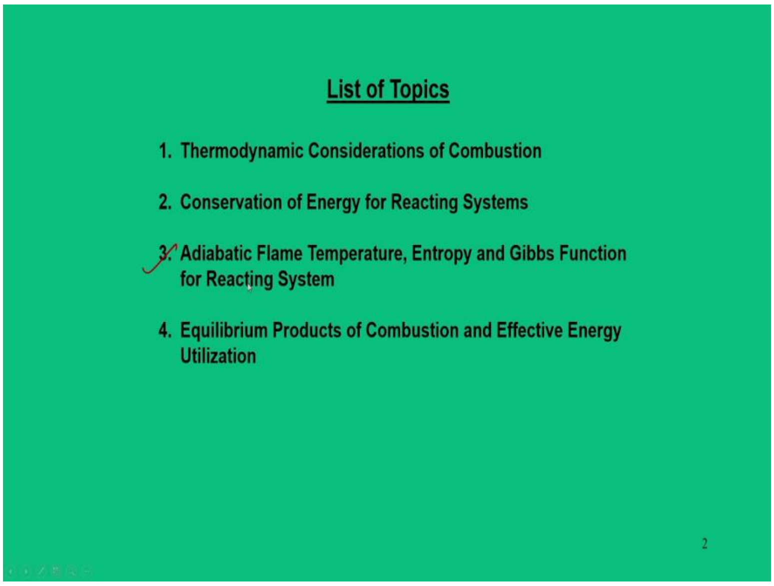
Advanced Thermodynamics and Combustion
Prof. Niranjan Sahoo
Department of Mechanical Engineering
Indian Institute of Technology, Guwahati

Module - 05
Combustion and Thermochemistry
Lecture - 21
Adiabatic Flame Temperature, Entropy and Gibbs Function for Reacting System

Dear learners, greetings from IIT Guwahati. We are in the MOOCs course Advanced Thermodynamics and Combustion, module 5 - Combustion and Thermochemistry.

(Refer Slide Time: 00:42)

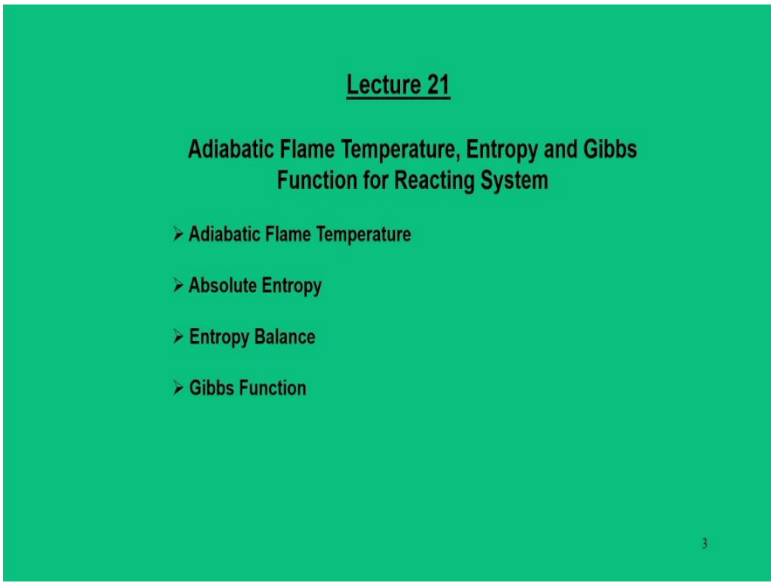


List of Topics

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 have covered two lectures, that is thermodynamic considerations of combustion, then conservation of energy for reacting systems. Today we will be dealing with another important topics that is lecture number 3 on this module, which will cover Adiabatic Flame Temperature, Entropy and Gibbs Function Evaluation for Reacting Systems.

(Refer Slide Time: 01:17)



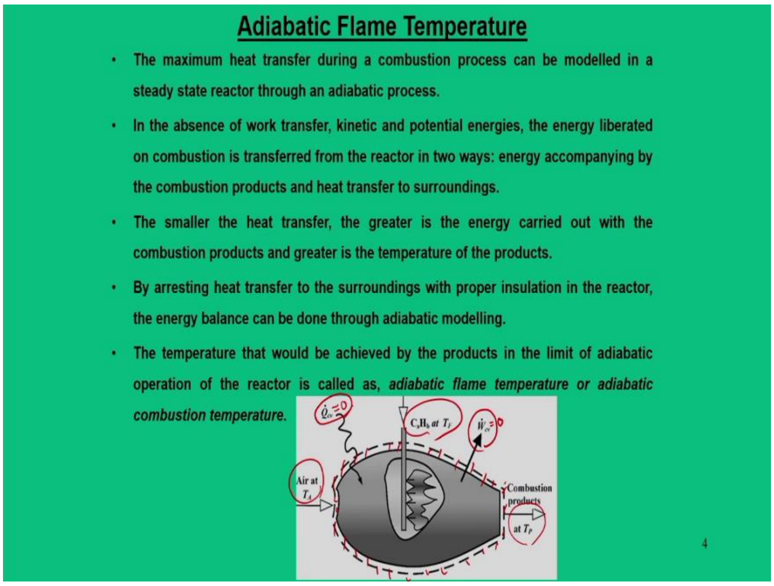
Lecture 21

Adiabatic Flame Temperature, Entropy and Gibbs Function for Reacting System

- Adiabatic Flame Temperature
- Absolute Entropy
- Entropy Balance
- Gibbs Function

So, in this lecture we will try to emphasize upon the very fundamental parameter that is adiabatic flame temperatures for reacting systems, then we will move on to evaluation of entropy and with a concept of absolute entropy. Then we will see the importance of Gibbs function for reacting systems.

(Refer Slide Time: 01:44)



Adiabatic Flame Temperature

- The maximum heat transfer during a combustion process can be modelled in a steady state reactor through an adiabatic process.
- In the absence of work transfer, kinetic and potential energies, the energy liberated on combustion is transferred from the reactor in two ways: energy accompanying by the combustion products and heat transfer to surroundings.
- The smaller the heat transfer, the greater is the energy carried out with the combustion products and greater is the temperature of the products.
- By arresting heat transfer to the surroundings with proper insulation in the reactor, the energy balance can be done through adiabatic modelling.
- The temperature that would be achieved by the products in the limit of adiabatic operation of the reactor is called as, *adiabatic flame temperature or adiabatic combustion temperature.*

So, let me start with the first segment that is adiabatic flame temperatures. As you know adiabatic process do not convey any kind of heat transfer into the system or out of the systems. And in fact, when you arrest the heat transfer in a closed system this will be the typically maximum temperature that we can achieve during some thermodynamic processes.

Now, with the view point of reacting systems, what you can see in this figure is that if you imagine that there is a reactor in which some fuel is coming at certain temperatures, air is entering into the reactor at certain temperature and we get the combustion product out of this reactor at certain pressure and temperatures.

And through this process we get heat out of the system and sometimes, we also get work out of the systems. Now, we can imagine a situation that as if that if you can arrest this, there is no heat transfer is possible into and out of the systems. And there is no work transfer to be possible for this case. And imagine that this reactor is completely adiabatic in nature. And of course, whatever combustion products remains they remain within this reactor.

