Advanced Thermodynamics and Combustion
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Module - 05
Combustion and Thermochemistry
Lecture - 20
Conservation of Energy for Reacting System

Dear learners, greetings from IIT Guwahati; we are in the MOOCs course Advanced Thermodynamics and Combustions, module 5 that is Combustion and Thermochemistry.

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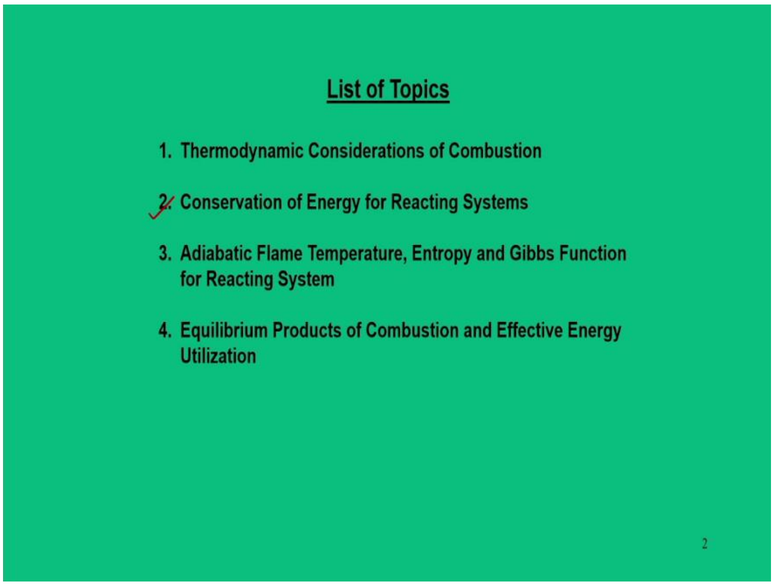

List of Topics

1. Thermodynamic Considerations of Combustion
2. Conservation of Energy for Reacting Systems
3. Adiabatic Flame Temperature, Entropy and Gibbs Function for Reacting System
4. Equilibrium Products of Combustion and Effective Energy Utilization

So, in this module we are going to cover 4 lectures; now, today we are going to discuss about the second one that is conservation of energy for reacting systems. Prior to these lectures, in our last class we discussed basic considerations combustion fundamentals with respect to thermodynamic view point.

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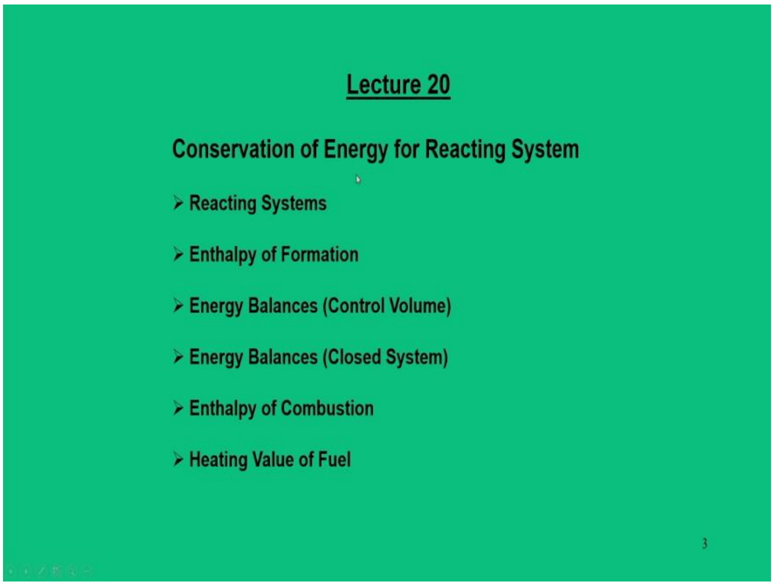

Lecture 20

Conservation of Energy for Reacting System

- Reacting Systems
- Enthalpy of Formation
- Energy Balances (Control Volume)
- Energy Balances (Closed System)
- Enthalpy of Combustion
- Heating Value of Fuel

Today we will see that how energy balance equations can be applied for a reacting systems. Now, with this what are the learning components we are going to gain is that, we will discuss about some basic introduction to a reacting systems. Then we will touch upon the enthalpy of formations, energy balance for reacting systems for control volume and for closed systems.

Then you will introduce the terms like which were commonly used in the combustion process that is enthalpy of combustions and heating value of the fuel. So, let us start our lecture number 20 that is conservation of energy for reacting systems.

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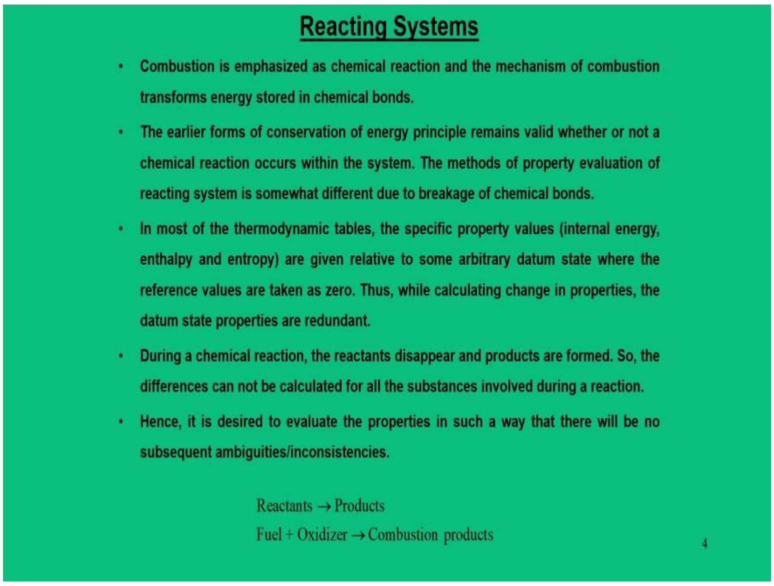

Reacting Systems

- Combustion is emphasized as chemical reaction and the mechanism of combustion transforms energy stored in chemical bonds.
- The earlier forms of conservation of energy principle remains valid whether or not a chemical reaction occurs within the system. The methods of property evaluation of reacting system is somewhat different due to breakage of chemical bonds.
- In most of the thermodynamic tables, the specific property values (internal energy, enthalpy and entropy) are given relative to some arbitrary datum state where the reference values are taken as zero. Thus, while calculating change in properties, the datum state properties are redundant.
- During a chemical reaction, the reactants disappear and products are formed. So, the differences can not be calculated for all the substances involved during a reaction.
- Hence, it is desired to evaluate the properties in such a way that there will be no subsequent ambiguities/inconsistencies.

$$\text{Reactants} \rightarrow \text{Products}$$
$$\text{Fuel} + \text{Oxidizer} \rightarrow \text{Combustion products}$$

So, just to give the introduction to reacting system, we all know that the combustion process is nothing but a chemical reactions, and through this mechanism the energy stored in the chemical bonds is utilized for some other purposes. Now, prior to this when we look at this energy balance equations, we assume that there is no reactions taking place during this thermodynamic process.

So, the earlier forms of conservation principle which was used without chemical reactions; now, we are going to say that similar principle also can be utilized for reacting systems as well. But if that has to be utilized then what are the points that needs to be remembered. So, we will revisit the basic thermodynamic energy principles from first law, second law and entropy analysis, all those things will study for the reacting system as well.

Now, when you deal with the earlier version of thermodynamic systems, we have introduced thermodynamic tables, specific property values in the form of equations for internal energy, enthalpy and entropy. And which are related to some arbitrary datum states; that means, when you evaluate the property values that was done with respect to some arbitrary datum value.

And the choice of arbitrary datum value are meaningless, because all our most of our analysis was concentrated towards the change; so, ultimately the effect of the datum numbers gets nullified. For example, when you calculate the internal energy change when a system goes from state 1 to state 2; so, the internal change is $U_2 - U_1$. So, while calculating $U_2 - U_1$ we are really do not bother what is the absolute value of U_1 as well as U_2.

So, it means that while calculating change in the properties datum state properties are redundant. But this is a very vital point during a chemical reactions, because during a chemical reactions the reactant vanish and new products are formed. So, this is the important aspects that we cannot calculate the difference, just by the change and second thing the temperatures during this process also changes.

