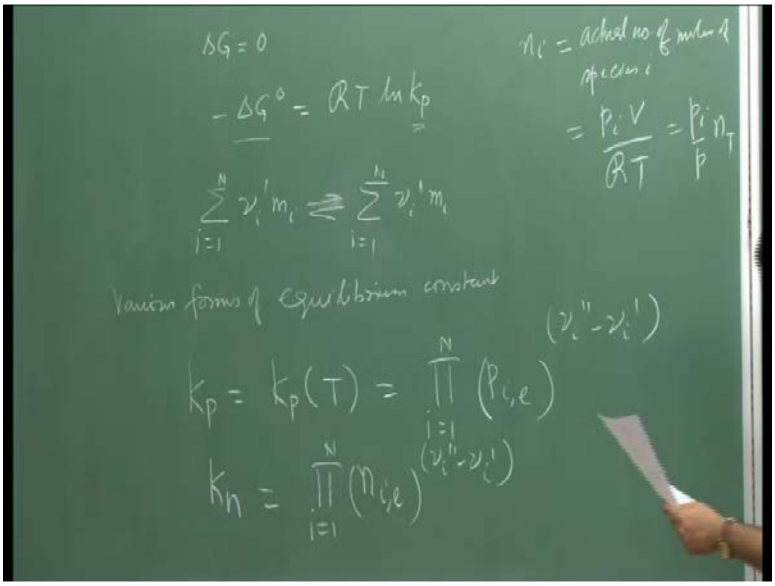
Jet and Rocket Propulsion

Prof. Dr. A. Kushari.
Department of Aerospace Engineering
Indian Institute of Technology, Kanpur

Lecture – 36

(Refer Slide Time: 00:25)

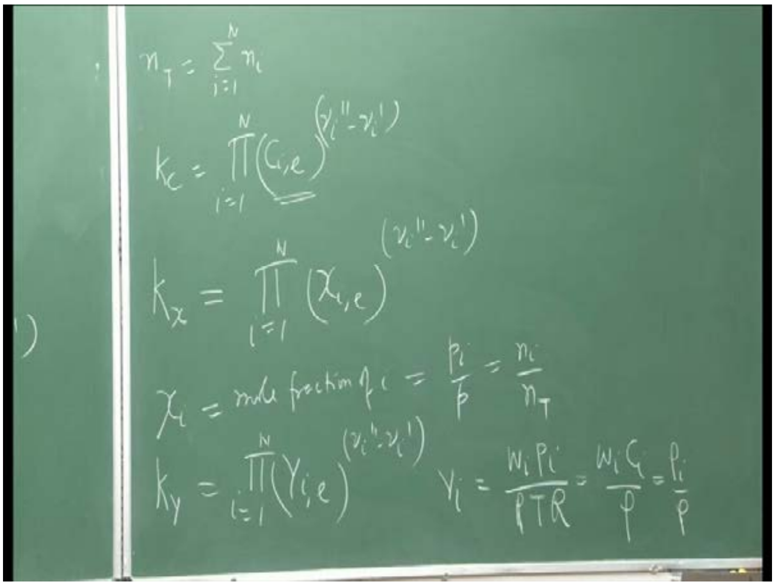


Good evening. So, in the last class we started discussing chemical equilibrium and we have shown that at equilibrium delta G is equal to 0, which is the change in Gibbs free energy; is 0 for a chemical equilibrium process. And from there we have shown that delta G naught is equal to R T l n K P, where delta G naught is the change in Gibbs free energy at standard state. And R this R is the universal gas constant, temperature in Kelvin, and K P is the equilibrium constant, this is defined for standard pressure. So, P naught is 1 atmosphere. Now, we have also shown that the Gibbs free energy for standard state can be obtain by knowing the molar gibbs free energy of formation of different species.

We have also shown that for the formation reactions; since we can estimate how much is the since we know the gibbs free energy of formation. We can estimate the K P for formation reactions then for a complex reaction not a formation reaction, we have shown in the last class that by combining different reactions, we can get the expression for K P for little more complex reaction by combining certain few formation reactions. Now, let us continue from there; we have been discussing this K P in the last class. Now, let us look at various forms of this constant; let us consider this chemical reaction, the generic chemical reaction that we have been discussing so far. This is our generic chemical reaction, what we are now going to talk about is various forms of equilibrium constant for this chemical reaction generic chemical reaction at equilibrium. Let us consider at equilibrium.

So, first of all K P; we have defined K P, we know that K P is a function of temperature. And we have defined it defined it as pie i equal to 1 to n that is product of partial pressure at equilibrium of different species, raise to the power the difference in Stoichiometric coefficient. This we have done in the previous class. Now, we can define the equilibrium constant in terms of moles also K n. So, K n is defined as pie i equal to 1 to n, the number of moles of particular species i at equilibrium, raise to the power again the differencing Stoichiometric coefficient. Where, in this reaction sorry, in this equation n i represent the actual number of moles of species i, which is typically given as the partial pressure multiplied by volume divided by R T. So, this is equal to p i by p by total number of moles multiplied by total numbers of moles, where n T is the total number of moles in the mixture.

(Refer Slide Time: 03:54)



$$n_T = \sum_{i=1}^{N} n_i$$

$$k_c = \prod_{i=1}^{N} \left(C_{i,e}\right)^{(\nu_i'' - \nu_i')}$$

$$k_x = \prod_{i=1}^{N} \left(\chi_{i,e}\right)^{(\nu_i'' - \nu_i')}$$

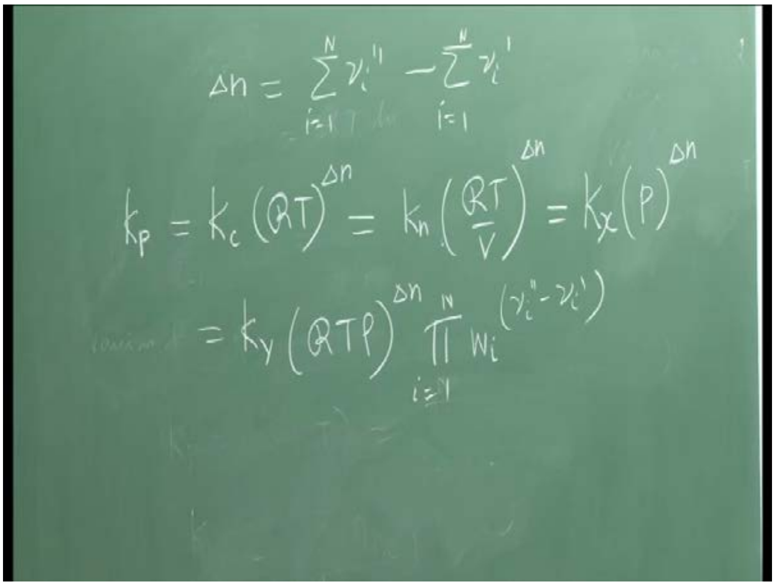
$$\chi_i = \text{mole fraction of } i = \frac{p_i}{p} = \frac{n_i}{n_T}$$

$$k_y = \prod_{i=1}^{N} \left(Y_{i,e}\right)^{(\nu_i'' - \nu_i')} \qquad Y_i = \frac{W_i P_i}{\rho T R} = \frac{W_i C_i}{\rho} = \frac{\rho_i}{\rho}$$

