even if you are working in a mechanical turbine you are not going to operated it for half a second two seconds so on.

You are going to work it as steady state and ask what happens what how much worked you can extract at steady state the mass going will be equal to mass going out DM out and dm in will both be equal and nothing will change in the box you can have a turbine into which fluid is coming in with the certain kinetic energy leaving with the other kinetic energy but it always the change U will always be the same.

So du will be 0 ds will be 0 and you will ask questions about, you can either you can ask questions about $\delta w_s$ you will say how much after can I get out of the system under steady state conditions, per unit mass flowing through the system so you will answer that question the only concept so far are simply the introduction view and as into laws those are asserted.

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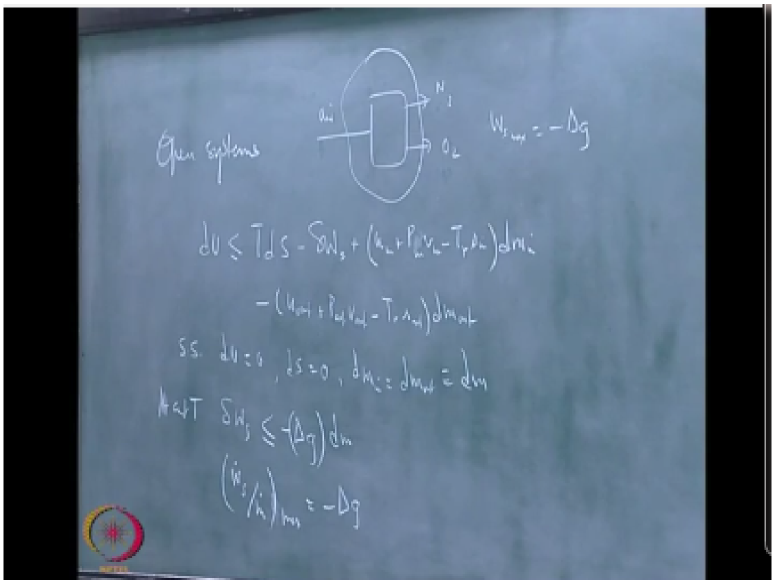

Their only un-contradicted human experience so far open systems, we would the last down we say du, we just want to complete one small statement at steady state du=0, ds=0 so we can rewrite this as $\delta w_s$ is less than or equal to we said constant T this T reservoir becomes Tn = T, so u + Pv – Ts is g, so you will get – Δg this will become dm, just call it dm. rewrite this as Ws./m., so the maximum work that you can get per unit flow of mass through this system = change in the gib energy with a – sign. This is also the minimum work you have to put in, so if I had the nice thing about thermodynamics it can, it is very nice for the student but it is absolutely irritating for the industrialist.

Because here is the guy who has a huge plan that separates air into nitrogen, oxygen and all that and you go and tell him oh this is your process yeah, nitrogen, oxygen and you sya the work done in the whole process. It is actually a factory you have got all things of things coming and going out this comes in it $25^0$ one atmosphere this each of these at $25^0$ one atmosphere and you say Wsmax that you have to put in - Δg.

That means g x1 times the g1 for nitrogen + x2 g2 for oxygen – that for air, so if you know g for air as a function of composition you are true with the calculation and you can get a model and you can write down models and you can write the answer 2minutes. You can ignore the fact that he has the high temperatures, low temperatures inside. If you are doing air liquid fraction for example you will go down for liquid nitrogen and blow a temperatures and all that is ignored.

Because this is T this is room temperature that is all counts, if thermodynamics is concerned you can completely contempt of what he is doing inside you said that is detail, I will not come into your factory. Here is an envelope where does the air come and the dust is come in that is all you have the task. So the whole thing is severe, now what I want to do now is, I just want to point out here you can trusty argue, that even in non isothermal systems it is Δg, isothermal system reversible process.

But Δh can be derived that Ws./m. maximum in adiabatic system is Δh can be derived without any concept of reversibility. We will go ahead with calculation for various systems, the purpose of the entire course will be to calculate thermodynamics properties the rest of it is practically downstream.

So purpose is, the purpose of the course is simply to calculate changes in internal energy, enthalpy and g, this is work calculation, maxima and minima work, you have to calculate changes in u, a because a close system under isentropic conditions and rebate conditions the maximum work you can get is Δu. The maximum isothermal work you can get out of this system is Δa¸ actually this is the – sign, Δu – Δa.

In a flow system the maximum work you can get in re adiabatic system is Δh – Δa, and – Δg for an isothermal flow system. So if I can calculate changes in u, a, h and g is no difficulty at all. For pure system it is trivial, what is difficult is mixtures, so we will set aside pure substances or system with constant composition, these two cases and then mixtures. In all these cases we will list what are called measurable quantity.

Measurable quantities as far as we are concerned would Pv temperature you can put brackets absolute temperature and then what is measurable, these are not properties, measurable quantity I have written, these are properties, you can also measure q the heat but that leads to a measurement of enthalpy, for example if I have du for the close system is $\delta$q – $\delta$w, $\delta$w in Pvt systems, the $\delta$q – Pdv.

So d H as $\delta$q – VdP + Vdp, d H is simply is du + dfp, so I add Pdv and Vdp and get this, so if I make measurement at a constant pressure I can measure changes in h by measuring q therefore, h becomes measurable this is in constant pressure systems h are changes in h I will write it as Δh really interested in changes in enthalpy and along with that it becomes independent of the part under certain conditions when pressure is constant it becomes a function of state you can differentiate it with respect to t, and get derivative property which we call the specific heats cp is an example cv is another measurable quantity cσ which is long saturation line that is measurable.