So, these two things is very critical for analysis of reacting systems. So, it is desired to evaluate the properties in such a way that there will not be any subsequent ambiguity and inconsistencies. Means, reference state must be taken into account and it cannot be any arbitrary state, it has to be fixed arbitrary states.

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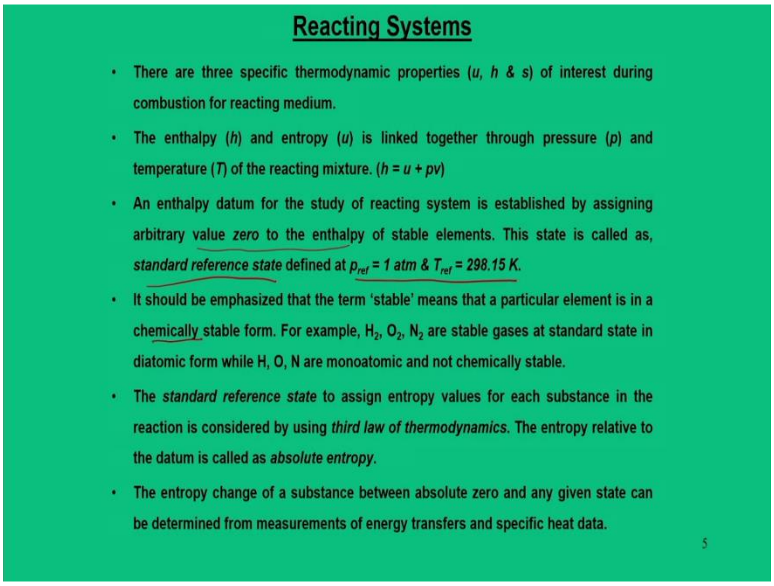

Reacting Systems

- There are three specific thermodynamic properties (u, h & s) of interest during combustion for reacting medium.
- The enthalpy (h) and entropy (u) is linked together through pressure (p) and temperature (T) of the reacting mixture. ($h = u + pv$)
- An enthalpy datum for the study of reacting system is established by assigning arbitrary value *zero* to the enthalpy of stable elements. This state is called as, *standard reference state* defined at $p_{ref} = 1$ atm & $T_{ref} = 298.15$ K.
- It should be emphasized that the term 'stable' means that a particular element is in a chemically stable form. For example, H_2, O_2, N_2 are stable gases at standard state in diatomic form while H, O, N are monoatomic and not chemically stable.
- The *standard reference state* to assign entropy values for each substance in the reaction is considered by using *third law of thermodynamics*. The entropy relative to the datum is called as *absolute entropy*.
- The entropy change of a substance between absolute zero and any given state can be determined from measurements of energy transfers and specific heat data.

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Now, how do you do that? For example, in a reacting systems we are mainly bothered three important properties; like, internal energy, enthalpy, and entropy. And of course, if you know pressure and volume, then one of the information either internal energy or enthalpy is sufficient to calculate one of them.

And because in a chemical reactions, the reactants and products; they will have multiple number of species, components, and the reactants vanish, products are formed. And when the products are formed it is formed at some temperatures. But what we need to find out that we need to define a state which we called as standard reference state and this is considered at atmospheric pressure and atmospheric temperature that is 1 atmosphere and 298.15 K.

So, this is given as a arbitrary reference zero values, what does this means? That means, at this reference states the components are stable, when the components are stable means they are stable in chemical form. For example, hydrogen, oxygen, nitrogen they are stable gases under atmospheric conditions. But hydrogen atom, oxygen atom, they are mono atomic in nature, but they are not chemically stable. When the component is stable you can assign this arbitrary zero value of enthalpy, internal energy; so, this is about enthalpy and internal energy treatment.

Now, at this same situations when you deal with entropy; so, entropy concept comes from the second law. And the second law also says that there is a temperature scale kelvin scale and the lowest temperature that we can achieve is 0 K. And at that point of time the third law of thermodynamics was defined, which says that entropy related to datum is absolute entropy and the absolute entropy values for all the substance at absolute zero temperature is 0.

So, this concept was introduced; that means, while talking about reacting systems we need to discuss the absolute entropy for the components at which they are formed and by that things we are trying to assign the entropy values. So, down the line we will see how we were going to assign the values of internal energy, enthalpy, entropy for the reactants and products during a chemical reactions.

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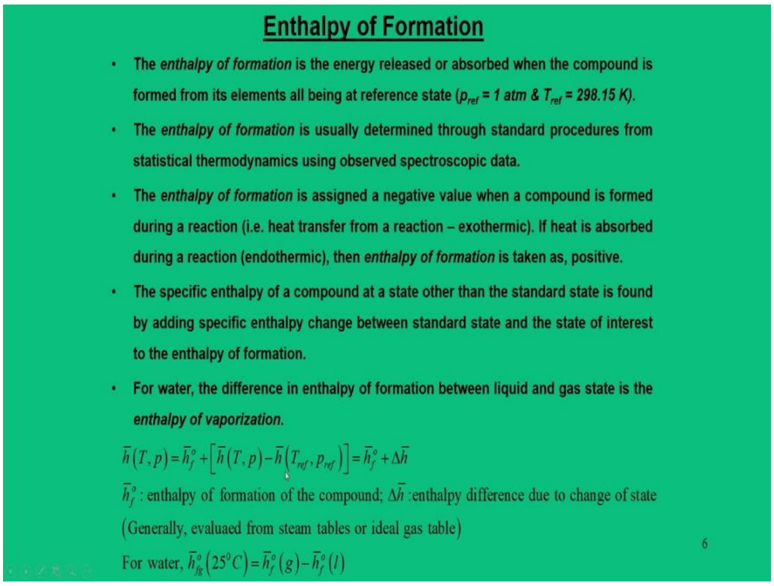

Enthalpy of Formation

- The *enthalpy of formation* is the energy released or absorbed when the compound is formed from its elements all being at reference state (p_{ref} = *1 atm* & T_{ref} = *298.15 K)*.
- The *enthalpy of formation* is usually determined through standard procedures from statistical thermodynamics using observed spectroscopic data.
- The *enthalpy of formation* is assigned a negative value when a compound is formed during a reaction (i.e. heat transfer from a reaction – exothermic). If heat is absorbed during a reaction (endothermic), then *enthalpy of formation* is taken as, positive.
- The specific enthalpy of a compound at a state other than the standard state is found by adding specific enthalpy change between standard state and the state of interest to the enthalpy of formation.
- For water, the difference in enthalpy of formation between liquid and gas state is the *enthalpy of vaporization.*

$$\bar{h}(T,p)=\bar{h}_f^o+\left[\bar{h}(T,p)-\bar{h}\left(T_{ref},p_{ref}\right)\right]=\bar{h}_f^o+\Delta\bar{h}$$

$\bar{h}_f^o$: enthalpy of formation of the compound; $\Delta\bar{h}$:enthalpy difference due to change of state (Generally, evaluaed from steam tables or ideal gas table)

For water, $\bar{h}_{fg}^o\left(25^0C\right)=\bar{h}_f^o(g)-\bar{h}_f^o(l)$

Now, we are going to introduce a term what is called as enthalpy of formations. So, by definition enthalpy of formation is nothing but the energy released or absorbed, when a compound is formed from its elements all being at reference states. So, all the elements are in reference states and a new compound is formed, the amount of energy which is released or absorbed is called enthalpy of formations.

The enthalpy of formation is usually determined through standard procedures of statistical thermodynamics. Because it involves information about the molecular and atomic level, and also we require the spectroscopic data. But we are not dealing with the statistical thermodynamics and in our viewpoint, we look at this enthalpy of formation as a global phenomena and we will assign it as a negative value when a compound is formed.

So, by default enthalpy formation is negative, when a compound is formed; when a compound is form means heat transfer from the reaction. So, heat transfer from the reaction; that means, heat is transferred from the reaction and it is exothermic in nature. Now, during a chemical reactions if heat is absorbed; so, we call this as endothermic reactions, we assign this enthalpy formation as a positive number. Then once we have this enthalpy of formation, then specific enthalpy of the compound at any other state can be found out with respect to standard state.

