Applied Thermodynamics for Engineers
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Lecture – 36
Thermodynamic Analysis of Reacting Systems

Morning friends, welcome to the last lecture of our course where we are going to discuss about the second part of chemical reactions. In the previous lecture you are introduced to the concept of stoichiometric or theoretical mixtures. And you have also learnt that using the information about the composition of the fuel and also the information about the amount of air supplied how can you frame the chemical reaction equations associated with any combustion. Of course, I must clarify that whatever we are discussing in this week they are equally applicable to any kind of chemical reaction, but primarily we are discussing everything in the context of combustion that is a kind of exothermic chemical reaction between fuel and oxidizer, because that is the primary mode of heat generation that we generally associated with any kind of heat engines.

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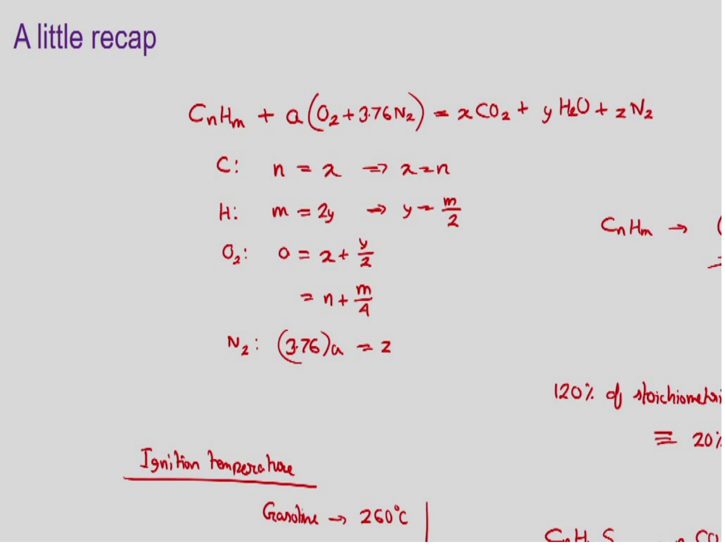

A little recap

$$C_nH_m + a(O_2+3.76N_2) = xCO_2 + yH_2O + zN_2$$

C: $n = x \Rightarrow x = n$

H: $m = 2y \Rightarrow y = \frac{m}{2}$

O_2: $a = x + \frac{y}{2}$

$= n + \frac{m}{4}$

N_2: $(3.76)a = z$

$C_nH_m \rightarrow$

120% of stoichiometri

$\equiv$ 20

Ignition temperature

Gasoline → 260°C

Now just to have a quick recap of whatever we have done in the previous lecture. There we have seen that if we are given with fuel having composition of say C_nH_m then we now know how to estimate the quantity of theoretical air requirement. Because we know that if *a* is the quantity or number of moles of oxygen required to have complete combustion of 1 mole of this particular fuel, then we can write this to be equal to, actually do not use square bracket commonly.

$$C_mH_n + a\ (O_2 + 3.76\ N_2) \rightarrow CO_2 + H_2O + N_2$$

We are a talking about stoichiometric mixture only. And now we have to perform chemical balance, If I assume say x CO_2 moles of x moles of CO_2 and y moles of H_2O and z moles of nitrogen appears in a product.

$$C_mH_n + a\ (O_2 + 3.76\ N_2) \rightarrow x\ CO_2 + y\ H_2O + z\ N_2$$

Then we can easily perform a chemical balance of the number of atoms. Like,

$$C:\ n = x \rightarrow x = n$$

$$H:\ m = 2y \rightarrow y = m/2$$

and for the one we interested in that is oxygen. Let us do in a different way, let us use O_2 for balance, instead of O. Like in the previous lecture we have done one balance similarly using N_2, let us do in terms of O_2. Then we have:

$$O_2:\quad a = x + y/2 = n + m/4$$

and nitrogen we can easily get now because if we write N_2 does not participate in any kind of reaction. So,

$$N_2 : (3.76)\ a = z$$

so z we can calculate. But the important thing that is coming out of this is that for a fuel having composition of C_nH_m we shall be requiring ($n + m/4$) moles of O_2/mole of fuel to have complete combustion. I should this is the minimum quantity of oxygen required to have complete combustion. Accordingly, you can easily calculate the mass of stoichiometric air-fuel mixture requirement or rather mass of stoichiometric air requirement and also the stoichiometric air-fuel ratio. And we have also been introduced to equivalent ratio from which we know that the information available to us about the amount of oxygen supply and the air supplied how can a couple that to the excess of air or deficiency of air. Commonly we know that quite often the quantity of air supplied is expressed as a percentage of this a. Something like say, if information is given that,

$$120\ \%\ \text{of stoichiometric air} \equiv 20\ \%\ \text{of excess air}$$

That is as per this calculation the number of moles of oxygen supplied is 1.2 times of this a or every mole of fuel. Let us quickly see another numerical application or numerical example for this particular concept, like the one that we have done in the previous lecture in quite similarly doing another one.

But, last one that I would like to mention in this case is that it is not that once it take this air in contact with each other, with correct proportion or even excess quantity of you are going to have combustion. Because every fuel will start participating in the combustion reaction only after it receives or it is taken to certain level of temperature. That particular temperature we generally called ignition temperature and it is a property of the fuel.

Or, I should say is a characteristic of the fuel that you are using. Some volatile type of fuels like say gasoline has quite less ignition temperature something of the order of about 260 ^{0}C. Whereas carbon have something in the range of 400 ^{0}C whatever I am writing a this is all approximate numbers; you can say ±10 with this. For hydrogen, it is even higher. I cannot remember the exact value; it is something in the order of 580 ^{0}C something like this. The ignition temperature for each fuel to have combustion, we have to take the fuel air mixture at least to this temperature or even preferably to higher temperature and then only we can have the combustion reaction been initiated. And also, the process that you have seen to calculate the quantity of stoichiometric oxygen requirement is $n + m/4$.

That is, assuming that only carbon and hydrogen are present in the fuel, but it is also possible that sulphur can be present in the fuel than that also we need to take into consideration. Like suppose if we have a fuel C_nH_m and sulphur say of T quantity, $C_nH_mS_t$ then corresponding you know that we shall be having on the product side i.e, right hand side as follows:

$$C_nH_mS_t \rightarrow n\ CO_2 + (m/2)\ H_2O + t\ SO_2$$

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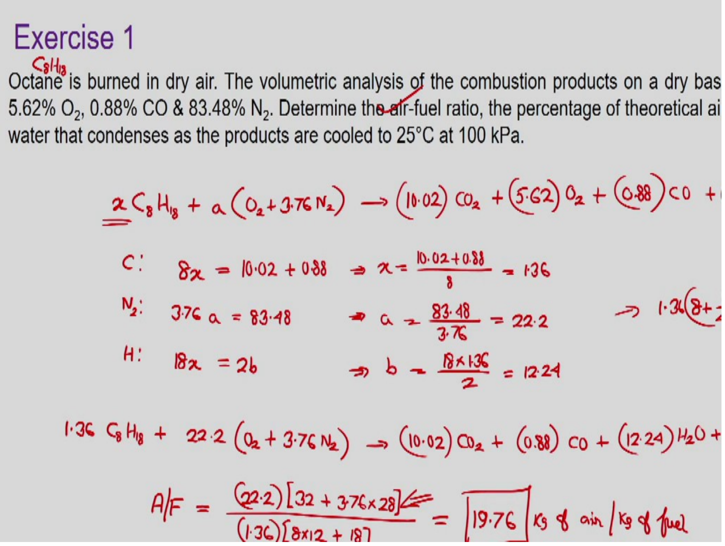

Exercise 1

C_8H_{18}

Octane is burned in dry air. The volumetric analysis of the combustion products on a dry bas
5.62% O_2, 0.88% CO & 83.48% N_2. Determine the air-fuel ratio, the percentage of theoretical ai
water that condenses as the products are cooled to 25°C at 100 kPa.

$$\underline{\underline{x}}\, C_8H_{18} + a(O_2 + 3.76 N_2) \rightarrow (10.02)\, CO_2 + (5.62)\, O_2 + (0.88)\, CO +$$

$$C: \quad 8x = 10.02 + 0.88 \Rightarrow x = \frac{10.02 + 0.88}{8} = 1.36$$

$$N_2: \quad 3.76\, a = 83.48 \Rightarrow a = \frac{83.48}{3.76} = 22.2 \qquad \rightarrow 1.36(8+$$

$$H: \quad 18x = 2b \Rightarrow b = \frac{18 \times 1.36}{2} = 12.24$$

$$1.36\, C_8H_{18} + 22.2\,(O_2 + 3.76 N_2) \rightarrow (10.02)\, CO_2 + (0.88)\, CO + (12.24)\, H_2O +$$

$$A/F = \frac{(22.2)[32 + 3.76 \times 28]}{(1.36)[8 \times 12 + 18]} = \boxed{19.76}\ \text{kg of air / kg of fuel}$$

So, accordingly the number of moles of oxygen required for a mole of fuel should be equal to:

$$\rightarrow \left(n + \frac{m}{4} + t\right)$$

this t is the additional contribution coming because of the sulphur present. So, this is the exercise that I am going to talk about now. Here the fuel is octane, it is burnt in dry air. Dry air means the air contains only oxygen and nitrogen and we are not having any kind of water vapour present in the air. Like in the previous example that we did yesterday, there it was moist air. So initially calculated neglecting the portion of moist air and then we added that to get the final composition on the product.

Here it is dry air so we do not have to bother about that. The volumetric analysis of the combustion products on the dry basis gives certain fractions of carbon dioxide, oxygen, carbon monoxide and nitrogen. Now here is another important term, the analysis of the combustion product has been done on dry basis. Dry basis means on the product, look at that the composition that is given there is no water vapour present.

