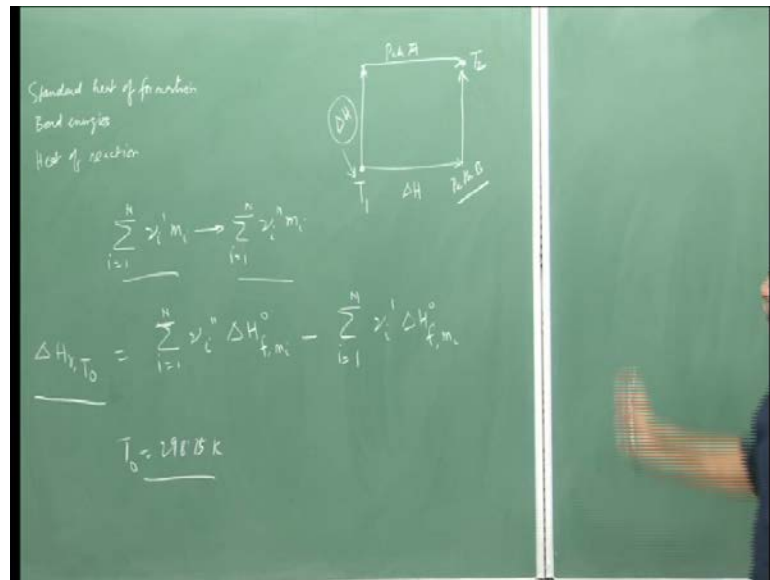


Jet and Rocket Propulsion
Prof. Dr. A. Kushari
Department of Aerospace Engineering
Indian Institute of Technology, Kanpur

Lecture - 33

(Refer Slide Time: 00:29)



So, in the last class we have been discussing certain definitions for heat of reactions. We discuss the standard heat of formation, then we discuss the bond energies, and then we started discussing heat of reaction. We did a thermodynamic analysis for the heat of reaction. We defined heat of reaction. And towards the end of the last class what we have shown is that if we consider a general chemical reaction given like this, where m_i is the species. So, there are n species that are present, and these are the stoichiometric coefficient for the reactants; this represents the reactant, this represents the product. So, this is the general chemical reaction that we have been discussing.

Now, we have also shown towards the end of the last class that the heat of reaction at standard temperature T_0 , then for this specific chemical reaction will be nothing but the heat of formation of all the products minus the heat of formation of summation of heat of formation of all the reactants. And this is, this definition at the standard temperature is applicable, because of our heat of formation is also defined for standard temperature and pressure. So, if the reaction is carried out at that standard temperature then the heat of this reaction is nothing but the difference of heat of formation. So, we have discussed up to this.

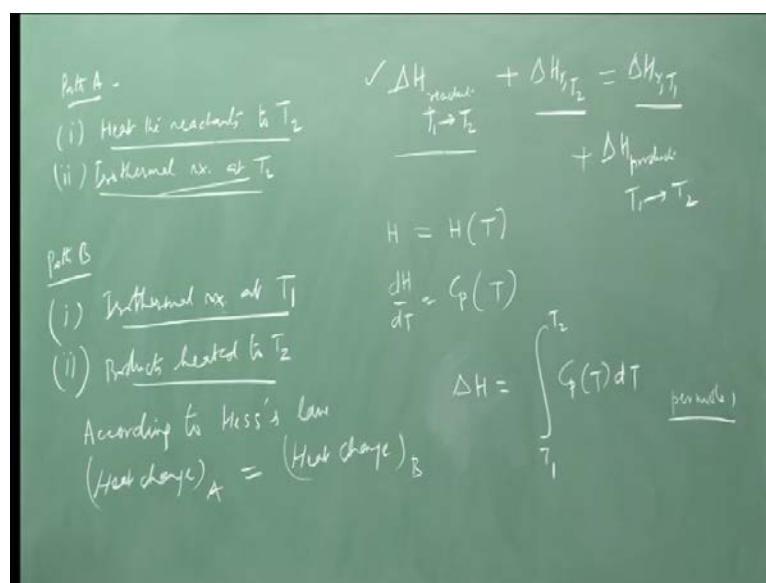
Now, very really actually always ever the reaction will actually occur at that temperature which is standard temperature is 298 degree Kelvin; most of the time the reaction will be occurring at some other temperature, typically higher temperature. So, the question arises is that if the temperature is different from the standard temperature how do we estimate the heat of reaction.

