#### **Indian Institute of Technology Madras**

## NPTEL

## National Programme on Technology Enhanced Learning

## **Chemical Engineering Thermodynamics**

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#### Lecture 9

#### **Illustrative calculations II**

In today's session I would like to discuss the calculation of maximum work that can be obtained from a device. In particular we will discuss the following problem have an under-sea potable device consisting of two tanks connected by a reversible engine.

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The natural the engine thermodynamics is com temperature of just and I need to two tanks and an engine in between. Compressed air from tank 1 initially at 10 bar expands through the engine into tank 2, which has air initially at one bar okay. The apparatus is to operate 100 meters below sea level it means it about a pressure of 10 bar so the idea of releasing the compressed air into the water does not arise because the pressure is very high.

Assume that air is a perfect gas and the holdup in the engine is negligible, some numbers are given for the volume of tank 1 and tank 2 and you are asked to calculate the maximum work that can be obtained from the system.

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Here is a picture of the situation I have tank 1 and tank 2 the volumes are given 0.1 m<sup>3</sup> 0.5m<sup>3</sup> and then the air flows from 1 to 2 to in work Ws shaft work. the initial pressures are given you can calculate the final pressure we will do that now and the maximum work that you can obtained to the system. There are two reasons why I want to do this problem one is to show you how the calculation is termed, secondly to show you that depending on the definition of the system the calculation of the work can be somewhat complicated or very simple.

So it is important in thermodynamics always to choose your system and in general to choose system to be as large as possible without leaving out the detail that you are looking for. Now in this case for example, we will start off with this analysis first to calculate the final pressure.

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You realize the gas initially in one condition in tank 1 and other condition in tank 2, and since it is under water and it is assumed with the whole processes isothermal a temperature is given as 5°C so in the isothermal process first we can calculate the final condition, notice that the two tanks together is a close system so you can take n0 the total number of moles n1+n2, n1 and tank 1, n2 and tank 2 to be a constant the sum. Since you are told it is an ideal gas you have PV=nRT, so  $P_f(V_1+V_2)$  should be equal to  $P_1^{0}V_1+P_2^{0}V_2$  the left hand side as essentially equal to  $n^0RT$ , the right hand side is also equal to n0RT.

So we know  $P_1^0P_2^0$  we know  $V_1$  and V2 so you can calculate  $P_f$  so it comes to 1.75 bar, so it is 10 bar in tank 1, 0.1 bar in tank 2 in the initial stage finally both tank 1 and 2 are at 1.75 bar. We will calculate the number of moles before we actually tackle them actual problem of calculating work,  $n_1^0$  is the number of moles initially in tank 1 clearly given by  $P_1^0V_1/RT$  so you can put in all the numbers here and  $10^5$  is to convert is the conversion for bars and you get essentially 43g moles in  $n_1^0$ ,  $n_2^0$  is 2.15g moles so the total is 45.15.

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At the end of the process the number of moles in tank 1 is 7.525 it is decreased from 43 to 7.525 and from moles and tank 2 as increased from 2.15 23.625. There are two ways of calculating work and trace the thermal operation. First thing is I take consider the open system consisting of the contents of the valve. You told that the contents are not the valve actually I should have said contents of the engine sorry.

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 $= dn_2 (\Delta g) = dn_2 \int v dP = dn_2 RT \ln (P_2 / P_1)$ P2 and P1 vary with moles transferred to tank 2; since P = n RT / V  $\delta W_{max} / RT = \{ \ln [(n_2 / n_1) (V_1 / V_2)] \} dn_2$  $= \ln \left[ 0.2 * n_2 / (n_0 - n_2) \right] dn_2 = \left[ -\ln 5 + \ln (n_2) - \ln (n_0 - n_2) \right] dn_2$ 

So if you have the contents of the engine as the system and the system has negligible holdup if you means the total moles flowing through in this case exactly 37.625-2.15 of 335g moles for in through is much larger than the amount contained in the engine. So I write  $dU=\partial Q-\partial Ws+gi_n dm_{in}-g_{out}dm_{out}$  this is for an isothermal system then this is in class. So the first time here is 0 this is negligible holdup so it is negligible holdup therefore that 0 then we are discussing  $\partial Ws$  and  $g_{in}-g_{out}$ ,  $g_{in}dm_{in}$  is the free energy coming in  $g_{out}dm_{out}$  is the free energy going out.