But we know that the fuel is octane and octane is C_8H_{18} and this hydrogen has to get combusted must have been converted to H_2O and therefore water vapour should have been there in the product. But we have done the analysis of combustion of the product on dry basis. That means the water vapour part has been removed while performing this analysis. So, the proportion of combustion part that is given that is excluding the water vapour, but still there in the product. So, we have to determine the air-fuel ratio, the percentage of theoretical air used and the amount of water that contains as the product cools to a certain temperature. We will be coming back to the third one later on. Let us try to do the analysis first. Here let us first try to write the chemical reaction for this. So, we have C_8H_{18} as the octane and nothing is mentioned about the proportion of fuel and here used in this.

So, let us assume, we are using extraction of are x moles of fuel plus a mole of air or a mole of oxygen rather, so 3.76 time a nitrogen also comes into picture and because of the reaction then we have as the product 10.02 moles of CO_2 so the we are taking this x because nothing is mentioned about the analysis or rather it is never mentioned in the problem statement that the volumetric analysis of the combustion products has been done for per mole of fuel. So, it is wrong to have x = 1, we have to consider x as some number. So here we are having 10.02

moles of CO2 plus 5.62 moles of oxygen plus 0.88 moles of CO plus 83.48 moles of nitrogen plus some quantity of water vapour which has not been considered while performing this dry analysis or rather the analysis of the commercial product on dry basis.

$$x\,C_8H_{18} + a\,(O_2 + 3.76\,N_2) \rightarrow (10.02)\,CO_2 + (5.62)\,O_2 + (0.88)\,CO + (83.48)\,N_2 + (b)H_2O$$

So, we can easily perform this analysis to get the values of these unknowns. We have unknowns as *x, a* and *b.* So from where we can start? We can easily start with the carbon, so

$$C\text{: } 8x = 10.02 + 0.88$$

$$\rightarrow x = \frac{10.02 + 0.88}{8} = 1.36$$

So, the analysis that is given that actually corresponds to 1.36 moles of fuel. Now we can perform for hydrogen, but let us do it for nitrogen. It is not that you always have to go by this route: carbon, hydrogen, oxygen, nitrogen, rather just from observation we can see that in this particular case, nitrogen is more or less independent I should say more or less redundant in most of the cases. But here it can give the state for the solution because if you balance the N_2 we can see that,

$$N_2\text{: } 3.76\,a = 83.48$$

$$\rightarrow a = \frac{83.48}{3.76} = 22.2$$

so this much of moles of oxygen has been supplied. And only unknown information is now *b*. To do that let us balance hydrogen. So,

$$H\text{: } 18\,x = 2\,b$$

$$\rightarrow b = \frac{18\ \times 1.36}{2} = 12.24$$

if required you can perform the oxygen balance to check whether that is satisfying it or not, but in this case, it is not required. So, the analysis done, let us write the equation again the complete equation now becomes:

$$1.36\,C_8H_{18} = 22.2\,(O_2 + 3.76\,N_2)$$

$$\rightarrow (10.02)\,CO_2 + (0.88)\,CO + (12.24)\,H_2O + (5.62)\,O_2 + (83.48)\,N_2$$

It is interesting that the product we have both oxygen and carbon monoxide present, that indicates that you have supplied excess quantity of oxygen probably, but the carbon monoxide presence in the product side indicates that has been incomplete combustion or because of some incomplete or imperfect mixing maybe. What should be the stoichiometric quantity of air requirement in this case. How can you calculate that to calculate the stoichiometric quantity of air requirement?

We know that chemical composition of the fuel C_8H_{18}, so the number of moles of oxygen requirement will be equal to:

$$1.36\left(8+\frac{18}{4}\right)=1.36\ \times(8+4.5)=??$$

this much moles of oxygen will be required. I do not need to calculate this value. So, I am not putting the number you can calculate this you will find that this value 22.2 is much larger than this. So, we have definitely we have supplied excess air. Here now generally for combustion reaction we would like to express the chemical equation or the equation that I have every time a as per moles of fuel. So, we can also write this equation by dividing all these numbers by 1.36, but for calculation purpose that may not be necessary. So, the next part that we have is to calculate the air-fuel ratio. So, can you calculate the air-fuel ratio in this particular case? The air-fuel ratio, *A/F* or whatever would you like to write that represents the:

$$A/F=\frac{m_{air}}{m_{fuel}}=\frac{22.2[32+3.76\times 28]}{(1.36)[8\times 12+18]}=19.76\ kg\ of\ air/kg\ of\ fuel$$

This is the first answer that you are looking for the air-fuel ratio. Now we have to calculate the percentage of theoretical air used. To have the percentage of theoretical air used, we need to know the stoichiometric mixture or stoichiometric quantity of air requirement which we have written here.

So, the percentage of theoretical air, you can easily calculate. Percentage of theoretical air should be equal to:

$$\%\ of\ theoretical\ air=\frac{m_{air\ ,actu\ al}}{m_{air\ ,stoi}}$$

so if we divide both by the molecular weight of air, actually here we are always writing the molecular weight of air is a combination of nitrogen and oxygen, but sometimes the molecular weight of air is taken to be 29 or 28.9 as the molecular weight. So, in that case, the numerator of this particular calculation could have also done as:

$$(22.2)\ (4.76)\ (29)$$

Would have given more or less similar number. So instead of writing [32 + 3.76 × 20] we can also write 4.76 multiplied by 29, you are more or less likely to get similar values. So, if you calculate that way, then in this particular case you can easily say that the mass of air requirement in actual case. In actual combustion we are using 22.2 moles of air and mass will be, let us use the molecular weight of air. So, 22.2 moles of oxygen we are using, so corresponding mass of air in actual case will be equal to 4.76 multiplied by 29 and the theoretical case, what you are having? We had 1.36 times 12.5, first ratio we should get multiplied by 4 corresponding mass of air is 4.76 multiplied by 29 see it is only little issue of mole.

$$= \frac{(22.2)(4.76 \times 29)}{(1.36 \times 12.5)(4.76 \times 29)}$$

So, the molecular part actually cancels out. So, could have easily written just as:

$$= \frac{(22.2)}{(1.36 \times 12.5)} = 131\ \%$$

So, 31 %, excess air has been supplied for this particular combustion to happen. But still you are having carbon monoxide present in the product. And now the final thing that we have to calculate is the amount of what are the contents of the product to cool to 25 ^{0}C and 100 kPa.

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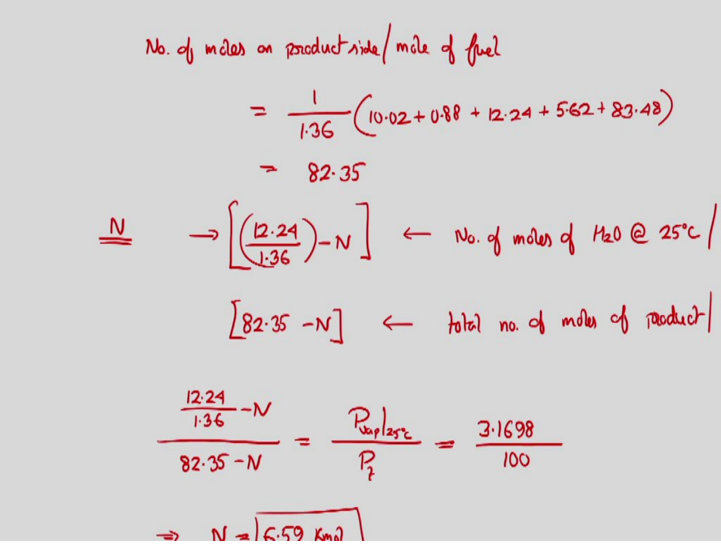

No. of moles on product side / mole of fuel

$$= \frac{1}{1.36}(10.02 + 0.88 + 12.24 + 5.62 + 83.48)$$

$$\Rightarrow 82.35$$

$$\underline{\underline{N}} \quad \rightarrow \left[\left(\frac{12.24}{1.36}\right) - N\right] \leftarrow \text{No. of moles of } H_2O \text{ @ } 25°C$$

$$[82.35 - N] \leftarrow \text{total no. of moles of product}$$

$$\frac{\frac{12.24}{1.36} - N}{82.35 - N} = \frac{P_{vap}|_{25°C}}{P_T} = \frac{3.1698}{100}$$

$$\Rightarrow N = \boxed{6.59\ Kmol}$$

Now for each mole of fuel that we have burnt, the total number of things that we have on the product side, what is the number of moles on product side per mole of fuel?

Number of moles on product side/mole of fuel

$$= \frac{1}{1.36}(10.02 + 0.88 + 12.24 + 5.62 + 83.48) = 82.35$$

So, this total approximately 82.35 number of moles are present on the products side for every mole of fuel participating in the combustion. Now the Dew point temperature of the product, if you assume that the Dew point temperature of the product is above 25 ^{0}C, then as we are cooling the product some part of water vapour will get condensed and only a lesser fraction. Like in this case, we are having 12.24 moles of H_2O present. Or, rather 12.24/1.36 number of moles of H_2O present on the product side for any mole of fuel. But as you are cooling it down and coming to 25 ^{0}C it will reduce to a lesser value while the other products such as carbon dioxide, carbon monoxide, oxygen and nitrogen will be present there. So, you have to calculate that, let us assume *N* moles of water vapour gets condensed as your cooling down to 25 ^{0}C, then once it reaches the 25 ^{0}C, then the number of moles of H_2O present in this composition is:

$$N \rightarrow \left[\left(\frac{12.24}{1.36}\right) - N\right]$$

For every mole of fuel this number of moles of water vapour will continue to be present in the product once you have cooled it down to the 25 ^{0}C value temperature. Then the total number of moles, So, this is the number of moles of H_2O at 25 ^{0}C / mole of fuel.

