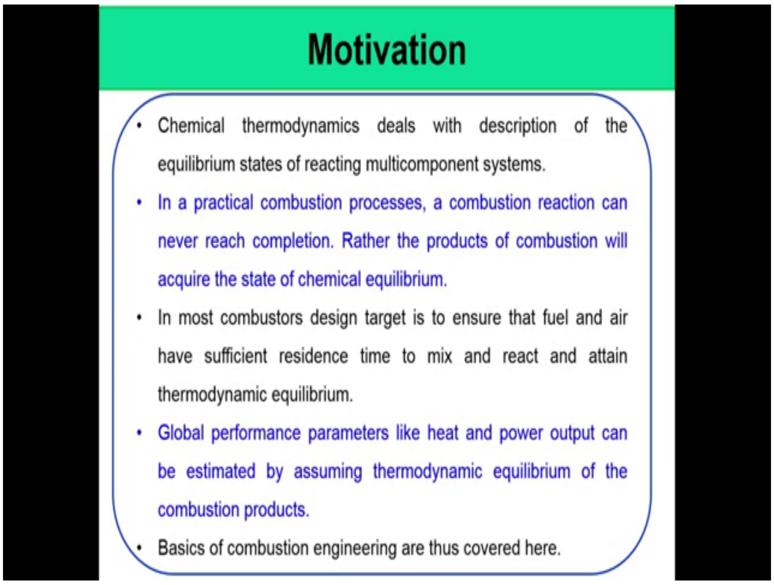
Combustion in Air Breathing Aero Engines
Dr. Swetaprovo Chaudhuri
Department of Aerospace Engineering
Indian Institute of Science, Bangalore

Lecture – 03
Chemical Equilibrium II

So, welcome back we were talking about a chemical thermodynamics.

Student: sir, you can start from the first sir.

(Refer Slide Time: 00:32)

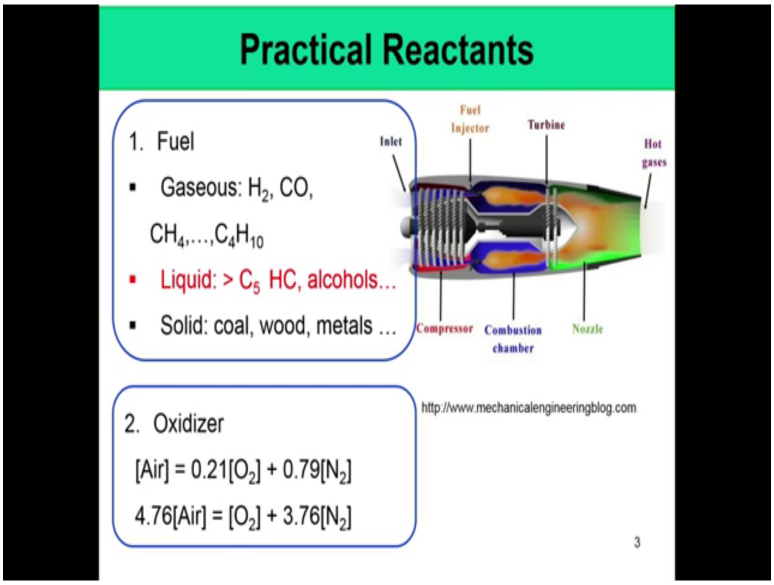


Motivation

- Chemical thermodynamics deals with description of the equilibrium states of reacting multicomponent systems.
- In a practical combustion processes, a combustion reaction can never reach completion. Rather the products of combustion will acquire the state of chemical equilibrium.
- In most combustors design target is to ensure that fuel and air have sufficient residence time to mix and react and attain thermodynamic equilibrium.
- Global performance parameters like heat and power output can be estimated by assuming thermodynamic equilibrium of the combustion products.
- Basics of combustion engineering are thus covered here.

So welcome back we were talking about chemical thermodynamics in last class that is where we left and we were talking about reviews of different; why it was needed to understand chemical thermodynamics and why that the products you need to understand the composition on temperature of the products which are in a state of a chemical equilibrium, and that in a combust of the design target is to ensure that the fuel in the air have sufficient residence time to mix and react and attain thermodynamic equilibrium.

(Refer Slide Time: 00:54)



Practical Reactants

1. Fuel
- Gaseous: H_2, CO, CH_4,…,C_4H_{10}
- Liquid: > C_5 HC, alcohols…
- Solid: coal, wood, metals …

2. Oxidizer

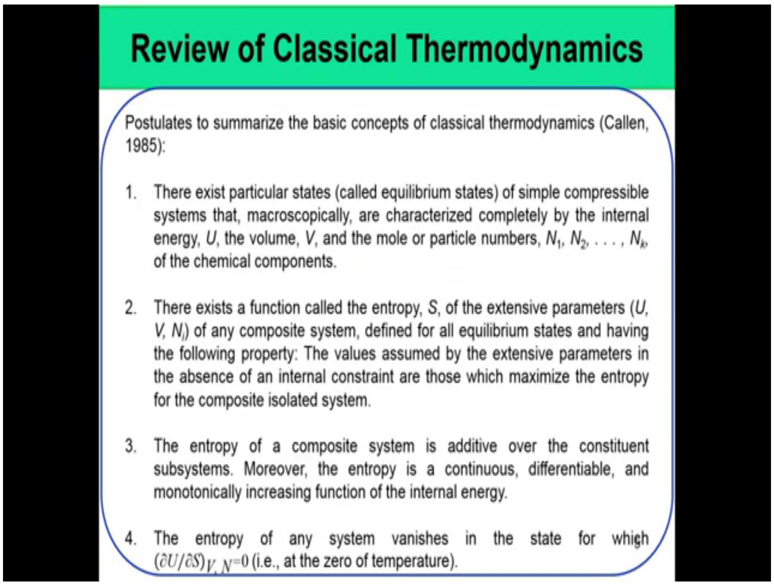
$[Air] = 0.21[O_2] + 0.79[N_2]$

$4.76[Air] = [O_2] + 3.76[N_2]$

http://www.mechanicalengineeringblog.com

And often chemical equilibrium as we have seen gives us good engineering parameters the total heat release the total power output this sort of things which are the first most important parameters that you need before you design an engine.

(Refer Slide Time: 01:13)



Review of Classical Thermodynamics

Postulates to summarize the basic concepts of classical thermodynamics (Callen, 1985):

1. There exist particular states (called equilibrium states) of simple compressible systems that, macroscopically, are characterized completely by the internal energy, U, the volume, V, and the mole or particle numbers, N_1, N_2, . . . , N_k, of the chemical components.

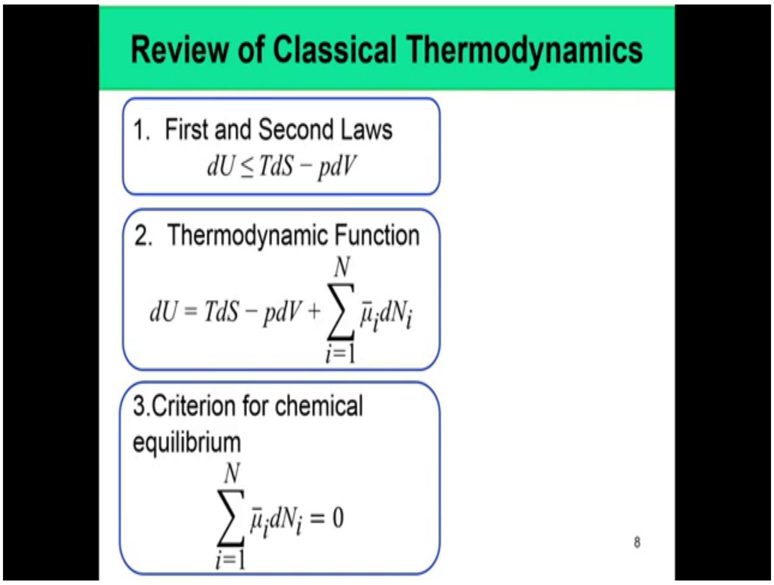
2. There exists a function called the entropy, S, of the extensive parameters (U, V, N_i) of any composite system, defined for all equilibrium states and having the following property: The values assumed by the extensive parameters in the absence of an internal constraint are those which maximize the entropy for the composite isolated system.

