**Material and Energy Balances**
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**Lecture - 67**
**Energy Balances: A Review - Part 4**

Welcome back for today's lecture on material and energy balances. So we have looked at energy balances and we covered all the fundamentals. We looked at the basics and performed a lot of example problems. In the last few lectures, we have been summarizing all the concepts that we have learnt through energy balance calculations.

So today, we will be solving a problem which actually tries to summarize all the concepts that we have learnt from both material and energy balances. In this problem we would actually be performing material balances first in an extensive way for this multiunit process and then we will actually move on to working on the energy balance aspects which will again cover most of the fundamental concepts that we have learnt throughout this course. So this problem nicely summarizes all the aspects which have been covered over the past few weeks in this course.

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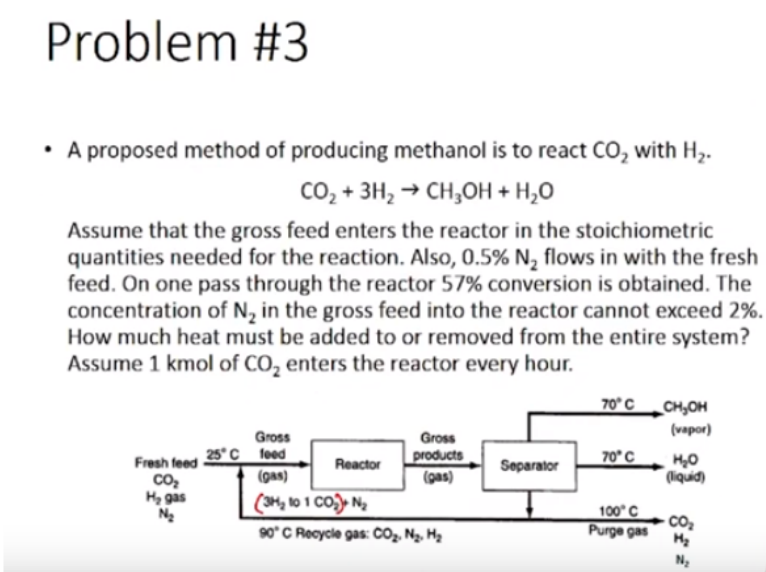


So let us now go to the problem. So the problem statement says a proposed method of producing methanol is to react CO2 with hydrogen. 1 mole of CO2 reacts with 3 moles of hydrogen to form 1 mole of methanol and 1 mole of water. Assume that the gross feed enters the reactor in the stoichiometric quantities needed for the reaction. Also, 0.5% nitrogen flows in with the fresh feed. On one pass through the reactor, 57% conversion is obtained.

The concentration of nitrogen in the gross feed into the reactor cannot exceed 2%. How much heat must be added or removed from the system given here? Assume 1 kmol of carbon dioxide enters the reactor every hour. So here is the flowchart. So you have a fresh feed which is coming in at 25 degree Celsius containing CO2, hydrogen, and nitrogen. It is getting mixed with a recycle feed which again contains carbon dioxide, nitrogen, and hydrogen.

However, this recycled gas is at 90 degree Celsius and here you end up having a gross feed which would contain carbon dioxide and nitrogen and hydrogen. Here what you have been given is it is 3 moles of hydrogen per mole of carbon dioxide which is the stoichiometric ratio with which it is coming in. It has been told that the gross feed enters the reactor in the stoichiometric quantities needed for the reaction.

And based on the reaction equation we know that for every mole of carbon dioxide there are 3 moles of hydrogen required. So that would be the ration which has been given here and this gross feed enters the reactor where 57% conversion for a single pass is obtained. So the gross feed, if you were to take reactor as the system then you would have 57% conversion.

So if you remember the lectures which we had on systems with recycle and reactions we would have discussed what single pass and overall conversion is. Here we have been given the single pass conversion. So this means the feed which is passing through the reactor a single time gets a 57% conversion and this results in the formation of product gases.

And as you can see the product gas then goes into a separator where methanol vapor at 70 degree Celsius, water liquid at 70 degree Celsius are taken out as products and you have a stream of gases which are the non-condensable components namely carbon dioxide, hydrogen, and nitrogen which are actually leaving the separator. So this is split into 2 streams. One is purged and the other is recycled.

The purged stream is at 100 degree Celsius and the recycle gas is at 90 degree Celsius. So this is the system which we are looking at. The 90 degree Celsius is recycled, is basically mixed with the fresh feed. So now we have this process given to us. We have been asked to identify how much heat must be added to or removed from this entire system. Let us look at this process and try to perform all the required calculations.

So I always say, the first step for performing any energy balance calculation is to perform material balances. Here we have been given 1 kmol of CO2 enters the reactor every hour so which means the basis we have to use would be 1 kilo moles of CO2 in the gross feed. So with that we would be able to perform the required material balance calculations.

So the first part would be to perform the extensive material balances that are required for getting the flow rates for all the streams. Once we have that, we can actually perform the energy balances. Let us go to the problem. Let us try to solve this problem.

