Material and Energy Balances Prof. Vignesh Muthuvijayan Department of Biotechnology Indian Institute of Technology-Madras

Lecture - 60 Energy Balances on Reactive Processes - Part 3

Welcome back to today's lecture for energy balances on reactive processes. In the previous lecture we looked at two different techniques where we can account for reactions in energy balance calculations. Those were the heat of reaction method and the heat of formation method. We also looked at how heat of formation implicitly uses Hess's law principles to account for heat of reaction and to perform energy balance calculations.

So these problems and this basic technique helps us in performing energy balances for any reactive system. So as I had already mentioned in the previous lectures, heat of reaction method is preferred when you have a single reaction where the heat of reaction is explicitly given to you and the heat of formation method is usually preferred when you either do not know the heat of reaction directly or if you have multiple reactions.

So in such scenario you tend to use the heat of formation method. So today we will actually perform a couple of example problems where the first problem we will try to use the heat of reaction method because it will be a single reaction with the heat of reaction explicitly given to you and the second example would be an example problem where there are multiple reactions and the heat of reaction is not explicitly stated. So we will use the heat of formation method.

So practicing these problems will help us get familiarized with the principles which I had discussed in the previous lectures. So let us now go to the problem statement. (Refer Slide Time: 01:49)

Example #1

 The standard heat of reaction for the oxidation of ammonia is given below:

 $4NH_3 (g) + 5O_2 (g) \rightarrow 4NO (g) + 6H_2O (v): \Delta \hat{H}_r^\circ = -904.7 \text{ kJ/mol}$ 100 mol NH₃/s and 200 mol O₂/s at 25°C are fed into a reactor in which the ammonia is completely consumed. The product gas emerges at 300°C. Calculate the rate at which heat must be transferred to or from the reactor, assuming operation at approximately 1 atm.



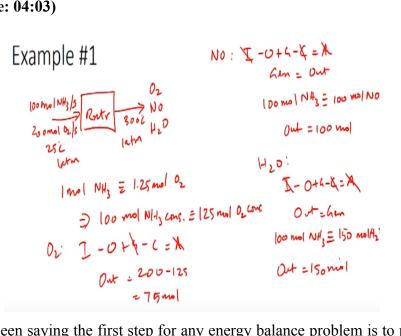
So the first example which we will start with is given here. The standard heat of reaction for the oxidation of ammonia is given below. 4 moles of ammonia gas reacts with 5 moles of oxygen gas to form 4 moles of nitric oxide gas plus 6 moles of water vapor and the heat of reaction, standard heat of reaction is given as -904.7 kJ/mol. 100 moles of ammonia gas per second and 200 moles of oxygen gas per second at 25 degree Celsius are fed into a reactor in which the ammonia is completely consumed. The product gas emerges at 300 degree Celsius.

You are asked to calculate the rate at which heat must be transferred to or from the reactor. You can assume that the operation is approximately at 1 atmosphere. So let us try to draw the flowchart. So you have a reactor. So this reactor is where ammonia is getting oxidized and you have been told that there are two components coming in which is 100 moles of ammonia and 200 moles of oxygen per second. So you have these 2 components coming in.

So as they are at same temperature as is 25 degree Celsius. I am just putting it as one inlet stream and you have a product gas stream which is emerging at 300 degree Celsius. We have been told that ammonia is fully consumed. So we still have, might have oxygen which is remaining. So because the ratio of ammonia to oxygen in the stoichiometric coefficients is 1:1.25 and oxygen is supplied as 1:2 compared to ammonia.

So this means there will be unreacted oxygen which is leaving and you would also have nitric oxide, water vapor in addition to the oxygen which are the products which are formed leaving the system. All of these are leaving at 300 degree Celsius. So we can assume 1 atmosphere for both the streams as given in the problem.

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As I had always been saying the first step for any energy balance problem is to perform material balance calculations. Here the exit stream information is not available readily. So we need to perform material balances to actually get the flow rates for the exit stream. So let us use the flow chart which we developed. So we have 100 moles of ammonia and 200 moles of oxygen entering. We have been told that ammonia is reacting fully.