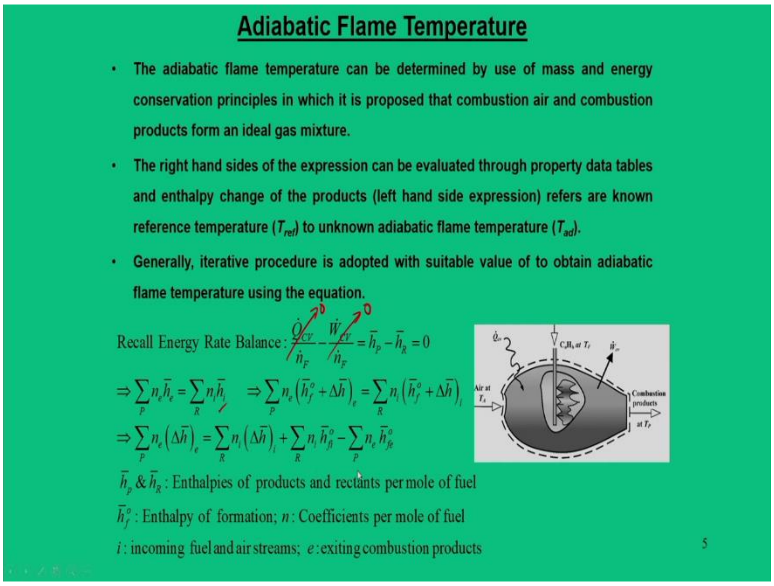
So, what we can see is that through this reaction process, if we arrest all kind of all modes of energy transfer out of the systems, then the temperature within the reactor will increase. And it will increase to a maximum possible extent and that temperatures we call this as an adiabatic flame temperature or many a times we call this as adiabatic combustion temperatures.

So, to summarize these things, what we can say that is that maximum heat transfer during a combustion process can be modeled in a steady state reactor through an adiabatic process. In the absence of work transfer kinetic energy, potential energy, the energy liberated out of the combustion is transferred into the reactor in 2 ways; one is through this combustion product, other is heat transfer to the surroundings.

Now, the smaller the heat transfer, greater is the energy carried out by the combustion products. And greater will be the temperature of the products. Now, by arresting this heat transfer to the surroundings with proper insulation in the reactor, the energy balance can be modeled through an adiabatic modeling. What it says is that if you know all the details of the combustion products, pressure and temperature precisely and by arresting all other modes of heat transfer we can evaluate what is the maximum temperature during a combustion process.

So, by definition what we say is that temperature that would be achieved by the products in the limit of adiabatic operation of the reactor is known as adiabatic flame temperature. Or sometimes it is also referred as adiabatic combustion temperature.

(Refer Slide Time: 04:56)



Adiabatic Flame Temperature

- The adiabatic flame temperature can be determined by use of mass and energy conservation principles in which it is proposed that combustion air and combustion products form an ideal gas mixture.
- The right hand sides of the expression can be evaluated through property data tables and enthalpy change of the products (left hand side expression) refers are known reference temperature (T_{ref}) to unknown adiabatic flame temperature (T_{ad}).
- Generally, iterative procedure is adopted with suitable value of to obtain adiabatic flame temperature using the equation.

Recall Energy Rate Balance: $\frac{\cancel{\dot{Q}_{CV}}^{\nearrow 0}}{\dot{n}_F} - \frac{\cancel{\dot{W}_{CV}}^{\nearrow 0}}{\dot{n}_F} = \bar{h}_P - \bar{h}_R = 0$

$\Rightarrow \sum_P n_e \bar{h}_e = \sum_R n_i \bar{h}_i \quad \Rightarrow \sum_P n_e \left(\bar{h}_f^o + \Delta\bar{h}\right)_e = \sum_R n_i \left(\bar{h}_f^o + \Delta\bar{h}\right)_i$

$\Rightarrow \sum_P n_e \left(\Delta\bar{h}\right)_e = \sum_R n_i \left(\Delta\bar{h}\right)_i + \sum_R n_i \bar{h}_{fi}^o - \sum_P n_e \bar{h}_{fe}^o$

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

$\bar{h}_f^o$: Enthalpy of formation; n: Coefficients per mole of fuel

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

Now, how do you evaluate this concept or how do we evaluate this adiabatic flame temperatures? The adiabatic flame temperature can be determined by the use of mass and energy conservation principle in which it is proposed that combustion air and combustion products form an ideal mixture.

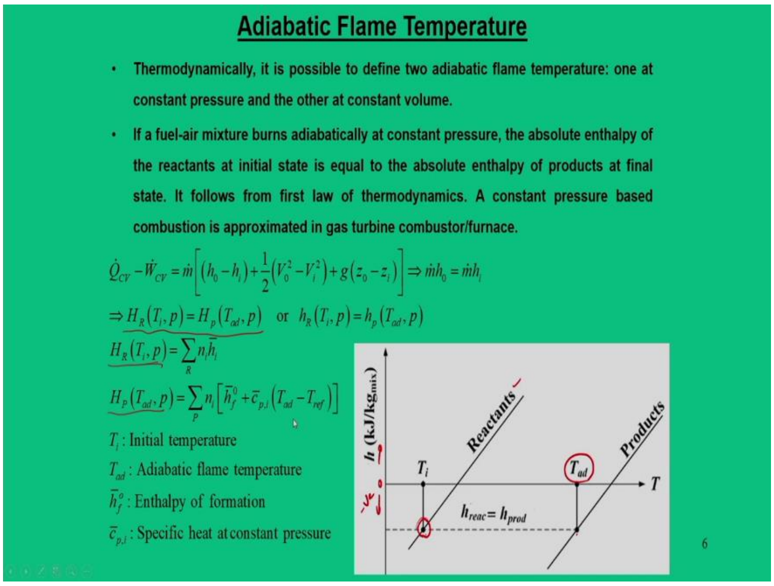
So, if you do that, we can write down this energy balance equations $\frac{\dot{Q}_{CV}}{\dot{n}_F} - \frac{\dot{W}_{CV}}{\dot{n}_F} = \bar{h}_P - \bar{h}_R = 0$, because we are saying $\dot{Q}_{CV}$ and $\dot{W}_{CV}$ to be 0. And in such a situation what we get is that enthalpy of products and reactions per mole of the fuel are equal.

So, this can be given through this summation form $\sum_P n_e \bar{h}_e = \sum_R n_i \bar{h}_i$. Then what we can write is that for reactant and products we can write in terms of its enthalpy of formations and enthalpy change. So, from this we can derive one important expressions, that enthalpy change of the products a function of enthalpy change of reactants plus difference in the summation of enthalpies of formation for reactants and products. So, this is the basic fundamental equations that is used to calculate the adiabatic flame temperature.

$$\sum_P n_e \left(\Delta\bar{h}\right)_e = \sum_R n_i \left(\Delta\bar{h}\right)_i + \sum_R n_i \bar{h}_{fi}^o - \sum_P n_e \bar{h}_{fe}^o$$

In fact, if you look at this enthalpy and if you say that this mixture is treated as an ideal gas, then the enthalpy of the mixture can be represented through this temperature change and the specific heat. And that specific heat has to be evaluated at certain temperature.

(Refer Slide Time: 06:44)



Adiabatic Flame Temperature

- Thermodynamically, it is possible to define two adiabatic flame temperature: one at constant pressure and the other at constant volume.
- If a fuel-air mixture burns adiabatically at constant pressure, the absolute enthalpy of the reactants at initial state is equal to the absolute enthalpy of products at final state. It follows from first law of thermodynamics. A constant pressure based combustion is approximated in gas turbine combustor/furnace.

$$\dot{Q}_{CV}-\dot{W}_{CV}=\dot{m}\left[\left(h_0-h_i\right)+\frac{1}{2}\left(V_0^2-V_i^2\right)+g\left(z_0-z_i\right)\right]\Rightarrow \dot{m}h_0=\dot{m}h_i$$

$$\Rightarrow \underline{H_R\left(T_i,p\right)=H_p\left(T_{ad},p\right)} \quad \text{or} \quad h_R\left(T_i,p\right)=h_p\left(T_{ad},p\right)$$

$$\underline{H_R\left(T_i,p\right)}=\sum_R n_i\bar{h}_i$$

$$\underline{H_P\left(T_{ad},p\right)}=\sum_P n_i\left[\bar{h}_f^0+\bar{c}_{p,i}\left(T_{ad}-T_{ref}\right)\right]$$

T_i : Initial temperature

T_{ad} : Adiabatic flame temperature

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

$\bar{c}_{p,i}$: Specific heat at constant pressure

So, let us see how we can do that. So, there are two ways to view this adiabatic flame temperatures, one can say that the reaction can take place at constant pressure or the reaction can take place at constant volume.

