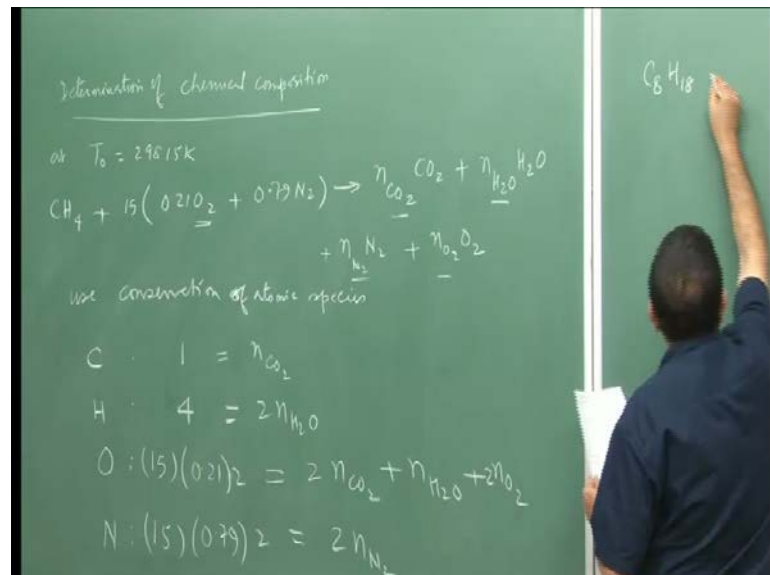


**Jet and Rocket Propulsion**  
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**Lecture - 35**

Good afternoon. So, for the last few lectures we have been discussing the chemistry part of rocket propulsion that is the combustion. We have talked about how to estimate the adiabatic flame temperature. We have defined the heat of reaction, heat of formation, etcetera. When we discuss the adiabatic flame temperature, we stated that the final composition of the product is very important in order to estimate the final temperature. At that time we have said that for the time being, let us assume that the composition is known and we estimated the final temperature based on that. However we have pointed out that when we have to do the actual calculations then that will also be unknown. So, we have to follow an iterative technique in order to converge both the concentration as well as the final temperature. So, today what we are going to discuss is the how do we estimate the chemical composition of after the reaction, the chemical composition of the products.

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So, the topic is Determination of chemical composition that is our topic of discussion today. Let us consider that we have a chemical reaction at say  $T$  naught, which is 298.15 degree Kelvin. Let us consider a very simple reaction hydrocarbons, say methane

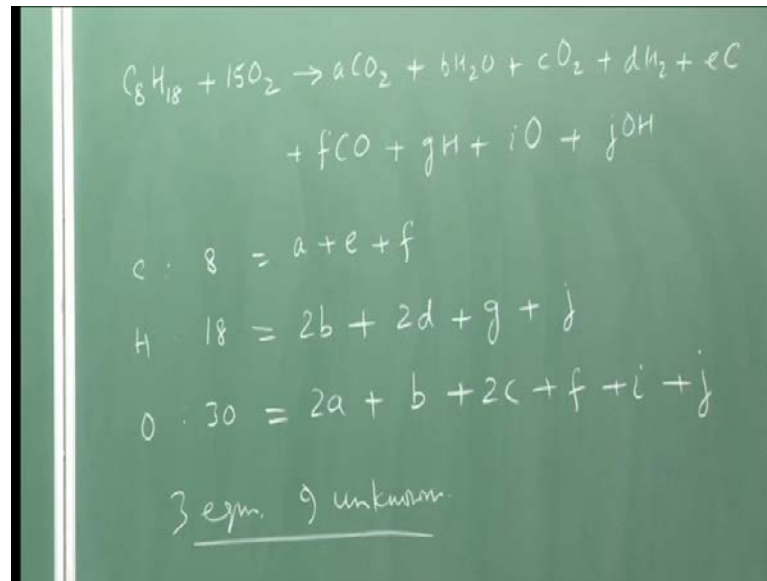
burning in air. So, this is the reaction we say that we have after the reaction we have  $n$   $\text{CO}_2$  moles of  $\text{CO}_2$  being produced  $n$   $\text{H}_2\text{O}$  moles of water vapor is produced. Apart from that we have nitrogen which remains unburned and some oxygen may also remain unburned. Because this is if I look at the stoichiometric reaction, then according to that this reaction is swirling. So, therefore some oxidizer will remain unburned.