So based on the stoichiometry for 1 mole of ammonia consumed, you would have 1.25 moles of oxygen consumed. So this implies for 100 moles of ammonia consumed you would have 100 moles of 125 moles of oxygen consumed. So now we can write an oxygen balance. So it would be input - output + generation – consumption = accumulation. At steady state there would not be any accumulation.

So now you can, you would not have any generation of oxygen because it is a reactant. So you would have input, output and consumption. So we have already identified consumption of oxygen as 125. We know the input is 200. So output for oxygen would be 200 -125 which is 75

moles of oxygen leaving the system. So similarly we can write material balances for nitric oxide. So nitric oxide would be input – output + generation – consumption = accumulation.

So this is a product, so there is no consumption and there is no accumulation at steady state. There is no input of nitric oxide either. So you would have generation = output. So generation can be identified using stoichiometry. So we have seen that for 4 moles of ammonia being consumed you have 4 moles of nitric oxide produced. So you would have for 100 moles of ammonia consumed you would have 100 moles of nitric oxide which is formed.

So this means your output for nitric oxide would actually be = 100 moles and similarly we can calculate for water. So we have seen that for every mole of ammonia consumed 1.5 moles of water is formed. So we can write the general material balance equation as input – output + generation – consumption = accumulation. Accumulation goes to 0 at steady state.

Consumption will go to 0 because it is a product and input goes to 0 because you do not have any feed of water. So you would end up with output equals generation. So generation can be calculated using the stoichiometry so which means 100 moles of ammonia would produce 150 moles of water. So your output for water would be = 150 moles of water.

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So using this we have the completed flowchart given here. So this is 100 moles of ammonia and 200 moles of oxygen at 25 degree Celsius coming in and this ends up producing 100 moles of nitric oxide and 150 moles of water and 75 moles of unreacted oxygen which are all leaving the system at 300 degree Celsius. We now need to identify Q dot which is the heat which is supplied or removed.

So now that we have performed the material balance calculations we can start with the energy balance component. So first thing is this system is an open system. So the general energy balance equation would be Q dot - W s dot = delta H dot + delta E k dot + delta E p dot. So E k, E p do not change. There is no moving part. so shaft work is also 0. So you are left with Q dot = delta H dot. So this is a simple equation. Now we need to calculation delta H dot.

So how do we go about doing that? Here we have a single reaction and the heat of reaction is given which means we would prefer the heat of reaction method. So as I had already said if we are going to use the heat of reaction method you would have to use the components in the reaction the equation as the reference state.

So as the standard heat of reaction is given you will use these components as they occur in the reaction equation basically the same phase and at 25 degree Celsius and 1 atmosphere as the reference states. So let us look at the reference states first. So the reference state for this would be ammonia gas and oxygen gas, nitric oxide gas and water vapor so which are all the components as they occur in the reaction at 25 degree Celsius and 1 atmosphere would be the reference state.

So let us not worry about the pressure here because it is at constant pressure. So the components which are involved are ammonia, oxygen, nitric oxide and water. So let us now write the, build the enthalpy table. So you would have n in dot, H cap in, n out dot and H cap out. So ammonia coming in is 100 moles. Oxygen coming in is 200 moles. No nitric oxide and water are coming in. Outlet stream contains no ammonia but it contains 75 moles of oxygen and 100 moles of nitric oxide and 150 moles of water. So let us look at which of these terms can go to 0.

So you have ammonia and oxygen entering at 25 degree Celsius which is the same as the reference state. So your inlet ammonia and oxygen are the same as the reference state so the enthalpies would be 0 and outlet streams everything is at 300 degree Celsius compared to the reference state of 25 degree Celsius. So we need to account for all these enthalpies. Let us call then H 1 cap, H2 cap and H 3 cap. Now we need to calculate H 1 cap, H 2 cap and H 3 cap.

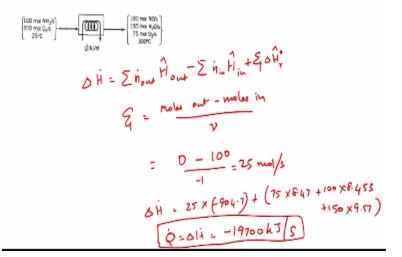
What is H 1 cap? H 1 cap is basically the process where oxygen at 25 degree Celsius which is the reference state is heated to oxygen at 300 degree Celsius which is the exit stream. So this is basically only change in temperature. So you can get this enthalpy value directly from combustion gas tables. So using that you can get H 1 cap as 8.47 kJ/mol. So now H 2 cap is the process where nitric oxide is heated from 25 degree Celsius which is the reference state to nitric oxide at 300 degree Celsius which is the exit stream.

