Material and Energy Balances

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Lecture - 61
Energy Balances on Reactive Processes - Part 4

Welcome back to today's lecture on energy balances on reactive processes. So we have actually looked at the fundamentals associated with reactive processes and performed some energy balance calculations. We looked at the heat of reaction method and heat of formation method. We performed a couple of example problems which gave us familiarity with these techniques. So today we will look at more problems related to energy balances for reactive processes.

Here we will actually focus on something different compared to what we have been looking at till now. Until now the focus has been to learn the techniques, basically try to understand heat of reaction method and heat of formation method works and what are the principles behind them, what to choose as reference states and how to perform the calculations. Today, the focus will not be on the technique itself.

However, we will look at how the system is working and what kind of parameter we are trying to estimate. So taking that into account, I have designed 3 example problems. The first example problem will actually talk about estimating the outlet temperature. So we will actually perform energy balance and material balance calculations to finally identify what would be the exit temperature for a particular reactor.

And the next problem will actually talk about performing material balance calculations and energy balance calculations simultaneously. So this is an example where you would have degrees of freedom greater than 0. So meaning that there will be more variables than the number of equations if you were to account only for material balance calculations. So if you use the energy balance equation along with the material balance calculations you can actually solve the problem.

So we will look at a problem of that kind and the last problem which we will be looking at as part of this session will be a problem where we will look at a close system. So most of the systems which we have studied are open systems. So because they are open systems we have always been calculating change in specific enthalpy and change in total enthalpy. So we have been building the enthalpy table.

Also, we will look at a close system which means we will be trying to calculate internal energy changes. So what is important is because we have a close system here we would also have to account for internal energy change in reaction instead of the heat of reaction directly. So if you remember, we have already looked at the correlation between internal energy of a reaction and the change in heat or the heat of reaction.

So using that correlation, we will be able to calculate the internal energy of a reaction and perform the necessary calculations.

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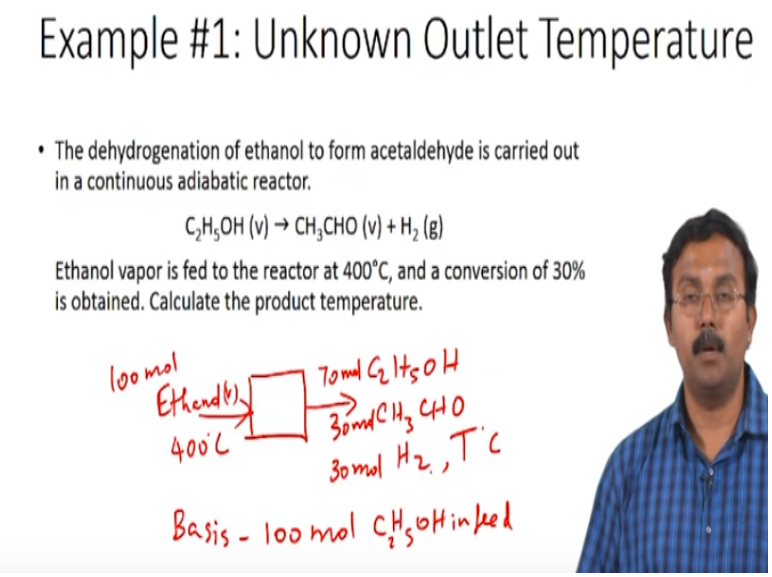

Example #1: Unknown Outlet Temperature

- The dehydrogenation of ethanol to form acetaldehyde is carried out in a continuous adiabatic reactor.

$$C_2H_5OH\ (v) \rightarrow CH_3CHO\ (v) + H_2\ (g)$$

Ethanol vapor is fed to the reactor at 400°C, and a conversion of 30% is obtained. Calculate the product temperature.

Basis - 100 mol C_2H_5OH in feed

Let us now start with the first problem. So the problem statement states that the dehydrogenation of ethanol to form acetaldehyde is carried out in a continuous adiabatic reactor. So you have 1 mole of ethanol forming acetaldehyde and hydrogen. So all of this are in gas phase. Ethanol vapor is fed to the reactor at 400 degree Celsius and the conversion is given as 30%. So you are asked to calculate the product temperature. So here we have only been given conversion.

