Material and Energy Balances
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Lecture - 59
Energy Balances on Reactive Processes - Part 2

Welcome to the lecture on energy balances on reactive processes. So we had in the earlier class we had looked at two techniques for accounting for reactive processes and reactions when you perform energy balances. Those were the heat of reaction and the heat of formation. So we described them in detail. We actually solved one problem where we looked at both these techniques.

We actually went through step by step as to how to preform energy balances for both these techniques. As you might remember, I had highlighted the difference between the reference states which are choses which actually requires us to use these either the heat of reaction explicitly or heat of reaction is actually accounted for implicitly. So in the heat of reaction method, the reference states you used were the compounds and elements which are actually present in the reaction as they are present in the reaction.

So if you had propane gas at 25 degree Celsius taking part in the reaction then you use the propane gas at 25 degree Celsius. You need to be clear that this is the reaction equation which is given, not the process which we talk about. So because in the previous example the process we had was oxygen at 300 degree Celsius coming in. But we still used oxygen at 25 degree Celsius because that is how we can actually use the standard heat of reaction.

Because the standard heat of reaction value can actually be obtained only when you have these components reacting at 25 degree Celsius. So for us to use that value we ensured that we use the component which are taking part in the reaction equation and use those components in the phase and temperature as they were taking part in that equation given. Please understand it is the equation given which we are accounting for, not the process itself.

So please do not get confused as to why I say reaction and then go ahead and use 25 degree Celsius instead of 300 degree Celsius. The 300 degree Celsius is what you see in the process. When I say reaction, I am taking about the equation which we have, okay? So that is for the heat of reaction. So in the last class, in the last lecture, towards the end I had actually asked you to try out how Hess's law is used to implicitly account for heat of reaction when we perform the heat of formation method for energy balances.

I hope you have tried that and I hope some of you at least have been able to answer that question. If not, I will try to explain it here. I will try to walk you down with the calculations and the derivation. Hopefully, that will clarify things in a better way for you.

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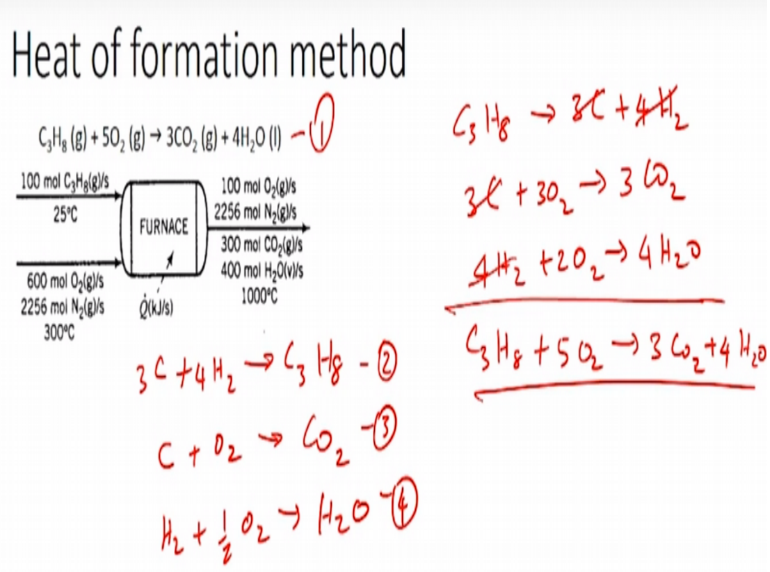

Heat of formation method

$C_3H_8\,(g) + 5O_2\,(g) \rightarrow 3CO_2\,(g) + 4H_2O\,(l)$ – ①

$3C + 4H_2 \rightarrow C_3H_8$ - ②

$C + O_2 \rightarrow CO_2$ -③

$H_2 + \frac{1}{2}O_2 \rightarrow H_2O$ -④

$C_3H_8 \rightarrow \cancel{3C} + \cancel{4H_2}$

$\cancel{3C} + 3O_2 \rightarrow 3CO_2$

$\cancel{4H_2} + 2O_2 \rightarrow 4H_2O$

$C_3H_8 + 5O_2 \rightarrow 3CO_2 + 4H_2O$

Now let us look at the same example. So I do not want to change an example here to make it complicated. So I am going to use the same example. As you see propane gas reacts with oxygen gas to form carbon dioxide gas and water liquid. So this is the chemical reaction which has been given to us. So here we are not worried about the heat of reaction. So we are not writing down what the heat of reaction is.