This is similar to a philosophy that constant pressure based combustion in a diesel engine and constant volume combust combustion in a SI engine. So, with this we are going to model this adiabatic flame temperatures. So, first case let us analyze a situation, where adiabatic flame temperature is reached through a constant pressure process.

So, if a fuel air mixtures burns adiabatically at constant pressure, the absolute enthalpy of the reactants at the initial state is equal to absolute enthalpy of products at the final states. So, this is the conditions what we do, what we derived in our last slide and this also follows from the first law of thermodynamics.

So, the very basic expression that we can see $H_R(T_i,p) = H_p(T_{ad},p)$. Then we can evaluate the total enthalpy of the reactants and total enthalpy of the products. So, this can be represented as a functional form, like one can represent enthalpy as a function of temperatures.

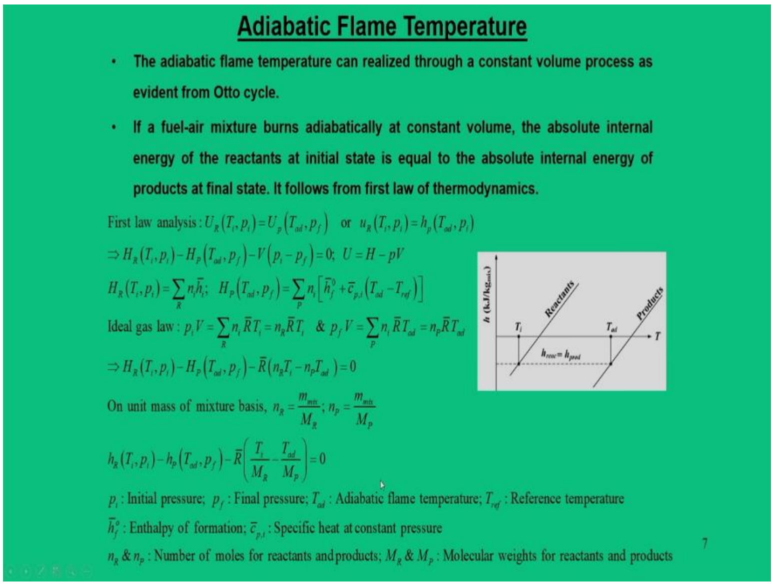
So, these reactants can have many number of species and this species will have different enthalpies at different temperatures. Let us say all the reactants, when they are at initial state T_i and at that temperature corresponding enthalpy value of combustion, of course, it is negative that is what this is in positive side and this is in negative side and this number is this point.

Now, when the reaction proceeds at one point of time, the products are completely formed and when these products are completely formed and the process is completely an adiabatic process, the temperature that it released is adiabatic flame temperatures. And at that point of time we expect that the enthalpy of reactants and products should be equal.

So, you can draw a horizontal line starting from this initial point and wherever it reaches this product, we can estimate this adiabatic flame temperature. So, this is all about how you can represent in graphically, but theoretically we can represent these things, like for reactants all the enthalpy has to be evaluated at the initial conditions $H_R(T_i, p) = \sum_R n_i \bar{h}_i$, for products all the enthalpies values will be decided at adiabatic flame temperatures and at that pressure and which is nothing but the function of the enthalpy of formations and Cp times difference in the temperatures, for all the constituents.

$$H_P(T_{ad}, p) = \sum_P n_i\left[\bar{h}_f^0 + \bar{c}_{p,i}\left(T_{ad} - T_{ref}\right)\right]$$

(Refer Slide Time: 09:56)



Adiabatic Flame Temperature

- **The adiabatic flame temperature can realized through a constant volume process as evident from Otto cycle.**
- **If a fuel-air mixture burns adiabatically at constant volume, the absolute internal energy of the reactants at initial state is equal to the absolute internal energy of products at final state. It follows from first law of thermodynamics.**

First law analysis: $U_R(T_i, p_i) = U_p(T_{ad}, p_f)$ or $u_R(T_i, p_i) = h_p(T_{ad}, p_i)$

$\Rightarrow H_R(T_i, p_i) - H_P(T_{ad}, p_f) - V(p_i - p_f) = 0;\ U = H - pV$

$H_R(T_i, p_i) = \sum_R n_i \bar{h}_i;\ \ H_P(T_{ad}, p_f) = \sum_P n_i\left[\bar{h}_f^0 + \bar{c}_{p,i}\left(T_{ad} - T_{ref}\right)\right]$

Ideal gas law: $p_i V = \sum_R n_i \bar{R} T_i = n_R \bar{R} T_i$ & $p_f V = \sum_P n_i \bar{R} T_{ad} = n_P \bar{R} T_{ad}$

$\Rightarrow H_R(T_i, p_i) - H_P(T_{ad}, p_f) - \bar{R}(n_R T_i - n_P T_{ad}) = 0$

On unit mass of mixture basis, $n_R = \frac{m_{mix}}{M_R};\ n_P = \frac{m_{mix}}{M_P}$

$h_R(T_i, p_i) - h_P(T_{ad}, p_f) - \bar{R}\left(\frac{T_i}{M_R} - \frac{T_{ad}}{M_P}\right) = 0$

p_i: Initial pressure; p_f: Final pressure; T_{ad}: Adiabatic flame temperature; T_{ref}: Reference temperature

$\bar{h}_f^o$: Enthalpy of formation; $\bar{c}_{p,i}$: Specific heat at constant pressure

n_R & n_P: Number of moles for reactants and products; M_R & M_P: Molecular weights for reactants and products

7

This is what we view the adiabatic flame temperature for a constant pressure process. Now, we will move on to constant volume process and here the concept is same but pressure is no longer the same. Pressure will not be same, but volume remains same; that means, reaction takes at constant volume; its like a closed system. So, here the fuel air mixture burns adiabatically at constant volume, the absolute internal energy of the reactants at initial state is equal to the absolute internal energy of the products at the final stage.

So, what really matters here is internal energy balance you have to do for reactants and products. Now, here if you look at this reactants, the reactants are at initial pressure p_i and temperature T_i, while products are formed at final pressure p_f and its adiabatic flame temperatures. Then what you do? Normally it is difficult to calculate the internal energy. So, you have to find this internal energy through enthalpy route, because enthalpy data table it is available to us.

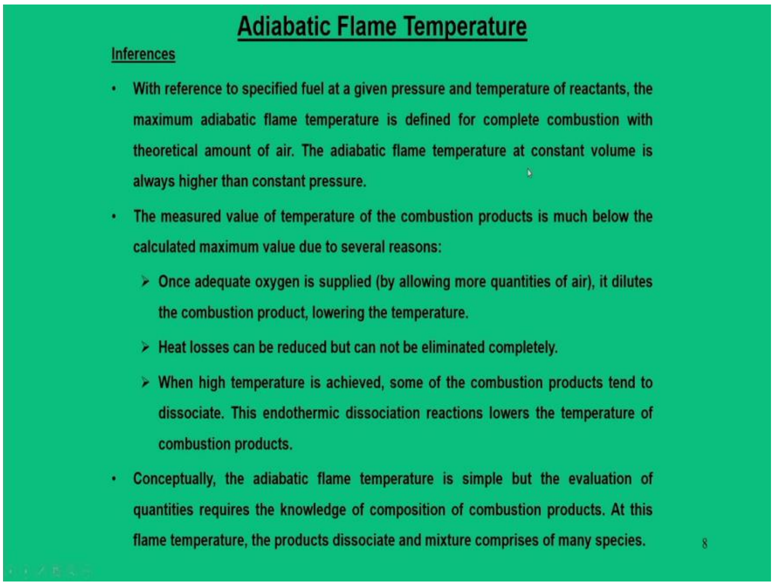
So, you can get it through enthalpy information. So, $U = H - pV$ and pressure you know because the pressure is a measurable quantity and volume is also measurable quantity. So, that equations when you put $U = H - pV$ and what remains same is your volume remains same. So, it is a pressure $p_f - p_i$. So, the equation now becomes simple. So, here the similar philosophy the enthalpy of reactants has to be evaluated at the initial conditions and for products, you have to find it through enthalpy of formation with cp information and change in the temperatures.