So, n T is the total number of moles in the mixture n T is nothing but the summation of number moles of all the species i ok. Similarly, we can define K C that is the equilibrium constant based on concentration. So, that is defined as pie i equal to 1 to N C i e to the power the differencing the stoichiometric coefficient, where this C i, e represent the concentration of C i e at equilibrium. So, that is equilibrium constant based on concentration. Similarly, we can define based on moles fraction K x. So, on mole fraction based on mole fraction; we can get again the concentration of species i, as a mole fraction of species i at equilibrium raise to the power the differencing Stoichiometric coefficient. Here, once again kappa i is the mole fraction of i, which is nothing but is equal to p i by p that is n i by n T. p i is the partial pressure at equilibrium of species I, p is the total pressure of system. n i is number of moles of a particular species i, n T is total number of moles. So, this is how defined for based on mole fraction.

Now, similarly, we can also define this property equilibrium constant based on mass fraction y. So, based on mass fraction I can define it as very similar definition where, y i is the mass fraction of species i. So, y i is mass fraction. So, that is equal to molecular weight of species i times partial pressure times rho T R. So, that is nothing but molecular by times concentration divided by density. Or, the density of species i divided by total mass average density, right that is the definition of mass fraction. So, these are defined properties. Now, I would like to point out more things the relationship between all this different representations of equilibrium constant. For that let us first define the change in number of moles in a chemical reaction.

(Refer Slide Time: 06:45)



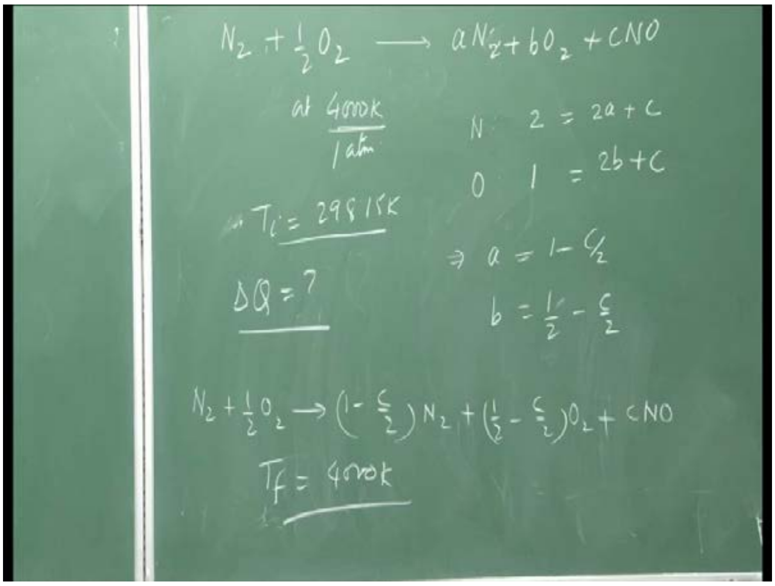
$$\Delta n = \sum_{i=1}^{N} \nu_i'' - \sum_{i=1}^{N} \nu_i'$$

$$k_p = k_c (RT)^{\Delta n} = k_n \left(\frac{RT}{V}\right)^{\Delta n} = k_x (P)^{\Delta n}$$

$$= k_y (RTP)^{\Delta n} \prod_{i=1}^{N} W_i^{(\nu_i'' - \nu_i')}$$

So, change in number of moles in a chemical reaction given by delta n is equal to the sum of the number of moles in the product side minus sum of moles number of moles in reacting side. So, that is the definition the total change in the number of moles. Then, it can be shown that K P is equal to K C R T to the power delta n, this is also equal to K n R T by V to the power delta n also equal to K kappa P to the power delta n. It is also equal to K y R T rho to the power delta n times pie i equal to 1 to n omega i to the power this. So, these are the different equilibrium constant based on different properties and this is the relationship among them. Now, depending on what is known to us; we can estimate the other. So, this is something this is very important information, which is typically used to estimate one of this equilibrium constant other knowing the other properties. Now, before we proceed further with the chemical equilibrium; let us solve the problem to essentially make this concept clearer.

(Refer Slide Time: 08:37)



$N_2 + \frac{1}{2}O_2 \longrightarrow aN_2 + bO_2 + cNO$

at 4000K
1 atm

$T_i = 298.15K$

$\Delta Q = ?$

N $2 = 2a + c$

O $1 = 2b + c$

$\Rightarrow a = 1 - \frac{c}{2}$

$b = \frac{1}{2} - \frac{c}{2}$

$N_2 + \frac{1}{2}O_2 \longrightarrow (1 - \frac{c}{2})N_2 + (\frac{1}{2} - \frac{c}{2})O_2 + cNO$

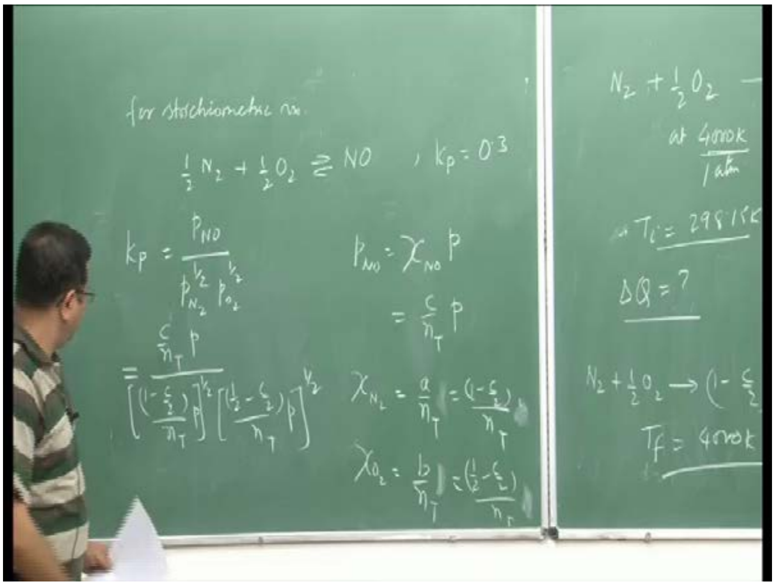
$T_f = 4000K$

Let us consider that we have a mixture of 1 mole of nitrogen and half mole of oxygen, and they are heated at 4000 degree Kelvin. So, because and 1 atmosphere pressure and 1 atmosphere pressure. So, because of that they is a resulting reaction, and we get the final equilibrium mixture consist of nitrogen oxygen and some nitrogen oxide nitric oxide N O nox. We can also assume the initial temperature of both nitrogen and oxygen T i is 298.15 Kelvin that is essentially the standard temperature. So, nitrogen and oxygen are supplied at standard temperature and then, they were heated steadily.