So, what we have said is that looking at the thermo chemical loss whether the reaction takes place in one step or multiple steps, we are going to have as long as the initial and final stages are same, we are going to have same change in the enthalpy. So, based on that we devise a schematic; let us say that initially the standard state or say the reactants are at state T 1, and we say that we know the heat of reaction at this state, state T 1.

Now we have to find out if the reactants where at state T 2 what will be the heat of reaction. We said that we can take two paths to reach from T 1 to T 2. We can have the reactions occurring at temperature T 1. Because of that some heat is liberated, and then this heat actually, sorry; we said that first we supply some ΔH amount of heat to the reactants which are at temperature T 1, so that heats up the reactants to the temperature T 2.

After that we carry out the isothermal reaction at temperature T 2. So, we reach this state. So, we call that path A. Another part can be that the reactions occur at temperature T 1 itself. So, because of that the products are formed and some amount of heat ΔH is liberated. Now this heat ΔH goes to heat up the products so that they go to temperature T 2. So, this is my path B.

(Refer Slide Time: 04:59)



So, once again if I have to summarize the 2 paths, path A corresponds to 2 steps. First, heat the reactants to temperature T_2 , that is done here, for that we need to supply some amount of heat ΔH ; and then second step is isothermal reaction at T_2 . Now, isothermal reaction is important because if you recall the way we defined the heat of reaction, heat of reaction is defined when the chemical reaction is taking place at constant pressure and constant temperature. Only change is in the number of moles, the composition. So, therefore, the heat of reaction is defined for isothermal reaction. So, therefore, we consider the reaction to be isothermal at temperature T_2 .

Path B on the other hand is an alternative path where first we have the isothermal reaction at temperature T_1 , and then products heated to temperature T_2 . Now, however, for both this cases, we are going from state 1 to state 2. So, the initial stage and the final stage is same for both this cases. Then, according to the Hess's law which we have discussed in the last class, the total heat evolved in this path is equal to the heat evolved in this path because the total heat is independent of the path. So, therefore, it will just depend on the initial and final state.

So, therefore, according to Hess's law, heat change for path A is equal to heat change for path B. Now, what is this heat change? Both, path A and path B are two step processes. Let us first look at path A. Path A, what we are doing is first heating the reactants to temperature T_2 which were initially at temperature T_1 . So, let us say that involves some

change in enthalpy. So, ΔH for the reactants going from temperature T_1 to T_2 , and then the reaction is occurring at temperature T_2 , here.

So, that is ΔH_r at temperature T_2 , that is the heat of reaction, right. So, there is some ΔH_r at T_2 ; here it is ΔH_r at T_1 ; and this is ΔH . So, this is the path taken in process A or path A, where first we have, we heat the reactant some temperature T_1 to T_2 and then have isothermal reaction at T_2 .

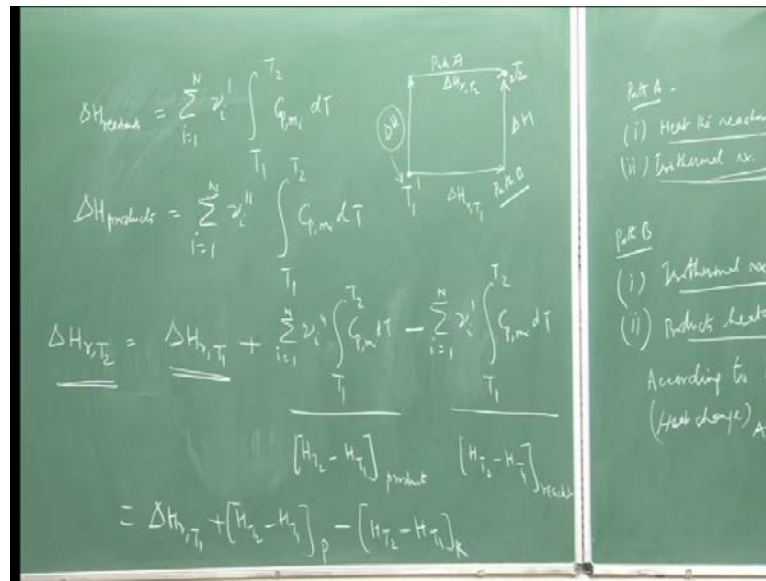
On the other hand if I look at path B, here first I have isothermal reaction at T_1 . So, that is ΔH_r at T_1 . And then heating the products to temperature T_2 , so that is ΔH for the products going from temperature T_1 to T_2 . So, this is according to the Hess's law, the left hand side and the right hand side of this two are equal.