So under isothermal conditions we have already seen this because Q is simply TdS is less than or equal to TdS and we have split that into  $S_{in} S_{out}$  for the system that have gone into the terms containing  $g_{in}$  and  $g_{out}$  done this in class in the remaining term there as the entropy change of the contents of the engine this also 0 for the same reason again negligible holdup. Then you have this so  $\partial S \partial Ws$  in fact this is at the reversible state so this gives you the maximum work in the maximum work is given by dn2 we working in moles instead of mass into  $\partial g$ ,  $\partial g$  being  $g_{out}$ - $g_{in}$ .

But you know that dg=-SdT+VdP is since the temperature is constant SdT term a 0 you have VdP so it integral of vdP from inlet conditions to outlet conditions, that is it goes from 1 to 2 so this gives you dn2 into RTlog(P2/P1) for an ideal gas V is RT/P so if you integrate this, this is the differential amount of work done when a small amount of moles dn2 are transferred from tank 1 to tank 2.

Now P2 and P1 vary with the moles transferred and since P=n0T/V  $\partial$ Wsmax/RT it si convenient to divide to make it dimensionless is equal to log(P2/P1), P2 is proportional to n2/V2 so you get

n2/V2 and then n2/n1xV1/V2 this is the logarithm of this dn2. As now substituted for n1 it is n0n2, n1+n2 is always equal to n0, n0 is a constant so you get this expression log(V1/V2) is 0.2 times n2/n0-n2 dn2 so you can integrate this you still get the differential amount of work done when dn2 moles are transferred from tank 1 to tank 2. So you have -ln5 logn2 should be integrate -log(n0-n2) should be integrate.

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 $W_{s\,max} \ /RT = \ (-ln \ 5 \ ) \ n_2 + n_2 \ [ \ ln \ (n_2) \ -1 ] \ + \ (n_0 - n_2) \ [ \ ln \ (n_0 - n_2) \ -1 ] + C$ Applying the limits on  $n_2$  , namely  $n_2^{\ \circ}$  to  $n_2^{\ \dagger}$  gives  $\ensuremath{W_{s\,max}}\xspace$  /RT = -68.8 2. CLOSED SYSTEM: Contents of both tanks  $= \Delta A = n_1^{\circ} (a^{\dagger} - a_1^{\circ}) + n_2^{\circ} (a^{\dagger} - a_2^{\circ})$ 

You can carry out this integration and you get  $W_{smax}/RT$ =-ln5 the first term into  $n_2$ +ln( $n_2dn_2$ ) will give you  $n_2ln n_2$ -1 and then  $n_0$ - $n_2 dn_2$  will give you  $n_0$ - $n_2 ln(n_0$ - $n_2$ -1), so you get this expression for the work done plus a constant which constant to be take these. Would you applying this between n2 and between n20 and n2f initially n2 is n20 finally n2 is n2f and if you substitute these values in here you get Wsmax/RT is -68.8 it is dimensionless number.

So you just have to substitute this number at n2f and subtract the value at n20 and this C will cancel out, so this is the final result that you get. So what you have done is you have discussed in open system, you have discuss the differential amount of work done when a small differential quantity of gas is transferred from one tank to the other and then integrated it as the process proceeds into changes continuously we have taken that into account. So this is the work calculation, now you can do this in another way, you can consider a close system contains of both tanks then you know from thermodynamics that the maximum work that can be done by the system is simply the change in the Helmholtz free energy.