Then we also assume that reactants and products form an ideal gas mixtures. So, we can use the ideal gas law. Now, to use this ideal gas law through this, we should be able to correlate the pressure volume as a function of its number of moles of reactants and the initial temperatures and similarly for products number of moles for the products and with its adiabatic flame temperatures.

By putting all these things, the working equation now becomes $h_R(T_i, p_i) - h_P(T_{ad}, p_f) - \bar{R}\left(\frac{T_i}{M_R} - \frac{T_{ad}}{M_P}\right) = 0$. So, T_i and T_{ad} is their temperatures at initial condition and adiabatic conditions, final temperature and n_R and n_P are number of moles per reactants and products.

And we can also use them through their mass fraction analysis, by converting moles into mass. So, if you do this, the workable equations becomes through this enthalpy information through their molecular weight, for reactants and products.

(Refer Slide Time: 12:53)



Adiabatic Flame Temperature

Inferences

- With reference to specified fuel at a given pressure and temperature of reactants, the maximum adiabatic flame temperature is defined for complete combustion with theoretical amount of air. The adiabatic flame temperature at constant volume is always higher than constant pressure.
- The measured value of temperature of the combustion products is much below the calculated maximum value due to several reasons:
  - Once adequate oxygen is supplied (by allowing more quantities of air), it dilutes the combustion product, lowering the temperature.
  - Heat losses can be reduced but can not be eliminated completely.
  - When high temperature is achieved, some of the combustion products tend to dissociate. This endothermic dissociation reactions lowers the temperature of combustion products.
- Conceptually, the adiabatic flame temperature is simple but the evaluation of quantities requires the knowledge of composition of combustion products. At this flame temperature, the products dissociate and mixture comprises of many species.

Now, this is the overall philosophy of adiabatic flame temperatures. If you want to draw certain inferences what message it gives for a reaction? First thing it gives is that although adiabatic flame temperature is a theoretical number and in fact, it is difficult to achieve in a reaction process, but it gives an estimate that during a combustion process what is the maximum temperature that we can achieve during a reaction.

So, with reference to a specific fuel at given pressure and temperature of reactants, the maximum adiabatic flame temperature is defined for a complete combustions with theoretical amount of air. Now, we define this adiabatic flame temperatures at two situations, at constant pressure and constant volume. Always we will see that at constant volume, adiabatic flame temperature is always higher than that of constant pressure. That is mainly because we are not allowing this heat to go out of the system or the reactor.

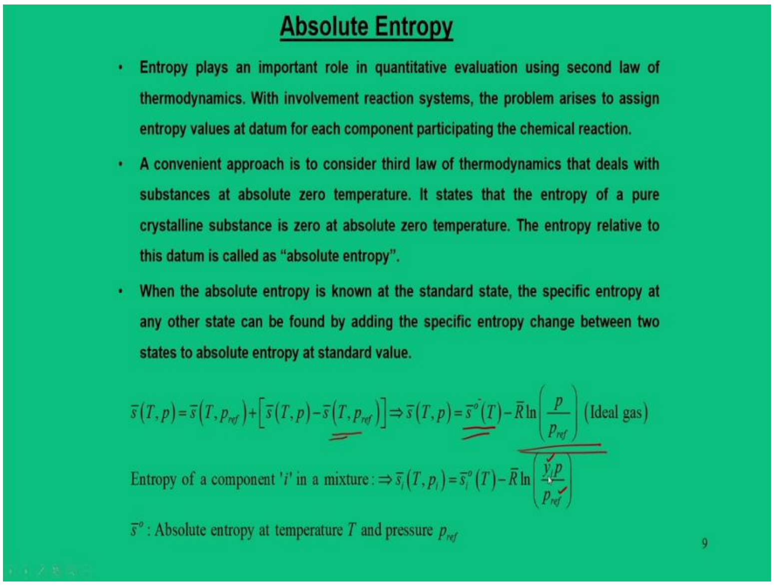
Although this is a theoretical number, but the measured value of temperature during combustion products is much below the calculated maximum values. That means, always for the reaction we can predict this should be the adiabatic flame temperature, but actual measured value will be always less, even several degrees less.

That is because for several reasons first once adequate oxygen is supplied, by allowing more quantities of air; that means, we expect the reaction to be complete or say complete combustions; that means, you should be able to supply sufficient quantity of air just to make a complete combustions.

So, when you do this, it dilutes the combustion products and thus lowers the temperatures. While modeling adiabatic temperature, we say it is an adiabatic modeling by putting insulations, but through this insulation it is possible to reduce heat, but it cannot be eliminated completely. Now, when the high temperature is achieved for example, when the combustion products are formed and high temperature is achieved there are some products which can tend to dissociate.

Now, when they dissociate, the endothermic dissociation reaction lowers the temperature of the products. So, these are the reasons, but conceptually the adiabatic flame temperature is a simple, but its evaluation requires the knowledge of the composition of combustion products. At this flame temperatures, always the products dissociate and they form many species.

(Refer Slide Time: 15:38)



Absolute Entropy

- Entropy plays an important role in quantitative evaluation using second law of thermodynamics. With involvement reaction systems, the problem arises to assign entropy values at datum for each component participating the chemical reaction.
- A convenient approach is to consider third law of thermodynamics that deals with substances at absolute zero temperature. It states that the entropy of a pure crystalline substance is zero at absolute zero temperature. The entropy relative to this datum is called as "absolute entropy".
- When the absolute entropy is known at the standard state, the specific entropy at any other state can be found by adding the specific entropy change between two states to absolute entropy at standard value.

$$\bar{s}(T,p)=\bar{s}(T,p_{ref})+\left[\bar{s}(T,p)-\bar{s}(T,p_{ref})\right]\Rightarrow\bar{s}(T,p)=\bar{s}^{o}(T)-\bar{R}\ln\left(\frac{p}{p_{ref}}\right)\text{ (Ideal gas)}$$

$$\text{Entropy of a component '}i\text{' in a mixture}:\Rightarrow\bar{s}_i(T,p_i)=\bar{s}_i^{o}(T)-\bar{R}\ln\left(\frac{y_i p}{p_{ref}}\right)$$

$\bar{s}^{o}$: Absolute entropy at temperature T and pressure p_{ref}

Now, having said this next target that we are going to discuss the concept of absolute entropy. So, previously we have also talked about information during a combustion reaction, we find how enthalpy needs to be calculated, internal energy needs to be calculated. Here we will try to emphasize how entropy will be going to be calculated.

And because entropy word comes from the second law of thermodynamics and it will tell us whether in which direction the reaction is going to proceed. So, the entropy plays an important role in the quantitative evaluation using the second law.

