Turbulent Combustion: Theory and Modelling
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Lecture – 6
Thermo - Chemistry (Contd.,)

So let us continue the discussion what you are doing it that the enthalpy of formation and enthalpy of reaction, enthalpy of combustion. And we took an example let us see what the example was.

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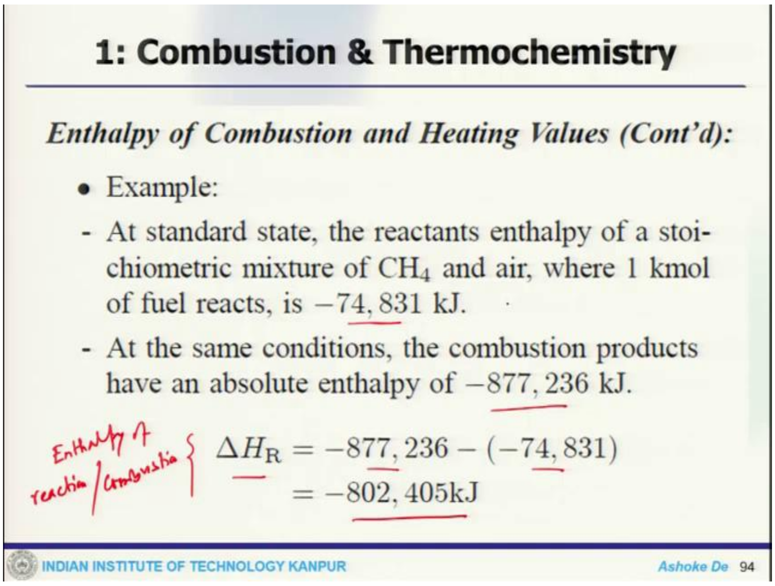

1: Combustion & Thermochemistry

Enthalpy of Combustion and Heating Values (Cont'd):

- Example:
  - At standard state, the reactants enthalpy of a stoichiometric mixture of CH_4 and air, where 1 kmol of fuel reacts, is $-74,831$ kJ.
  - At the same conditions, the combustion products have an absolute enthalpy of $-877,236$ kJ.

Enthalpy of reaction / Combustion

$$\Delta H_R = -877,236 - (-74,831) = -802,405 \text{kJ}$$

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So, we took an example of methane this is where we stop which is at the standard state of the reactant and product are at the standard state so we get the enthalpy and then we find out per unit, mass.

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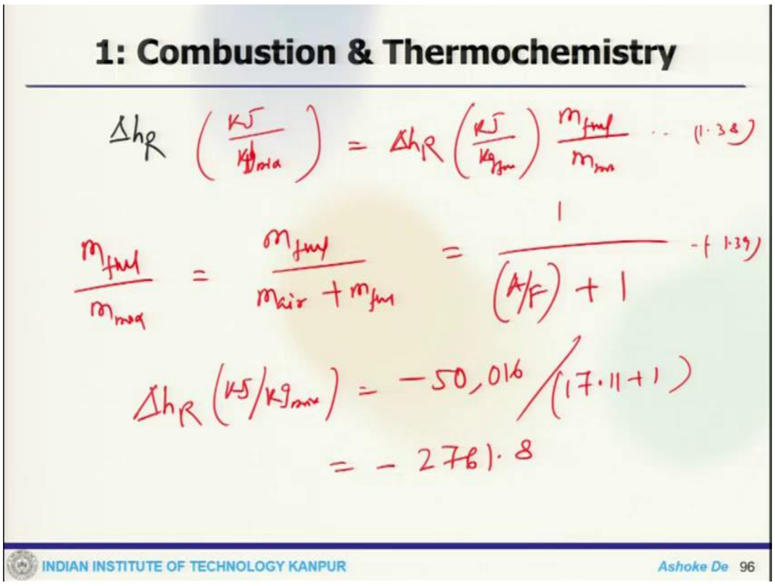

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$$\Delta h_R \left(\frac{kJ}{kg_{mix}}\right) = \Delta h_R \left(\frac{kJ}{kg_{fuel}}\right) \frac{m_{fuel}}{m_{mix}} \quad \cdots (1.38)$$

$$\frac{m_{fuel}}{m_{mix}} = \frac{m_{fuel}}{m_{air} + m_{fuel}} = \frac{1}{(A/F) + 1} \quad -(1.39)$$

$$\Delta h_R (kJ/kg_{mix}) = -50{,}016/(17.11+1)$$

$$= -2761.8$$

So, one can also look at that so that is per kg$_{mix}$ is Δh_R which is:

$$\Delta h_R = \frac{m_{fuel}}{m_{mix}}$$

Where,

$$\frac{m_{fuel}}{m_{mix}} = \frac{m_{fuel}}{m_{air} + m_{fuel}} = \frac{1}{\left({}^{A}/_{F}\right) + 1}$$

So, no one can see how this can be used to find out this is:

$$\Delta h_R = {}^{-50016}/_{(17.11 + 1)} = -2761.8$$

So, one can do this kind of simple example one can take and you this calculation.

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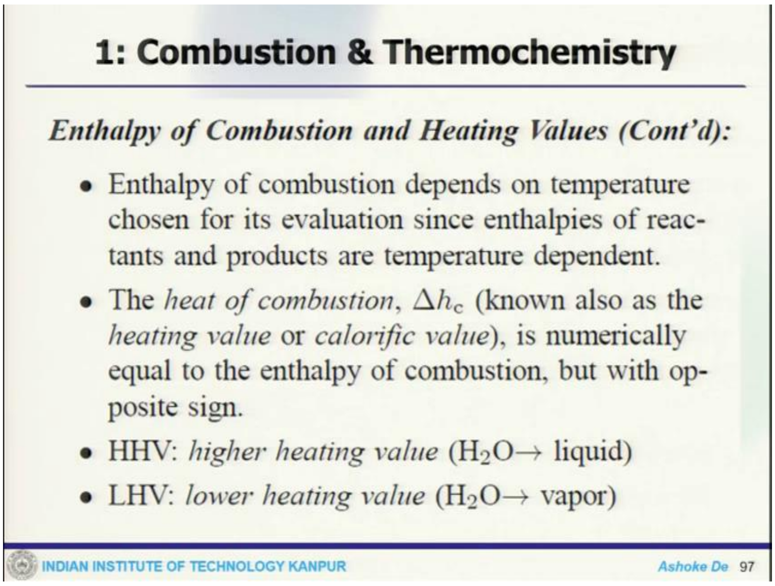

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Enthalpy of Combustion and Heating Values (Cont'd):

- Enthalpy of combustion depends on temperature chosen for its evaluation since enthalpies of reactants and products are temperature dependent.
- The *heat of combustion*, Δh_c (known also as the *heating value* or *calorific value*), is numerically equal to the enthalpy of combustion, but with opposite sign.
- HHV: *higher heating value* ($H_2O \rightarrow$ liquid)
- LHV: *lower heating value* ($H_2O \rightarrow$ vapor)

Now enthalpy of combustion also depends on temperature chosen for its evaluation and enthalpy of reactants and products are the temperature dependent because you have reactance which are coming in and when they are reacting there is a heat release which takes place so obviously the product will have a different temperature. Now, the heat of combustion Δh_c which is known as heating value or calorific value is typically equal to the enthalpy of combustion but with opposite sign.

And there are two different types of heating values. One is the high heating value or higher heating value and another is the lower heating value and that depends on what you get as a product H_2O. If the product state is in liquid form, then you get the high heating value and when the product and H_2O in the product is in vapour state it’s a lower heating value.

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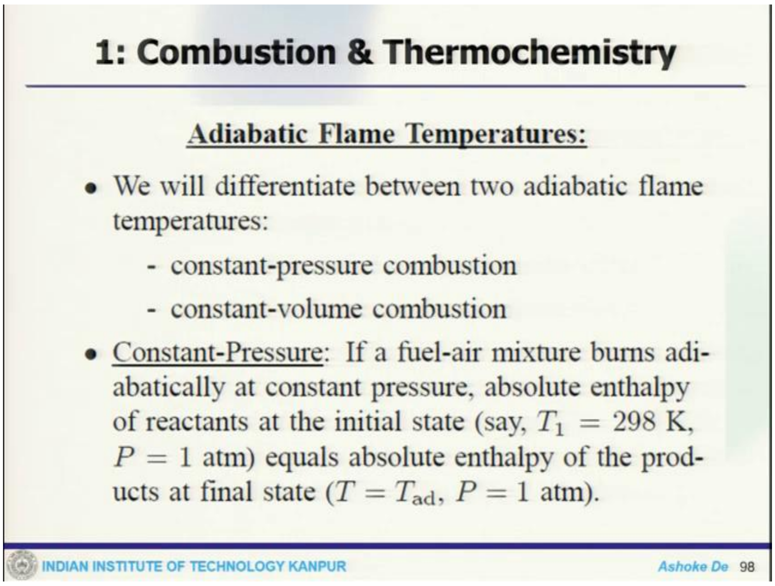

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Adiabatic Flame Temperatures:

- We will differentiate between two adiabatic flame temperatures:
  - constant-pressure combustion
  - constant-volume combustion
- Constant-Pressure: If a fuel-air mixture burns adiabatically at constant pressure, absolute enthalpy of reactants at the initial state (say, $T_1 = 298$ K, $P = 1$ atm) equals absolute enthalpy of the products at final state ($T = T_{\text{ad}}$, $P = 1$ atm).