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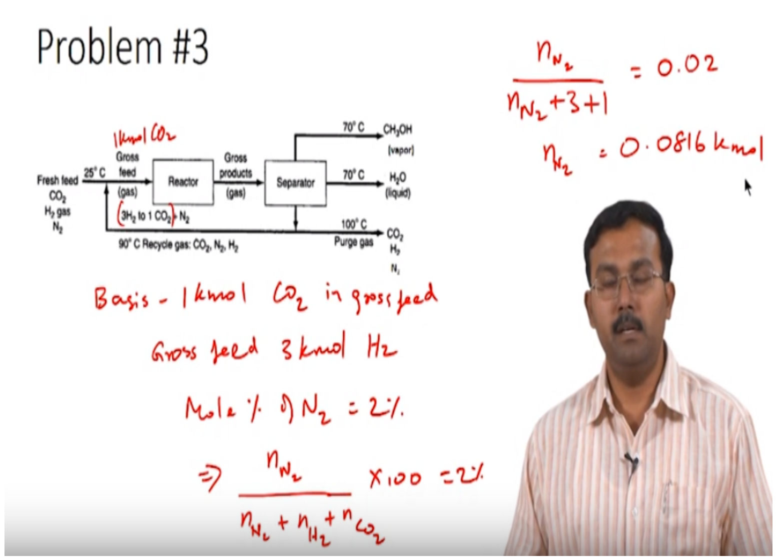


Based on the information given to us in the problem we can use the basis as 1 kmol of CO2 in gross feed. So we have been told that 1 kmol of CO2 enters into the reactor. So which means this is the gross feed and you have 1 kmol of CO2 entering here. So this is the basis given. So we have also been told that the feed which is entering the reactor contains stoichiometric ratio of CO2 and hydrogen which is 3:1 so which is also been given to us.

So now that we have that information it would mean that the gross feed actually would contain 3 kilo moles of hydrogen as well. So you have 1 kilo mole of $CO_2$ and 3 kilo moles of hydrogen. So in addition to carbon dioxide and the hydrogen, you also have nitrogen. We need to find out how much nitrogen is accompanying this $CO_2$ and hydrogen. How would we do that? We have been told that the concentration of nitrogen in the gross feed cannot exceed 2%.

So which means we will use 2% as the concentration of nitrogen in the gross feed and using that concentration, assuming that it is at the maximum threshold given, we will be able to identify how much nitrogen is present. So if we were to assume nitrogen concentration, the nitrogen mole percentage is 2%. So mole percent of nitrogen = 2%.

This implies what you have would be number of moles of nitrogen/number of moles of nitrogen + number of moles of hydrogen + number of moles of carbon dioxide times 100 = 2%. So what you would have from here is, the only value we do not know is $n_{N_2}$ which is the number of moles of nitrogen. The other values are already known. We know that hydrogen is kilo moles and carbon dioxide is coming in at 1 kilo mole and the concentration, the mole percentage is 2%.

So the mole fraction is 0.02. So using this, we can actually calculate the value for the number of moles of nitrogen and the value we would get would be 0.0816 kmol. So we have 0.0816 kmol of nitrogen coming in. So we also have been given that the single pass conversion is 0.57 or 57%. How would we be able to use the single pass conversion?

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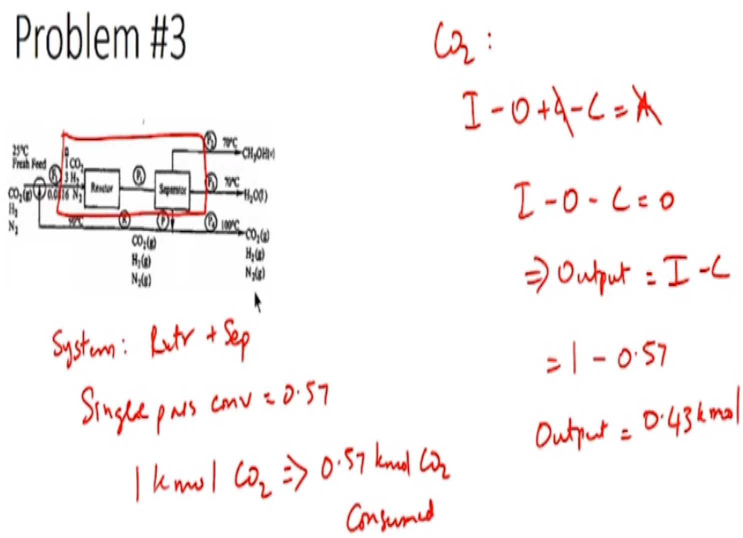


For using this value, we need to ensure that the reactant which is entering the reactor only passes through the reactor a single time. So which means we have to take the reactor, the gross feed as the component which is crossing the system boundary and we need to ensure that whatever is leaving does not come back through the recycle stream and the system needs to be chosen appropriately.

So for this reason, we would choose, we could either choose just the reactor or the reactor and the separator. If we were to choose just the reactor, we do not have much information about the gross product. However, if we were to choose the reactor along with the separator then we have a lot of information about the streams which are leaving the separator. So for this reason, we will choose the system of interest as reactor + separator.

So the system we are using would be reactor + separator. So now that we have used the system, we can use the single pass conversion. Single pass conversion = 0.57, right? So this means we have 1 kmol of $CO_2$ entering. So if 1 kmol of $CO_2$ is entering how much is actually getting consumed. This implies 57% of this is getting consumed because of the single pass conversion. So which means 0.57 kmol of $CO_2$ is consumed.

