Engineering Thermodynamics

Prof. S. R. Kale
Department of Mechanical Engineering
Indian Institute of Technology, Delhi

Lecture - 52
Thermodynamics of Reacting Systems: Analysis of Closed and Open Systems. Enthalpy of formation.

This is the third lecture on Reacting Systems. We continue where we left off from last time, where we have defined what type of a system we are going we have developed, how are going to approach it and now we will go into the analysis of that. And begin to answer the question that we are posing in terms of what is energy release and what is the type of temperatures that we get. So, we write that same equation that we were looking at earlier.

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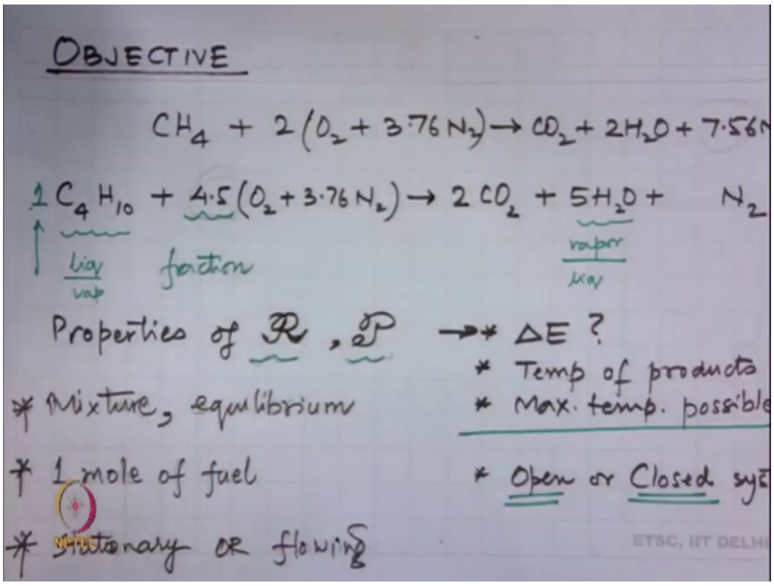

OBJECTIVE

$CH_4 + 2(O_2 + 3.76 N_2) \rightarrow CO_2 + 2H_2O + 7.56$

$\underset{\substack{\uparrow \\ \frac{liq}{vap}}}{\underbrace{1}} C_4H_{10} + \underset{fraction}{\underbrace{4.5}}(O_2 + 3.76 N_2) \rightarrow 2 CO_2 + \underset{\frac{vapor}{liq}}{\underbrace{5H_2O}} + \quad N_2$

Properties of $\mathcal{R}$, $\mathcal{P}$ → * ΔE ?

* Temp of products
* Max. temp. possibl

* Mixture, equlibrium
* 1 mole of fuel
* Stationary OR flowing

* Open or Closed sy

The burning of methane in air, these are stoichiometric reaction. We are defined what is stoichiometric mixture, what is equivalence ratio, what is percent excess air, all those quantities we are defined. So, instead of this we it hydrocarbon could have been any other hydrocarbon, in this second reaction is for butane. And only reason for putting it here is that first out here what we are seeing is that number of moles need not be an integer as we are seeing here it is fraction. And we do that, so that the number of moles on this side for the fuel this remains 1 that is one thing.

The second thing to note here is that C 4 H 10 which is LPG the main constituent of LPG in the cylinder, this is in the liquid phase, but then when it burns this is in the vapour phase. Another point to note is that this H 2 O which is a in the domestic burner it just goes out a H 2 O vapour, we do not see it, but if you have put the gas flame low and put a vessel of cold water, you will see some H 2 O condensing outside it. So, this could be that the H 2 O leaves the reacting system the device in vapour form, vapour phase or in liquid phase. We will see the applications of this on energy that is released by this reaction in a few minutes.

So, what we want now is that we want the properties of the reactants and the mixtures to answer the question that we are posing like heat release, temperature, maximum temperature possible. We will develop this analysis for two situations; open system and a close system. And as we have already convinced ourselves that we will treat the reactants as a mixture which is at equilibrium and we will then put all the properties of a mixture that we have learned earlier, all the parameters the symbols everything that we have already learned this is what we will bring into our use over here.

Then we will always write the reaction, so that we have 1 mole of fuel simply everything else become easy. And we will often refer to various things particularly energy release rates on a per fuel kg or per fuel mole basis per fuel mass. So, we will keep the fuel as 1 mole. And as we have seen that does not matter whether this reaction does not tell us whether the fuel is stationery or it is moving. The reaction is applicable to both cases, where the whole system or the flows, there is no flow taking place with the stationery system or there is a flow system that is also ok. The reaction remains the same; the analysis remains the same.

So, going back to our mixtures, so how do we quantify our reactants and products? And this is exactly the same of what we are defined earlier in mixtures. Mass fraction of every species is capital y i is a mass of that species divided by mass of the mixture in a given system that the volume is fixed.

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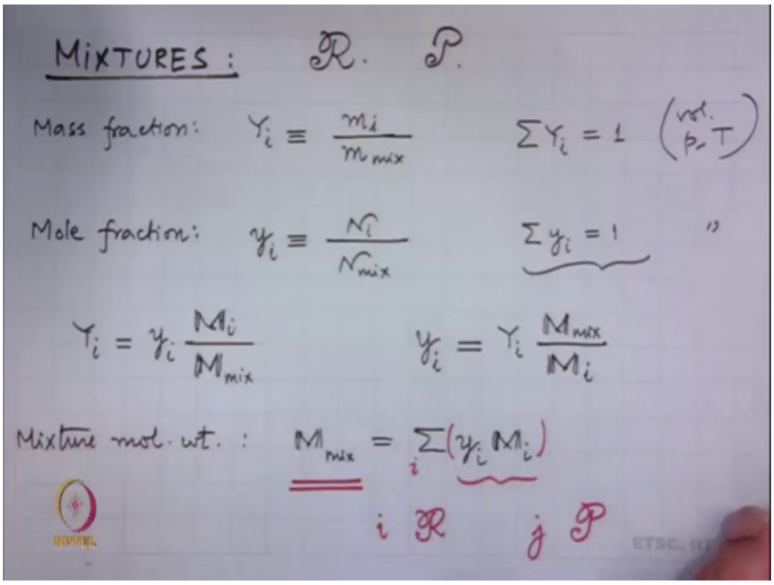

MIXTURES : $\mathcal{R}$. $\mathcal{P}$.

Mass fraction: $Y_i \equiv \frac{m_i}{m_{mix}}$ $\qquad \sum Y_i = 1$ (vol. p, T)

Mole fraction: $y_i \equiv \frac{N_i}{N_{mix}}$ $\qquad \underbrace{\sum y_i = 1}$ "

$$Y_i = y_i \frac{M_i}{M_{mix}} \qquad y_i = Y_i \frac{M_{mix}}{M_i}$$

Mixture mol. wt. : $\underline{\underline{M_{mix}}} = \sum_i (\underbrace{y_i M_i})$

i $\mathcal{R}$ $\qquad$ j $\mathcal{P}$

So, we have same volume and same pressure and same temperature. Mole fraction for the same conditions, the number of moles of the species i here divided by the total number of moles in the mixture. And in both cases, these are normalized things. So, the sum of all the mole fraction is 1 and this thing is also 1. And these two are related to one another that the mass fraction is mole fraction multiplied by the mass molar mass ratio and the opposite there in this case.

And an important thing that comes out is that the mixture molecular weight is summation of the molar mass molar fraction multiplied by the molecular weight of that species and this is summed of for all the species which in the case of reactants. We will denote by i and in the case of products, we will put j as the here and all the species in the products. Later on in the calculations this becomes something called easy to use, sometimes we will be also using this one.

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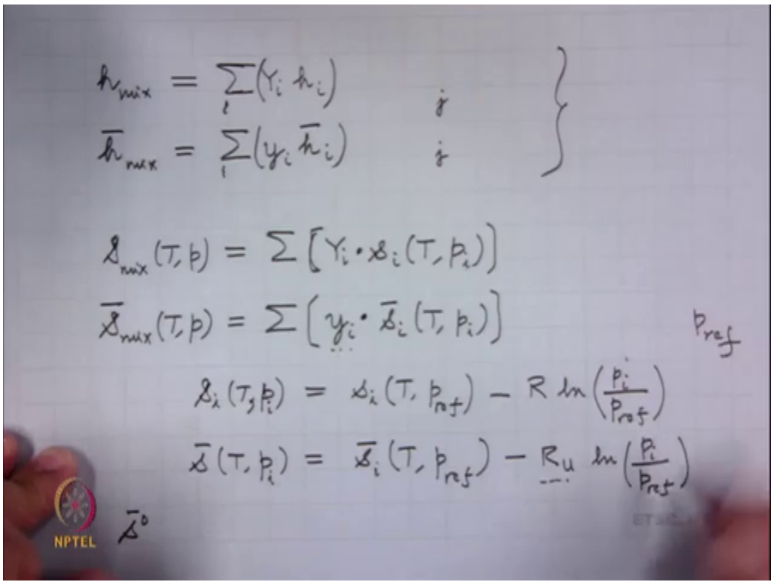

$$\left.\begin{array}{ll} h_{mix} = \sum_i (Y_i h_i) & j \\ \bar{h}_{mix} = \sum_i (y_i \bar{h}_i) & j \end{array}\right\}$$

$$s_{mix}(T, p) = \sum [Y_i \cdot s_i(T, p_i)]$$

$$\bar{s}_{mix}(T, p) = \sum [\underset{\cdots}{y_i} \cdot \bar{s}_i(T, p_i)]$$

p_{ref}

$$s_i(T, p_i) = s_i(T, p_{ref}) - R \ln\left(\frac{p_i}{p_{ref}}\right)$$

$$\bar{s}(T, p_i) = \bar{s}_i(T, p_{ref}) - \underset{\cdots}{R_u} \ln\left(\frac{p_i}{p_{ref}}\right)$$

$\bar{s}^0$

Then mixtures you also defined that the specific enthalpy of the mixture can be defined as the mass fraction multiplied by the specific enthalpy of each component summed up over for all the species in the component. This could be either i or as we said this could also be j. On a molar basis, the molar specific molar enthalpy is summation of the molar ratio multiplied by the molar enthalpy specific molar enthalpy which you denote by a bar, so that is how we get the enthalpy so of the products or enthalpy of the reactants.

Now, we will look at specific entropy of the mixture. For a given temperature and pressure this is the sum of the mass fraction multiplied by specific entropy at the temperature, but the pressure for i th species is its partial pressure in that mixture, so that is a difference here. That the mixture specific enthalpy is at T and p, but the species specific enthalpy is at the same T, but at the partial pressure of that species in that mixture. And we can express this in terms of a molar specific enthalpy which we put a bar there and this is s i bar and this is the molar mass fraction.

And we know that specific entropy of any species or in general a specific entropy for T and p is specific entropy at T and reference pressure minus R ln p upon p ref. So, we need a reference pressure for defining the specific entropy. And we have said that if this was ambient as 1 bar as this reference pressure, we have got terms like s 0 bar and from there we could get everything else. The molar definition of specific entropy is given by this relation which is nothing but the same one si bar at T and p ref minus the universal gas constant and the logarithm ratio of pi over p ref. So, this is all what we have already got from mixtures. And we know that if you have a mixture of molecules how to get h, u, s all these properties.

