

Indian Institute of Technology Kanpur

National Programme on Technology Enhanced Learning (NPTEL)

Course Title

Engineering Thermodynamics

Lecture – 19

First Law of Thermodynamics to Reacting Systems

By

Prof. D. P. Mishra

Department of Aerospace Engineering

Let us start this lecture and before that we can recall as usual like what we learned in the last lecture and also previously. So if you look at we are trying to basically apply the first law of thermodynamics both for the control mass system and control volume system right. And we have also taken few examples and how to apply that and if look at whatever the systems we have discuss is basically non reacting kind of flows.

For example, like you know like if I consider example of heart of a human being which is giving the blood supply to your whole body right it will be very interesting component to be analyzed by using the first law of thermodynamics. But there if look at there is no chemical reaction is taking place right, but if I consider let us say digestion of your food right in your digestive track, so what is happening some reaction will be occurring there right metabolism kind of.

So if I want to analyze by using thermodynamics you know laws then you know we will have to consider some of the reactions as well and some examples you know like is very important, because chemistry is very important in life therefore Jim Eadon of the Sheffield University.

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Lecture 19

"You are a big chemical reaction. Everything you say, all that you do, all that you see, decide or remember, think or feel is nothing but the manifestation of the chemical reaction that is you."

Jim Eadon
Sheffield University

Rightly said, "You are a big chemical reaction. Everything you say, all that you do, all that you see, decide or remember, or think or feel is nothing but the manifestation of the chemical reaction that is you." So how beautifully he has really told and what we will be doing today we will be basically looking at how to handle the problems wherever there is a some chemical reactions will be occurring, because whenever chemical reaction occurs there will be either you know some heat will be released or some heat will be what you call absorb right exothermic reaction or endothermic reaction will be taking place.

So what we will do will be basically taking some kind of problem which is related to combustion.

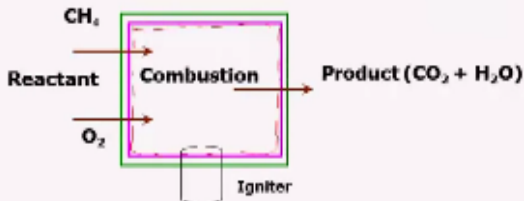
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What do we mean by Combustion?

Combustion is setting fire to fuel in a controlled manner.

In combustion, chemical reactions are sustained itself.

Combustion: A chemical process in which **Fuel** is reacted with **Oxidizer** while releasing heat and light.



Ignition: Initial energy to initiate combustion.

So what do you mean by combustion can anybody tell me right, is it something like setting well to how to call fire to fuel. So it is basically you can think of in layman's term that combustion is a process by which you can just burn the fuel in a controlled manner, right and so in the combustion basically there will be several chemical reactions which will be occurring, but they are self sustained that means once it is initiated you need not to give any further energy it will be taking care of themselves right.

So in a more technical way we can define a combustion is a process during which fuel is reacted with oxidizer while releasing heat and light of course you know heat is always has to be released some total of that, but the light you may not see some time right. But most of the combustion process you could see right what are the examples of combustion process you see can anybody tell me, you might have seen, you know like burning of what you call your LPG burner right what we use for cooking food.

And you might have seen like cigarette burnings and then they are you know like weak flames we have seen and several other things what we do. And so for example if we will consider a burner let us say or a combustors where the chemical reaction is taking place, I am like this into this chamber the one mole of methane is entering so also along with the oxygen right, it will be reacting with each other.

And it is giving right to product of carbon dioxide and water you take this as a system boundary right you can take this as a system boundary right, and then it has to be mixed properly and is it

like it will go to directly combustion carbon dioxide and water. Suppose there is a chamber where you are just adding fuel let us say methane fuel and oxidizer and it mixed properly unless otherwise you give some ignition energy it would not ignite it will remain as it is you know is not it.

So if you look at that is in a stable state, but once you give you know ignition energy then it will going directly to the, what you call to the end product that is carbon dioxide and water keep in mind there might be several reaction which are occurring before really the methane and oxidizer or oxygen getting into the end product carbon dioxide water, but we are considering only one step kind of reaction.

So and that you know is very important you should have of course sufficient amount of ignition energy to the combustion to take place or in other words for initiation of combustion. So we will have to see that how to handle as I told that this whether we could consider this as a control mass system or control volume if it is the flow is taking place right and the, you know then we will consider as a basically control volume in this case flow is taking place I mean like methane is entering so also oxidizer and then some reaction is occurring in the what we call in the combustors.

So therefore we can consider as a control volume system very easily and for analysis, but however if some reaction is taking place in a chamber closed chamber like you.

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Example: $\text{CH}_4 + 2 \text{O}_2 \Rightarrow \text{CO}_2 + 2 \text{H}_2\text{O} + \Delta H$

1 mol + 2 mol \Rightarrow 1 mol + 2 mol

16 g + 64 g \Rightarrow 44 g + 36 g

\Rightarrow Mass is conserved

In this process chemical bonds are broken & new bonds are formed which releases heat.

Mostly air is used as an oxidizer.

$\text{CH}_4 + 2(\text{O}_2 + 79/21 \text{N}_2) \Rightarrow \text{CO}_2 + 2 \text{H}_2\text{O} + 7.52 \text{N}_2$

Stoichiometric: Minimum amount of oxidizer (air) required for complete combustion of fuel.

\Rightarrow 274.66 kg of air is required for 16 kg of CH_4 .

Stoic. Air/Fuel Ratio = $m_A/m_F = 277.66/16 = 17.166$

For example, you take some acid and react with some you know base kind of things and then what will happen some kind of product will be coming out there you know in chemistry what we do you add some you know kind of to liquid for reacting you know like and then you will see that there is a some kind of control mass system in it to use it. But in this case we are using a control volume system.