Now, the question is here; how much heat will be required to take this to 4000 degree Kelvin temperature. So, how much delta Q is equal to what how much heat is required? So, first for this problem; let us look at what is known to us, first we wanted to estimate a b and C, how much is a total, what is the total what are the final composition. In order to do that first us do the atomic species balance? So, we have 2 species nitrogen and oxygen in the reacting side we have 2 atoms of nitrogen. So, this is equal to then 2 a plus C in the product and the oxygen in the reacting side we have 1 atom of oxygen; this is equal to then 2 b plus C. So, if you simplify this; we get a is equal to 1 minus C by 2, b equal to half minus C by 2. So, then at equilibrium this is what is our final composition. So, if we can estimate C we know, how much is the final product composition. So, my final equilibrium reaction then is this looks like 1 minus C by 2 times N 2 plus half minus C by 2 times O 2 plus C N O.

Now, what is given to us that the initial temperature is T i; the final temperature of the mixture is 4000 Kelvin. So, here what we are solving is that what we are saying is that initially the mixtures were at this temperature; first they were heated to this temperature then reaction occurs. It is equivalent to saying that the reaction occurs at this temperature and then the heat takes this to this temperature. So, both of them are equivalent that we have already discussed. Now, if we had a Stoichiometric reaction.

(Refer Slide Time: 12:05)

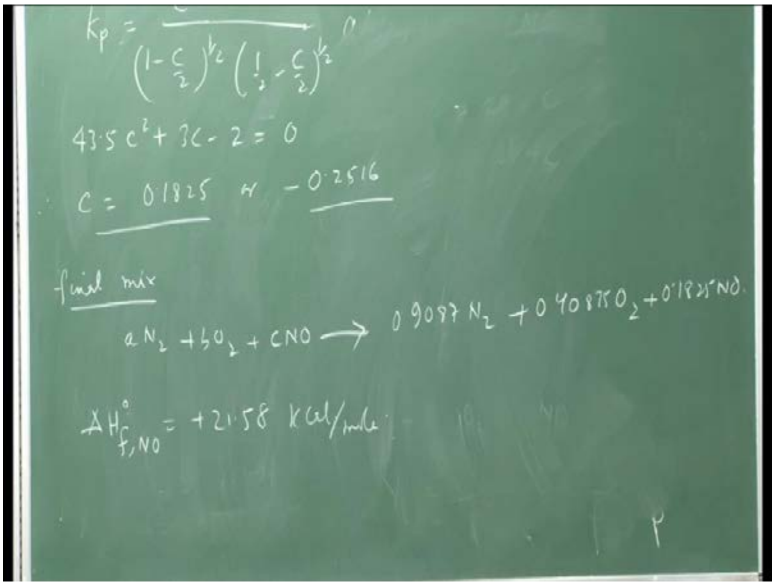


So, this reaction as you can see clearly is not stoichiometric, but for a Stoichiometric reaction it will be half N 2 plus half O 2 giving N O, right. So, if you have to produce 1mole of N O we need half N 2 and half O 2. That is what Stoichiometric reaction and the value of K P for this reaction can be obtained from thermo chemical tables, this is equal to 0.3. Now, as we can see here from our discussion we had 2 species, we had 3 unknowns. So, we were not able to solve this. Now, we are using that information the K P information to solve this. Now, this K P is applicable at equilibrium right and this Stoichiometric reaction is the equilibrium Stoichiometric reaction. So, for this reaction K P is equal to p N O by p N 2 to the power half p O 2 to the power half.

Now, what is the partial pressure of N O in this mixture, it is the number of moles times the total pressure divided by total number of moles, right. This is a mole fraction times a pressure. So, first of all p N O x kappa N O times a total pressure right, and the mole fraction is the number of moles of N O in the final mixture which is C divided by total number of moles which is let say at the time being is n T we will estimate that also, times pressure. Similarly, the mole fraction of N 2 in the final mixture is a by n T times p, and a according to this estimate is 1 minus C by 2 times n 2 by y n T times p. Similarly, mole fraction of O 2 is b by n T times p. So, this is equal to half minus C by 2 by n T times p.

Now, these are our actual mole fractions. So, we can estimate the partial pressure for every molecule here. Now, using this because the partial pressure of N 2 will be nothing but mole fraction multiplied by the total pressure sorry, this p will not come here sorry, because we are talking about just the mole fraction. So, now we come back to this equation we write the partial pressure for all of them power half minus C by 2 by n T times p to the power half. So, you can see here now, we have one equation which relates which is a function of only C, right. So, if I now expand this first of all this n T will cancel off pressure will cancel off. So, we have simplified expression which gives us the value of C in terms of k p.

(Refer Slide Time: 15:36)



$$k_p = \frac{\quad}{\left(1-\frac{c}{2}\right)^{1/2}\left(\frac{1}{2}-\frac{c}{2}\right)^{1/2}}$$

$$43.5c^2 + 3c - 2 = 0$$

$$c = \underline{0.1825} \text{ or } \underline{-0.2516}$$

final mix

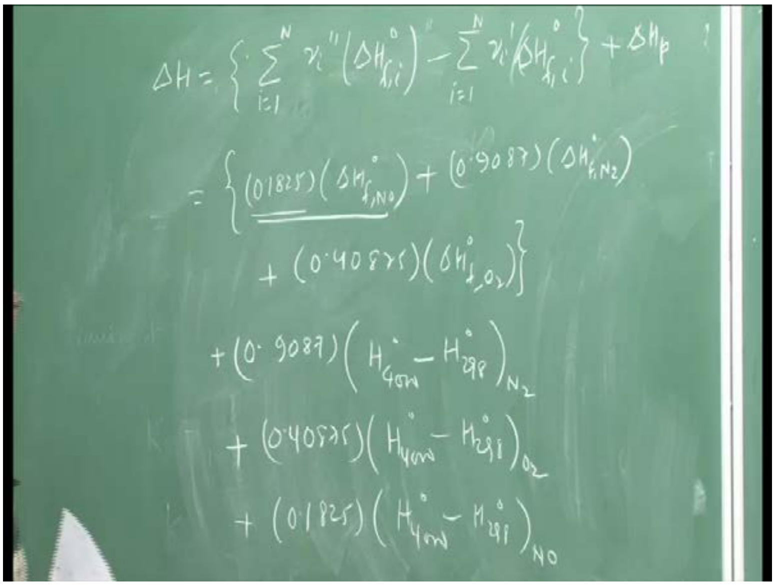
$$aN_2 + bO_2 + cNO \longrightarrow 0.9087 N_2 + 0.40875 O_2 + 0.1825 NO.$$

$$\Delta H^{\circ}_{f,NO} = +21.58 \text{ kcal/mole}$$

So, by simplifying this we get K P is equal to C upon 1 minus C by 2 to the power half times half minus C by 2 to the power half. After we expand this; putting K P equal to 0.3 to get this. Now, let us solve for C is the quadratic equation. So, it can be very easily solved, this gives C is equal to 0.1825 or minus 0. 2516. Now, if I look at these 2 numbers; the negative value is physically not possible, because there has to be some amount of nitrogen oxide to be present. So, therefore this is the correct value once we have C then, we can estimate a and b also. So, my final mixture is final mixture which is a N 2 plus b O 2 plus C N O is equal to point 0.927 N 2 plus 0.40875 O 2 plus 0.8125 N O. This is how we get the final composition right.