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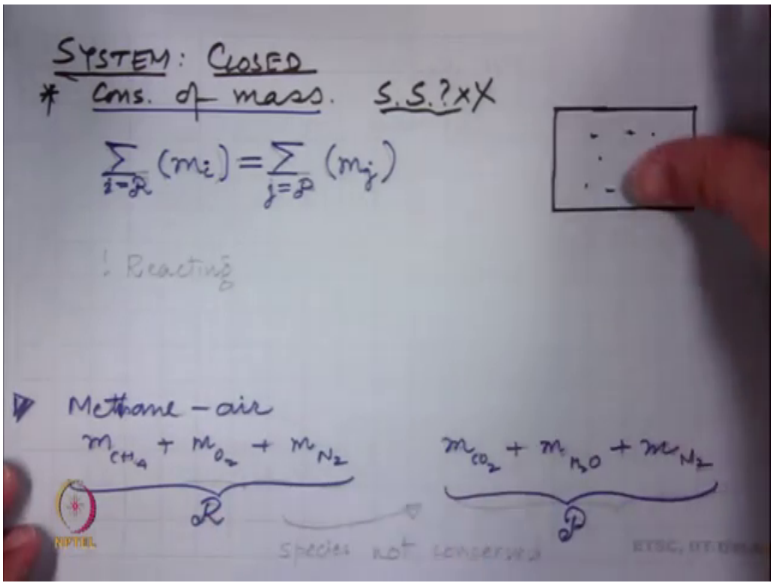

SYSTEM: CLOSED

* Cons. of mass. S.S.?XX

$$\sum_{i=R}(m_i) = \sum_{j=P}(m_j)$$

! Reacting

Methane – air

$$\underbrace{m_{CH_4} + m_{O_2} + m_{N_2}}_{R} \rightarrow \underbrace{m_{CO_2} + m_{H_2O} + m_{N_2}}_{P}$$

Species not conserved

Let us now start by looking at a closed system and we will do two things apply conservation of mass and then the conservation of energy. So, the first thing is a closed system. There is no issue of steady state, because it is stationary. And we apply the conservation of mass to this, so that equation there is straight forward from the mixture thing. We say that whatever mass was there before the react reaction took place is exactly the same after the reaction.

So, we write that summation of all the mass of every species from i equal to R, this is for every reactant species, this is equal to the summation for every react product species where j is the product and these two are equal. So, this is mass conservation. And it is different from the mixtures that we had done where there was no reaction, was in that case we said that the mass of individual species is also conserved. But that is not the case here, because there is a reaction taking place some of the species here got disappeared and they do not exist in the products and new species are appeared in the products which did not exist in the reactants.

So, species conservation though it can written, you will have to write that for that there is a source term or a sync term where the species has disappeared. We will not bother to write at this point of time. In the case of our example which was the methane air reaction, we have mass of methane plus mass of oxygen and mass of nitrogen all of this is a reactance. And in the product side, we will have to a mass of carbon dioxide, mass of H 2 O the water that is formed and mass of nitrogen all of which is the products which is here, so that is what this equation would become practically in solving problems, it will become like this. So that is for conservation of mass and now for the same system we will look at conservation of energy.

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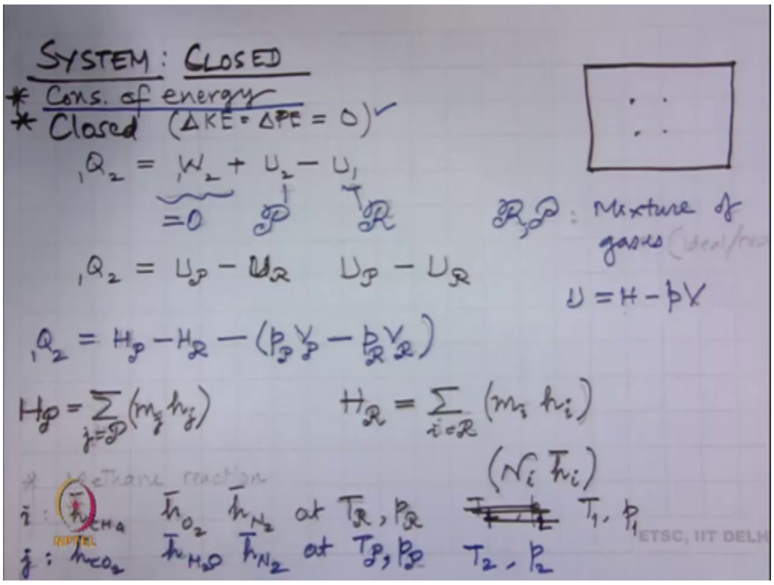

SYSTEM : CLOSED

* Cons. of energy

* Closed $(\Delta KE = \Delta PE = 0)$ ✓

$${}_1Q_2 = \underbrace{{}_1W_2}_{=0} + \underbrace{U_2}_{\mathcal{P}} - \underbrace{U_1}_{\mathcal{R}}$$

$\mathcal{R}, \mathcal{P}$: Mixture of gases (ideal/rea

$${}_1Q_2 = U_{\mathcal{P}} - U_{\mathcal{R}} \qquad U_{\mathcal{P}} - U_{\mathcal{R}}$$

$$U = H - pV$$

$${}_1Q_2 = H_{\mathcal{P}} - H_{\mathcal{R}} - (p_{\mathcal{P}}V_{\mathcal{P}} - p_{\mathcal{R}}V_{\mathcal{R}})$$

$$H_{\mathcal{P}} = \sum_{j \in \mathcal{P}} (m_j h_j) \qquad H_{\mathcal{R}} = \sum_{i \in \mathcal{R}} (m_i h_i)$$

$$(N_i \bar{h}_i)$$

* Methane reaction

i : $\bar{h}_{CH_4}$ $\bar{h}_{O_2}$ $\bar{h}_{N_2}$ at $T_{\mathcal{R}}, p_{\mathcal{R}}$ T_1, p_1

j : $\bar{h}_{CO_2}$ $\bar{h}_{H_2O}$ $\bar{h}_{N_2}$ at $T_{\mathcal{P}}, p_{\mathcal{P}}$ T_2, p_2

And we assume that there is no change in kinetic and potential energies. And so we can write the first law equation as Q from state 1 to state 2 is work done plus U 2 minus U 1. And it is a closed system and for the time being let us assume that there is no work transfer and we put this at 0. U 2 is at some temperature and pressure and this is nothing but the condition of the products and U 1 is nothing but the condition of the reactants. And as we said reactants and products each one of them individually can be analyzed as a mixture of gases. And U has we have learned earlier in the course is H minus p V. The reason for writing this is that we have tables and data for H in many cases U is not tabulated, but that is the way to get U.

So, now let us write down this reaction further and see what happens. We can say that Q 1 2 is H P minus H R minus pressure product of p V for the products minus the same product, but now for the reactants. And now we expand the equation we had just put a few minutes back that the extensive property enthalpy of the products this is summation of enthalpy of the individual species which is m j h j and j is taken for every product.

And similarly H R is summation for every species for m i h i, instead of writing in terms of mass of the individual species we can also represent this by the number of moles and call use the molar specific heat, number of moles of i multiplied by the specific enthalpy of i. So, both this bracket terms can be made into this form.

So, in this case, if suppose this mixture was methane plus air, then the reactants we will have to get the h here or h bar for CH 4, say h bar for O 2, h bar for N 2 and all of this will be at the state at which the reactants are which could be T R and p R or if it is state 2 we can say that this is T 2, p 2. So, this is what the products work. For the reactants or for the products, so this was the reactants we have h bar CO 2, h bar H 2 O, h bar N 2 and this we will evaluate at the temperature and pressure at which the react of the products.

These are reactions this will be T 1 and p 1, this is T 2 and p 2. So, the reactants are at temperature T 1 and p 1 and products at T 2 and p 2. So, what the problem has now come to is that if we know these enthalpy values, we can then put them here and calculate what are the heat transfer during the reaction or how do we get this. We will come back to this question in a few minutes after looking at open systems.

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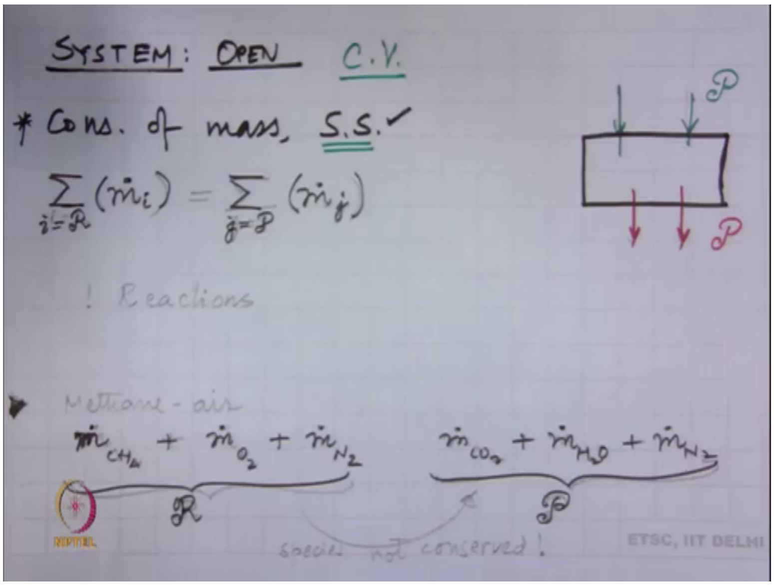

SYSTEM: OPEN C.V.

* Cons. of mass, S.S. ✓

$$\sum_{i=\mathcal{R}} (\dot{m}_i) = \sum_{j=\mathcal{P}} (\dot{m}_j)$$

! Reactions

Methane - air

$$\underbrace{\dot{m}_{CH_4} + \dot{m}_{O_2} + \dot{m}_{N_2}}_{\mathcal{R}} \qquad \underbrace{\dot{m}_{CO_2} + \dot{m}_{H_2O} + \dot{m}_{N_2}}_{\mathcal{P}}$$

species not conserved !

So, first the open system conservation of mass, it is the same type of system that we had made earlier, where we had inflows of the reactance and out flow of the products. And we apply the conservation of mass for a control volume with that assumption that there is steady state; that means, m cv dt term that becomes 0. So, it we are left with the fact that mass in flow rates is equal to mass out flow rates. So, inflow rates are again by m dot i, where i is every species in the reactants. And this has to equal the mass flow rates of every species that is flowing out with the products. Again as before some of the reactants disappear new species appear and so species conservation is not strictly the way we are writing this.

And in the case of them if this was the fuel was methane and going with air and coming out as carbon dioxide, water and nitrogen, then we would have to need mass flow rate of CH 4 plus mass flow rate of O 2 plus mass flow rate of N 2, this is what we have in the reactants. And for the products it will be mass flow rate of carbon dioxide plus mass flow rate of H 2 O plus mass flow rate of N 2 and this is all the products. So, that is one part of the story. And now we will look at the same system and look at the conservation of energy.

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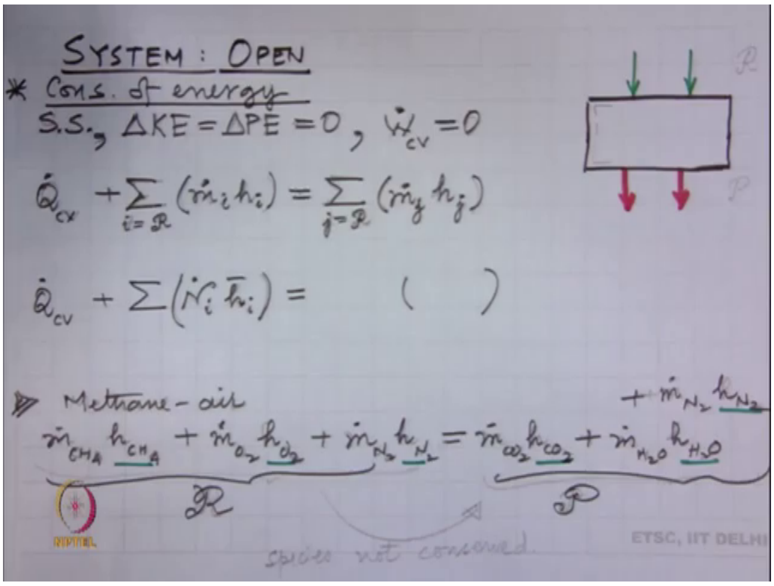

SYSTEM : OPEN

* Cons. of energy

S.S., $\Delta KE = \Delta PE = 0$, $\dot{W}_{cv} = 0$

$$\dot{Q}_{cv} + \sum_{i=\mathcal{R}} (\dot{m}_i h_i) = \sum_{j=\mathcal{P}} (\dot{m}_j h_j)$$

$$\dot{Q}_{cv} + \sum (\dot{N}_i \bar{h}_i) = (\qquad)$$

▷ Methane - air

$$\underbrace{\dot{m}_{CH_4} h_{CH_4} + \dot{m}_{O_2} h_{O_2} + \dot{m}_{N_2} h_{N_2}}_{\mathcal{R}} = \underbrace{\dot{m}_{CO_2} h_{CO_2} + \dot{m}_{H_2O} h_{H_2O} + \dot{m}_{N_2} h_{N_2}}_{\mathcal{P}}$$

species not conserved.