We have not been given what is the amount of ethanol which is coming into the system. So we will have to assume some basis and we will have to perform simple material balances to identify the composition of the exit gas as well. So what you have is a reactor where the dehydrogenation of ethanol is taking place. So let us assume that the inlet is only ethanol.

So you have ethanol vapor and it has been given that it is coming in at a temperature of 400 degree Celsius and you would have a product stream which would have unreacted ethanol. We know that the conversion of ethanol is only 30%. That means 70% of ethanol entering will actually be leaving the system. So you would have ethanol which is C_2H_5OH and you will also have the acetaldehyde which has been formed CH_3CHO and hydrogen which has been formed.

So all these components will actually be leaving the system. We now need to identify the molar flow rates for each of these components. So let us assume a basis for performing these simple material balances. So we will assume that 100 moles of ethanol is actually entering the system. So we will just call this as 100 moles of C_2H_5OH in feed. So once we have this we can fill out the flow chart as 100 moles of ethanol coming in by performing simple material balance on ethanol, we know that 30% is converted which means 30% of ethanol is consumed.

So outlet would be equal to inlet minus, input minus consumption. So this means you would have 70 moles of ethanol leaving the system. Based on the stoichiometry, we can identify that 1 mole of acetaldehyde is produced per mole of ethanol consumed and 1 mole of hydrogen is produced per mole of ethanol consumed. So based on that we know 30 moles of ethanol has been consumed.

So output for acetaldehyde and hydrogen would be equal to the generation which is basically 30 moles. So you have 30 moles of acetaldehyde and 30 moles of hydrogen which are leaving the system. You are asked to calculate the temperature at which they are leaving. Let us just call that as T degree Celsius. So now this is the flow chart and this is the process for which we need to identify the outlet temperature.

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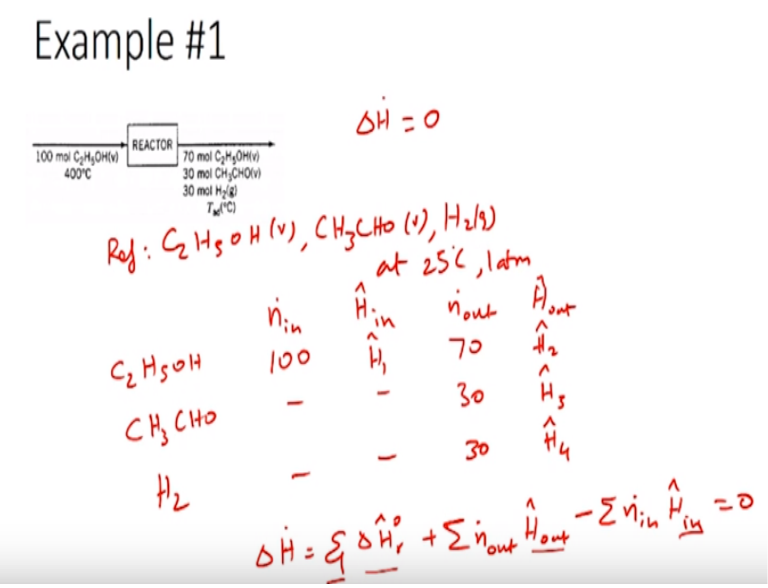

Example #1

$\Delta\dot{H} = 0$

Ref: $C_2H_5OH(v)$, $CH_3CHO(v)$, $H_2(g)$ at 25°C, 1atm

	$\dot{n}_{in}$	$\hat{H}_{in}$	$\dot{n}_{out}$	$\hat{H}_{out}$
C_2H_5OH	100	$\hat{H}_1$	70	$\hat{H}_2$
CH_3CHO	–	–	30	$\hat{H}_3$
H_2	–	–	30	$\hat{H}_4$

$$\Delta\dot{H} = \underline{\xi}\,\underline{\Delta\hat{H}_r^\circ} + \sum \dot{n}_{out}\underline{\hat{H}_{out}} - \sum \dot{n}_{in}\underline{\hat{H}_{in}} = 0$$

