# Indian Institute of Technology Madras

# NPTEL

# National Programme on Technology Enhanced Learning

# Chemical Engineering Thermodynamics

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## Lecture 8

## Work Calculation

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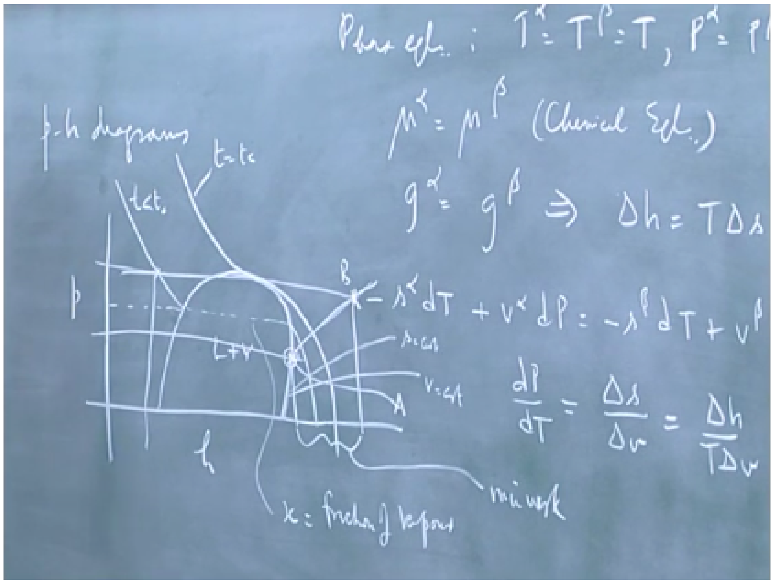

So we are discussing this pH diagrams discussing U was h t come along a isotherm at a particular pressure here this equation μ α = μm is phase equilibrium, but we also have seen this is a same as G α = Gβ for pure substances the chemical potential is simply be free energy gives the energy promo, so this can be written as we have said that phase equilibrium T α = T β = T T α = P β = P pressures are the same because you have mechanical equilibrium and thermal equilibrium and so this gives you chemical, so thermo dynamic equilibrium as the components.

Thermal mechanical and chemical equilibrium so you have $S\alpha$ dT so you have a Gibbs Duhen equation that tells you that $dP / dt = \Delta S / \Delta V$ answer this in place that $\Delta H = t \Delta S$, now this is $\Delta H / T \Delta V$ this is your pressures Gibbs Duhen equations you quite familiar with in the idea is that the pressure becomes related to the temperature by this equation at some if you take substance in lower the pressure at some temperature below the critical temperature this is $t = tc$ so below tc you take any isotherm should be lowering the pressure and move along the isotherm.

You reach a pressure at which two phases form the here if you decrease the pressure further you have the gas phase of fe so we have in this region of course we have already isotropic lines this is S = constant this is V = constant and so on you can read any of the I will use and takes two coordinates to fix the position of a state for example here any H and P we will fix the position then you can do it in terms we need two variables if you fix the temperature and the pressure which point is fixed.

If you fix temperature in enthalpy this is point of the game fixed so any two variables will specify the state of the system inside this region and this is where liquid = vapor typically and given you the charge for methane we plotted to an experimental data here also you need to variables because you have one variable temperature which will determine the pressure and therefore all the values at saturation similarly at the vapor and that in between how much of vapor and how much of liquid is present is specified by an extensive variable and the variable here so if we denote by x = fraction of vapor.

So two variables are required to specify the state two system and need to we will do know if you want to calculate work for example you want to know how what is the maximum work with typically for example you compress a fluid you compress it as I said radio by typically simply because compression is usually done by it can be done by a rotary device or a reciprocating device and the compression find is very small it so small that the amount of heat transferred to the fluid is negligible.