So now to get information about $CO_2$ which is leaving the system we would have to write a $CO_2$ balance. So the $CO_2$ balance for the system would be input – output + generation – consumption

= accumulation. At steady state there would not be any accumulation and as CO2 is a reactant, it is only getting consumed. There is no generation of CO2. So you would have input – output – consumption = 0 implying that output = input – consumption.

So we know that the input is 1 kmol and consumption is 0.57 kmol giving the output for CO2 as 0.43 kmol. So this CO2 is actually leaving only through the stream P because you have other streams here which are P 2, P 3, and P 4. P 4 does not cross the system boundary here. Only the streams which are crossing the system boundary are P 2, P 3 and P. So out of this P 2 has only methanol. P 3 has only water. P has carbon dioxide, hydrogen, and nitrogen. So the number of moles of carbon dioxide in the stream P is 0.43 kmol.

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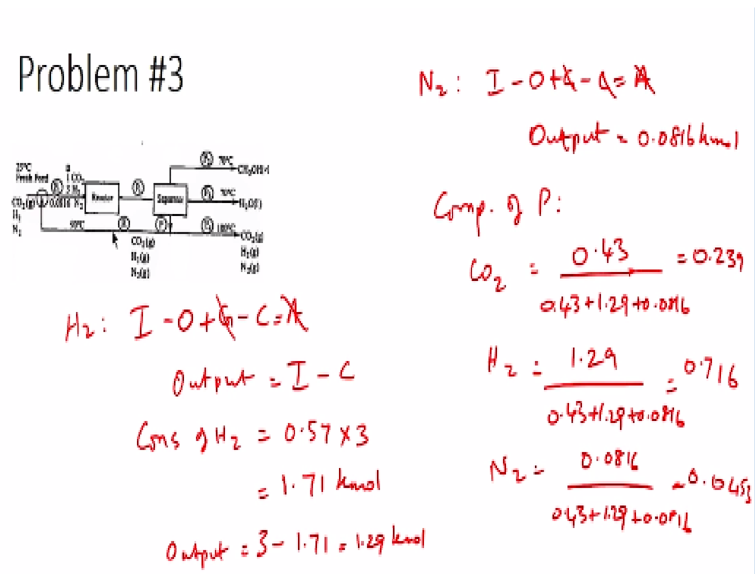


We now have to calculate the number of moles of hydrogen in the stream P. So using the same system, we need to now write a hydrogen balance. The hydrogen balance again is input – output + generation – consumptions = accumulation. At steady state there is no accumulation. Again, hydrogen is a reactant so there is no generation of hydrogen. So your output again would become input – consumption. So input we already know is 3 kmol. So what is consumption?

So consumption of hydrogen would also be equal to 0.57 times 3 because this is 57% conversion for a single pass applies for both carbon dioxide and hydrogen because they are fed at stoichiometric ratios. So this means the number of moles of hydrogen consumed would be 1.71

kmol. So substituting this value for consumption and the value for input we can calculate the output for hydrogen from the system would be 3 – 1.71 which is 1.29 kmol.

So now we know that the product stream P contains 1.29 kmol of hydrogen and 0.43 kmol of carbon dioxide. We now need to identify how much nitrogen is actually leaving the system. Nitrogen does not take part in the reaction. So the nitrogen balance which initially would be input – output + generation – consumption = accumulation.

Can be simplified as input = output because at steady state accumulation goes to 0 and as it is not taking part in the reaction, generation and consumption would also be equal to 0 giving us nitrogen output as the same as input which would be 0.0816 kmol. So now that we have the information about the product stream, we can actually identify the mole fraction of all of these components in the product stream. So which is this important?

If we have the mole fraction of these product streams, we can actually identify the composition of the recycle stream and the purged stream which can then be used for further calculations, okay? So we will try to find the composition of the stream P. So composition of P would be it contains carbon dioxide which is 0.43/0.43 + 1.29 + 0.816 giving a mole fraction of 0.239 and we have hydrogen which is 1.29/0.43 + 1.29 + 0.0816 giving a value of 0.716 and for nitrogen the composition would be 0.0816/ 0.43 + 1.29 + 0.0816 giving a value of 0.0453.

So now we have the composition for the stream P which in turn gives us the composition for recycle and the purge stream. As it is a splitter we know that the composition would not have changed.

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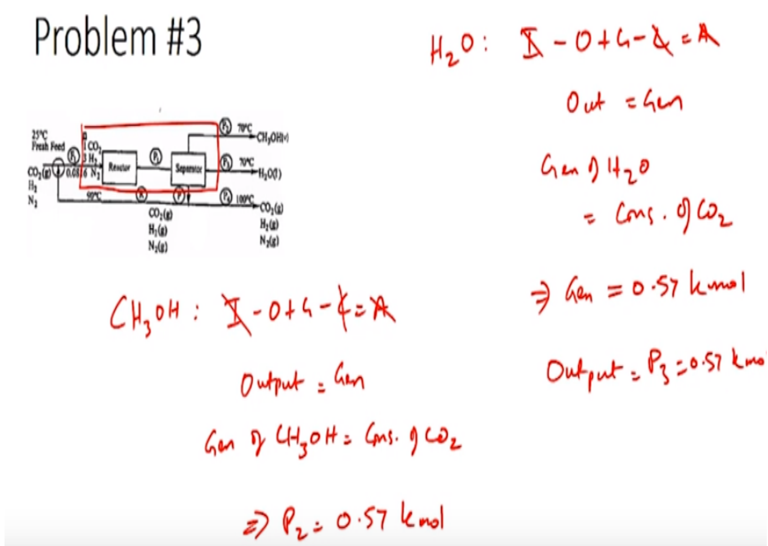


So we also need to identify how much of methanol and water are leaving the system which we had chosen. The system we had been working on is this, which is the reactor + separator. So to identify the amount of methanol, we have to write a methanol balance. So methanol balance would be input – output + generation – consumption = accumulation. At steady state accumulation goes to 0 and methanol is not being consumed as it is a product.