3. The entropy of a composite system is additive over the constituent subsystems. Moreover, the entropy is a continuous, differentiable, and monotonically increasing function of the internal energy.

4. The entropy of any system vanishes in the state for which $(\partial U/\partial S)_{V,N}=0$ (i.e., at the zero of temperature).

And then we talked about practical reactants stoichiometry and postulates, and we derived the Gibbs free energy the equilibrium condition in terms of Gibbs free energy the criteria for chemical equilibrium volume element conservation.

(Refer Slide Time: 01:17)



Review of Classical Thermodynamics

1. First and Second Laws

$$dU \le TdS - pdV$$

2. Thermodynamic Function

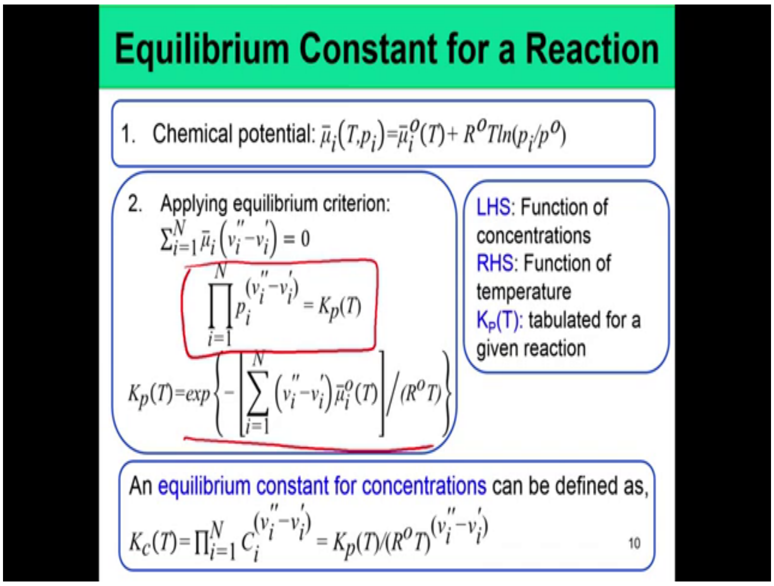
$$dU = TdS - pdV + \sum_{i=1}^{N} \bar{\mu}_i dN_i$$

3.Criterion for chemical equilibrium

$$\sum_{i=1}^{N} \bar{\mu}_i dN_i = 0$$

And then we obtain the chemical potential and we obtain the derived the equilibrium constant KPT which is given by this which was given by this formula.

(Refer Slide Time: 01:25)



Equilibrium Constant for a Reaction

1. Chemical potential: $\bar{\mu}_i(T,p_i)=\bar{\mu}_i^o(T)+ R^oTln(p_i/p^o)$

2. Applying equilibrium criterion:

$$\Sigma_{i=1}^{N} \bar{\mu}_i \left(v_i^{''}-v_i^{'}\right) = 0$$

$$\boxed{\prod_{i=1}^{N} p_i^{(v_i^{''}-v_i^{'})} = K_p(T)}$$

$$\underline{K_p(T)=exp\left\{-\left[\sum_{i=1}^{N} \left(v_i^{''}-v_i^{'}\right)\bar{\mu}_i^o(T)\right]/(R^oT)\right\}}$$

LHS: Function of concentrations

RHS: Function of temperature

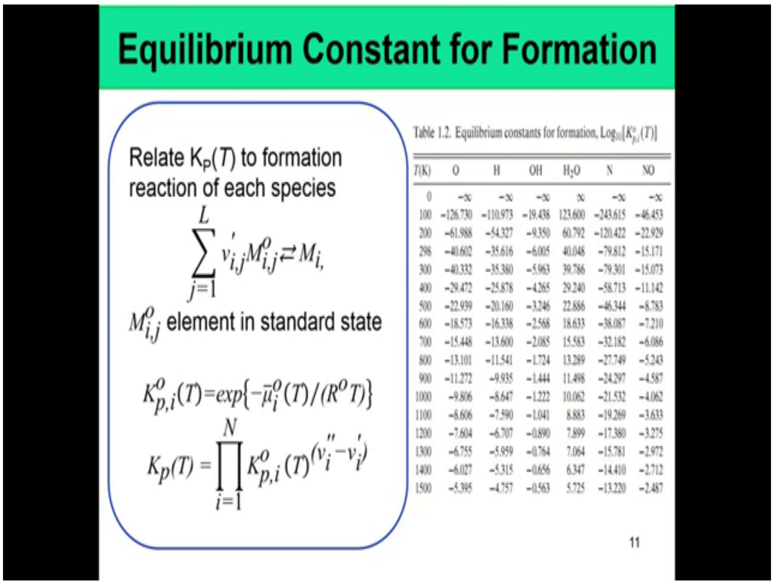
$K_p(T)$: tabulated for a given reaction

An equilibrium constant for concentrations can be defined as,

$$K_c(T)=\prod_{i=1}^{N} C_i^{(v_i^{''}-v_i^{'})} = K_p(T)/(R^oT)^{(v_i^{''}-v_i^{'})}$$

Now, and of course, there is also a Kc that is equilibrium constant in terms of concentrations and we said.

(Refer Slide Time: 01:44)



Equilibrium Constant for Formation

Relate $K_P(T)$ to formation reaction of each species

$$\sum_{j=1}^{L} \nu'_{i,j} M^o_{i,j} \rightleftarrows M_i,$$

$M^o_{i,j}$ element in standard state

$$K^o_{p,i}(T) = exp\{-\bar{\mu}^o_i(T)/(R^o T)\}$$

$$K_p(T) = \prod_{i=1}^{N} K^o_{p,i}(T)^{(\nu''_i - \nu'_i)}$$

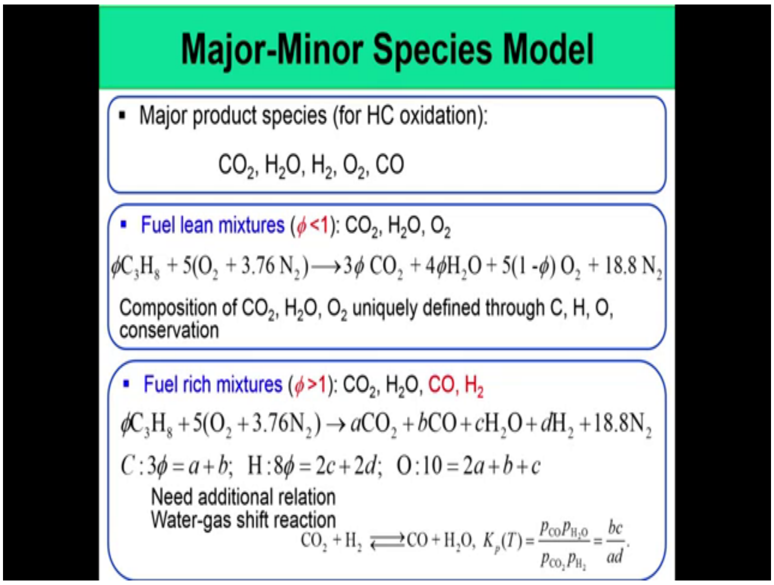
Table 1.2. Equilibrium constants for formation, $Log_{10}[K^o_{p,i}(T)]$