If you take a rotary device for example typically it rotates the 1000 rpm for 1200rpm for convince that means per second you have 20 rotations so in 20 times as second it gets compressed so 120th of a second how much heat can be transferred to the fluid, so effectively it is radio biotic  you know that the entire work done is simply the enthalpy change so if you take an S = constant line adiabatic reversible in case then if you are compressing from some pressure.

To some other pressure from this point let say do not need to be instauration line then matter c have draw it here, so this point is a I take vapor at this pressure and compress it from a to b the amount of minimum work that I have to do this is the enthalpy along the isotropic line, so this will represent for example the minimum work for unit mass of per mole depending on what the plot is, so essentially calculating minimum works simply means on this chart.

Identifying position a and position b the initial state in the final state if it is isothermal you will along an isotherm and calculate $\delta$G if it is adiabatic if it is a close system when you will calculate $\delta$U and if it is finally that enclose the isothermal system we will calculate $\delta$A let me do an example yeah this is adiabatic cases.

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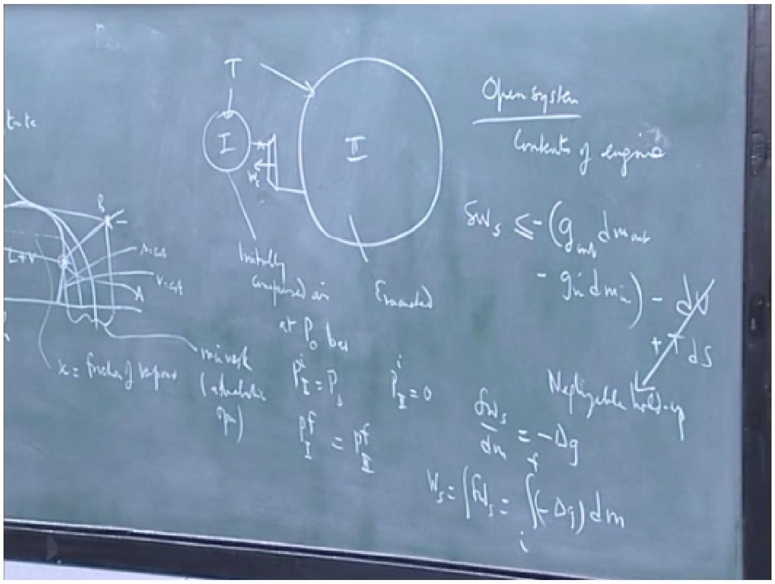

And device that we will carry on the back for under water operations as a huge tank and we have small tank and a huge time two tanks and you have valve here, you have a expansion device as we put into this okay I have tank 1 and tank 2 this contains at P = 0 this contains initially compressed here at same P0 bar you know the what units on this chapter the old units are all okay made it the SI units and pass mega paschal no matter at some pressure and this is initially evacuated.

What you do is a $T = 0$ or you will open a valve allow this here to expand here into this you could let it out in the open to pressure is sufficiently low but example for deep see activity if your 10m is below sea level you turn of 10 bar already the pressure there so in this fill to 10 bar into gas only but all if you open the valve, so you have to have another container secondly there are environmental considerations whether the gas that you put in if it here it is okay if you are taking some other gas their operations.

We do not want to it let out into the sea so what you do is pas it through and expansion within this engine will rotate this will give you work stop so as the gas expands from one tank to the other it turns a chart which will do work for you, you may do a minor repairs and simply be we may take the hallow of ship and break up the crush that are formed at some places and so on.

Whatever the into repair job that you are doing you need an engine to help you to do his work and this is a typical device this is get it on the back so you can calculate how much you can first fall the weight of the device that a person get carried the size of the device and all that, so the some limitations in terms of how much a person can carry on and get back and do the work, but the question of thermodynamics interest is if it is works under sea water for example.