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Now that brings to another important parameter, which is an adiabatic flame temperature. This is again, very specific to a particular and when it is reacted with an oxidizer or reactant. So, let us say even for example Methane is reacted with air and methane is reacted with oxygen. The temperature of the product will be different. Similarly, adiabatic temperature would be different but any given condition for a given fuel this is one of the theoretical temperature that what is possible can happen.

Now we will differentiate between two adiabatic flame temperature one is the constant pressure combustion process and other is the constant volume combustion process. Now what happens when it is a constant pressure process? So fuel air mixture bonds adiabatically at constant pressure absolute enthalpy of reactants are the initial state say T_1 and equal to absolute enthalpy of the product and final state. So that is at the adiabatic and pre atmospheric that means there is no pressure change.

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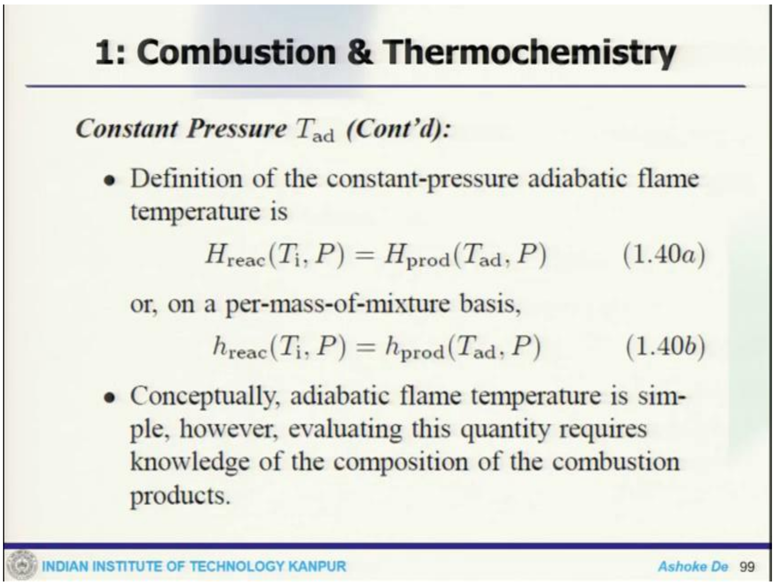

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Constant Pressure T_{ad} *(Cont'd):*

- Definition of the constant-pressure adiabatic flame temperature is
  $$H_{reac}(T_i, P) = H_{prod}(T_{ad}, P) \quad (1.40a)$$
  or, on a per-mass-of-mixture basis,
  $$h_{reac}(T_i, P) = h_{prod}(T_{ad}, P) \quad (1.40b)$$
- Conceptually, adiabatic flame temperature is simple, however, evaluating this quantity requires knowledge of the composition of the combustion products.

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So, the adiabatic flame temperature definition will get you the reactant enthalpy at the T_i or P would be the product enthalpy adiabatic P and per unit mass you can find out from this to this. So, one can calculate the adiabatic flame temperature and it is a simple calculation. What is required some knowledge of composition of the combustion products that means if I have in Methane or propane which is reacting the combustion product needs to be known.

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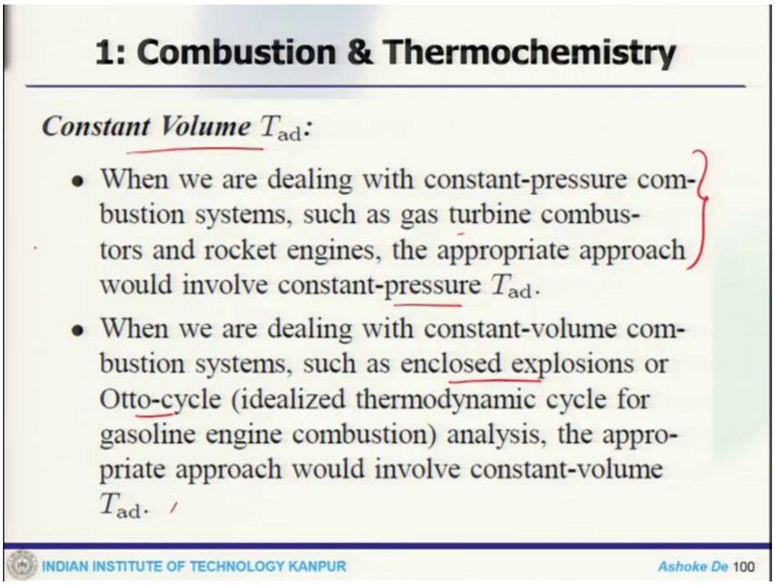

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Constant Volume T_{ad}*:*

- When we are dealing with constant-pressure combustion systems, such as gas turbine combustors and rocket engines, the appropriate approach would involve constant-pressure T_{ad}.
- When we are dealing with constant-volume combustion systems, such as enclosed explosions or Otto-cycle (idealized thermodynamic cycle for gasoline engine combustion) analysis, the appropriate approach would involve constant-volume T_{ad}.

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Now second one is the constant volume and adiabatic temperature. So that $T_{adiabatic}$ and what is dealing with constant pressure combustion systems such as gas turbine, rocket engine the appropriate approach would involve constant pressure adiabatic temperature. Depending on the example one can use different approach whether constant pressure temperature constant volume is constant volume expansion. Now when you are dealing with constant volume combustion system in enclosed explosion or Otto-cycle analysis, the appropriate approach would involve constant volume adiabatic temperature.

So there is a big difference between these two process one is constant pressure this is T constant, this is V constant.

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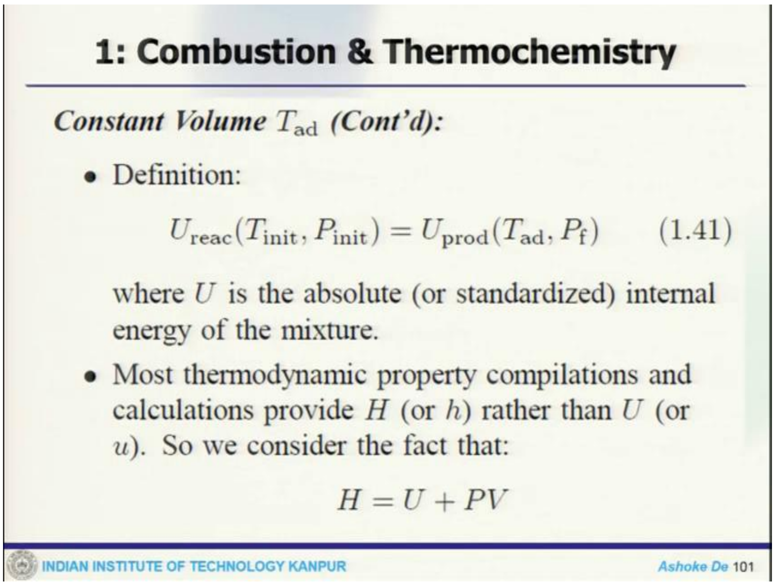

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Constant Volume T_{ad} (Cont'd):

- Definition:

$$U_{reac}(T_{init}, P_{init}) = U_{prod}(T_{ad}, P_f) \qquad (1.41)$$

  where U is the absolute (or standardized) internal energy of the mixture.
- Most thermodynamic property compilations and calculations provide H (or h) rather than U (or u). So we consider the fact that:

$$H = U + PV$$

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Now when you come to constant volume adiabatic flame temperature calculation, so you get $U_{reactant}$ that is the absolute internal energy. U stands here velocity internal energy at initial temperature and pressure it should be the product internal energy of the absolute energy at adiabatic flame temperature and pressure. Now most of the thermodynamics property compilations and calculation involved H and U.

So, we now compile them the enthalpy is essentially an information gets from internal energy and PV.