The other case it was the Gibbs free energy here it is the Helmholtz free energy, now if you go from the initial state to the final state notice that n10 moles and n10 and n20 are the numbers of moles initially in the tank this n10 moles goes from an initial state of where it is Helmholtz free energy is a10 their final state where it is Helmholtz free energy is af, is a specific Helmholtz free energy this per mole multiplied by the number of moles. Whereas n20 goes from a20 to af.

For example the n10 moles in tank 1 go from 10 bar to 1.75 bar it is an expansion still do work for you, here n20 moles are compressed from the initial condition of 0.1 bar to 1.75 bar.

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So if you try to calculate a the change in a, a is again -SdT+PdV and the SdT will go to 0 because the temperature is constant, so PdV is RT dlnv for an ideal gas, so Wmax/Rt is simply the integral of this which will give you Wmax/Rt then it comes to integral of dlnv and if you are calculating n10 times the integral of dlnv which gives you  $\ln(v1f/v10)+n20$  times  $\ln(v2f/v20)$ . There is a minus sign here which I have carried over and then since v1 is constant v1f/v10 is the same as n1f/n10<sup>-1</sup> so the minus sign can be removed you get n10 log(n1f/n10)+n20ln(n2f/n20).

So this gives you a-74.95 which represents the work done by the system in the compressed air expanding from n10 at 10 bar to 1.75 bar. In n20 being compressed requires work of 6.15 so the network quarters -68.8. Now this is Wmax what we calculated earlier was Wsmax but the two come out to be the same, the reason for that is the difference between W and Wsmax, Wmax and

Wsmax is in fact flow work. Now flow work in a simply  $p_{in}$ ,  $v_{in}$ ,  $dm_{in}$  and flow work out this  $p_{out}$ ,  $v_{out} dm_{out}$ .

Because the holdup is negligible you know that dm<sub>in</sub>=dm<sub>out</sub> and pin vin=pout vout=RT because it is isothermal operation flow in and exactly equal to flow out at rather work done by flow in and work out by flow out by the fluid flowing out are both equal, therefore W must be equal to Ws which is indeed the result you get. But notice that this calculation using the close system concept is much faster, is much simpler than the calculation using the open system.

In this case the problem is fairly simple in the two do not matter but in many cases by choosing the system correctly it is possible in fact to simplify the problem considerably, so the thumb rule in these cases is as far as possible choose a system that is as large as you can identify without loss of detail. Next the thumb rule in thermodynamics then you get the simples formulation. Today we will discuss a thermodynamic analysis of the process for the manufacture of solid carbon dioxide or dry ice as it is called. I want to illustrate the use of the pH chart and we have already discussed the chart in theory it will this.

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Problem solving session will illustrate how the pH chart makes life very easy to do such analysis. Basically carbon dioxide is manufactured solid carbon dioxide you manufactured by mixing makeup carbon dioxide with recycle carbon dioxide and the resulting carbon dioxide gas say 1kg and thus a compressor this compression is done adiabatically compression is so fast that is effectively adiabatic you need to compress it to very high pressures 6400 kPa, this is done in three stages because in every stage the temperature rise can then can otherwise get too high.

Therefore, what you do is compressed it in stages and the thumb rule is usually is used equal compression ratios, so if you are compressing from 100 kPa to 6400 kpa we are talking of the factor 64 so to the power 1/3th is 4, so you will go from 100 to 400, 400 to 1600 and 1600 to 6400 at the end of each compression you will cool it back to roughly 25° or whatever, whatever is the convenient temperature.

And then you isobarically condensed to a saturated liquid this liquid is then throttled down to 100 H kPa, where solid and vapour are in equilibrium. The solid is removed as the product and the vapour is recycled so it is fairly straight forward process and.

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So the process flow sheet we shown here you have make a carbon dioxide and this make a carbon dioxide is at 100 kPa and 30°C the recycle is also at 100 kPa and this recycle is saturated vapour corresponding to the throttling operation, post throttling operation. So at 100 kPa this is saturated vapour so this recycle I will just show you on the chart what the temperature is, this these two are mixed and you have 1kg of carbon dioxide let us say entering the compressor this

is compressed the 400 kPa and from 400 kpa this is cooled to whatever temperature it is appropriate I will show you on the chart again.