This is a temperature $T$ which is fixed and both are a temperature $T$ so isothermal operation effectively because a temperature of the water outside will determine the temperature of the whole process, so under isothermal operation what is the total work that is done, so there are two ways of calculating it and this is the trouble about thermodynamics one way tends out to be trials other ways turns out to be somewhat it complex but the answers are the same.

They have to be same in any case so for example if I want to calculate the work I can calculate I can take the engine alone I can do it as an open system where I dependent condense of the engine, that is my system so I have gas coming and gas going out and I can ask what is the work done derived an expression for the work done if you remember this expression had $\delta ws$ or less than or equal to the n isothermal and $dT_S$ of which at steady state we said the $U$ and $TdS$ and $dS$ are 0.

But apart from steady state if you have system like this where the total amount of gas flowing through the systems over a finite period of time of interest and do not make that time too short, the total mass flowing through is much larger than the hold up in the system the this $d_U$

represents change in internal energy of the contents of this device, and this condense is not at steady state because this pressure is falling this pressure is raising so the pressure will change.

So the condense will change but the mass inside is negligibly small therefore the internal energy is negligibly small that change in internal energy is even smaller therefore we through these two terms out in case, if you try to analyze this system for a micro second or something will be a wrong answers because tends this assumptions is not valid but you normally you worried about finite period of time during which the amount of gas passing through this system.

His much larger than the negligible I mean negligible compared to the mass passing through the system during the period of interest, so if I have gas passing through this and turn to negligible hold up then d amount = $d_{min}$ because that mass inside is negligible so you simply get $\delta W_S$ / dm = $\delta g$ if you are trying to calculate the maximum amount of work you are talking about $P_1 = P_0$ initially $P_2 = 0$ or near 0 P1 final this is initial final should be equal to P2 final till the pressures and different.

There will be work that you can extract in this case I am talking about isothermal operation this is why I got this result $\delta g$, because I want to calculate $W_S$ simply integral of $\delta w_S$, so the entire of the same and equal to integral of – $\delta g$ and dm from the initial conditions to the final condition on this diagram one this plotted or constant specific volume lines so instead of the m there mass is simply equal to volume by this specific volume in the volume of the so in this case for example.

You can take the mass here you can integrate over this condition here and the mass here will be simply the total volume of cylinder 2 divided by specific volume in cylinder okay this is actually the hard way I will do this calculation until and this in minute, but in the easier way just we take over flow system.

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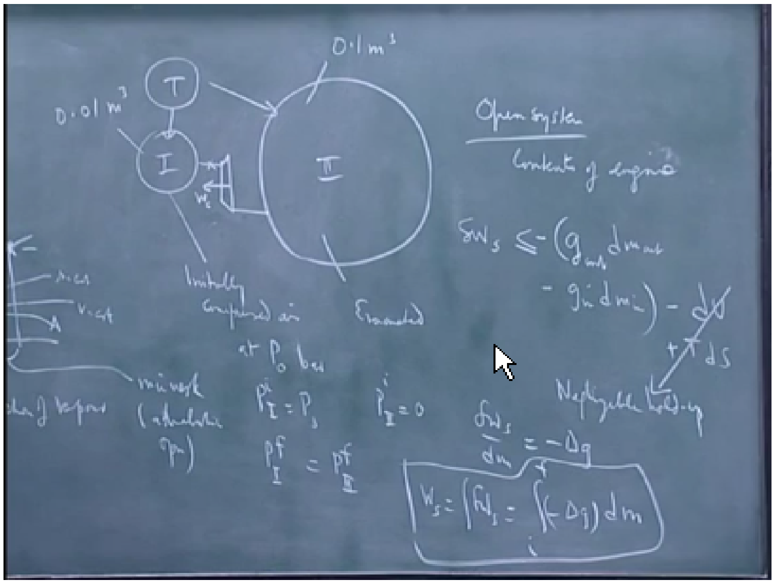

Fact as a thumb rule as far possible define a close system which will still five you then system you need in this case it is tank 1 = contents of engine plus tank 2 I take all of them together or contents of tank 1 = engine = tank this a close system no mass change and this is change if it is a close system you know that $\delta$w is less or equal to – $\delta$A under isothermal conditions.