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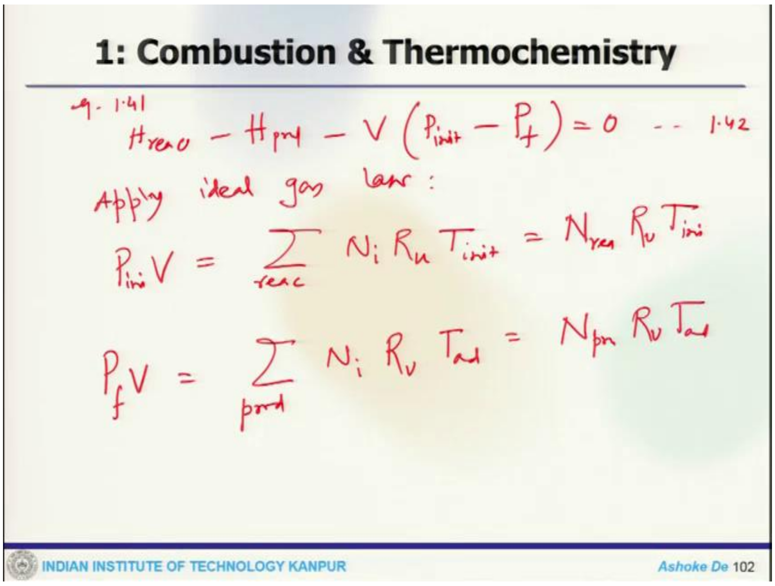

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eq. 1.41

$H_{reac} - H_{prod} - V\left(P_{init} - P_f\right) = 0$ -- 1.42

Apply ideal gas law :

$P_{ini}V = \sum_{reac} N_i R_u T_{init} = N_{rea} R_u T_{ini}$

$P_f V = \sum_{prod} N_i R_u T_{ad} = N_{pro} R_u T_{ad}$

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Now what you can write that from equation 1.41 that:

$$H_{reac} - H_{prod} - V\left(P_{initial} - P_{final}\right) = 0$$

If you apply the ideal gas law here, so we apply ideal gas law so:

$$P_{initial}V = \sum_{reac} N_i R_u T_{initial} = N_{reac} R_u T_{initial}$$

Similarly one can find out:

$$P_{final}V = \sum_{prod} N_i R_u T_{ad} = N_{prod} R_u T_{ad}$$

So it is just a pressure volume relationship using ideal gas one can find out.

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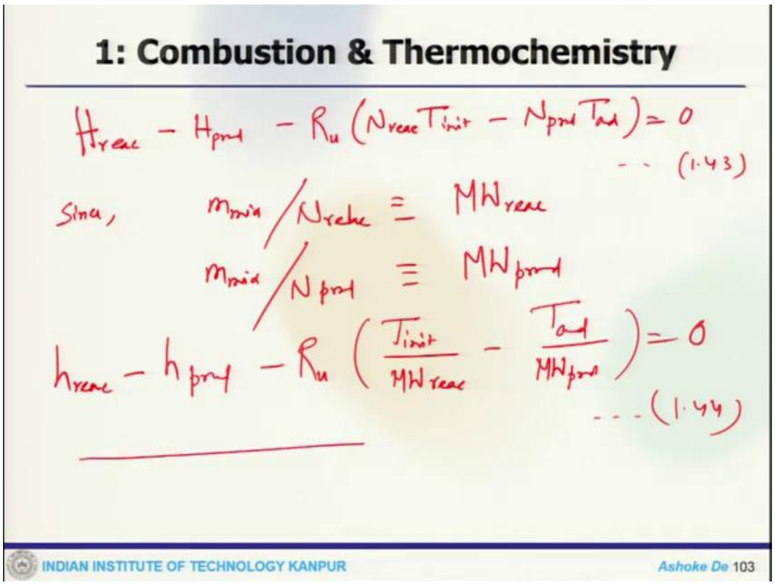

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$H_{reac} - H_{prod} - R_u\left(N_{reac}T_{init} - N_{prod}T_{ad}\right) = 0$ -- (1.43)

Since, $m_{mix}/N_{reac} = MW_{reac}$

$m_{mix}/N_{prod} = MW_{prod}$

$h_{reac} - h_{prod} - R_u\left(\frac{T_{init}}{MW_{reac}} - \frac{T_{ad}}{MW_{prod}}\right) = 0$ --- (1.44)

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Now this, the first equation 1.42 what we get:

$$H_{reac} - H_{prod} - R_u\left(N_{reac}T_{initial} - N_{prod}T_{ad}\right) = 0$$

Now we have:

$$m_{mix}/N_{reac} = MW_{reac}$$

$$m_{mix}/N_{prod} = MW_{prod}$$

If we write we get:

$$h_{reac} - h_{prod} - R_u\left(\frac{T_{initial}}{MW_{reac}} - \frac{T_{ad}}{MW_{prod}}\right) = 0$$

So that is your equation what you can get.

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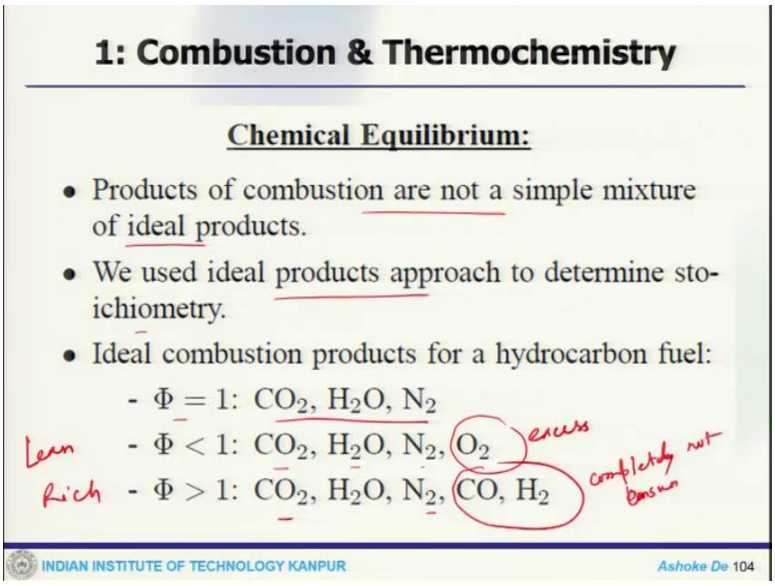

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Chemical Equilibrium:

- Products of combustion are not a simple mixture of ideal products.
- We used ideal products approach to determine stoichiometry.
- Ideal combustion products for a hydrocarbon fuel:
  - $\Phi = 1$: CO_2, H_2O, N_2
  - Lean - $\Phi < 1$: CO_2, H_2O, N_2, O_2 excess
  - Rich - $\Phi > 1$: CO_2, H_2O, N_2, CO, H_2 completely not consum

Now, we move to chemical equilibrium. So what one can note here what you get as a product of combustion cannot be a simple mixture of ideal products. so se can use standard ideal products approach to determine the stoichiometry that means for example methane is burning with air you get CO_2, H_2O and excess nitrogen and that the standard ideal product that you use. So for example ideal combustion products for hydrocarbon fuel if it is stoichiometry it will be CO_2 H_2O N_2 O_2 if it is to lean, you get CO_2 H_2O N_2 this is a lean condition so excess oxygen.

If this is rich you get CO_2 H_2O N_2 but then you get some CO and H_2 because that is a rich so hydrocarbon this should remain, not this is completely not consume. So you get back these kind of things.

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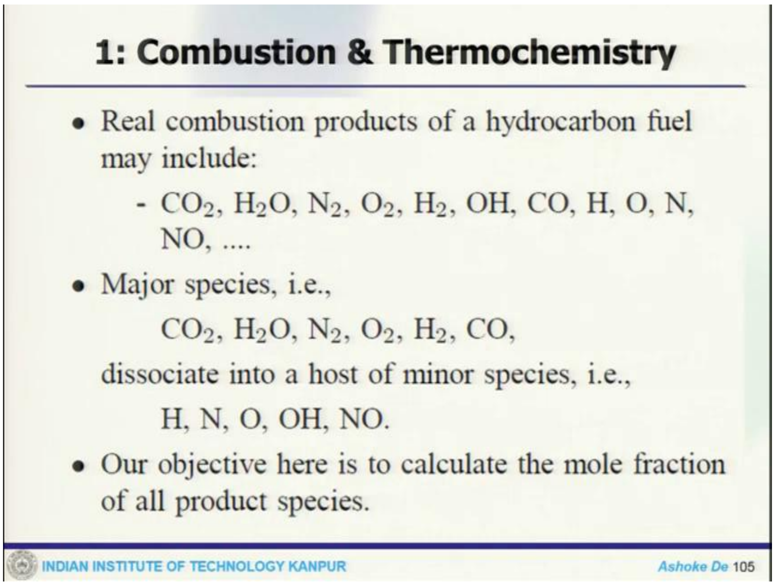

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- Real combustion products of a hydrocarbon fuel may include:
    - CO_2, H_2O, N_2, O_2, H_2, OH, CO, H, O, N, NO, ...
- Major species, i.e.,

  CO_2, H_2O, N_2, O_2, H_2, CO,

  dissociate into a host of minor species, i.e.,

  H, N, O, OH, NO.
- Our objective here is to calculate the mole fraction of all product species.

