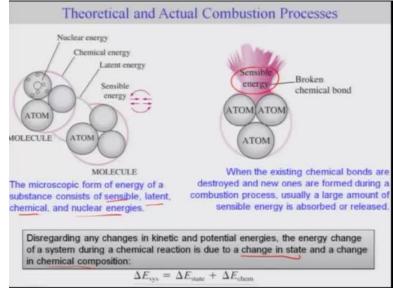
Engineering Thermodynamics Professor Jayant K Singh Indian Institute of Technology Kanpur Department of Chemical Engineering Module 8 Lecture No 57 Enthalpy of formation and combustion, adiabatic flame temperature

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	Learning Objectives
•	Give an overview of fuels and combustion.
•	Apply the conservation of mass to reacting systems to determine balanced reaction equations.
•	Define the parameters used in combustion analysis, such as air-fuel ratio, percent theoretical air
•	Apply energy balances to reacting systems for both steady-flow control volumes and fixed mass systems.
•	Calculate the enthalpy of reaction, enthalpy of combustion, and the heating values of fuels.
•	Determine the adiabatic flame temperature for reacting mixtures.

Ok welcome back uh, we were discussing the chemical reaction and in this particular lecture we will be looking at the enthalpy of reaction, enthalpy of combustion and particularly the first law of chemical reaction systems for close system and as well as for the study flow systems and in the end we will look at the adiabatic frame temperature for reacting mixtures ok.

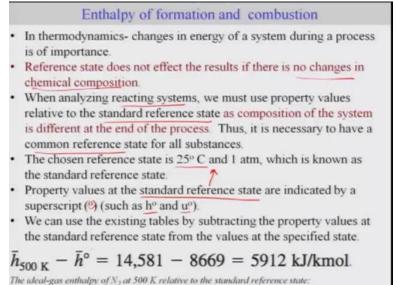
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So let me just go through the basics of combustion processes, now as we know that microscopic form of energy of a substance consist of sensible radiant chemical and nuclear energies and thus when there is a specific reaction which occurs particularly combustion then usually a large amount of sensible energy gets released or absorbed. Now this is represented in terms of broken chemical pot ok.

So if you disregard any changes in kinetic and potential energies, the energy change of a system during a chemical reaction will be due to the change in state ok, state of the system that means temperature pressure and due to the change in the chemical composition which means when the reaction occurs there is a change in species or change in the chemical composition and hence there will be change in energies due to that and thus the change in the energy of the system is due to the state and change and due to the contribution of chemical composition change ok.

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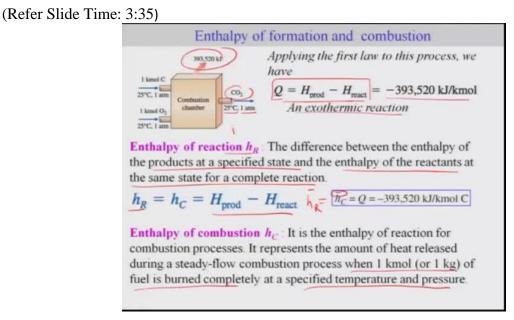


In thermodynamics what we are interested in in the changes in the energies ok not the absolute energy, so when the reaction occurs we are not interested in the final total energy but whatever the energy change because if you recall, the first law of thermodynamics talks about the change in energies. So that is relevant for us and in fact that makes our life bit easier. So as I said the changes in energy of the system during a process is of importance in thermodynamics and thus if there is no change in the chemical potential, the reference state which is used to find the energy of the system, you can make use of any reference state will not affect the final results ok.

But we know during the chemical reaction, the composition will change. So for analysing the reacting system first of all we must use property values with reference to a standard reference state because as I said the composition of the system at the end of the process is different from the at the initial conditions because initially you have the set of reactants ok and they undergo reactions and there is a set of products will come and the product composition will be different from that of the reactant composition. Thus it is necessary for the reacting system to make use of a common reference state for all the substances.

Uh chosen reference state is 25 degree Celsius at one atmosphere which is a typical standard reference state and this is what we are going to make use of as a, as a standard reference state for calculating all the properties ok. the property values at the standard reference state that is this ok

are indicated by super script, that means H super scripts are zero or UO this would be indicative of the properties at the standard reference state ok.