So I all I need to know is A final w is simply = A final – A initial $\delta$ – A and this is also easy to write down because this is mf remember in the final state the pressure is a same in both so I can take the total mass mf into $A_f$ it is a homogenous this should be – here so we will take the minus in sign + m initial in tank 1 times A initial in tank 1 + m initial in tank 2 A initial in tank when I derived result for closer systems the system does not have to be homogenous it can consist of several homogenous parts.

You have to add all the thermodynamic properties so Ai is actually A in this tank let us say A in this tank engine mass negligible I mean the mass the contents of the engine is negligible in this particular case I have taken initial mass is 0 here so I can strike this out negligible mass initially I evacuate this cylinder so I have simply mf Af + in this case these two are equal m is simply $m_f$ = mi in 1 tank 1 = v of tank 1 / V initial in tank 1, so I must give you the size the two cylinders.

Capital V is total volume of tank 1 $V_1$ $V_2$ will be volume of tank 2 to calculate $V_1$ I know the temperature and I know the pressure initially P0 so we will take some numbers here for example if you take let us take some numbers from here for example I will take.

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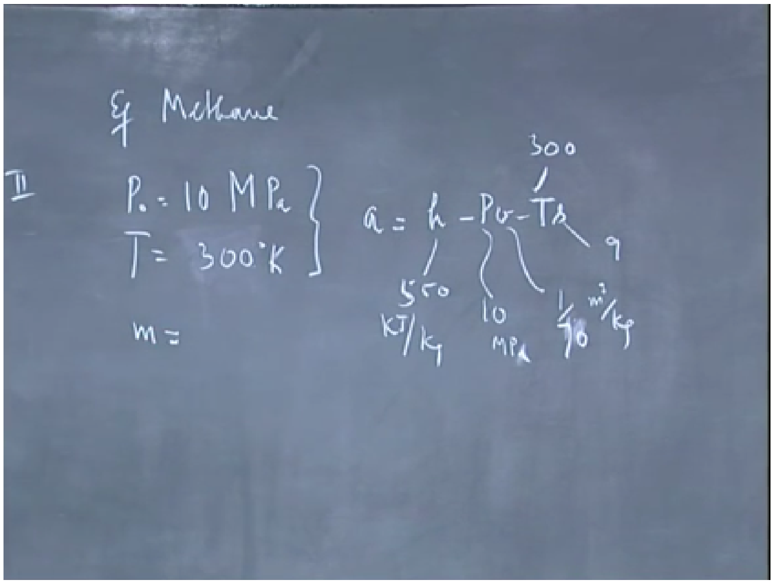

Example I am taking methane only because I have a chart and methane nobody will be foolish in after run this with methane I mean this way do run such an engineer with here, so if air leaks you do not have to worry about this trying the ecology in this fashion all that stuff, but I just write for example let me take some reasonable temperatures so let me take 10mpa let me say I filled up to 10MP, I can take temperature I do not think I have a choice here this is sea water.

So we will take something like $20^0$C of the about 73 let me take $300^0$C for convenience that line was here, so we can read the 300k line here so 300 is k and 10 what I need is simply A at these conditions this is the initial condition, so what does A = A is H you need to get several variables because H – $P_V$ – Ts right I have a H $P_V$ P and S all these are available on the chart so P is known you have to read S from the table in the so you just take the intersection o $300^0$ k line.

Which is an isotherm you can see that line there it comes down and needs the tend NPA line at something like 550 enthalpy roughly that means far ways from here so you can read some numbers out you tell me the numbers, so this is about 550 for example and whatever units this is kilo joules / kilogram.