T(K)	O	H	OH	H_2O	N	NO
0	$-\infty$	$-\infty$	$-\infty$	∞	$-\infty$	$-\infty$
100	−126.730	−110.973	−19.438	123.600	−243.615	−46.453
200	−61.988	−54.327	−9.350	60.792	−120.422	−22.929
298	−40.602	−35.616	−6.005	40.048	−79.812	−15.171
300	−40.332	−35.380	−5.963	39.786	−79.301	−15.073
400	−29.472	−25.878	−4.265	29.240	−58.713	−11.142
500	−22.939	−20.160	−3.246	22.886	−46.344	−8.783
600	−18.573	−16.338	−2.568	18.633	−38.087	−7.210
700	−15.448	−13.600	−2.085	15.583	−32.182	−6.086
800	−13.101	−11.541	−1.724	13.289	−27.749	−5.243
900	−11.272	−9.935	−1.444	11.498	−24.297	−4.587
1000	−9.806	−8.647	−1.222	10.062	−21.532	−4.062
1100	−8.606	−7.590	−1.041	8.883	−19.269	−3.633
1200	−7.604	−6.707	−0.890	7.899	−17.380	−3.275
1300	−6.755	−5.959	−0.764	7.064	−15.781	−2.972
1400	−6.027	−5.315	−0.656	6.347	−14.410	−2.712
1500	−5.395	−4.757	−0.563	5.725	−13.220	−2.487

We showed that the how we do not need to tabulate equilibrium constant for individual reactions. What we can obtain it from the formation if we write hypothetical reaction by which a species is formed by given reaction, when we can write the equilibrium constant for given reaction in terms of the equilibrium constant of those reactions that form the given species involved in the present reaction.

So, and of course, the most important thing to notice that as you have seen that this equilibrium constant this is essentially, this is our equilibrium constant definition and this is given by the product the continued product of the partial pressures of a given species, raise to their the difference of their stoichiometric factors right. The stoichiometry constants that are being involved, so, this is the definition.

(Refer Slide Time: 02:42)



Major-Minor Species Model

- Major product species (for HC oxidation):

  CO_2, H_2O, H_2, O_2, CO

- Fuel lean mixtures ($\phi<1$): CO_2, H_2O, O_2

$$\phi C_3H_8 + 5(O_2 + 3.76\,N_2) \longrightarrow 3\phi\, CO_2 + 4\phi H_2O + 5(1-\phi)\, O_2 + 18.8\, N_2$$

Composition of CO_2, H_2O, O_2 uniquely defined through C, H, O, conservation

- Fuel rich mixtures ($\phi>1$): CO_2, H_2O, CO, H_2

$$\phi C_3H_8 + 5(O_2 + 3.76N_2) \rightarrow aCO_2 + bCO + cH_2O + dH_2 + 18.8N_2$$

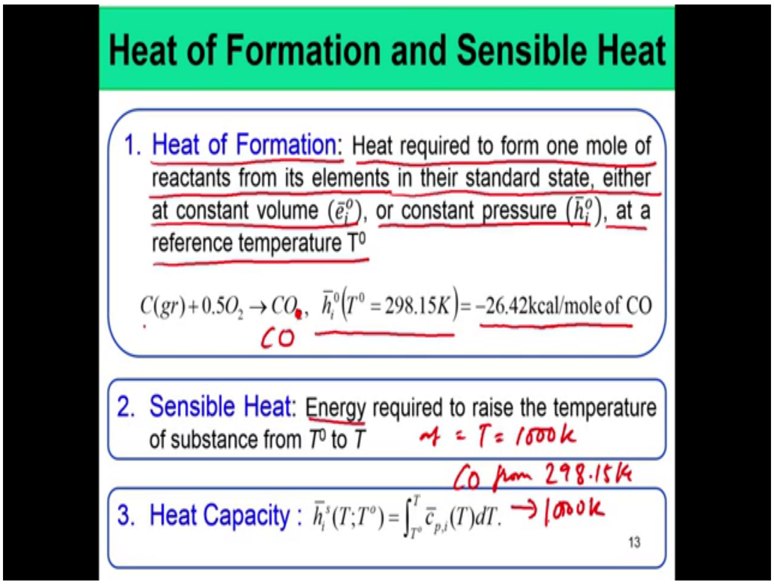
$$C: 3\phi = a + b;\quad H: 8\phi = 2c + 2d;\quad O: 10 = 2a + b + c$$

Need additional relation
Water-gas shift reaction

$$CO_2 + H_2 \rightleftarrows CO + H_2O,\ K_p(T) = \frac{p_{CO}p_{H_2O}}{p_{CO_2}p_{H_2}} = \frac{bc}{ad}.$$

And now as we have also shown the importance of equilibrium constant when you have even you involve more species which are invariably present in a in the equilibrium in the chemical equilibrium in the equilibrium situation of the products. Then you can get away for fuel lean mixtures for phi less than one, but for phi greater than one for rich mixtures you knew which we have more species formed especially carbon monoxide. And hydrogen and then you need the equilibrium constant of additional reactions which is the water gas shift reaction to give us give you all the equilibrium composition essentially, but then the next important thing is that how do you obtain the temperature. And for that you need to introduce few concepts which are called heat of formation and sensible heat.

(Refer Slide Time: 03:33)



Heat of Formation and Sensible Heat

1. **Heat of Formation:** Heat required to form one mole of reactants from its elements in their standard state, either at constant volume ($\bar{e}_i^o$), or constant pressure ($\bar{h}_i^o$), at a reference temperature T⁰

$$C(gr) + 0.5O_2 \rightarrow CO, \quad \bar{h}_i^0\left(T^0 = 298.15K\right) = -26.42\text{kcal/mole of CO}$$

CO

2. **Sensible Heat:** Energy required to raise the temperature of substance from T^0 to T

eg : T = 1000k

CO from 298.15K

3. **Heat Capacity :** $\bar{h}_i^s(T;T^o) = \int_{T^o}^{T} \bar{c}_{p,i}(T)dT.$ → 1000k

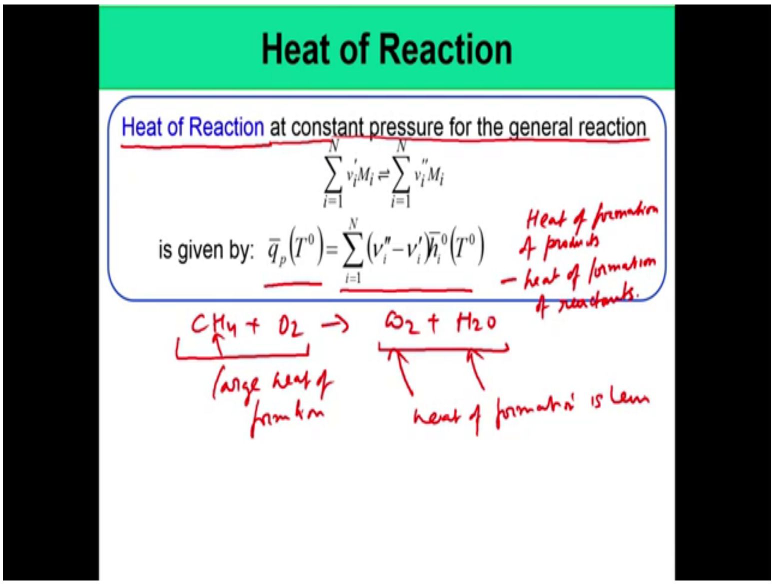
So, heat of formation the heat of formation is very important concept. The heat of formation is defined as a heat required to form one mole of reactants from it is elements. Remember reactants need not be elements reactants are essentially in in molecules right. Methane CH4 is formed from C and hydrogen carbon and hydrogen. Hydrogen molecule itself is formed from 2 atoms of hydrogen so on and so forth.