So now let me just take a look of describe this particular example of a combustion of a carbon leading to the formation of CO2 so you have 1 kilo mole of C and 1 kilo mole of oxygen at 25 degree Celsius at one atmosphere in a combustion chamber leading to the formation of a CO2 at 25 degree Celsius atmosphere. During this combustion the energy is being released to the amount of 393520 kg ok.

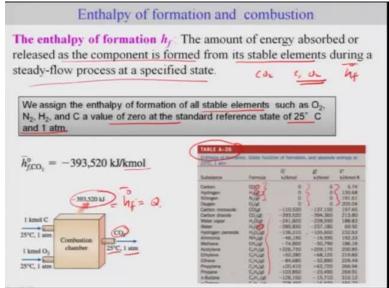
Ok so if you apply the first law of to this process, now considering that there is no work involved then this would be a simply Q is equal to the change in the enthalpies, that means the difference in the enthalpies between the product and the reactant. This is a study flow system and that is what we can make use of this first law for a study flow system. Now this particular reaction is exothermic reaction which essentially means that it releases energy and thus Q is negative of this value ok because this is being released ok.

We will be introducing the enthalpy related to formation of this CO2 by something called combustion enthalpy or in order to further analyse such kind of a processes let me first define two terms, one is a the enthalpy of reaction which is nothing but the difference between the enthalpy of the products at the specified state and the enthalpy of the reactants at the same state for a complete reaction. So enthalpy of reaction is nothing but the difference between the enthalpy of the product at the same state. So essentially for the case of this CO2 formation or combustion of carbon at 25 degrees at one atmosphere where the reactants are also at 25 degree one atmosphere that is standard state and as well as the CO2.

uh For this case your HR is nothing but your Q itself which is minus 39352 kilo joules per kg kilo mole. Here we have used bar which is indicative of your reference as a 1 kilo mole of carbon, the other term which we are going to make use of it is called enthalpy of combustion, it is the enthalpy of reaction for combustion process as in this case. It represent the amount of heat released during a steady flow combustion process where 1 kilo mole or 1 kg of fuel is burnt completely at a specified temperature and pressure.

So for the above example your HC is HR ok and essentially the heat of combustion is nothing but also heat of reaction for the case of your combustion of carbon to CO2 which is a complete combustion as in the case shown here ok.

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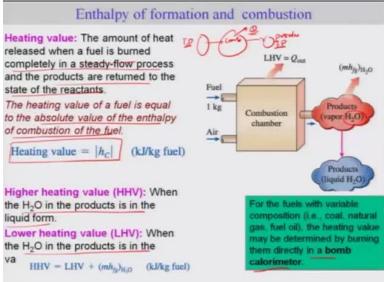
There is another aspect which we should also look at it and that is your CO2 is being formed from individual elements at this standard condition and thus we also define another term or another variable or which is we call it enthalpy of formation ok, this is the definition where we, the enthalpy of formation is nothing but the amount of energy absorbed or released as the component is formed from a stable element. So for the case of CO2, C and O2 are the steerable elements ok.

So this is the amound of energy absorbed or released as the component is formed from a stable element during a steady flow process at a specified state. So specified state could be anything, the enthalpy of formation at typical standard state would be HF0, if it is a mole bases then it is going to be bar on top of it ok. For the generalisation or for the usage of this enthalpy of formation what we do is, we assign the enthalpy of formation for all stable elements such as O2, N2, H2, C value of 0 at the standard reference state of 25 degree Celsius at one atmosphere and based on this definition it is very clear that for the case of CO2 this amount itself is nothing but HF0 at 25, this is a heat of formation, 0 stands for that this heat of formation is nothing but at 25 degree at one atmosphere and thus the 0 represent there and super script and the bar represent it is in kilo mole unit ok.

So this is your heat of formation with a negative sign would be your H bar F ok or this was nothing but Q which is this. Heat of formation for various different elements or various different compounds are being tabulated for us to make use of it directly from the table, so that we can use those tables to solve problems instead of finding out heat of formation for each individual compounds and a common compounds or the molecules are tabulated in table A26.