So all these are measurable qualities in the rule thermodynamic when you derive any expression if I want you to get dU or dA or dH instantly s is not direct interest here but you find u and s then you can calculate these derivate the thumb rule is that on the right hand side if you get measurable qualities stop otherwise you can keep going around in circles and come back to you first part so, our purpose will be to get calculate changes in terms of measurable properties in measurable quantities are these and all the derivatives are considered measurable so the change in volume with respect to temperature at constant pressure is a measurable quantity.

The expansion volume expansion coefficient is measurable similarly the change in volume with pressure is measurable quantity and so on all derivatives are considered measurable all though if you ask a PVT guy who is actually making these measurements its pure help making a accurate measurements at low pressure as for example pure help because, the volume changes negotiable and to measure it accurately it becomes very, very difficult what we will do is we look at only these changes we look at when you can express it in terms of PVT.

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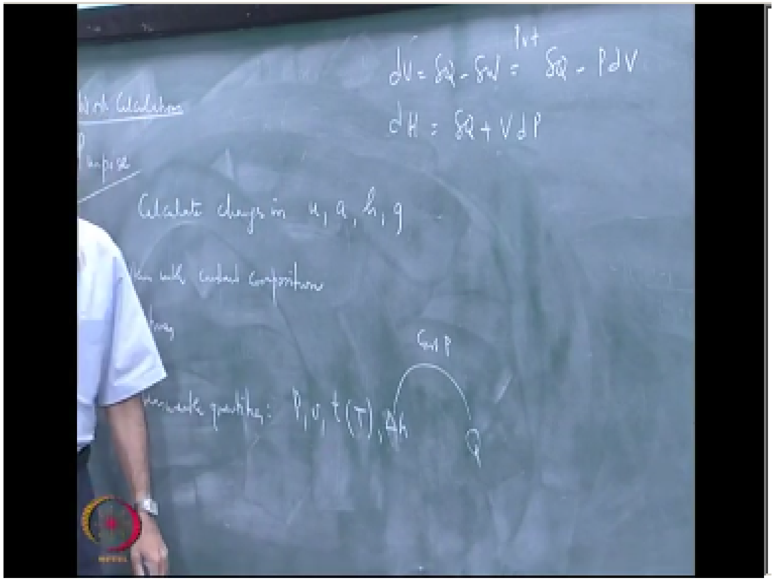

So the basic equation we will deal with close systems here if you are looking at systems of constant composition you need to look at only close systems so far I will start with dU=Tds-Pdv for PV systems we will be looking at PVT systems strictly speaking in thermodynamics you should write de which is the total energy but in thermodynamics you do not worry about changes in potential and kinetic energies of the system as the whole you are not worried about moving the box up and down where as in fluid mechanics du will be negotiable we will be only looking at potential energy changes.

And kinetic energy changes of the macroscopic systems that is the only difference where as the equation are the same so I will be looking at this so I have to express ds and this is where s is function of if you want you have to choose your variables T and P or s is the function of T and V you can choose either simply a matter of what information you need in order to calculate these changes.

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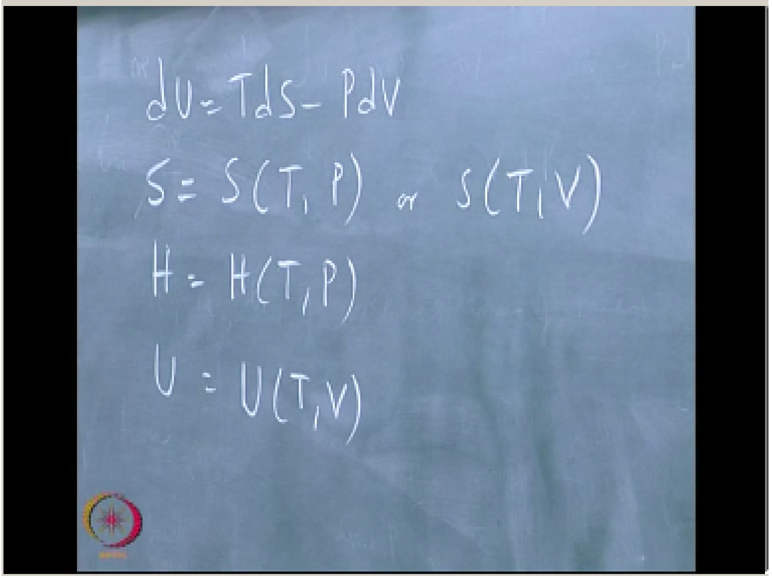

$$dU = TdS - PdV$$

$$S = S(T,P) \text{ or } S(T,V)$$

$$H = H(T,P)$$

$$U = U(T,V)$$

Normally it is convince to choose  H as the function of T,P U is the function of T,V actually U is said to be natural function of S and V the way the equation occurs here so gives this equation of state we simply du as a function of S and V for thermo dynamic theoretical arguments such much more convenient but in practice you can measure TP or V so you have to express everything in terms of TP between these two if you use volume you have to integrate from infinite volume.

So it is much added for pressure you integrate from zero pressure so it is easier to do TP but your equations of state empirical equations that connect PVT or all explicit in P I mean explicit in V p is the function of volume that is how you express it not volume as the function of P so even if you take the equation you have to solve the cubic equation to get the volumes where as pressure is given explicitly.

So the more convenient variable in terms of expressions the concrete variables are T and V but the convenient variable for integrations are T and P so you can choose either of them what we will do is write down the equations for pure component systems in the case of pure component systems I do not mind does no0t matter if I write capital H or small h I can write it per unit mass much more convenient to write for unit mass so we will derive the expressions for DH and DS in certain orbit their calculation but the orbit is does not matter because you are going to find differences in entropy and differences in en therapy so I will derive that those expressions next class.

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