And we assume that in most of the system and which is a reasonably good assumptions that we have steady state that kinetic energy changes and potential energy changes are 0. And we also further assume that work done is 0, work transfer during the process, but there could be and will be heat transfer. So, the whole energy equation now becomes Q dot c v plus m dot i h i, where i is every reactants species, this is equal to summation of the same product for every product species.

Alternately, we could write these as mass flow rates of the moles multiplied by the molar specific heat molar specific enthalpy. So, for the methane air reaction, we have to have m dot of CH 4 multiplied by h CH 4 plus mass flow rate of oxygen and specific enthalpy of oxygen, mass flow rate of nitrogen and specific enthalpy of nitrogen, this is mass flow rate of carbon dioxide and specific enthalpy of CO 2, mass flow rate of H 2 O and specific enthalpy of H 2 O plus mass flow rate of nitrogen multiplied by specific enthalpy of nitrogen. So, this is all our reactants, all of these are our products.

And again now what we see here is we have to get these terms, the specific enthalpy of each of these and specific enthalpy of these that is our the issue before us. So, now we got the same question when we looked at the closed system. There also we needed this specific enthalpies. So, what is the issue? Well, we have studied in properties of a pure substance that you had tabulated specific enthalpies.

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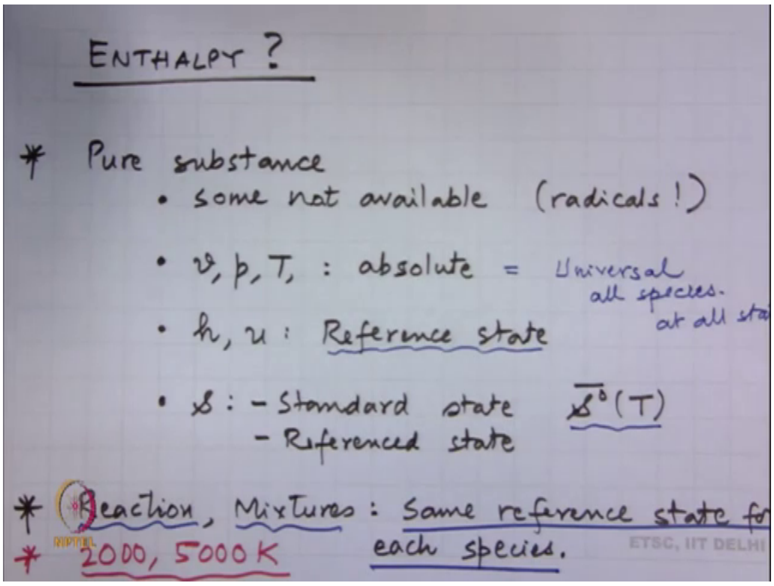

ENTHALPY ?

* Pure substance
  - some not available (radicals !)
  - $v, p, T,$: absolute = Universal all species. at all sta
  - h, u : Reference state
  - s : - Standard state $\bar{s}^0(T)$
    - Referenced state

* Reaction, Mixtures : Same reference state fo each species.

* 2000, 5000 K

First in reacting systems we got so many substances that maybe we do not have this tables data for every species. It may be there, but not be readily available. Second they could also be some radicals in the certain chemical reactions for which data is not there. The next thing to note is that while pressure, volume, specific volume and temperature are absolute quantities in the sense that they do not depend on the reference state. And the meaning for them is same for every substance. So, there is no ambiguity in it. So, this is common to all species. So, universal and this is applicable to all species at all states.

But as we saw with pure substance, specific enthalpy and specific internal energy and also specific entropy were all with reference to a particular state which we called the reference state. For water the reference state was that the specific enthalpy of saturated liquid at the triple point is 0. It was completely a choice of convenience. For some materials it was that instead of 0 degrees the temperature was minus 40 degree Celsius or minus 60 degree Celsius.

In the case of the psychometric chart, the reference state was different. So, all the viewer getting values of h numerically there values would be all different, which was all fine if you are only looking at a system with one pure substance; if you are looking at a mixture, we realize that the reference state for both the substances must be the same.

Now, we have a issue coming up here that h, u and s have different reference state for different materials. For ammonia, it is something, for carbon dioxide it must be something else. H 2 O itself somebody could have some value, somebody else would have some other value. And the reason why everybody does not use 0 Kelvin at this fixed reference state, it simply because all the numbers becomes very large and we say we do not want to deal with a very large numbers in most day-to-day calculations. So, we will shift our scale, it is a matter of convenience there.

For s we developed a standards state entropy definition is 0 bar and that to care of much of these issues, but not for h and u. The second complicating factor that is coming into this case is that we have reactions. There are many species in this and we have mixtures of these species. And in order to calculate h and u of a mixture, we have a very important requirement coming up is that we should have the same reference state for each species; otherwise we could end up in a big mess.

So, what this means is that while the earlier property data were there, we are now going to shift and change and relook at it in a different way with a reference state which is a unique, unambiguous for all species. So, this is what we have to define the specific enthalpy. There is one more issue that is coming up in the case of reacting systems particularly combustion is that all these properties that we had for properties of a pure substance work for temperatures in a particular range.

In combustion we get much higher temperature than we saw in those cases temperatures of several 1000, 2000, 4000, 5000 Kelvin or even more are not uncommon. And most of these property tables do not go anywhere near these temperatures. So, we need property data that goes up to this high temperature that is one.

And second at these high temperatures the pure substance also undergoes a change in that there could be some dissociation. So, that also needs to be taken care of. And so we need a completely different set of properties that firstly, are consistent across species and go to much higher temperatures and from that we can do are combustion calculations.

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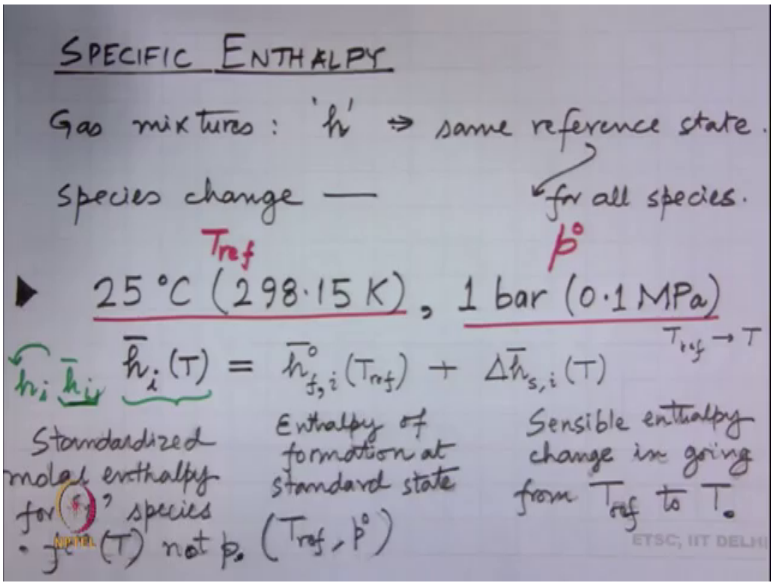

SPECIFIC ENTHALPY

Gas mixtures : 'h' ⇒ same reference state.

species change — for all species.

▶ $\underset{T_{ref}}{25\,°C\ (298.15\,K)}$, $\underset{p^{\circ}}{1\ bar\ (0.1\,MPa)}$

$h_i\ \bar{h}_i\ \underbrace{\bar{h}_i(T)} = \bar{h}^{\circ}_{f,i}(T_{ref}) + \Delta\bar{h}_{s,i}(T)\quad T_{ref} \to T$

Standardized molar enthalpy for 'i' species

Enthalpy of formation at standard state

Sensible enthalpy change in going from T_{ref} to T.

• $f^n(T)$ not p. (T_{ref}, p°)

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So, the first thing we do is define a reference state. And we say that for all enthalpy referencing we will use 25 degree Celsius which is 298.5 15 Kelvin as a reference temperature and the reference pressure we will call it as p superscript 0 is 1 bar or 0.1 mega Pascal. And then we will say that we are now going to redefine or specific enthalpy and instead of working with a mass basis we will from now on all the property data we will get is a moral basis.

So, h i bar T, where i is any particular species. This is what we are calling as all the enthalpies that we were looking at earlier. What we said was h i or h i bar is this now.

And this multiplied by the molecular mass of i species will give us this. So, the two are it very easily converted and we will concentrate on this part. And to be explicit and say that this is enthalpy at a particular temperature for a particular species, this is the expression we are going to use.

So, this is what we will call standardized molar enthalpy for the ith species, h i T which is a function of temperature and not of pressure, so that is h i T bar. This is standardized molar enthalpy. And this we will refer we will express as sum of two properties, one we call h 0 f, i is the species and write a particular reference temperature plus delta h and which is the change. So, what we are saying is that at this temperature, we have a particular value of a fixed enthalpy to which we add a change in enthalpy from that reference state to the actual state. So, actual state is T, reference state was 25 degree Celsius.

So, this with a f subscript is enthalpy of formation at standard state. So, this is a new term that we are now introducing enthalpy of formation at standard state which means this was done at T ref and p 0 and all the property data that we have will be for this condition 25 degree Celsius and 1 bar. So, this is like a fixed parameter that at about some reference temperature, it is T is the enthalpy is fixed. And this is now made consistent across all species.

And then there is change from the reference state temperature to the actual temperature T. So, either it will be call it T or this is from T ref to T. So, this is a sensible enthalpy what you are calling the subscript s sensible enthalpy change. And in some cases you may just see enthalpy change in going or transiting from the reference state temperature T ref to the temperature at which we need the property. So, this is a new thing that has come up enthalpy of formation is something that is come as a new thing. And we will see look at this much more detail in a few minutes.