So, heat of formation is essentially the heat required to form one mole of reactants from it is elements in their standard state either at constant volume which involves the internal energy note the change in the notation, here we are denoting the specific the specific internal energy by small e i or at constant pressure which we are mentioning it as enthalpy at a and that a reference temperature T 0.

So, the heat required to form one mole of reactants from it is elements in their standard state either at constant volume or at constant pressure at a given reference temperature T 0. So, this is the heat of formation. So, as an example if you are interested in the heat of formation of CO2 or rather the heat of formation this is essentially not CO2 this is heat of formation of rather CO, which is formed from which is formed from one mole of carbon, solid carbon graphite and half mole of oxygen, and that gives you one mole of carbon monoxide. And then it is heat of formation at the standard temperature at the standard reference temperature of 298.15 kelvin is minus 26.42 kilo calorie kilo cal cal per mole of CO.

So, that is the heat of formation of CO. Now it is important to note that the elements do not by definition the heat of formation of elements is equal to 0 only molecules of heat of formation. Now what is sensible heat? This is the heat of formation essentially it is the energy you can think of it like the energy that is stored in the chemical bonds, what is the heat of formation. What is sensible heat sensible heat is the energy that is required to raise the temperature of a substance from T 0 that is a reference state to T. So, then the then the amount of energy is essentially the energy sensible heat for CO at a temperature of say 1000 kelvin is equal to the amount of heat required to raise the require to raise the energy is required to raise the temperature of CO from 298.15 kelvin 2000 kelvin. And of course, you are right that to estimate that we need to know the specific heat capacities and there is where the C p is coming. So, it is called that is where the C p is come which actually functions of temperature the specific.

(Refer Slide Time: 06:48)



Heat of Reaction

Heat of Reaction at constant pressure for the general reaction

$$\sum_{i=1}^{N} v_i' M_i \rightleftharpoons \sum_{i=1}^{N} v_i'' M_i$$

is given by: $\bar{q}_p(T^0) = \sum_{i=1}^{N} (v_i'' - v_i')\bar{h}_i^0(T^0)$

Heat of formation of products − heat of formation of reactants.

$CH_4 + O_2 \rightarrow CO_2 + H_2O$

large heat of formation

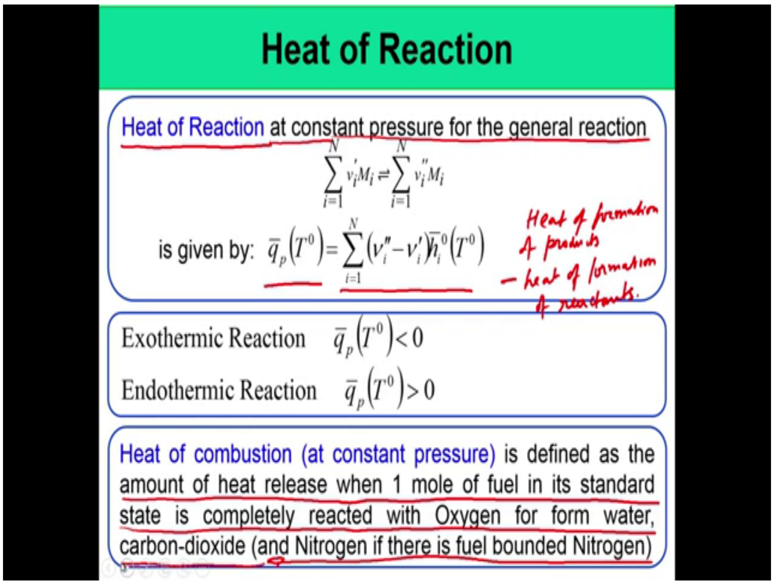
heat of formation is less

So, now we can define; what is the heat of reaction? Now the heat of reaction this is a very important concept. Now we must also distinguish and never get confused between the heat of formation and the heat of reaction. By definition the heat of formation is a property of a given molecule. It is a property of a species. Heat of reaction is a property of a reaction. So, there is a basic difference. So, what is that, the heat of reaction at a constant pressure for a general reaction of this form as we are defined this is the general reaction is given by this is the heat of reaction is given by the heat of formation of the products, minus the heat of formation of the reactants. That is the heat of reaction which is clearly given in a generalized form by this equation.

Now, suppose a reaction is exothermic, it releases heat. The question is will the heat of formation be positive or negative. Now if it releases heat the heat of formation, if the; it is the heat of the formation of the products which is a property of the product, will definitely be less then the heat of formation of the reactants. Because the reactants have given up this heat release this heat which the products didnt have right. Now the products can be heated because the products have been heated by this heat of formation of the reactants right. You see the point there is the reactants suppose we consider the methane air combustion reaction CH for O2 goes to CO2 plus water. Now yes our common sense suggest that on the normal conditions if you do combustion at a constant a pressure your CO2 and water will be at high temperature. And of course, your CO H4 and oxygen was at low temperature.

Now, but then you need to see why is the CO2 and water at high temperature. It is at high temperature because these had CH4 had large heat of formation, which it has given up by the combustion reaction and these heat of formation has now been absorbed by the CO2 and water in form of a sensible heat which has raised it temperature, but you must know that this heat of formation of these quantities is less. And that is why the reaction is exothermic.

(Refer Slide Time: 10:04)



Heat of Reaction

Heat of Reaction at constant pressure for the general reaction

$$\sum_{i=1}^{N} v_i' M_i \rightleftharpoons \sum_{i=1}^{N} v_i'' M_i$$

is given by: $\bar{q}_p\left(T^0\right) = \sum_{i=1}^{N} \left(v_i'' - v_i'\right) \bar{h}_i^0\left(T^0\right)$

Heat of formation of products − heat of formation of reactants.

Exothermic Reaction $\bar{q}_p\left(T^0\right) < 0$

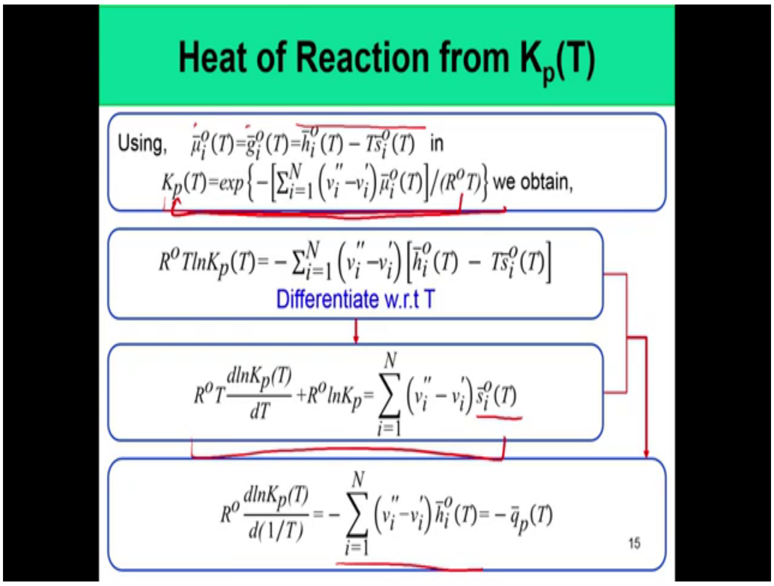
Endothermic Reaction $\bar{q}_p\left(T^0\right) > 0$

Heat of combustion (at constant pressure) is defined as the amount of heat release when 1 mole of fuel in its standard state is completely reacted with Oxygen for form water, carbon-dioxide (and Nitrogen if there is fuel bounded Nitrogen)

So, for an exothermic reaction, your heat of reaction is less than 0. And for an endothermic reaction your heat of reaction is greater than 0 because your endothermic reaction means the heat is been absorbed. Now once the heat has been absorbed; where does it go. So, the products has absorbed the heat, to increase it is own heat of formation. So, the heat of formation of an in an endothermic reaction the heat of formation of the products is higher than the heat of formation of the reactants and that is why the heat of reaction is greater than 0, for the endothermic reaction whereas, for an exothermic reaction the heat of reaction is less than 0.