For example, let us consider this parameter molar enthalpy at particular temperature and pressure for any component which is being formed. So, we start with $\bar{h}_f^o$; that means, molar specific enthalpy of formation of that compound, if we say carbon dioxide is going to be formed and you want to find out its enthalpy of formation at a given temperature and pressure.

Then what you are going to find out the enthalpy of formation of CO_2 at reference state, and reference state means one atmosphere and 298.15K plus the $\Delta\bar{h}$ that is nothing but the difference of molar enthalpy at given pressure and temperature and the molar enthalpy at reference temperature and pressure.

So, these data values are typically available in any thermodynamic books if you look for, and towards the end of these thermodynamics books you have lot of tables figures and we can get all this information. So, basically this information is required from the data table, enthalpy of formation and enthalpy at reference pressure and temperatures.

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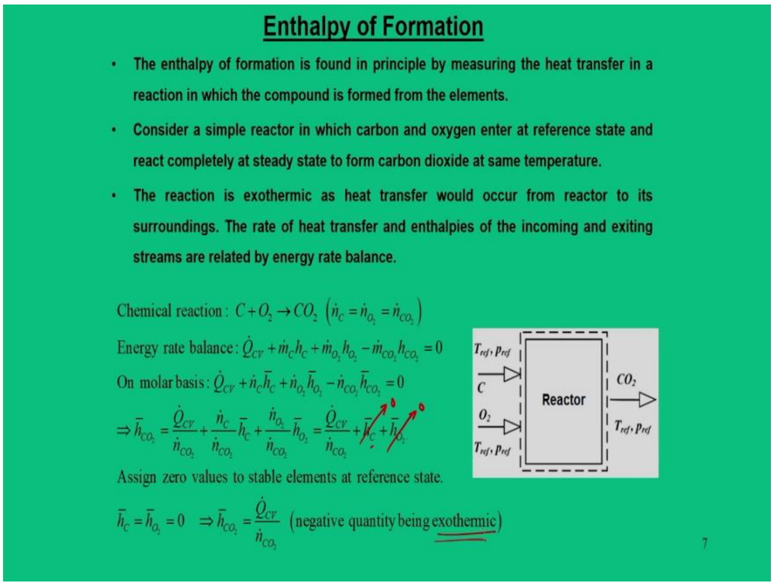

Enthalpy of Formation

- The enthalpy of formation is found in principle by measuring the heat transfer in a reaction in which the compound is formed from the elements.
- Consider a simple reactor in which carbon and oxygen enter at reference state and react completely at steady state to form carbon dioxide at same temperature.
- The reaction is exothermic as heat transfer would occur from reactor to its surroundings. The rate of heat transfer and enthalpies of the incoming and exiting streams are related by energy rate balance.

Chemical reaction : $C+O_2 \rightarrow CO_2 \ \left(\dot{n}_C=\dot{n}_{O_2}=\dot{n}_{CO_2}\right)$

Energy rate balance : $\dot{Q}_{CV}+\dot{m}_C h_C+\dot{m}_{O_2} h_{O_2}-\dot{m}_{CO_2} h_{CO_2}=0$

On molar basis : $\dot{Q}_{CV}+\dot{n}_C\bar{h}_C+\dot{n}_{O_2}\bar{h}_{O_2}-\dot{n}_{CO_2}\bar{h}_{CO_2}=0$

$$\Rightarrow \bar{h}_{CO_2}=\frac{\dot{Q}_{CV}}{\dot{n}_{CO_2}}+\frac{\dot{n}_C}{\dot{n}_{CO_2}}\bar{h}_C+\frac{\dot{n}_{O_2}}{\dot{n}_{CO_2}}\bar{h}_{O_2}=\frac{\dot{Q}_{CV}}{\dot{n}_{CO_2}}+\cancelto{0}{\bar{h}_C}+\cancelto{0}{\bar{h}_{O_2}}$$

Assign zero values to stable elements at reference state.

$$\bar{h}_C=\bar{h}_{O_2}=0 \ \Rightarrow \bar{h}_{CO_2}=\frac{\dot{Q}_{CV}}{\dot{n}_{CO_2}} \ \text{(negative quantity being }\underline{\underline{\text{exothermic}}}\text{)}$$

Then moving further let us talk about a particular example that how enthalpy of formation is calculated. So, by principal, enthalpy of formation is found by measuring the heat transfer in a reaction in which the compound is formed from the elements. So, you can think of a simple reactor where carbon and oxygen are entering at reference state and pressure and set at same reference pressure and temperature where CO 2 is formed

So, basically this reference temperature at pressure is one atmosphere and 298.15 K. So, through this reaction ($C + O_2 \rightarrow CO_2$) we are getting it, and during this formation process if you want to calculate what is the enthalpy of formation of CO_2, one can find it through the energy balance equations. First thing that you have to do is that, you have to write the chemical reactions that is $C + O_2 \rightarrow CO_2$. And for all these things we can find out its molar number or stoichiometric coefficients and number of moles.

Then you can write the energy balance, because there is no work transfer in the systems, but there is heat transfer because it is a heat of formation or heat transfer or either reaction is a exothermic or endothermic. So, $\dot{Q}_{CV}$ is your energy balance and then we have to find out on mass basis and molar basis. For example, in the first equation of energy balance talks about $\dot{Q}_{CV} + \dot{m}_C h_C + \dot{m}_{O_2} h_{O_2} - \dot{m}_{CO_2} h_{CO_2} = 0$, that is for energy mass of carbon and enthalpy of carbon and mass flow rate of oxygen and enthalpy of oxygen, mass flow rate of CO_2 and enthalpy of CO_2. And there is a negative sign here because it is coming out.

And same thing we have written in the form of molar form, on molar basis, $\dot{Q}_{CV} + \dot{n}_C \bar{h}_C + \dot{n}_{O_2} \bar{h}_{O_2} - \dot{n}_{CO_2} \bar{h}_{CO_2} = 0$, mass flow rate is replaced with the molar flow rate of carbon, similarly for oxygen and CO_2. Now, after solving these equations we get a simplified form of molar enthalpy of CO_2 that is $\bar{h}_{CO_2} = \frac{\dot{Q}_{CV}}{\dot{n}_{CO_2}} + \bar{h}_C + \bar{h}_{O_2}$.

Now, here while calculating the enthalpy of formation for carbon dioxide, then we have to assign these two enthalpies $\bar{h}_C = \bar{h}_{O_2} = 0$, that is because carbon and oxygen they are stable components and they at the reference conditions. So, if you are assigning this value as 0, then the enthalpy of formation molar enthalpy $\bar{h}_{CO_2} = \frac{\dot{Q}_{CV}}{\dot{n}_{CO_2}}$. And this is a negative quantity, because reaction is exothermic.

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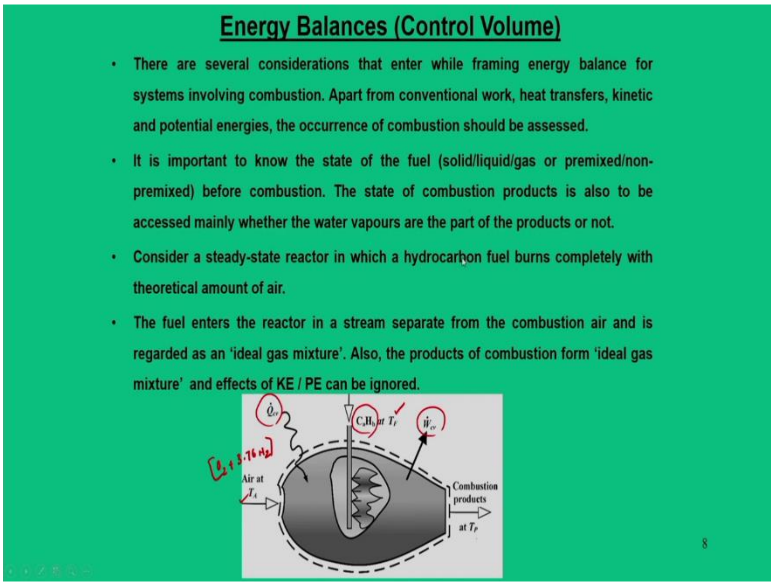

Energy Balances (Control Volume)

- There are several considerations that enter while framing energy balance for systems involving combustion. Apart from conventional work, heat transfers, kinetic and potential energies, the occurrence of combustion should be assessed.
- It is important to know the state of the fuel (solid/liquid/gas or premixed/non-premixed) before combustion. The state of combustion products is also to be accessed mainly whether the water vapours are the part of the products or not.
- Consider a steady-state reactor in which a hydrocarbon fuel burns completely with theoretical amount of air.
- The fuel enters the reactor in a stream separate from the combustion air and is regarded as an 'ideal gas mixture'. Also, the products of combustion form 'ideal gas mixture' and effects of KE / PE can be ignored.