Once we have the final composition now we know how much our final temperature, we can get how much heat is required, right. So, let us look at that. First of all delta H of formation for N O is equal to plus 21 per 58 kilocalorie per mole. Now, this is a constant pressure process. So, delta Q is equal to delta H, right. So, essentially we have to find out the total enthalpy change in this process, which is equal to how do we do it? we assume that first the reaction had occurred at standard state right and then, the products are heated to the final temperature.

(Refer Slide Time: 18:08)



$$\Delta H = \left\{ \sum_{i=1}^{N} \nu_i'' \left(\Delta H^\circ_{f,i}\right) - \sum_{i=1}^{N} \nu_i' \left(\Delta H^\circ_{f,i}\right) \right\} + \Delta H_p$$

$$= \left\{ \underline{(0.1825)\left(\Delta H^\circ_{f,NO}\right)} + (0.9087)\left(\Delta H^\circ_{f,N_2}\right) + (0.40875)\left(\Delta H^\circ_{f,O_2}\right) \right\}$$

$$+ (0.9087)\left(H^\circ_{4000} - H^\circ_{298}\right)_{N_2}$$

$$+ (0.40875)\left(H^\circ_{4000} - H^\circ_{298}\right)_{O_2}$$

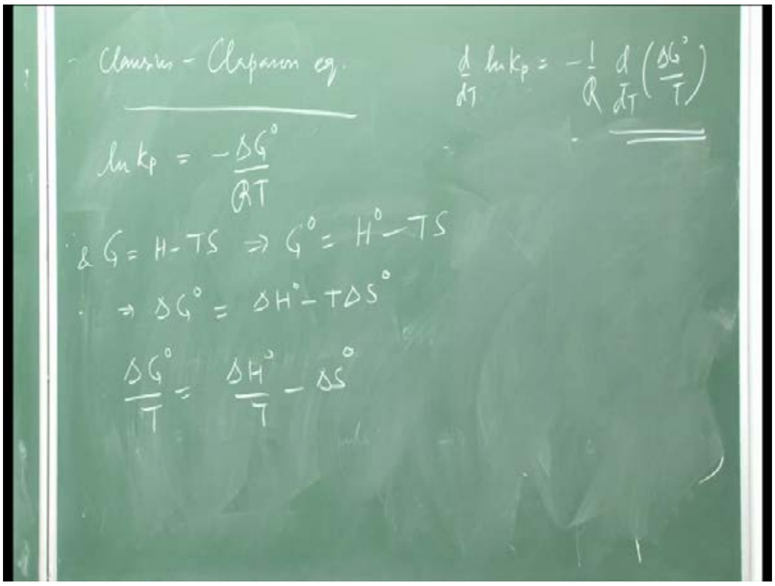
$$+ (0.1825)\left(H^\circ_{4000} - H^\circ_{298}\right)_{NO}$$

So, the total delta H is equal to first of all heat of formation total heat of formation, which is equal to nothing but this we have seen in the previous class, other 2 class back I think. So, this is a total heat evolved in the formation reaction, this total heat of formation of all the products species, total heat of formation of all the reactants species. So, that is the heat evolves during the reaction at standard state. And then the products are heated delta H p from this standard rate of 298 Kelvin to 4000 Kelvin which is final temperature.

Now, if I look at this; in the product side we have that composition right. So, we have 0.1825 times delta H f of N naught, right. So, delta H f of N naught plus 0.90987 times delta H f naught of N 2 plus 0.40875 delta H f naught of O 2. So, this is the total change in the formation enthalpy and then, the heat require to heat it up. So, that will be equal to now, this amount of nitrogen is heated from 298 to 4000. So, that is; first of all let us look at nitrogen. So, this amount of nitrogen is there initially in the final which is heated now for nitrogen then, oxygen is heated again from the initial temperature of 298 to the final temperature. And N O is heated again from 2 98 to final temperature ok.

Now, what is a heat formation of nitrogen? Is 0, because nitrogen appears as nitrogen molecule here. So, this is 0, heat of formation of oxygen is also 0 and these values we can get from thermo chemical tables; the enthalpy for nitrogen for oxygen for N O at different temperatures as tabulated thermo chemical tables. So, we can get that once we do that if I estimate the final heat is 5.53 kilocalorie. So, 5.53 kilocalorie must be supplied, in order to take to carry out this reaction this is an endothermic reaction. So, so much heat is required. So, that explained how we estimate. So, in this problem we showed first that how do we estimate the final composition and then, instead of solving for adiabatic flame temperature we said that flame temperature is known how much heat is require. So, this is how we do it. I like to point out one more things here; let for estimate for K P we talked about Gibbs free energy. Many times Gibbs free energy is not available to us, but typically the enthalpy variation the changes are given.

(Refer Slide Time: 22:25)



Clausius - Clapeyron eq.

$$\ln K_p = -\frac{\Delta G^0}{RT}$$

& $G = H - TS \Rightarrow G^0 = H^0 - TS$

$\Rightarrow \Delta G^0 = \Delta H^0 - T\Delta S^0$

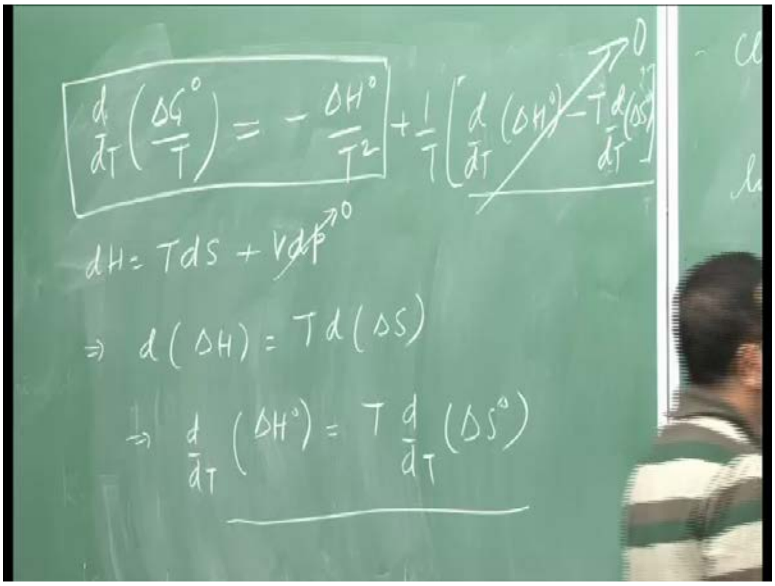
$$\frac{\Delta G^0}{T} = \frac{\Delta H^0}{T} - \Delta S^0$$

$$\frac{d}{dT}\ln K_p = -\frac{1}{R}\frac{d}{dT}\left(\frac{\Delta G^0}{T}\right)$$

So, how do we get the Gibbs free energy or other the K P if enthalpy changes are given? So, for that we use Clausius Clrparon equation; let us see how we get that we have already shown that ln K P is equal to minus delta G naught by R T. And we have shown that Gibbs free energy is equal to H minus T S. Therefore, at standard pressure this was defined as standard pressure H naught minus T S. So, therefore the change in Gibbs free energy is equal to delta H naught minus T delta S naught. And therefore we can write delta G naught by T is equal to delta H naught by T minus delta S naught ok.