And you can clearly see here ok where the carbon states are given in solids, gas and later on in liquid also and for the elements which are stable such as your carbon, hydrogen, nitrogen, oxygen there reference values are considered to be 0 so ok. That is only for the heat of enthalpies or Gibbs free energy here. Further values are given for other molecule values are given here ok, so this is something which we will be able to use it in solving problems related to chemical reactions.

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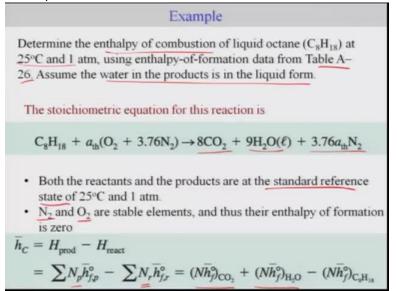
Now as we have already discussed that the fuels are of different types. Some fuels yield larger energy. That means it has more value for energy generation or ok and it is more environmentally friendly and in order to quantify the fuel quality one can make use of something called heating value ok.

So what is a heating value? Heating value is the amount of a heat released when a fuel is burnt completely in a steady flow process and the product are returned to the state of reactant. So that means the reactants are also at T and P, there is a combustion which occurs ok and this releases certain heat and the product here ok also is brought to the same state which means T and P. And whatever the corresponding heat being released is basically your heating value. So heating value of a fuel is equal to the absolute value of the enthalpy of combustion of the fuel, so this is what we call heating value ok.

Now it depends whether the heating value whether the product is in vapour state or liquid state. For fuel particularly fuel will contain certain amount of hydrogen ok, for hydro carbons it is very very relevant and it will obviously yield certain water which can be in a vapour state or a liquid state. Now if it is the water and the vapour state is in the product which means the water vapour will consume the heat of vaporization energy or the latent heat and thus it will reduce the amount of the heat being released from the combustion chamber ok. So it will reduce the heating value, so that heating value where the product water vapour of product water is in vapour state is called low heating value. If water is being condensed or if the final product of the water is in the liquid state then essentially the latent heat of vaporization is also released as a part of the heating value and then that will be your high heating value ok. So the higher heating value is when water is in the product is in the liquid form and the lower heating value is when water in the product is in the vapour form ok.

So one can determine the heating value of the fuel by burning the fuel directly in a something called bomb calorimetery.

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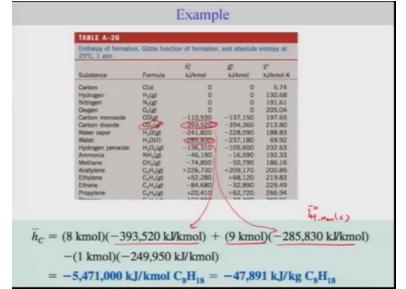
So let me now do an example of where we can calculate the enthalpy of combustion for liquid octane and so this is at 25 degree Celsius in one atmosphere and we have to make use of the table A 26 and assuming the water in the product is in the liquid form ok. So the first step is to write down the reaction of for this particular combustion of the liquid octane. Ok let me start with that, so the reaction should be in stoichiometric form stoichiometrically balanced, so this is your stoichiometric equation for this reaction ok.

And A we can calculate it being a stoichiometrically balanced it should be a theoretical value of A should be your 8, you can clearly see that ATH should be 8 here. So one can do this balance, now this particular reaction where the reactants are at 25 degree once atmosphere and as well as

the product is at 25 degree at one atmosphere, so that means they are both at the standard reference state ok and we know that we have taken the assumption or we have taken the reference value for the standard reference state for elemental stable elements to be 0.

That means the enthalpy of formation of stable elements at standard states are going to be 0, that means for N2 and O2 the enthalpy of formation is going to be 0 which is associated with this particular combustion reaction ok. So let us see which is your enthalpy of combustion as we already discussed earlier the SC is nothing but for this reaction is nothing but your Q is H product minus H reactant ok and what is the H product?