Now, let us look at the enthalpy term little closely. Here I have 4 changes in enthalpy, out of them 2 that is heating the reactant from temperature T_1 to T_2 and heating the product from temperature T_1 to T_2 does not involve the reaction; it is just heating, whereas this 2 involve the heat of reaction. So, now, let us look at the enthalpy little more closely.

We are talking about the working substance which is a pure substance and ideal gas. So, if the working substance is an ideal gas then we know that enthalpy is a function of only temperature and dH/dT is equal to c_p which is also a function of temperature. We know this from thermodynamics.

Therefore, looking at this expression, dH is nothing but integral for this process; heating the reactants from temperature T_1 to T_2 is nothing but integrating $c_p dT$ from temperature T_1 to T_2 . So, this will be $c_p \Delta T$ from temperature T_1 to T_2 ; and of course, this will be per mole basis. So, now, with this if I now come back to this equation, ΔH for the reactant, sorry; let me come back to this equation; we come back to this equation now and put this back into this expression.

(Refer Slide Time: 10:53)



Then we get; so this term is delta H for the reactants, taking it from T 1 to T 2. So, I write it as delta H reactants which will be equal to; this was for every species in the reactant, right. So, the total change in enthalpy will be the sum over all of them. So, therefore, that will be equal to sigma i equal to 1 to n; there are n species multiplied by the psychometric coefficient for the reactants, integral T 1 to T 2. And now we represent C p for every species by C p m i, where m i has, I have said at the beginning represents a particular chemical species. So, that is the total change in enthalpy of the reactants.

Similarly, this term here is changing enthalpy of the products. So, I can write it here as delta H products is equal to, once again sigma 1 to n mu i double prime integral T 1 to T 2 C p i m i, C p m i d T. So, this gives me the total changing enthalpy of the products, in heating the products from temperature T 1 to T 2.

Now, we take all of this and put it back once again into this equation. Then, what we get is by rearranging that equation delta H heat of reaction at temperature T 2 is equal to heat of reaction at temperature T 1 plus, this term which is the change in enthalpy in heating the products from temperature T 1 to T 2 minus, change in enthalpy in heating the reactants from temperature T 1 to T 2. So, we are just replacing this term and this term with those expressions, and then just rewriting this equation.

Let us look at what are this 3 terms. As I can see that the heat of reaction at temperature T 2 consists of 3 terms. First is heat of reaction at temperature T 1. Then, there is this term; what is this? This is nothing but change in enthalpy of the products when they are

heated from temperature T 2 to T 1, sorry, T 1 to T 2. And, this term here is change in enthalpy of the reactants when they are heated from temperature T 1 to T 2. So, we can see here then that $\Delta H_r T 2$ is equal to nothing but the heat of reaction at temperature T 1, the change in enthalpy of the products minus, change in enthalpy of the reactants.

So, here what we are listing, actually at two ways in estimating the heat of reaction. If we know the composition and the C p values for every species we can use this equation and get the heat of reaction. On the other hand if we know even the species we can find out the total enthalpy of the species of different temperatures. So, for the product we can estimate, for the reactants we can estimate. So, from the thermo chemical table depending on whether this enthalpy values are given or C p values are given we can estimate the heat of reaction. So, essentially it is the same, different representation of the same thing.

(Refer Slide Time: 15:06)

The image shows a chalkboard with the following handwritten equations:

$$p = 1 \text{ atm.}, T_1 = T_0 = 298.15 \text{ K.}$$

$$\Delta H_{r,T} = \left[\sum_{i=1}^N \nu_i'' \Delta H_{f,i}^0 - \sum_{i=1}^N \nu_i' \Delta H_{f,i}^0 \right]$$

$$+ \sum_{i=1}^N \nu_i'' \int_{T_0}^T C_{p,m,i} dT - \sum_{i=1}^N \nu_i' \int_{T_0}^T C_{p,m,i} dT$$

$$= \Delta H^0 + f(T)$$

$$\text{At } T = T_0, f(T) = 0 \quad f(T) = \sum_{i=1}^N \nu_i'' \int_{T_0}^T C_{p,m,i} dT - \sum_{i=1}^N \nu_i' \int_{T_0}^T C_{p,m,i} dT$$

Now, let us take a step backward. Let us consider if the pressure is 1 atmosphere; the reactions are occurring at 1 atmosphere pressure, and the initial temperature T 1 which is equal to T naught that is the standard state, 298.15 kelvin. Then what happens? The conditions at which now the reactions are occurring are standard temperature and pressure, right. Therefore, this term here, heat of reaction occurring at standard temperature of pressure. So, that can be then projected as the standard heat of formation, right.