Then we will move to next segment of our discussion that is energy balance we will be looking at a control volume system. And all our reactions we can thought of in a control volume approach, like in this particular figure what we can see is that some component C_aH_b is a fuel. And any arbitrary fuel, and air is $O_2 + 3.76\ N_2$, this is the model and it enters at certain temperature T_A, fuel temperature is T_F, and this reaction takes place.

And we get the combustion products at the product temperature T_P. And during this process we may have a possibility of heat transfer into the control volume and work transfer out of the control volume. So, this is the description of how a reactor works or you can view this chemical reaction as a reacting system. And it is a steady state reactor in which hydrocarbon fuel burns completely with theoretical amount of air.

And the combustion products are formed it is treated as an ideal gas mixtures. Conventionally, we are trying to ignore the effects of kinetic and energy and potential energy, also you need to see that the combustion products form an ideal gas mixtures. Another view point is that this many a times this air and fuel they can come as a mixer or they can come separately; so, accordingly you will have a single inlet or multiple inlet. So, in this way you call this as pre mixed or non pre mixed combustion and fuel can be solid, liquid, or gas.

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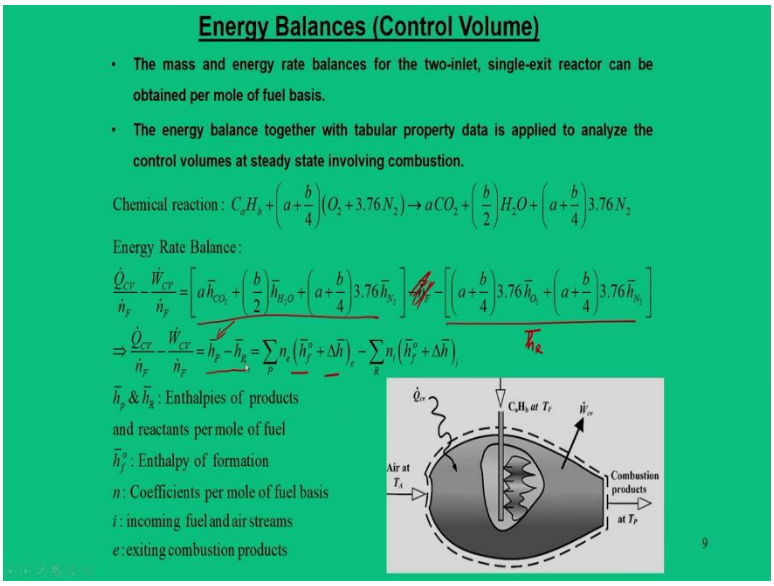

Energy Balances (Control Volume)

- The mass and energy rate balances for the two-inlet, single-exit reactor can be obtained per mole of fuel basis.
- The energy balance together with tabular property data is applied to analyze the control volumes at steady state involving combustion.

Chemical reaction: $C_aH_b+\left(a+\frac{b}{4}\right)(O_2+3.76N_2)\rightarrow aCO_2+\left(\frac{b}{2}\right)H_2O+\left(a+\frac{b}{4}\right)3.76N_2$

Energy Rate Balance:

$$\frac{\dot{Q}_{CV}}{\dot{n}_F}-\frac{\dot{W}_{CV}}{\dot{n}_F}=\left[a\bar{h}_{CO_2}+\left(\frac{b}{2}\right)\bar{h}_{H_2O}+\left(a+\frac{b}{4}\right)3.76\bar{h}_{N_2}\right]\cancel{\bar{h}_F}-\underbrace{\left[\left(a+\frac{b}{4}\right)3.76\bar{h}_{O_2}+\left(a+\frac{b}{4}\right)3.76\bar{h}_{N_2}\right]}_{\bar{h}_R}$$

$$\Rightarrow\frac{\dot{Q}_{CV}}{\dot{n}_F}-\frac{\dot{W}_{CV}}{\dot{n}_F}=\bar{h}_P-\bar{h}_R=\sum_P n_e\left(\bar{h}_f^o+\Delta\bar{h}\right)_e-\sum_R n_i\left(\bar{h}_f^o+\Delta\bar{h}\right)_i$$

$\bar{h}_p$ & $\bar{h}_R$: Enthalpies of products and reactants per mole of fuel

$\bar{h}_f^o$: Enthalpy of formation

n: Coefficients per mole of fuel basis

i: incoming fuel and air streams

e: exiting combustion products

So, with this view point if you are going to find the mass and energy rate balance, first thing you have to do is write the chemical reactions. So, chemical reaction for this is $C_aH_b+\left(a+\frac{b}{4}\right)(O_2+3.76N_2)\rightarrow aCO_2+\left(\frac{b}{2}\right)H_2O+\left(a+\frac{b}{4}\right)3.76N_2$. Now, for this reaction we are going to find the energy balance; and of course, all this energy balance when you treat we have to find out what is the molar flow rate of the fuel all this reference point is with respect to fuel.

So, we can write $\frac{\dot{Q}_{CV}}{\dot{n}_F}-\frac{\dot{W}_{CV}}{\dot{n}_F}$. So, if you do this, then we have basically three entries and out of which two are entering into the systems and one is living out of systems. So, when you are entering medium is air; so, air is modeled with oxygen and nitrogen with its appropriate compositions, and stoichiometric coefficient value, products which are formed is $CO_2, H_2O, and\ N_2$.

$$\frac{\dot{Q}_{CV}}{\dot{n}_F}-\frac{\dot{W}_{CV}}{\dot{n}_F}=\left[a\bar{h}_{CO_2}+\left(\frac{b}{2}\right)\bar{h}_{H_2O}+\left(a+\frac{b}{4}\right)3.76\bar{h}_{N_2}\right]$$
$$-\left[\left(a+\frac{b}{4}\right)3.76\bar{h}_{O_2}+\left(a+\frac{b}{4}\right)3.76\bar{h}_{N_2}\right]$$

So, through this process we can write this enthalpy of reactants and products as $\frac{\dot{Q}_{CV}}{\dot{n}_F}-\frac{\dot{W}_{CV}}{\dot{n}_F}=\bar{h}_P-\bar{h}_R$. So, from this equation ultimately what we get is $\frac{\dot{Q}_{CV}}{\dot{n}_F}-\frac{\dot{W}_{CV}}{\dot{n}_F}=$

$\sum_P n_e\left(\bar{h}_f^o + \Delta\bar{h}\right)_e - \sum_R n_i\left(\bar{h}_f^o + \Delta\bar{h}\right)_i$. And $\bar{h}_P$ and $\bar{h}_R$ is nothing but the molar enthalpy of the products and reactions per mole of the fuel.

So, this can be correlated with the summation of two parameters, first is enthalpy of formation for that component and the enthalpy change. That means, if there are multiple entries of the components, then we can make a summation by multiplying their number of moles; so, in this case we have two things, one is oxygen other is air.

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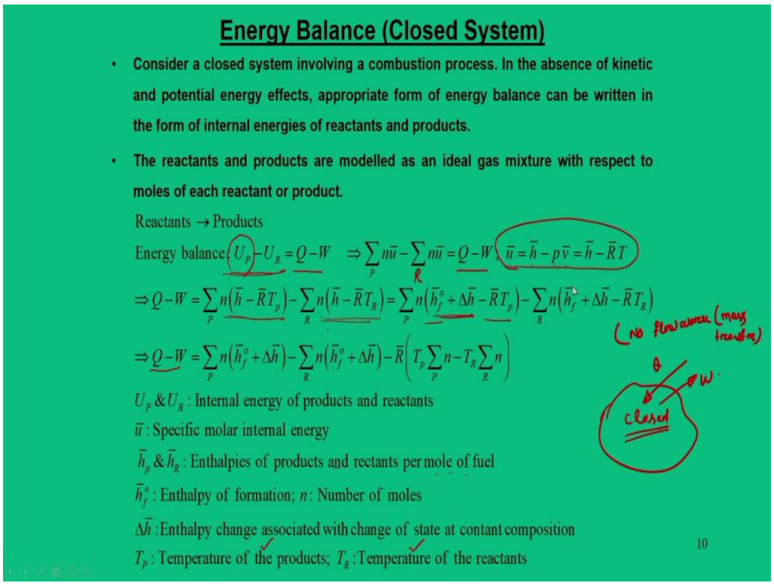

Energy Balance (Closed System)

- Consider a closed system involving a combustion process. In the absence of kinetic and potential energy effects, appropriate form of energy balance can be written in the form of internal energies of reactants and products.
- The reactants and products are modelled as an ideal gas mixture with respect to moles of each reactant or product.