And then compressed again to 1600 kPa so this is 400 kPa to 1600 this is compressed one is cooled again and then it is compressed once more here the pressure is 6400, this compressed carbon dioxide is now cooled to liquid carbon dioxide at 6400 kPa, this liquid is now throttled and it goes into a separation drum where you have the product which is dry ice or snow as it is called and here you have saturated vapour. The pressure in this chamber is 100 kPa so the process is clear this the three compression steps each of these is treated as if it was isentropic and actual practice it is adiabatic I am not quite reversible.

Therefore, you will have to make a correction for it we would not discuss that correction today but basically we will treat this as an adiabatic reversible process so you have isentropic compression, and you can follow this the steps on this diagram on the pH chart and pH chart gives you all the data required for you to do the calculations that are required. Now what are the calculations that are required, you have to calculate the dry ice produced per kg of G entering the show chamber.

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Per kg of the liquid carbon dioxide entering the chamber through the throttling valve, you should say through the throttling valve okay. The coolant is available at 20° with the difference of 5° in temperature between the coolant at inlet and the hot stream at outlet okay, this is specified so you

can expect after cooling at the end of the heat exchange process the temperature to be 25°. Now you trace the process on the pH chart you are asked to calculate the work done per kg of dry ice produced. I think tracing this on the pH chart will be somewhat instructive.



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This is the pH chart that I have here which is downloaded from the web it is you can get this chart for carbon dioxide, carbon dioxide has a solid vapour region a sublimation region this is here at the bottom you have solid and on this side you have the vapour and little higher above 500 kPa the transition happens between liquid and vapour, the process let us say we start with 1kg at the point A is it actually a mix of two things what we have is a compression isentropic compression I follow the line of constant entropy up to 400 kPa then you cool down to C which happens to be at 25°.

Because your coolant is available at 20 and you have to maintain a 5° difference between the cool stream leaving the heat exchanger and the coolant entering so 25° is all that you can cool to, so the point B is 400 kPa after isentropic compression it is identified by entropy at A equal to entropy at b so you move along the isentropic line. Remember that every point on this chart is completely identified by specifying two properties so we start here A is known and come back to how you get the position of A exactly.

But from A to B is isentropic compression then cooling to C, C is at the pressure is 400 and there is a temperature change goes down to 25 and then you have another isentropic compression to B, now the temperature is the pressure is 1600 kPa and the temperature is whatever you read on chart in this case for example this temperature is like 120° you can imagine if you keep going the temperature could raise very high. So at this point you cool it again to 25° this is isobaric cooling to just a heat exchanger and remaining like the pressure drops, so the pressure the effectively 1600 and the temperature is 25 at the point E.

Then you do an isentropic compression again to 6400 and then cool it all the way to G, the temperature at G happens to be 25°C in fact the cooling the coolant in this case really determines the pressure up to which you go in order to then throttled and obtain the product. In this case the saturation temperature at the point G where the pressure is 6400 PSIA I am sorry 6400 kPa kilo Pascal's is exactly 25°. Now here there is a pH case transition you keep cooling it till all of it becomes a liquid.

So the point G essentially if you start with 1kg at A of gas at point G you have 1kg of liquid at 6400 kPa, then you do a throttling operation it comes right down the throttling operation is a nice enthalpy operation as we have seen in theory, so it will come right sown you go down to the pressure of 100 kPa. But at 100 kPa carbon dioxide is a mixture of solid and vapour in the amount of vapour and the amount of liquid is determined by the position in this case which between the saturated solid which is a P and the saturated vapour which is at R in this diagram.