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Now if you look at the list of real combustion products as we listed here. It Wwll be plenty because any hydrocarbon reaction goes to a series of multiple reactions and that you will see wants to go to the kinetics that how a particular reaction actually goes to multiple so typically you get the global products like CO_2 H_2O N_2 O_2 H_2 OH and there are plenty of other radicals.

There will be plenty of other radicals which will be there. So, the radicals they are found and they actually carrier of any reaction but they are getting consumed. So, at the end you get to see the global product. And rather you can say there are some major species so always any combustion systems you can have some major species and there would be some minor species. So, major species like CO_2 H_2O N_2 CO and there are minor species like radicals H, N, O, OH, and NO.

So, what we want to do here we want to calculate the mole fraction of all products species that means if your combustion product contains major and both minor species then we can evaluate that.

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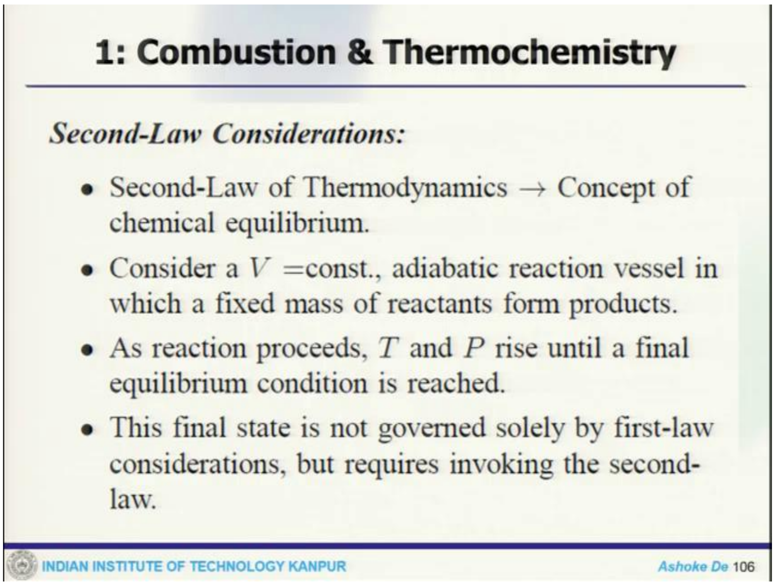

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Second-Law Considerations:

- Second-Law of Thermodynamics → Concept of chemical equilibrium.
- Consider a V =const., adiabatic reaction vessel in which a fixed mass of reactants form products.
- As reaction proceeds, T and P rise until a final equilibrium condition is reached.
- This final state is not governed solely by first-law considerations, but requires invoking the second-law.

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Now you get to the second law consideration so the second law of thermodynamics, which actually gives you the idea of equilibrium. For example, if you considered in constant volume adiabatic reaction vessel in which a fixed mass of reactants and products. As the reaction go along T and P rise until final equilibrium condition is reached. So this final state what the first law gives you that gives you the energy balance and you can find out how much heat is evolved due to the reaction but when the second law will tell you the final state that it reaches.

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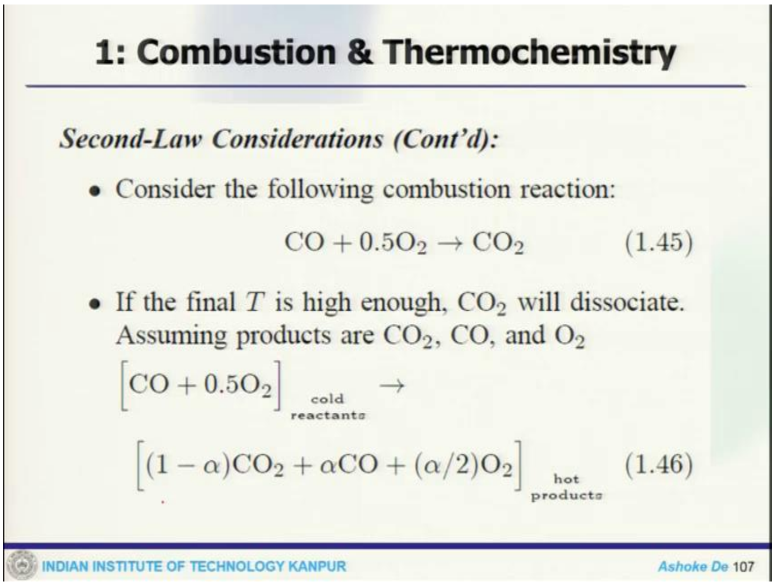

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Second-Law Considerations (Cont'd):

- Consider the following combustion reaction:

$$CO + 0.5O_2 \rightarrow CO_2 \qquad (1.45)$$

- If the final T is high enough, CO_2 will dissociate. Assuming products are CO_2, CO, and O_2

$$\left[CO + 0.5O_2\right]_{\text{cold reactants}} \rightarrow$$

$$\left[(1-\alpha)CO_2 + \alpha CO + (\alpha/2)O_2\right]_{\text{hot products}} \qquad (1.46)$$

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For example consider the following reaction where CO is bond with oxygen to form CO_2 if the temperature is high enough the CO_2 disassociate and you get to see the reverse reaction. So, this particular reaction it is not only one way reaction it could be a reversible reaction also, so as you mean now CO and O_2 confirm CO_2. At the same time, if the temperature is high the CO_2 itself form to form CO and O_2. So, everything would be part of your combustion product or hot product.

And that is why we use a factor that you will get this much of dissociation will take place it is not that complete CO_2 get dissociated. There is some percentage of the CO_2 dissociated and that will from this much of Oxygen and CO.

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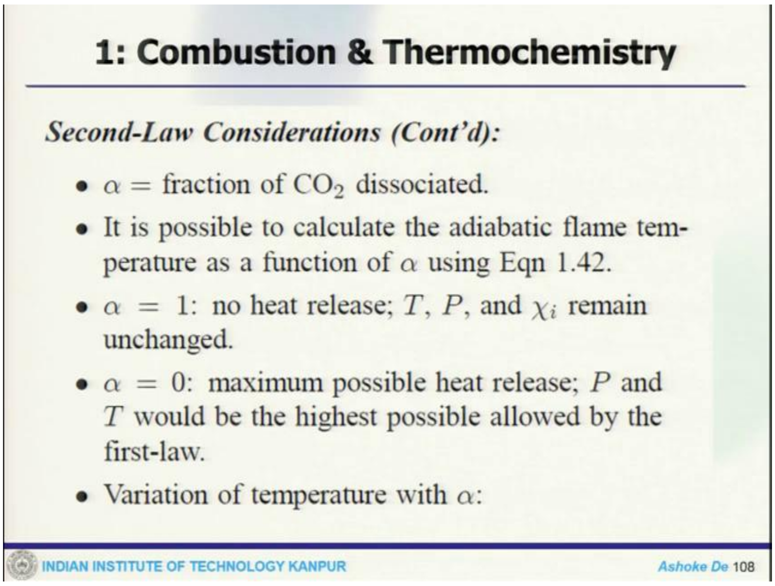

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Second-Law Considerations (Cont'd):

- α = fraction of CO_2 dissociated.
- It is possible to calculate the adiabatic flame temperature as a function of α using Eqn 1.42.
- $\alpha = 1$: no heat release; T, P, and χ_i remain unchanged.
- $\alpha = 0$: maximum possible heat release; P and T would be the highest possible allowed by the first-law.
- Variation of temperature with α:

Now this is as I said alpha (α) is the function of the CO_2 dissociation. If we calculate the adiabatic flame temperature as a function of α then you can see what happened. So α is one that means no heat release if you go back and see here α one means CO_2 one. So, there is no heat released because whatever comes in they remain CO and CO_2. α is zero that means there is no dissociation of CO_2.

So, O_2 and CO_2 in one and form completely CO_2 so that would be the maximum possible heat release that is there and if α between 0 and 1 there will be variation of T with α.

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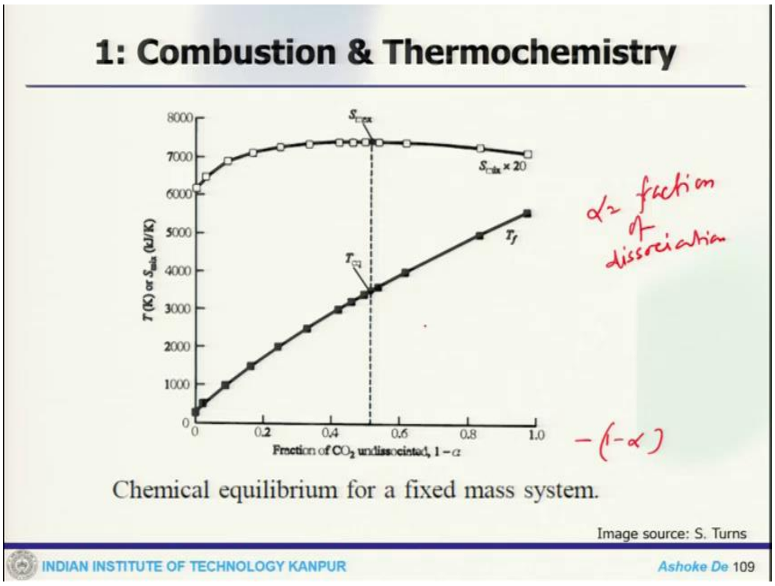

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α = fraction of dissociation

$-(1-\alpha)$

Chemical equilibrium for a fixed mass system.