So you have H 2 cap which would be equal to integral C p of nitric oxide dT from 25 degree Celsius to 300 degree Celsius. You can look up the C p value for nitric oxide gas and you would be able to perform this integration and you would end up with H 2 cap = 8.453 kJ/mol. And for water vapor you would have H 3 cap which would be nothing but water vapor which is the reference state water vapor at 25 degree Celsius is heated to water vapor at 300 degree Celsius and this would mean your H 3 cap would be = 9.57 kJ/mol.

So these values you can actually obtain from the enthalpy table for combustion gases. So you can fill out the enthalpy table with H 1 cap, H 2 cap and H 3 cap.

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Example #1



So you can calculate your delta H dot as delta H dot would be = sigma of outlet streams which is n dot out times H cap out – sigma of n dot in times H cap in + we also have to account for the reaction, heat of reaction would be psi times delta H r cap. So heat of reaction is given to us. It was given as -904.7 kJ/mol. So what we do not have is psi which is the extent of reaction. Let us now calculate the extent of reaction. It is moles out – moles in/stoichiometric coefficient.

So if you were to take ammonia then moles out would be 0 and if you were to take so moles in would be 100 and if you divide it by the stoichiometric coefficient which I am calling as negative 1 because you have it as a reactant and this would be = 25 mol/s. So extent of reaction is 25 mol/s and you already have the heat of reaction. You have the specific enthalpies for the individual components in the outlet stream and the molar flow rates of the outlet streams.

Inlet stream everything goes to 0. So you can substitute these values here and you would be able to calculate delta H dot as 25 times -904.7 which is basically the psi times delta H r degree + 75 times 8.47 + 100 times 8.453 + 150 times 9.57 and the other two terms are going to 0. So you would end up with delta H dot = -19700 kJ/s. As the energy balance equation was Q dot = delta H dot, Q dot is also equal to the same value of -19700 kJ/s.

With this we have solved a simple problem where you had a single reaction and you had also been given the value for the heat of reaction. Let us look at one more example where we would actually be using the heat of formation method because there are going to be two reactions which are happening simultaneously. You are going to have the next example where you have 2 reactions which are happening simultaneously and the heat of reactions have not been explicitly given. So we would use the heat of formation method.

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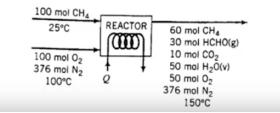
Example #2

 Methane is oxidized with air to produce formaldehyde in a continuous reactor. A competing reaction is the combustion of methane to form CO₂.

 $CH_4 (g) + O_2 (g) \rightarrow HCHO (g) + H_2O (v)$

 $\mathsf{CH}_4\left(\mathsf{g}\right)+\mathsf{2O}_2\left(\mathsf{g}\right)\to\mathsf{CO}_2\left(\mathsf{g}\right)+\mathsf{2H}_2\mathsf{O}\left(\mathsf{v}\right)$

The flowchart for the process is shown in the diagram.

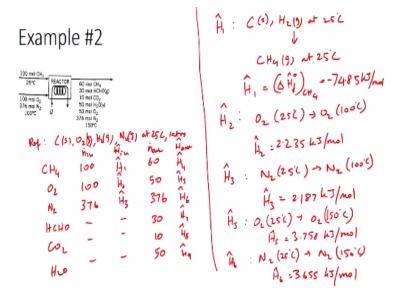


So here is the example problem. Methane is oxidized with air to produce formaldehyde in a continuous reactor. A competing reaction is the combustion of methane to form carbon dioxide. So you have 1 mole of methane reacting with 1 mole of oxygen to form formaldehyde and water. You also have 1 mole of methane reacting with 2 moles of oxygen to form carbon dioxide and water. So the flowchart for the process is given and you have all the flow rates given.