The pressure of course is 10 can you tell me what V is at that point we just identify the intersection point and then read everything from the graph, this is great fun somebody else draw graph where you and we just read numbers from it so the whole calculation is trivial what is your

V the V lines I pointed out you that V is the slope of the V lines you remember we got the slope for V and theirs line actually these are marked here, so the S lines have just deep or slope.

The flatter lines on the right hand side or the V lines the line that passes through this about 10 these lines are lines of just mark density z okay if change this is not specific volume actually density is given and this chart has changed since the last addition so this is actually 1/ that so this is about 1/10 m/kg I am reading numbers approximately you read the more carefully and normally the $P_V$ product is negligible compared to H so H – $P_V$ H and U can be equated.

For most purposes and then you have TS, S you can read here what is the value of S that you get here, 17 this line say me 17 70 sorry no it is much idea right, okay then what about the entropy this is mines 15 20 it is higher raise in okay 30 50 and 70 it is almost 70 no it is not sorry I take it back and one or two mistakes and you are not, so one of my problems is that it is about 10 yeah you write about 10 9 okay and this is of course 300 so that is the initial value and you have to know the volume as well.

I mean the mass the mass is simply the total volume what you think even carry I mean you have back what kind of volumes can we carry $1m^3$ will be cubic let say point this is the larger one will about $0.1m^3$ this about $0.01m^3$ and this will be your some numbers so we start turn here back okay, so the m will be 0.o1 which is meter cube / multiplied by the density in this case see giving you density actually those are constant volume lines with same as constant density lines.

We marked the density units 01 into the density is we just say 1/70 no 70 okay $V/m^3$ so you will multiply M into A this is A initial this is M initial, so you have got this figure to get the final state we have to realize that the total volume is given it is an isothermal operation so if the mass the is the same so to get the $M_f$ is the same is also = mf so with final density the $\partial$f or 1 / $\partial$ Vf final density is simply mf which is this divided by $V_1 + V_2$ so it is 0.11 it is 11th of the initial density.

So you has already 70 /11 so you have to find the 70/11 curve here and that is one fixed point then you are moving along the isotherms so along with $300^0$ line we locate the second coordinate the simply the volume, so 70/11 is got 6 so you see the volume line is 6 some here in about 6.6 if we intersects the $300^0$ line in some enthalpy which is about 650 you have to locate that point the enthalpy at that point again we are calculating the $A_f = H_f – Pf\ Vf – TS_f$ is $H_f$ is about you can read it more carefully 650.

And the reason these numbers decrees you go to it and as we more left for example as we move from vapor to liquid because this 0. Of energy is considered when two molecules are infinitely a path so as they move closer attractive forces between the molecules work is done the if you push the 1 molecule towards the other work is actually done by the system itself on new, on the second molecule the first molecule is attract in line the second molecule is attracted in the first molecule.

So the energy will actually deicers so it will always go less you take the ideal gas infinitely separated molecule as the 0 of the energy so this is $H_f$ this you can read Pf you have already seen what this is 11/70 you can read PF on that intersection again in order it comes to get something like 1 $P_f$ is approximately 1 when T is known P is again 300 and finally Sf, Sf is about 10.5 or something at 10.5 we got to the lower pressure is this higher intrepid greater movement of the molecule is more freedom for the molecules.

So you calculate this Af mean multiply by MF which is same and you get a number which will tell you the maximum work you can get out of the system what you want is actually shaped work what you get there is w right how would you find the shaft work, this will give you shaft work directly you open system analysis will give you shaft from directly but on the other hand that so much easier to do the calculation here, so get shaft work all you do is go back to the definition WS is w total work done.

Shaft work is – total work – the flow work flow work done by the system is here and the outside – I will simply say flow work calculation because flow work calculation depends on the outlet conditions in the outlet conditions keep changing, so I have to integrated from initial state to the final state, normally if it was an ideal gas for example PV would be RT regardless of the state here the pressure in the volume change but PV is RP so in a isothermal operation the work here will be the same as the work in.