So in this example one mole of methane is reacting with two moles of the protocol oxygen going to the product of car one mole of carbon dioxide and two moles of water and giving rise to you know certain amount of heat release and if you look at the you know of course in this example the moles are balanced and so also the mass because 16 gram of methane is reacting with 64 grams of oxygen going to the product of 44 grams of carbon dioxide and 36 grams of you know water.

So in this case mass is conserved you know like kind of things and if you look at the mole in this example is also you know balance both the left and right hand side but in other reaction it need not work but how mass has to be you know balance, so of course in this process as I told like the chemical bonds are broken and new bonds are formed of course which religious seat and in some reactions particularly endothermic reactions where the heat has to be absorbed and you need to provide the heat for the reaction to occur.

So mostly air is used an oxidizer right and if you now replace in the chemical reaction that is instead of oxygen if we will use the air like an air we are saying that 79% of nitrogen and 21 %

oxygen we are neglecting the other you know gases which are in very, very small proportion negligibly small, so if you look at the one mole of methane is react to it two moles of air is going to the one mole of carbon dioxide and two moles of water.

And of course 7.5 two moles of nitrogen if you look at this is the balance am I right if you look at if you take this balance this is a balanced equation and that we call it a stoichiometric you know kind of things and stoichiometric means the minimum amount of oxidizer required for complete combustion of you know but let us say one gram of fuel or one mole of kind of thing in this case the two 74.66 kg of air is required for 16 kg of methane you can call it also you know grams.

So the stoichiometric air-fuel ratio will be mass of air divided by mass of F which is happens to be 17.166 that means the ratio of air will you need to provide that is 17.166 for complete combustion right, so I am like this we need to have a balance that is your stoichiometric.

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But, usually, excess air is supplied for complete combustion in actual case.

120 % theoretical air = 1.2 x theoretical air.

$$\text{Equivalence ratio} = \phi = (F/A)_{\text{act.}} / (F/A)_{\text{Stoic.}}$$

$\phi < 1 \Rightarrow$ Fuel lean = Less fuel $\phi = 1.0$

$\phi > 1 \Rightarrow$ Fuel rich = More Fuel

$$(A/F)_{\text{mol}} = n_A/n_F$$

But usually what we do we will have to give excess amount of air for complete combustion in actual you know case because that what we have just now saw that for methane and air we need to give what you call something 17.16 around that ratio has to be maintained that is the 17.16 is basically a air to fuel ratio but that is theoretical even if you give in actual case you cannot really have a complete combustion therefore we always give excess amount of air so that complete combustion can take otherwise it will be what will happen it will be causing pollution because some carbon monoxide and some other unburned hydrocarbons will be remaining and also it will be inefficient he means the entire energy would not be released during these chemical reactions.

Or burning of fuel so if I consider 120% of theoretical air basically it 1.2 times of theoretical air that will have to give and you know like we will have to define a equivalence ratio which will tell you like you know basically whether it is a lean fuel or the rich that is defined as Π is ratio of fuel air actual /fuel a stoichiometric that means this is your equivalence ratio kind of things you can define other way around that is you know air-fuel stoichiometric /air-fuel actual that also some people do define.

That is the same thing and if Π is equal to 1 what is the meaning if, is the Π is equal to 1 that is equivalence ratio 1 that means you are basically operating on a stoichiometric fuel air ratio right or air fuel ratio whatever you got and if it is Π is less than 1 means what that is basically fuel in you are giving less amount of fuel as compared to the stoichiometric you know air what is required you are given less.

And if Π is greater than 1 that means you are giving more amount of fuel than the what whatever the available air is there you know kind of things so therefore we call it as a fuel rich and this will help you to you know like to see with how far you are deviating from the stoichiometric mixture ratio, so that is that is why equivalence ratio is being used and if you keep in mind both the fuel air ratio is a non-dimensional number, so also equivalence ratio right.

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Example: The gasoline (Octane = C_8H_{18}) is burned with dry air. The volumetric analysis of products on dry basis is $CO_2 = 10.02\%$, $O_2 = 5.62\%$, $CO = 0.88\%$ & $N_2 = 83.48\%$. Determine (a) A/F ratio (b) % theoretical air used (c) equivalence ratio.

$$XC_8H_{18} + a(O_2 + 3.76 N_2) \Rightarrow 10.02 CO_2 + 0.88 CO + 5.62 O_2 + 83.48 N_2 + b H_2O$$

By mass balance;

N: $3.76 a = 83.48$;

C: $8 X = 10.02 + 0.88$;

H: $18 x = 2b$;

O: $2a = 10.02 \times 2 + 0.88 + 2 \times 5.62 + b$

$44.4 = 44.4$ (checked)

$a = 22.2$
 $x = 1.36$
 $b = 12.24$

And let us take an example how to you know do the stoichiometric calculation, so the gasoline that is we can model it as an octane C_8H_{18} is burnt with dry air it can be moisture also right you know like for example rainy season is on the way, so at that time you cannot consider the air to be dry right because we generally take air from the atmosphere and then use it for combustion purposes but we are considering dry air that means, it would not be having any water particulates or the you know steam other this thing moisture rather not still moisture and volumetric analysis of product on the dry basis.

Right is something carbon dioxide 10.02%, oxygen 5.62 % and Co 0.88% and nitrogen of course 83.48% kind of things and determine air fuel ratio and we will have to find out percentage of theoretical air use and equivalence ratio you know to point it out so what we will do will basically take this equation that is X moles of the octane is reacting a moles of air and going to the product is given like if you look at carbon dioxide is 10.02 and CEO is 0.88 and 5.62 is oxygen and 83.48 nitrogen of course the be the amount of water you know is not given.