Now, let us look back again at this equation and let us differentiate it with respect to temperature. So, if we do d d T of ln K P this is equal to nothing but 1 by R minus 1by R d d T of delta G naught by T right. That comes from by differentiating this. So, we defined first of all from here, we have shown the d d T of ln K P is equal to this. Now, let us look at this term d d T of d ln T.

(Refer Slide Time: 24:14)



$$\boxed{\frac{d}{dT}\left(\frac{\Delta G^\circ}{T}\right) = -\frac{\Delta H^\circ}{T^2}} + \frac{1}{T}\left[\cancelto{0}{\frac{d}{dT}(\Delta H^\circ) - T\frac{d}{dT}(\Delta S^\circ)}\right]$$

$$dH = TdS + \cancelto{0}{Vdp}$$

$$\Rightarrow d(\Delta H) = Td(\Delta S)$$

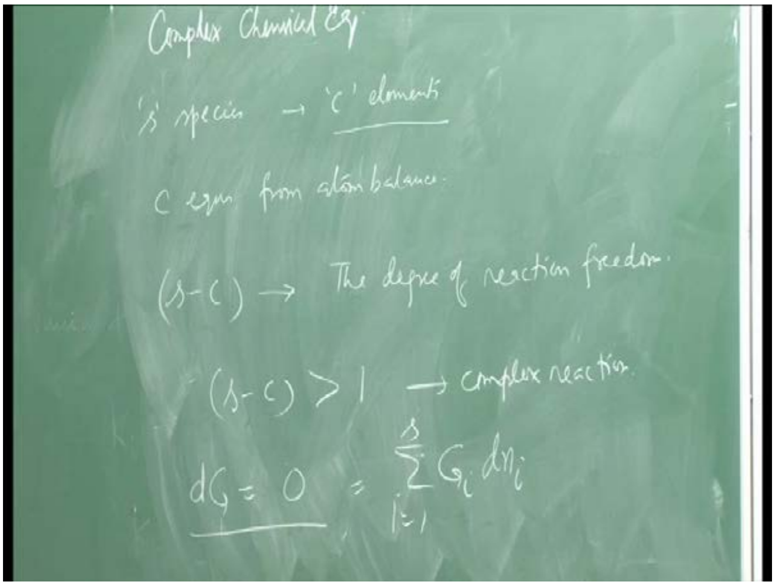
$$\Rightarrow \frac{d}{dT}(\Delta H^\circ) = T\frac{d}{dT}(\Delta S^\circ)$$

So, first let us look at d d T of delta G naught by T delta G naught by T for according to this equal to delta H naught by T minus T delta s naught by ln of delta S naught. So, this will be equal to minus delta H naught by T square plus 1 by T d d T of delta H naught minus T d d T of delta S naught. So, because H naught is also a function of temperature. So, we can write this like this. Now, let us look at the Gibbs equation; it says that d H equal to T d s plus v d p. Since, we are considering a constant pressure process therefore, d p is 0. So, this term is 0. So, d H is equal to T d s therefore, we can write this as d of delta H is equal to T d of delta S. Therefore, d d T of delta H naught is equal to T times d d T of delta S naught. Here, we are now we are imposing the condition that the enthalpy and the entropy here at essentially their process at standard pressure.

Now, if I look at this expression and this expression we have this minus this appearing here. Therefore, this term is 0, right. So, therefore, this term goes to zero. So, what we are left with only this portion of this expression; therefore, once we put it here this term d d T of G naught by T delta G naught by T is equal to nothing but minus delta H by T naught by T square. So, if I put it here this comes to be equal to delta H naught by R T square. So, here now we have got an expression for K P in terms of delta H naught which is something typically a known property universal gas constant and temperature. So, this equation is called Clausius Clrparon equation which gives us the value of K P if delta H naught is known ok.

So, now so far we have been discussing typically simpler reaction one step reaction, but in our rockets we have complex reactions involving may be multiple reactions. What we know is initially the reactants that we are supplying; we may not even know what is the final products, if you know the final products let say we know the final products we do not know what are the reaction occurring. So, now let us try to get the reactions, which are occurring in the practical system, where we have more complex chemical equilibrium. So, the next thing that we are going to discuss is complex chemical equilibrium and how to get that condition.

(Refer Slide Time: 27:36)



Complex Chemical Eq

's' species → 'C' elements

C eqn from atom balance.

$(s-C) \rightarrow$ The degree of reaction freedom.

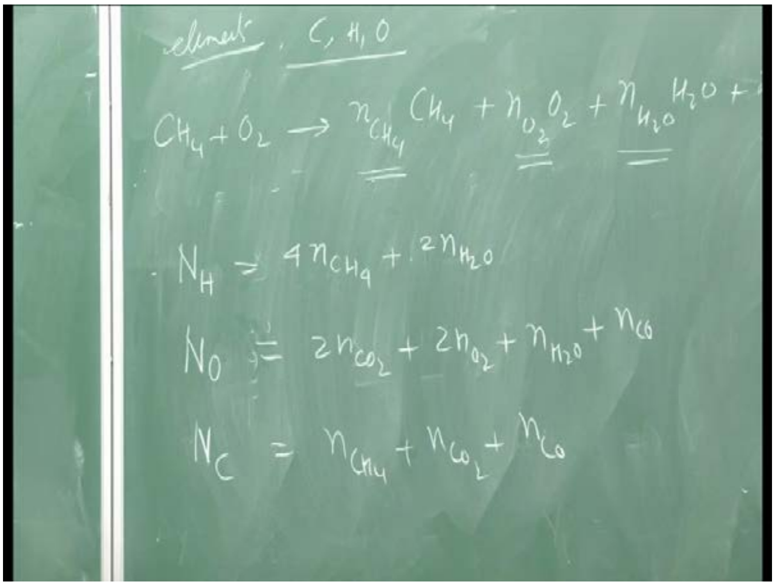
$(s-C) > 1 \rightarrow$ complex reaction.

$\underline{dG = 0} = \sum_{i=1}^{s} G_i \, dn_i$

So, next is complex chemical equilibrium; now, we have seen some example in the previous class that at one of the example where the reaction was occurring at high temperature, we have 4 species and 9 unknowns. So, the atom balance was not able to provide us enough equations to solve the problem. Even in the previous case we used one K P equation, right. But when we are going to more complex systems if we have s species and from C elements then, from atom balance for C elements we get C equations. So, we get C equations from atom balance which we have already discussed many times.