So, now, if I combine all this together I get heat of reaction at any temperature T . So, that is why we are saying it is that we know the heat of formation. So, what we say is that for estimating the heat of reaction at any other temperature we say that the reaction occurs at the standard temperature and pressure. Therefore, the heat of reaction is the heat of formation for the species. And then we account for the enthalpy change for the reactants and products.

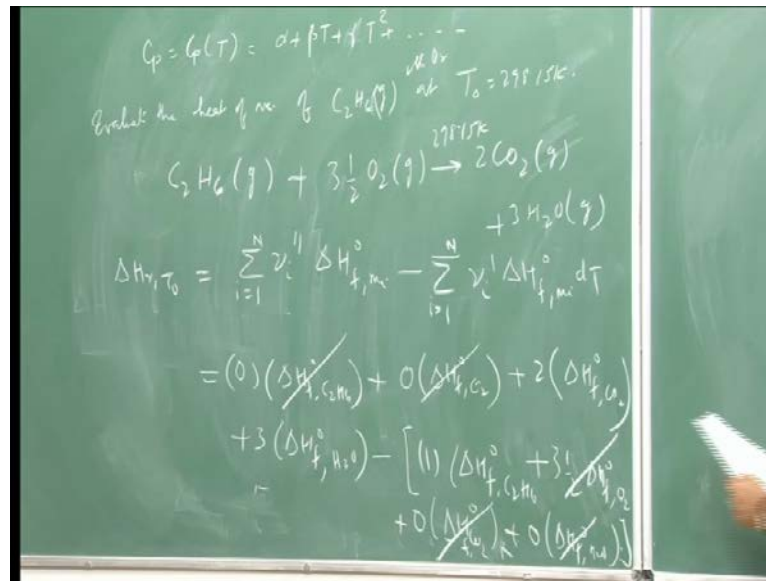
So, therefore, at any temperature heat of reaction is equal to standard heat of the, heat of formation. So, therefore, in that case my ΔH_r becomes equal to the heat of formation. So, I can write it as this, for every species of course. This is the heat of formation for the products. Similarly, I have heat of formation for the reactants. So, that gives the total heat of formation plus, the change in enthalpy. So, first for the products.

Now, the temperature now will change from T_{naught} to T . The T_{naught} is the standard temperature plus, sorry, minus $\sum_{i=1}^n \nu_i' \int_{T_{\text{naught}}}^T C_{p,m,i} dT$. So, now, this is the expression for heat of reaction at any temperature, but still at one atmosphere pressure that we have to understand. If I look at this expression then this is nothing but the enthalpy change as standard temperature, $\Delta H_{\text{as a standard temperature plus, a function of temperature}}$; as you can see that both this terms are function of temperature T . So, this is the function of temperature.

So, if I take a closer look at this, the heat of reaction at any temperature is the heat evolved by the reaction of standard temperature or heat of reaction at standard temperature plus, some function of temperature. Then, once again if my, this temperature T is the standard temperature then $f(T)$ is 0, right. If the standard temperature $f(T)$ is 0, so therefore, this term here is essentially the heat of reaction at standard temperature.

And, $f(T)$ is a function of temperature; so I can write an expression for $f(T)$ which is equal to essentially $\sum_{i=1}^n \nu_i'' \int_{T_{\text{naught}}}^T C_{p,m,i} dT$ minus, $\sum_{i=1}^n \nu_i' \int_{T_{\text{naught}}}^T C_{p,m,i} dT$. So, that is the expression for $f(T)$. Now, C_p is the specific heat at constant pressure.

(Refer Slide Time: 19:39)



So, once again these values for different species or chemicals are given in thermochemical tables. C_p can be given as a polynomial of temperature. So, typically, as we have seen that C_p should be a function of temperature, and it is typically expressed as $\alpha + \beta T + \gamma T^2$, etcetera. So, depending on the accuracy we can choose the order. So, typically these values of α , β , and γ , etcetera, are given in standard thermochemical tables. So, this is how we estimate the heat of reaction.