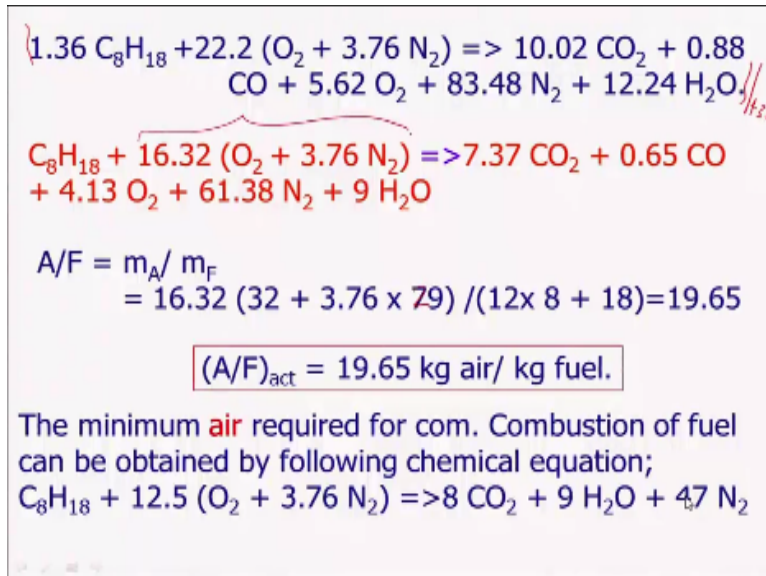
So you need to find out so basically what we will have to do we will have to find out this you know a and then B and then put the X that you need to find it out and keep in mind this is one problem where the products are given in some cases there will be full will be given will be known well let us say CNG gas or some other you know let us say a producer gas it will be several constituents so you need to find out you know like this thing so we will have to use a procedure which is be easier and also the effective way of doing that.

We will be doing basically a mass balance you know that we have already done but we will do in a little systematic way what we'll do we will take the nitrogen if you look at left hand side right what is the nitrogen, nitrogen 3.76 a is equal to in the right hand side there is 80 3.48 then you can get very easily a write a happens to be 22.2 similarly will take see the carbon that is in this case left hand side it is 8x is equal to right hand side 10.02 and carbon monoxide that is point 0.8 and you will find out x is equal to 1.36.

And now we will consider the hydrogen H that is 18x is equal to 2b that is for the water it comes and then you will get the B is equal to two 12.24 and then we can look at oh that is oxygen on the left hand side is 2a is equal to for the carbon dioxide 10.02 into 2 and 0.8 it for carbon monoxide and then for oxygen to into 5.6 and from water that is be so if you look at you know be you know X you know really a why I need this it is just to check whether you have done any mistake or not otherwise there is no need you can already you know this all unknown right these are all known these are unknown you know that thing.

So it is balanced but we just to cross check that you know you have done the right so you can look at it and it is left hand side is equal to the right hand side so therefore it is the right one so this is a systematic way of balancing a equation even for the complex 11 can do that.

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So I mean if you look at these all those coefficients would then what will can do we can divide this entire equation right by 1.36 then you will get per mole kind of things right and that is this expression okay so from this I can find out air and fuel ratio that is m_A by mass of well so if you look at the mass of a is basically this portion right that is 16.3 to into I can take the molecular weight of oxygen plus you know 3.76 into 3.76 into basically it should be 29 plus divided by 12 into 8 + 18 right and that will give 19.65 and the air-fuel ratio is basically 19.6 k 5 kg of a 4 kg of whether that means for burning 1kg of well.

You need you know like in this case 19.6 kg of air is being supplied in this example right then we need to find out for 1kg of this often right how much of air you will have to give for complete combustion in theoretically right. So that we will have to find it out because we are interested to find out equivalence ratio so minimum air required for complete combustion of well can be obtained by following chemical reaction that you can do balance right and that is one mole of the octane is reacting with 12.5 moles of a and giving to the 8 moles of carbon dioxide 9 moles of water and of course 47 moles of nitrogen kind of things so and if you look at them.

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$$\% \text{ of theoretical air} = \frac{m_{air,act}}{m_{air,theo}} = \frac{N_{air,act}}{N_{air,theo}} = \frac{16.32}{12.5} \times 100 = 131 \%$$

$$\left(\frac{F}{A}\right)_{Stoi} = \frac{m_F}{m_A} = \frac{(12 \times 8 + 18)}{12.5(32 + 3.76 \times 28)} = \frac{114}{1716} = 0.06643$$

$$\left(\frac{A}{F}\right)_{Stoi} = \frac{m_A}{m_F} = \frac{1716}{114} = 15.05$$

$$\phi = \frac{\left(\frac{m_F}{m_A}\right)_{actu}}{\left(\frac{m_F}{m_A}\right)_{theo}} = \frac{0.0508905}{0.06643} = 0.766$$

$\phi = 0.766 < 1 = \text{Fuel Lean mixture}$

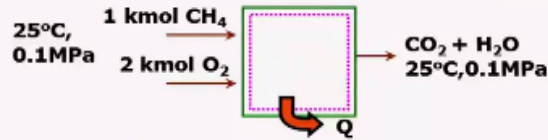
Percentage theoretical air that comes the particle mass of air actual divided mass of theoretical and that will give me the 16 what you call one hundred thirty percent kind of theoretical air will give right and the fuel a stoichiometric will be equal to mass of the fuel of the mass of air that is if we just put these numbers here you will get that is 0.06 643 that you will get and if you look at air fuel ratio right what it would be air fuel ratio is around something 15.05 this is your case so if you look at this is basically hydrocarbon right.