And total number of moles will be how much? Total number of moles will be:

$$[82.35 - N]$$

this is the total number of moles of product or on the product side/mole of fuel. So now we can easily calculate the partial pressure for this has to be as, we know that the final pressure of the mixture is 100 kPa. Then we can easily calculate the number of moles of water vapour present on the product at 25 ^{0}C. That is

$$\frac{\left(\frac{12.24}{1.36}\right) - N}{82.35 - N} = \frac{P_{vap\,|25^0C}}{P_t}$$

where

$P_{vap|25^0C}$ is the vapour pressure at 25 ^{0}C

P_t is the total pressure of the mixture

And from the chart we can find that, you can use the steam table or property table, we will find the 25 ^{0}C as I just noted the value. The vapour pressure of water is 3.1698 kPa and total pressure is given to 100 kPa, i.e.,

$$\frac{P_{vap\,|25^0C}}{P_t} = \frac{3.1698}{100}$$

So, we can easily solve this one to get:

$$N = 6.59 \text{ kmol}$$

So you can find that, for every kmol of octane bound for combustion, 6.5 moles of water vapour will get separated out once we are cooling the product down to 25 ^{0}C. So that way you can use the concept of chemical combustion or combustion reaction and the stoichiometric mixture or stoichiometric air to perform any simple combustion reaction.

Just look at this problem statement again, we are given only with two information one is the chemical composition of the fuel which is octane C_8H_{18} and volumetric analysis of the product on dry basis. But still so many information we are able to calculate. We can easily calculate the equivalence ratio the stoichiometric mass of air which we have used as a part of calculation and several other things also.

Now, this is an application of what we did in the previous lecture. Now today there are several other things also I have in to offer and let me go to quickly because I am in very short of time.

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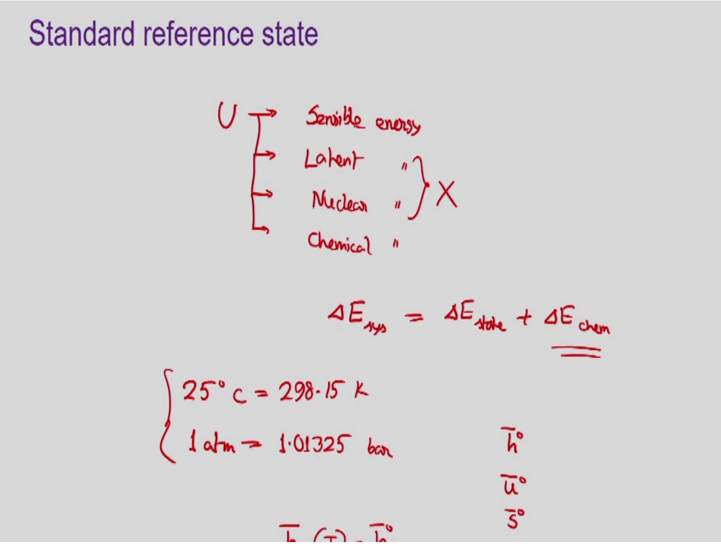

Standard reference state

$U \rightarrow$ Sensible energy

$\rightarrow$ Latent " $\}$ X

$\rightarrow$ Nuclear " $\}$ X

$\rightarrow$ Chemical "

$$\Delta E_{sys} = \Delta E_{state} + \underline{\underline{\Delta E_{chem}}}$$

$$\begin{cases} 25^\circ C = 298.15\ K \\ 1\ atm \rightarrow 1.01325\ bar \end{cases}$$

$\bar{h}^\circ$

$\bar{u}^\circ$

$\bar{s}^\circ$

$\bar{h}(T) - \bar{h}^\circ$

The first concept that I would like to introduce is the enthalpy of combustion, but before the right into the standard reference state. Now we know that how to identify the chemical reaction corresponding to a combustion, once we know the chemical combustion of fuel and some information about the amount of air supplied or maybe analysis of the combustion product. Now, we have to identify how much amount of energy that we are gaining from this combustion because that is ultimate objective. Ultimately, we want to have an exothermic chemical reaction simply to utilise the energy released during the combustion process. And so that is something that you are going to do in the subsequent slides. But before that I have to define one standard reference states. Remember that in thermodynamics like what you have done in your basic thermodynamics or all the previous 11 modules of this course, we always talked about the change in properties. We never bothered about absolute magnitude of properties like internal energy, enthalpy and entropy you always have to use the change in the property values. But that is not the case in case of combustion because assume combustion, we are not talking about the same spaces rather we talk about different spaces. And therefore, whenever we are going for combustion calculation or combustion related thermodynamic analysis.

We have to identify your standard reference state and this standard reference date can be defined such a way that for a given particular state point we know the values of properties for whatever chemical spaces that we are dealing with. You know that internal energy for any substance can as several components likes say if U represent the internal energy, we can have a sensible part of that as I am mentioned yesterday also, sensible energy is there is phase change involved. We can have latent part of that, then in certain cases we can have nuclear energy as well. And the final form is the chemical part. For nuclear case the internal energy that we are talking about that is associated with the orientation of the subatomic particle inside the atom unless you are breaking the atoms, we do not need to bother about that.

But in case of chemical part, we are talking about the orientation of atoms inside the molecules. During the chemical reaction as the orientation of atoms gets altered so the chemical part is important. So, for the moment let us neglect the latent and nuclear parts, we have only the sensible energy part which is associated with the temperature change and the chemical part which is associated with the atomic orientation inside molecule.

Then the change in energy of a system during any chemical reaction ΔE system can be given as the sum of ΔE associated with the state point which is the conventional that you are always using and the energy that has been released because of the chemical reaction are changing the orientation of atoms inside the molecules.

$$\Delta E_{sys} = \Delta E_{state} + \Delta E_{chem}$$

So, the second part we are not bothered about so far. It is the first one that you have dealt through are entire analysis. Now, the first part is associated with the change in energy because of the change in state. Now if the change the state of the product and of the reactant that remains to be same, then ΔE_{state} also will not come into picture. And then whatever change in energy that you have to talk about that is only the one associated with the chemical reactions.

And that is why the concept of standard reference state comes into play. Generally, for combustion calculation we consider 25 ^{0}C temperature and 1 atmospheric pressure, i.e., 1.01325 bar pressure as the standard atmospheric condition. So, 25 ^{0}C i.e., 298.15 K and 1 bar pressure or rather 1.01325 bar pressure is only considered as the standard reference point.

And to denote any property at the standard reference point or corresponding standard reference point, we use the superscript zero. Like if we are talking about the enthalpy corresponding this condition, we shall be putting h^{o}, if we are talking about internal energy we shall be writing u^{o}, if you are writing for entropy we shall be writing again s^{o}. These are the standard reference properties.

And in combustion calculation we generally use property values on molar basis and not mass basis. In all previous 11 weeks have always defined enthalpy or entropy on per unit mass basis, but here it is much easier to work on molar basis because it is the chemical reactions. We write chemical equations in molar basis. So, if we have to write in molar basis, then there is over bar coming to picture, these are properties, specific properties and are defined as per unit mole on molar bases and evaluated the standard reference state of 25 ^{0}C and 1 atmospheric pressure. They are represented as follows:

$$\bar{h}^{0}, \bar{u}^{0}, \bar{s}^{0}$$

And once we know the value of these at any condition you can easily calculate the properties. Like suppose we want to evaluate the property of something or the change in the value of enthalpy at a particular temperature that is given. Then we can easily calculate the value of the enthalpy at that temperature minus this *h^{0} over bar*.

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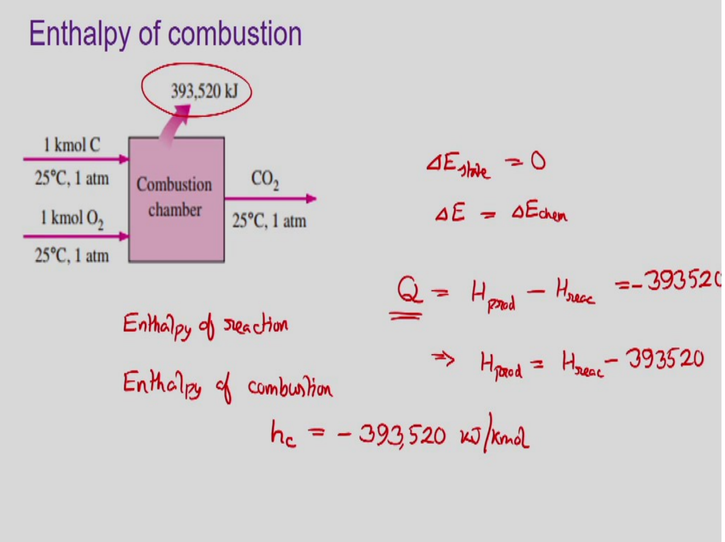

Enthalpy of combustion

$\Delta E_{state} = 0$

$\Delta E = \Delta E_{chem}$

$\underline{\underline{Q}} = H_{prod} - H_{reac} = -39352$

$\Rightarrow H_{prod} = H_{reac} - 393520$

Enthalpy of reaction

Enthalpy of combustion

$h_c = -393{,}520$ kJ/kmol

Now, we have the enthalpy of combustion. Let us talk about a simple chemical reaction. 1 kmol of carbon at the standard reference state is supplied to combustion chamber which is also receiving 1 kmol of oxygen again at the same state. And at the end of combustion, we are having carbon dioxide coming out of the chamber. It has also been reduced back to the end state. And as a result of the entire reaction we are having this much amount of energy being released from this combustion chamber. Now as this chemical reaction, for this chemical reaction both the reactants and products are all the same standard reference state. So, the ΔE_{state} has to be equal to zero in this case.

$$\Delta E_{state} = 0$$

So, the change in energy content is only because of this chemical part, that is because of the orientation of the carbon and oxygen atoms to form carbon dioxide. And now if we perform a simple first law balance, then the amount of energy released from this Q should be equal to the enthalpy on the product side minus enthalpy on the reactant side and Q in this case is found to be 393520 kJ.

$$Q = H_{prod} - H_{react} = 393520 \text{ kJ}$$

rather minus of this, because it supplied to the system is taken as positive. So this 393520 kJ is negative. That is, we can write as:

$$Q = H_{prod} - H_{react} = -393520 \text{ kJ}$$

That means

$$H_{prod} = H_{react} - 393520 \text{ kJ}$$

and this particular thing this Q is called the enthalpy of reaction and it can be associated to any chemical reaction process. When the enthalpy of reaction is negative, like in this case the enthalpy of the product is less than enthalpy of the reactants and therefore, the chemical reaction is going to be an exothermic one. Whereas in case of endothermic reaction energy will be absorbed by the combustion chamber so the enthalpy of reaction will be positive and the product is going to have enthalpy higher than the reactants.