Image source: S. Turns

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This particular curve shows how that variation actually takes place. This is a fraction of CO_2 and $(1-\alpha)$ so this axis you have $(1-\alpha)$, α is the fraction of disassociation so that you get and you see how the temperature and other things.

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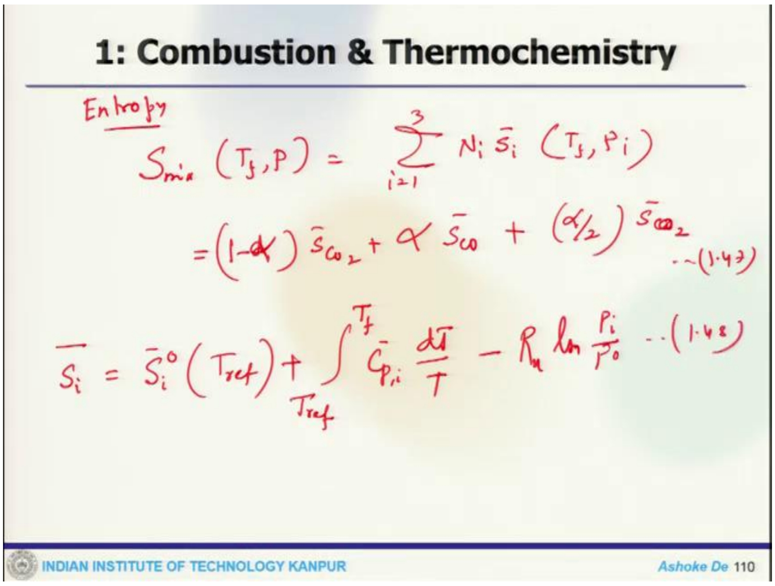

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Entropy

$$S_{mix}(T_f, P) = \sum_{i=1}^{3} N_i \bar{s}_i (T_f, P_i)$$

$$= (1-\alpha)\bar{s}_{CO_2} + \alpha \bar{s}_{CO} + (\alpha/2)\bar{s}_{O_2} \quad \ldots(1.47)$$

$$\bar{s}_i = \bar{s}_i^o(T_{ref}) + \int_{T_{ref}}^{T_f} \bar{c}_{p,i} \frac{dT}{T} - R_u \ln \frac{P_i}{P^o} \quad \ldots(1.48)$$

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Now if you apply the second law in these things then you can find out the entropy. And entropy how you find out if mixture in entropy in the final we would be these are the species N_i at T_a and T_i, so this will get:

$$S_{mix} = (1-\alpha)\bar{S}_{CO_2} + \alpha\bar{S}_{CO} + (\alpha/2)\bar{S}_{O_2}$$

So it is 1.47. So, the mixture entropy would be:

$$\bar{S}_i = \bar{S}_i^0(T_{ref}) + \int_{T_{ref}}^{T_f} \bar{C}_{p,i}\frac{dT}{T} - R_u ln\frac{P_i}{P_0}$$

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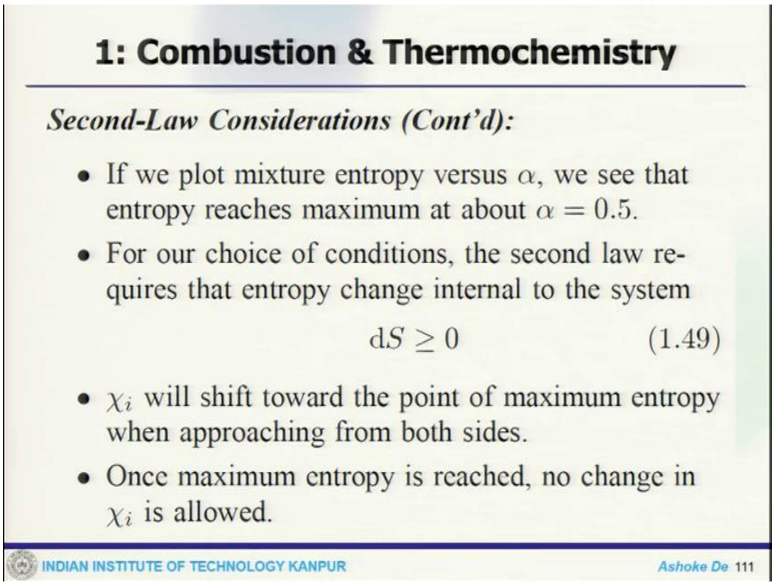

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Second-Law Considerations (Cont'd):

- If we plot mixture entropy versus α, we see that entropy reaches maximum at about $\alpha = 0.5$.
- For our choice of conditions, the second law requires that entropy change internal to the system

$$dS \geq 0 \qquad (1.49)$$

- χ_i will shift toward the point of maximum entropy when approaching from both sides.
- Once maximum entropy is reached, no change in χ_i is allowed.

Now if you plot the mixture entropy versus α you see that entropy reaches maximum at $\alpha = 0.5$ around that time it will be maximum. Now for second law requires that entropy change in internal to the system which is greater than required. And the mole fraction in shift towards the point of maximum entropy when approaching from both side and as soon as you reach the maximum entropy, there would be no change in the mole fraction which is not allowed.

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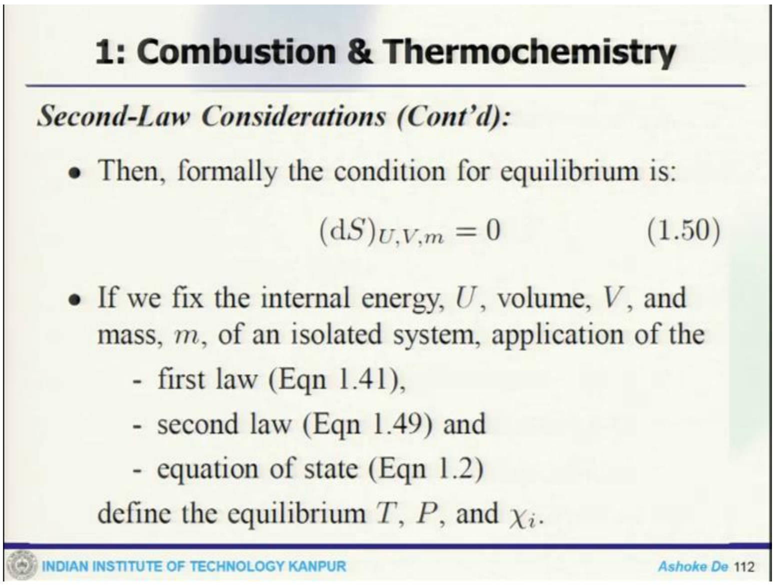

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Second-Law Considerations (Cont'd):

- Then, formally the condition for equilibrium is:

$$(dS)_{U,V,m} = 0 \qquad (1.50)$$

- If we fix the internal energy, U, volume, V, and mass, m, of an isolated system, application of the
  - first law (Eqn 1.41),
  - second law (Eqn 1.49) and
  - equation of state (Eqn 1.2)

  define the equilibrium T, P, and χ_i.

So that will form the basis of your equilibrium and one can formally put the condition for the equilibrium is that change of entropy is going to be zero for given U, V and m. Now if you fixed the internal energy and volume and mass for isolated system. So, one can apply first law which is your equation 1.41 that we have derived. It can be second law and equations of state 1.2 define the equilibrium T, P and mole fraction so, you get all these things.