And so also the methane is an hydrocarbon but in methane in case of methane we have seen the air fuel ratio is around 17 point 16 but in this case it is 15 you keep in mind that for unsaturated hydrocarbon right except the methane most of the things will be air fuel ratio will be roughly 15 you know you can keep in mind that bulk pack number that ratio which is required you know air fuel ratio is required for complete combustion and then equivalence ratio this is mass of well divided by mass of air actual divided by the mass of air, air to fuel ratio theoretical right.

And that will be giving you 0.766 right and this is if you look at the equivalence ratio is lean or reach which is this one it will be basically lean it is less than one right and if it is greater than one we call it as a rich full reach okay and if it is equal to one that is basically Stoichiometric mixture, so as I told that in this case the mixture basically is well lean.

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Standard Heat of Reaction:



Applying First Law,
Steady Flow $\Delta KE = 0, \Delta PE = 0, W=0$

$$Q = dH = H_p - H_R = \sum_p n_{i,p} \bar{h}_{i,p} - \sum_R n_{i,R} \bar{h}_{i,R} = \Delta H_{R,298}^0$$

Where, $n_{i,R}$ = No of moles of the reactant

$n_{i,P}$ = No of moles of the Product

$\bar{h}_{i,R}$ = Enthalpy of reactant per unit mole;

$\bar{h}_{i,P}$ = Enthalpy of product per unit mole;

$\Delta H_{R,298}^0$ = Heat of reaction ($T = 298.15 \text{ K}, P = 0.1 \text{ MPa}$)

So we will now look at certain you know terminologies what we will be using for analyzing this and most of the things you will be knowing but I am just trying to make you to recall again so that you will be comfortable as you go along, so that is the standard heat of reactions in this case what we will consider that one kilo mole of methane is basically reacting with this what you call burner right or a chamber.

With two kilo moles of oxygen and then it is going to the product of carbon dioxide water keep in mind that it is entering with the 0.1 mega Pascal of pressure and 25 degree Celsius it is also leaving at 25 degree Celsius and 0.1 mega Pascal right that is the things what we are saying that means that whatever the heat is going out of the system will be taken out then only it will be otherwise temperature will suit up because it is a an exothermic you know a reaction heat will be released.

So if that is the case then we will have to apply the first law of thermodynamics and this is our what you call the control volume I can take okay, this is my system boundary control volume and if I apply this first law of thermodynamics for a control volume system so we will have to make some assumption what are the Assumption we are making here you can say that the change in kinetic energy you know will be negligibly small and so also the potential energy and then what else and we can assume it is to be a steady process right.

And there is no work done if we will do that then what will be your first law I mean what will be the then first law of thermodynamics what it will be it will be basically the Q is equal to that is

the heat is going out nothing but H P that is DH right and which is nothing but hp- HR what is HP is the enthalpy of the product these are the product these are product right and the reactants minus the enthalpy of the reactant.

And that is nothing but summation of the moles the number of moles of each constituents of the product in this case I is for the product in this case it can be carbon dioxide and water and enthalpy of the product minus the summation of the moles of the reactant into their corresponding heat of reactants you know enthalpy of the reactants and these if you look at by definition you know is basically ΔH zero not R at 298 and this is your nothing but your standard heat of reactions right.

So as I told that HIR is basically enthalpy of reactant per unit mole and HIV the enthalpy of product per unit more and this $\Delta H_{R,298}$ that is at 298 is basically heat of reactions and this is the things which is you can get you know basically from a table and kind of things and that is the standard heat of reaction because it is being you know at the ambient temperature and ambient pressure.

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Example: $\text{CH}_4 + 2\text{O}_2 = \text{CO}_2 + 2\text{H}_2\text{O}$

$$n_{\text{CO}_2} = 1, n_{\text{H}_2\text{O}} = 2, n_{\text{O}_2} = 2, n_{\text{CH}_4} = 1$$

$$\Delta H_{R,298}^0 = \left(n_{\text{CO}_2} \bar{h}_{f,\text{CO}_2}^0 + n_{\text{H}_2\text{O}} \bar{h}_{f,\text{H}_2\text{O}}^0 \right) - \left(n_{\text{CH}_4} \bar{h}_{f,\text{CH}_4}^0 + n_{\text{O}_2} \bar{h}_{f,\text{O}_2}^0 \right)$$

$h_{f,i}^0$ = heat of formation of i^{th} species at standard state (298.15 K and 101,325 Pa).

So let us consider an example again the methane one mole of methane is reacting with two moles of oxygen going to the one mole of carbon dioxide and two moles of water so in this case if you

look at the N CO₂ is 1 and n water that is the number of moles of water is 2 and oxygen is also 2 and methane is one mole, so ΔH_{OR} is basically the heat of reaction and that is equal to NH, NCO₂ in HFCO₂ and this is basically heat of formations of co₂ and the number of moles of course we know and then heat of formation of water.

And these are of course for the methane heat of formation and oxygen, so now we need to of course find out this heat of formation of the spaces at standard state that is 2908.15 Kelvin and of course 101.3 25 Pascal's.

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Heat of Formation = Energy change during formation of one mole of a single compound from the constituent elements.

Example: $C + O_2 \Rightarrow CO_2$

At 25°C and 0.1MPa, 1 kmol C and 1 kmol O₂ enter a process box, and 1 kmol CO₂ exits. The energy change is 393,520 kJ.