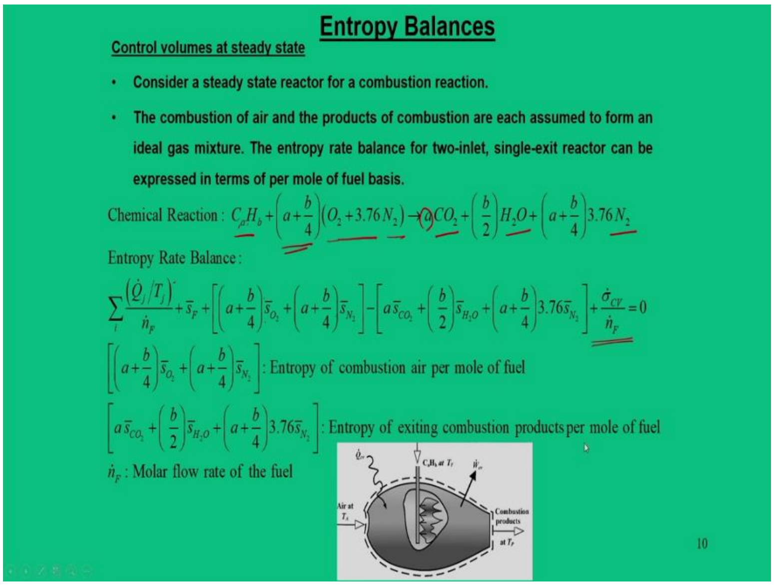
With the involvement of reacting system the main problem that arises is to assign the absolute entropy values with respect to datum or certain datum conditions. To this datum conditions for entropy is considered at absolute 0 temperatures and that is nothing but your third law of thermodynamics. So, the entropy value related to this datum is called as "absolute entropy".

Now, when this absolute entropy is known at the standard state, the specific entropy at other state can be found out by adding specific entropy change. So, this is the expression that is represented here. Now, in a combustion process how you are going to calculate this entropy, first thing entropy on a molar basis, if you need to entropy at certain pressure and temperatures. First we have to find out what is the reference entropy.

And this reference entropy and reference pressure and temperature, it has to be found out through absolute entropy, that means, there you talk about enthalpy of formation, here we will talk about absolute entropy is zero which is a function of temperature only, there is no requirement of pressure because the third laws thermodynamics says that pressure has no role at absolute zero. So, that point of time we can say the entropy that is calculated it is $\bar{s}^o(T)$ and this other reference state that can be approximated that is $\bar{R}\, ln\left(\frac{p}{p_{ref}}\right)$.

So, this we can get it from ideal gas through an ideal gas relations. Now, we know that typically reference pressure is known and total pressure will be known, but we do not know the respective composition or mole fractions. So, for entropy of a component 'i' in the mixture can be calculated by knowing its mole fraction. So, this is the workable formula for entropy $\bar{s}_i(T, p_i) = \bar{s}_i^o(T) - \bar{R}\ln\left(\frac{y_i p}{p_{ref}}\right)$.

(Refer Slide Time: 18:30)



Entropy Balances

Control volumes at steady state

- Consider a steady state reactor for a combustion reaction.
- The combustion of air and the products of combustion are each assumed to form an ideal gas mixture. The entropy rate balance for two-inlet, single-exit reactor can be expressed in terms of per mole of fuel basis.

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

Entropy Rate Balance:

$$\sum_j \frac{(\dot{Q}_j/T_j)}{\dot{n}_F} + \bar{s}_F + \left[\left(a+\frac{b}{4}\right)\bar{s}_{O_2} + \left(a+\frac{b}{4}\right)\bar{s}_{N_2}\right] - \left[a\bar{s}_{CO_2} + \left(\frac{b}{2}\right)\bar{s}_{H_2O} + \left(a+\frac{b}{4}\right)3.76\bar{s}_{N_2}\right] + \frac{\dot{\sigma}_{CV}}{\dot{n}_F} = 0$$

$\left[\left(a+\frac{b}{4}\right)\bar{s}_{O_2} + \left(a+\frac{b}{4}\right)\bar{s}_{N_2}\right]$: Entropy of combustion air per mole of fuel

$\left[a\bar{s}_{CO_2} + \left(\frac{b}{2}\right)\bar{s}_{H_2O} + \left(a+\frac{b}{4}\right)3.76\bar{s}_{N_2}\right]$: Entropy of exiting combustion products per mole of fuel

$\dot{n}_F$: Molar flow rate of the fuel

Now, when you have information about entropy, then you can make this entropy balance. There are two types of equations for entropy balance, one is control volume at steady state, other is the closed system entropy. So, when you consider a steady state reactor for a combustion system, we assume that air and products of combustion each are assumed to form ideal gas mixture. In this case for an 2 inlet single exit reactor systems, they can be expressed in terms of per mole of fuel basis.

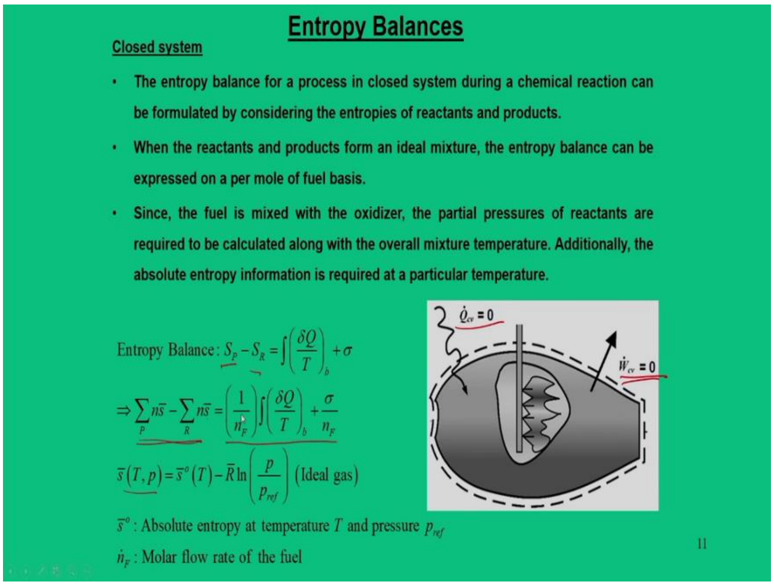
So, a chemical reaction that takes place we have fuel and we have air, they mix together with their appropriate molar basis. We get $aCO_2 + \left(\frac{b}{2}\right)H_2O + \left(a+\frac{b}{4}\right)3.76N_2$. Now, for this we need to find out the entropy balance.

So, entropy balance that can be calculated if you can recall this entropy balance equations, first is entropy through heat transfer. So, we have to find the different routes how heat transfer takes place at a given temperature and per mole of fuel that can be calculated by dividing it then $\bar{s}_F$; that means, entropy of this formation for fuel, then in this case other components that are there is like here we have O$_2$, we have N$_2$.

$$\sum_i \frac{\left(\frac{\dot{Q}_j}{T_j}\right)}{\dot{n}_F} + \bar{s}_F + \left[\left(a+\frac{b}{4}\right)\bar{s}_{O_2} + \left(a+\frac{b}{4}\right)\bar{s}_{N_2}\right] - \left[a\bar{s}_{CO_2} + \left(\frac{b}{2}\right)\bar{s}_{H_2O} + \left(a+\frac{b}{4}\right)3.76\bar{s}_{N_2}\right] + \frac{\dot{\sigma}_{CV}}{\dot{n}_F} = 0$$

So, this number is for this fuel and this number is for O2 and this coefficients are for nitrogen. Similarly, in the right hand side expressions are given as a minus number. So, you can write this and finally, last term refers to the entropy production rate for control volume. And what we have the information is entropy of combustion of air per mole of the fuel, entropy of the existing combustion products per mole of the fuel.

(Refer Slide Time: 20:43)



Entropy Balances

Closed system

- The entropy balance for a process in closed system during a chemical reaction can be formulated by considering the entropies of reactants and products.
- When the reactants and products form an ideal mixture, the entropy balance can be expressed on a per mole of fuel basis.
- Since, the fuel is mixed with the oxidizer, the partial pressures of reactants are required to be calculated along with the overall mixture temperature. Additionally, the absolute entropy information is required at a particular temperature.