Reactants → Products

Energy balance $U_P - U_R = Q - W \quad \Rightarrow \sum_P n\bar{u} - \sum_R n\bar{u} = Q - W$; $\bar{u} = \bar{h} - p\bar{v} = \bar{h} - \bar{R}T$

$$\Rightarrow Q - W = \sum_P n\left(\bar{h} - \bar{R}T_p\right) - \sum_R n\left(\bar{h} - \bar{R}T_R\right) = \sum_P n\left(\bar{h}_f^o + \Delta\bar{h} - \bar{R}T_p\right) - \sum_R n\left(\bar{h}_f^o + \Delta\bar{h} - \bar{R}T_R\right)$$

$$\Rightarrow Q - W = \sum_P n\left(\bar{h}_f^o + \Delta\bar{h}\right) - \sum_R n\left(\bar{h}_f^o + \Delta\bar{h}\right) - \bar{R}\left(T_p\sum_P n - T_R\sum_R n\right)$$

U_p & U_R : Internal energy of products and reactants

$\bar{u}$: Specific molar internal energy

$\bar{h}_p$ & $\bar{h}_R$: Enthalpies of products and rectants per mole of fuel

$\bar{h}_f^o$: Enthalpy of formation; n : Number of moles

$\Delta\bar{h}$: Enthalpy change associated with change of state at contant composition

T_p : Temperature of the products; T_R : Temperature of the reactants

Then when you deal with the closed systems similar explanation can be given here as well, but here our attention is that instead of enthalpy we need to calculate the internal energy. So, because in a closed system that involves combustion process and in the absence of kinetic energy and potential energy, one can write the appropriate form of energy balance equation in the form of internal energies of reactants and products and with same logics both reactants and products are modeled as an ideal gas mixture. All the analysis are with respect to moles of each components each reactant or products. Because in a closed systems, there is no mass transfer. So, for a closed systems whatever changes takes place that changes takes place with respect to this internal energy.

So, basically in a closed system what happens we can say heat or work interaction is possible, but no flow work or mass transfer. With these conditions due to heat and work interactions, the change in the work and heat transfer will lead to internal energy change.

And in this closed systems reaction is taking place and when this reaction is taking place, we view them as reactants and products.

So, we can take this $Q - W = \sum_P n\bar{u} - \sum_R n\bar{u}$ that is the total energy of the products that is molar internal energy multiplied by its number of moles for the products and number of moles for reactants multiplied by the molar enthalpies of each species of the reactants; so, there is a summation here. Now, what you know is these closed systems, the system is at final temperature T_P; so, T_P is your temperature of the products, T_R is your temperature of the reactants.

So, we also know that the internal energy is can be written as a function of enthalpy, pressure and volume. And for an ideal gas $p\bar{v} = \bar{R}T$. By doing so in the end what you get is that we can find out Q minus W that is for each component we need to evaluate the enthalpy of formation, enthalpy change minus $\bar{R}T_p$.

So, we replace $\bar{u} = \bar{h} - p\bar{v} = \bar{h} - \bar{R}T$, then once you do that products we can write this expression for reactants we can write also this expressions.

$$\Rightarrow Q - W = \sum_P n\left(\bar{h} - \bar{R}T_p\right) - \sum_R n\left(\bar{h} - \bar{R}T_R\right)$$

$$= \sum_P n\left(\bar{h}_f^o + \Delta\bar{h} - \bar{R}T_p\right) - \sum_R n\left(\bar{h}_f^o + \Delta\bar{h} - \bar{R}T_R\right)$$

$$\Rightarrow Q - W = \sum_P n\left(\bar{h}_f^o + \Delta\bar{h}\right) - \sum_R n\left(\bar{h}_f^o + \Delta\bar{h}\right) - \bar{R}\left(T_p \sum_P n - T_R \sum_R n\right)$$

And from this equation if you want to go to this equation, what happens is enthalpy of the product and reactants per mole of fuel is represented with respect to enthalpy formation plus the enthalpy change. And that we have to do it for products as well as for the reactants; so, if you do this a simplified expressions between Q and W can be found out.

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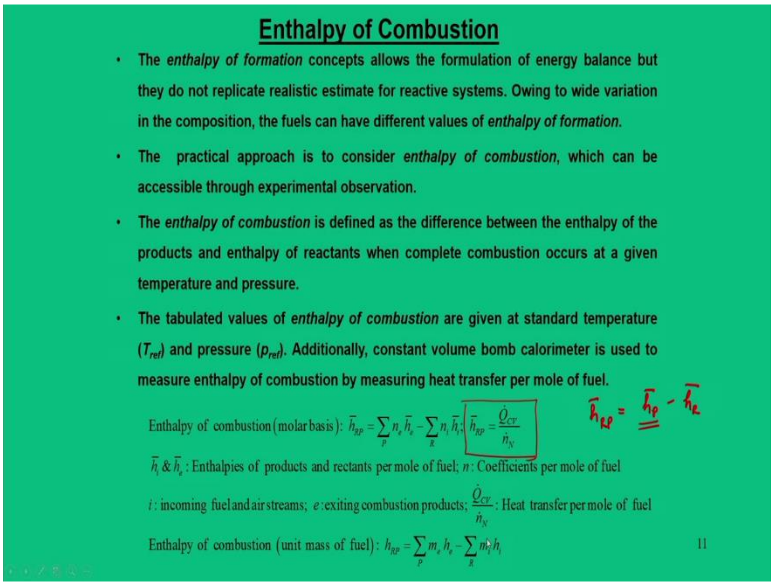

Enthalpy of Combustion

- The *enthalpy of formation* concepts allows the formulation of energy balance but they do not replicate realistic estimate for reactive systems. Owing to wide variation in the composition, the fuels can have different values of *enthalpy of formation*.
- The practical approach is to consider *enthalpy of combustion*, which can be accessible through experimental observation.
- The *enthalpy of combustion* is defined as the difference between the enthalpy of the products and enthalpy of reactants when complete combustion occurs at a given temperature and pressure.
- The tabulated values of *enthalpy of combustion* are given at standard temperature (T_{ref}) and pressure (p_{ref}). Additionally, constant volume bomb calorimeter is used to measure enthalpy of combustion by measuring heat transfer per mole of fuel.

Enthalpy of combustion (molar basis): $\bar{h}_{RP} = \sum_P n_e \bar{h}_e - \sum_R n_i \bar{h}_i$; $\boxed{\bar{h}_{RP} = \frac{\dot{Q}_{CV}}{\dot{n}_N}}$

$\bar{h}_{RP} = \underline{\underline{\bar{h}_P}} - \bar{h}_R$

$\bar{h}_i$ & $\bar{h}_e$: Enthalpies of products and rectants per mole of fuel; n : Coefficients per mole of fuel

i : incoming fuel and air streams; e : exiting combustion products; $\frac{\dot{Q}_{CV}}{\dot{n}_N}$: Heat transfer per mole of fuel

Enthalpy of combustion (unit mass of fuel): $h_{RP} = \sum_P m_e h_e - \sum_R m_i h_i$

Now, next topic of discussion is enthalpy of combustions. Now, prior to this we know that the enthalpy of formation concepts which we discussed earlier it allows the formulation of energy balance. But they really do not replicate the realistic estimate of the reactive systems, why? Because, many a times a components can be formed at different conditions or different compositions that mean there are many sources in which a components can be formed.