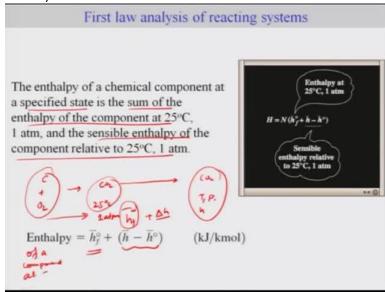
H product is sum of the enthalpy of formation for each individual product which means CO2, H2O, N2 that means sum of NP multiplied by the heat of formation per unit moles, so NP is nothing but the moles for the product and similarly this is also moles for the reactant and this is the heat of formation of the reactants at standard state ok. So when you consider the product, product you have CO2 and S2O, so that means your N times H F0 bar CO2 plus that of H2O and then since this is a stable element and we are talking about the standard reference state then this is 0, so there is no N2 here in the product state because HF 0 for N2 is going to be 0 and then for the reactant we have only this C8 H8 that 18 that is octane and the other elements being a stable elements are going to be 0, so this becomes your heat of combustion analysis ok.



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Now you can make use of this table, the table has all the important values, so what we need is for the heat of formation for the CO2, H2O, C8, H18 which can be directly taken from here and based on the stoichiometric analysis this will be your 8 and thus you have 8 kilo moles, this comes from your CO2 in a gas state ok, similarly this will be for the water, water is in the liquid state and hence this water is 9, N for water is 9 kilo moles multiplied by HF for water which liquid particularly liquid state, so this comes from here, this was, this should be from here ok and this comes here ok and then you have this in the reactant for C8 H18 the the liquid octane and this you can get it from the table as well ok.

From here we can do the simple calculation which will lead this heat of combustion per unit mole in this value, you can convert this to in per kg as well ok. So this is a simple exercise making use of table and a stoichiometric equation analysis of the reaction. Now let me just take to the next step and try to first explain the first law of the reacting system. Before we go through this we must understand the enthalpy calculations at a given state ok, let us say T and P.



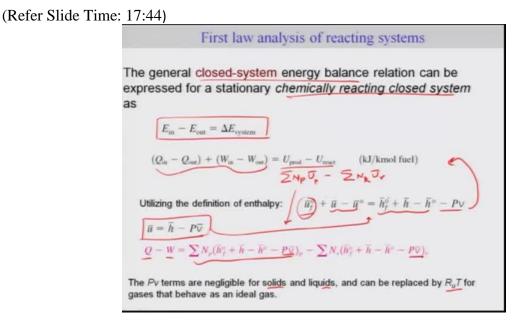
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The enthalpy of a chemical compound at a specified state that is your TP ok is nothing but the sum of the enthalpy of the component at 25 degree Celsius one atmosphere and the sensible heat enthalpy of the component related to the 25 degree Celsius and one atmosphere. So in order to understand this we can consider let us say the formation of CO2 at 25 degree Celsius one atmosphere ok. And if you are interested to find out the enthalpy of the CO2 at a certain T and P

then enthalpy here is going to be enthalpy of from the stable element to here, so that will be your enthalpy of formation at standard state and from here to we take this gas whatever is formed at 25 degree Celsius take it to this T and P, so that will be the change in enthalpy of this particular path ok.

So thus the enthalpy of the component at TP is nothing but enthalpy of formation plus the change in the enthalpy taking the compound chemical compound from the reference or from the standard state to the specific state of our interest which would be given by the sensible enthalpy difference or in another word the your delta H ok. So this is your enthalpy of formation of that particular compound plus the difference with respect to the standard state the or the change in the enthalpy with reference to the standard state.

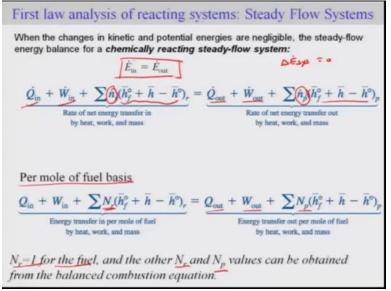
So this is how we are going to calculate enthalpy of a compound at a given T and P ok.



So now we take a look at other general closed system energy balanced relation, so for chemical reactants closed system E in minus E out is nothing but your delta E system, E in minus E out can also be written without any sign convention, Q in minus Q out plus W in minus W out and delta E system will be simply the change in the internal energy ok or between the product and the reactant, so this will be your simply U product minus U reactor because this is a closed system, there is no no mass flow at all.