Let us see how we go about performing the calculations. Okay, so now we have to identify what type of a system it is. This is an open system so the equation would be Q dot – W s dot = delta H dot + delta E k dot + delta E p dot. So obviously where kinetic energy changes and potential energy changes will go to 0 giving you an equation which is nothing but Q dot = delta H dot. So we need to identify delta H dot. So for this we have to build the enthalpy table.

For that we first need to identify the reference states. We could use either the compounds which are taking part in the reaction as the reference state or the elements as the reference state. So here I have chosen to use the compounds as it take part in the reaction as the reference states. Although the heat of reaction is not given here we can actually calculate the heat of reaction using the heats of formation for ethanol, acetaldehyde and hydrogen or you can use heat of combustion to calculate that. So basically we would be able to get the value for heat of reaction.

So I have used the heat of reaction method for performing the calculations. So here you choose the reference state as C2H5OH vapor, CH3CHO vapor and hydrogen gas, all at 25 degree Celsius and 1 atmosphere as the reference state. So this is the condition in which these components are taking part in the reaction. So again please remember that when I say reaction I am talking about the equation and not the process itself.

Obviously, in the process, ethanol is coming in at 400 degree Celsius and it is leaving at a temperature of T degree Celsius. So we are interested in identifying using the heat of reaction which is the standard heat of reaction. So therefore we are using these values at 25 degree Celsius. So let us build the table. So you would have C2H5OH and CH3CHO and hydrogen. So you have let us say you have n in dot H cap in, n out dot and H cap out.

So the number of moles of ethanol coming in is 100. You do not have acetaldehyde and hydrogen entering. You have 70 moles of ethanol leaving and 30 moles of acetaldehyde and hydrogen leaving each. So we need to calculate the enthalpy for all the components because they are coming in at 400 degree Celsius in the inlet and the outlet we do not know the temperature. So obviously we have to identify the enthalpies for all these components.

So we will call them H 1 cap, H 2 cap, H 3 cap and H 4 cap. So now our goal is to calculate these things and basically use it in the delta H dot equation. So here we have Q dot = delta H dot but the process has also been told that it is an adiabatic process which means Q dot = 0. So giving you delta H dot = 0. So because you have delta H dot = 0 we can actually substitute the values for H 1, H 2, H 3, H 4 into this equation.

And you will end up with a polynomial with temperature and we can actually solve the polynomial to get the temperature of the exit stream. Let us go ahead and do that. So your delta H dot would actually be equal to psi times delta H r + sigma of n out dot H cap out – sigma of n in dot H cap in. So this value would be equal to 0. So we need to calculate delta H r which is the heat of reaction. We need to identify psi which is the extent of reaction.

We also need to get the enthalpies for the outlet streams and the inlet streams. So let us go about calculating these factors.

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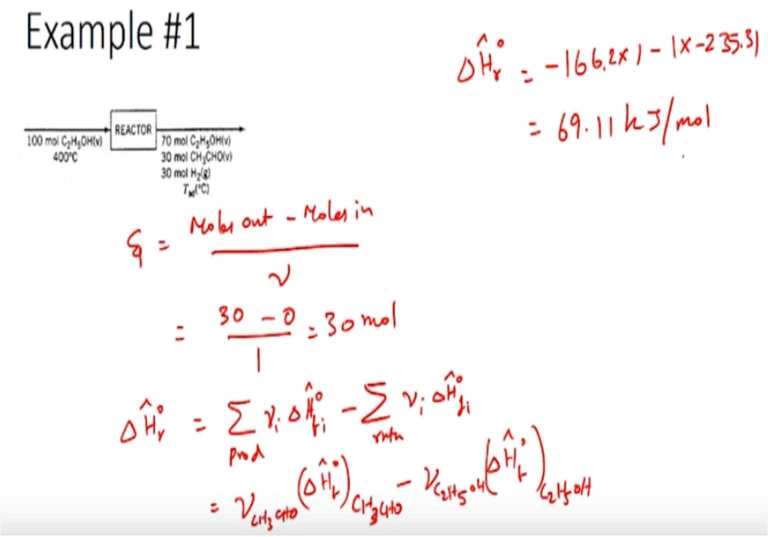