So, heat of reaction is defined for any general raised reaction whereas, the heat of combustion at constant pressure is defined as the amount of heat release when one mole of fuel in it is standard state is completed reacted with the oxygen to form water carbon dioxide and nitrogen, if there is fuel bind nitrogen. You do not need to worry about this these are typically for different kind of propellants and etcetera. Now of course, there is one thing here that is when you form water can be in gaseous state, it can be in liquid state. So, depending on that you can have a higher heating value or lower heating value.

(Refer Slide Time: 11:43)



Heat of Reaction from $K_p(T)$

Using, $\bar{\mu}_i^o(T)=\bar{g}_i^o(T)=\bar{h}_i^o(T)-T\bar{s}_i^o(T)$ in

$K_p(T)=exp\left\{-\left[\sum_{i=1}^{N}\left(v_i''-v_i'\right)\bar{\mu}_i^o(T)\right]/(R^oT)\right\}$ we obtain,

$$R^oT\ln K_p(T)=-\sum_{i=1}^{N}\left(v_i''-v_i'\right)\left[\bar{h}_i^o(T)-T\bar{s}_i^o(T)\right]$$

Differentiate w.r.t T

$$R^oT\frac{d\ln K_p(T)}{dT}+R^o\ln K_p=\sum_{i=1}^{N}\left(v_i''-v_i'\right)\bar{s}_i^o(T)$$

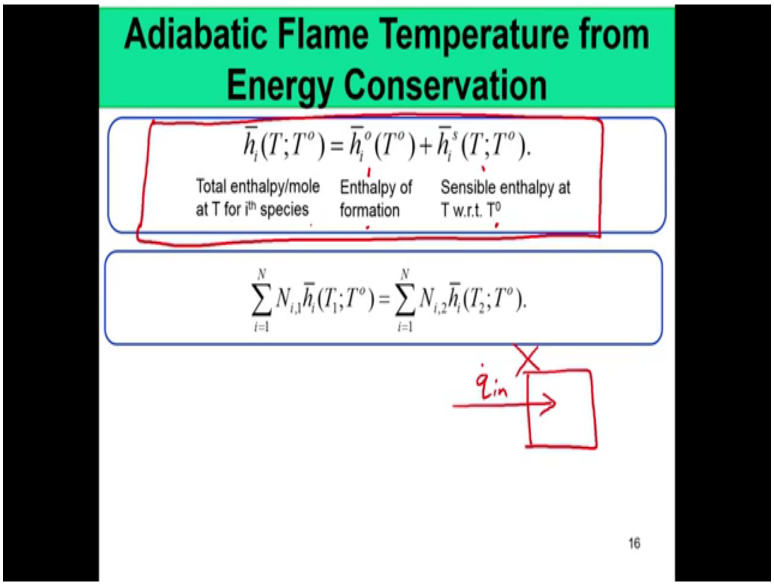
$$R^o\frac{d\ln K_p(T)}{d(1/T)}=-\sum_{i=1}^{N}\left(v_i''-v_i'\right)\bar{h}_i^o(T)=-\bar{q}_p(T)$$

15

Now, you can also define I will just quickly go over this derivation that you can also obtain the heat of reaction from KPT. That is when you define this; the standards the specific chemical potential can be shown to be equal to the specific these 3 energy and which is given by this form. And then of course, this is our relationship for the equilibrium constant. And we can basically write we can take basically here this on this side and then we differentiate with T and once we differentiate with T at constant pressure we will see that this that derivatives of d h I and d s I will dropout and only this will remain. And this is what we will get and it can be shown that your KP this r 0 times deal on KPT divided by d 1 T is essentially is equal to your minus of heat of formation of products minus heat of formation of reactants, which is the heat of reaction negative of the heat of reaction. So, that is how we can obtain this.

(Refer Slide Time: 12:54)

.



Adiabatic Flame Temperature from Energy Conservation

$$\bar{h}_i(T;T^o) = \bar{h}_i^o(T^o) + \bar{h}_i^s(T;T^o).$$

Total enthalpy/mole at T for i^{th} species

Enthalpy of formation

Sensible enthalpy at T w.r.t. T^0

$$\sum_{i=1}^{N} N_{i,1}\bar{h}_i(T_1;T^o) = \sum_{i=1}^{N} N_{i,2}\bar{h}_i(T_2;T^o).$$

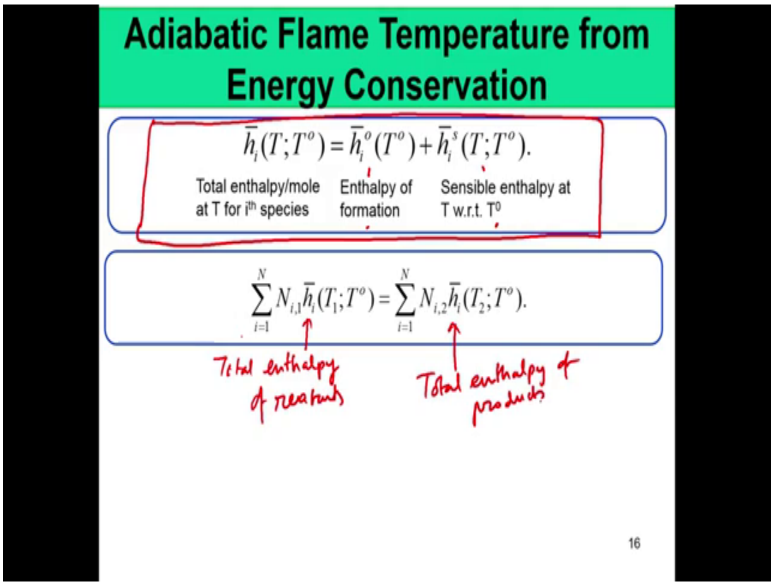
16

Now, how do you obtain adiabatic flame temperature from energy conservation? Adiabatic flame temperature is a temperature which will see is essentially the temperature of the equilibrium products. Now the total enthalpy this is a very important definition, the total enthalpy at a given temperature T per mole for an ith species ith species one can be anything, it can be methane oxygen water CO2 etcetera, is essentially sum of 2 things the enthalpy of formation and the sensible enthalpy. That is, you can think of it like this it is the inherent energy it had because of it is different kinds of bounds and the energy that has been absorbed in the bonds, because it has been raised from the standard state to a high temperature state.

So, the total enthalpy is a sum of these things. Now of course, you see in a when you have a; suppose a combustion happening at cons pressure inside a vessel, now the vessel walls can be sealed. So, there is no heat that is crossing this control volume boundaries or a system boundaries. So, essentially it is energy from the chemical bonds becoming sensible enthalpy or vice versa. There is no external energy coming from anywhere. You must remember this thing. So, it is essentially rearrangement of the enthalpy, between the enthalpy of formation and the sensible enthalpy that is happening in combustion.

So, please understand this thing in combustion when you model combustion in a given engine or something there is no it is not that, it is not like this. There is no energy you cannot moderate like an energy crossing the system boundaries. It is basically rearrangement of the enthalpy from the heat of formation to the sensible part sensible enthalpy part. So, if there is no energy coming in.