So but you can as we already discussed that our table A 26 or the table which we have used contains the enthalpy values A and we can rewrite this expression of the energy balance for the closed system reacting chemical reactor system in terms of the enthalpy, one can make use of this definition of the the relation of the internal energy with enthalpy and the bar represent per unit mole and rewrite this expression so, rewrite this expression of UF, UF is a this internal energy of the formation at different system plus the change in internal energy with reference to different system is nothing but this minus this, this comes directly from this relation ok.

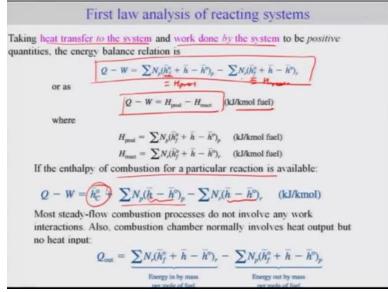
And then you can use this expression directly in this expression where U earlier was nothing but your NPU bar ok minus summation NP NR reactant U reactant ok. So this can be written here and this itself can be written in terms of a using the sign convention simply Q minus W ok. Thus you have the chemical reactive closed system energy balance can be written as in this form Q minus W is equal to the change in enthalpy due to the product minus total enthalpy due to the reactant ok. In this PV term, note that we can neglect this for solid and liquids and this can be replaced by RUT for gases that behave as an ideal gas ok. (Refer Slide Time: 19:57)



For the case of a stea dy flow system, we can consider delta E in to be 0 and thus your rate of change in energy in should be equal to rate of change in energy out. This E in can be written due to the contribution of a heat in W work in and as well as the energy transfer due to a mass ok which includes your moral flow rate of the reactant multiplied by the enthalpy of the reactant. This should be equal to Q out plus W out in a rate form plus the energy transfer out due to the product where that is nothing but summation of the modal flow rate of the product or multiplied by the enthalpy of the individual product components.

One can rewrite this in terms of per mole of fuel bases where we divide with respect to the fuel and then you have this Q in plus W in and this becomes your NR, number of moles of the reactants where NR is equal to one fourth of case of the fuel and other NR NP values can be obtained from the balance combustion equation ok. So here instead of the rate you have Q out for the product for this side, Q out plus W out and summation of the moles of the product multiplied by the corresponding mole of enthalpy or enthalpy per unit mole bases ok for the product.

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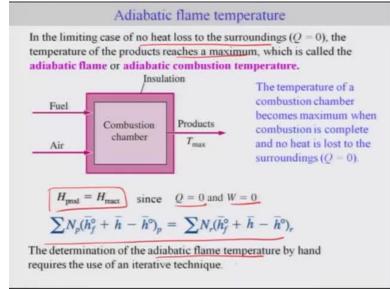


Ok so this is a straight forward balance and we can consider now typical and a sign convention where heat transfer to the system is going to be considered positive work done by the system also going to be considered positive and thus you have the relation Q minus W ok minus is equal to sum of the energy transfer energy of the product minus energy due to the reactant and one can replace this in a more generic form where this is nothing but your H of product and this is nothing but your H of reactant.

Note that this is a per unit kilo mole fuel bases ok. Now if there is a specific combustion which occurs during the reaction then you can take out the reference part ok directly as a part of your combustion and thus this comes out from here and H bar 0C comes out here separately and then you what remains is nothing but your NP multiplies by H bar minus H, that only the sensible enthalpy change ok with respect to the reference value ok for the case of product and reactant. And this is due to the enthalpy of combustion you know at a standard state.

So if this is available we can directly make use of this expression ok. Ok for the case usually for most study flow combustion process, the work involvement is not usually there, that means they do not involve any work interaction and hence this would be 0 and one can write Q out the heat generated is nothing but difference between the enthalpy of the reactant entering the combustion chamber and enthalpy of the product leaving the combustion chamber.

Ok so when the combustion chamber is being operated the temperature of the combustion changes during the reaction ok and it can reach a certain maximum value as well and this is something which we can represent in terms of adiabatic flame temperature.