So what I will do step by step take you through the calculations convenient way to start at G because the stream is identified it is saturated liquid at 6400 so if you start with G and then do the throttling then you can locate the position R and you know what the make at carbon dioxide state is so you can mix these two and obtain the position A and then complete the diagram.

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So you start with stream G which is saturated liquid at 6400 kPa from G I go to H what I need to know is the enthalpy there this isenthalpic you can read hG which is equal to hH on the diagram, in the diagram it is about -40 kJ/kg I have not been very careful in reading these numbers you can do more accurate job but I want to illustrate how this calculation is done, so you go from G to H at 100 kPa this is an H is at 100 kPa and the enthalpy is -40, this stream H splits into a product ice and saturated vapour.

And all this is isobaric so you equate the enthalpies before and after mixing you have -40 is equal to the enthalpy of the solid is -420 times x is the fraction of the solid and 120 is happens to be the enthalpy of the saturated gas at R. so if you combine this you can calculate x from this equation. The x value that you get this point 0.31kg dry ice per kg of carbon dioxide entering the compression.

Our basis is 1 kg entering the compression that means for every kg entering 0.31 of snow is formed dry ice is formed and 0.69 is recycled, so the recycle you can see on this chart you can see where is the recycle is and where the product is, you can see that the product enthalpy which I read out for you is -420 the enthalpy of the saturated vapour at 100 kPa is 120 and H is at -40 so you come to the conclusion that the fraction of solid produced is 0.31, so that completes our analysis of just the throttling operation, throttling operation and the separation into product and recycle vapour. The next step they make up carbon dioxide at 30° we have given this.

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And make a gas to be equal to the amount of dry ice removed so 0.31 kg at 100 kPa 30° I read the enthalpy on the chart it is 220 is mixed with recycle, the recycle is 0.69 kg at 100kPa and enthalpy of 120 the temperature which happens to be  $-80^{\circ}$  at you can read on the chart. Now if you mix these two you get an enthalpy at A of 151 kJ/kg okay it is an average of 220 and 120 in the ratio of 0.31 to 0.69 so 0.31x220 + 0.69x120 will give you 151, this locates point A is at 100kPa that we know and 151 kJ/kg so that locates point A on the chart.

Once you know point A you follow the isentropic line the entropy constant I do not have to read the value but if you do you will find it is fairly close to 4.6 it is just little over 4.6 so you follow that line up to 400kPa and you get the point B. The point B you move left you move isobarically along the horizontal line towards 25°C which is the point C, so you have here at each point I read of data that I need seen A is compressed isentropically to 400kPa the final enthalpy at the point B is 230 you know that the enthalpy at the point A is 151.

So the difference between these two is 79 kJ which is what which is the cooling I am sorry, which is the compression work this is the compression work, once you got the compression work at the point B then stream B is cooled it is cooled to the point C where the enthalpy is 210,so from 210, 230 to 210 this is has a cooling load of 20kJ/kg stream C is then compressed isentropically again on this chart you go along the isentropic line and in this case the entropy is 4.6 you go up to 1600 which is point B.

Now if you read the enthalpy at D you get the enthalpy at D is 300 and you already know that the enthalpy at C is 210 so between these two you know that the compression work is 90 kJ/kg. So you got one first stage compression work second stage compression work, then again from 300 it is cooled down to the point E here cooling load cooling equal to 100 kJ/kg so you go from the point B to point E and if you read the difference in enthalpies it gives you the cooling load.

Remember for isentropic compression the work done a simply  $\delta H$  from point D again you compressed to point F this is the third stage of compression so E to F is 200 to 285 so again I can write compression work is equal to 85 kJ/kg and finally from F to G there is a huge cooling this heat exchanger is a very big heat exchanger and the cooling load is 285-40 which is 235 kJ/kg. remember the condensation occurs at exactly at 25° so you just need a lot more cool and to bring it down to the point G instead of stopping at the vapour.

So this gives you the state F calculations that you need for answering all the questions and the questions are simply let me recall the questions for you first question is calculate dry ice produced per kg of G entering this no chamber we have already calculated that we showed you that the dry ice produced is 0.31 this is A.