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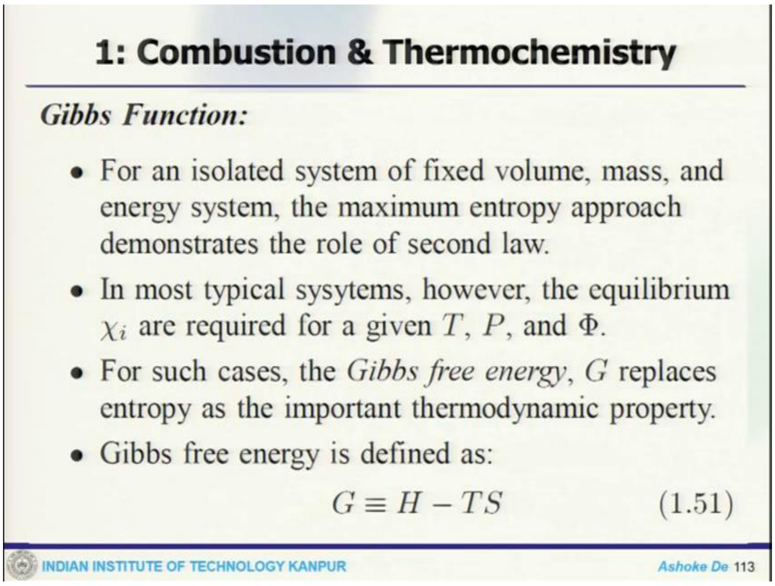

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Gibbs Function:

- For an isolated system of fixed volume, mass, and energy system, the maximum entropy approach demonstrates the role of second law.
- In most typical sysytems, however, the equilibrium χ_i are required for a given T, P, and Φ.
- For such cases, the *Gibbs free energy*, G replaces entropy as the important thermodynamic property.
- Gibbs free energy is defined as:

$$G \equiv H - TS \qquad (1.51)$$

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Another important function which is the Gibbs function for an isolated system of fixed volume mass and energy system the maximum entropy approach demonstrate the role of second law. In most difficult system how equilibrium were is given for T, P and φ. Now Gibbs energy which is designated as 1 Enthalpy and T and S that gives you an idea what happens to the reaction.

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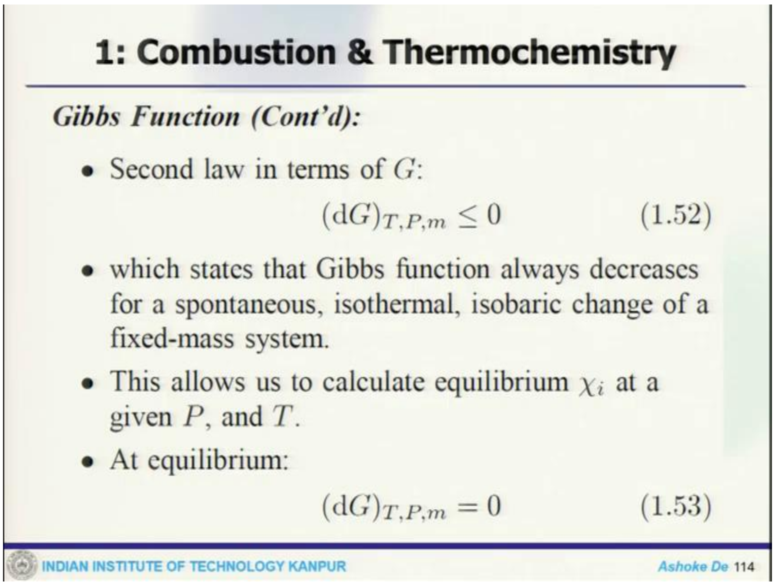

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Gibbs Function (Cont'd):

- Second law in terms of G:

$$(\mathrm{d}G)_{T,P,m} \leq 0 \qquad (1.52)$$

- which states that Gibbs function always decreases for a spontaneous, isothermal, isobaric change of a fixed-mass system.
- This allows us to calculate equilibrium χ_i at a given P, and T.
- At equilibrium:

$$(\mathrm{d}G)_{T,P,m} = 0 \qquad (1.53)$$

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So, in terms of second law, Gibbs energy gives energy is always less than equal to zero which clearly state that it always decreases spontaneously isothermal isomeric change of fixed mass system. So, this allow us to calculate the mole fraction at a given pressure and temperature. And when it is an equilibrium, this should be the zero.

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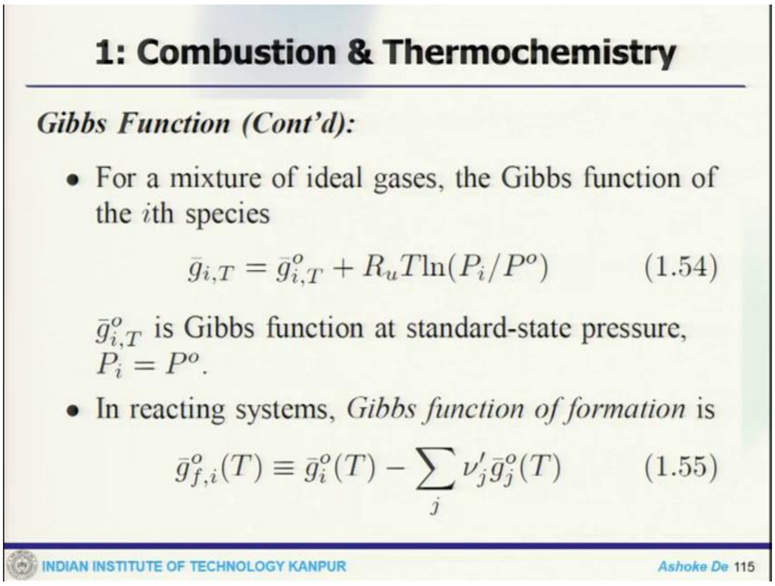

1: Combustion & Thermochemistry

Gibbs Function (Cont'd):

- For a mixture of ideal gases, the Gibbs function of the ith species

$$\bar{g}_{i,T} = \bar{g}^o_{i,T} + R_u T \ln(P_i/P^o) \qquad (1.54)$$

$\bar{g}^o_{i,T}$ is Gibbs function at standard-state pressure, $P_i = P^o$.

- In reacting systems, *Gibbs function of formation* is

$$\bar{g}^o_{f,i}(T) \equiv \bar{g}^o_i(T) - \sum_j \nu'_j \bar{g}^o_j(T) \qquad (1.55)$$

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Ashoke De 115

Once the change is zero from equilibrium one can find out this function. Now for mixture of ideal gases, the Gibbs function of the ith species can be given. So again these are very, very basics of your thermodynamics or rather basics of your combustion process and it should be very much required once we go along. This is a Gibbs function at standard state and pressure.

Now we have to consider a reacting system that means there are multiple species which are involved in the reaction.

So, which function of formation can be represented as this function at a particular temperature at the reference 1 then the stoichiometric coefficient or the reactant this are the number of reactants which are present in the particular system and their Gibbs function.

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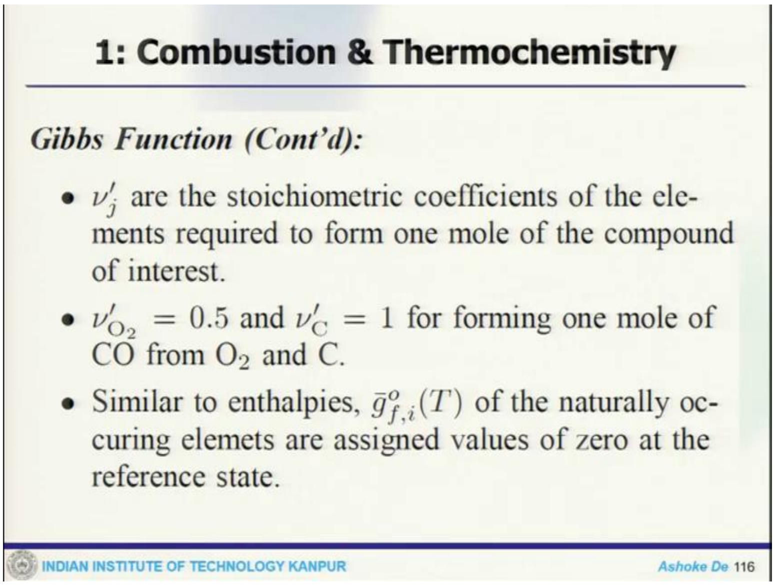

1: Combustion & Thermochemistry

Gibbs Function (Cont'd):

- ν_j' are the stoichiometric coefficients of the elements required to form one mole of the compound of interest.
- $\nu_{O_2}' = 0.5$ and $\nu_C' = 1$ for forming one mole of CO from O_2 and C.
- Similar to enthalpies, $\bar{g}_{f,i}^o(T)$ of the naturally occuring elemets are assigned values of zero at the reference state.

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Ashoke De 116

So as I said ν_j^i are the stoichiometric coefficients of the elements required to form 1 mole of the compound of interest. Let us say that the example that we had to O_2 will be .5 and ν_C' will be 1 mole of CO from O_2 and C, similar to the enthalpies Gibbs function of the naturally occurring elements are having zero values at reference state. So, this is very, very important when you talk about the enthalpy of formation or ah the formation energy at reference state for a particular element.