So, I repeat for exothermic chemical reaction enthalpy of reaction is negative and the product is having lesser enthalpy compute the reactants. For endothermic chemical reaction enthalpy of reaction is positive and the product is going to have higher enthalpy compared to the reactants. Now when we are talking on the combustion reaction, we generally call this more commonly we call this enthalpy of combustion. There is no difference between the definition of these two quantities, but enthalpy of reaction is a more generalized term, enthalpy of combustion is associated with the combustion process.

So, the enthalpy of combustion for then h_c is for this carbon dioxide is going to be – 393,520 kJ, that is going to be the enthalpy of reaction rather per kilo mole the enthalpy of combustion is going to be this much for carbon dioxide.

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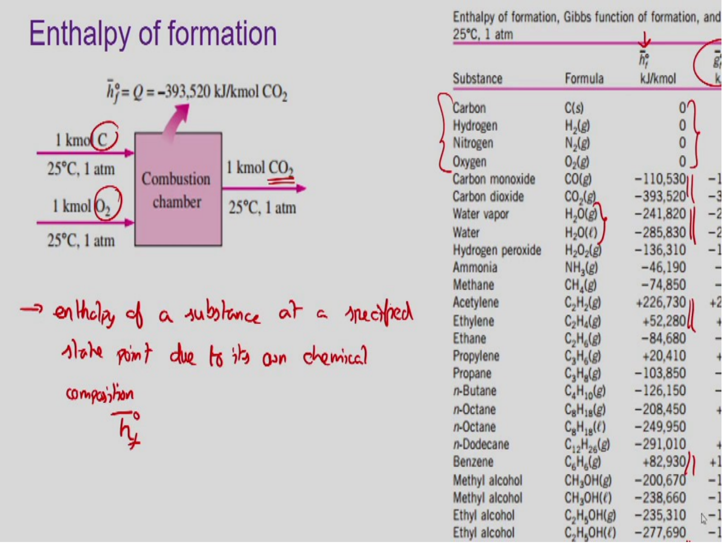

Enthalpy of formation

→ enthalpy of a substance at a specified state point due to its own chemical composition

$\bar{h}_f^\circ$

Enthalpy of formation, Gibbs function of formation, and
25°C, 1 atm

Substance	Formula	$\bar{h}_f^\circ$ kJ/kmol
Carbon	$C(s)$	0
Hydrogen	$H_2(g)$	0
Nitrogen	$N_2(g)$	0
Oxygen	$O_2(g)$	0
Carbon monoxide	$CO(g)$	−110,530
Carbon dioxide	$CO_2(g)$	−393,520
Water vapor	$H_2O(g)$	−241,820
Water	$H_2O(\ell)$	−285,830
Hydrogen peroxide	$H_2O_2(g)$	−136,310
Ammonia	$NH_3(g)$	−46,190
Methane	$CH_4(g)$	−74,850
Acetylene	$C_2H_2(g)$	+226,730
Ethylene	$C_2H_4(g)$	+52,280
Ethane	$C_2H_6(g)$	−84,680
Propylene	$C_3H_6(g)$	+20,410
Propane	$C_3H_8(g)$	−103,850
n-Butane	$C_4H_{10}(g)$	−126,150
n-Octane	$C_8H_{18}(g)$	−208,450
n-Octane	$C_8H_{18}(\ell)$	−249,950
n-Dodecane	$C_{12}H_{26}(g)$	−291,010
Benzene	$C_6H_6(g)$	+82,930
Methyl alcohol	$CH_3OH(g)$	−200,670
Methyl alcohol	$CH_3OH(\ell)$	−238,660
Ethyl alcohol	$C_2H_5OH(g)$	−235,310
Ethyl alcohol	$C_2H_5OH(\ell)$	−277,690

Now, there is another term let we use that is called the enthalpy of formation. The enthalpy of formation is obviously very useful for analyse the combustion process of fuels. However, there are so many different kinds of fuels or fuel mixtures that quite often it is useless. Like to calculate the enthalpy of combustion during the particular reaction, you need to know the enthalpy for all the reactants and the products.

And then only we can calculate the amount of heat released. Rather the concept of enthalpy of formation is more fundamental and is also much easier to make use of. Now, what is the enthalpy of formation then? Enthalpy of formation is that also, I should also mention that when we are talking about incomplete combustion then enthalpy of combustion is of no use. Because enthalpy of combustion is always associated with the complete combustion or stoichiometric chemical reaction.

But when you are having excess or when you have incomplete combustion, then the enthalpy of combustion is not usable. Then we go for this enthalpy of formation which is a more fundamental one. Enthalpy of formation can be viewed as the enthalpy of a substance at a specified state point due to it is own chemical composition. The enthalpy of formation of all elements are set to zero. Like carbon, oxygen, they all set to zero. But that is not true for products like this or compounds like this. They will be having certain value of enthalpy of formation, like the one shown here this same chemical reaction that we use your previous slide. 1 kmol of carbon and 1 kmol of oxygen coming to the combustion chamber at the standard condition and we are having 1 kmol of carbon dioxide coming out in the same condition. Then that amount of heat released is the enthalpy of formation.

Because that is the amount of energy required to form this 1 kmol of carbon dioxide at the standard reference state. And as shown here is a symbol h_f^0 *over bar* to denote this enthalpy of formation. Here the subscript *f* refers to formation *over bar* represents that it is a per mole quantity or per kmol quantity that this on defined on molar basis and that superscript zero represents that it has evaluated at the standard reference condition.

So, enthalpy of formation, quite similarly we can calculate for different kind of substances. Like I have a table shown here, there are several things given. This one we do not need to bother about for the moment or at least for this particular course. You make a note of this on or I should be coming back to this in the last slide. But here our interest is this one:

$$\overline{h_f}^0$$

You can see that for basic elements like carbon, hydrogen, nitrogen, and oxygen, enthalpy of formation is equal to zero, because for elements it is equal to zero. But for other substances it is having some value some cases negative and some case it is positive. Also, there are some interesting things to note that for water and water vapour there are two different values because under 1 atmospheric pressure at 25 ^{0}C, water generally remains only as a single-phase liquid.

But if you change the pressure then it is possible have water vapour under 25 ^{0}C and water as vapor state also at 25 ^{0}C. Now enthalpy generally is very weakly variant on pressure and accordingly we can define water vapour and water as two different stable state of the substance. This enthalpy of formation always corresponds to a stable state like here water vapour and water.

Both are considered to be stable state and the difference between their enthalpy of formation values, that is actually associated with, what it can be from, where the difference can come in? That is nothing but h_{fg}, the latent heat of vaporization. The solid substances like say carbon can have two stable state at this temperature: one is graphite and other is diamond. Then in that case it is defined in case of graphite.

And similarly, other substance we can see carbon monoxide and carbon dioxide. They have negative values; certain substances are positive values as well. Like benzene is one we have ethylene or acetylene in this case. Oxygen molecules, hydrogen molecules, nitrogen molecules they all can be formed through endothermic chemical reaction and so they are having positive values of enthalpy of formation.

The values of the enthalpy formation shown in this table make the combustion calculations very easy. Because as we have seen in the previous slides, we can easily calculate the enthalpy of a chemical spaces using the value with respect your standard reference state and the standard reference state now, we know the values in terms of the enthalpy of formation.

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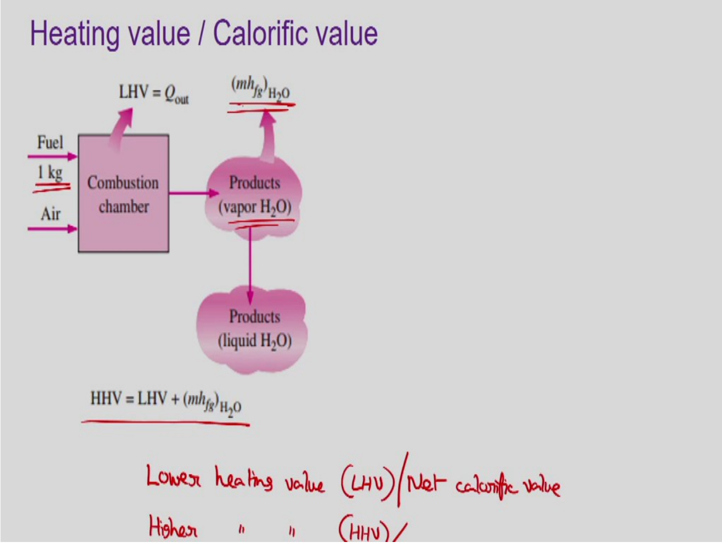

Heating value / Calorific value

$HHV = LHV + (mh_{fg})_{H_2O}$

Lower heating value (LHV)/Net calorific value

Higher " " (HHV)/

The final one that I would like to incorporate that is the heating value or calorific value, the name probably you have already heard, it refers to the amount of energy that we can get by complete combustion of 1 kg of fuel. The previous two definitions are on molar basis this is on mass basis. If we burn 1 kg of fuel and we have complete combustion, then amount of energy that is released is called the heating value or calorific value.

But there are two definitions: one is *LHV*, that is the lower heating value, other is the higher heating value which is *HHV*. Now the difference between them is in terms of the water vapour that can present in the product. Now the heat that is released immediately on combustion that we call the lower heating value and then once we allowed the water vapour present in the product to condense back to the liquid water., then some more energy will be released which will be equal to the corresponding mass of water vapour multiplied by the corresponding latent heat. So there we have:

$$HHV = LHV + (mh_{fg})_{H2O}$$

The lower heating value is quite often also called the net calorific value. The higher heating value is called the gross calorific value. We always want to use fuels having higher calorific value simply because we are going to have more amount of energy released from a given quantity of fuel or a given mass of fuel.