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So the answer to A is 0.31 kg of dry ice produced per kg entering the compression, the second question is what is the compression work.

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Compression work for producing 0.31 kg of dry ice I simply the compression work in the three stages which we already showed you it is (hB-hA)+(hD-hC)+(hF-hG) and this whole thing is simply equal to 79+90+85 which we showed you on in individual steps giving u2 and add 54 kg so the work done per kg of dry ice is simply 254/0.31 or 819 kJ. So this is the work you have to put in, in order to produce 1kg of dry ice.

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So this actually completes the problem but the second part of the problem is trace the process on the pH chart we have already done that let me go over it again, you have make up carbon dioxide you have recycle carbon dioxide the recycle can be located very easily to know the amount of recycle you have to do the calculations staring from G you do the throttling operation you know the enthalpy at G because it saturated liquid at 6400 kPa so the enthalpy there is -40 it splits into vapour and dry ice and how it splits it can be done by an enthalpy balance so this gives you the amount of dry ice produced per kg.

Say of liquid at G or per kg entering the compresses so this gives you a split of 0.31 kg per kg entering the compressor. This 0.31 is the recycle with an enthalpy of 120 kJ/kg it is mixed with the makeup which is at 30°C you can located on the graph and then you mix them the two 0.69 of makeup will give you an enthalpy of 151 okay, that on the chart go isentropically to be B to C is a very small heat exchanger then C to D C is located by the temperature  $25^{\circ}$  and the pressure 400 from there again isentropic compression and from D to E you have to go you have isobarically at back to  $25^{\circ}$  so this is the cooling required then E to F is again a compression.

So in each stage this certain amount of work done work is approximately equals not exactly equal but you have to add these three to get the total work. From F you do an isobaric condensation again you do a cooling followed by condensation and this is throttled. So you can see how easy it is on the chart, now let me illustrate here what would happen if the compressor was not isentropic but not reversible okay, compression is effectively adiabatic what would

happen then is for example third stage if you take the third stage let us look at the third stage compression.

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3 smp hE2 = 85 103/14 compression = 85% (say) = = 200 + 100 = 300 kJ/kg

As an example, you have the enthalpy at E and the enthalpy at F are known we have already read those values, the enthalpy at E we have seen this 200 and the enthalpy at F is 285 so we concluded that the work was equal to remember this is minimum work 85 kJ/kg. Now if you are given that the efficiency of the compressor actual compressors of the compression I say 85% this is given a typical values for compressor efficiencies then the actual work is actually 85/0.85 or it is 100 kJ/kg. Then enthalpy at F' the actual at the end of compression the enthalpy is now remember that the work done is always equal to  $\delta$ H in an adiabatic process so hF' is actually 200 hE+100 which is 300 kJ/kg.

So on this diagram for example you have to locate hF' at 300 this is F this is F' 300 and the actual compression line will is on the right, on this side is ideal compression this side is actual. So your work will increase by that amount so correspondingly if all the compressors having efficiency of 0.85 the total work that we calculated earlier the sum of the three terms that we calculated we got 819 kJ, so correspondingly the total work in isentropic case is 819 kJ/kg of dry ice.

Now actual work is equal to 819/0.85 you can calculate this 120 the approximately 940, so you can see that with the chart available knowing the efficiencies you can actually get the actual

work done therefore you can get the work required in order to produce 1kg of dry ice. So if you do have the pH chart it makes calculations much easier, if you where to do the calculations with an equation state you can get equally good numbers provided you have a good equational state for carbon dioxide.

But the pH chart makes life that much easier so this is simply to illustrate to you the use of laws as we derive them the first law actually in effect both the laws because remember while I am using only enthalpy balances we are locating the points through an identification of the compression as an isentropic process that means we need the entropy as a property of state which is what the second law defines for you. So effectively this illustrates for you how calculations can be done with the pH chart on any process.

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