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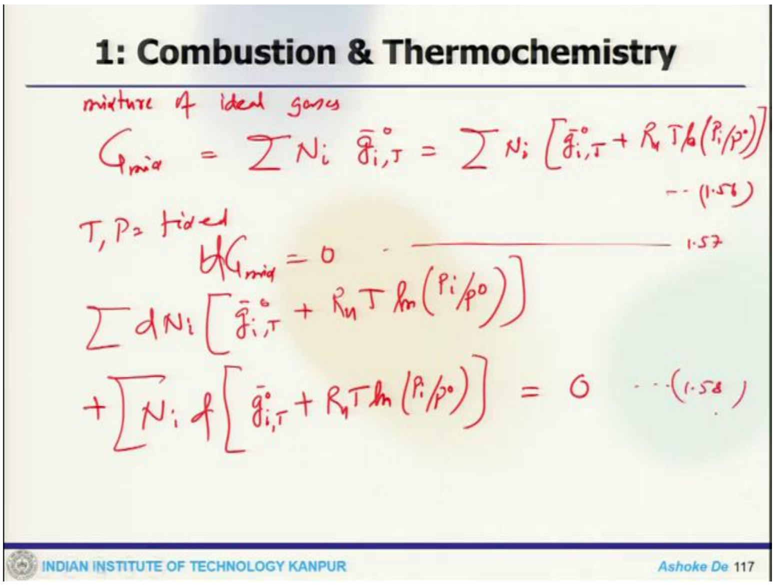

1: Combustion & Thermochemistry

mixture of ideal gases

$G_{mix} = \sum N_i \bar{g}^o_{i,T} = \sum N_i \left[\bar{g}^o_{i,T} + R_u T \ln(P_i/P^o)\right]$ -- (1.56)

T, P = fixed

$dG_{mix} = 0$ ---- 1.57

$\sum dN_i \left[\bar{g}^o_{i,T} + R_u T \ln(P_i/P^o)\right]$

$+ \sum N_i d\left[\bar{g}^o_{i,T} + R_u T \ln(P_i/P^o)\right] = 0$ ...(1.58)

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Now when you have a mixture of ideal gas all gases the G_{mix} would be:

$$G_{mix} = \sum N_i \left[\bar{g}^0_{i,T} + R_u T ln\left({P_i}/{P_0}\right)\right]$$

So, that is your equation. Now for a fixed T and P, these are fixed so you can find out the equilibrium condition that G_{mix} is zero so that:

$$\left[dN_i \left[\bar{g}^0_{i,T} + R_u T ln\left({P_i}/{P_0}\right)\right]\right] + \left[N_i d\left[\bar{g}^0_{i,T} + R_u T ln\left({P_i}/{P_0}\right)\right]\right] = 0$$

This is your 1.57 and this is 1.58. So that will get you the equilibrium condition.

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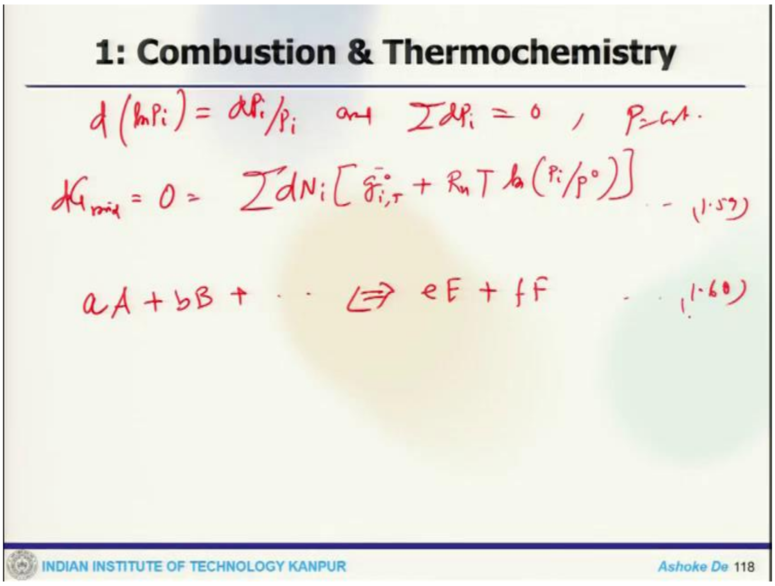

1: Combustion & Thermochemistry

$d(\ln P_i) = dP_i/P_i$ and $\sum dP_i = 0$, $P = cst.$

$dG_{mix} = 0 = \sum dN_i \left[\bar{g}^o_{i,T} + R_u T \ln(P_i/P^o)\right]$ - (1.59)

$aA + bB + \cdots \rightleftharpoons eE + fF$ ... (1.60)

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Now second term in the last equation essentially these term is zero because:

$$d(lnP_i) = {}^{dP_i}/_{P_i}$$

And,

$$\sum dP_i = 0$$

because total pressure is constant. Then we get:

$$dG_{mix} = 0 = \sum dN_i \left[\bar{g}_{i,T}^0 + R_u T ln \left({}^{P_i}/_{P_0}\right)\right]$$

Which is 1.59 for a general system one can write:

$$aA + bB + \cdots = eE + fF$$

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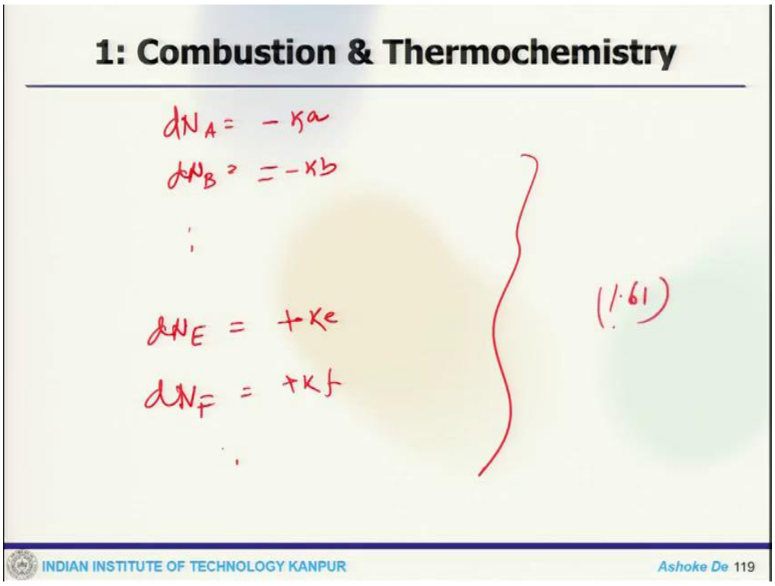

1: Combustion & Thermochemistry

$$\left.\begin{aligned} dN_A &= -\kappa a \\ dN_B &= -\kappa b \\ &\vdots \\ dN_E &= +\kappa e \\ dN_F &= +\kappa f \\ &\vdots \end{aligned}\right\} \quad (1.61)$$

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So, one can define a very generic system and do that. So, change in number of each species is proportional to its stoichiometric coefficient, so:

$$dN_A = -\kappa a$$

And

$$dN_B = -\kappa b$$

And so long:

$$dN_E = -\kappa e$$

$$dN_F = -\kappa f$$

So, that is how if you do that.

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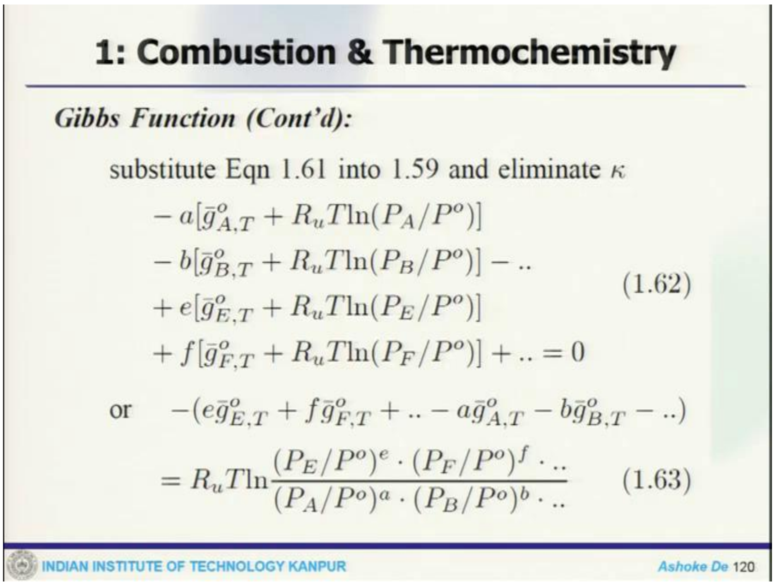

1: Combustion & Thermochemistry

Gibbs Function (Cont'd):

substitute Eqn 1.61 into 1.59 and eliminate κ

$$\begin{aligned}&-a[\bar{g}^o_{A,T} + R_uT\ln(P_A/P^o)]\\&-b[\bar{g}^o_{B,T} + R_uT\ln(P_B/P^o)] - ..\\&+e[\bar{g}^o_{E,T} + R_uT\ln(P_E/P^o)]\\&+f[\bar{g}^o_{F,T} + R_uT\ln(P_F/P^o)] + .. = 0\end{aligned} \qquad (1.62)$$

or $\quad -(e\bar{g}^o_{E,T} + f\bar{g}^o_{F,T} + .. - a\bar{g}^o_{A,T} - b\bar{g}^o_{B,T} - ..)$

$$= R_uT\ln\frac{(P_E/P^o)^e \cdot (P_F/P^o)^f \cdot ..}{(P_A/P^o)^a \cdot (P_B/P^o)^b \cdot ..} \qquad (1.63)$$

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Now you put everything together so this looks little messy. Put 1.61 into 1.59 and eliminate k so you get the equation that will be your equilibrium condition, zero and if you find out do little bit of algebra, you finally get this and that is an simple algebra one can do.