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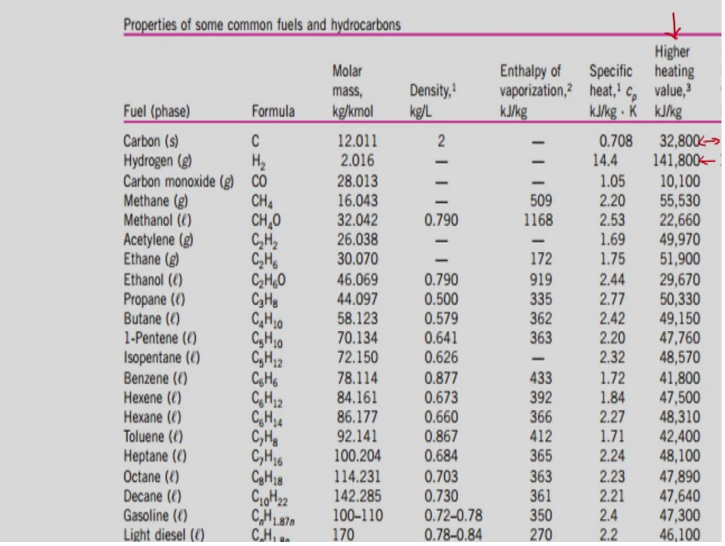

Properties of some common fuels and hydrocarbons

Fuel (phase)	Formula	Molar mass, kg/kmol	Density,[1] kg/L	Enthalpy of vaporization,[2] kJ/kg	Specific heat,[1] c_p kJ/kg · K	Higher heating value,[3] kJ/kg
Carbon (s)	C	12.011	2	—	0.708	32,800
Hydrogen (g)	H_2	2.016	—	—	14.4	141,800
Carbon monoxide (g)	CO	28.013	—	—	1.05	10,100
Methane (g)	CH_4	16.043	—	509	2.20	55,530
Methanol (ℓ)	CH_4O	32.042	0.790	1168	2.53	22,660
Acetylene (g)	C_2H_2	26.038	—	—	1.69	49,970
Ethane (g)	C_2H_6	30.070	—	172	1.75	51,900
Ethanol (ℓ)	C_2H_6O	46.069	0.790	919	2.44	29,670
Propane (ℓ)	C_3H_8	44.097	0.500	335	2.77	50,330
Butane (ℓ)	C_4H_{10}	58.123	0.579	362	2.42	49,150
1-Pentene (ℓ)	C_5H_{10}	70.134	0.641	363	2.20	47,760
Isopentane (ℓ)	C_5H_{12}	72.150	0.626	—	2.32	48,570
Benzene (ℓ)	C_6H_6	78.114	0.877	433	1.72	41,800
Hexene (ℓ)	C_6H_{12}	84.161	0.673	392	1.84	47,500
Hexane (ℓ)	C_6H_{14}	86.177	0.660	366	2.27	48,310
Toluene (ℓ)	C_7H_8	92.141	0.867	412	1.71	42,400
Heptane (ℓ)	C_7H_{16}	100.204	0.684	365	2.24	48,100
Octane (ℓ)	C_8H_{18}	114.231	0.703	363	2.23	47,890
Decane (ℓ)	$C_{10}H_{22}$	142.285	0.730	361	2.21	47,640
Gasoline (ℓ)	$C_nH_{1.87n}$	100–110	0.72–0.78	350	2.4	47,300
Light diesel (ℓ)	$C_nH_{1.8n}$	170	0.78–0.84	270	2.2	46,100

This is a table shown again, I am taking all the tables from the book of Cengel and Boles and the for some common fuels and hydrocarbons in the enthalpy of vaporization and higher or lower heat values are given. Just look at these two columns higher and lower heating values. So, like for carbon you can see both values are equal because for combustion of carbon, the product is carbon dioxide and there is no water vapour present in the product. So, we cannot get any additional amount of energy released by combustion. But for hydrogen we have H_2O produced and once that get condensed, we have this additional amount of energy that is released. Accordingly, we are having the values for several other products. For natural gases it is quite high in the range of 50,000 which is quite high value of higher heating value. Hydrogen has extremely high heating value, but again hydrogen has its own problems as a fuel, but is very prospective as a fuel.

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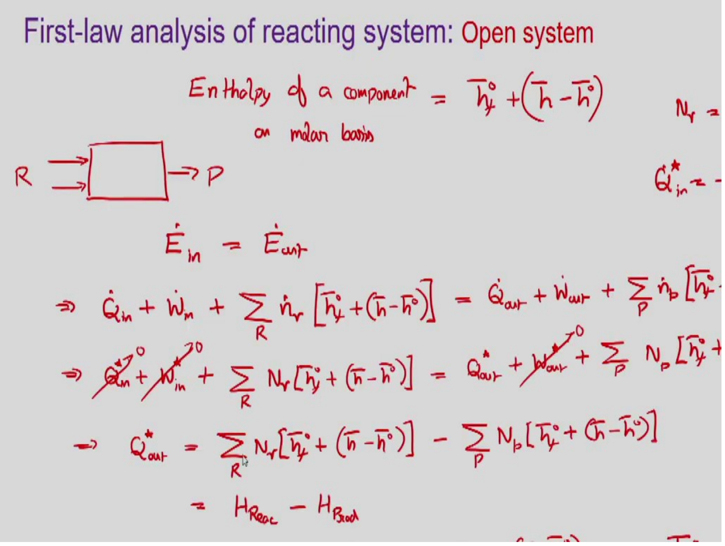

First-law analysis of reacting system: Open system

Enthalpy of a component on molar basis $= \bar{h}_f^\circ + (\bar{h} - \bar{h}^\circ)$

$N_r =$

R → → P

$\dot{Q}^*_{in} = -$

$\dot{E}_{in} = \dot{E}_{out}$

$\Rightarrow \dot{Q}_{in} + \dot{W}_{in} + \sum_R \dot{n}_r \left[\bar{h}_f^\circ + (\bar{h} - \bar{h}^\circ)\right] = \dot{Q}_{out} + \dot{W}_{out} + \sum_P \dot{n}_p \left[\bar{h}_f^\circ\right.$

$\Rightarrow \cancelto{0}{Q^*_{in}} + \cancelto{0}{W^*_{in}} + \sum_R N_r \left[\bar{h}_f^\circ + (\bar{h} - \bar{h}^\circ)\right] = Q^*_{out} + \cancelto{0}{W^*_{out}} + \sum_P N_p \left[\bar{h}_f^\circ +\right.$

$\Rightarrow Q^*_{out} = \sum_R N_r \left[\bar{h}_f^\circ + (\bar{h} - \bar{h}^\circ)\right] - \sum_P N_p \left[\bar{h}_f^\circ + (\bar{h} - \bar{h}^\circ)\right]$

$= H_{Reac} - H_{Prod}$

Now, let us quickly try to do the thermodynamic analysis of a reacting system, first for an open system and then for a closed system. So, for an open system, enthalpy of a component on molar basis if you like to define, then that can always be represented as the enthalpy of formation plus the change enthalpy corresponding to the change in state from the standard reference state.

Enthalpy of a component on molar basis

$$= \overline{h_f}^{0} + (\bar{h} - \bar{h}^{0})$$

Here the concept of enthalpy of formation comes into play. The first part, that is this one this is giving with the enthalpy of formation at the standard reference state and also the amount of energy required to form this one. Like elements which are having stable atoms like oxygen, hydrogen and carbon, for them this is value is 0, for others like for carbon dioxide we have seen the values. That is the enthalpy of formation, the amount of energy required to form this, to make this atom happen. And then we have this second part, which talks about the change in its enthalpy once you are taking it away from the standard reference to some other state. So, this is the enthalpy of a component on molar basis at any given condition. So, let us say this is a chemical reaction that we are talking about. We are having reactants coming in, we are having product going out and we would like to write the energy balance for this. Assuming that there is no heat loss from the system, then we can easily write that, assuming steady flow condition rate of energy coming in should be equal to the rate of energy going out.

$$\dot{E}_{in} = \dot{E}_{out}$$

So, we can write the first law of thermodynamics that is,

$$\dot{Q}_{in} + \dot{W}_{out} + \sum_{R} \dot{n}_r \left[\overline{h_f}^{0} + (\bar{h} - \bar{h}^{0})\right] = \dot{Q}_{out} + \dot{W}_{out} + \sum_{P} \dot{n}_p \left[\overline{h_f}^{0} + (\bar{h} - \bar{h}^{0})\right]$$

And now if we divide this entire equation by the number of by per mol of fuel or fuel flow rate. Let us say, $n_{dot\ f}$ refers to the molar rate of supply of fuel that is per unit time, the number of fuel moles that is kmols supplied to the combustion chamber. If we divide the entire equation by this, then this become:

$$Q_{in}{}^{*} + W_{in}{}^{*} + \sum_{R} N_r \left[\overline{h_f}^{0} + (\bar{h} - \bar{h}^{0})\right] = Q_{out}{}^{*} + W_{out}{}^{*} + \sum_{P} N_p \left[\overline{h_f}^{0} + (\bar{h} - \bar{h}^{0})\right]$$

where

$Q_{in}*$ *star* actually is equal to the total amount of heat supplied by the molar flow rate of the fuel here are let is exclusively,

$$Q_{in}{}^{*} = \frac{\dot{Q}_{in}}{\dot{n}_{fuel}}$$

Here *Nr* refers to the molar flow rate of any particular reactant divided by molar flow rate of the fuel; it is mathematically expressed as:

$$N_r = \frac{\dot{n}_r}{\dot{n}_{fuel}}$$

here in the similar way *Np* refers to the molar flow rate of a particular product divided by the molar flow rate of the fuel. So here we have divided this entire equation by the molar flow rate of the fuel because that is quite convenient in most of the cases. Now, we can write this equation in several ways, but generally in combustion analysis we do not bother about the work transfer does not involved in the process involved work transfer. And we generally also do not have any kind of heat input so we interested primarily at the amount of heat output that we are getting.