So we can discuss this aspect by considering a limiting case where the no heat loss to the surrounding is considered, that means Q is equal to 0 and you will consider this to be insulation an insulating combustion chamber. So the temperature of the product here reaches a specific maximum or reaches the maximum and this particular temperature is called adiabatic flame or adiabatic combustion temperature and you can try to find out this adiabatic combustion temperature by considering Q equal to 0 considering there is insulation on this combustion chamber and of course we have considered that there is no work interaction ok.

And thus your H product is H reactant, that means you can write this expression in this form and then what you can do is you can determine this adiabatic flame temperature because the temperature of the product will keep changing, so that becomes a variable and one can iterate this as that left hand side expression is or the values are same as the right hand side, so one can do iterative analysis to come up with the value of adiabatic flame temperature.

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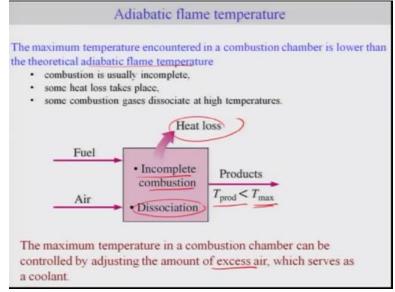
Adiabatic flame temperature
The adiabatic flame temperature of a fuel depends on (1)the state of the reactants
(2)the degree of completion of the reaction (3)the amount of air used
For a specified fuel at a specified state burned with air at a specified state, the adiabatic flame temperature attains its maximum value when complete combustion occurs with the theoretical amount of air.
The adiabatic flame temperature is an important consideration in the design of combustion chambers, gas turbines, and nozzles.
In combustion chambers, the highest temperature to which a material can be exposed is limited by metallurgical considerations.

So the adiabatic flame temperature of this fuel is not unique, it depends on couple of things or couple of variables, it depends on the state of the reactant it depends on the degree of the completion of the reaction and amount of the air used. For a specified fuel at a specified state burned with A at a specified state which means given state the adiabatic flame temperature attains its maximum when there is a complete combustion with the theoretical amount of air ok.

So there would be a theoretical adiabatic flame temperature which will assume that there is a theoretical amount of air is being used for complete combustion of the fuel. Now this adiabatic flame temperature becomes an important characteristic because this is something which has to be considered for the design of the combustion chamber gas turbine and nozzle, so this is important for metallurgical aspect of the combustion chamber ok. In combustion chamber the highest temperature to which a material can be exposed is limited by the metallurgical consideration.

So you need to be aware of the adiabatic flame temperature. That means what maximum temperature or reaction can yield ok or the product can reach.

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Now the maximum temperature which is encountered in a combustion chamber is typically lower than the theoretical adiabatic flame temperature because there could be a heat loss from the combustion chamber, there could be a incomplete combustion, there could be a dissociation of the gas at high temperature thus the T product usually is less than T maximum or the maximum adiabatic flame temperature or theoretical temperature.

However one can control this maximum temperature because if these are the constraint we have to deal with, that means heat loss, incomplete combustion, dissociation then you can make use of by adjusting the excess amount, you can control the maximum temperature in the combustion chamber. The excess amount acts like a coolant as well ok, so that is about the adiabatic flame temperature of the combustion chamber, so that would be the something which is relevant for chemically reacting system and one can also make use of second law analysis of chemical reactor system. However we will not cover this aspect in this course.

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Summary

- Fuels and combustion.
- · Theoretical and actual combustion processes
- · Enthalpy of formation and enthalpy of combustion.
- · First-law analysis of reacting systems
 - Steady-flow systems
- Closed systems
- · Adiabatic flame temperature

I will end this particular chapter with summary of what we have gone through, we have gone through the definition of the fuel and combustion, theoretical and actual combustion processes, enthalpy of formation and enthalpy of combustion and as well as the first law analysis of the reacting system where including steady flow system and close system and we also discussed the adiabatic flame temperature which acts like a theoretical limit for the design of the chambers and in general we should be aware of the maximum temperature which can it yield and we can control this by use of excess air.

So with that I will be completing this course, I will this will be the end of this course and I hope that you have learned fundamentals of first law and second law, its analysis for engineering systems and hope you can take it further for practical applications ok, so good luck, see you next time.