So for an ideal gas there will be no difference at all flow work will be 0 WS will = W in many cases flow work is negligible so WS will be approximately W but we can calculate that exactly I will do this other calculation then it will become clear just what we are talking about is that calculation clear, why did it looks a bit mainly when you first see it we can see that once you have a chart you are empowered is essentially you have the chart then you can do any calculation.

If be as somebody has done the chart for you and all you do is locate these things in a mystery as a way if you are impressing a lay man we can always do this and move your fingers locate the point in say 0.A 0.B and then calculate the differences but the calculation self is trivial and you can get out of the thermodynamics only the maximum work that you can get from the system in actual practice we will get less because a variation friction losses and reversibilities.

Then you can design your system better and better and you can say if it gets you within 99% of the thermodynamic result you said stop improving this system will help you, now let me do the second calculation although it is quite illustrate and finally you will be able to match that to.

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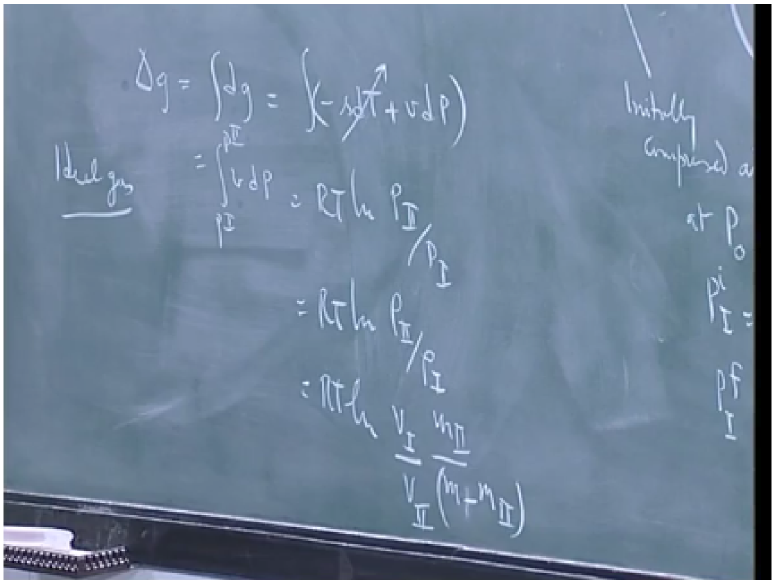

What is want to do is to calculate Δg into dm this is the integral I want to calculate this mass could be any of them because the mass leading 1 is the same as a mass entering two so I can start with either one let me start with this m dm = dm in tank 2 because in tank 2 mass is increasing we are looking at the floor through these system, it is also equal to – of dm1 could be either 1 Δg is the difference in flew energy between tank 1 and tank 2 so this is integral dg = ∫ - SdT + VdP and this is just a thermodynamic property per mole and therefore it is like the close system equations.

Which is 0 because it is isothermal operation so I all I have to do is the calculate ∫ VdP this is from inlet to outlet so this is from P outlet this $P_2$ inlet this P1 $\delta$g is g out to – gn g out is the same as g in tank 2 g in this same as g in tank 1 at this stage you have to do a numerical calculation because in the chart you will have to start with $P_1$ to $P_2$ at any given mass, so when the mass is equal to m2 which will go from 0 all the way to the final total mass that was initially in the system.

At agree mass you have to calculate that you assume m2 start from 0 make small increments at every point you have to know V from P1 to P2 that is you go along the isothermal line from P1 to P2, let me do this calculation for an ideal gas so that it is explicitly clear, so at this stage we want to assume ideal gas actually you can do this for an ideal gas you can do this analytically because this is simply RT ln P2 / P1 I am going to integrate this over m2.