Now, therefore this S minus C is our additional require equations which we need to close this problem. So, this term s minus C is called the degree of reaction freedom. A reaction having only one degree of reaction freedom is called a simple reaction, like the reaction we took in the example, right. But if the degree of reaction freedom is greater than one then, the reaction is said to be complex. So, if S minus C is greater than one that is called a complex reaction. Now, we want to work with a complex reaction; we have seen earlier that for any reaction no matter with a simple or complex. We have seen that at equilibrium d G equal to 0, right. And what is d G? If we have s species what is total d G for that total change in free energy? This is nothing but sum over this s species the Gibbs free energy for individual species times the change in number of moles of the species, right. So, that is the total d G and this is equal to 0 at equilibrium. We will use this relationship to obtain the equilibrium relation.

(Refer Slide Time: 30:25)



elements: C, H, O

$$CH_4 + O_2 \rightarrow n_{CH_4} CH_4 + n_{O_2} O_2 + n_{H_2O} H_2O +$$

$$N_H = 4 n_{CH_4} + 2 n_{H_2O}$$

$$N_O = 2 n_{CO_2} + 2 n_{O_2} + n_{H_2O} + n_{CO}$$

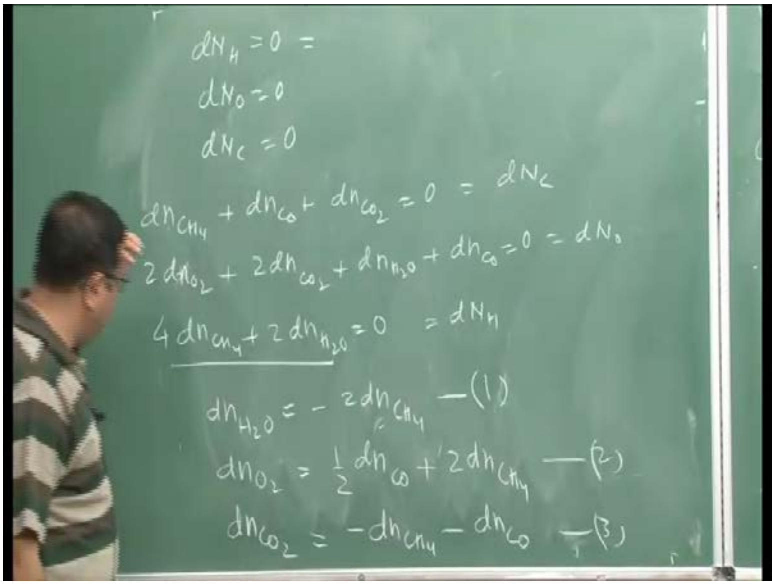
$$N_C = n_{CH_4} + n_{CO_2} + n_{CO}$$

Let us start with an example that will make it easier to explain. The example we have already seen similar example before; that we let say we have some methane, and some oxygen as reactant. And the products what we have is some unburned methane, some oxygen, some water vapor, some carbon monoxide, some carbon dioxide these are the products. Now, this is typically what happens we have carbon monoxide, carbon dioxide, water vapor ,unburned hydrocarbon, oxygen everything is present at equilibrium. We want to find out then, what are the reaction equilibrium reactions that are occurring? What are our elements in this case? The elements are carbon, hydrogen and oxygen. So, we will get 3 equations from there then, in the final products. So, our chemical reaction is something I am not mentioning how much it is there. The final composition will have something like this.

So, in the final composition we have n C H 4 moles of methane, n O 2 moles of oxygen, n H 2 O moles of water vapor, n C O moles of carbon monoxide and n C O 2 moles of carbon dioxide. Now, we want to find out relationship to get this, only then our final composition will be known. So, in order to do that let us first to get the equations that we are looking for. First the 3 elements are these; let us say that depending on the initial composition we have N H number of hydrogen. So, then N H is equal to in this product side we will have 4 n C H 4 plus 2 n H 2 O right, because 1 C H 4 molecule will give 4 hydrogen atoms, 1 H 2 O molecule will give 2 hydrogen atoms. So, if N H is the initial number of hydrogen atoms this is will be the product side.

Similarly, we can get N O number of atoms of oxygen. So, that will be from atom balance 2 n C O 2 plus 2 n O 2 plus n H 2 O plus n C O. Similarly, we have n C is the number of atoms of carbon. So, that is equal to n C H 4 plus n C O 2 plus n C O. So, now our atom balance is done. We get only 3 reactions and we have 5 unknowns. So, we need 2 more equations somehow, right.

(Refer Slide Time: 33:32)

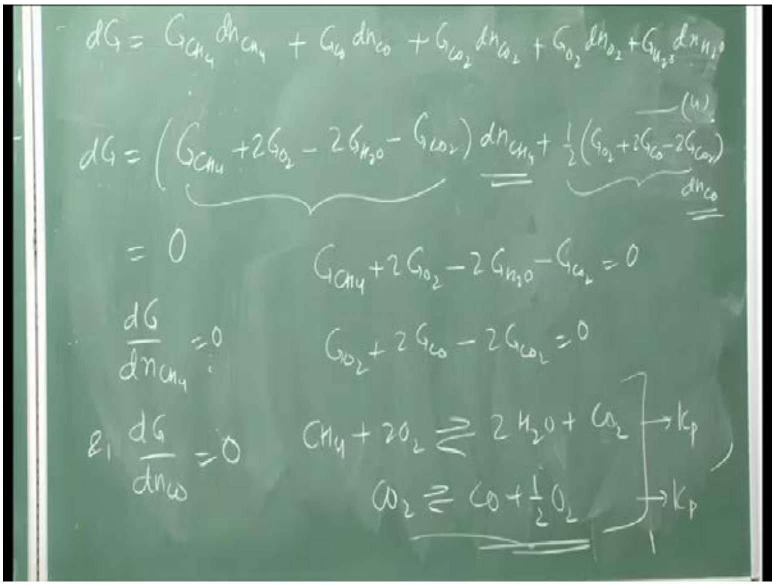


So, let us look at the changes; first of all what is the change in number of atoms of hydrogen d H N N H is 0 right. Because that is going to be conserve. So, this is equal to 0, and this then is equal to nothing but change in this plus change in this. So, this is equal to this. Therefore, from these 3 equations similarly, we get d N O equal to 0 and d N C equal to0. So, from these 3 we get 3 equations, these are d n C H 4 plus d n C O plus d n C O 2 is equal to 0, 2 d n O 2 plus 2 d n C O 2 plus d n H 2 O plus d n C O equal to 0, 4 d n C H 4 plus 2 d n H 2 O equal to 0, right. So, this represents d N C, this represents d N O, and this represent d N H. So, the change in number of atoms we get 3 equations here.