So, $Q_{out}*$ can then be written as:

$$Q_{out}{}^{*} = \sum_{R} N_r \left[\overline{h_f}^{0} + (\bar{h} - \bar{h}^{0})\right] - \sum_{P} N_p \left[\overline{h_f}^{0} + (\bar{h} - \bar{h}^{0})\right]$$

or maybe you can write this one as:

$$= H_{Reac} - H_{Prod}$$

where

H_{Reac} is the total enthalpy for the reactant

H_{Prod} is the total enthalpy for the product. This also we can write but generally not required for most of the cases. If we have the enthalpy of combustion available during a particular case then we can also simplify this equation. If the enthalpy of combustion is available. Then we can also write as:

$$Q_{out}{}^{*} = \overline{h_c}^{0} + \sum_R N_r \left(\bar{h} - \bar{h}^{0} \right) - \sum_P N_p \left(\bar{h} - \bar{h}^{0} \right)$$

This is of course once we have the enthalpy of combustion available to us with a minus sign on this. Because this enthalpy of combustion under standard reference state can easily be calculated using the enthalpy of formation. We have seen earlier right? When the enthalpy of formation is known, then from there we can easily calculate the enthalpy of combustion for this.

Like in this particular case,

$$\overline{h_c}^{0} = \sum_P N_p \overline{h_f}^{0} - \sum_R N_r \overline{h_f}^{0}$$

which is the enthalpy of combustion. If that is known we can easily go by this particular route. So for one final time combustion chamber does not involve any kind of heat input and any kind of work interaction, then this is the way we can easily calculate. We just need to know the molar composition. So, if N_r and N_p are commonly known, then if we write any standard chemical reaction as you are always writing earlier.

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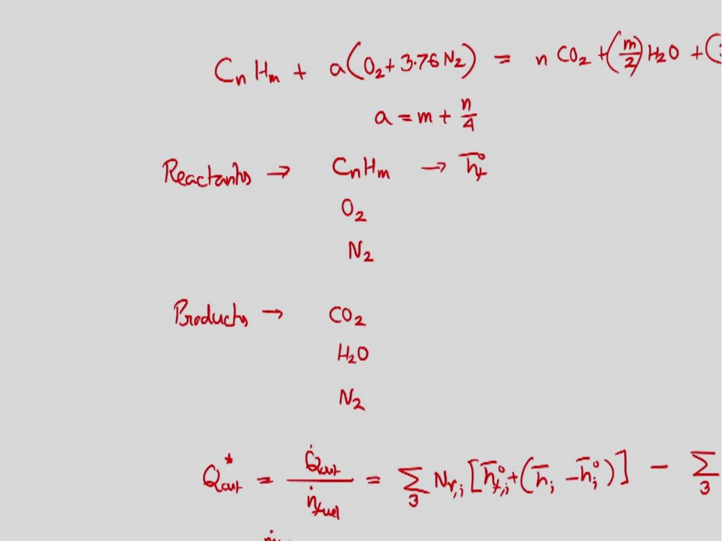

$$C_nH_m + a(O_2 + 3.76N_2) = n\,CO_2 + \left(\frac{m}{2}\right)H_2O +$$

$$a = m + \frac{n}{4}$$

Reactants → C_nH_m → $\bar{h}_f^{\circ}$

O_2

N_2

Products → CO_2

H_2O

N_2

$$Q_{out}^{*} = \frac{\dot{Q}_{out}}{\dot{n}_{fuel}} = \sum_{3} N_{r,i}\left[\bar{h}_{f,i}^{\circ} + \left(\bar{h}_i - \bar{h}_i^{\circ}\right)\right] - \sum_{3}$$

So, say,

$$C_nH_m + a(O_2 + 3.76N_2) = n\,CO_2 + \frac{m}{2}H_2O + (3.76a)N_2$$

we know that in this case,

$$a = m + \frac{n}{4}$$

Now, how many reactants you have? In this case you have three reactants: we have hydrocarbon, we have oxygen and we have nitrogen.

And we have on the product side, as this is a complete reaction. We have CO_2, we have H_2O and we have nitrogen. So, you can get the value for each of them. For each of them you can get the enthalpy of formation for this. And also their enthalpy values, the sensible enthalpy values can be obtained from the table, assuming each of them as an ideal gas or some relevant assumptions and accordingly, you can easily calculate then whatever we wrote earlier this equation you can easily make use of to get the total heat output. Where

$$Q_{out}{}^{*} = \frac{rate\ of\ heat\ release}{molar\ fuel\ rate} = \frac{\dot{Q}_{out}}{\dot{n}_{fuel}}$$

is going to be equal to just look at what we wrote earlier from this particular thing so here on the reactants side we are having three elements. So,

$$= \sum_{3} N_{r,i}\left[\overline{h_{f,i}}^{\,0} + (\bar{h}_i - \bar{h}_i^{\,0})\right] - \sum_{3} N_{p,j}\left[\overline{h_{f,j}}^{\,0} + (\bar{h}_j - \bar{h}_j^{\,0})\right]$$

This we can calculate and if you know the rate at which fuel is being supplied to the combustion chamber then you can easily calculate,

$$\dot{n}_{fuel} = \frac{\dot{m}_{fuel}}{M_{fuel}}$$

from there we can calculate this molar flow rate of the fuel itself. So, once we multiply this entire equation using suitable parameter you are going to get the total heat output from this combustion chamber in per unit mass basis or flow rate of mass. I am going to read quickly to this, but I hope I am able to reach all of you. This just a sample to show how to do such combustion calculations.

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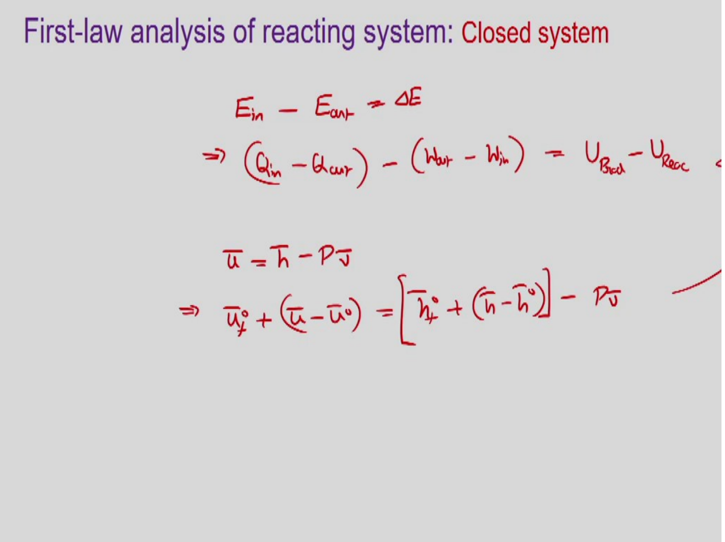

First-law analysis of reacting system: Closed system

$$E_{in} - E_{out} = \Delta E$$

$$\Rightarrow (Q_{in} - Q_{out}) - (W_{out} - W_{in}) = U_{Prod} - U_{Reac}$$

$$\bar{u} = \bar{h} - P\bar{v}$$

$$\Rightarrow \bar{u}_f^{\circ} + (\bar{u} - \bar{u}^{\circ}) = \left[\bar{h}_f^{\circ} + (\bar{h} - \bar{h}^{\circ})\right] - P\bar{v}$$

I shall be showing one numerical example quickly. And then if you are talking about a closed system, for closed system, we generally do not talk at rate basis rather we take in quantity basis. So, in that case,

$$E_{in} - E_{out} = \Delta E$$

that is, energy in minus energy out is equal to change in the total energy content of the system. Accordingly, we can write,

$$(Q_{in} - Q_{out}) - (W_{out} - W_{in}) = U_{Prod} - U_{Reac}$$

because conventionally we take heat input as it is positive and work done by the system is positive, to be equal to rate of change of, neglecting any changes in potential and kinetic energies is going to be internal for the product (U_{Prod}) minus internal energy for the reactants (U_{Reac}). And the internal energy can be calculated, if calculating U we know that as per the definition it can be written as:

$$\bar{u} = \bar{h} - P\bar{v}$$

Pressure is an intensive property but h and v here are represented on mole basis.

Now, you can have similar representation of like similar to enthalpy of formation, we can define an internal energy for formation, as the equation below:

$$\left[\overline{u_f}^{0} + (\bar{u} - \bar{u}^{0})\right] = \left[\overline{h_f}^{0} + (\bar{h} - \bar{h}^{0})\right] - P\bar{v}$$

so, from there we can easily take this into this equation and solve for closed systems as well.

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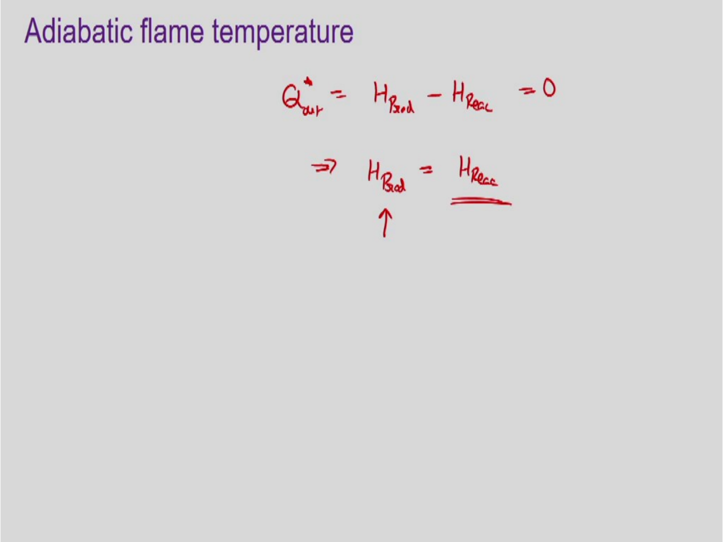

Adiabatic flame temperature

$$Q^{*}_{out} = H_{Prod} - H_{Reac} = 0$$

$$\Rightarrow \underset{\uparrow}{H_{Prod}} = \underline{\underline{H_{Reac}}}$$

Now, one final term that I would like to define is adiabatic flame temperature. What do you mean by adiabatic flame temperature? Adiabatic flame temperature refers to the maximum temperature which can be reached by the combustion products. Now during the combustion reaction, the energy is going to get lost to the surrounding or I should say not lost, energy will be going to the round stream application.