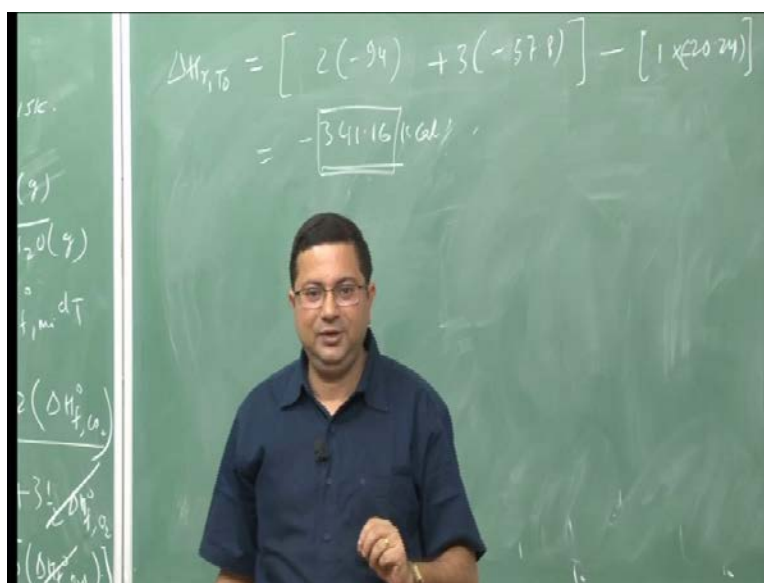
Let us look at an example to make it a little clearer. The example I will be looking at is to evaluate the heat of reaction of ethane gas at T_{naught} which is 298.15 kelvin at standard temperature and pressure; so here the heat of reaction of ethane, with oxygen. So, this is my chemical reaction, giving me 2 CO_2 gas plus 3 H_2O gas; and this is occurring at 298.15 degree kelvin. So, we have to estimate the heat of reaction for this.

Here this is straight forward because the $f(T)$ term is 0; we are talking of the standard temperature. So, we just have to get, $\Delta H_{r,T_{naught}}$, heat of reaction at standard temperature. So, here what we have is only this term which is nothing but this. So, $\Delta H_{r,T_{naught}}$ is equal to this, according to the derivation which we had just worked out.

Now, let us see, first let us start with the product. We have 4 species here- ethane, oxygen, carbon dioxide, and water vapor. So, in the product side we do not have any ethane; so 0 times this. We do not have any hydro oxygen also; so once again 0. We have

some carbon dioxide; so 2 moles of carbon dioxide are there. So, 2 times heat of formation of carbon dioxide plus, 3 times heat of formation of water vapor; that is the product side, minus; let us come to the reactant side. We have 1 mole of ethane, then plus three and half moles of oxygen plus, 0 mole of carbon dioxide plus, 0 mole of water vapor. So, that is why thermo chemical equation. Now, oxygen in molecular form is the standard state. So, heat of formation of oxygen is 0; so that is 0. So, what I will have now is a very simple expression.

(Refer Slide Time: 23:37)



It says that delta H r T naught is equal to 2 times, let me see here, 2 times heat of formation of carbon dioxide which is minus 94 kilo calorie we have seen before. So, this is 2 times minus 94 roughly, approximately; 3 times heat of formation of water vapor; heat of formation of water vapor is minus 57.8 kilo calorie per mole, that again we can get from the thermo chemical tables, minus; 1 times heat of formation of ethane. So, that is 1 into 20.24, minus 20.24.

So, now, if I just do the maths it comes out to be 341.16 kilo calorie. So, this is the heat of reaction at standard state. Notice, that this value is coming out to be negative which means that this reaction is exothermic. So, this explains how we estimate the heat of reaction. Now, if it works to be at different temperature we get the C p terms in which we will work out later.

The value that we are getting here for standard state has a particular significance. If this product, if this species which is ethane here which is burning is a fuel, then we call this

the heating value of the fuel. So, heating value of the fuel is defined as a positive number that is equal to the enthalpy of combustion, but of opposite signs. So here, this value here is the enthalpy of combustion because we are burning ethane in oxygen. So, this is the enthalpy of combustion, but with opposite sign because if it is a heating value you always mean it is a exothermic reactions. So, therefore, only the magnitude of this that is this 341.16 this value with the positive sign; that is the heating value of ethane. So, when ethane is burned in pure oxygen this is the amount of heat it is going to give.