So I have to relate the pressures to the mass this is the same as $R_T$ ln P2 is ρ RT because it is ideal gas this is equal to $R_T$ ln the density is simply mass in tank 2 by volume of tank 2 and this is volume of tank 1 in mass in tank 1 mass in tank 1 as m – m2 this is I am not doing it from methane and doing it for ideal gas right now, for methane you have to do the same thing that you have to do the same thing but you have to numerically by going along the isotherm or I can give you an equation state and use intervals equation of state describe methane.

Then you will do the integration using V from the ventalog equation, now I have to do this integral over dm, dm2 so I will simply get Δg.

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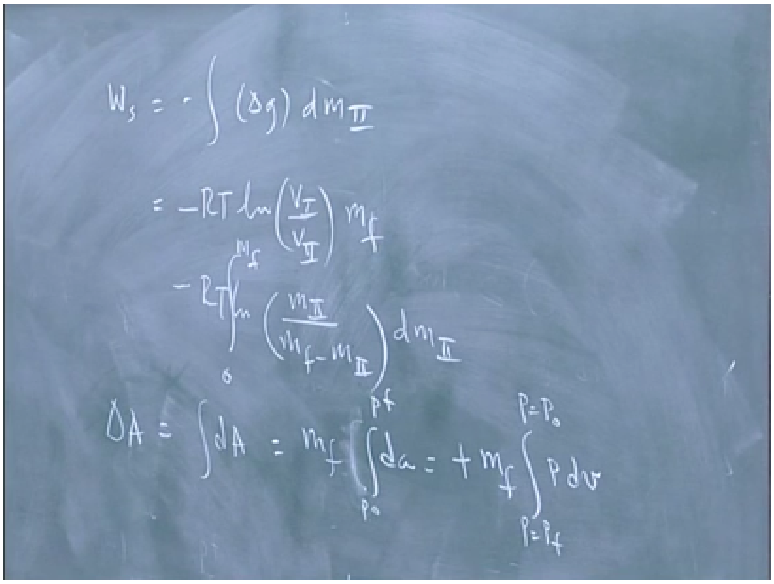

$$W_s = -\int (\Delta g)\, dm_{II}$$

$$= -RT \ln\left(\frac{V_I}{V_{II}}\right) m_f - RT \int_0^{m_f} \ln\left(\frac{m_{II}}{m_f - m_{II}}\right) dm_{II}$$

$$\Delta A = \int dA = m_f \int_{P_0}^{P_f} da = + m_f \int_{P=P_f}^{P=P_0} P\, dv$$

Since I want to get Ws = - ∫ Δg dm 2 and I get $R_T$ ln $V_1$ / $V_2$ which is a constant times $m_2$ not m2 in total integral of m2 = 0 to total mass into mf integral of this from m2 = 0 to mf this is the other example of $V_1/V_2$ + logarithm of the second term, so I splitted into two parts log of $V_1/V_2$ this is a geometric factor this is a constant therefore I just integrated over the entire mass, so I get the total mass flowing through the system which is equal to total mass in tank 2 at end of the process this simply mf – RT ln this you know how to integrate this log x bx in log of A – x bx in the same case for an ideal gas for ΔA this would have been simply equal to again I have to integrate the same thing dA convert A final – A initial that is all.

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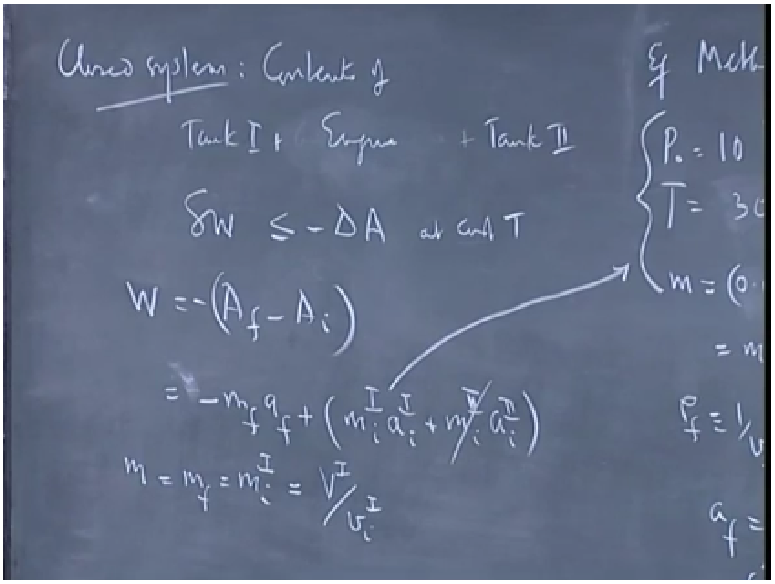