If we make the combustion chamber perfectly insulated so that no heat is able to come out of the combustion chamber, then your Q_{dot} is also 0. Like in the previous case we have written that

$$Q_{out}{}^{*} = H_{Prod} - H_{Reac}$$

Now if the combustion is insulated this is equal to zero, that means

$$H_{Prod} = H_{Reac}$$

In that case the temperature of the product, will be reaching the maximum temperature in that case that temperature is called the adiabatic flame temperature. So when we perform the combustion equation is perfectly insulated chamber we stop any kind of heat leakage or heat loss. Then the combustion product will be available to, is the maximum temperature and maximum temperature is defined as the adiabatic flame temperature.

It since quite straight forward the calculation procedure, for practically it is not. Because while we can easily calculate the enthalpy of the reactant, we cannot directly calculate enthalpy of the product, because that itself is a function of this temperature. So generally, we have to go for some kind of iterative procedure. We guess a temperature for the product calculate H_{Prod} and compare that with the H_{Reac}.

And depending upon how much difference is that we modify our guessed temperature and try to get a better solution. Some kind of iterative computational algorithms are generally followed to get these values. Those who of you are those of you who are interested in numerical simulation or computer simulations this will be really very good exercise for you to do. You can pick up any standard chemical reaction, like the one that we are showing earlier and you can perform the chemical analyse for this. Now, I would like to quickly solve one problem to show the first balance for a reacting system. Liquid propane enters a combustion chamber at a given temperature and mass flow rate it is given as 0.05 kg/min.

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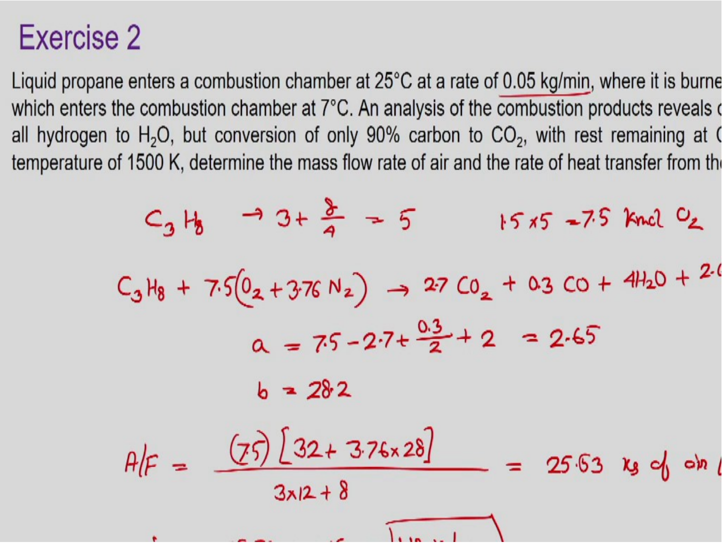

Exercise 2

Liquid propane enters a combustion chamber at 25°C at a rate of 0.05 kg/min, where it is burne
which enters the combustion chamber at 7°C. An analysis of the combustion products reveals c
all hydrogen to H_2O, but conversion of only 90% carbon to CO_2, with rest remaining at C
temperature of 1500 K, determine the mass flow rate of air and the rate of heat transfer from th

$$C_3H_8 \rightarrow 3 + \frac{8}{4} = 5 \qquad 1.5 \times 5 = 7.5 \text{ Kmol } O_2$$

$$C_3H_8 + 7.5(O_2 + 3.76 N_2) \rightarrow 2.7 CO_2 + 0.3 CO + 4H_2O + 2.$$

$$a = 7.5 - 2.7 + \frac{0.3}{2} + 2 = 2.65$$

$$b = 28.2$$

$$A/F = \frac{(7.5)[32 + 3.76 \times 28]}{3 \times 12 + 8} = 25.63 \text{ kg of air}$$

It is burned with 50% excess air which enters the combustion chamber at 7 ^{0}C. So, combustion product analysis has been done. It is shown that complete conversion of all hydrogen to H_2O, but combustion of only 90 % of carbon to CO_2 with rest remaining at CO. Taking a gas exit temperature of 1500 K, we have to define the mass flow rate of air and the rate of heat transfer from the combustor.

So, let us first try to calculate the stoichiometric quantity of air requirement in this case. So, we have the fuel is C_3H_8, then the minimum number of oxygen molecules required is:

$$C_3H_8 \quad \rightarrow 3+\frac{8}{4}=5$$

So, let us write the chemical reaction. It is 50 percent excess air so for theoretical case or stoichiometric equivalent reaction we need to have 5 moles of oxygen.

In this case we shall be requiring 1.5 times of 5 that is 7.5 kilo moles of oxygen is required. So, let us write the chemical reaction:

$$C_3H_8+7.5(O_2+3.76N_2)=2.7\,CO_2+0.3\,CO+4H_2O+aO_2+bN_2$$

Now, had it been complete combustion it would have had $3CO_2$. Here it is mentioned that only 90 % of carbon gets converted to CO_2. So, 90 % of 3 that is 2.7 kilo moles of CO_2 is getting, rest this 0.3 remains as CO. Hydrogen has been completely converted to H_2O. So, we shall be having in this case as $4H_2O$ plus some say *a* quantity of oxygen measurement and *b* quantity of nitrogen.

So, we can easily perform the calculation, then in this case

$$a=7.5-2.7+\frac{0.3}{2}+2=2.65$$

And accordingly,

$$b=28.2$$

So, we can now put the values of a and b in the chemical reaction equation. And it is written as follows:

$$C_3H_8+7.5(O_2+3.76N_2)=2.7\,CO_2+0.3\,CO+4H_2O+2.65O_2+(28.2)N_2$$

Now the first part of calculation has to calculate the mass rate of air. We can do it very easily. Let us first calculate the air-fuel ratio. Air-fuel ratio in this case is going to be 7.5 kmol of air has been used, so it is:

$$A/_F=\frac{7.5\,[32+3.76\times 28]}{[3\times 12+8]}=25.53\,kg\ of\ air/kg\ of\ fuel$$

Now fuel flow rate is given. So, accordingly,

$$\dot{m}_{air}=25.53\ \times 0.05=1.18\,kg/min$$

the first part is solved. Now we calculate the rate of heat transfer, we have to do the first level.

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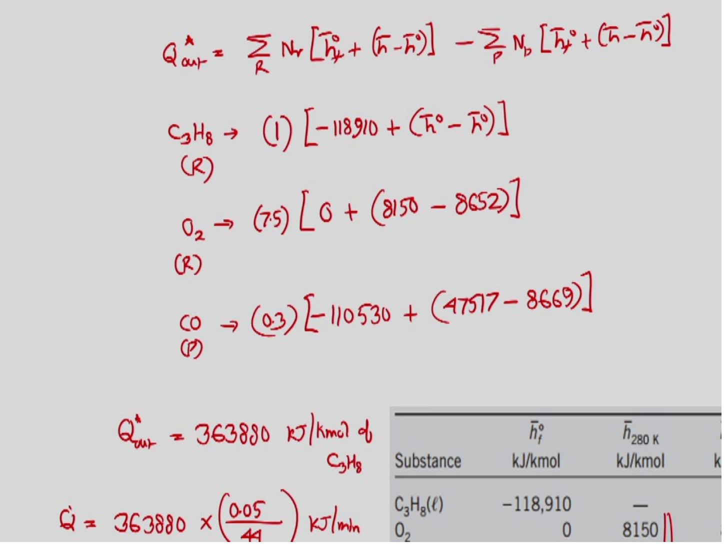

$$\dot{Q}^*_{out} = \sum_R N_r [\bar{h}_f^\circ + (\bar{h} - \bar{h}^\circ)] - \sum_P N_p [\bar{h}_f^\circ + (\bar{h} - \bar{h}^\circ)]$$

$$\underset{(R)}{C_3H_8} \rightarrow (1) [-118910 + (\bar{h}^\circ - \bar{h}^\circ)]$$

$$\underset{(R)}{O_2} \rightarrow (7.5) [0 + (8150 - 8652)]$$

$$\underset{(P)}{CO} \rightarrow (0.3) [-110530 + (47517 - 8669)]$$

$$\dot{Q}^*_{out} = 363880 \text{ kJ/kmol of } C_3H_8$$

$$\dot{Q} = 363880 \times \left(\frac{0.05}{44}\right) \text{ kJ/min}$$

Substance	$\bar{h}_f^\circ$ kJ/kmol	$\bar{h}_{280\text{ K}}$ kJ/kmol
$C_3H_8(\ell)$	−118,910	—
O_2	0	8150

For this let us make use of this table. Here the enthalpy of formation is given for all the components. Air is been supplied at 7 ^{0}C to K, so *h* $_{bar\ for\ air}$ is given at 280 K, *h* $_{bar}$ at 298 K, which is actually our *h* $_{bar\ dot}$ that is given for all the components. And at 1500 K is the final temperature, so *h* $_{bar}$ at 1500 K is also given. Methane is supplied at 25 ^{0}C only, so for methane we need not bother about this value, enthalpy of formation is available. So we can easily perform the analysis. Then as per our notation,

$$Q_{out}{}^* = \sum_R N_r \left[\overline{h_f}^0 + (\bar{h} - \bar{h}^0)\right] - \sum_P N_p \left[\overline{h_f}^0 + (\bar{h} - \bar{h}^0)\right]$$

So, we have to put all these values to get, I am just showing you some numbers. Let us say if you want to do the calculation say for the fuel C_3H_8 which will be coming on the reactant side. It is one of the reactants so far which we know that we are having total 1 kmol, so, number is 1. It is given $h_{f\ not\ bar}$ to be − 118910 plus it is being supplied at 25 ^{0}C only. So being supplied, *h bar*, this two are getting cancelled in this case because it is being supplied at 25 ^{0}C only.

$$C_3H_{8(R)} \quad \rightarrow (1)[-118910 + (\bar{h}^0 - \bar{h}^0)]$$

If you want to do the same calculation say for oxygen, which is again another reactant, now for oxygen, we are having 7.5 kmols. So, 7.5 kmols, we have, enthalpy of formation for oxygen is equal to 0. Oxygen is been supplied at 7 ^{0}C at 280 K. So, we have 8150 minus 8652 for oxygen.

$$O_{3(R)} \quad \rightarrow (7.5)[0 + (8150 - 8652)]$$

If you want to do for any of the products let us pick up the product of carbon monoxide which is 0.3 moles. Carbon monoxide which is appearing on product side, it is having 0.3 moles, it has its enthalpy of formation for carbon monoxide as minus 110530 plus carbon monoxide appears in the product which is at 1500 K. SO, to take this value which is 47517 minus is corresponding enthalpy at standard reference states is 8669.

$$CO_{(R)} \quad \rightarrow (0.3)[-1105300 + (47517 - 8669)]$$

So, this way you can calculate for any of the components that we are looking for. And finally the values of:

$$Q_{out}{}^{*} = 363880\ kJ/kmol\ of\ C_3H_8$$

Remember the entire calculation has been done for 1 kmol of fuel. So, if we want to calculate *Q dot out*. We have to multiply this 363880 to the molar flow arte. And mass fluoride it is given as 0.05 kg/min, so the molar flow rate it is going to be:

$$\dot{Q} = 363880 \times \left(\frac{0.05}{44}\right) kJ/min$$

where 44 is the molecular weight

So final number is going to be coming as:

$$= 6.89 \text{ kW}$$

This way using the information all the constituents and the corresponding states, we can calculate the total amount of energy released during combustion chamber.