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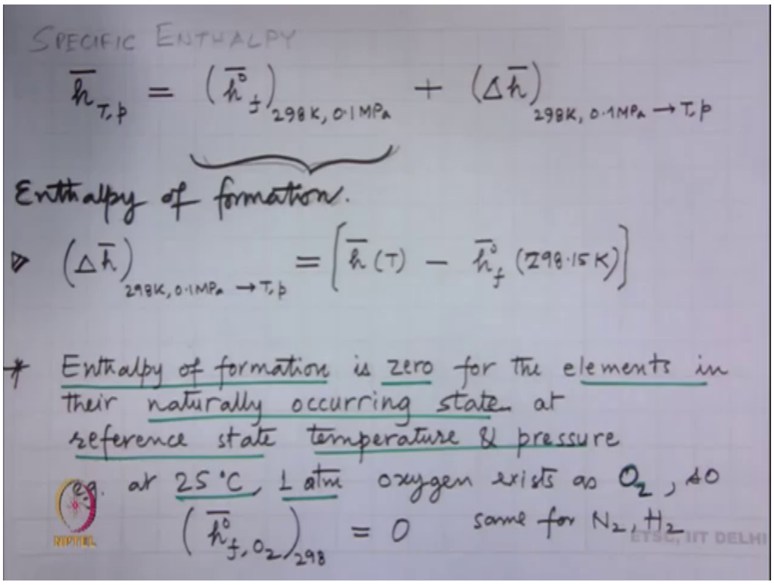

SPECIFIC ENTHALPY

$$\bar{h}_{T,p} = \underbrace{(\bar{h}^{o}_{f})_{298K,\, 0.1MPa}}_{\text{Enthalpy of formation.}} + (\Delta\bar{h})_{298K,\, 0.1MPa \to T,p}$$

▷ $(\Delta\bar{h})_{298K,\, 0.1MPa \to T,p} = \left[\bar{h}(T) - \bar{h}^{o}_{f}(298.15K)\right]$

* Enthalpy of formation is zero for the elements in their naturally occurring state at reference state temperature & pressure

e.g. at 25 °C, 1 atm oxygen exists as O_2, so

$(\bar{h}^{o}_{f,O_2})_{298} = 0$ same for N_2, H_2

So, now we can write the same expression and it will more convenient way is for any species we can then put the subscript i. So, we have did drop that subscript i for the time being and such that the molar specific enthalpy at temperature and pressure is molar specific enthalpy of formation at standard state plus change of enthalpy from standard state to the actual temperature and pressure, where this part is the enthalpy of formation.

And we can rearrange this terms and say that delta h for this change is delta h at T and we can say that the effect of pressure on specific enthalpy is not very significant minus the enthalpy of formation at 298.15 Kelvin or somewhere you will see only 298 is written, somewhere it is 25 degree C is written. So, this is something we are getting.

And the convention that is followed and it is consistent is what we have written in the next statement that the enthalpy of formation is 0 for the elements in their naturally occurring state at reference state temperature and pressure which is 25 degree C and 1 atmosphere. So, at 25 degree C, 1 atmosphere oxygen exists as O 2 diatomic structure. And we say that enthalpy of formation of O 2 at 298 Kelvin is 0. So, instead of oxygen we are looking at nitrogen or hydrogen, this should be the same case.

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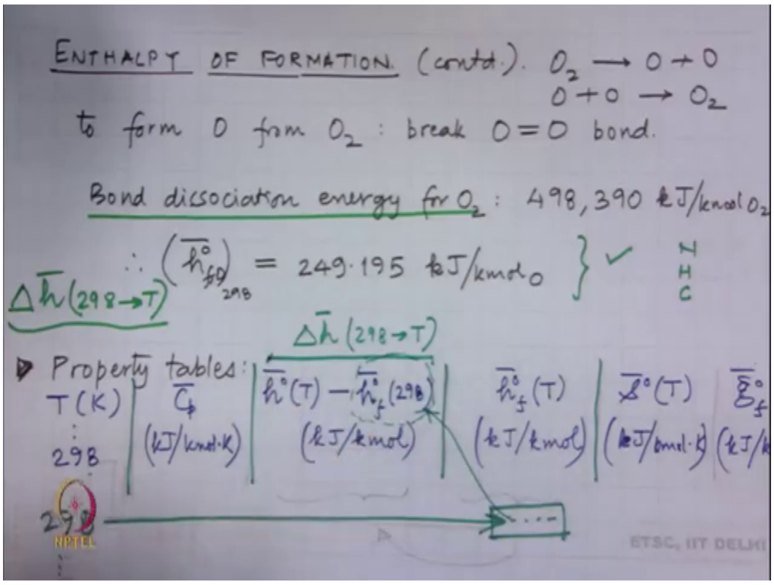


ENTHALPY OF FORMATION (contd.). $O_2 \longrightarrow O + O$

$O + O \longrightarrow O_2$

to form O from O_2 : break O=O bond.

Bond dissociation energy for O_2 : 498,390 kJ/kmol O_2

$\therefore (\bar{h}^{\circ}_{f,O})_{298} = 249.195$ kJ/kmol$_O$ } ✓ N H C

$\Delta\bar{h}(298 \to T)$

▶ Property tables:

T(K)	$\bar{c}_p$ (kJ/kmol·K)	$\overbrace{\bar{h}^{\circ}(T) - \bar{h}^{\circ}_f(298)}^{\Delta\bar{h}(298\to T)}$ (kJ/kmol)	$\bar{h}^{\circ}_f(T)$ (kJ/kmol)	$\bar{s}^{\circ}(T)$ (kJ/kmol·K)	$\bar{g}^{\circ}_f$ (kJ/k
⋮					
298					
298		...			
⋮					

So, what it means is that having said this as a reference state as 0, we can now go and ask the question that if I have to break oxygen to form O plus O or you look at O 2 becoming O plus O or O plus O becoming O 2 what is the energy involved in this? In the first case, if you have to go like this the bond which is the O-O bond, this bond has to be broken. For that you need to give energy and that is called the bond dissociation energy for oxygen.

And this is known as known to be from data tables as 498,390 kilo Joules per kilo mole of oxygen. So, when you give that much energy to 1 kilo mole of oxygen, we produce 1 kilo mole of O plus 1 kilo mole of O 2 kilo moles of O. So, the enthalpy of formation of atomic oxygen O at 298 Kelvin is half of this value which is 249.15 kilo Joules per kilo mole O.

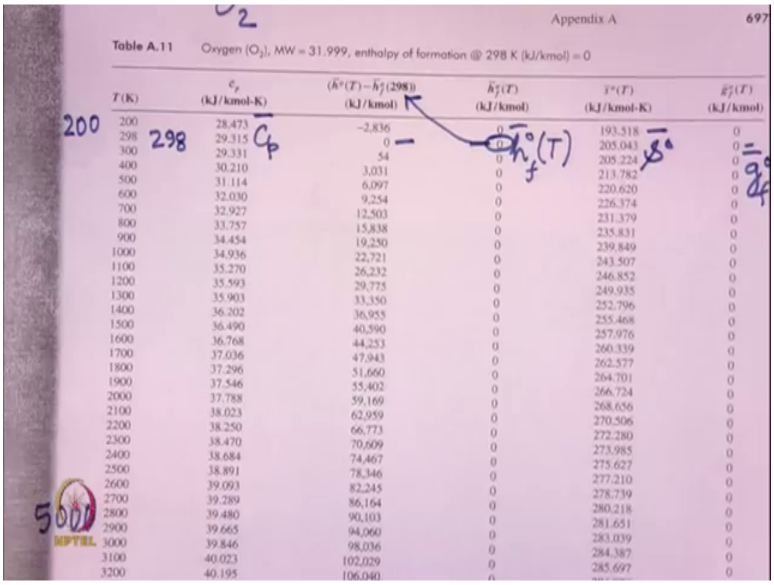
So, now we have got something the enthalpy of formation of atomic oxygen is known and like that we can get the enthalpy of formation for every element like this. So, we can have N, we can have H O is already there, you can add more chemicals to it. And then so, you can even add say C like that. And then what one can do is select in this case if O and O to be combined, we knew how much energy would be released. We can then say if I have to combined C and H and H and H, I would create 4 bonds what is the amount of energy required from knowing the formation enthalpies of individual atoms we can get the formation of any complex molecule all reference to the same state.

So, we have a consistent method of getting the data. So, where do we get this data? First we need the enthalpy of formation and then we need the other part which was delta h bar going from standard state 298 k going to T. So, how do we get this data? For this we now start using yet another set of property tables where they have listed this different things and I will show you the tables in a few minutes. The first column has the temperature in Kelvin; the second column gives the molar specific heat; the third column gives what we have been talking of here delta h which is h 0 T minus h f 0 at 298 k that is molar specific enthalpy at temperature t minus enthalpy of formation at the reference state that is the third column.

So, this is one column, second column, third column. The forth column give the enthalpy of formation at that particular at any temperature T. And in this will get various numbers coming down then s 0 t and then finally, Gibbs function for formation g f t. In this temperature column, there will be some temperatures below and then finally, everyone will have an common temperature at 298 k and then it goes there. And so if you look at h f t at 298 k, this is the value that were are looking at to put over here.

So, this value you can say is popping up into this part from here it comes. So, you will get 298 k pick up this value, it goes into this expression. And then we can use the same relation that enthalpy is this plus delta h; delta h came from here. So, we can write this even on the top of this, this is delta h bar going from 298 to T ok.

(Refer Slide Time: 34:17)



Appendix A 697

Table A.11 Oxygen (O_2), MW = 31.999, enthalpy of formation @ 298 K (kJ/kmol) = 0

T (K)	$\bar{c}_p$ (kJ/kmol-K)	$(\bar{h}^\circ(T)-\bar{h}^\circ_f(298))$ (kJ/kmol)	$\bar{h}^\circ_f(T)$ (kJ/kmol)	$\bar{s}^\circ(T)$ (kJ/kmol-K)	$\bar{g}^\circ_f(T)$ (kJ/kmol)
200	28.473	−2,836	0	193.518	0
298	29.315	0	0	205.043	0
300	29.331	54	0	205.224	0
400	30.210	3,031	0	213.782	0
500	31.114	6,097	0	220.620	0
600	32.030	9,254	0	226.374	0
700	32.927	12,503	0	231.379	0
800	33.757	15,838	0	235.831	0
900	34.454	19,250	0	239.849	0
1000	34.936	22,721	0	243.507	0
1100	35.270	26,232	0	246.852	0
1200	35.593	29,775	0	249.935	0
1300	35.903	33,350	0	252.796	0
1400	36.202	36,955	0	255.468	0
1500	36.490	40,590	0	257.976	0
1600	36.768	44,253	0	260.339	0
1700	37.036	47,943	0	262.577	0
1800	37.296	51,660	0	264.701	0
1900	37.546	55,402	0	266.724	0
2000	37.788	59,169	0	268.656	0
2100	38.023	62,959	0	270.506	0
2200	38.250	66,773	0	272.280	0
2300	38.470	70,609	0	273.985	0
2400	38.684	74,467	0	275.627	0
2500	38.891	78,346	0	277.210	0
2600	39.093	82,245	0	278.739	0
2700	39.289	86,164	0	280.218	0
2800	39.480	90,103	0	281.651	0
2900	39.665	94,060	0	283.039	0
3000	39.846	98,036	0	284.387	0
3100	40.023	102,029	0	285.697	0
3200	40.195	106,040	0		

So, we have a look at the tables now. These are available as standard data ok. So, I have mentioned these are standard data tables, which have been generated from statistical mechanics and kinetic theory of gases. And this is here is given for oxygen O 2 its molecular weight 31.99, enthalpy of formation at 298 Kelvin kilo Joules per kilo mole is 0. So, the 1st column is temperature in Kelvin starts at 200 Kelvin and this table ends at 5000 Kelvin. So, we are looking at this temperature going from a low value 200 k and all the way it goes to 5000 that so, much higher temperature than what we have looked at a in the properties of a pure substance and that is required because in chemical reactions you do get this type of temperatures.

The second column is the molar specifics heat at constant pressure. So, this is C p bar and it goes in this column and you can see that specific heat increases. And this is one of the important things of this table is that unlike all the earlier calculations that we did quite often we assumed that specific heat is constant with temperature. We see here that there is a substantial change in the specific heat; it increases as the temperature increases. So, constant pressure specific heat is only an approximation. You will actually if you integrate for enthalpy integral C p delta t, you will get much more accurate value and that is what the table does.

Then you have this column here, this is h 0 f at any T. And here at second temperature we can see is 298 and for this the value here is 0. And you can also see that delta h for this value which is here this is also 0. So, second column was h 0 at T minus h f 0 at 298 Kelvin. So, h f 0 at 298 k is this value that we are getting, this is what is coming here.

And so now, this table gives series of numbers which is a difference of enthalpy minus standard state enthalpy and that is what we get from here. And even that going down below this value, you get minus values. This column is s 0 bar at the temperature, standard state entropy and finally, here it is we will see later on g 0 formation at any temperature. The Gibbs function for formation. Right now we are only interested in this and this part, so that is why we are getting this table.