So, instead of targeting how it is formed, let us target that when two components react then how they behave or view this as a change of enthalpies between reactants and products and that is defined in terms of enthalpy of combustion. So, it is defined as the difference between the enthalpy of products and enthalpy of reactants when complete combustion occurs at a given pressure and temperatures. That means, in a complete combustion process, one can define the enthalpy of combustions.

If that is the case this $\bar{h}_{RP} = \bar{h}_P - \bar{h}_R$. And $\bar{h}_P$ is nothing but the summation of all the incoming fuel air streams or for the products, or summation of all outgoing combustion products multiple with their respective mole fraction. And for reactants it is the number of entries for the reactants $\bar{h}_{RP} = \sum_P n_e \bar{h}_e - \sum_R n_i \bar{h}_i$.

And finally, we can get that $\bar{h}_{RP} = \frac{\dot{Q}_{CV}}{\dot{n}_N}$, N stands for number of moles for the fuel. And this was defined with respect to molar basis, one can also write it with respect to mass basis.

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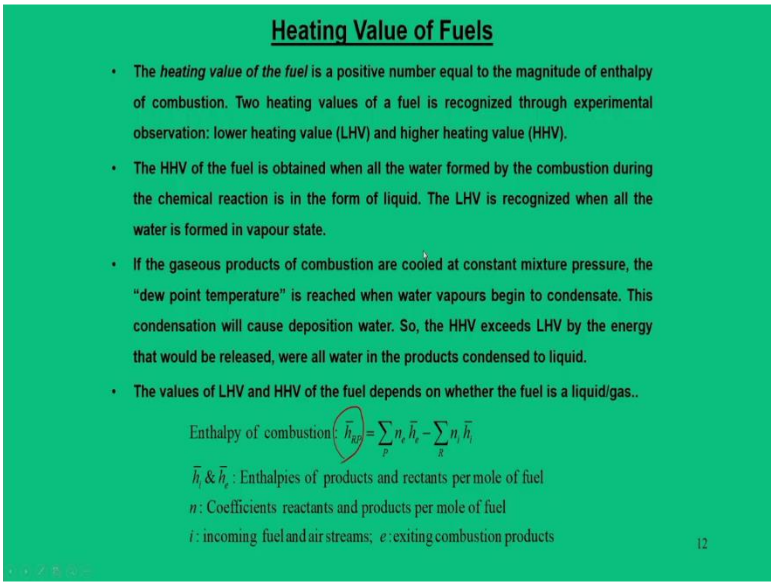

Heating Value of Fuels

- The *heating value of the fuel* is a positive number equal to the magnitude of enthalpy of combustion. Two heating values of a fuel is recognized through experimental observation: lower heating value (LHV) and higher heating value (HHV).
- The HHV of the fuel is obtained when all the water formed by the combustion during the chemical reaction is in the form of liquid. The LHV is recognized when all the water is formed in vapour state.
- If the gaseous products of combustion are cooled at constant mixture pressure, the “dew point temperature” is reached when water vapours begin to condensate. This condensation will cause deposition water. So, the HHV exceeds LHV by the energy that would be released, were all water in the products condensed to liquid.
- The values of LHV and HHV of the fuel depends on whether the fuel is a liquid/gas..

Enthalpy of combustion: $\bar{h}_{RP} = \sum_{P} n_e \bar{h}_e - \sum_{R} n_i \bar{h}_i$

$\bar{h}_i$ & $\bar{h}_e$: Enthalpies of products and rectants per mole of fuel

n : Coefficients reactants and products per mole of fuel

i : incoming fuel and air streams; e : exiting combustion products

And the last segment that we are going to discuss is that heating value of the fuel. So, we have enthalpy of formation, then we move to enthalpy of combustions and then now we are moving to heating value. So, when we are talking about enthalpy of formation, we are bothered about how that component during a reaction is formed.

But when you are moving for enthalpy of combustions, we view that lets say all the components have been formed and reactants and products has been formed. And then we are really bothered what is the difference between the enthalpies between products and reactants.

Now, having said this we are now going to introduce the heating value of the fuel. So, basically all it matters, because if fuel enters and when it reacts with oxidizer air, the combustion is initiated. So, it is the fuel heating value that really matters a lot to all the audience. So, the ideal way of looking at the enthalpy of combustion during a reaction is with respect to heating value of the fuel.

In fact, when any fuel is defined, we have to also specify its heating value; for example, petrol, diesel, kerosene all of them will have some heating value, we define them in terms of heating value. So, as a matter of common audience it is better that we should talk about the heating value and moreover then when you deal with the enthalpy of combustions that number is always a negative quantity.

So, what you do is that, we replace that enthalpy of combustion as heating value of the fuel which is widely accepted. And it is always a positive number and which is equal to magnitude of enthalpy of combustion; that means, during a chemical reaction whatever magnitude of enthalpy of combustion that is assigned as the heating value of the fuel.

Now, there are two heating value of the fuel can be possible; one is at lower heating value, other is the higher heating value. So, during a chemical reaction what may happen is that combustion products are formed they are at already at elevated temperatures. And we say we know that during the combustion process always water is one of the entity and this water at that elevated temperature will exist in vapour form.

So, if you calculate the heating value of the fuel during a combustion process, we assign it as a lower heating value. Now, when this combustion products are released, from this combustion environment to atmospheric condition it is basically cooled. So, when it is cooled, the water vapours try to condensate and when all the water vapour try to condensate; that means, similar amount of heat is also released; so, that number is assigned as a higher heating value.

So, higher heating value of the fuel is defined when all the water vapour formed during combustion chemical reactions is in the form of liquid state. And lower heating value is recognized when all the products are in the vapour state. When the gaseous products of the combustions are cooled at constant mixture pressure, the dew point temperature is reached; so, water vapours begins to condensate.

This will cause the condensation or that is deposition of water. And; that means, in other words we can say higher heating value of the fuel exceeds the lower heating value that is nothing but the difference in the energy that will be released. So, here in the final note we can say whatever $\bar{h}_{RP}$ enthalpy of combustion is always a negative quantity and we assign that as a positive number as the heating value of the fuel.

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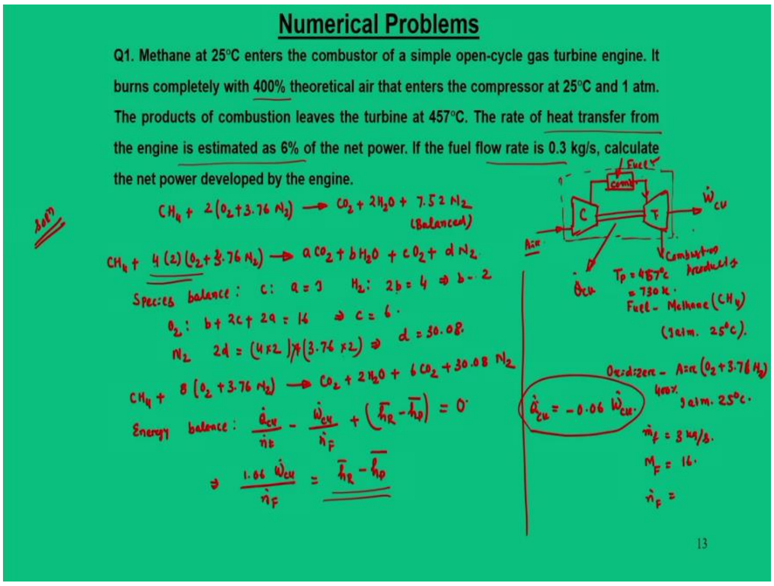

Numerical Problems

Q1. Methane at 25°C enters the combustor of a simple open-cycle gas turbine engine. It burns completely with 400% theoretical air that enters the compressor at 25°C and 1 atm. The products of combustion leaves the turbine at 457°C. The rate of heat transfer from the engine is estimated as 6% of the net power. If the fuel flow rate is 0.3 kg/s, calculate the net power developed by the engine.