You do not have any input of methanol. You only have output and generation of methanol which means output for methanol which is P 2 would be equal to generation of methanol. So looking at the stoichiometry, generation of methanol would be equal to the consumption of carbon dioxide. So generation of methanol = consumption of carbon dioxide. This implies P 2 is actually = 0.57 kmol. Similarly, we can perform material balance for water.

So for the water, you would have input – output + generation – consumption = accumulation getting simplified to output = generation. So this is the same logic as we used for methanol. So generation again looking at stoichiometry, generation of water = consumption of CO2. This implies generation of water = 0.57 kmol. So therefore, output which is P 3 = 0.57 kmol.

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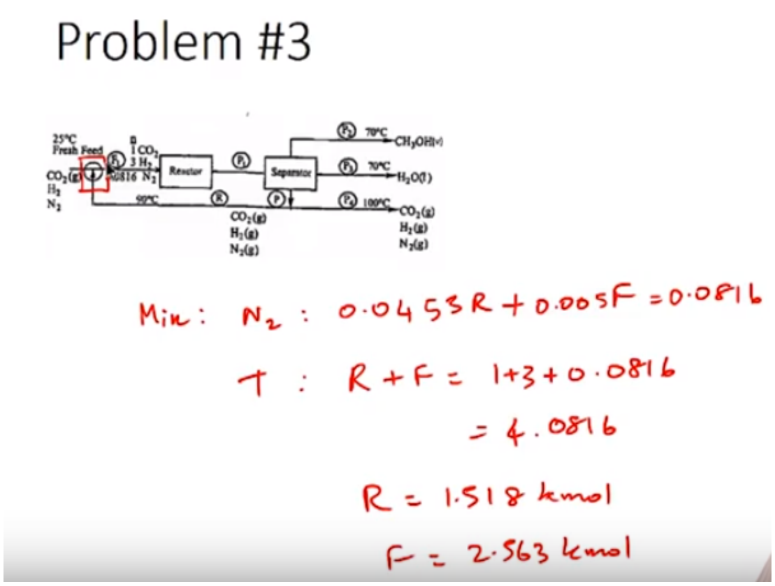


Now to get the information on the fresh feed and the recycled feed, we need to choose a different system. So here we could use the mixing point as the system. So if we were to use mixing point as the system then we can actually write two different balances. One would be for nitrogen and the other could be for the total balance and using these we will be able to solve for the two unknowns. The first unknown is the recycle amount R and the other is the feed rate F.

So let us try to get this. So let us first write the nitrogen balance. The nitrogen balance would be simple. You would have 0.0453 R. So we have already calculated the mole fraction for nitrogen in R which is equal to the mole fraction of nitrogen in P, right? So using that we get this equation which is 0.0453 times R amount of nitrogen entering into the mixing point through the recycle plus 0.005F. so we have been told that the nitrogen in the fresh feed is 0.5%.

So that means the amount of nitrogen entering through the fresh feed would be 0.005F and this is = 0.0816 which is the total number of kilo moles of nitrogen in the gross feed. So we can also write a total balance. The total balance would be R + F = 1 + 3 + 0.816. So this would then become 4.0816. So now we have 2 equations and 2 unknowns. So solving these two equations simultaneously, you would be able to get the values for R and F.

So let us see what the values would be. Solving these we get R = 1.518 kmol and F = 2.563 kmol. So this gives us the values for R and F. However, we still do not have the information on how much carbon dioxide, hydrogen, and nitrogen are actually entering through the fresh feed. So how would we get that?

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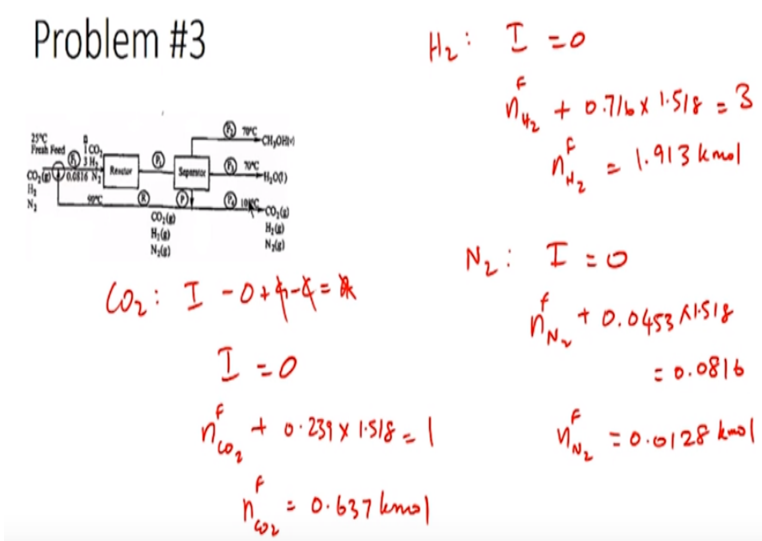


So that we can get by writing individual component balances for the mixing point. Let us now write the carbon dioxide balance for the mixing point. It would be input – output + generation – consumption = accumulation. So no accumulation at steady state. No generation or consumption. It is a nonreactive system. So input = output. So your input actually has two terms. One is through the fresh feed. Other is through the recycle feed.