Now, as I have just mentioned that we have 5 species in the product and 3 elements. So, the degree of the reaction freedom in this cases 2. So, we need to have 2 more equations. Now, what we do is since; we have 5 variables what we will do is first let us choose 2 of these variables as independent variables, and express the other variables as function of these 2. So, what will be the most logical choice? Let say we choose methane because that is our fuel. So, we choose one of them methane one of the independent variable. And the other independent variable let say is carbon monoxide, because typically in stoichiometric reaction we should get carbon dioxide. Since, we are getting carbon monoxide that is intermediate reaction occurring. So, we choose that as one of the reactant independent variable.

So, then what we can do is from these 3 equations; we can write from this equation d n H 2 O is equal to minus 2 d n C H 4 let me call this equation 1. Then, from this other equations we get d n O 2 is equal to half d n C O plus 2 d n C H 4, let me call this equation 2. And similarly we get d n C O 2 from this equation is equal to minus d n C H 4 minus d n C O let me call this equation 3. So, essentially what we are doing is; we are representing d n H 2 O d n O 2 and d n C O 2 as function of d n C H 4and d n C o. So, change in moles of methane and carbon monoxide. Now, we have chosen methane and carbon monoxide as independent variables. So, now we have these 3 equations.

(Refer Slide Time: 37:08)



$$dG = G_{CH_4}\,dn_{CH_4} + G_{CO}\,dn_{CO} + G_{CO_2}\,dn_{CO_2} + G_{O_2}\,dn_{O_2} + G_{H_2O}\,dn_{H_2O} \quad (4)$$

$$dG = \underbrace{\left(G_{CH_4} + 2G_{O_2} - 2G_{H_2O} - G_{CO_2}\right)}_{=0} dn_{CH_4} + \underbrace{\tfrac{1}{2}\left(G_{O_2} + 2G_{CO} - 2G_{CO_2}\right)}\,dn_{CO}$$

$$\frac{dG}{dn_{CH_4}} = 0 \qquad G_{CH_4} + 2G_{O_2} - 2G_{H_2O} - G_{CO_2} = 0$$

$$G_{O_2} + 2G_{CO} - 2G_{CO_2} = 0$$

$$\& \quad \frac{dG}{dn_{CO}} = 0 \qquad CH_4 + 2O_2 \rightleftarrows 2H_2O + CO_2 \rightarrow K_p$$

$$CO_2 \rightleftarrows CO + \tfrac{1}{2}O_2 \rightarrow K_p$$

Next step now is bringing our discussion on free energy. What is the total free energy? The total free energy change is d G, right. So, that free energy total free energy is nothing but free energy change is d G C H 4 species times d n C H 4 plus G C O times d n C O plus G C O 2 times d n C O 2 plus G O 2 times d n O 2 that is it one 2 3 4 d n H 2 o. So, this is my total change in Gibbs free energy all size species are considered. So, let me call this equation 4 ok. Now, what we do is from this expression; let us eliminate this, this and this. Then, it will remain only as function of d H C H 4 and C O.

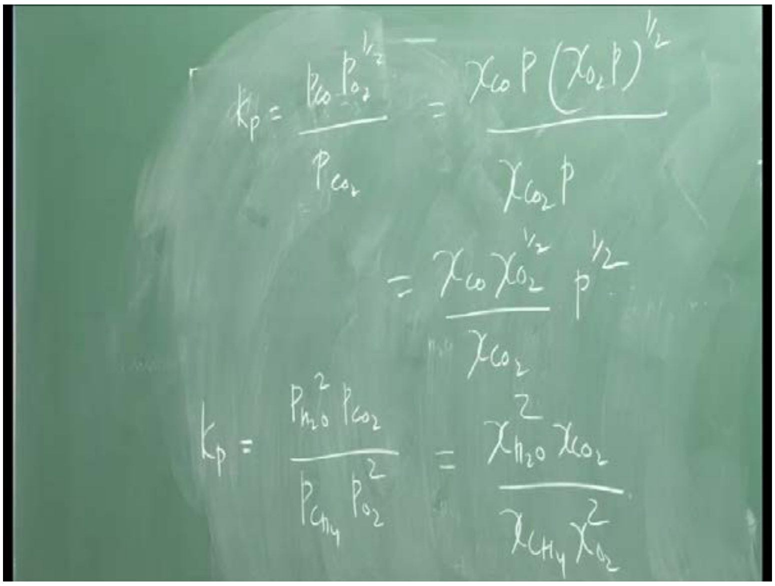
So, after eliminating this we get d G is equal to G C H 4 plus 2 G O 2 minus 2 G H 2 O minus G C O 2 times d n C H 4 plus half G O 2 plus 2 G C O minus 2 G C O 2 times d n C O. So, that is the total change in Gibbs free energy in term of the free energy of all those species we are considering times the change in number moles of methane and carbon monoxide. Now, from the equilibrium d G is 0, right. So, this term must be equal to 0. Now, let us see this is not 0 right, and this is not 0. Therefore, in order and this is positive this is actually this is none 0, this is none 0 therefore, in order for this to be 0 this must be 0, and this must be 0, right. So, in order for this to be 0; mathematically what we have is right, d G d n C H 4 equal to 0, d G d n C O equal to 0. And that means; that this term is equal to 0, and this term is equal to 0.

So, what we get is G C H 4 plus 2 G O 2 minus 2 G H 2 O minus G C O 2 equal to 0. This thing gives me after eliminating these things, and from this I get G O 2 plus 2 G C

O minus 2 G C O 2 equal to 0, I get these 2 equations. Now, these 2 equations correspond to the 2 equilibrium condition for 2 equilibrium reactions. First of them comes from here, this will be valid for an equilibrium reaction at standard temperature and pressure, which will be C H 4 plus 2 O 2 equal to 2 H 2 O plus C O 2 right. If I have an equilibrium equation at standard temperature and pressure then, the total change in Gibbs free energy delta G naught for this is equal to 0, we have already talked about it.

So, therefore this is in order for this to be correct we need to have this condition, right. And actually it may not be at standard temperature and pressure any reaction can do that because delta G naught as delta G for a chemical reaction at equilibrium is 0. So, therefore, in order for this to be correct we have this equilibrium reaction. Similarly, for this to be correct we have another equilibrium reaction which is ok. Now, this reaction C O is something as I said is appearing as one of the intermediate products, right. So, this is appearing from this reaction. So, now I have these 2 equilibrium reactions; once we have these 2 reactions what is the advantages I am gaining now? For this equilibrium reaction I have a K P, for this equilibrium reaction I have another K P, right. So, and those K P s can be easily obtained.