$\bar{h}_{f,CO_2}^0 = \text{heat of formation} = -393,520 \text{ kJ/kmol}$

$\bar{h}_{f,C}^0 = 0, \bar{h}_{f,O_2}^0 = 0$; As heat of formation of elements at STP = 0

Standard heat of formation are available in table.

$$\bar{h}_{f,i}(T) = \bar{h}_{f,i}^0(298) + \int_{298}^T \bar{C}_{p,i} dT$$

(Note: $\bar{C}_{p,i}$ is specific heat capacity)

So heat of formation is basically energy change during the formation of one mole of single compound from the constituent elements you know during that whenever it is being formed you know like some heat will be liberated or some heat has to be supplied for example if I take CO is C is reacting with the oxygen going given to the carbon dioxide then a certain amount of heat you know is being to be released that is 393, 520 kilo Joule has to be you know supply for that.

That means the heat has to be released so these HF CO₂ is nothing but heat of formation you know that is 393, 000 520 kilo Joule per kilo mole kind of things so and also the heat of

formation of carbon you know is zero and heat of formation of oxygen zero because that is at the natural state at the standard temperature and pressure and this has been you know considered as that a reference.

So the standard heat of formation you know can be obtained from the table and you can use that let me just show you one table was that and this standard heat of formation is basically can becomes two terms one is what you call standard heat of formations you know at standard state this is the like standard heat of formation and this is your sensible enthalpy, enthalpy so this heat of formation at a particular temperature you can get by just taking the data of heat of standard heat of formations right, and also the take care of sensible enthalpy.

For example like let us say you want to have something heat of formation at let us say 500 Kelvin so what we will have to do you have to get this data of h_f^0 at 298 Kelvin and then allowed to integrate this you know CPI values will take and integrate the sensible energy from 298 to T is let us say if I say it is something 600 Kelvin right, so from that you can get at any temperature you can get the heat of formation.

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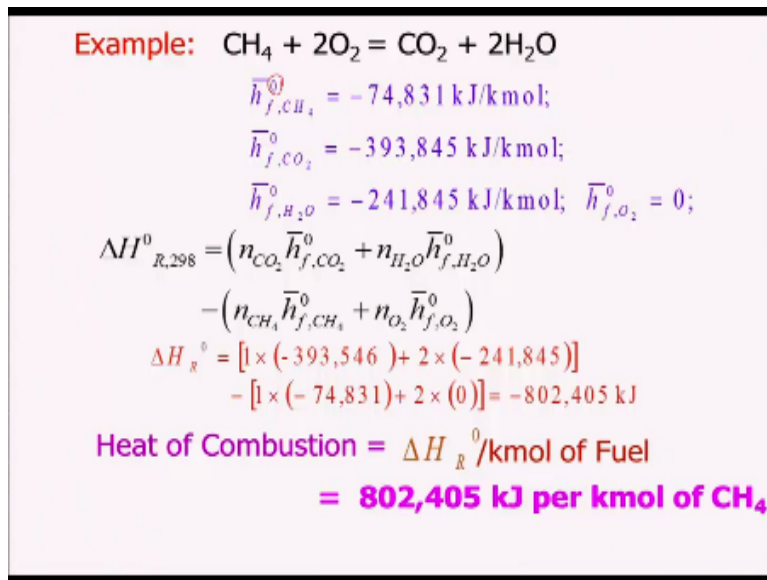
Heat of formation of important species at 25 °C and 0.1 MPa			
Species	Formula	State	Heat of formation(kJ/mol)
Oxygen	O ₂	Gas	0
Hydrogen	H ₂	Gas	0
Hydroxyl	OH	Gas	42.3
Water	H ₂ O	Gas	-242
Water	H ₂ O	Liquid	-286
Carbon monoxide	CO	Gas	-110.5
Carbon dioxide	CO ₂	Gas	-394
Methane	CH ₄	Gas	-74.5
Propane	C ₃ H ₈	Gas	-103.8
Butane (n)	C ₄ H ₁₀	Gas	-124.7
Kerosene	CH _{1.842}	Liquid	-51.6
Nitrogen dioxide	NO ₂	Gas	33.9
Nitric acid	NO	Gas	90.4

So these are the heat of formation of important species like is given here I have given some very few examples here like if you look at as I told earlier that the standard state like for oxygen is a standard state at the gaseous state that is why it is 0 so also hydrogen and whereas the water you

know will be -2142 if it is gaseous state if it is a liquid state it is 286 that means this he if you look at the difference is due to the heat of vaporization right.

And there are several other gases have given here carbon monoxide and then you know like a methane and the several of them and that you need not to remember this number is very difficult you will have to use the table for that, and then keep in mind that there is a negative these are all exothermic reactions here but let us say night nitrogen dioxide is basically positive the endothermic kind of things that sign indicates the nature of the reaction.

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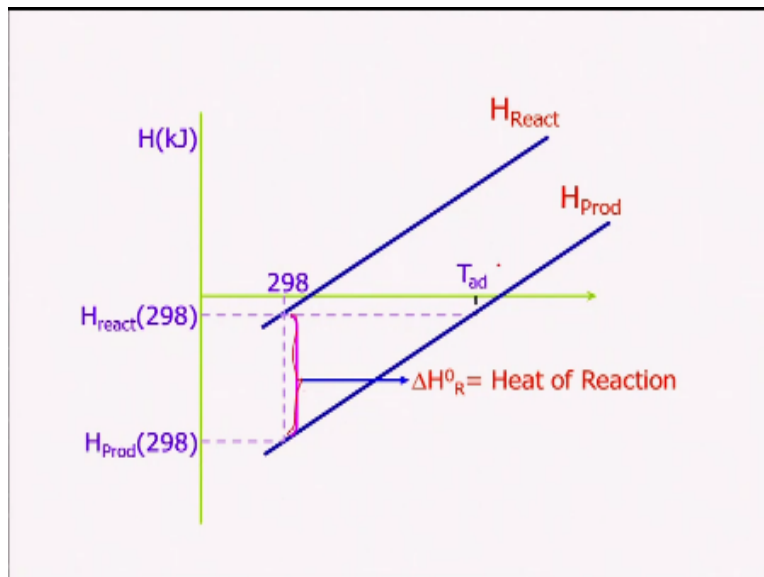


So we will continue that example like what will they from the table we can get for methane is basically 74831 kJ/km similarly for carbon dioxide and water and of course the oxygen at the standard state is 0 keep in mind that this 0 is considered this 0 is basically considered standard state you know just as a reference that to take that symbol. So what we will do we will basically substitute these values for you know standard state of heat of formations or heat of formation at standard state like for carbon dioxide water and methane and oxygen.