So, if you go to this table, we get all this data. And we can pick up the temperature get this properties and if we have working with a temperature that is not listed here, but lies between two values say between 2000 and 2100 Kelvin, we will have to do linear interpolation. Alternately all these are now available as computerized property tables;

one can always put the value there and get the exact value that you want. Calculations are now much easier this has been programmed. So, now if that was so oxygen let us see what happens for atomic oxygen.

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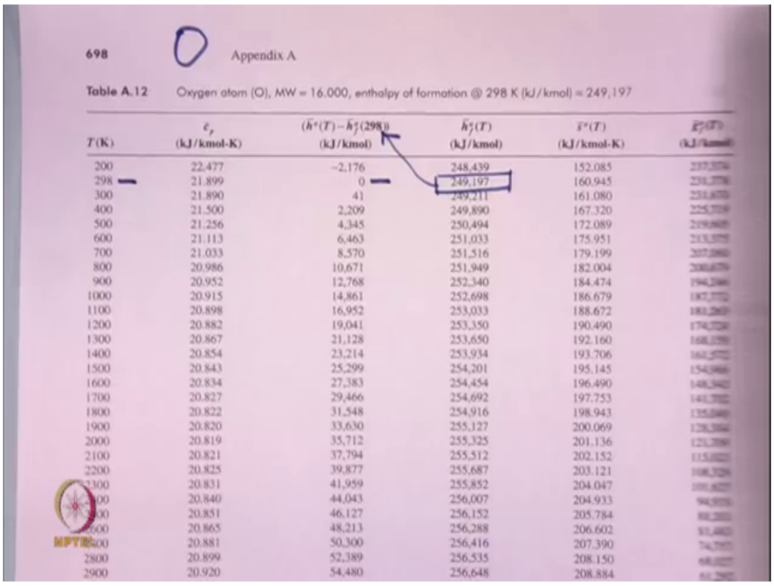


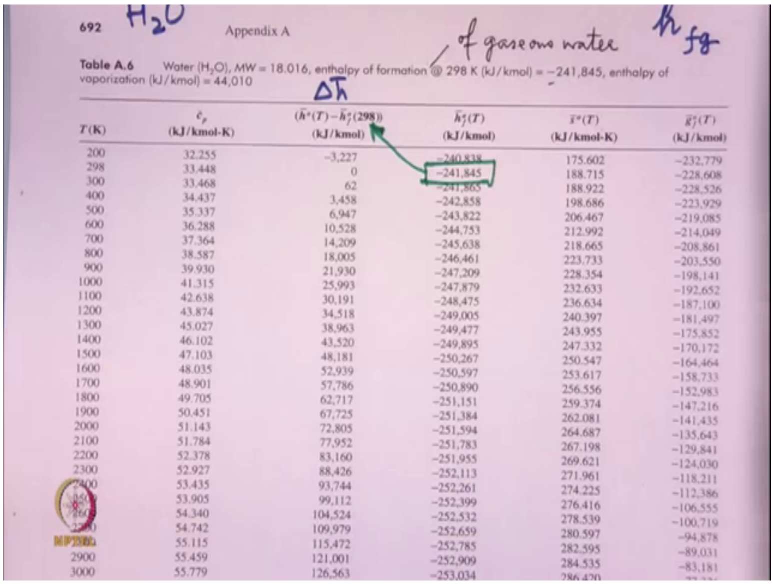
698 O Appendix A

Table A.12 Oxygen atom (O), MW = 16.000, enthalpy of formation @ 298 K (kJ/kmol) = 249,197

T (K)	$\bar{c}_p$ (kJ/kmol-K)	$(\bar{h}^\circ(T)-\bar{h}_f^\circ(298))$ (kJ/kmol)	$\bar{h}_f^\circ(T)$ (kJ/kmol)	$\bar{s}^\circ(T)$ (kJ/kmol-K)	$\bar{g}_f^\circ(T)$ (kJ/kmol)
200	22.477	-2,176	248,439	152.085	[illegible]
298	21.899	0	$\boxed{249,197}$	160.945	[illegible]
300	21.890	41	249,211	161.080	[illegible]
400	21.500	2,209	249,890	167.320	[illegible]
500	21.256	4,345	250,494	172.089	[illegible]
600	21.113	6,463	251,033	175.951	[illegible]
700	21.033	8,570	251,516	179.199	[illegible]
800	20.986	10,671	251,949	182.004	[illegible]
900	20.952	12,768	252,340	184.474	[illegible]
1000	20.915	14,861	252,698	186.679	[illegible]
1100	20.898	16,952	253,033	188.672	[illegible]
1200	20.882	19,041	253,350	190.490	[illegible]
1300	20.867	21,128	253,650	192.160	[illegible]
1400	20.854	23,214	253,934	193.706	[illegible]
1500	20.843	25,299	254,201	195.145	[illegible]
1600	20.834	27,383	254,454	196.490	[illegible]
1700	20.827	29,466	254,692	197.753	[illegible]
1800	20.822	31,548	254,916	198.943	[illegible]
1900	20.820	33,630	255,127	200.069	[illegible]
2000	20.819	35,712	255,325	201.136	[illegible]
2100	20.821	37,794	255,512	202.152	[illegible]
2200	20.825	39,877	255,687	203.121	[illegible]
2300	20.831	41,959	255,852	204.047	[illegible]
2400	20.840	44,043	256,007	204.933	[illegible]
2500	20.851	46,127	256,152	205.784	[illegible]
2600	20.865	48,213	256,288	206.602	[illegible]
2700	20.881	50,300	256,416	207.390	[illegible]
2800	20.899	52,389	256,535	208.150	[illegible]
2900	20.920	54,480	256,648	208.884	[illegible]

So, this is now O, molecular weight 16, enthalpy of formation at 298 Kelvin, 249.197 kilo Joules per kilo mole. Again the columns are exactly the same. The difference now is that s h 0 T minus h f 0 at 298 k, at the 298 Kelvin temperature this number is 0, but the formation h f 0 298 k which is there in the 2nd column, this is a finite number, this is going there it is nonzero, that is because this is the amount of energy that we got when we have to break the O-O bond. And for O 2 we had put the specific enthalpy as 0. So, the formation of O atom requires energy and that is what is showing up over here; rest of it is very similar to what we have had earlier.

(Refer Slide Time: 38:58)



692 H_2O Appendix A

Table A.6 Water (H_2O), MW = 18.016, enthalpy of formation @ 298 K (kJ/kmol) = −241,845, enthalpy of vaporization (kJ/kmol) = 44,010

of gaseous water

$\bar{h}_{fg}$

$\Delta\bar{h}$

T(K)	$\bar{c}_p$ (kJ/kmol-K)	$(\bar{h}^\circ(T) - \bar{h}^\circ_f(298))$ (kJ/kmol)	$\bar{h}^\circ_f(T)$ (kJ/kmol)	$\bar{s}^\circ(T)$ (kJ/kmol-K)	$\bar{g}^\circ_f(T)$ (kJ/kmol)
200	32.255	−3,227	−240,838	175.602	−232,779
298	33.448	0	$\boxed{-241,845}$	188.715	−228,608
300	33.468	62	−241,865	188.922	−228,526
400	34.437	3,458	−242,858	198.686	−223,929
500	35.337	6,947	−243,822	206.467	−219,085
600	36.288	10,528	−244,753	212.992	−214,049
700	37.364	14,209	−245,638	218.665	−208,861
800	38.587	18,005	−246,461	223.733	−203,550
900	39.930	21,930	−247,209	228.354	−198,141
1000	41.315	25,993	−247,879	232.633	−192,652
1100	42.638	30,191	−248,475	236.634	−187,100
1200	43.874	34,518	−249,005	240.397	−181,497
1300	45.027	38,963	−249,477	243.955	−175,852
1400	46.102	43,520	−249,895	247.332	−170,172
1500	47.103	48,181	−250,267	250.547	−164,464
1600	48.035	52,939	−250,597	253.617	−158,733
1700	48.901	57,786	−250,890	256.556	−152,983
1800	49.705	62,717	−251,151	259.374	−147,216
1900	50.451	67,725	−251,384	262.081	−141,435
2000	51.143	72,805	−251,594	264.687	−135,643
2100	51.784	77,952	−251,783	267.198	−129,841
2200	52.378	83,160	−251,955	269.621	−124,030
2300	52.927	88,426	−252,113	271.961	−118,211
2400	53.435	93,744	−252,261	274.225	−112,386
2500	53.905	99,112	−252,399	276.416	−106,555
2600	54.340	104,524	−252,532	278.539	−100,719
2700	54.742	109,979	−252,659	280.597	−94,878
[illegible]	55.115	115,472	−252,785	282.595	−89,031
2900	55.459	121,001	−252,909	284.535	−83,181
3000	55.779	126,563	−253,034	286.420	[illegible]

And one more we will see this is water. So, this H 2 O would come by taking 2 hydrogen atoms and 1 oxygen atom and making certain bonds. And the way to make those atoms was (Refer Time: 39:15) from thereby from the natural state for which the enthalpy was known and then we find out from joining what happens 2 H 2 O. So, basically you can calculate this H 2 O as then for enthalpy of formation from the enthalpy of formation of its atomic constituents.

So, what we here is that again the same set of things is there. This is your delta h bar and say it that enthalpy of formation at 298 Kelvin is minus 241845 kilo Joules per kilo mole and enthalpy of vaporization kilo Joules per kilo mole is 44010. So, enthalpy of vaporization is nothing but what we have learned in the earlier course as this is in kilo mole basis. So, this is h bar f g, same number.

So, what you have here is that the formation enthalpy of formation at 298 Kelvin for water is given over here, this is the value that will be taken in this calculation. And this is nonzero. And here again after that the numbers keep changing again the property data goes to 5000 Kelvin. So, this is our way to get all the property data that we have been looking for in doing all the calculations that when we wanted the value of h, this is how we get it from this and this table.

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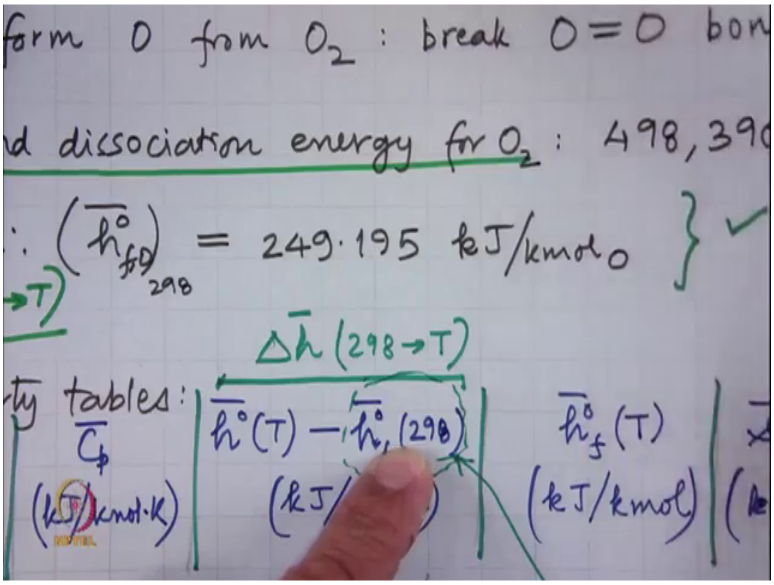

form O from O_2 : break O=O bon

d dissociation energy for O_2 : 498,39

$\therefore \left(\bar{h}^{\circ}_{f,O}\right)_{298} = 249.195$ kJ/kmol$_O$ } ✓

→T)

$\Delta \bar{h}\,(298 \rightarrow T)$

ty tables: | $\bar{C}_p$ (kJ/kmol·K) | $\bar{h}^{\circ}(T) - \bar{h}^{\circ}_{f}(298)$ (kJ/ | $\bar{h}^{\circ}_{f}(T)$ (kJ/kmol) | (

The values are different simply because the reference state is same and enthalpies, difference of enthalpies in any two states will be the same whether we use the earlier tables or we are using these tables.