100 moles of methane is entering and you have 100 moles and 376 moles of 100 moles of oxygen and 376 moles of nitrogen entering at 100 degree Celsius and you have unreacted methane, formaldehyde produced carbon dioxide produced water vapor produced unreacted oxygen and nitrogen which are leaving, all at 150 degree Celsius. So you have all the information to perform the problem.

So you do not have the heat of reaction and you have multiple reactions so you would prefer to use the heat of formation method.

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As we are going to use the heat of formation method we have to choose the appropriate reference states. So the reference states for this system would be carbon solid, oxygen gas, hydrogen gas, and nitrogen gas all at 25 degree Celsius and 1 atmosphere. So these are the elements as they occur in nature at 25 degree Celsius. This would ensure that we can use the heat of formation values which are the standard heats of formations obtained from the tables available to you.

So now let us build the enthalpy table. The components you would have are methane, oxygen, nitrogen, formaldehyde, carbon dioxide and water. So you have n in dot H cap in, n out dot and H cap out. So let us write down the molar flow rates. You have 100 moles of methane, 100 moles of oxygen and 376 moles of nitrogen which are coming in. You do not have any moles of formaldehyde, carbon dioxide or water coming in.

So in the exit stream you have 60 moles of methane, 50 moles of oxygen, 376 moles of nitrogen, 30 moles of formaldehyde, 10 moles of carbon dioxide and 50 moles of water are all leaving the system. So here the inlet stream for methane is at 25 degree Celsius. So this enthalpy would only account for the formation of methane from carbon and hydrogen. So this would be H 1 cap and you would have H 2 cap and H 3 cap for oxygen and nitrogen because you are heating it from 25 degree Celsius to 100 degree Celsius. We do not have to worry about these 3 components.

So you would have H 4 cap, H 5 cap, H 6 cap, H 7 cap, H 8 cap and H 9 cap, all that have to be calculated because you either have, here you have both formation of the compound and then heating. So in case of nitrogen and oxygen you just have the heating process. So you need to account for 9 different enthalpies needed to calculate all of them and then you would be able to calculate the delta H dot. Let us start with the calculations. So delta you have the H 1 cap.

So the H 1 cap is a process where you have carbon solid and hydrogen gas at 25 degree Celsius forming methane gas at 25 degree Celsius. So this is nothing but the formation reaction. So your H 1 cap would be equal to the heat of formation for, standard heat of formation for methane. So which using the tables you would be able to identify as -74.85 kJ/mol. Now for H 2 cap. So H 2 cap is nothing but oxygen being heated from 25 degree Celsius to 100 degree Celsius.

So this value you can get from combustion gases table. So this H 2 cap would be = 2.235 kJ/mol. So similarly H 3 cap is the process where nitrogen at reference state of 25 degree Celsius is heated to nitrogen at 100 degree Celsius and this H 3 cap = 2.187 kJ/mol from the enthalpy table for combustion gases. Now you have H 4 to H 9 for the exit streams. Let us first finish H 5 and H 6 cap because those values can be obtained directly from the tables.

So H 5 cap would be again oxygen at 25 degree Celsius being heated to oxygen at 150 degree Celsius. So this H 5 cap would be = 3.758 kJ/mol and you have H 6 cap which would be oxygen sorry nitrogen at 25 degree Celsius being heated to nitrogen at 150 degree Celsius which is the exit condition so and this would be H 6 cap = 3.655 kJ/mol. So the values H 2 cap, H 3 cap, H 5 cap and H 6 cap can actually be obtained from the specific enthalpy table for combustion gases. Now let us identify the values for H 4 cap, H 7, H 8 and H 9.

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Example #2

$$\hat{H}_{7} : C(s), O_{2}(s), H_{2}(y) \rightarrow H(Ho(2sc)) \\
 H(Ho(2sc)) + H(H$$

So let us start with H 4. So what is H 4 cap? What is the process we are looking at? So you have carbon solid and hydrogen gas forming methane gas so which is one thing. These are all at 25 degree Celsius. So this is methane at 25 degree Celsius which is formed and this is then heated to methane at 150 degree Celsius which is the exit stream temperature. So you have two steps. The first one is the heat of formation and the second step is the heating of methane from 25 to 150.