So in the process, we actually have propane gas entering at 25 degree Celsius and oxygen and nitrogen entering at 300 degree Celsius and you have an exit gas which contains unreacted oxygen 100 moles per second and you have nitrogen which is just coming in and going out as inert gas and you have 300 moles of carbon dioxide and 400 moles of water which are leaving the system. So for this particular system we had used the heat of formation method.

So if you remember, the reference states where the elements as they occur in nature at 25 degree Celsius and 1 atmosphere. So what we did was we had the carbon solid at 25 degree Celsius and 1 atmosphere, oxygen gas at 25 degree Celsius and 1 atmosphere, nitrogen and hydrogen gases at 25 degree Celsius and 1 atmosphere. So those were the reference states we used. So from that reference state when we actually had to account for the enthalpy of propane gas we assume that carbon and hydrogen reacts to form propane and then we use that as the enthalpy.

So what we did there was the enthalpy for propane gas in the specific enthalpy table would have been for the process of $3C + 4H2$ forms $C3H8$, okay? So this is the heat of formation value which we have accounted for. So for the time being let us not worry about the change in temperatures. We will only account for the heat of formations which have been accounted for in the reaction.

So if you remember for propane carbon dioxide and for water we had two components. The first component was the heat of formation and the next component was the change in temperature. So the change in temperature is the same thing as we had for the heat of reaction method as well, right? So because in the heat of reaction method as well we had the reference state as carbon dioxide gas at 25 degree Celsius which meant that the process of heating it from 25 degree Celsius to 1000 degree Celsius was accounted for as the change in enthalpy.

So that component still remains in the heat of formation method as well. So let us not worry about that component where the temperature increase is looked at. We will only look at the component where you actually have the compound being formed from these elemental aspects which you are looking at, carbon, hydrogen and oxygen. So for carbon dioxide what we would have for formation reaction would be carbon + oxygen gives carbon dioxide.

So this would be the formation reaction for carbon dioxide. Similarly, for water the formation reaction would be hydrogen + 1/2 oxygen gives water. So these are the 3 equations. Using Hess's law, can we get this equation? Let us call this equation 1. Now these equations we will just call them as equations 2, 3 and 4. So using equations 2, 3 and 4 how would we get equation 1? So you have 1 mole of propane reacting here. We have 1 mole of propane forming here.

So if we multiply the second equation by -1 so basically flip the equation then you would have propane moving to the reactant side. So that would be the first step. So the next concept is carbon dioxide. So we have 3 moles of carbon dioxide being formed in the reaction 1 whereas you have only 1 mole of carbon dioxide being formed in the reaction 3. So if you were to multiply the reaction 3 with numerical value of 3, you would have 3 moles of carbon dioxide being produced.

So that would be the operation which has to be performed. What about the fourth equation. What you see is 4 moles of water being produced and here it is only 1 mole of water produced. So let us multiply this equation 4 by 4 and then we would get the 4 moles of water liquid being formed. So if you were to do this, what you end up with is C3H8, so this is the reverse of this reaction gives 3C + 4H2 and you have multiplied the third equation by 3.

So you have 3C + 3O2 gives 3CO2 and the fourth equation becomes 4H2 + 2O2 gives 4H2O. Now 3 carbon and 3 carbon gets cancelled. 4 hydrogen and 4 hydrogen gets cancelled. So you now have 3 moles of oxygen and 2 moles of oxygen adding up to 5 moles of oxygen. You have 1 mole of propane. So this is C3H8 + 5 moles of oxygen forming 3 moles of carbon dioxide + 4 moles of water. So this is the equation 1.

So we got the equation 1 and all we did was multiply equation 3 by 3 and equation 4 by 4 and flipped the equation 2 to get our equation, get the equation of interest. So now, let us see what our enthalpy table looked like when we prepared it for the heat of formation method.

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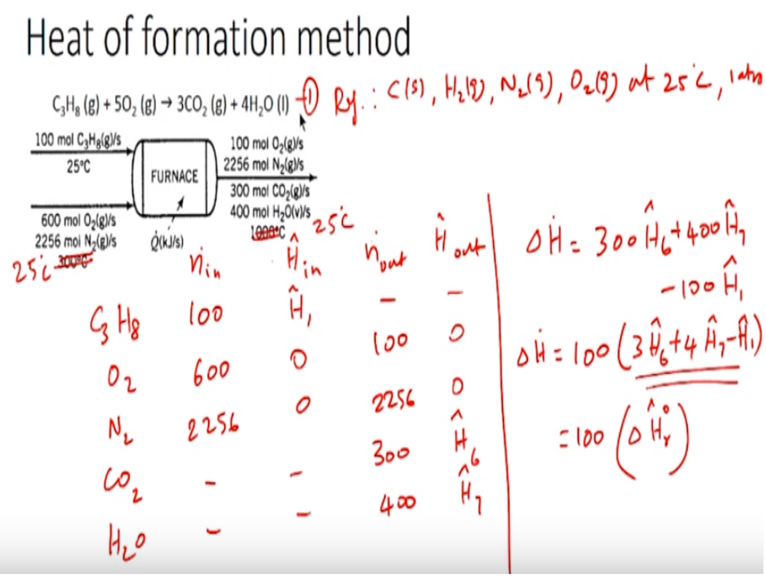