Example #1

$$\Delta\hat{H}_r^\circ = -166.2\times 1 - 1\times -235.31$$
$$= 69.11\ \mathrm{kJ/mol}$$

$$\xi = \frac{\text{Moles out} - \text{Moles in}}{\nu}$$
$$= \frac{30 - 0}{1} = 30\ \mathrm{mol}$$

$$\Delta\hat{H}_r^\circ = \sum_{\text{prod}} \nu_i \Delta\hat{H}_{fi}^\circ - \sum_{\text{rxtn}} \nu_i \Delta\hat{H}_{fi}^\circ$$
$$= \nu_{CH_3CHO}\left(\Delta\hat{H}_f^\circ\right)_{CH_3CHO} - \nu_{C_2H_5OH}\left(\Delta\hat{H}_f^\circ\right)_{C_2H_5OH}$$

So the first one is the extent of reaction. Extent of reaction would be = number of moles out – moles in/stoichiometric coefficient. So we have 30 moles of acetaldehyde which is leaving the system. 0 moles of acetaldehyde entering the system divided by stoichiometric coefficient of acetaldehyde which is 1 giving you an extent of reaction of 30 moles. So now we have the extent of reaction. Next thing is for us to identify the heat of reaction.

So the standard heat of reaction can be calculated from the heats of formation. So what you would have would be heat of formation for the products – heat of formation of the reactants. So basically a product of the stoichiometric coefficient and the heat of formation for the products and the summation of that and subtracting that with the heat of formation of the reactants. So let us try and do that so you would have sigma nu i delta H f cap.

So this is the standard heat of formation for products minus similar value for reactants would have stoichiometric coefficient times heat of formation for the reactants. So here the products are acetaldehyde and hydrogen. So hydrogen is a gas which is an element. So it would actually not have any heat of formation. So heat of formation for hydrogen would be 0.

So you would have this as stoichiometric coefficient of acetaldehyde CH3CHO times heat of formation, standard heat of formation of acetaldehyde minus stoichiometric coefficient of ethanol times the standard heat of formation of ethanol. So using this we can actually calculate the heat of reaction given. So from the tables we can get the heat of formation for acetaldehyde and the heat of formation for ethanol and if we were to plug those values in you are left with delta H r cap = -166.2 times 1 – 1 times -235.31.

So the value for the heat of reaction is 69.11 kJ/mol. So now we have identified the heat of reaction as well. So the next step is to identify the enthalpy for the inlet and the outlet streams.

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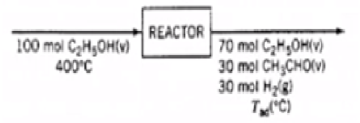
Example #1



$$\hat{H}_1 : C_2H_5OH(25^\circ C) \rightarrow C_2H_5OH(400^\circ C)$$

$$\hat{H}_1 = \int_{25}^{400} (C_p)_{C_2H_5OH(v)} \, dT$$

$$\hat{H}_1 = 33.79 \text{ kJ/mol}$$

So let us calculate the enthalpy for the inlet stream H 1 cap. So H 1 cap is basically the process where you have ethanol at 25 degree Celsius. So we are using ethanol vapor at 25 degree Celsius being heated to ethanol vapor at 400 degree Celsius. So your H 1 cap would actually be equal to integral 25 to 400 C p of ethanol vapor C2H5OH vapor dT. So we need to get the C p for ethanol and we will be able to perform this calculation and this would give us a value H 1 cap of 33.79 kJ/mol. So you can get the C p value from your textbooks or other reference books.