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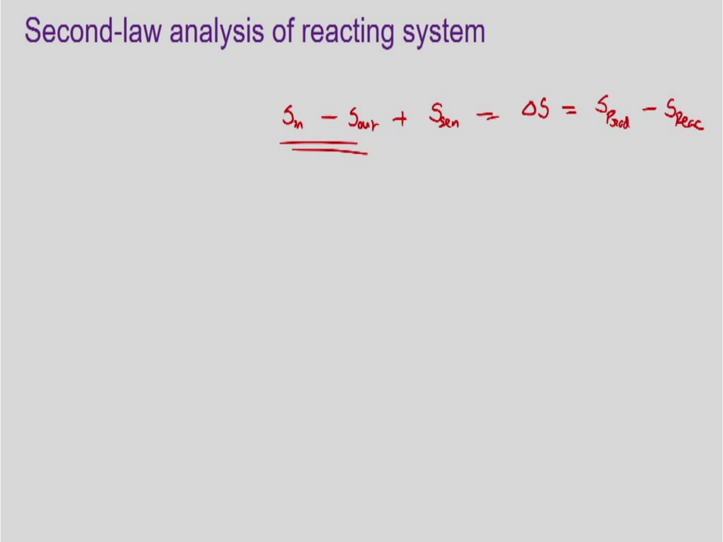

Second-law analysis of reacting system

$$\underline{\underline{S_{in} - S_{out}}} + S_{gen} = \Delta S = S_{Prod} - S_{Reac}$$

And very quickly to transfer upon the second law it is we have never done second law analysis for any of the cases. But here it is important because here the second law this calculation requires a concept of the third law of thermodynamics. Because we know that for performing the second law base calculation unit know the entropy. And now for any system though if you want to perform in energy balance,

$$S_{in} - S_{out} + S_{gen} = \Delta S$$

While these quantities can easily be calculated using the concepts of heat transfer and corresponding temperature, but to calculate the enthalpy of the reactant and the product for this ΔS corresponds to:

$$\Delta S = S_{Prod} - S_{Reac}$$

We need to set up a common base. Again, we need a standard reference condition for which the third law of thermodynamics comes into play. The third law, I think I have mentioned that earlier but just to repeat it. Third law of thermodynamics says that the entropy of a pure crystalline substance at absolute zero temperature is equal to zero. That sets up a base for calculating the absolute entropy of any substance. Remember in all the non-reacting thermodynamic systems, we can always calculate with the entropy change. So, we do not need the value of absolute entropy, we can always take entropy with respect to any particular level. But here as we are talking about different substances quite similar to the enthalpy based analysis we need to know the absolute entropy value and therefore the third law is important. I do not want to go any further on this because that will take me to more complicated constants like the Gibbs function etc. which are beyond the scope of this course.

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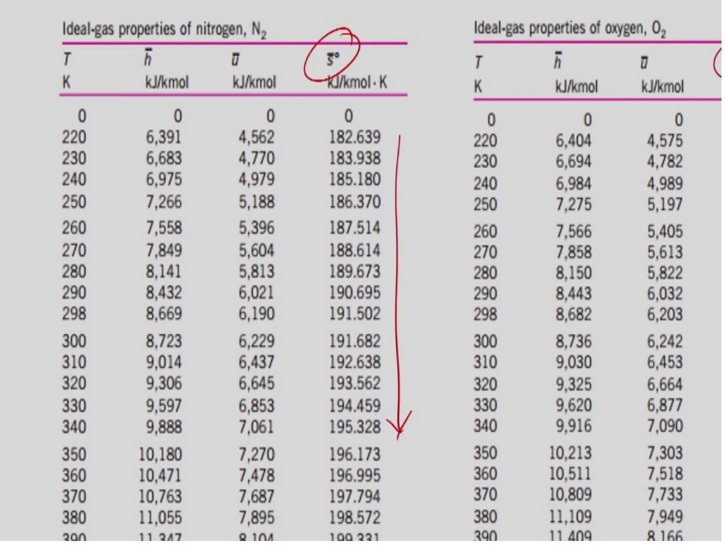

Ideal-gas properties of nitrogen, N_2

T K	$\bar{h}$ kJ/kmol	$\bar{u}$ kJ/kmol	$\bar{s}^\circ$ kJ/kmol · K
0	0	0	0
220	6,391	4,562	182.639
230	6,683	4,770	183.938
240	6,975	4,979	185.180
250	7,266	5,188	186.370
260	7,558	5,396	187.514
270	7,849	5,604	188.614
280	8,141	5,813	189.673
290	8,432	6,021	190.695
298	8,669	6,190	191.502
300	8,723	6,229	191.682
310	9,014	6,437	192.638
320	9,306	6,645	193.562
330	9,597	6,853	194.459
340	9,888	7,061	195.328
350	10,180	7,270	196.173
360	10,471	7,478	196.995
370	10,763	7,687	197.794
380	11,055	7,895	198.572
390	11,347	8,104	199.331

Ideal-gas properties of oxygen, O_2

T K	$\bar{h}$ kJ/kmol	$\bar{u}$ kJ/kmol
0	0	0
220	6,404	4,575
230	6,694	4,782
240	6,984	4,989
250	7,275	5,197
260	7,566	5,405
270	7,858	5,613
280	8,150	5,822
290	8,443	6,032
298	8,682	6,203
300	8,736	6,242
310	9,030	6,453
320	9,325	6,664
330	9,620	6,877
340	9,916	7,090
350	10,213	7,303
360	10,511	7,518
370	10,809	7,733
380	11,109	7,949
390	11,409	8,166

Just before stopping I would like to show one table where we can get the absolute entropy values for some common substances, these are available in standard books. These are the *S not bar* and also I referred to one of the tables earlier where the enthalpy of formation was given. there the third column give this absolute entropy per unit mole or per unit kilo mole for common substances. It varies with temperature as you can see it is continuously increasing as we are going to higher temperature.

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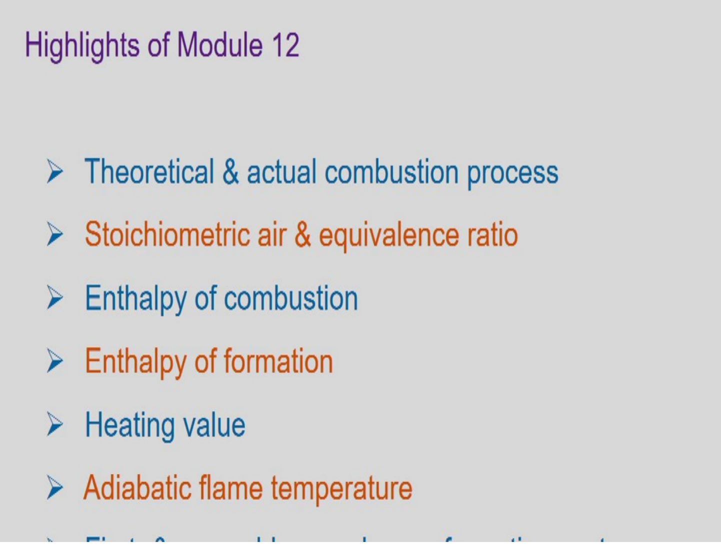

Highlights of Module 12

- Theoretical & actual combustion process
- Stoichiometric air & equivalence ratio
- Enthalpy of combustion
- Enthalpy of formation
- Heating value
- Adiabatic flame temperature

So, in this module 12, we have talked about the theoretical and actual combustion process. I introduced you to the concept of stoichiometric mixture, stoichiometric air and equivalence ratio, which can also be expressed in terms of excess of air or deficiency of air. Then today you are introduced to the concept of enthalpy of combustion and more fundamental concept of enthalpy of formation.

Then we talked about the higher and lower heating values and the concept of adiabatic flame temperature is the maximum possible temperature if substance or rather the combustion products can reach. It is actually very important term from design point of view because the metallurgical limits always has to be adhered with and so your combustion chamber design should be such that it is able to sustain up to the adiabatic flame temperature.

Practical cases of course temperature will be much lower because of incomplete combustion and dissociation reaction and also by supplying excess air, we can lower the temperature because additional quantity of air left after combustion can provide a bit of cooling effect by absorbing energy from this. And finally I have shown a brief way of performing the first law analysis of the system and just touched upon the second law analysis.

So, that take me to the end of the module number 12 and also to the end of this course. I hope I have been able to reach you by all the concepts that I have discussed. I am continuously getting your feedback. And if you have any query, please write keep on writing back to me and it is a really happy association for 12 weeks and I hope we shall be able to meet in some other course very soon and if you have any queries even beyond this course also keep on writing to me on my personal email ids, which have definitely all of you must be having by now. So, hopefully I shall be able to meet you sometime again, discussing sometime again. And with this I am signing off for one final time on this particular course. Thank you very much.