Entropy Balance: $S_P - S_R = \int \left(\frac{\delta Q}{T}\right)_b + \sigma$

$\Rightarrow \sum_P n\bar{s} - \sum_R n\bar{s} = \left(\frac{1}{n_F}\right)\int \left(\frac{\delta Q}{T}\right)_b + \frac{\sigma}{n_F}$

$\bar{s}(T,p) = \bar{s}^{o}(T) - \bar{R}\ln\left(\frac{p}{p_{ref}}\right)$ (Ideal gas)

$\bar{s}^{o}$: Absolute entropy at temperature T and pressure p_{ref}

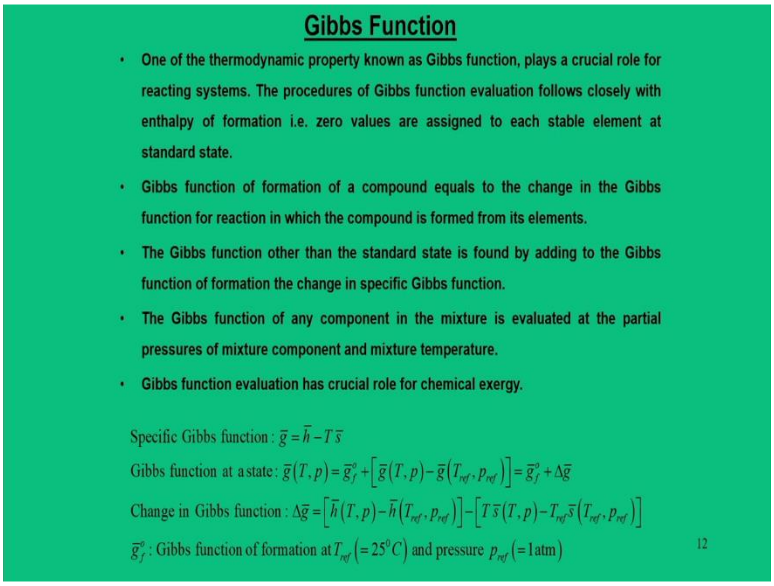
$\dot{n}_F$: Molar flow rate of the fuel

Now, same things when you assign that there is no work transfer, no heat transfer and it is a closed system, then we can write it as entropy for the closed systems as $S_P - S_R = \int \left(\frac{\delta Q}{T}\right)_b + \sigma$. And then this equation can be per products and reactants, they can be summed up with their respective number of moles. And we also can find out the right hand expressions per mole of fuel and $\bar{s}(T,p)$ through information of absolute entropy.

$$\sum_P n\bar{s} - \sum_R n\bar{s} = \left(\frac{1}{n_F}\right)\int \left(\frac{\delta Q}{T}\right)_b + \frac{\sigma}{n_F}$$

$$\bar{s}(T,p) = \bar{s}^o(T) - \bar{R}\ln\left(\frac{p}{p_{ref}}\right) \text{(Idealgas)}$$

(Refer Slide Time: 21:29)



Gibbs Function

- One of the thermodynamic property known as Gibbs function, plays a crucial role for reacting systems. The procedures of Gibbs function evaluation follows closely with enthalpy of formation i.e. zero values are assigned to each stable element at standard state.
- Gibbs function of formation of a compound equals to the change in the Gibbs function for reaction in which the compound is formed from its elements.
- The Gibbs function other than the standard state is found by adding to the Gibbs function of formation the change in specific Gibbs function.
- The Gibbs function of any component in the mixture is evaluated at the partial pressures of mixture component and mixture temperature.
- Gibbs function evaluation has crucial role for chemical exergy.

Specific Gibbs function : $\bar{g} = \bar{h} - T\bar{s}$

Gibbs function at a state: $\bar{g}(T,p) = \bar{g}_f^o + \left[\bar{g}(T,p) - \bar{g}(T_{ref}, p_{ref})\right] = \bar{g}_f^o + \Delta\bar{g}$

Change in Gibbs function : $\Delta\bar{g} = \left[\bar{h}(T,p) - \bar{h}(T_{ref}, p_{ref})\right] - \left[T\bar{s}(T,p) - T_{ref}\bar{s}(T_{ref}, p_{ref})\right]$

$\bar{g}_f^o$: Gibbs function of formation at $T_{ref}\left(=25^0 C\right)$ and pressure $p_{ref}\left(=1\text{atm}\right)$

And the last segment of this chemical reaction is the Gibbs functions, the word Gibbs function comes into picture when you dealt with the thermodynamic property relations. And in fact, this Gibbs function has a very vital or important role in the reacting systems and this information is also similar to what we do it with for enthalpy.

So, this Gibbs function of formation of a compound is equal to the change in the Gibbs function for the reaction in which the compound is formed from this element. And this Gibbs function treatment is almost similar to what we do it for enthalpies. So, the information that is required is the enthalpy of formation plus enthalpy change. Here also same thing, Gibbs function of formation and Gibbs function change between any given state with respect to its reference states.

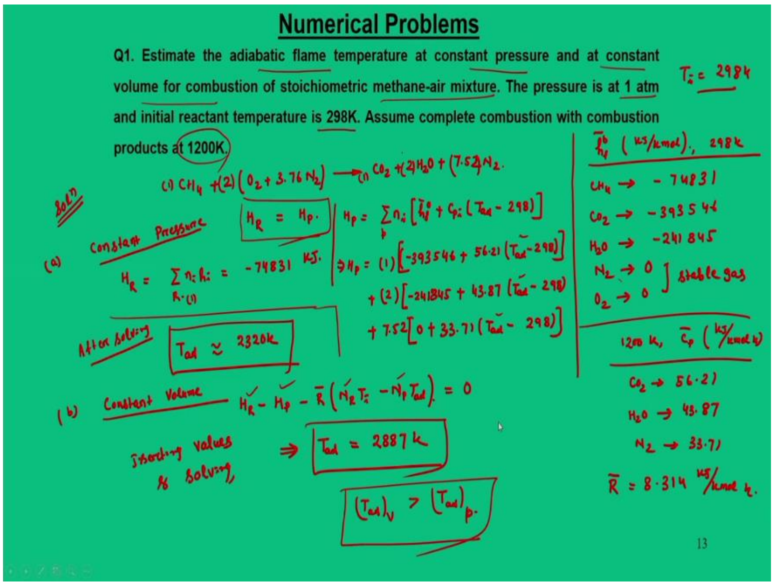
So, if you can recall this Gibbs function $\bar{g} = \bar{h} - T\bar{s}$ and this Gibbs function when you calculate they can also be evaluated through this enthalpy route. Through this process we can find out this Gibbs function with respect to molar basis, Gibbs function at given temperature at pressure with knowledge of Gibbs function of formation and this gives function change and this Gibbs function change can be found out from this enthalpy and temperature and entropy.

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

$$\Delta\bar{g} = \left[\bar{h}(T,p) - \bar{h}\left(T_{ref}, p_{ref}\right)\right] - \left[T\bar{s}(T,p) - T_{ref}\bar{s}\left(T_{ref}, p_{ref}\right)\right]$$

So, to calculate this Gibbs function, we also know the information of enthalpy and entropy. Another point I need to emphasize that this Gibbs function evaluation plays a very crucial role for chemical exergy and which will not be covering in this particular course. But chemical exergy is very important point for the learners, who are in the areas of chemical engineering. With this we complete this lecture and based on this content of this lecture, we will try to solve some of the numerical problems.

(Refer Slide Time: 23:45)



Numerical Problems

Q1. Estimate the adiabatic flame temperature at constant pressure and at constant volume for combustion of stoichiometric methane-air mixture. The pressure is at 1 atm and initial reactant temperature is 298K. Assume complete combustion with combustion products at 1200K.