We already calculated the value for the recycle feed, the molar flow rate for the recycle feed as 1.518 kmol. So now we also have the composition of the recycle feed. So we will have these two things separated. You would have one which is n F CO2 which is the carbon dioxide entering through fresh feed plus 0.239 times 1.518 which is the number of moles of carbon dioxide entering through the recycle stream equals the total number of moles of carbon dioxide in the gross feed which is 1.

So this means the fresh feed would contain 0.637 kmol of carbon dioxide. Similarly, we can write a balance for hydrogen. The hydrogen balance would basically be again input = output for a nonreactive system. At steady state it would be input = output and the equation would be n H2

F + 0.716 times 1.518 = 3. So solving this you would get the number of moles of hydrogen coming through the fresh feed as 1.913 kmol.

Similarly, we can write a balance for nitrogen which would be again input = output. So you have nitrogen from fresh feed + 0.0453 times 1.518 which is the number of moles of, amount of nitrogen entering through the recycle stream. This would be = 0.0816. So solving this equation we would get number of moles of nitrogen entering from the fresh feed would be = 0.0128 kmol.

So with this we now have the information about the fresh feed. So we also need to have the information about the purged stream if we want to perform energy balance calculations for the overall system.

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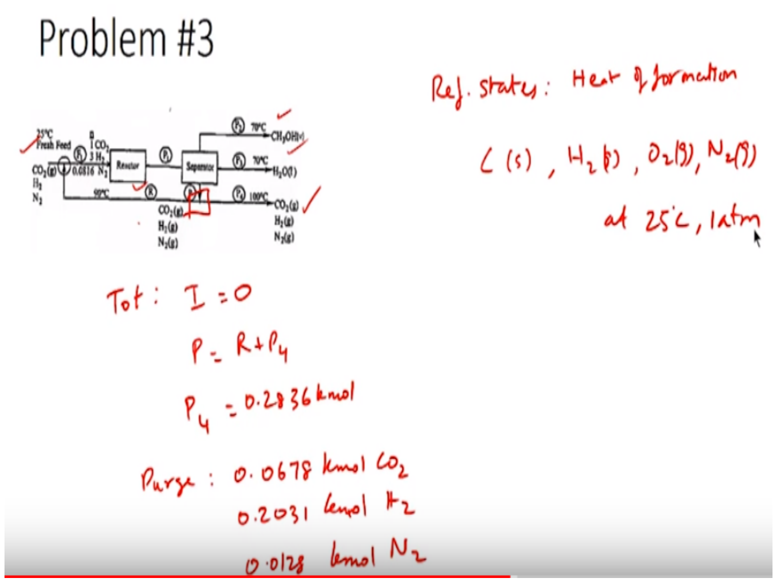


So for doing that we will have to write a balance for the splitter as we now have the information about the fresh feed. We have information about the recycle stream. We have information about P 2, P 3. We just need to get the information about P 4. For this we can write the total balance equation for the splitter. The total balance for the splitter would just be input = output and input is actually P. This is = R + P 4. So solving for this we will actually get P 4 = 0.2836 kmol.

So we knew the value for R. we had also calculated the value for P earlier. So using these two values, we can calculate the value for P 4. We already know the composition of the purge stream.

The composition of the purge stream would be the same as the composition of the stream P and the recycle stream. Using that we can calculate the number of moles of the amount of carbon dioxide, hydrogen, and nitrogen in the purge stream.

So the purge stream basically contains 0.0678 kmol of $CO_2$, 0.2031 kmol of hydrogen and 0.0128 kmol of nitrogen. So this gives us the information about the purge stream as well. So now, we have all the information. So we have the information about fresh feed. We have the information about the product stream for methanol, product stream for water and the purge stream which contains all the $CO_2$, hydrogen and nitrogen.

So we have information about the overall system. All the flow rates for the overall systems are available. So the amounts now that are available can be used for performing the energy balance calculations. So what is the energy balance we can perform? So for performing energy balance calculations for the overall system, we need to first identify appropriate reference states. So here in this problem, if you look at the problem statement we have been given the reaction.

So this is the problem statement, right? So the problem statement says that carbon dioxide reacts with hydrogen to form methanol and water. We have not been given the heat of reaction. So we could either choose to calculate the heat of reaction using Hess's law explicitly and then apply this heat of reaction while we perform the calculations for energy balances.

Or we could use the heat of formation method where the heat of reaction is implicitly calculated while performing the calculations building the enthalpy table itself. So here I have chosen to use the heat of formation method. So for heat of formation method we have to choose appropriate reference states. So the reference states I have chosen are determined because of the method I am using. So I am using the heat of formation method.