Many possible heating values are there depending on the phase of the products or on the reactants. For example, here we have taken everything as gas, right, but for some other reaction we may have solid, liquid, gas, all combined. So, depending on the phase we can have different heating value. So, we have to specify the heating value for a particular phase. And of course, it depends on the condition of combustion. Here everything is a standard temperature and standard pressure, but if pressure and temperatures are different particularly temperature is different we are going to have different heating value. So, heating value is defined for a given temperature.

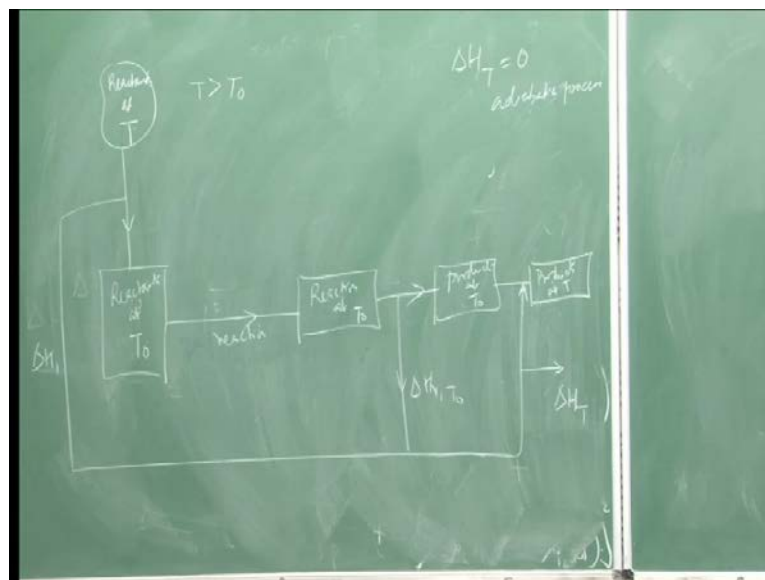
Now, on the other hand, as a special case if I consider again this reaction, ethane is burning with oxygen is a special case of heat of reaction. So, when the heat liberated where the fuel reacts with oxygen to yield carbon dioxide and water vapor which is done here then the heat of that reaction is called heat of combustion. The combustion is defined as something burning in oxygen, pure oxygen. So, therefore, that is how it is defined.

Now, heat of reaction can be deduced by using the Hess's law as we have just discussed to and we summed the appropriate reaction for which the heat of reaction is known. We can also get heat of formation from heat of reaction that is another thing. Many times we do not know heat of formation, but we can estimate only the heat of reaction then we can get the heat of formation from there. So, this is the basics of the heat of reaction.

Now, let us look at another thing. In all over discussing so far, we said that the reaction is occurring at standard state, temperature T_{naught} , some heat is liberated which is by heat of reaction; here this was the standard temperature was at, standard, the reaction was at standard state so that is given $\Delta H_r T_{\text{naught}}$; but if it was, the final temperature was something else it will be $\Delta H_r T$. So, that is how much heat is liberated.

Now, for the argument sake let us say that we know how much it is liberated. We do not know how much is a temperature, then how are we going to handle it. And, what will be the final temperature, how it is defined; in order to do that we have to now define the process.

(Refer Slide Time: 29:04)



So, if I consider a schematic of a reaction path, let us consider a reaction path like this. Let us say that we have reactants initially at some temperature T , and then we want to find out what will be the final product temperature where it is assumed that this temperature is greater than T_{naught} , as T_{naught} is the standard temperature. What we are saying now is that the standard heat of reaction is something that is known to us because we know the heat of formation of all the product species, product as well as reactants. So, we can estimate the standard heat of reaction.

So, we are saying that our reaction is occurring at standard temperature. So, that is the case; only then we know how much is the heat evolved at that condition. That is the case then what we will do is first let us say we choose the temperature of the reactants and take them to the standard temperature. After that, we said that the reaction occurs; so now the reaction is at standard state. And because of that some ΔH is; so reaction at temperature T_{naught} . After that now we have the products because the reaction has occurred we have products at temperature T_{naught} . Now let us see this entire schematic.