Sol^n

$$CH_4 + 2(O_2 + 3.76\,N_2) \longrightarrow CO_2 + 2H_2O + 7.52\,N_2$$

(Balanced)

$$CH_4 + \underline{\underline{4(2)}}(O_2 + 3.76\,N_2) \longrightarrow a\,CO_2 + b\,H_2O + c\,O_2 + d\,N_2$$

Species balance : C: $a = 1$ H$_2$: $2b = 4 \Rightarrow b = 2$

O_2: $b + 2c + 2a = 16 \Rightarrow c = 6.$

N_2 $2d = (4 \times 2) \times (3.76 \times 2) \Rightarrow d = 30.08.$

$$CH_4 + 8(O_2 + 3.76\,N_2) \longrightarrow CO_2 + 2H_2O + 6\,CO_2 + 30.08\,N_2$$

Energy balance : $\frac{\dot{Q}_{cv}}{\dot{n}_F} - \frac{\dot{W}_{cv}}{\dot{n}_F} + (\bar{h}_R - \bar{h}_P) = 0.$

$$\Rightarrow \frac{1.06\,\dot{W}_{cv}}{\dot{n}_F} = \underline{\underline{\bar{h}_R - \bar{h}_P}}$$

$T_P = 457°C$
$= 730\,K.$

Fuel - Methane (CH_4)
(1 atm. 25°C).

Oxidizer - Air ($O_2 + 3.76\,N_2$)
400%
1 atm. 25°C.

$\boxed{\dot{Q}_{cv} = -0.06\,\dot{W}_{cv}.}$

$\dot{m}_f = 3\,kg/s.$

$M_F = 16.$

$\dot{n}_F =$

Now, whatever we have discussed so far, we will try to solve a numerical problems based on the concepts that we covered today. As the learning components we covered about mainly on enthalpy of formation, enthalpy of combustion, and heating value of the fuel. So, based on this we will try to solve a problem which talks about a methane and air combustion system in a simple gas turbine unit.

So, if you look at a gas turbine unit typically, we have a compressor that compressor is coupled with a turbine and fuel is introduced in a combustor. So, we say and the combustion products comes and enters into the turbine and when they expand in the turbine, we get power output. And air enters into the compressor and fuel enters to the combustor, and if you treat entire things as a control volume then we can say there are two entries, one for air other for fuel.

There is one output that is a combustor products and this combustion products goes out and what are the things that has given to us this fuel is methane CH_4 and it enters at 1 atmosphere 25 C. And we have oxidizer is air which is $O_2 + 3.76N_2$ and we are saying it is 400 percent theoretical air.

Then when you say combustion products, it is at 457 C or 730 K. And this oxidizer is also at same conditions as that of fuel; so, this is 1 atmosphere 25 C. And what is given is the fuel flow rate $\dot{m}_f = 0.3\ kg/s$; so, we know the molecular weight of fuel that is CH_4 that is 16; so, we can find out $\dot{n}_f$.

So, if this is the problem the first thing that, we need to do is that we have to write the balanced chemical reactions. $CH_4 + 2(O_2 + 3.76N_2) \rightarrow CO_2 + 2H_2O + 7.52N_2$

Now, with 400 percent theoretical layer what the reaction is going to be there; so, we have to write $CH_4 + 4 \times 2(O_2 + 3.76N_2) \rightarrow aCO_2 + bH_2O + cO_2 + dN_2$.

$$Species\ balance - \quad C: a = 1, \qquad H_2: 2b = 4; b = 2 \quad O_2: b + 2c + 2a = 16; c = 6$$

$$N_2:\ 2d = 4 \times 2 \times 3.76 \times 2; d = 30.08$$

$$CH_4 + 4 \times 2(O_2 + 3.76N_2) \rightarrow CO_2 + 2H_2O + 6O_2 + 30.08N_2$$

Now, we are in a position for to write the energy balance; so, heat comes from the fuel, work comes out from the turbine.

$$\frac{\dot{Q}_{CV}}{\dot{n}_F} - \frac{\dot{W}_{CV}}{\dot{n}_F} + \bar{h}_R - \bar{h}_p = 0$$

Now, what other information is given is that heat transfer from this engine is 6 percent of net power; so, $\dot{Q}_{CV} = -0.06\dot{W}_{CV}$, because heat is coming out, W work is also coming out. So, $1.06\frac{\dot{W}_{CV}}{\dot{n}_F} = \bar{h}_R - \bar{h}_p$.

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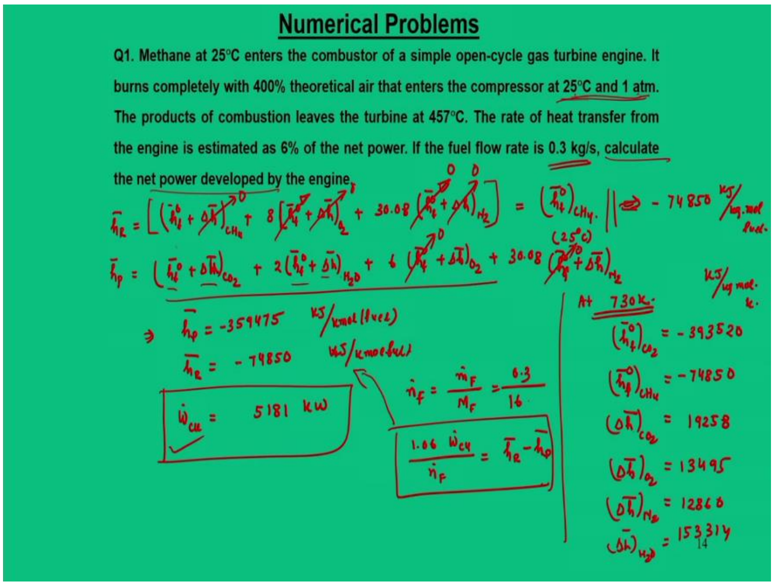

Numerical Problems

Q1. Methane at 25°C enters the combustor of a simple open-cycle gas turbine engine. It burns completely with 400% theoretical air that enters the compressor at 25°C and 1 atm. The products of combustion leaves the turbine at 457°C. The rate of heat transfer from the engine is estimated as 6% of the net power. If the fuel flow rate is 0.3 kg/s, calculate the net power developed by the engine.

$$\bar{h}_R = \left[(\bar{h}_f^0 + \cancel{\Delta\bar{h}})_{CH_4} + 8[\cancel{\bar{h}_f^0} + \cancel{\Delta\bar{h}}]_{O_2} + 30.08(\cancel{\bar{h}_f^0} + \cancel{\Delta\bar{h}})_{N_2}\right] = (\bar{h}_f^0)_{CH_4} \Rightarrow -74850\ kJ/kg.mol\ fuel$$

$$(25°C)$$

$$\bar{h}_p = (\bar{h}_f^0 + \Delta\bar{h})_{CO_2} + 2(\bar{h}_f^0 + \Delta\bar{h})_{H_2O} + 6(\cancel{\bar{h}_f^0} + \Delta\bar{h})_{O_2} + 30.08(\cancel{\bar{h}_f^0} + \Delta\bar{h})_{N_2} \quad kJ/kg\ mol.k.$$

$$\Rightarrow \bar{h}_p = -359475\ kJ/kmol(fuel)$$

$$\bar{h}_R = -74850\ kJ/kmol\,fuel$$

$$\boxed{\dot{W}_{CV} = 5181\ kW}$$

$$\dot{n}_F = \frac{\dot{m}_F}{M_F} = \frac{0.3}{16}$$

$$\boxed{\frac{1.06\,\dot{W}_{CV}}{\dot{n}_F} = \bar{h}_R - \bar{h}_p}$$

At 730K.

$$(\bar{h}_f^0)_{CO_2} = -393520$$

$$(\bar{h}_f^0)_{CH_4} = -74850$$

$$(\Delta\bar{h})_{CO_2} = 19258$$

$$(\Delta\bar{h})_{O_2} = 13495$$

$$(\Delta\bar{h})_{N_2} = 12860$$

$$(\Delta\bar{h})_{H_2O} = 153314$$

So, now we are going to find out what is this h_R and h_P; so, to do that what we need to know we have to write down this equation.

$$\bar{h}_R = \left(\bar{h}_f^o + \Delta\bar{h}\right)_{CH_4} + 8\left(\bar{h}_f^o + \Delta\bar{h}\right)_{O_2} + 30.08\left(\bar{h}_f^o + \Delta\bar{h}\right)_{N_2}$$