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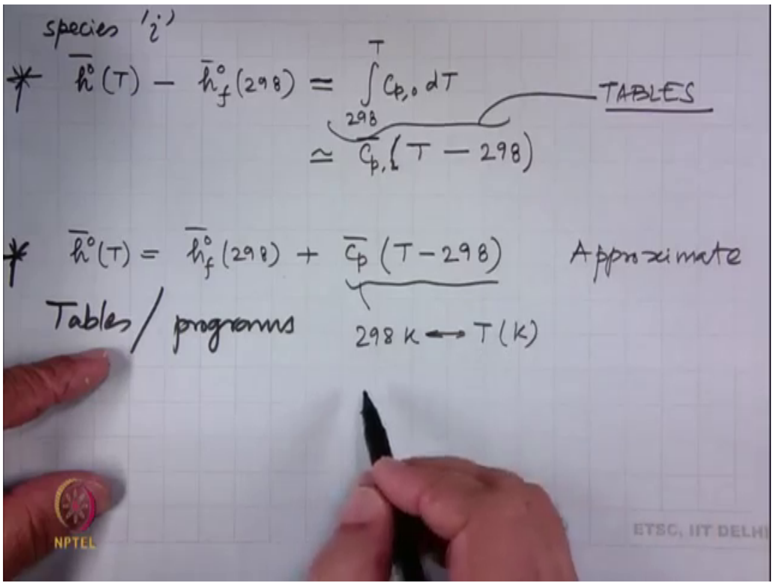

species 'i'

$$* \quad \bar{h}^{\circ}(T) - \bar{h}^{\circ}_{f}(298) = \underbrace{\int_{298}^{T} c_{p,i}\, dT}_{\text{TABLES}}$$

$$\simeq \bar{c}_{p,i}(T - 298)$$

$$* \quad \bar{h}^{\circ}(T) = \bar{h}^{\circ}_{f}(298) + \underbrace{\bar{c}_p\,(T - 298)}_{298\,K \leftrightarrow T(K)} \qquad \text{Approximate}$$

Tables / programs

So, to summarize how are we getting this specific enthalpy for any species i and the subscript i have been dropped from here. Method one we have just looked at is the use the tables or you could be computerized programs or interactive software that does not matter which is h 0 at T which is h f 0 at T into 298 k plus average specific a T minus 298, so that is one way to do it, but this is of course the approximate way.

The correct thing would have been to it is a this is integral of C p 0 T from 298 to T approximation is this the exact value of this integral is what is there in the tables, so that is for some quick calculations one can do this is to use average C p value over that temperature range 298 to T. So, this is over 298 K to T whatever was in Kelvin some sort of an average value.

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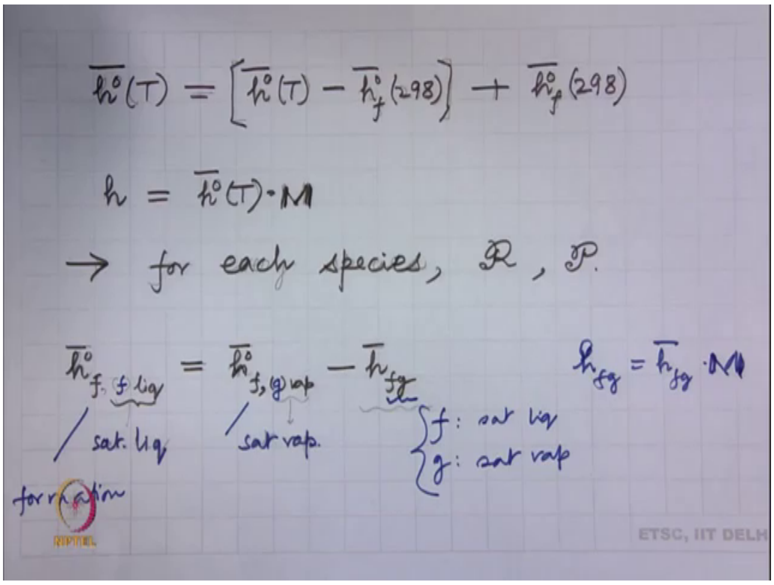

$$\bar{h}^0(T) = \left[\bar{h}^0(T) - \bar{h}^0_f(298)\right] + \bar{h}^0_f(298)$$

$$h = \bar{h}^0(T)\cdot M$$

→ for each species, $\mathcal{R}$, $\mathcal{P}$.

$$\bar{h}^0_{f,\,\underbrace{f\,liq}} = \bar{h}^0_{f,\,(g)\,vap} - \underbrace{\bar{h}_{fg}}$$

$$h_{fg} = \bar{h}_{fg}\cdot M$$

/ sat. liq

/ sat vap.

formation

f : sat liq

g : sat vap

ETSC, IIT DELH

But the tables what they gave us is h 0 of T this is equal to one column data that we read h 0 of T at bar minus h f 0 T at 298 plus h 0 f bar at 298 and to get this is all molar basis. Mass basis this is h 0 bar at T which came from here multiplied by the molar mass of that particular species. And so we can do this for each species. This could be either in the reactants or in the products.

For phase change, we will do that h 0 f; for liquid in the bracket this I left it blank because now f has got two meanings coming up here and so it is causing confusion. I will come back to it the minute this is h 0 f which is a formation; in the vapour states minus h bar f g and this is where you can see the confusion coming in. We are using now f g from what you have learned in properties of a pure substance, where f is saturated liquid and g was saturated vapour. But now f is being used in this case as formation.

So, what we are saying is the enthalpy of formation of saturated liquid. So, ideally this f will be f and this will be a g. So, just to minimize the confusion, I have put different colors on it, but that is one of the problems that we have same subscript appearing for two different things, it does not matter. We keep our book keeping straight that this f means that we are looking at saturated liquid and this means that you are looking at saturated h f g bar is nothing but your h f g is h f g bar times the molar mass of that particular material. So, two are exactly the same. So, numbers values and all the same as what we had earlier tables.

So, now we come to the last part of the lecture. We have now developed all the tools that we required to do any analysis of this system. We will now use those for few specific things to learn about chemical a particular reaction and for a particular type of fuel. And these are important numbers that we will look at and come across quiet often.

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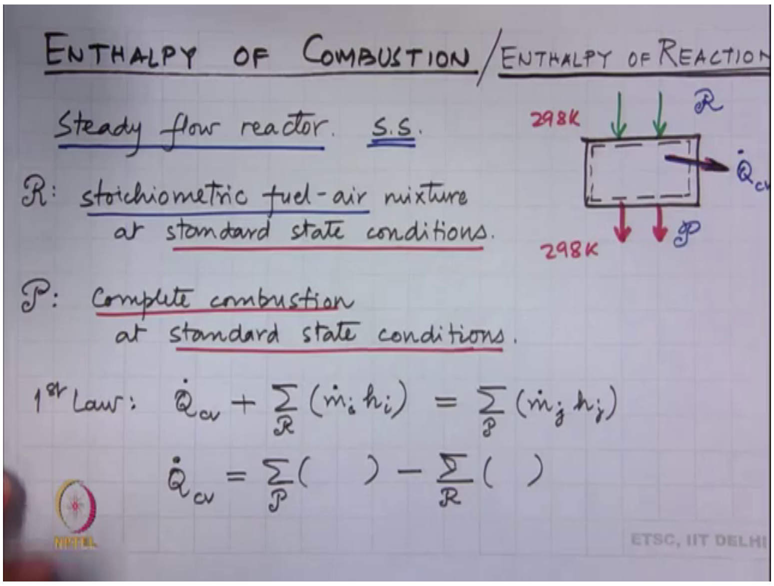

ENTHALPY OF COMBUSTION / ENTHALPY OF REACTION

Steady flow reactor. S.S.

R: stoichiometric fuel-air mixture
at standard state conditions.

P: Complete combustion
at standard state conditions.

1st Law: $\dot{Q}_{cv} + \sum_{\mathcal{R}} (\dot{m}_i h_i) = \sum_{\mathcal{P}} (\dot{m}_j h_j)$

$$\dot{Q}_{cv} = \sum_{\mathcal{P}} (\quad) - \sum_{\mathcal{R}} (\quad)$$

So, for any general reaction, the first thing that we would like to we talk about is what is called enthalpy of reaction, in the case of a reaction being a combustion reaction, we are looking at enthalpy of combustion. So, what you are doing is same thing, but we are now looking at a steady flow reactor that means we have steady state you have the reactants going in and the products coming out and there is some heat transfer taking place. So, in defining the enthalpy of reaction what will now start calling it enthalpy of combustion is that the reactants are going in are firstly, it is a stoichiometric air fuel ratio that is number 1. And second they are at standard state conditions 298 k and 1 bar.

And what comes out is next first that there is complete combustion and it is a stoichiometric mixture anyway and the products are also at standard state conditions 298 k. So, this went in at 298 K 1 bar; this came out as 298 K which can be only possible when there is heat transfer out of this system Q dot c v. So, when we write the 1st law it is Q dot c v plus m dot i h i for the reactants is equal to summation of the same thing for the products, where Q dot c v is what was h summation for products minus summation for the reactants.

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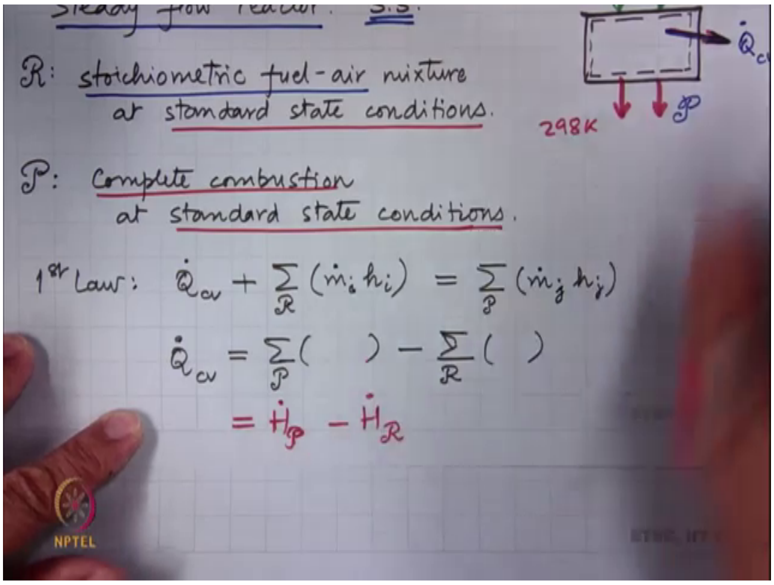

Steady flow reactor: S.S.

$\mathcal{R}$: stoichiometric fuel-air mixture at standard state conditions.

$\mathcal{P}$: Complete combustion at standard state conditions.

1st Law: $\dot{Q}_{cv} + \sum_{\mathcal{R}} (\dot{m}_i h_i) = \sum_{\mathcal{P}} (\dot{m}_j h_j)$

$$\dot{Q}_{cv} = \sum_{\mathcal{P}} (\quad) - \sum_{\mathcal{R}} (\quad)$$
$$= \dot{H}_{\mathcal{P}} - \dot{H}_{\mathcal{R}}$$

And this can also be represent as H dot for the products minus H dot for reactants.