$T_i = 298\text{K}$

Solⁿ

$(1)\,CH_4 + (2)(O_2 + 3.76N_2) \rightarrow (1)\,CO_2 + (2)H_2O + (7.52)N_2.$

(a) Constant Pressure

$\boxed{H_R = H_p.}$

$H_R = \sum_{R\cdot(1)} n_i h_i = -74831$ kJ.

$H_p = \sum_p n_i\left[\bar{h}_f^o + C_{p_i}(T_{ad} - 298)\right]$

$\Rightarrow H_p = (1)\left[-393546 + 56.21(T_{ad} - 298)\right]$

$+ (2)\left[-241845 + 43.87(T_{ad} - 298)\right]$

$+ 7.52\left[0 + 33.71(T_{ad} - 298)\right]$

After solving $\boxed{T_{ad} \simeq 2320\text{K}}$

(b) Constant Volume $H_R - H_P - \bar{R}(N_R T_i - N_P T_{ad}) = 0$

Inserting values & solving, $\Rightarrow \boxed{T_{ad} = 2887\text{K}}$

$\boxed{(T_{ad})_V > (T_{ad})_P.}$

$\bar{h}_f^o$ (kJ/kmol), 298K

$CH_4 \rightarrow -74831$

$CO_2 \rightarrow -393546$

$H_2O \rightarrow -241845$

$N_2 \rightarrow 0$] stable gas

$O_2 \rightarrow 0$

1200 K, $\bar{C}_p$ (kJ/kmol K)

$CO_2 \rightarrow 56.21$

$H_2O \rightarrow 43.87$

$N_2 \rightarrow 33.71$

$\bar{R} = 8.314$ kJ/kmol K.

So, the first problem is about this calculation of adiabatic flame temperature at constant pressure and constant volume during a combustion process for a methane air mixture. And the conditions that are given is initial conditions are one atmosphere and 298 kelvin and complete combustion process. But the combustion product temperature T_p is 1200 kelvin, this information is required mainly because all the properties needs to be evaluated at this temperature.

To solve this problem and there are two cases, one is constant pressure case, other is the constant volume case. So, before you do that first thing that you need to write what is methane air combustions.

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

Now, for this reaction we know that this is 1 mole, this is 2 mole and here also 1 mole and here 2 mole and this is 7.52 mole.

So, Case 1 we say constant pressure.

$\bar{h}_f^o \left(\frac{kJ}{kmol}\right)$ @ 298 K	$\bar{c}_{p,i} \left(\frac{kJ}{kmol}\right)$ @ 1200 K
$CH_4 \rightarrow -74831$	$CO_2 \rightarrow 56.21$
$CO_2 \rightarrow -393546$	$H_2O \rightarrow 43.87$
$H_2O \rightarrow -241845$	$N_2 \rightarrow 33.71$
$N_2 \rightarrow$ 0 (Stable gas)	
$O_2 \rightarrow$ 0 (Stable gas)	

$$H_R(T_i, p) = H_p(T_{ad}, p)$$

$$H_R(T_i, p) = \sum_R n_i \bar{h}_i = -74831 \times 1 = -74831\ kJ$$

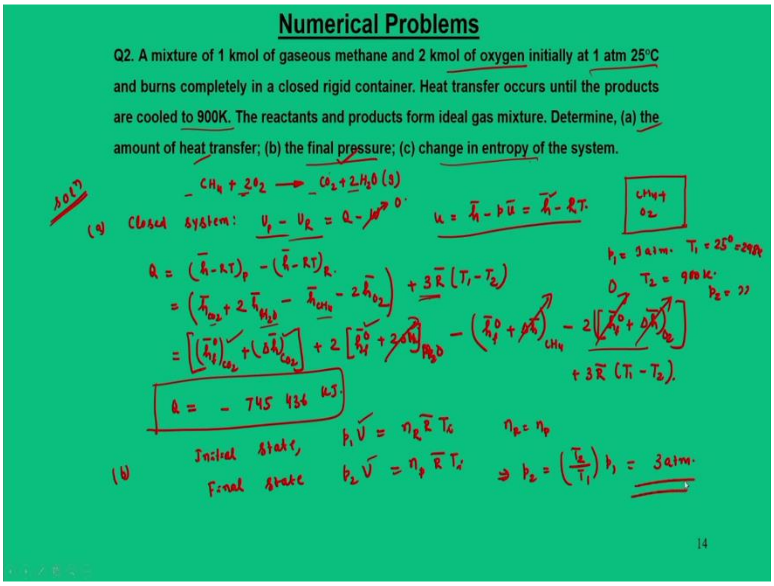
$$\begin{aligned} H_P(T_{ad}, p) &= \sum_P n_i\left[\bar{h}_f^0 + \bar{c}_{p,i}(T_{ad} - 298)\right] \\ &= (1)[-393546 + 56.21(T_{ad} - 298)] \\ &+ (2)[-241845 + 43.87(T_{ad} - 298)] \\ &+ (7.52)[0 + 33.71(T_{ad} - 298)] \end{aligned}$$

$$Upon\ solving, H_R(T_i, p) = H_p(T_{ad}, p); T_{ad} = 2320\ K$$

Now, by using the same data we are going to find out what is the adiabatic flame temperature at constant volume. So, for constant volume, $H_R(T_i, p_i) - H_P\left(T_{ad}, p_f\right) - \bar{R}(n_R T_i - n_P T_{ad}) = 0$. This is the working equation that we derived in our earlier slides. All the information of H_R and H_P are known to us, number of moles reactants and products also known to us from this equations. Initial temperature T_i is known. So, adiabatic temperature is unknown. And $\bar{R} = 8.314\ kJ/kmol - K$

So, by inserting this values and solving we can reach that this will imply that T adiabatic flame temperature is 2887 K. So, if you can closely write all these equations separately and in this equation all the parameters are known except the unknown parameters is T adiabatic. So, we can put it and find this. So, what you see here T adiabatic at constant volume is greater than T adiabatic at constant pressures. So, this is about the adiabatic flame temperatures.

(Refer Slide Time: 32:45)



Numerical Problems

Q2. A mixture of 1 kmol of gaseous methane and 2 kmol of oxygen initially at 1 atm 25°C and burns completely in a closed rigid container. Heat transfer occurs until the products are cooled to 900K. The reactants and products form ideal gas mixture. Determine, (a) the amount of heat transfer; (b) the final pressure; (c) change in entropy of the system.

Sol^n

$CH_4 + 2O_2 \longrightarrow CO_2 + 2H_2O\,(g)$

(a) Closed system: $U_p - U_R = Q - \cancel{W}^{\,0}$ $\qquad u = \bar{h} - p\bar{v} = \bar{h} - \bar{R}T$

$\boxed{CH_4 + O_2}$

$p_1 = 1\,atm$. $T_1 = 25^\circ = 298\,K$

$T_2 = 900\,K$.

$p_2 = ??$

$Q = (\bar{h} - RT)_p - (\bar{h} - RT)_R$

$= (\bar{h}_{CO_2} + 2\bar{h}_{H_2O} - \bar{h}_{CH_4} - 2\bar{h}_{O_2}) + 3\bar{R}(T_1 - T_2)$

$= [(\bar{h}_f^0)_{CO_2} + (\Delta\bar{h})_{CO_2}] + 2[\bar{h}_f^0 + \cancel{\Delta\bar{h}}]_{H_2O} - (\bar{h}_f^0 + \cancel{\Delta\bar{h}})_{CH_4} - 2[\cancel{\bar{h}_f^0} + \cancel{\Delta\bar{h}}]_{O_2} + 3\bar{R}(T_1 - T_2)$.

$\boxed{Q = -745\ 436\ kJ}$

(b) Initial state, $p_1\bar{V} = n_R\bar{R}T_1$ $\qquad n_R = n_p$

Final state $p_2\bar{V} = n_p\bar{R}T_2$ $\qquad \Rightarrow p_2 = \left(\frac{T_2}{T_1}\right)p_1 = 3\,atm$.