Closed system: Content of

Tank I + Engine + Tank II

$\delta W \le -\Delta A$ at const T

$W = -(A_f - A_i)$

$= -m_f a_f + (m_i^{I} a_i^{I} + \cancel{m_i^{II}} a_i^{II})$

$m = m_f = m_i^{I} = V^{I} / v_i^{I}$

Eg Meth

$P_0 = 10$

$T = 3$

$m = (0$

$= m$

$\rho_f = 1/v$

$a_f =$

The same calculation I have to do which gives me $m_f$ I can pull out mf times $\int$dA for initial condition $P_0$ to $P_f$ and that constant temperature $d_A$ is $d_A$ is actually – sDT – pdV, so this is simply – or + $\int m_f$ times pdV from P = pf to P = P0 as we switch the two for the – switch the limits, so this again is $R_P$ / V.

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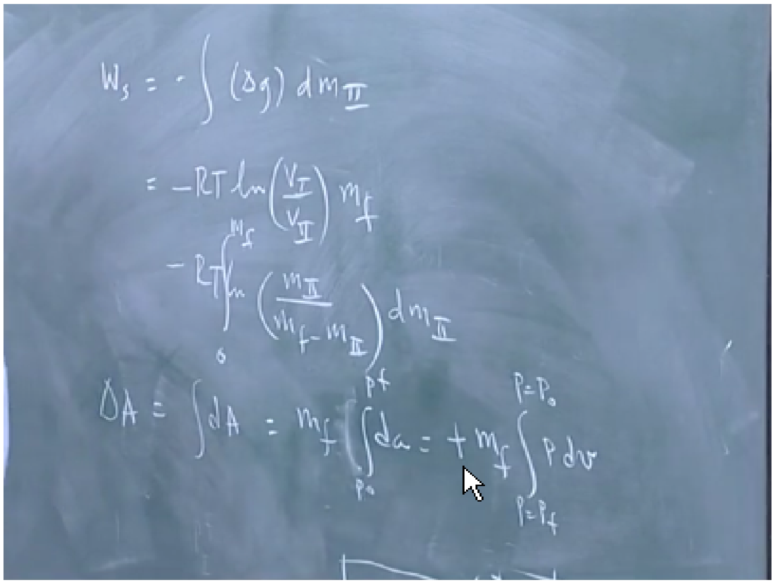

So you get mf or ΔA = mf into $R_P$ ln V initial at $R_T$ ln V by Δ prime so V = mf into $R_T$ into ln because the same is the same I can multiply by the mass in it V initial into m initial would give me simply $V_1$ in V final length the m final will give me $V_1 + V_2$ and I want to you compare this which gives you actually w in this which gives $W_S$ complete this integration and you will find that the two expressions are identically because flow work in an isothermal idea gas system is not flow work is 0.

Flow in is equal to flow out if you want to a proper at profession analysis for industrial something they have to get to data base many of them have access to data base in these cases as far as this course is concerned you can use trapezoidal rule for all integrations if you are doing VdP numerical integration this simply take $V_2 + V_1/ 2$ under those conditions and just integrate using trapezoidal would that will do then for accuracy you can go to any level of accuracy later okay I will stop here.

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