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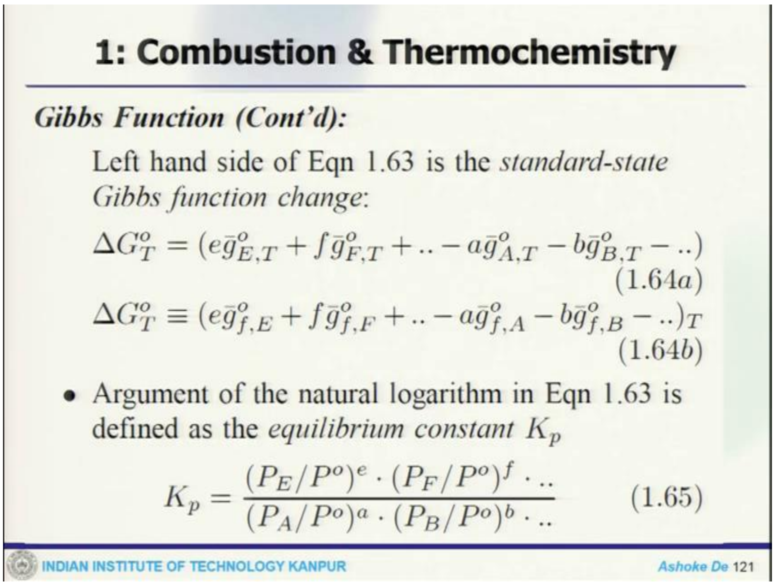

1: Combustion & Thermochemistry

Gibbs Function (Cont'd):

Left hand side of Eqn 1.63 is the *standard-state Gibbs function change*:

$$\Delta G^o_T = (e\bar{g}^o_{E,T} + f\bar{g}^o_{F,T} + .. - a\bar{g}^o_{A,T} - b\bar{g}^o_{B,T} - ..) \qquad (1.64a)$$

$$\Delta G^o_T \equiv (e\bar{g}^o_{f,E} + f\bar{g}^o_{f,F} + .. - a\bar{g}^o_{f,A} - b\bar{g}^o_{f,B} - ..)_T \qquad (1.64b)$$

- Argument of the natural logarithm in Eqn 1.63 is defined as the *equilibrium constant* K_p

$$K_p = \frac{(P_E/P^o)^e \cdot (P_F/P^o)^f \cdot ..}{(P_A/P^o)^a \cdot (P_B/P^o)^b \cdot ..} \qquad (1.65)$$

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Now what? You can look at it that the previous equation 1.63. The left hand side is a standard state Gibbs function. So this is what we are talking about. This is a standard state Gibbs function change so that one can write that change of Gibbs function would be this much and this should be another one. So, natural logarithm of the previous equation. If you take you get the equilibrium constant K_P in terms of all the partial pressure.

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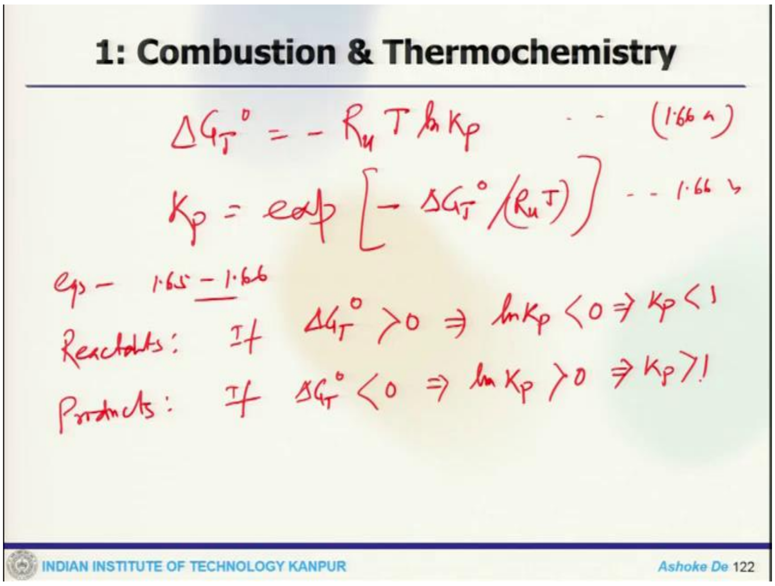

1: Combustion & Thermochemistry

$\Delta G_T^0 = -R_u T \ln K_p$ - - (1.66 a)

$K_p = \exp\left[-\Delta G_T^0/(R_u T)\right]$ - - 1.66 b

eqs – 1.65 – 1.66

Reactants: If $\Delta G_T^0 > 0 \Rightarrow \ln K_p < 0 \Rightarrow K_p < 1$

Products: If $\Delta G_T^0 < 0 \Rightarrow \ln K_p > 0 \Rightarrow K_p > 1$

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Ashoke De 122

So, then one can write that:

$$\Delta G_T^0 = -R_u T ln K_P$$

which is your 1.66a and K_P is exponential component of $\left[{-\Delta G_T^0}/{(R_u T)}\right]$ which is 1.66b. Now this 1.65 and 1.66 qualitative indication of whether a particular reaction so that means these 2 equations 1.65 and 1.66 will give you an indication whether a particular reaction favours products or reactants are the equilibrium.

If it is reactance then if:

$$\Delta G_T^0 > 0$$

That will give you lnK_P which means K_P would be less than 1 or if it favour the products. Then your ΔG_T^0 which would be less than zero, lnK_P is greater than zero, K_P would be greater than 1 so that is how you get it.

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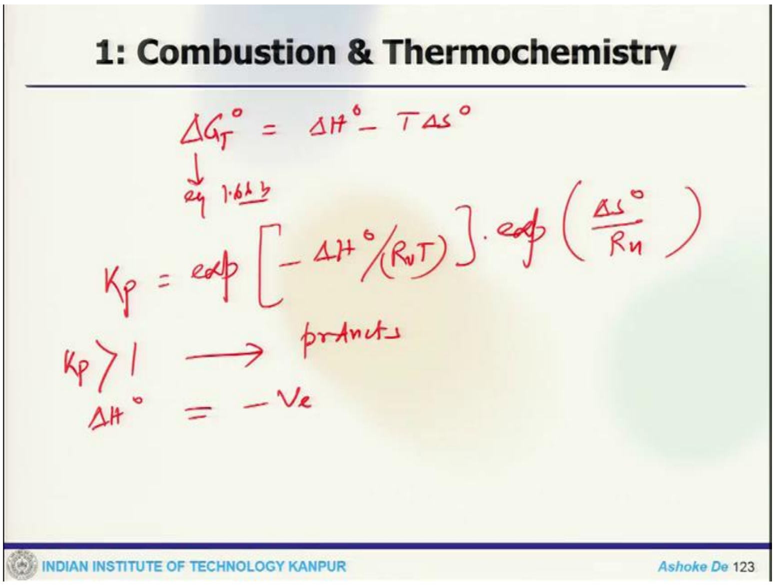

1: Combustion & Thermochemistry

$$\Delta G_T^o = \Delta H^o - T\Delta s^o$$

$\downarrow$ eq 1.66 b

$$K_p = \exp\left[-\Delta H^o/(R_u T)\right] \cdot \exp\left(\frac{\Delta s^o}{R_u}\right)$$

$K_p > 1 \longrightarrow$ products

$\Delta H^o = -$Ve

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Ashoke De 123

Now similar physical inside one can obtain by considering the definition of ΔG_T^0 in terms of enthalpy and entropy change, which is:

$$\Delta G_T^0 = \Delta H^0 - T\Delta S^0$$

And if you put this one back in equation 1.66b you get:

$$K_p = exp\left[{-\Delta H^0}/{(R_u T)}\right] exp\left(\frac{\Delta S^0}{R_u}\right)$$

Now for $K_p > 1$ this favours products and ΔH^0 should be negative or should be always negative and it would be also positive changes in entropy to $K_p > 1$.

So, this is how you can find out the relation between this Gibbs function and all these things. So, we will stop here today and continue the discussion in the next lecture.