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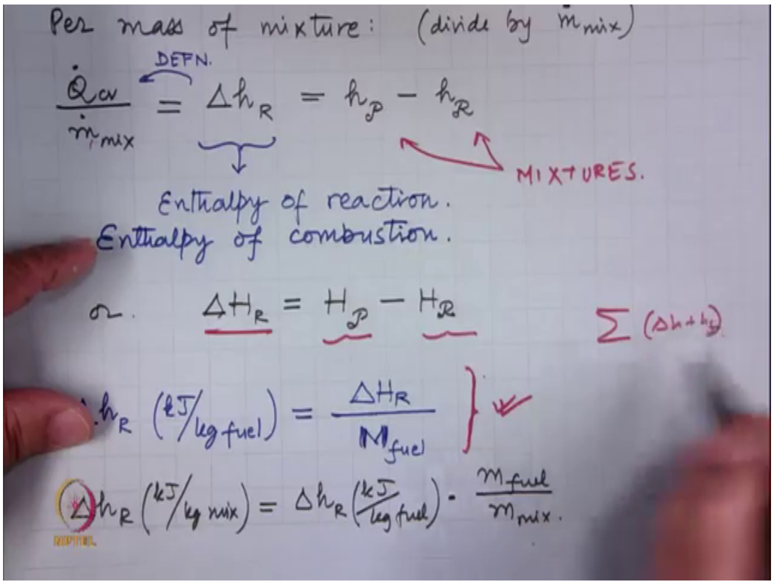


Per mass of mixture: (divide by $\dot{m}_{mix}$)

$$\frac{\dot{Q}_{cv}}{\dot{m}_{mix}} \overset{\text{DEFN.}}{=} \underbrace{\Delta h_R}_{\text{Enthalpy of reaction.}} = h_P - h_R$$

MIXTURES.

Enthalpy of combustion.

or. $\underline{\Delta H_R} = H_P - H_R$ $\Sigma(\Delta h + h_f)$

$$h_R\,(\text{kJ/kg fuel}) = \frac{\Delta H_R}{M_{fuel}}$$

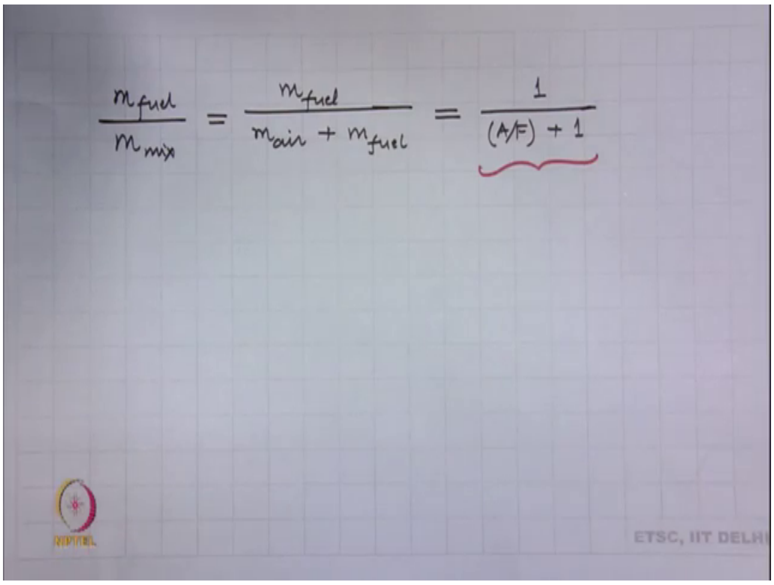
$$\Delta h_R\,(\text{kJ/kg mix}) = \Delta h_R \left(\frac{\text{kJ}}{\text{kg fuel}}\right) \cdot \frac{m_{fuel}}{m_{mix}}.$$

If we do it on per mass basis, we divided it throughout by mixture mass flow rate in the mass flow rate of in going in and coming out is going to be the same with that is not an issue 2 dot c v over m dot mix. Now, remember m dot mix is same as m dot P which is same as m dot R. This we call is delta h R enthalpy of reaction or enthalpy of combustion which is h of P minus h of R and in a P and R are mixtures.

So, these have to be get for mixture properties or delta h R is h P minus h R. So, if you express this as a total one or this was a mixture thing, then delta h R is kilo Joules per kg of fuel is this value divided by molar mass of the fuel or per kilogram basis delta h R is kilo Joules per kilogram of mixture which is delta h R upon this into mass flow rate of fuel over mass flow rate of mixture.

So, this is more common one to be found and this is what we use is how much kilo Joules is released per kilogram of fuel that is the thing that we are always interested in and that is the way to get it. We are not going into the full details of it, because now we know how to get H P and how to get H R, from the summations and then using delta h and h formation from there we can get all these numbers.

(Refer Slide Time: 49:02)



$$\frac{m_{fuel}}{m_{mix}} = \frac{m_{fuel}}{m_{air} + m_{fuel}} = \underbrace{\frac{1}{(A/F) + 1}}$$

A small change that can be done over there is that mass of fuel over mass of mixture can be rewritten as 1 upon air fuel ratio plus 1. So, this is a connection that we can put there with the heat of reaction. A common term we use in defining fuels is the heating value or the calorific value.

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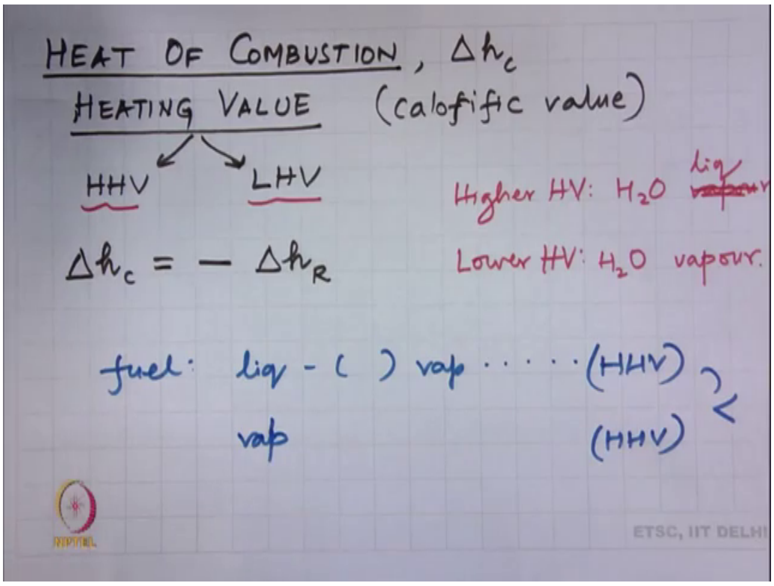

HEAT OF COMBUSTION, Δh_c

HEATING VALUE (calofific value)

HHV LHV

$\Delta h_c = - \Delta h_R$

Higher HV: H_2O ~~vapour~~ liq

Lower HV: H_2O vapour.

fuel: liq - ( ) vap ..... (HHV) >
vap (HHV) <

So, we say heating value; heating value is nothing but heat of combustion and this is not enthalpy of combustion, this is now heat of combustion delta h c or the heating value is nothing but numerically it is the same as heat of reaction, but of opposite sign exactly the same, there is no change.

The only complication or variables various that come into it is that the heating value could be defined as del higher heating value or lower heating value. Higher heating value means after combustion the H 2 O is in vapour state and the sorry this is in liquid state, because when H 2 O condense that also energy was taken out from the system. The lower heating value is the one that you have when H 2 O stays in the vapour phase, so that enthalpy of evaporation or condensation is not available to be taken out from the system.

We would also like you should also keep in mind that another thing could happen that the fuel itself as we had mentioned earlier it could be in liquid phase or it could be in vapour phase. If it was a liquid, it will take energy to become a vapour and then the chemical reactions will start. So, the enthalpy the heat of combustion from a liquid fuel will be less than the heat of combustion of a vapour fuel whether it is H H V or in both cases that means the water vapour condition is the same, but this will be less than this value.

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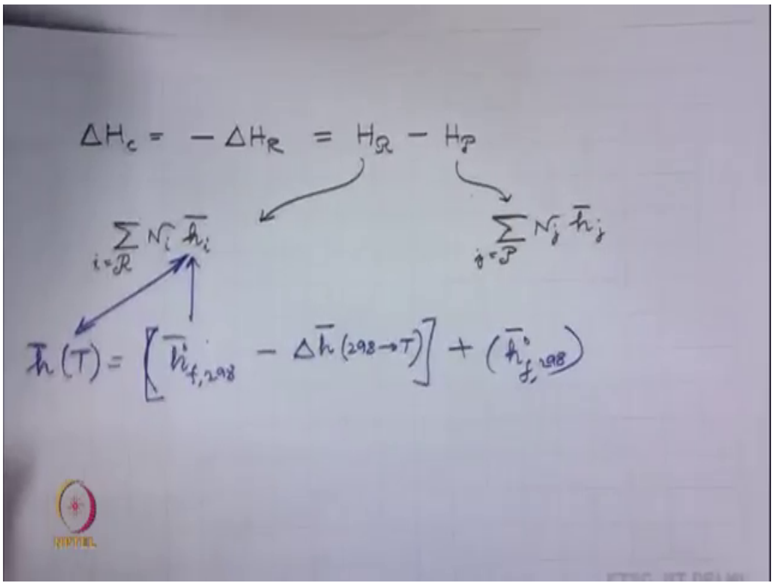

$$\Delta H_c = -\Delta H_R = H_R - H_P$$

$$\sum_{i \in R} N_i \bar{h}_i \qquad \sum_{j \in P} N_j \bar{h}_j$$

$$\bar{h}(T) = \left[\bar{h}_{f,298} - \Delta\bar{h}(298 \to T)\right] + \left(\bar{h}^{0}_{f,298}\right)$$

Just to recap what we had at earlier delta H C is minus delta H R which is H R minus H P enthalpy of reactance is number of moles of every species in the reactant multiplied by the molar specific enthalpy. And this we have already learned, is a new thing that has come about this was h 0 f at 298 minus delta h bar in 298 to T, this is what we got from the tables there. So, this is what we have wanted. So, we get this plus we added the particular values to it. So, this is h basically what you have looking at h bar at T. So, this is what is we have seen.

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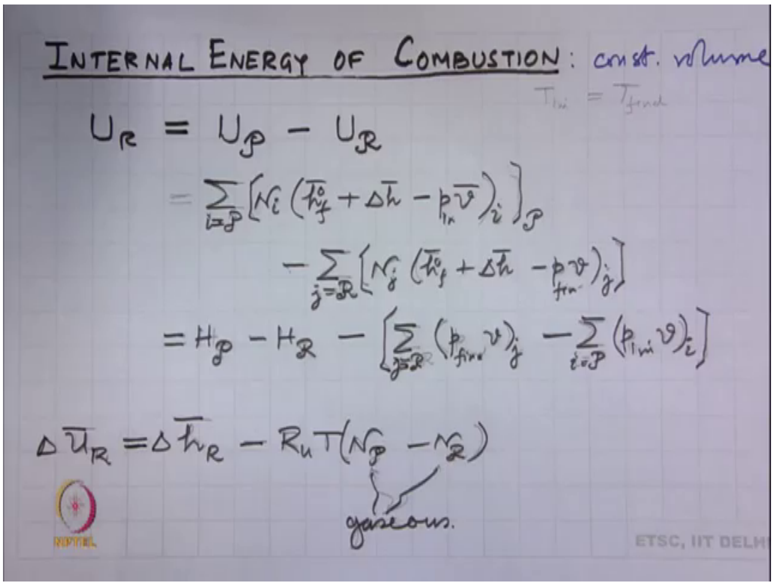

INTERNAL ENERGY OF COMBUSTION: const. volume

$T_{ini} = T_{final}$

$$U_R = U_P - U_R$$

$$= \sum_{i=P} \left[N_i \left(\bar{h}^0_f + \Delta \bar{h} - p_{in} \bar{v} \right)_i \right]_P - \sum_{j=R} \left[N_j \left(\bar{h}^0_f + \Delta \bar{h} - p_{fin} v \right)_j \right]$$

$$= H_P - H_R - \left[\sum_{j=R} \left(p_{fin} v \right)_j - \sum_{i=P} \left(p_{ini} v \right)_i \right]$$

$$\Delta \bar{u}_R = \Delta \bar{h}_R - R_u T \underbrace{\left(N_P - N_R \right)}_{\text{gaseous.}}$$

Now, we look at another condition, where the combustion instead of taking plate place at constant pressure which is what we have looked at in earlier case. Now, it takes place in a closed system which is at now constant volume combustion. So, now U R may be becomes now the internal energy of combustion is U P minus U R and this we can now write as i is equal to P N i into h 0 f plus delta h minus p v for each species. And this is at the product state. And similar expression we can write for the reactants N j h 0 f plus delta h bar minus p this was a initial temp pressure, this is the final pressure specific volume at j.