So, here we can see that all are at both reactants that is methane as well as air they are at same reference condition 1 atmosphere and 25 C. So, we can simply assign this $\Delta\bar{h}$ value to 0 and oxygen O_2 and N_2 they are stable components, we can assign this 0 for their enthalpy of formations. $\bar{h}_R = \left(\bar{h}_f^o\right)_{CH_4} at\ 25C = -74850 kJ/kg.mol.$

$$\bar{h}_p = \left(\bar{h}_f^o + \Delta\bar{h}\right)_{CO_2} + 2\left(\bar{h}_f^o + \Delta\bar{h}\right)_{H_2O} + 6\left(\bar{h}_f^o + \Delta\bar{h}\right)_{O_2} + 30.08\left(\bar{h}_f^o + \Delta\bar{h}\right)_{N_2}$$

Now, we can assign to 0 enthalpy of formation for stable component this numbers to be 0. So, left out numbers you have to calculate these conditions at 730 K.

$$\left(\bar{h}_f^o\right)_{CO_2} = -393520;\ \left(\Delta\bar{h}\right)_{CO_2} = 19258;\ \left(\bar{h}_f^o\right)_{H_2O} = -74850;\ \left(\Delta\bar{h}\right)_{O_2} = 13495;$$

$$\left(\Delta\bar{h}\right)_{N_2} = 12860;\ \left(\Delta\bar{h}\right)_{H_2O} = 153314$$

So, by inserting this we can get the final number as $\bar{h}_p = -359475\ kJ/kg.mol$. So, once you say this then we can find out from this equation about $\dot{W}_{CV} = 5181 kW$.

So, this is our requirement that we need to find out what is the net power developed by the fuel. So, of course, here you have use $\dot{n}_F = \frac{\dot{m}_F}{M_F} = \frac{0.3}{16}$. So, this is all about the problem that is associated with the power developed in a gas turbine combustor which mainly uses methane as the fuel.

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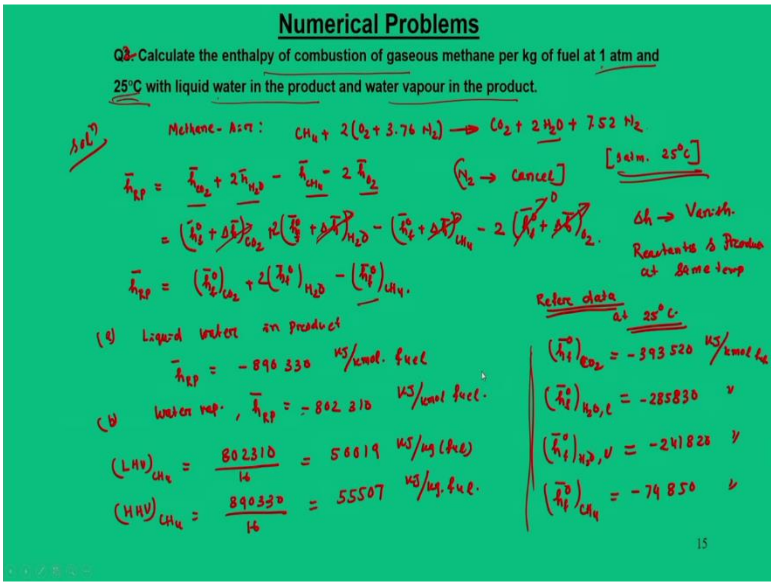

Numerical Problems

Q3. Calculate the enthalpy of combustion of gaseous methane per kg of fuel at 1 atm and 25°C with liquid water in the product and water vapour in the product.

Sol^n

Methane-Air: $CH_4 + 2(O_2 + 3.76N_2) \rightarrow CO_2 + 2H_2O + 7.52N_2$

[1atm. 25°C]

$\bar{h}_{RP} = \bar{h}_{CO_2} + 2\bar{h}_{H_2O} - \bar{h}_{CH_4} - 2\bar{h}_{O_2}$ ($N_2 \rightarrow$ cancel]

$= (\bar{h}_f^o + \cancel{\Delta\bar{h}})_{CO_2} + 2(\bar{h}_f^o + \cancel{\Delta\bar{h}})_{H_2O} - (\bar{h}_f^o + \cancel{\Delta\bar{h}})_{CH_4} - 2(\cancel{\bar{h}_f^o} + \cancel{\Delta\bar{h}})_{O_2}$

$\Delta h \rightarrow$ Vanish.

Reactants & Products at same temp

$\bar{h}_{RP} = (\bar{h}_f^o)_{CO_2} + 2(\bar{h}_f^o)_{H_2O} - (\bar{h}_f^o)_{CH_4}$

(a) Liquid water in product

$\bar{h}_{RP} = -890330$ kJ/kmol. fuel

(b) water vap., $\bar{h}_{RP} = -802310$ kJ/kmol fuel.

$(LHV)_{CH_4} = \frac{802310}{16} = 50019$ kJ/kg (fuel)

$(HHV)_{CH_4} = \frac{890330}{16} = 55507$ kJ/kg. fuel.

Refer data at 25°C.

$(\bar{h}_f^o)_{CO_2} = -393520$ kJ/kmol fuel

$(\bar{h}_f^o)_{H_2O,l} = -285830$,,

$(\bar{h}_f^o)_{H_2O,v} = -241820$,,

$(\bar{h}_f^o)_{CH_4} = -74850$,,

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The next problem is about the calculation of enthalpy of combustion of gaseous methane at 1 atmosphere and 25 C. And here we need to calculate the enthalpy of combustions for gaseous methane at two conditions; one is when the liquid water is in the products, and other is water vapor is in the products. So, to do that; first thing you have to write the methane air reaction.

$$CH_4 + 2(O_2 + 3.76N_2) \rightarrow CO_2 + 2H_2O + 7.52N_2$$

And here we say that both reactants and products they are at 1 atmosphere and 25 C. So,

$$\bar{h}_{RP} = \bar{h}_{CO_2} + 2\bar{h}_{H_2O} - \bar{h}_{CH_4} - 2\bar{h}_{O_2}\ (N_2\ cancel)$$

$$\bar{h}_{RP} = \left(\bar{h}_f^o + \Delta\bar{h}\right)_{CO_2} + 2\left(\bar{h}_f^o + \Delta\bar{h}\right)_{H_2O} - \left(\bar{h}_f^o + \Delta\bar{h}\right)_{CH_4} - 2\left(\bar{h}_f^o + \Delta\bar{h}\right)_{O_2}$$

So, let us see what we can assign and they are at 1 atmosphere and 25 C. So, stable compounds they will vanish; means this number will vanish. And other points other components like $\Delta\bar{h}$ will vanish, because reactants and products at same temperature.

$$\bar{h}_{RP} = \left(\bar{h}_f^o\right)_{CO_2} + 2\left(\bar{h}_f^o\right)_{H_2O} - \left(\bar{h}_f^o\right)_{CH_4}$$

So, we have to refer data, this data has to be referred at 25 C. $\left(\bar{h}_f^o\right)_{CO_2} = -393520 kJ/kmolfuel$; $\left(\bar{h}_f^o\right)_{H_2O,l} = -255830$; $\left(\bar{h}_f^o\right)_{H_2O,v} = -241820$; $\left(\bar{h}_f^o\right)_{CH_4} =$

$-74850.$ So, we have all the numbers we can insert it, then we can find it out first part liquid water in the products. So, we can calculate $\bar{h}_{RP} = -890330\ kJ/kmol - K$. Second part water vapour which is $\bar{h}_{RP} = -802310\ kJ/kmolfuel$. So, we can assign each LHV,

$$(LHV)_{CH_4} = \frac{802310}{16} = 50019 kJ/kgfuel;\ (HHV)_{CH_4} = \frac{890330}{16} = 55507 kJ/kgfuel$$

So, what it means that at 25 C, the lower heating value of methane is about 50 mega joule per kg of fuel and higher heating value of methane would be about 55 mega joule per kg fuel. So, remember this was taken at 25 C and that point of time for our simplicity this $\Delta\bar{h}$ value was neglected, because both reactants and products they are at same temperatures.

Now, if I ask you to calculate the reactants are at 1 atmosphere and 25 C, products are at different pressure and temperature. Then the problem will be more complicated, this $\Delta\bar{h}$ terms has to be evaluated with respect to that product temperatures and during that point of time, these numbers will also be different. But; however, for the simplicity of problem solving it was simplified that we have assumed that both fuel and air they are at same temperature and pressures; so, this is all about the lecture for today.

Thank you for your attention.