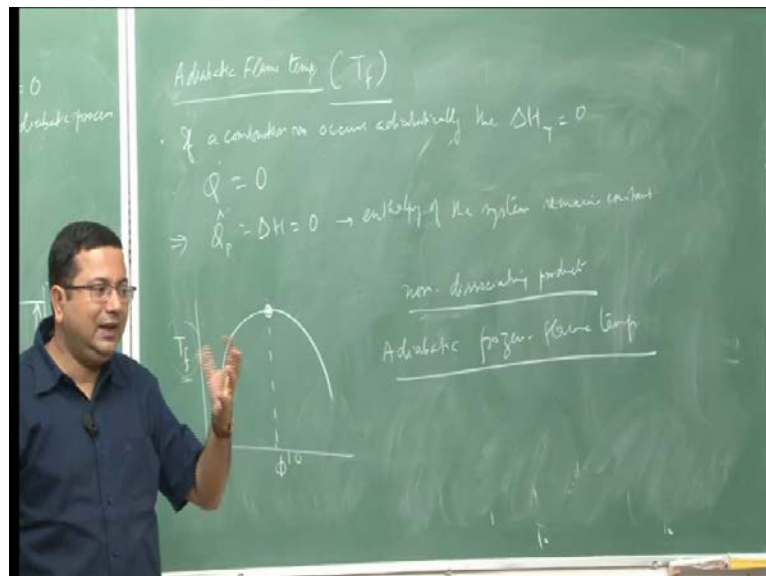
In cooling this reactants from temperature T to T_{naught} we had to take out some heat. Let us say we take out some heat ΔH_1 which we are not giving anywhere, we are

keeping it in same deposit. Then, when the reaction is occurring here during the reactions some amount of it ΔH_r is released, $\Delta H_r T$ is not released. So, that is also with us. Now, this two, ΔH_1 and $\Delta H_r T$ naught, they have to be some more utilized, they have to be reduced. So, what happens is that this heat goes in and heats the product.

So, therefore, we get products at temperature T , where T is the final temperature where all this heat is now going to heat the products. Now, how much heat is taken out and how much is actually utilized depends on the process, right. So, depending on that let us say that; when we will get the maximum heat or the maximum temperature? When all the heat that is generated here is completely supplied to this we get the maximum temperature.

So, in other words, if some, a part of heat is given to this and the part goes out, let us say ΔH that is going out then this temperature is going to be less; only if ΔH is 0 nothing goes out, everything is used up in the system; then this product will be at higher temperature. What is that process where no heat is leaving the system? That is adiabatic, right. So, therefore, that process when you have $\Delta H T$ is equal to 0; this is ΔH_c ; is equal to 0 we have, we call it at adiabatic process and for that we get the maximum temperature, right.

(Refer Slide Time: 33:13)



So, now, this temperature that we get is actually given a name; when we get the maximum temperature that is called adiabatic flame temperature. So, let us now look at what is adiabatic flame temperature. This is the temperature that we would like to

achieve in practical combustion systems, in practical rocket motor, that is why we put lot of insulations to prevent any heat transfer out of the system so that we trap all the energies that is produced by our chemical reaction to heat up the products.

So, we get the final temperature because of the fact that we have discussed in detail that higher our T_c is we get higher characteristic velocity c^* that increases the $i_s p$. So, we get higher $i_s p$ or higher thrust. So, therefore, we want to maximize the temperature. And, we know from now from this discussion the temperature will be maximum if it is done adiabatically that is why we need to have good insulation. So, now let us look at adiabatic flame temperature.

If a combustion reaction occurs adiabatically then ΔH_T is equal to 0; that is ΔH enthalpy that is going out of the system is 0. So, therefore, no heat leaves the system. So, the total system enthalpy remains constant, right. So, therefore, Q_{dot} is 0 which implies for this a constant pressure process. So, the enthalpy of the system remains constant. Now, this is something that how can that happen? Because we know that the chemical reaction, most of the combustion reactions are exothermic.

So, the chemical reaction is going to liberate some heat; where is that heat going? So, that heat is going to heat up the products. So, the reaction is supposed to occur in a different lower temperature then the heat of reaction that is evolved is going to heat up the products to a higher temperature; so we get a higher temperature; and so that the enthalpy of the system remains constant. So, whatever enthalpy was initially the same enthalpy remains at the end.

So, because of that this temperature of the systems increases. This temperature if it is done adiabatically as I have just said, the temperature, this temperature is going to be maximum for a given composition, right. We cannot have temperature more than this because as far as our energy conservation is concerned the optimum amount of range is available to the propellants. So, that is going to be the maximum temperature.