If you substitute these values you will find out heat of reaction is basically 802, 405 kJ for this you know reactions. And if you look at like we have basically used one kilo mole of fuel so therefore heat of combustion is nothing but the heat of reaction divided by the moles of fuel that will give me the what you call heat of combustion and that happens to the in this case 802, 405 kJ/kmol of methane.

And if you know basically use the multiply these or if you just you know express this heat of combustion per kg you will have to take you know in the denominator you will have to multiply the molecular weight and then you can get per unit mass kind of things. So that happens to be 50.15 mega Joule per kg methane if you that means if you burnt 1kg of methane you will get something 50.1 5 mega Joule of energy which is very, very large amount right. Of course unlike the nuclear reaction which is much higher but it is really you know quite a bit amount of energy.

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So if you want to this visualize what is the heat of reactions you can say that you know like what you are taking that is the your reactants here in this and which is at 298 Kelvin and the product is that again 298 Kelvin if you bring this is nothing but this portion is nothing but your heat of reaction keep in mind that this heat if it will be utilized then you know you will reach a temperature that is basically the adiabatic temperature product which is provided the heat is not going out we will be discussing how to calculate this you know temperature adiabatic temperature kind of things.

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Hess Law

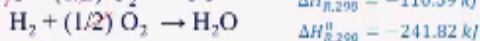
- In a chemical reaction, the resultant heat is same, irrespective of the number of steps

The net heat of reaction depends only on the initial and final states

Illustration: Determine the heat of reaction for water gas shift reaction



Intermediate reactions:



So if you look at we need to use this Hess law which is nothing but the first law of thermodynamics for the chemical reaction and we state that in a chemical reaction the resultant heat is the same irrespective of the number of steps it is being taken during the chemical reactions right. So let us that means the net heat of reaction depends only on the initial and the final step it does not depend what the path is being taken you know for which might be involved several number of reactions to give an example like if you look at like one mole of methane is reacting with.

Let us say two moles of oxygen going to the product of carbon dioxide and water there might be several reaction which will be taking place here we are just modeling it as you know if you when you will work with the actual system there will be several multi-step chemistry will be taking place right and then whatever the heat will be released in the single step it will be same as that of the whole if there might be something let us say 40 reactions are taking place right for to a methane combustion right with the air.

So then the heat release will be same so that is a saying that is the net heat of reaction depends only on the initial and final state it does not depend on the path taken by the chemical reactions you know kind of thing. So to illustrate let us take that an example of water gas shift reaction and we will have to find out heat of reaction for this, so if you look at the water shift gassy reaction is basically the one mole of carbon dioxide is react to me the one mole of mole of hydrogen.

And going to the product of one mole of carbon dioxide and water and the amount of heat release is basically something 41.16 kilo joule kind of things but it can you know really go in the very undergoing several intermediate reaction that means several reaction will be taking place in between let us say that carbon dioxide is being you know decomposed into c plus O₂ which is basically endothermic reaction in this case that is 393.5 kilo joules.

And this carbon is reacting with oxygen is going to the carbon monoxide this is an exothermic reaction which is you know one 10.59 kilo joule being energy being released and then hydrogen is reacting with the oxygen and going to the product water. So if you look at that is basically this will just add all those things this will be canceled it out and this together this half you know will be cancelling it out.

So what will get CO₂ Plus hydrogen going to the one mole of carbon monoxide and one mole of water so that you had together that you are getting 41.16 kilo Joule this is nothing but your what you call you are applying the first law of thermodynamics that is the heat whatever the what you call being it is released it will be basically not dependent on the what you call not on the path rather it will be dependent on the initial and final state in this case basically it is the enthalpy change right that is the what we are considering.

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ADIABATIC FLAME TEMPERATURE

1st Law of TD gives, $H_p = H_R$ (1)

Since, $\Delta KE = 0, \Delta PE = 0, \dot{Q} = 0, \dot{W}_{sh} = 0$

$$\Rightarrow H_p = \sum_p n_{i,p} \bar{h}_{i,p} = \sum_p n_{i,p} \left(\bar{h}_{f,i,p}^0 + \int_{T_0}^{T_p} C_{p,i}(T) dT \right)$$

hand of formation at STP *sensible enthalpy*

$$\Rightarrow H_R = \sum_k n_{i,k} \bar{h}_{i,k} = \sum_k n_{i,k} \left(\bar{h}_{f,i,k}^0 + \int_{T_0}^T C_{p,i,k}(T) dT \right)$$

So what we will be doing is basically adiabatic flame temperature will be considering, now let us consider that a burner in case the fuel is reacting with oxygen air and it is giving rise to the product and let us say that we will take a system here and we are taking the control volume and no heat being going out that we are considering right, so and if you look at what are the Assumption we are we are having same thing that means change in the kinetic energy is zero and change in potential energy is zero and no work is being done in this case and then heat release is zero.

So therefore it will be first law of thermodynamics give string to the heat of product or the total enthalpy of the product is equal to total enthalpy of reactant right okay, that already we have done when we are doing this heat of reaction in that the Q we are considering but now Q is 0 so therefore H P is equal to H R and if you look at H P is nothing but summation of the you know moles and then heat of what you call enthalpy of the product and that is nothing but your moles into this is your heat of formation standard heat of formation right this is heat of formation at STP standard temperature and pressure and this is your sensible enthalpy right.