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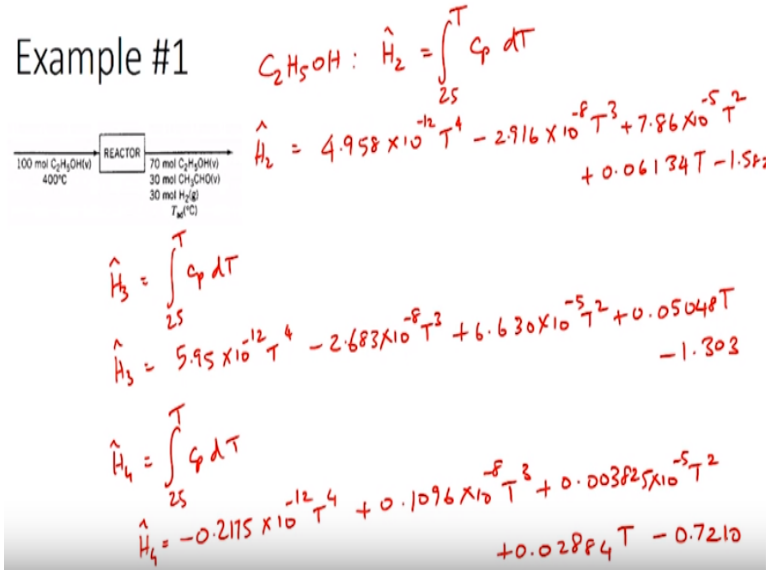

Example #1

C_2H_5OH: $\hat{H}_2 = \int_{25}^{T} C_p\, dT$

$\hat{H}_2 = 4.958 \times 10^{-12} T^4 - 2.916 \times 10^{-8} T^3 + 7.86 \times 10^{-5} T^2 + 0.06134 T - 1.5$

$\hat{H}_3 = \int_{25}^{T} C_p\, dT$

$\hat{H}_3 = 5.95 \times 10^{-12} T^4 - 2.683 \times 10^{-8} T^3 + 6.630 \times 10^{-5} T^2 + 0.05048 T - 1.303$

$\hat{H}_4 = \int_{25}^{T} C_p\, dT$

$\hat{H}_4 = -0.2115 \times 10^{-12} T^4 + 0.1096 \times 10^{-8} T^3 + 0.003825 \times 10^{-5} T^2 + 0.02884 T - 0.7210$

Now that we have calculated the enthalpy for the inlet streams we need to move on to calculate the enthalpy for the outlet streams. As you know the outlet stream temperature is not known. So which means we would have to use an integral from 24 degree Celsius which is the reference state to the temperature of outlet which we have assumed to be T degree Celsius and we will basically perform this calculation using the C p values for ethanol vapor, acetaldehyde vapor and hydrogen gas.

And we will be able to get polynomials for temperature which will be used for solving for the value of T. So let us try and do that. So what we have here is first thing is for ethanol. So ethanol in the exit stream you have you have H 2 cap. So here it basically the temperature is being increased from 25 degree Celsius to T degree Celsius. So you would have H 2 cap = integral 25 to T C p dT.

So using the C p of ethanol vapor you would be able to integrate this and get the value for H 2 cap as H 2 cap would be equal to 4.958 times 10 power -12 T power 4 – 2.916 times 10 power -8 T power 3 + 7.86 times 10 power -5 times T squared + 0.06134 times T – 1.582. So this is H 2 cap. So for calculating H 3 cap you have to again use the C p for acetaldehyde vapor. So this is not readily available in the table given in your text book.

However, this problem is an example problem in Felder Rousseau. So you would be able to get the value for C p of acetaldehyde vapor looking up the text book which is of Felder Rousseau. So I am going to give the solved solution here. You can always look it out for the C p values for acetaldehyde vapor.

So if we were to calculate the value for H 3 cap which is basically heating of acetaldehyde vapor from 25 degree Celsius to T degree Celsius you have this as 25 to T C p of acetaldehyde dT and using this you get H 3 cap = 5.95 times 10 power -12 T power 4 – 2.683 times 10 power -8 T cube + 6.630 times 10 power -5 T squared + 0.05048 T – 1.303. So similarly we can calculate the value for H 4 cap which would be integral C p of hydrogen gas dT from 25 to T temperature.