So, for a given composition depending on the heat of reaction we get the maximum temperature is our adiabatic flame temperature. So, therefore, this temperature is called adiabatic flame temperature designated by T_f . Now, this value of T_f then depends on what? Depends on heat of reaction, right. The heat of reaction depends on what? The reaction always will be at stichometric condition, right. It will essentially heat up all the

fuel or air, depending on which I will higher quantity. It will, the reaction will always stichometric.

Now, if you have a condition where we have either excess air or excess fuel, then that excess air or fuel does not take part in the reaction; only the stichometric amount of fuel and oxidizer will take part in the reaction. Now this excess amount of air and fuel then work as a heat sink. So, the heat that is generated is not only heating the products, but also this excess air or excess fuel. So, since the composition is now more number of molecules the overall temperature is going to be less, right.

So, therefore, the adiabatic flame temperature is going to be maximum for a stichometric mixture. And, for any other mixer the adiabatic flame temperature is going to be less. So, therefore, now what we can say is that we can control this adiabatic flame temperature by controlling the ratio of fuel and oxidizer, right. So, fuel oxidizer ratio will control this temperature.

So, if we, now let us look at how do we control. So, first of all what I have just said if I plot the flame temperature verses equivalence ratio then at equivalence ratio of 1, 1 we have stichometric mixer we get the maximum temperature. And, on both sides, that is fuel lean and fuel leach the temperature drops. So, therefore, depending on what fuel oxidizer ratio we have we get different temperatures.

Now, therefore, since we want to operate a rocket, always there is maximum temperature; then what is our ultimate objective is to operate at stichometric, right. So, would you like to operate at stichometric condition as much as possible. And, unlike a gas topped engine where we do not carry the oxidizer; it is freely available, as air is freely available there you operate in the lean slide because the freely available air is there which will give us this advantage.

Whereas for rocket since we are carrying both oxidizer and fuel, both of them are part of propellant, so we do not want to waste any of them. Now, if you are working on this side we have more fuel that is required, so therefore the fuel is wasted. Here, on the other hand, we have more oxidizer then that is required. So, oxidizer is wasted. So, we do not want to waste because we want to carry them. Therefore, for the rocket we would like to operate here.

So, therefore, for the rocket our operating condition should be such that we should be as close to the stichometric as possible, and the temperature then will of course be the

maximum temperature. So, then what happens? Now, this maximum temperature as we have seen was depending on equivalence ratio, now it will depend on the propellants, heat of reaction. So, we have a direct relationship now between the heat of reaction and the final flame temperature for the rocket application. Whereas, as I have just said, for air leak applications this will typically operate towards the lean side, but for rocket we would like to operate at this point. Now, typically this final temperature or the adiabatic flame temperature is quite high. It can be 3000, 4000 degree kelvin, and that is what the rocket temperatures are.

The problem is at such high temperature there is a possibility of dissociation of products and that does occur. So, we will discuss that the way the dissociation is going to affect the performance. The dissociation involves changes in the amount of it because dissociation reactions are endothermic. So, they absorb some energy. Therefore, we may not get this temperature because some energy is gone into dissociation. So, essentially what is dissociation doing? It is changing the final composition.

So, once again the test temperature it depends on the composition if the composition changes dissociation changes. So, dissociation will bring down the final flame temperature, and that is why you would say that the final temperature depends on the composition of the products.

Typically, then the adiabatic flame temperature for non-dissociating products; if the products are non-dissociating, for non-dissociating products the adiabatic flame temperature is called adiabatic frozen flame temperature because if the dissociation is not occurring we say that the composition is frozen. So, we say this is the adiabatic frozen flame temperature. So, this is the temperature that is going to be our T_c for our rocket motor.

So, now, we have discussed what is this temperature; the next step will be how do we estimate this temperature. So, remember for the last few lectures we have been talking about heat of reaction, etcetera, heat of formation, etcetera, but now we are coming back to what we were intended to do to get the temperature. But, the temperature as I have just mentioned is a function of the composition; that also needs to come out during our discussion. So, I will stop here now in this lecture.

In the next lecture, first we will talk about how do we estimate this adiabatic flame temperature. Once that is done then we will see that the composition and temperature are

interlinked. So, therefore, unless we talk about temperature we cannot talk about composition; similarly, unless we talk about composition we cannot talk about temperature also. So, we will bring out that interlink and then go in to the estimation of the composition as well. So, I will stop here now and in the next class we will continue from here.

Thank you.