So, what it this we can then simplify this and write it in terms of the specific enthalpy H P minus H R minus these two terms going in their which is summation p final v for j minus summation p initial v for each reactant problem. So, i is every product, j is a every reactant. And from there we get that u bar R is h bar R or we had called it delta h r minus R u T times N P minus N R. And these are in gaseous phase.

So, the internal energy of combustion is could be very different from that of the inter specific enthalpy of combustion. Finally, we ask the question what are the temperature that we can get? And in particular we ask the question what is the maximum temperature we can get from a reaction and that is called adiabatic flame temperature.

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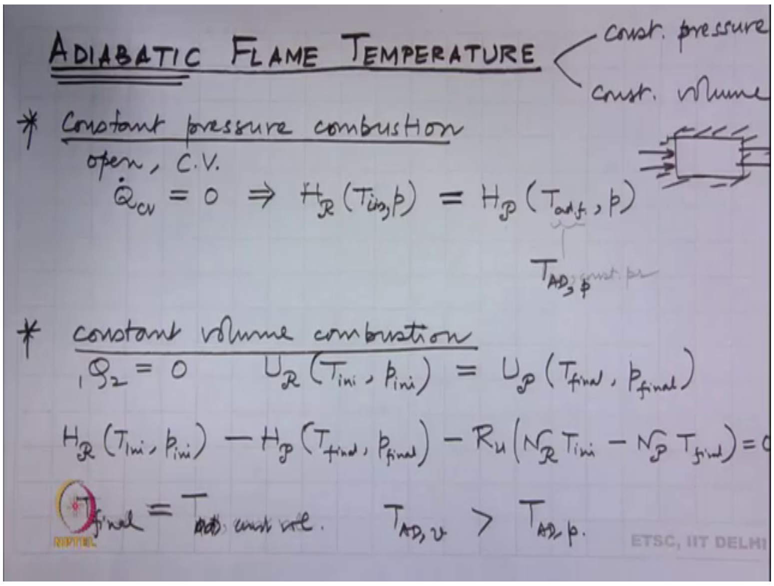

ADIABATIC FLAME TEMPERATURE < Const. pressure / Const. volume

* Constant pressure combustion

open, C.V.

$$\dot{Q}_{cv} = 0 \Rightarrow H_R(T_{in}, p) = H_P(\underbrace{T_{ad.f.}}_{T_{AD,p}\ \text{const. pr}}, p)$$

* constant volume combustion

$$ {}_1Q_2 = 0 \qquad U_R(T_{ini}, p_{ini}) = U_P(T_{final}, p_{final})$$

$$H_R(T_{ini}, p_{ini}) - H_P(T_{final}, p_{final}) - R_u(N_R T_{ini} - N_P T_{final}) = 0$$

$$T_{final} = T_{AD,\ const\ vol.} \qquad T_{AD,v} > T_{AD,p}.$$

ETSC, IIT DELHI

So, if you say that I have fuel and I am burning it with air, we now will develop a method we say that is the maximum possible temperature you can get. If you burn it with oxygen this is the maximum possible temperature you can get and that is sets an upper limit to all the energy conversion machinery that we design at the systems that we design. We by burning a fuel, you cannot get a temperature greater than that is an upper limit.

So, we will look at constant pressure combustion which is an open system control volume types Q dot c v is equal to 0 that means it is adiabatic no heat transfer from the system. So, we have a reactor into which things are flowing in and flowing out, and this was perfectly insulated. So, all the energy released by combustion went to increase the temperature of the products so which means that H R of the reactance at T in inflow temperature and pressure its enthalpy of the products at adiabatic flame temperature and the pressure. So, this we can say is T adiabatic at constant pressure, so that is one way to define it.

The other way is constant volume combustion, where Q 12 is 0 and now the two internal energies are equated. And if you convert that into terms of their enthalpies, let H R minus H P minus something else and this is equal to 0 because this is equal to this. So, this basically tells you in both cases that T final temperature that the system will get is the adiabatic flame temperature. In this case, it is constant volume. And we can see that because the system did not do come back to its original pressure, the adiabatic flame temperature at constant volume will be adiabatic flame temperature at constant pressure.

But in practice producing a constant volume continuous process is not entirely possible and so with most common referencing of adiabatic flame temperature is at constant pressure. So, this is what people would normally talk off. Say gas turbine your it is a cool steady flow process like this and the adiabatic flame temperature is that constant pressure.

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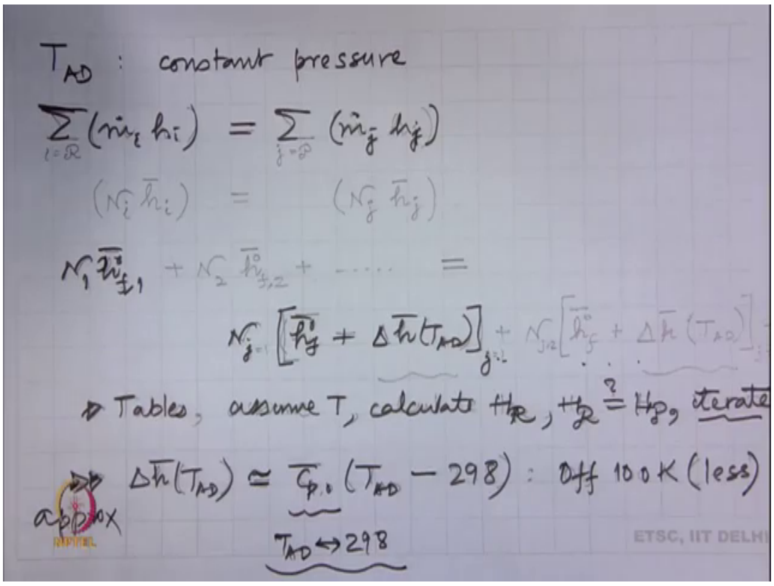

T_{AD} : constant pressure

$$\sum_{i=R} (\dot{m}_i h_i) = \sum_{j=P} (\dot{m}_j h_j)$$

$$(N_i \bar{h}_i) = (N_j \bar{h}_j)$$

$$N_1 \bar{h}^{\circ}_{f,1} + N_2 \bar{h}^{\circ}_{f,2} + \dots =$$

$$N_{j=1} \left[\bar{h}^{\circ}_f + \Delta \bar{h}(T_{AD})\right]_{j=1} + N_{j=2} \left[\bar{h}^{\circ}_f + \Delta \bar{h}(T_{AD})\right]_{j=2}$$

▸ Tables, assume T, calculate H_R, $H_R \overset{?}{=} H_P$, iterate

▸▸ $\Delta \bar{h}(T_{AD}) \simeq \bar{c}_{p,0} (T_{AD} - 298)$: off 100 K (less)

approx

$T_{AD} \leftrightarrow 298$

So, how do we calculate that? We have written those expressions there. We can now just write down for the constant pressure case m dot i h i this is equal to summation m dot j h f j r. And then we can equate these and get that for the inlet state, this becomes N dot 1 h 0 f 1 like that and for the reactants this will be h 0 f plus delta h bar at T adiabatic for each j species. And then we have two options; either we use the tables or the programs and to calculate the T in which case you assume a T, there from the tables you get you calculate H R. And then see if that H R matches with the enthalpy of the products, if yes, then the temperature is the adiabatic flame temperature otherwise iterate or we can even have a computer program that the iteration for us we do not need to do it now.

For the other case is approximate solution does not require iteration. It is quite simple straight forward. We can say that delta h for going up to T adiabatic, this is approximately equal to C p 0 into T adiabatic minus 298. So, you have assuming a constant specific heat over this range of T adiabatic to 298. And we can calculate T adiabatic without doing any iteration. It is easier calculation, but it could be off by at least about a 100 Kelvin and usually it will be under predicting the actual adiabatic flame temperature and that is because this is an approximation the tables would give the exact value. So, that brings us to the end of the thermodynamics of reacting systems where we learned how to took take the loss and the concepts that we learn for a pure substance and apply it to a reacting system.

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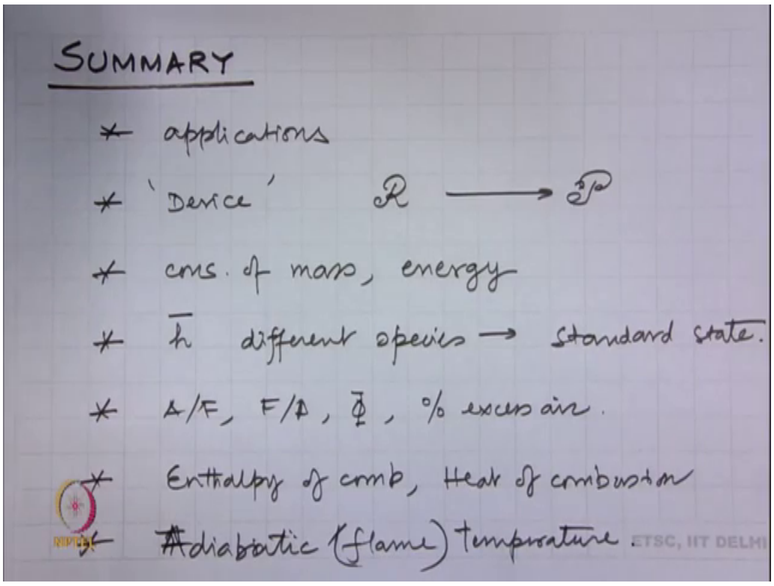

SUMMARY

- applications
- 'Device' $\mathcal{R} \longrightarrow \mathcal{P}$
- cns. of mass, energy
- $\bar{h}$ different species → standard state.
- A/F, F/A, Φ, % excess air.
- Enthalpy of comb, Heat of combustion
- Adiabatic (flame) temperature

We looked at various applications and realize that thermodynamics is one aspect of engineering combustion system which has got fluid mechanics heat transfer and many other considerations coming into it. We then made a simple system out of it and we say that we will only look at the reaction as a device or some sort of a black box in which all the micro details are completely subsumed. And we are only worried about saying that what we have is reactance and they go through a process and they become products. We make that model.

After that model we applied the conservation equations, conservation of mass and conservation of energy. And in doing the conservation of energy, we came across the need for how getting enthalpies for different species and referencing them in a consistent way to standard condition. So, we do we came across the use of a new set of tables which are consistent in this respect and for reactive systems we have to use those tables. And using this we then came across various definitions of the reacting system alone, we came across air fuel ratio which is at a gross level, fuel air ratio, equivalence ratio and then percent excess air like that.

And finally, we saw how from all these reactions we can get the enthalpy of combustion, then heat of reaction or heat of combustion. And finally, we said what is the maximum possible temperature for which we got the answer by way of a adiabatic flame temperature or just the adiabatic temperature.

So, with this we are now able to do a macro level analysis of a combustion system and that is good enough to do many calculations of use. So, this forms is the basis of how combustions happens, but as we have seen from the actual devices things are almost complicated. And to understand those one has to go to a advance course which is a postgraduate course in combustion and then we start begin to look at more and more realistic way how to design combustors or how to understand a combustor to achieve things like minimizing emissions. With that we will complete this sequence of lectures on the reacting system.

Thank you.