14

Now, next question we are going to solve about the entropy evaluation during a reaction process. So, this problem will give you understanding about entropy evaluation in a closed system. So, to do that, let us first find out what is the reaction, this is a methane oxygen reactions. So, same issue that is same reaction, here there is no nitrogen.

$$CH_4 + 2(O_2) \to CO_2 + 2H_2O\ (g)$$

Heat transfer occurs till the products are cooled to 900 K. So, you can imagine that the reaction is happening in a closed systems of CH_4 and O_2 and the products are formed, initial condition is P is 1 atmosphere, T is 25 C that is 298 K and final product T_2 that reaches is 900 K, p_2 we need to calculate, what is the final pressure. On top of that we are find out the heat transfer because for entropy calculation also we require heat transfer.

So, first part we can directly write the equation for closed system,

$$U_p - U_R = Q - W\ ; Here\ W = 0\ and\ u = \bar{h} - p\bar{v} = \bar{h} - \bar{R}T$$

$$Q = \left(\bar{h} - RT\right)_p - \left(\bar{h} - RT\right)_R = \left(\bar{h}_{CO_2} + 2\bar{h}_{H_2O} - \bar{h}_{CH_4} - 2\bar{h}_{O_2}\right) + 3\bar{R}(T_1 - T_2)$$

$$Q = \left(\bar{h}_f^o + \Delta\bar{h}\right)_{CO_2} + 2\left(\bar{h}_f^o + \Delta\bar{h}\right)_{H_2O} - \left(\bar{h}_f^o + \Delta\bar{h}\right)_{CH_4} - 2\left(\bar{h}_f^o + \Delta\bar{h}\right)_{O_2} + 3\bar{R}(T_1 - T_2)$$

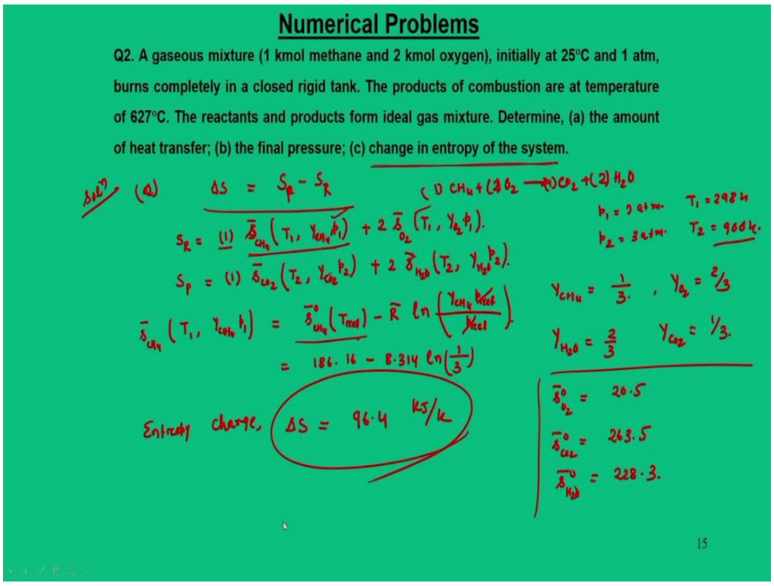
Now, here we need to now try to see which needs to be ignored and oxygen is a stable component. So, $\bar{h}_f^o$ is ignored, $\Delta\bar{h}$ is also ignored everywhere except CH_4 because that is the reactants and products are at same initial temperatures, CH_4 and O_2. Then what we does not know is this. So, using this data table we need to find this information and please refer my earlier slides for these numbers. Then you calculate Q as -745436 kJ.

Second part is final pressure. Now, to calculate the final pressures we require the ideal gas equations.

$$Initial\ state: p_1\bar{v} = n_R\bar{R}T_1; Final\ state: p_2\bar{v} = n_R\bar{R}T_2; as\ n_R = n_P$$

$$So, p_2 = \left(\frac{T_2}{T_1}\right)p_1 = 3\ atm$$

(Refer Slide Time: 39:29)



Numerical Problems

Q2. A gaseous mixture (1 kmol methane and 2 kmol oxygen), initially at 25°C and 1 atm, burns completely in a closed rigid tank. The products of combustion are at temperature of 627°C. The reactants and products form ideal gas mixture. Determine, (a) the amount of heat transfer; (b) the final pressure; (c) change in entropy of the system.

Sol^n (a)

$\Delta S = S_P - S_R$

$(1)\, CH_4 + (2)\, O_2 \rightarrow (1)\, CO_2 + (2)\, H_2O$

$p_1 = 1$ atm. $T_1 = 298$ K

$p_2 = 3$ atm. $T_2 = 900$ K.

$S_R = (1)\,\bar{s}_{CH_4}(T_1, y_{CH_4}p_1) + 2\,\bar{s}_{O_2}(T_1, y_{O_2}p_1).$

$S_P = (1)\,\bar{s}_{CO_2}(T_2, y_{CO_2}p_2) + 2\,\bar{s}_{H_2O}(T_2, y_{H_2O}p_2).$

$y_{CH_4} = \frac{1}{3}.\ ,\ y_{O_2} = 2/3$

$y_{H_2O} = \frac{2}{3}\quad y_{CO_2} = 1/3.$

$\bar{s}_{CH_4}(T_1, y_{CH_4}p_1) = \bar{s}^o_{CH_4}(T_{ref}) - \bar{R}\ln\left(\frac{y_{CH_4}\cancel{p_{ref}}}{\cancel{p_{ref}}}\right).$

$= 186.16 - 8.314\ln\left(\frac{1}{3}\right)$

Entropy change, $\boxed{\Delta S = 96.4\ kJ/K}$

$\bar{s}^o_{O_2} = 20.5$

$\bar{s}^o_{CO_2} = 263.5$

$\bar{s}^o_{H_2O} = 228.3.$

Then last part of this is, which we emphasized in this particular lecture, how to calculate this entropy. So, entropy evaluation requires that what is the final product entropy and what is the final reactant entropy, that is entropy of products minus entropy of reactants. So, this will give you the entropy change for this closed systems.

$$Given: p_1 = 1\ atm; p_2 = 3\ atm; T_1 = 298\ K, T_2 = 900\ K$$

$$Y_{CH_4} = \frac{1}{3}; Y_{O_2} = \frac{2}{3}; Y_{H_2O} = \frac{2}{3}; Y_{CO_2} = \frac{1}{3};\ \bar{s}^o_{CH_4} = 186.16;\ \bar{s}^o_{O_2} = 20.5;\ \bar{s}^o_{CO_2} = 263.5;\ \bar{s}^o_{H_2O} = 228.3$$

$$\Delta S = S_P - S_R = \bar{s}_{CO_2}(T_2, Y_{CO_2}p_2) + 2\bar{s}_{H_2O}(T_2, Y_{H_2O}p_2) - \bar{s}_{CH_4}(T_1, Y_{CH_4}p_1) - 2\bar{s}_{O_2}(T_1, Y_{O_2}p_1)$$

$$\bar{s}_{CH_4}(T_1, Y_{CH_4}p_1) = \bar{s}^o_{CH_4}(T\_ref) - \bar{R}\, ln\left(\frac{y_i p_{ref}}{p_{ref}}\right)$$

So, we are putting all these numbers and calculating each term, we can find out this entropy change ΔS as 96.4 kJ/K. So, in our previous lectures I emphasized how you are going to calculate change in the enthalpy in a reacting systems. In this particular lecture through this problem, I have made this calculations that how you are going to calculate the change in the entropy in a reacting systems.

Also, we have demonstrated during a chemical reactions what is the maximum possible temperature and that we calculated as adiabatic flame temperature one at constant pressure other at constant volume. So, with this I conclude this lecture.

Thank you for your attention.