So for the heat of formation method, the reference states have to be elements as they appear in nature at 25 degree Celsius and 1 atmosphere. So this means the reference states can be carbon solid + hydrogen gas sorry not plus hydrogen gas and oxygen gas and nitrogen gas all at 25 degree Celsius and 1 atmosphere. So now that we have taken this as the reference state we would have to build the enthalpy table.

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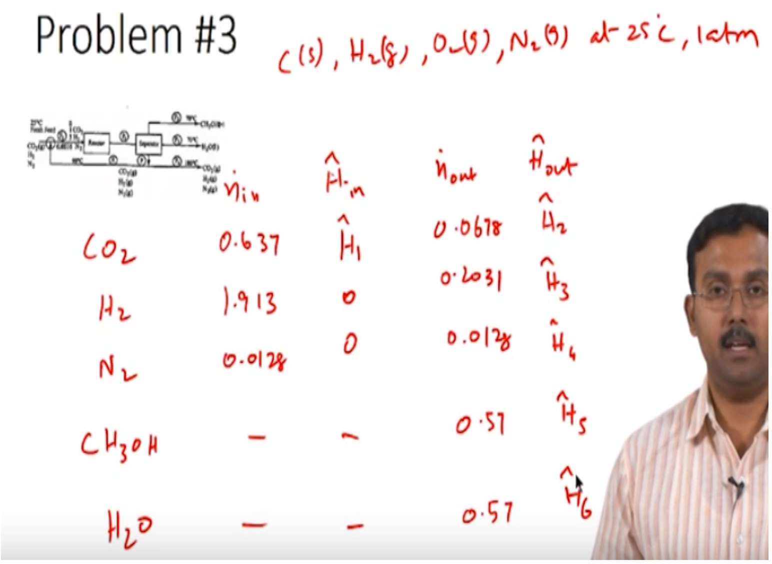


So let us build the enthalpy table for the overall system. So the overall system encompasses the mixing point, reactor and the separator. So the only streams which are crossing the system boundary are the fresh feed which contains carbon dioxide, hydrogen, and nitrogen and you have the product streams which are methanol and water and the purge stream which contains carbon dioxide, hydrogen, and nitrogen. So let us now write the enthalpy table for this.

You would have carbon dioxide, hydrogen, nitrogen, methanol, and water. So these are the components which are crossing the system boundary. So you have n in dot, H cap in, n out dot, and H cap out. So let us fill out the values. So based on the material balance calculations we have performed, we know that 0.637 kmol of carbon dioxide enters through the fresh feed. 1.913 kmol of hydrogen enters through the fresh feed and 0.0128 kmol of nitrogen enters through the fresh feed. There is no methanol or water entering through the fresh feed.

So let us look at the exit streams. We now have carbon dioxide leaving through the purge stream. We have calculated the number of moles of carbon dioxide leaving through the purge stream as 0.0678 kmol and the amount of hydrogen leaving through the purge stream is 0.2031 kmol. Amount of nitrogen leaving through the purge stream is 0.0128 kmol and you have methanol which is leaving the system as 0.57 kmol through the product stream P 2 and water is leaving, 0.57 kmol of water is leaving through P 3 and now we have all this information.

We had used the reference states as carbon solid, hydrogen gas, oxygen gas, nitrogen gas all at 25 degree Celsius and 1 atmosphere, right, so for the heat of formation method. So here the first component is carbon dioxide. Carbon dioxide coming in at 25 degree Celsius you would have some enthalpy associated with it compared to the reference state because you have the formation of carbon dioxide.

The next one is hydrogen which is coming in at 25 degree Celsius and 1 atmosphere. It is the same as the reference state so this would be 0. Now nitrogen coming in at 25 degree Celsius and 1 atmosphere is at reference state so which will also be 0. So the exit streams all of them are at different temperature or exiting as a compound rather than the element which means we would have to calculate all these enthalpies.

So this would be H 2 cap, H 3 cap, H 4 cap, H 5 cap and H 6 cap. So now we have to calculate 6 different enthalpy, specific enthalpy values.

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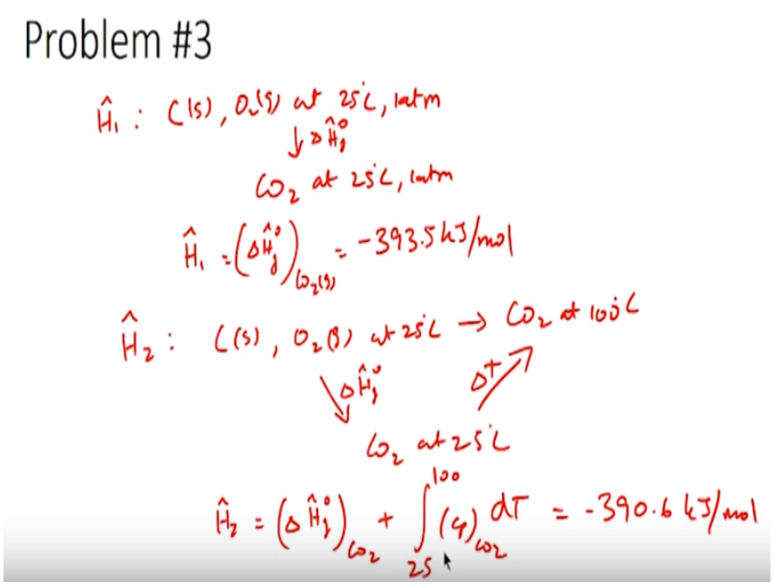


Let us first calculate H 1 cap. The H 1 cap is basically the first enthalpy where carbon and oxygen, carbon solid and oxygen gas at 25 degree Celsius forms carbon dioxide at 25 degree

Celsius and 1 atmosphere. So the reference state is carbon solid and so the reference state used is carbon solid and oxygen gas at 25 degree Celsius and 1 atmosphere. From here it goes to carbon dioxide at 25 degree Celsius and 1 atmosphere which is the fresh feed for carbon dioxide.