So your H 4 cap is actually equal to -0.2175 times 10 power -12 T power 4 + 0.1096 times 10 power -8 T cube + 0.003825 times 10 power -5 T squared + 0.02884 T – 0.7210. Please perform these calculations yourselves and try to get the values. Make sure that you use the appropriate C p values which you can get from the textbooks or handbooks and you can actually now use these values and plug them into the equation which we had for delta H dot.

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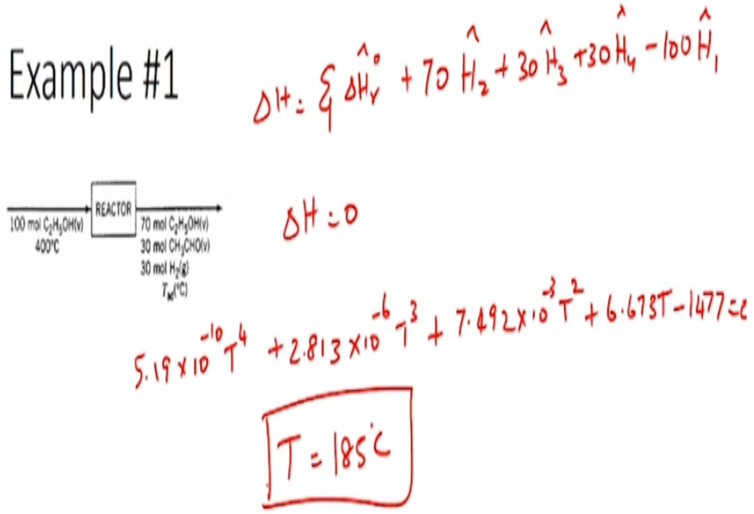

Example #1

$\Delta H = \xi \Delta \hat{H}_r^\circ + 70\hat{H}_2 + 30\hat{H}_3 + 30\hat{H}_4 - 100\hat{H}_1$

$\Delta H = 0$

$5.19\times10^{-10}T^4 + 2.813\times10^{-6}T^3 + 7.492\times10^{-3}T^2 + 6.673T - 1477 = 0$

$\boxed{T = 185^\circ C}$

So the equation would actually become delta H = psi delta H r + 70 times H 2 cap + 30 times H 3 cap + 30 times H 4 cap – 100 times H 1 cap. So this would be the equation. So if you were to substitute the values for H 2, H 3, H 4 in the form of the polynomials and we already have the numerical values for the extent of reaction and the heat of reaction and also for H 1 cap. So we can get the value for delta H and we know that because it is an adiabatic process, delta H = 0.

So what you end up with is a polynomial equation which would be 5.19 times 10 power -10 T power 4 + 2.813 times 10 power -6 T cube + 7.492 times 10 power -3 T squared + 6.673 times T – 1477 = 0. So this would be the polynomial you would have to solve to get the value for T. So you can actually solve this equation using excel or some other software.

Or if you do not have access to that you could try to ignore the higher powers of temperature which is the T power 4 and T power 3 because you see that the coefficients are actually 10 power -10 and 10 power -6. So meaning that the impact of this would actually be smaller. So if you did not have access to a good scientific calculator which can solve this kind of a polynomial or a computer then you can try to ignore these two.

But however if you have the access to such electronic gadgets, you would want to use this polynomial to get the value for the temperature and the temperature which you obtain by solving this polynomial would be 185 degree Celsius. So with this you get the outlet temperature for the system which we are looking at. So as you saw we were able to perform simple energy balance calculations with the goal of identifying an unknown temperature of the outlet stream.

And we were able to perform the calculations because we already knew that the process was adiabatic. We could also be given information about how much heat is transferred and we would be able to use that value for Q instead of using the value of 0 and would still be able to perform similar calculations and obtain the value for the temperature. So with this we come to the conclusion of the first example. Let us move on to the second example.