Heat of formation method

$C_3H_8(g) + 5O_2(g) \rightarrow 3CO_2(g) + 4H_2O(l)$ ① Ref.: $C(s), H_2(g), N_2(g), O_2(g)$ at 25°C, 1 atm

	$\dot{n}_{in}$	$\hat{H}_{in}$	$\dot{n}_{out}$	$\hat{H}_{out}$
C_3H_8	100	$\hat{H}_1$	—	—
O_2	600	0	100	0
N_2	2256	0	2256	0
CO_2	-	-	300	$\hat{H}_6$
H_2O	-	-	400	$\hat{H}_7$

$$\Delta\dot{H} = 300\hat{H}_6 + 400\hat{H}_7 - 100\hat{H}_1$$

$$\Delta\dot{H} = 100\left(\underline{\underline{3\hat{H}_6 + 4\hat{H}_7 - \hat{H}_1}}\right)$$

$$= 100\left(\Delta\hat{H}_r^\circ\right)$$

So the heat of formation method enthalpy table was basically this. We had components C3H8. We had oxygen, nitrogen, carbon dioxide and water. So all the 5 components were identified. You have n dot in, H cap in, n dot out and H cap out. So these values are 100, 600, 2256 and 0 and 0. So you do not have any propane leaving and these values are 100, 2256, 300 and 400 and now these values have to be accounted for.

So let us now for the time being not worry about the temperature. So we will just assume all these temperatures to be at 25 degree Celsius only okay as I said we are not worried about accounting for the change in temperature because that is anyways accounted for in both the techniques the same way. So we are only interested in knowing how the reaction itself is accounted for.

So for the time being we will assume these components to also be at 25 degree Celsius. This will help us understand this process. So this would be H 1 cap, this is H 2 cap. So this H 2 cap would be 0 because your reference state here now you have to also note down your reference states. Your reference states are carbon solid, hydrogen gas, nitrogen gas and oxygen gas all at 25 degree Celsius and 1 atmosphere, okay?

So what happens is you do not have any enthalpy here because based on our assumption we are only having temperature of 25 degree Celsius here. So these 2 values would be the same as the reference state. So you have 0 for this. And similarly our outlet condition is also 25 degree Celsius. So again oxygen and nitrogen would be 0. We have carbon dioxide and water forming.

So we have H, now let us just call this as H 6 cap and H 7 cap to be consistent with what we did last time, okay? Now, what we have is if for this particular system you would end up with the change in enthalpy delta H dot would be equal to 100 times 0 + 2256 times 0 + 300 times H 6 cap + 400 times H 7 cap – 100 times H 1 cap. So what you have done here is you have 3 different enthalpies. So 100 is common for all of these. So let us just take out the 100.

So what happens is here delta H dot becomes 100 times 3H 6 cap + 4 H 7 cap – H 1 cap. So what is H 1 cap? H 1 cap is nothing but carbon and hydrogen forming propane. So that would be the reaction 2 which we looked at. So in the previous equation we had reaction 2 where carbon and hydrogen forms propane. So that is the enthalpy change associated with formation of propane. So you now have that with a negative coefficient and you have H 6 cap multiplied by 3.

What is H 6 cap? It is nothing but carbon dioxide being formed from carbon and oxygen so which was reaction 3. So carbon + oxygen forms carbon dioxide. Now that is being multiplied by 3 and the reaction where water is formed from H2 and oxygen is multiplied by 4 which is reaction 4 which is exactly the operations which we did. So now this particular value gives us nothing but the heat of reaction for this system. It should be 100 times delta H r cap.

So this accounts for the heat of reaction for the equation 1. So we now have the heat of reaction. So what is this 100? That is nothing but the extent of reaction.