(Refer Slide Time: 15:39)



Adiabatic Flame Temperature from Energy Conservation

$$\bar{h}_i(T;T^o) = \bar{h}_i^o(T^o) + \bar{h}_i^s(T;T^o).$$

Total enthalpy/mole at T for ith species

Enthalpy of formation

Sensible enthalpy at T w.r.t. T^0

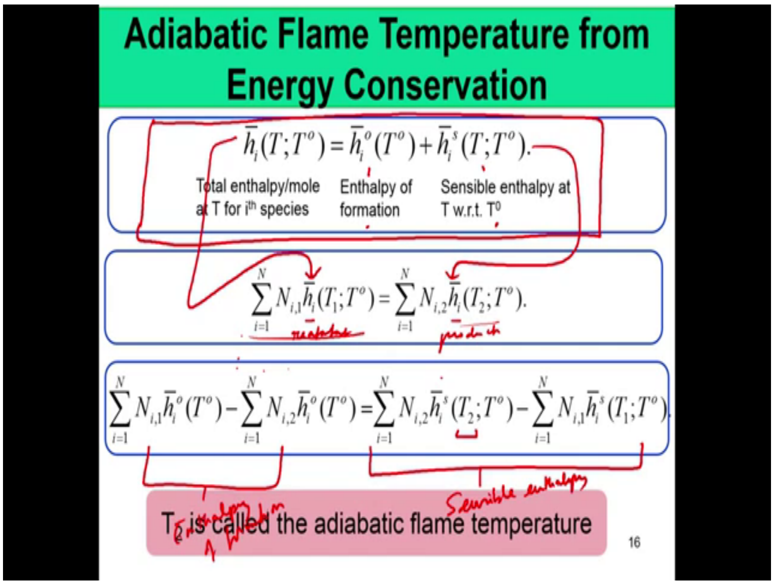
$$\sum_{i=1}^{N} N_{i,1}\bar{h}_i(T_1;T^o) = \sum_{i=1}^{N} N_{i,2}\bar{h}_i(T_2;T^o).$$

Total enthalpy of reactants

Total enthalpy of products

So then how do we model this? How do we write this? We can write that the total energy of the reactants; this can be this thing as essentially summation Ni Hi Ti at T z with respect T 0 is the total enthalpy of reactants which is equal to total enthalpy of products. It seems of course, this seems there is no additional energy coming in enthalpy of reactants is equal to enthalpy of products. And then we can put the enthalpy of formation on one side and the sensible enthalpy on the other side.

(Refer Slide Time: 16:20)



Adiabatic Flame Temperature from Energy Conservation

$$\bar{h}_i(T;T^o) = \bar{h}_i^o(T^o) + \bar{h}_i^s(T;T^o).$$

Total enthalpy/mole at T for ith species

Enthalpy of formation

Sensible enthalpy at T w.r.t. T^0

$$\sum_{i=1}^{N} N_{i,1}\bar{h}_i(T_1;T^o) = \sum_{i=1}^{N} N_{i,2}\bar{h}_i(T_2;T^o).$$

reactants

products

$$\underbrace{\sum_{i=1}^{N} N_{i,1}\bar{h}_i^o(T^o) - \sum_{i=1}^{N} N_{i,2}\bar{h}_i^o(T^o)}_{\text{Enthalpy of formation}} = \underbrace{\sum_{i=1}^{N} N_{i,2}\bar{h}_i^s(\underbrace{T_2}_{};T^o) - \sum_{i=1}^{N} N_{i,1}\bar{h}_i^s(T_1;T^o)}_{\text{Sensible enthalpy}}.$$

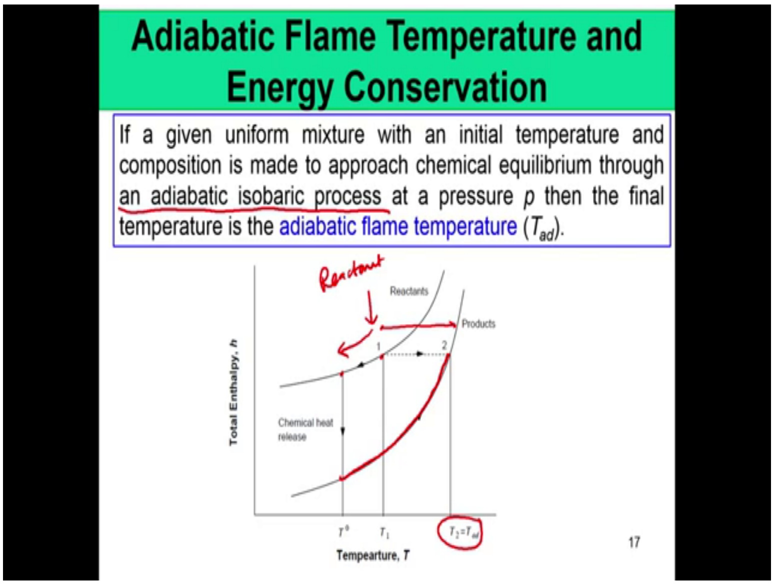
T_2 is called the adiabatic flame temperature

So, now what we have essentially done is that. So, this is the total enthalpy right. This is the total enthalpy of the reactants this is the total enthalpy of the products. So, you can use this one to substitute here and substitute here. So, once you have then you have basically on the left hand side you have the enthalpy of enthalpy of formation of the reactants, plus sensible enthalpy of the reactants. And you have enthalpy of formation of the products plus the sensible enthalpy of the products. Now what we have done in this step is essentially we have collected the enthalpy of formation of the reactants and the products on the left hand side, and we have collected the enthalpy the sensible enthalpy of the reactants and the products on the right hand side. Now what is happened is that the enthalpy of the, if this is the combustion reaction say then enthalpy of the reactants the enthalpy of formation of the reactants is much high and that when at it has been released it has been converted to sensible enthalpy of the products.

So, as a result of this because the sensible enthalpy of the products has been increased, it has been increased because it is temperature has increased. So, this T 2 is the temperature at which this sensible enthalpy can be realized. And hence T 2 is called the adiabatic flame temperature. So, you see the thing, that is the; you had the reactants have lot of enthalpy of formation, whereas, the it does not have to it did not have too much sensible enthalpy because it can be at a reference state itself. Whereas, the products have small enthalpy of formation, but it has very large sensible enthalpy. The very large sensible enthalpy is contiguous is the enthalpy is large because it is a function of temperature, and that temperature which it has been raised which this sensible enthalpy has been realized is called that a adiabatic flame temperature.

So, of course, you see this is not an explicit equation. This is still an implicit equation and we have to do some iteration to essentially find the enthalpy of the adiabatic flame temperature, but essentially the adiabatic flame temperature comes purely from the energy conservation. That is or rather it comes from the rearrangement of enthalpy between the sensible enthalpy and the enthalpy of formation.

(Refer Slide Time: 19:37)



Adiabatic Flame Temperature and Energy Conservation

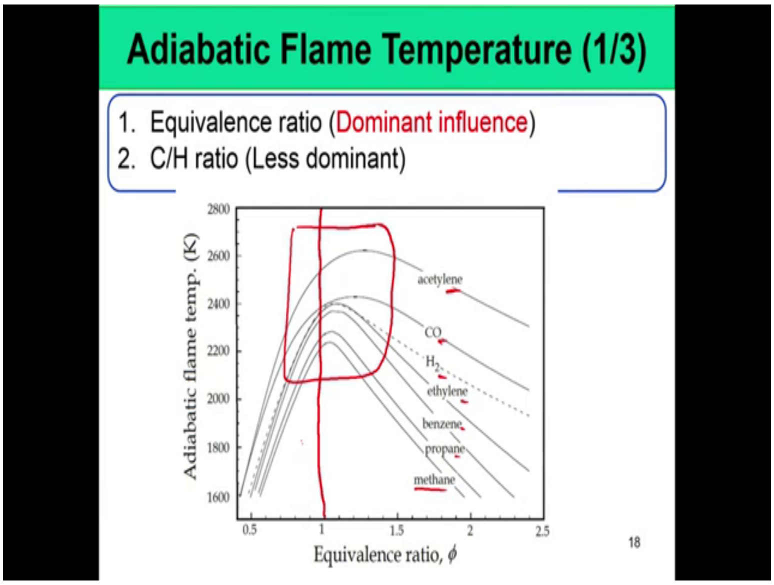
If a given uniform mixture with an initial temperature and composition is made to approach chemical equilibrium through an adiabatic isobaric process at a pressure *p* then the final temperature is the adiabatic flame temperature (T_{ad}).