(Refer Slide Time: 42:26)



$$K_p = \frac{p_{CO}\, p_{O_2}^{1/2}}{p_{CO_2}} = \frac{\chi_{CO} P \left(\chi_{O_2} P\right)^{1/2}}{\chi_{CO_2} P}$$

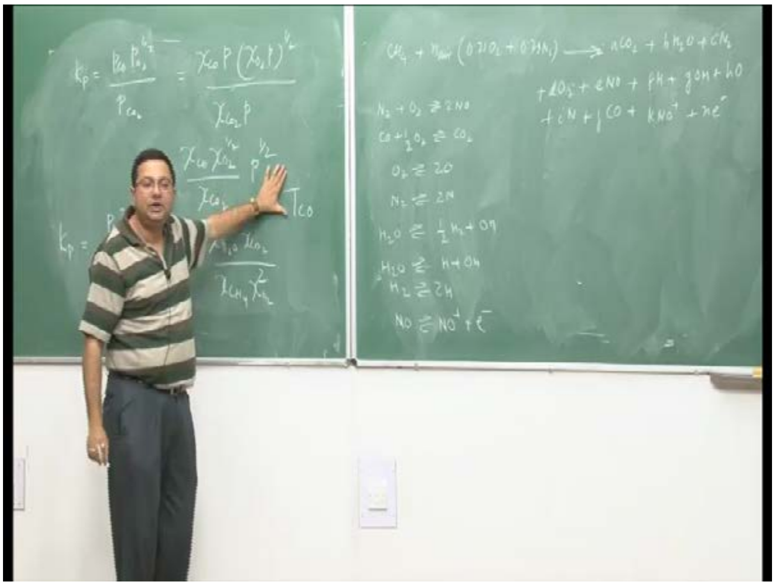
$$= \frac{\chi_{CO}\, \chi_{O_2}^{1/2}}{\chi_{CO_2}}\, p^{1/2}$$

$$K_p = \frac{p_{H_2O}^2\, p_{CO_2}}{p_{CH_4}\, p_{O_2}^2} = \frac{\chi_{H_2O}^2\, \chi_{CO_2}}{\chi_{CH_4}\, \chi_{O_2}^2}$$

for example, if I look at this reaction then, K P for that reaction is equal to p C naught p O 2 to the power half by p C O 2, right. This can be further written as mole fraction of C O times total pressure, mole fraction of O 2 times total pressure to the power half divided by mole fraction C O 2 times total pressure, right. So, this is equal to k C O k O 2 a kappa O 2 kappa C O 2 times pressure to the power half, right. So, for the given pressure if you know the value of K P, if you know the value of the total pressure we now get one relationship relating these 3, right. Similarly, we can get for the other reactions; K P is equal to p H 2 O square p C O 2 by p C H 4 p O 2 square. In this equation pressure term will not come out. So, finally this will be equal to this is square, this is square ok.

So, now I get these 2 equations sorry, anything is missing here this will be half there will be half here. So, I have these 2 equations for K P and K P as I said is available from standard table we can find out K P. So, once K P s are known or we can estimate K P from the definition that as Clausius Clrparon equation or from delta G you can estimate K P for this equilibrium reaction. Once K P s are known now, I have 1 and 2; these 2 equations relating these 5 mole fraction and 3 we have already got before from atom balance. So, now I have 5 equations 5 unknowns which can be then now, solve for the final composition. So, that is how now I will get final composition ok.

(Refer Slide Time: 45:08)



So, now let us look at more complex reaction I am not going to derive it, but I will show what are the reactions, equilibrium reactions that will be there. So, we will look at a very complex reaction; let us say we are looking at combustion of methane in air at very high temperature, this is air at very high temperature. So, that is as temperature is so high that we have dissociation also. Then, for that case the composition is going to be like this. As you can see there are considering lots of species including the formation of knocks. We are considering and then, we considering dissociation of knocks, we are considering these equations. So, this is my total number of species at the product species.

Now, let us say what are the degrees of reaction freedom here? I have carbon, hydrogen, nitrogen, oxygen. So, I have 4 atoms, and how many unknowns do I have one 2 3 4 5 6 7 8 9 10 11 12. So, we have 4 atomic species and 12 unknowns. So, my degree of reaction freedom is 8. So, I need to have 8 equilibrium reactions like we have done like here to close the problem. And those 8 reactions are going to be like this that essentially is obtained following the process I have just discussed. So, this 8 equations are 1 2 3 4 5 6 7 and 8. So, as you can see I have these 8 equilibrium equations and these 8 equilibrium equations now I can get 8 K P values. And now I will have the remaining 8 equations I can get from that K P values, I can complete the problem and solve for the entire composition. So, this is typically what is done in solving the complex chemical equilibrium problems.

So, this brings us to our discussion on the chemistry part. So, let me just summarize; what we have learned and what can we get from here. We have looked at chemical equilibrium, we have defined various properties like K P delta G naught etcetera, etcetera. And then we have shown that if only we know what are that species going to be in product side, we can form certain equilibrium reactions, once we formed those equilibrium reactions for those equilibrium reactions K P values can be obtained from the tables. Then, we have the additional equations to close the problem, particularly with complex reactions where the degree of reaction freedom is more than 1.

So, now 1 more point I like to point out here that here that this K P values as we have said it is a function of temperature, right. So, far in this case we are considering that we know the temperature. Now, if I combine this discussion with the discussion of adiabatic flame temperature, what did I said at that time that first we chose the value of adiabatic flame temperature. So, let us say we chose a value of adiabatic flame temperature then, we formulate this we get the K P value for that temperature we solve for the final composition like we have done also for the problem that we solved today. So, we solve for that we get the final composition.

Once we have a final composition we do the energy balance that is how much heat is going to heat up, like the problem we solved, right. Then, we see that from the energy balance this much energy is produced by the chemical reaction and finally, going to the final temperature this much is required. Do we have the match? if we do not we change the initial guess of the final temperature, and repeat this process. So, essentially the problem that have worked out, we repeat that again and again for different temperatures till we get the final composition as well as the final all the equilibrium reactions will you merge now, right. So, everything we will get, we get the final composition, we get the final temperature, what will that give me?

Once we have this we get the chamber temperature T C naught, and remember that pressure is also included here. So, pressure is something that needs to provide. So, pressure is one of the parameter that will be appear we will get T C naught and once we have the mixture; we can get the molecular weight first of all of the mixture, because we know the entire composition we can get the molecular weight of the mixture. Once we have the molecular weight, we can get the value of r for the mixture right. Similarly, we can get C P for the mixture because that is mass averaged; we can C V for the mixture because that is also a mass average. Once we have these 2, we can get gamma for the mixture which is C P by C V.

So, now we have gamma, we have T C naught pressure is already given. So, now we have all the things required to estimate thrust and start designing the nozzle also, right. So, therefore this is how this is what come from the combustor. Combustor design after the combustion, when specified the fuel and oxidizer, we know how much is coming at what pressure, and at what temperature we get the final temperature considering the adiabatic mixture as well as adiabatic combustion as well as the final composition. Then, we now have all the necessary ingredients to carry forward this analysis. So, that is what I wanted to discuss in the combustion part.

One point I made here is that we need to know the fuel composition. So, that is what I am going to start and discuss in the next couple of lectures. We will first talk dedicate one lecture to solid propellants, and then to liquid propellants. We talk about the fuels, we talk about how the fire propellants rockets work then, we talk about liquid propellants. What are the liquid propellants rockets, what are the components are and how they work. And that complete our discussion on chemical rockets. After that we will dedicate couples of lectures on electric propulsion. So, that will complete the course. So, I will stop here today and next class I will discuss solid propellants rockets.

Thank you.