So your H 4 cap basically has the standard heat of formation for methane as the first step plus integral C p dT where you use C p of methane gas and heat it from 25 to 150. So using the C p value from the table and the heat of formation, you would have these values as -74.85 + 4.9 giving you H 4 cap as -69.95 kJ/mol. Similarly, you can calculate H 7 cap.

So H 7 cap is nothing but formation of formaldehyde from carbon, hydrogen and oxygen which is carbon solid and oxygen gas and hydrogen gas all of which react to form formaldehyde at 25 degree Celsius and from here it is heated to formaldehyde at 150 degree Celsius and that would be the final condition for the exit stream. So this would mean H 7 cap actually has the standard heat of formation for formaldehyde plus integral C p dT where C p of formaldehyde has to be used and temperature range is from 25 to 150 degree Celsius.

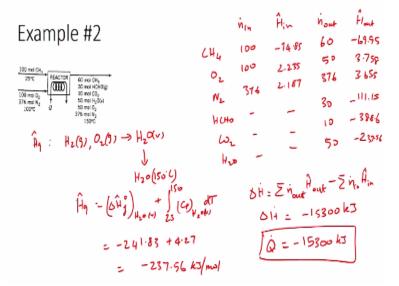
Using the tables we will be able to get the values for heat of formation and for C p of formaldehyde. Substituting these we can get H 7 cap as -115.9 + 4.75 which = -111.15 kJ/mol.

Similarly we can calculate H 8 cap. H 8 cap equal to so H 8 cap is the process where you have carbon solid and oxygen gas at 25 degree Celsius forms carbon dioxide gas at 25 degree Celsius which is then heated to form carbon dioxide at 150 degree Celsius.

So the first step for H 8 cap is the heat of formation of carbon dioxide. So you use the standard heat of formation of carbon dioxide and add it with integral 25 to 150 C p of carbon dioxide dT and substituting the value for heat of formation and the C p value for carbon dioxide you would be able to calculate H 8 cap as -393.5 + 4.75 which would be = -388.6 kJ/mol.

So this second term integral Cp dT could also be obtained from combustion tables because the enthalpy of carbon dioxide at 150 degree Celsius compared to 25 degree Celsius can be obtained directly from that table.

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So similarly for H 9 cap you have the process where hydrogen gas and oxygen gas at 25 degree Celsius react to form water vapor at 25 degree Celsius which is then heated to water vapor at 150 degree Celsius. So the first step is heat of formation of water vapor and the second step is the heat supplied for heating water vapor from 25 degree Celsius to 150 degree Celsius.

So your H 9 cap would actually be equal to delta H f cap of water vapor plus either integral C p dT or you can also use value from the enthalpy table for combustion gases. So you would have

25 to 150 C p of water vapor dT. So now H 9 cap would be = -241.83 + 4.27 which would be = -237.56 kJ/mol. So now we have all the specific enthalpy values. We can fill out the table and calculate delta H dot.

So the enthalpy table will basically look like this. Methane, oxygen, nitrogen, formaldehyde and carbon dioxide and water would basically have an n dot H cap in, n out dot and H cap out and you have 100, 100, 376 and then nothing here. So -74.85, 2.235, 2.187 and do not worry about these three. You have 60, 50, 376, 30, 10 and 50. So these enthalpies would be -69.95, 3.758, 3.655, -111.15, -388.6, -237.56.

So now that we have this, the total enthalpy of the outlet stream can be calculated as the product of individual flow rates times the specific enthalpies and the summation of that. And similarly you can calculate the total enthalpy of the inlet stream and the difference between the two can be your delta H dot which would basically be sigma n dot out times H cap out – sigma n dot in H cap in and this value delta H dot = -15300 kilo joules.

And we already have Q dot which is the heat supplied or removed would be also equal to the delta H dot and finally the value is 15300 kJ. So this gives us the heat which needs to be supplied or removed from the system. So with that we have actually performed the second example where we had used the heat of formation method and we were able to calculate the heat that needs to be supplied to the system.

Now that we have performed two examples where we have tried both heat of reaction and heat of formation technique we will come for the next class where we look at the problems slightly differently where we will try to calculate the unknown outlet temperatures and we will also try to use material and energy balances simultaneously to get the desired answers. Thank you.