Of course with n coming into picture otherwise it will be specific you know sensible enthalpy and H R will be similar things I mean only the, you know what you call it is the reactants it is mean for the reactants, so what you will do you will just you know use that thing and then find out what will be adiabatic temperature.

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$$\sum n_{IP} \bar{h}_{j,IP}^0 - \sum n_{IR} \bar{h}_{j,IR}^0 = \Delta H_{R,298}^0 = \text{Heat of Reaction}$$

$$\text{Sensible Enthalpy} = \sum n_{IR} \int_{T_0=298}^{T=600} C_{P,IR}(T) dT - \sum n_{IP} \int_{T_0=298}^{T=298} C_{P,IP}(T) dT$$

$$\frac{\bar{C}_{P,j}}{R_u} = A + BT + CT^2 + DT^3 \dots$$

where, A, B, C, D are constants.

So if you consider this that by definition this $n_{IP} \bar{h}_{j,IP}^0 - \sum n_{IR} \bar{h}_{j,IR}^0$ I mean minus $n_{IR} \bar{h}_{j,IR}^0$ for the reactant and this is nothing but your heat of it of reactions right you can get very easy and then other things what will say that this sensible enthalpy that is the terms which we have seen that when we are considering the balance of enthalpy of the product and is equal to the enthalpy of reactants and then this is basically from the some temperature standard temperature that is equal to 298 Kelvin you can say T is equal to anything let us say if it is six hundred Kelvin kind of things that is you know you can take if it is the inlet condition is 600.

Otherwise what will say this will be u 298 Kelvin also right but whereas the product will be this is 298 Kelvin and this is the adiabatic temperature that means this is a general equation which can be applied for anything right suppose the reactant is coming at 298 Kelvin what will happen to this term this term will be what 0 because it is integrated 298 to 298. So it will be 0 right and whereas the product always it has to go to certain temperature because no heat being going out of the system so therefore it has to go to the adiabatic temperature.

So what is saying that that means the reactant at the standard temperature it is going to the product at the standard temperature that is nothing but your it release right this is the heat of reaction and this heat of reaction right will be basically what you call you utilize here to raise this temperature right this heat of reaction whatever it is raising and then the product you are getting that is adiabatic temperature and keep in mind that this is a very important point that CP

whatever we are using here in the particularly product you know we'll be having very high temperature.

So therefore this is a function of temperature CP which is considered $A + BT$ and $C + CT^2 + TQ$ and this a b c d are constant and these constants will be varying for each species, species means for carbon dioxide it may be different oxygen it will be different and water it will be different so that has to be taken care. So it is a quite difficult to integrate this term you know this term to integrate is quite difficult.

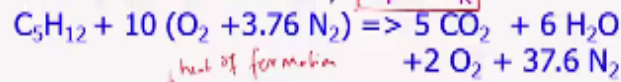
So therefore what we will be doing our calculation will be using some average properties of the CP and then trying to calculate but in actual case generally you know numerically it has to be integrated.

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Example: Estimate the adiabatic flame temperature of C_5H_{12} with 25% excess air. Both C_5H_{12} & air enter the burner at 25 °C. Assume Complete combustion.

$$\Delta KE = 0, \Delta PE = 0, Q = 0, \dot{W}_{sh} = 0$$

1st Law for CV becomes, $H_p = H_R$



$$H_p = 5 \times \bar{h}_{f,CO_2}^0 + 6 \bar{h}_{f,H_2O}^0 + 2 \bar{h}_{f,O_2}^0 + 37.6 \bar{h}_{f,N_2}^0 + (5 \bar{C}_{p,CO_2} + 6 \bar{C}_{p,H_2O} + 2 \bar{C}_{p,O_2} + 37.6 \bar{C}_{p,N_2}) (T_{ad} - 298)$$

$$H_R = \bar{h}_{f,C_5H_{12}}^0 + 10 \bar{h}_{f,O_2}^0 + 37.6 \bar{h}_{f,N_2}^0$$

But from 1st Law, We know that $H_p = H_R$

So we will take an example to estimate the adiabatic flame temperature of the product like that is C₅H₁₂ with 25% excess of air and both C₅H₁₂ and air enter the burner at 25°C. So same thing condition will be available that control volume system will be taking and then H_P is equal to H_R right and you can do this balance.

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Example: Estimate the adiabatic flame temperature of C₅H₁₂ with 25% excess air. Both C₅H₁₂ & air enter the burner at 25°C. Assume Complete combustion.

$\Delta KE = 0, \Delta PE = 0, Q = 0, \dot{W}_{sh} = 0$

1ST Law for CV becomes, $H_P = H_R$

$C_5H_{12} + 10(O_2 + 3.76 N_2) \Rightarrow 5 CO_2 + 6 H_2O + 2 O_2 + 37.6 N_2$

$$H_P = 5 \times \bar{h}_{f,CO_2}^0 + 6 \bar{h}_{f,H_2O}^0 + 2 \bar{h}_{f,O_2}^0 + 37.6 \bar{h}_{f,N_2}^0 + (5 \bar{C}_{P,CO_2} + 6 \bar{C}_{P,H_2O} + 2 \bar{C}_{P,O_2} + 37.6 \bar{C}_{P,N_2}) (T_{ad} - 298)$$

And if we look you know I can find outputs I can write down H_P is equal to 5 into of CO₂ + 6h F water and to HF oxygen and 37 points a of the nitrogen right and thesis your what you call heat of formation these are basically heat of formation you can get this these terms are heat of formation at standard state like estimate and whether these are your sensible enthalpy what we are assuming in this case you know the it disintegrated you know it day 2 minus T 298 Kelvin.