So, let us say that this is our chemical reaction. Here in the product side we have carbon dioxide, water vapor, nitrogen and oxygen. But we do not know the composition we do not know how many moles of each of this species are present in the product. We want to estimate that. So, first let us use the conservation of atomic species like we have discussed earlier. So, what are the atomic species that we have, we have carbon, we have hydrogen, oxygen and nitrogen. So, first let us look at the carbon. In the reacting side we have one mole of or one atom of carbon. So, therefore, this is equal to  $n$   $\text{CO}_2$  because in the product side also we should have exactly same number of atoms of carbon. Similarly, if I look at hydrogen we have 4 hydrogen here.

So, that will be equal to every molecule of water vapor contents, 2 atoms of hydrogen's. So, 2 times  $n$   $\text{H}_2\text{O}$  right that is going to be a number of atoms of hydrogen. Similarly, for oxygen in the reacting side we have 15 times 0.21 into 2, because every molecule of oxygen contains 2 atoms of oxygen. So, this is equal to our now, in the product side oxygen appears as a in the carbon dioxide. So, for every carbon dioxide molecule we have 2 atoms of oxygen. So, we write 2 and  $\text{CO}_2$  similarly, every water vapor molecule has 1 atom of oxygen plus we have the unburned oxygen available.

Similarly, for nitrogen we have in the product reacting side we have 15 times 0.79 times 2 and in the product side we have 2  $\text{N}_2$ . So, now if I look at this I have four equations 1, 2, 3, 4 and four and I have 4 unknowns  $n$   $\text{CO}_2$ ,  $n$   $\text{H}_2\text{O}$ ,  $n$   $\text{N}_2$  and  $n$   $\text{O}_2$ . So, 4 equations and 4 unknowns can be easily solved. So, this is quite straight forward we can solve for all the unknowns and I can get the composition, final composition. So, this is something which the number of atoms and or the primary atoms and the number of unknowns are same, but that may not be the case always.

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Let us look at another reaction. So, here we take a heavier hydrocarbon octane, burning in oxygen, for this I have all kind of products present and once again it depends on the final temperature also how much of each product will be present and what are the products present that we will discuss little later. So, let say here I have all this products present. Now, what are the primary atoms we have atomic species, we have carbon, hydrogen oxygen. So, essentially we have 3 atomic species, carbon we have 8, hydrogen we have 18, oxygen we have 30 atoms. Now in the product side carbon is appearing here and here and here a plus e plus f. Hydrogen is appearing here, in water vapor plus in the molecular hydrogen plus as the atomic hydrogen plus as part of O H.

Similarly, oxygen is appearing in carbon dioxide. So, 2 a is appearing in water vapor, it is appearing in molecular oxygen, it is appearing in C O then as atomic oxygen and in O H. So, from the number of atomic species we can form these 3 equations; however, total number of unknowns is 1, 2, 3, 4, 5, 6, 7, 8, 9. So, we have 3 equations and 9 unknowns. So, we cannot solve this and get all the unknowns. We need to know some additional equations to complete this problem. So, therefore we need the 6 additional equations which can be obtained from the chemical equilibrium theory. So, that is the justification of what we are going to discuss today. So, today we are going to discuss chemical equilibrium theory which gives us the additional equations.

So, first let us go back and start discussing chemical equilibrium theory. And I like to point out the one theory before we go there, that this reaction is not a fundamental reaction, because typically the fundamental reactions will be collision of 2 molecules giving us the most two more three products. But here in the product side we see 9. So, this cannot be fundamental single step reaction. Actually this involves a reaction sequence containing various reaction steps. So, the theory we are going to discuss now will also give us some indication of what will be the reaction steps ok. So, with that let us now look at the chemical equilibrium theory chemical equilibrium theory.

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Chemical Equilibrium Theory

Gibbs free energy  $G = H - TS = U + PV - TS$

$$dU = dH - d(PV) = dH - PdV - VdP$$

$$TdS = dH - VdP = TdS - PdV$$

$$dG = dU + PdV + VdP - TdS - SdT$$

$$dG = VdP - SdT$$

If we consider a reacting system without any velocity, let us say stationary system. So, we can neglect the potential energy and kinetic energy term. One of the energy terms, which are very important for reacting system is called Gibbs free energy. So, we define is a defined property gibbs free energy this defined as G equal to enthalpy H minus T S. This is a in thermodynamic you must of see that it gives us free energy defined like this. Now, here H is the enthalpy. By definition enthalpy is internal energy plus P V. So, this can be written as U plus P V minus T S. Where, U is the internal energy, P is pressure, V is the volume of system, T is temperature, S is entropy. So, this is gives free energy. Now, the change in internal energy d U can be written as then because my U is equal to H minus P V right. So, therefore d U is equal to d H minus d (P V) which is equal to d H minus P d V minus V d P. And in thermodynamics we have seen that Td S is equal to d

$H - P dV$  this called Gibbs equation, and you have seen this before in thermodynamics.