So here only formation of, standard heat of formation for carbon dioxide has to be accounted for. So H 1 cap would be equal to the standard heat of formation for carbon dioxide gas. So this value can be obtained from any table. So this value is actually -393.5 kJ/mol. Now we have to look at H 2 cap. So H 2 cap is again for carbon dioxide. However, the exit stream carbon dioxide is leaving at 100 degree Celsius.

So we now have a process where carbon solid and oxygen gas at 25 degree Celsius forms carbon dioxide at 100 degree Celsius. So the first step would be formation of carbon dioxide at 25 degree Celsius and from here you have the heating of carbon dioxide to form carbon dioxide at 100 degree Celsius. So the first step would have the heat of formation and the second step would be a delta T term.

So your H 2 cap would be equal to the standard heat of formation for carbon dioxide gas + integral 25 to 100 (C p) CO2 gas dT. So using the C p (CO2) gas from any table and the heat of formation we will be able to calculate this value as -390.6 kJ/mol. So since CO2 is a combustion gas, instead of performing integral C p dT, we would also be able to get the value for the enthalpy of carbon dioxide with reference to 25 degree Celsius from a table which is the combustion gas table which we had discussed earlier.

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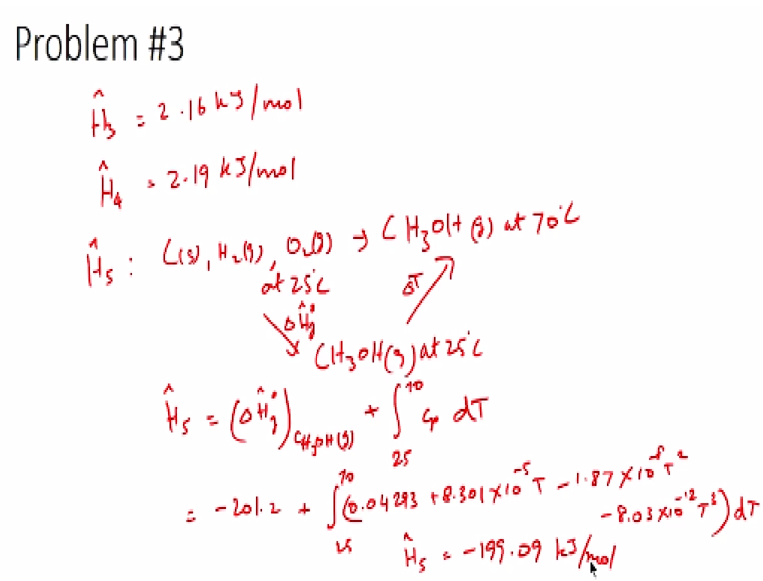


So we now have H 2 cap. Let us look at H 3 cap. H 3 cap is nothing but hydrogen gas at 100 degree Celsius. So this is only the heating of hydrogen gas from 25 degree Celsius which is the reference state to 100 degree Celsius which is the exit purge condition. So this value can be obtained from the table which would be 2.16 kJ/mol and H 4 cap can also be obtained from this kind of a table. So H 4 cap is for the nitrogen at 100 degree Celsius.

So again from combustion gas table, you will be able to get this value, which is 2.19 kJ/mol and we now have to look at H 5 cap and H 6 cap. So what is H 5 cap? So H 5 cap is the change in enthalpy for the process where carbon solid, hydrogen gas, and oxygen gas forms methane. So these are all at 25 degree Celsius, the reference state is at 25 degree Celsius, and if forms methanol gas at 70 degree Celsius.

Now, we need to perform calculations to get this. So the first step would be formation of methanol gas at 25 degree Celsius and then would be heating. So initial step you would be looking at the standard heat of formation for methanol gas and the second step is delta T. So your H 5 cap is actually equal to standard heat of formation of methanol gas plus integral 25 to 100 C p of methanol dT.

You have to use the C p of methanol gas and you will be able to perform this integration. So the value here would be -201.2 + integral 25 to 70. So this is 70, I am sorry, not 100. So 70 would be

0.04293 + 8.301 times 10 power -5 T – 1.87 times 10 power -8 T square – 8.03 times 10 power -12 T cube dT. So the value for C p I obtain from the tables. So from here I can calculate H 5 cap as -199.09 kJ/mol.