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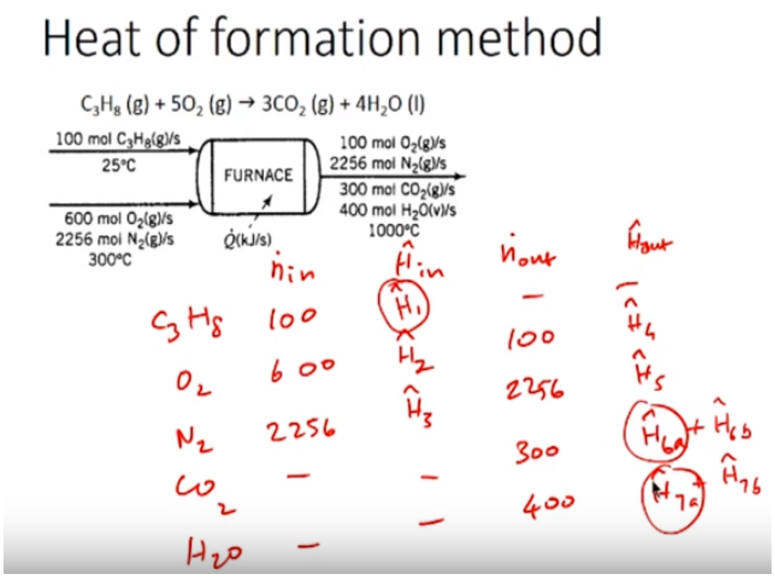

Heat of formation method

$C_3H_8 (g) + 5O_2 (g) \rightarrow 3CO_2 (g) + 4H_2O (l)$

	$\dot{n}_{in}$	$\hat{H}_{in}$	$\dot{n}_{out}$	$\hat{H}_{out}$
C_3H_8	100	$\hat{H}_1$	—	—
O_2	600	$\hat{H}_2$	100	$\hat{H}_4$
N_2	2256	$\hat{H}_3$	2256	$\hat{H}_5$
CO_2	—	—	300	$\hat{H}_{6a} + \hat{H}_{6b}$
H_2O	—	—	400	$\hat{H}_{7a}$ $\hat{H}_{7b}$

So we had calculated the extent of reaction earlier and that was identified to be 100 and here now we have 100 times heat of reaction which we have obtained which is nothing but extent of reaction times heat of reaction. So if we were to have the temperature differences as well what would happen is now this equation can actually have 2 components. So this table would have all these enthalpy values in the table would have 2 components.

So what you would end up with would be C3H8, we will call it n in dot H cap in, n out dot and H cap out, okay? So you have propane, oxygen, nitrogen, carbon dioxide and water. So in propane you have 100 moles coming in, oxygen 600 moles coming in and nitrogen 2256 moles coming in and these are not coming in. We do not have any propane leaving. You have 100, 2256, 300 and 400 moles of each of these components leaving.

So now we are going to account for the temperature as well. So you have H 1 cap, this is going to be H 2 cap. You have H 3 cap. You have H 4 cap, H 5 cap, H 6 cap and H 7 cap. So now what happens is all these are going to have different components. So H 1 cap is going to be only heat of formation where carbon and hydrogen react to form propane.

Whereas H 2, H 3, H 4 and H 5 are going to have only heating of these components from 25 degree Celsius which is the reference state to either 300 degree Celsius which is the inlet condition or 1000 degree Celsius which is the outlet condition. Your other two terms H 6 cap and

H 7 cap are going to have 2 different components. One being the formation of carbon dioxide and the other is your heating of carbon dioxide or water from 25 degree Celsius to 1000 degree Celsius.

So now if we were to break this down into two components, so let us just call this H 1, H 2 and all these things are fine so let us just call these alone as H 6 a + H 6 b and similarly this would also be H 7 a + H 7 b. So if we do this what happens is in comparison with what you had in the heat of formation technique sorry heat of reaction technique the only values which you have in addition to whatever you would have had in the heat of reaction technique are these values.

You have H 1 cap and you have this H 6 a and H 7 a. So which account for the heat of formations and again you would multiply them with these terms and you would again get the same Hess's law where the heat of formations for carbon dioxide and water are multiplied by 4 and the heat of formation for propane is multiplied by -1 and adding all these we would get the total change in enthalpy due to the reaction because you are also going to be multiplying it with 100 which is the extent of reaction.

So using this technique you have actually accounted for the heat of reaction in an implicit way and this is how heat of formation method actually accounts for the heat of reaction as well. So hope you have understood the principles. Please try to solve problems using both techniques. So we will be solving more problems as part of this understanding how to perform energy balances for reactive processes.

I hope you would try both techniques even if I try out only one technique during the class. Please take the problem and try to use the other technique and see whether you are able to take the, understand how to define the reference states and how each of the steps are defined and how actually a hypothetical path is filled for this type of a problem. So until then thank you.