And we are saying that the Cavallies are not function of temperature in this case we are SME right therefore we are taking out and doing that and of course HR will be with the heat of formation you can say all those for the pentane and oxygen and nitrogen right and there is no sensible enthalpy here because it is at the ambient temperature to start with right so therefore there is no sensible enthalpy in this case sow know that HP is equal to HR and Weill just do that and when we will do this we will find out this is nothing but H R .

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$$\Delta H_R^0 = (5 \times \bar{h}_{f,CO_2}^0 + 6 \bar{h}_{f,H_2O}^0 - \bar{h}_{C_5H_{12}}^0)$$

$$= -(5 \bar{C}_{P,CO_2} + 6 \bar{C}_{P,H_2O} + 2 \bar{C}_{P,O_2} + 37.6 \bar{C}_{P,N_2}) (T_{ad} - 298)$$

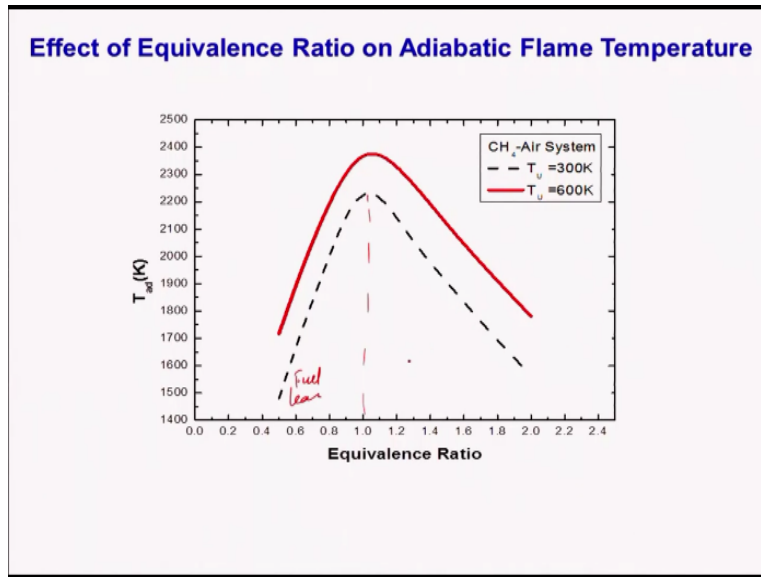
But, $5 \bar{h}_{f,CO_2}^0 + 6 \bar{h}_{f,H_2O}^0 - \bar{h}_{f,C_5H_{12}}^0 = \Delta H_R^0 = -3271.71$

Is equal to this portion right and this is nothing but your what you call and which is equal to the sensible enthalpy and this HR not is 327 1.71kilo joules right if you just do these values over here and put this average values of cps corresponding certain temperatures right these values are average values for example these are these average values of the co2 right this portion we have taken average values that will be given to you or it will have to find it out and then you will calculate T adiabatic is 18 52.3Kelvin keep in mind that if you are not taking proper values of CP then you won't get the you know proper adiabatic temperature.

You will be because that will be dictating the what temperature will be getting in your calculation right and keep in mind that here I mean we have used the control what you call

volume system right now if I say the control mass system how to you know calculate idiotic temperature that I am giving you as an assignment you do that what you will have to do there basically you'll have to say nah not the you know internal energy u of the product is equal to internal energy of the reactant that is all you will get okay and from that you will have to calculate what will be adiabatic temperature let me ask you another.

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Question which will be higher for the same system further let us say if I consider this print in aright whether the adiabatic temperature by using the control mass system will give me a higher a divot temperature or you know it will be lower as compared to the control volume system that i will leave with you and then we will then let us look at that what will happen two equivalents what you call ratios.

If you look at that it will be having peak temperature here at one at equivalency one this will be having peak temperature something 2250 kind of things and both the lean side this is your lean mixture side lean fuel inside right this is go em like it drops down and of course on the reefs side it drops down at lower slope this is well at each side equivalence is greater than one and as you increase this temperature inlet temperature to six hundred Kelvin the temperature also increases having similar features so if you look at like instead of you know.

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Adiabatic flame temperature of typical fuels at stoichiometric mixture

System	T_u (K)	P (MPa)	T_{ad} (K)
CH ₄ -air	300	0.1	2200
CH ₄ -air	300	2.0	2270
CH ₄ -air	600	2.0	2500
CH ₄ -O ₂	300	0.1	3030
C ₃ H ₈ -air	300	0.1	2278
H ₂ -air	300	0.1	2390
H ₂ -O ₂	300	0.1	3080
CO-air	300	0.1	2400

Methane air if we're reusing methane-oxygen if you look at there is an increase in temperature kind of things for the same pressure and same mixtures kind of things right that is an increase in temperature now if you look at like if I take hydrogen oxygen you know it is a very higher temperature right as compared to the hydrogen air right because the nitrogen is a diluent so therefore it is absorbing large amount of it and here the nitrogen or they are there for this bring higher.

So therefore the adiabatic temperature will be not only depending on the fuel air ratio. It will be depending on the inlet temperature it will be depending on the also the weather it is air or oxidized oxygen or any other things you know that way you will be so basically we will stop over we have learned how to apply the first law of thermodynamics to take care of reacting systems you know and we have also seen.

How to calculate adiabatic temperature and it will be also devotes temperature will be dependent on the pressure if you look at the one like you know pressure is point s and when it will increase per methane air two then the temperature has increased from 2202 2274 the same stoichiometric mixture so it is also dependent on the pressure right so will stop over here and we will in the next lecture discuss about basically the second.

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