So, it can be also thought of I mean formally it is defined like this, adiabatic flame temperature. That is if we have a given if a given uniform mixture with an initial temperature on composition is met to approach the chemical equilibrium, through an adiabatic isobaric process, adiabatic process because there is no heat entering into the into the into the control volume to the system that I was talking about. Isobaric means constant pressure, at a pressure p, when the final temperature is the adiabatic flame temperature T ad, why is T ad higher than the normal temperature. There is it is a very basic question right it is a almost an obvious question that I am asking that why is the combustion why is it temperature of the products higher than the temperature of the reactants because the reactants had once again very large enthalpy of formation. Because of the chemical reaction that enthalpy of formation is now converted into the sensible enthalpy of the products. Now the sensible enthalpy is of course, a function of temperature and because the sensible enthalpy is a very high the temperature must be high, and as a result of this the adiabatic flame temperature in which the sensible enthalpy is realized is large. So, that is why when you have combustion it basically have large final product temperature is high.

Now, you can also think of it like this that in this enthalpy temperature diagram. So, suppose this is the reactants. So, first it can be which essentially goes from this is the one is the reactant state 2 is the product state. It essentially goes like this, but we can think that it involves like 3 steps. So, first it goes to the T 0 that is the reference state. The products the reactants sorry; so, this is the reactant, so, it goes to this reference state and then it releases the energy. So, the as it energy releases it is enthalpy goes down the reactants enthalpy goes down, but then now that energy that chemical energy that has been released is essential taken up by the products. And then it becomes hot, because now it has absorbed all the enthalpy that is released by the reactants and now the sensible enthalpy of the products has increased and hence this T 2 is equal to T ad, is greater than 1, is greater than T 1.

So, please remember this that there is no additional energy coming from anywhere else. It is a chemical energy that is converted into sensible energy, sensible enthalpy and that energy conservation on the left on the between the reactants and the products gives you the adiabatic flame temperature.

(Refer Slide Time: 22:34)



Adiabatic Flame Temperature (1/3)

1. Equivalence ratio (Dominant influence)
2. C/H ratio (Less dominant)

Now, what does adiabatic flame temperature depend on? Now one of the most important parameters in combustion is adiabatic flame temperature. We do combustion because we want the temperature to be high. Once the temperature is high you can if you can as you remember from a thermodynamics cycle, if you have heat release at high pressure, if you have a system which is at high pressure and at high temperature you can extract work out of it. So, it is because of this high adiabatic flame temperature that is combustion is attractive. And that is why you have combustion in engines look what though. So, it is very important and to understand that why on what are the parameters on which adiabatic flame temperature depend on. Of course, it depends on the equivalence ratio phi which is the actual fuel ratio divided by the stoichiometry fuel ratio, and it also depends on the CH ratio that is the carbon to hydrogen ratio though that is less dominant.

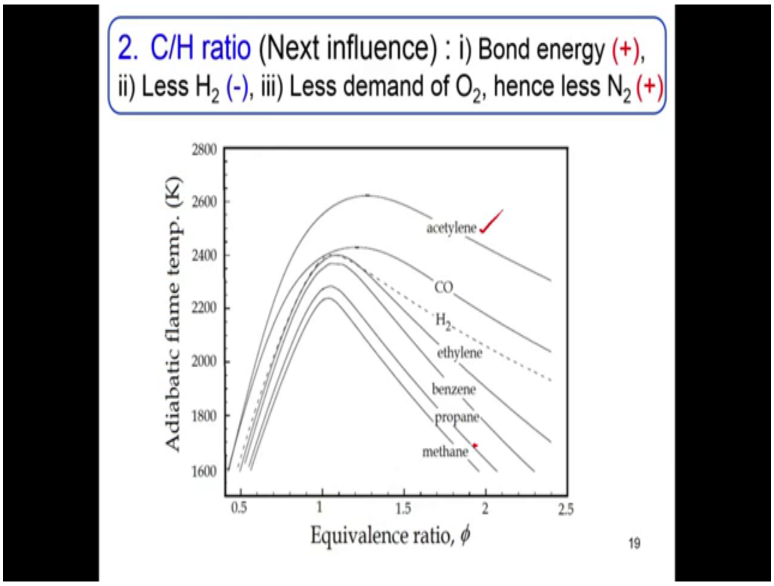
So, this is how the adiabatic flame temperature for different fuels looks like. So, this is you see methane, propane, benzene, ethylene, hydrogen, carbon monoxide and acetylene. And you see that it is a peaks at almost at equivalence ratio peaks at equivalent ratio of 1, though it is slightly shifted from 1, but the all the temperatures you see you see around this 2 2 0 0 2 2 6 0 0 kelvin when because this is adiabatic flame temperature in air in air.

Now, one more important thing is that to note is that adiabatic flame temperature you know, if you have there is all the adiabatic flame temperature is also depend on the medium in which you are burning. If you are burning in pure oxygen you are adiabatic flame temperature will be much higher than if you have burning in air. The reason is that the adiabatic flame temperature as you see is the essentially is a comes from the sensible enthalpy.

Now, if you have lot of nitrogen is not participating in the reactions. So, lot of the sensible enthalpy goes in heating of the nitrogen also. So, the adiabatic flame temperature in air which contains nitrogen for a hydrocarbon combustion reaction is definitely lower than that of the adiabatic flame temperature in a pure oxygen anyways. So, this is the adiabatic flame temperature in air and this is the range in which it is in which you have the adiabatic flame temperatures.

So, of course, you see the most important thing is that that on both sides of the; it is low on both sides of the equivalence ratio and it is this peak typed behavior we have received. Now of course, if equivalence ratio is less than one if bounding is lean you do not have you have a less supply of fuel. Of course, we do not supply much the given amount of fuel you do not achieve that kind of temperature. So, it is obvious, but why is adiabatic flame temperature low when you have a fuel rich combustion also. Because you see know the lot of the energy of the sensible enthalpy is now spent in heating up the unbound fuel. Of course, you do not have unbound fuel as such, but you have carbon monoxide and hydrogen. So, lot of the energy which is also a fuel actually. So, lot of the energy in is now spent in heating up of carbon monoxide and hydrogen, when you have fuel rich combustion as we have seen in the equilibrium composition calculation. So, on the adiabatic flame temperature basically is goes down on both sides of stoichiometry condition right.