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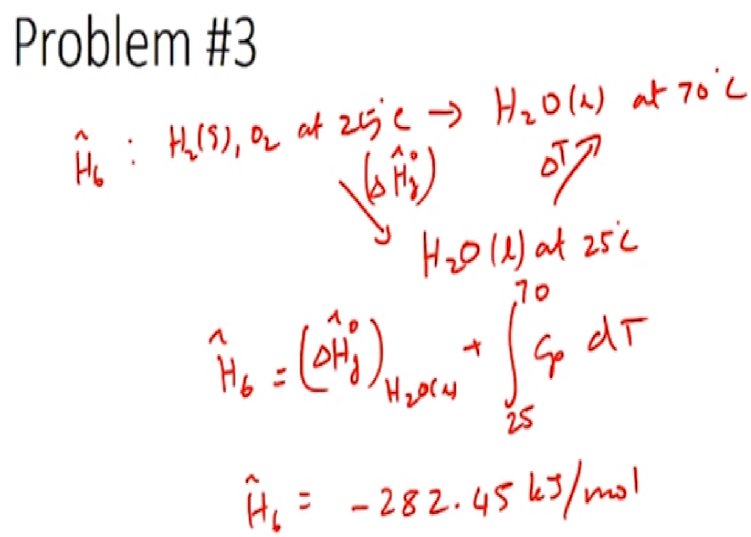


So similarly, we have to calculate the value for H 6 cap as well. So for H 6 cap you have hydrogen gas and oxygen gas at 25 degree Celsius forming water liquid at 70 degree Celsius. So the first step is formation of water liquid at 25 degree Celsius and from here it is heated. So the first step is just heat of formation, standard heat of formation for water liquid and the second step is delta T which will be integral Cp dT.

So your H 6 cap would be equal to standard heat of formation for water liquid plus integral C p of water liquid dT and the temperature is from 25 to 70. So using the value for C p for water you would be able to get this value for H 6 cap as -282.45 kJ/mol. So the C p for water would be 0.0754 kJ/mol degree Celsius. So using that we have been able to calculate H 6 cap.

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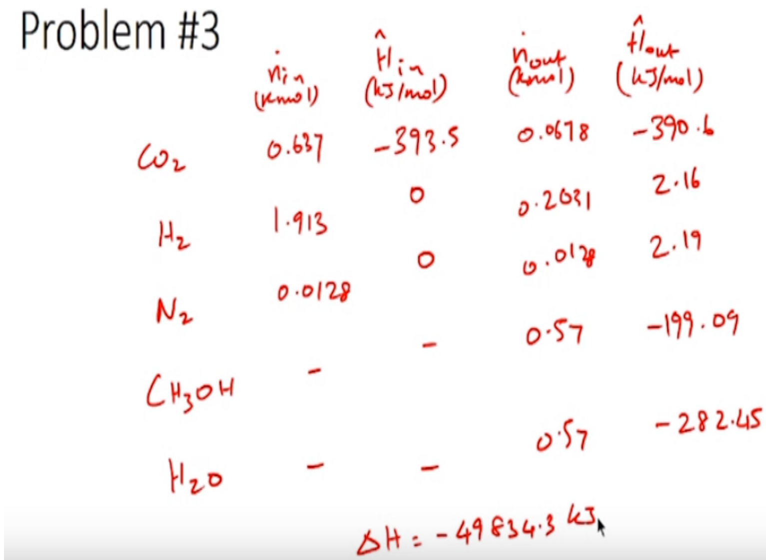


Now that we have calculated all the enthalpy values, let us go ahead and fill the enthalpy table. So the enthalpy table which we had was CO2, hydrogen, nitrogen, methanol, and water. So we had n in dot, H cap in, n out dot, and H cap out. So the values for n in and n out are 0.637 kmol, 1.913 kmol and 0.0128 kmol. So please note that these values are all in kilo moles and the values for H cap we calculated were all in kilo joules per mole.

So make sure you convert it appropriately while you perform the final calculations. These are all in kilo joules per mole, okay? So this value we have calculated as -393.5 0, 0, and here we have these values as 0.0678, 0.2031, 0.0128, 0.57 and 0.57. So this values for enthalpy are -390.6, 2.16, 2.19, -199.09 and -282.45. So now that we have all the enthalpies we can calculate delta H.

So delta H for this process would be, we can calculate the total enthalpy of the outlet stream and subtract the total enthalpy of the inlet stream from that value. So this would give us -49834.3 kJ.
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## Problem #3

$$Q - W_s = \Delta H + \Delta E_k + \Delta E_p$$

$$Q = \Delta H$$

$$Q = -49834.3\,kJ$$

So if we were to look at the general energy balance equation you would have used so for the open system the energy balance equation would have been Q – W s = delta H + delta E k + delta E p and you have no change in kinetic, potential energy, no moving parts. So this would give us Q = delta H and Q which is the amount of heat supplied or removed from the system would be -49834.3 kJ.

So with this we have performed all the required calculations to get the amount of heat transfer. So if you looked at this problem, here we actually had a multiunit system with recycle and purge and a reaction. So for this type of a system, we actually performed all the required material balances to get the information about the fresh feed, purge stream and the product streams and once we had this information, we went ahead to perform the energy balances for the overall system.

For this overall system, we have actually been able to calculate the amount of heat which needs to be transferred and here we took into consideration the heat of reaction in an implicit way by using the heat of formation method. So this particular problem summarizes all the aspects which we have been looking at and gives us a succinct overview of all the fundamental concepts that have been covered through this course till this point.

In the next lectures we will not start looking at systems which are not in steady state. Until this point, all the systems which we have been working with have been systems at steady state. So in the next lecture, from the next lecture onwards, we will actually look at systems which are not in steady state and we will look to see how material and energy balance calculations can be performed for such unsteady state processes. Until then thank you and goodbye.