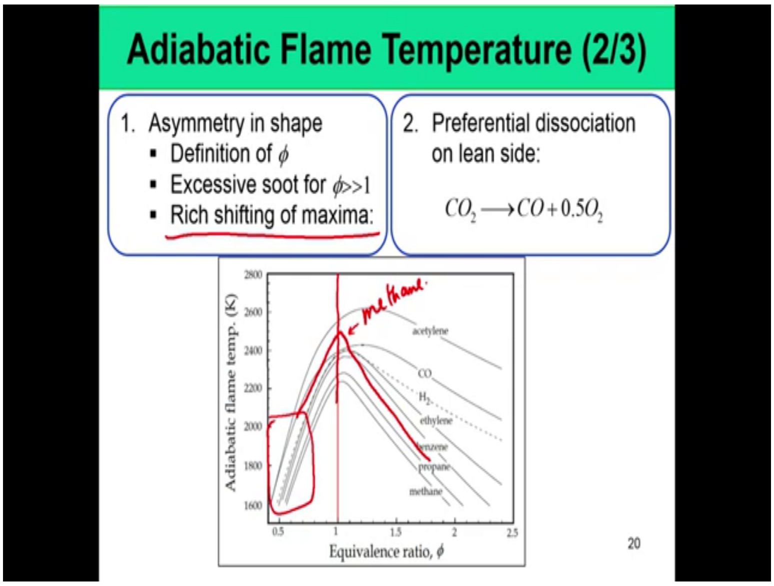
(Refer Slide Time: 25:53)



2. C/H ratio (Next influence) : i) Bond energy (+), ii) Less H_2 (-), iii) Less demand of O_2, hence less N_2 (+)

So, in the next parameter at that it depends on CH ratio. Because you see it depends on whether depends on whether it is methane propane benzene ethylene or acetylene of course, it is very clearly seen that acetylene has a much higher temperature then methane. There are the reason is that you see acetylene has a triple bond whereas, methane has a single bonds. So, when you have triple bonds the amount the bond energy is essentially high, but at the same time acetylene can contain less hydrogen then what methane can contain. So, it is that is reducing factor, but on the other hand because it has got less because it has got less hydrogen it is the it demands less oxygen for water formation. Hence if the requirement of oxygen is less you need less nitrogen also and nitrogen is basically you are just wasting energy in heating up the nitrogen right. So, these are the factor that determines the CH ratio in bond energy less hydrogen or more hydrogen and the demand of oxygen essentially determines that adiabatic flame temperature.

(Refer Slide Time: 26:51)



Adiabatic Flame Temperature (2/3)

1. Asymmetry in shape
   - Definition of ϕ
   - Excessive soot for $\phi >> 1$
   - Rich shifting of maxima:

2. Preferential dissociation on lean side:

$$CO_2 \longrightarrow CO + 0.5O_2$$

Now, finally, you now you see that there is an asymmetry in shape also. The adiabatic flame temperature this side is much smooth whereas, this side is much steep right now that has to do with the definition of equivalence ratio. And if you define the normalized equivalence ratio, you will that this is reasonably more symmetric. Of course, you must also note that there is lot of soot, if you burn in fuel rich because of the unburned hydrocarbons and particles that are being formed. And this CO there is some like ring formation ring structure formation and then there is polymerization then you form soot. And what that is what why fuel rich combustion is very much unwanted. And then there is a most important very important phenomenon of the rich shifting of the maxima. What is that? G intuition suggest that yes we understand why adiabatic flame temperature should peak at stoichiometry, but you see that it is not exactly peaking at stoichiometry. Stoichiometry is here whereas, this is peaking here, this is peaking here, this is peaking here this is peaking here this is peaking here and this is peaking here, why?

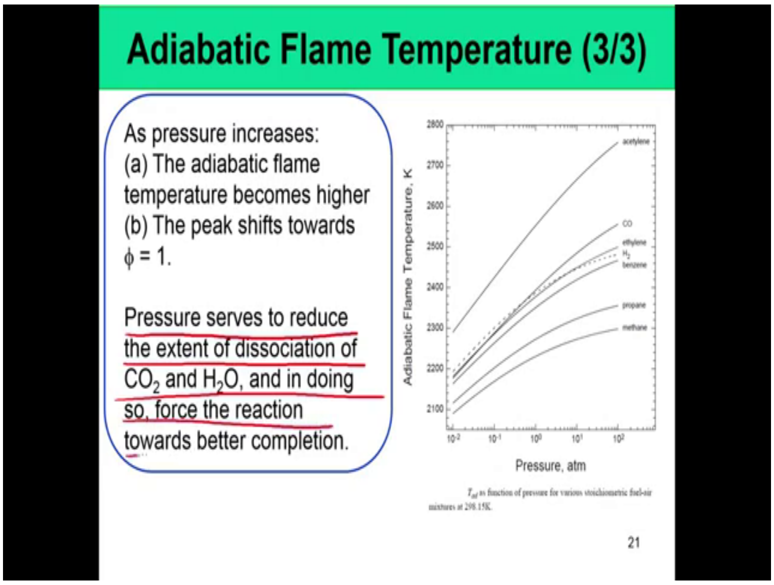
This is a very important question to answer and this has to do with essentially the equilibrium chemical equilibrium. The reason is that you must note that these products are not in a frozen state. If there were in a frozen state you will find that the adiabatic flame temperature peaks at phi equal to 1, but because they are in a equilibrium state the CO2 and the water that is being formed, they basically dissociate that is the CO2 become CO and oxygen and water also decomposes into hydrogen and oxygen. There is also continuous dissociation always in small amount that is going on.

Now, these dissociation reactions need some energy. And it turns out it can be shown that the dissociation reactions are stronger, that is there is preferential dissociation on the lean side. There is more dissociation going on the lean side both for CO2 and water, then you have the dissociation on the rich side. So, if you have more dissociation on the lean side, there is more requirement of the energy that is that was released some part of it is basically sucked backed to form to basically do this dissociation reactions. And this sucking back of energy happens more on the lean side then on the rich side. So, as a result of this energy that is ribbing reabsorbed because of the dissociation, your adiabatic flame temperature shifts to the rich side. And you do not have the adiabatic flame temperature maximum on the; at equivalent ratio 1.

Now, this is very important and this factor needs to be noted if you are designing a standard combustor. Of course, you will see that later this adiabatic flame temperature also determines the pollutants being that will be emitted. And presently we everybody wants to basically work on this regime. So, the temperature can be less there can be no soot, there can be no carbon monoxide formation and, but of course, there are other challenges that are associated with this will talk later.

But once again coming back to the dissociation, you will see that it increasing pressure we will we will see that with increasing pressure this basically this adiabatic flame temperature becomes more and more peak towards stoichiometry. So, this at a higher pressure decides what the adiabatic flame temperature graph for methane would look like. It would shift more towards the more towards equivalence ratio of one. This is because the dissociation reactions are diminishes; the intensity of the dissociation reactions diminishes at high pressure as a result of which the adiabatic flame temperature tends to shift back.

(Refer Slide Time: 31:03)



Adiabatic Flame Temperature (3/3)

As pressure increases:
(a) The adiabatic flame temperature becomes higher
(b) The peak shifts towards $\phi = 1$.

Pressure serves to reduce the extent of dissociation of CO_2 and H_2O, and in doing so, force the reaction towards better completion.

T_{ad} as function of pressure for various stoichiometric fuel-air mixtures at 298.15K.

And as a result of this once the dissociation reactions are diminished, your the energy that is consumed in this dissociation reaction is also diminished. And as a result of which the adiabatic flame temperature increases with pressure at a stoichiometry condition. And this is what you see that as pressure increases the adiabatic flame temperature becomes higher and the peak shift backs towards one because the pressure serve to reduce the extent of dissociation of CO2 and water and in doing. So, force the reaction towards better completion.

So, with that we would end this first module of like review of chemical thermodynamics, where we have obtained a KP the equilibrium constant, where we have obtained the concepts of enthalpy of formation the heat of formation the heat of reaction, we have obtained the concept of adiabatic flame temperature and the very important concept of why the adiabatic flame temperature shifts on the rich side rather it does not peak at equivalence ratio of 1. So, thank you very much for your attention and we will meet again and when we meet again we will discuss chemical kinetics.

Thank you.