So, now if I put this back into this equation  $dH - P dV$  becomes equal to  $T dS$  minus sorry,  $dH - V dP - P dV$ . So,  $T dS$  equal to  $dH - V dP$  therefore, this is equal to  $dU$  equal to  $T dS - P dV$ . Now, let me take this and put it back into this equation for that; first let us differentiate this expression for Gibbs free energy  $G$ . So, this will be equal to  $G$  equal to  $U + P V - T S$  if I expand this. This will be  $dU + P dV + V dP - T dS - S dT$ . Now,  $T dS - P dV - V dP - S dT$  is my  $dU$ . So, this will cancel off. So, I get  $dG$  equal to nothing but  $V dP - S dT$ , this is a simple expression representing the change in Gibbs free energy for a particular process.

Now, how do we define our chemical reaction? We define the chemical reaction occurring in isothermal condition, right. The reaction was occurring in isothermal temperature was not changing. What we say is that after the reaction, whatever heat of reaction is released that goes on to increase the temperature, but the reaction is isothermal.

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for isothermal m.  $dT = 0$

$$dG = V dP$$

for perfect gas -  $PV = nRT$

$$\Rightarrow V = \frac{nRT}{P}$$
$$dG = nRT \frac{dP}{P} = nRT d(\ln P)$$
$$P^0 \rightarrow P$$
$$\Delta G = G(P) - G(P^0) = nRT [\ln P - \ln P^0]$$

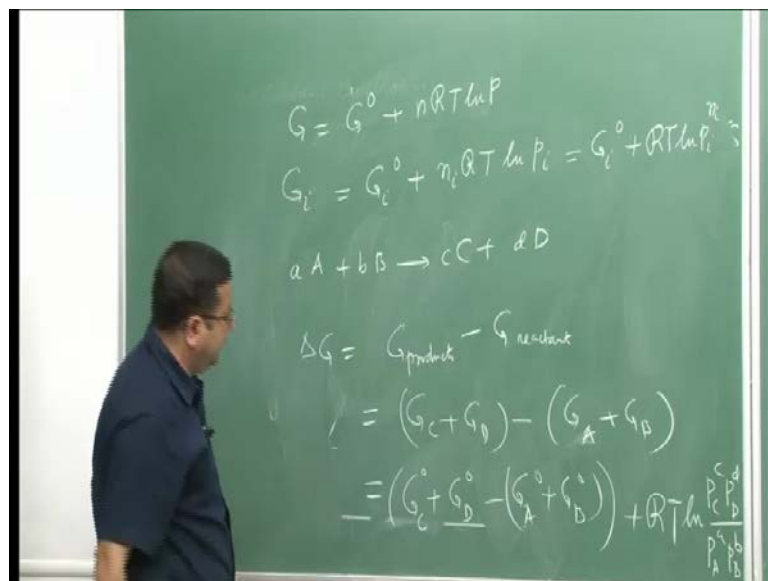
So, for isothermal reaction temperature change is 0, right. Therefore, this term here is 0 therefore now, my  $dG$  is equal to  $V dP$  or  $V$  is the volume;  $P$  is the pressure, ok. Now, since we have been saying that our working field is the perfect gas. So, for a perfect gas

we used perfect gas equation of state this says that  $P V$  equal to  $n$ ,  $n$  is the number of moles, universal gas constant  $R$  times  $T$ . So, therefore the volume can be represented as a function of the temperature and pressure like this  $V$  equal to  $n R T$  by  $P$ . Now, let us take this and put it back into this expression for Gibbs free energy change. So, my  $d G$  will be equal to then  $n R T d P$  by  $P$ . Now this is nothing but equal to  $n R T d \ln P$ , log natural of  $p$ , right.

Now, let us say that if you integrate this, from some reference pressure  $P$  naught to some actual pressure  $P$ . So, now we are bringing in the effect of pressure also. So, if we integrated from some reference pressure  $P$  naught to some actual pressure  $P$ . Then, we get  $\Delta G$  is the change in Gibbs free energy in this process, which is equal to  $G$  at this pressure minus  $G$  at  $P$  naught standard pressure. This is equal to the  $n R T \ln P$  minus  $\ln P$  naught. Now, this  $G P$  naught is my standard pressure. So, instead of writing it every time as  $P$  what I will say is that I will write for in any other pressure  $G$  is  $G P$  represented as  $G$  only. Only for standard state I represented as  $G$  naught.

So, then I can write it as  $G$  minus  $G$  naught, where  $G$  naught is the Gibbs free energy at the standard pressure. Previously, we had defined everything for standard temperature. Now, it is standard pressure equal to  $n R T \ln P$  by  $P$  naught. Now, what is our standard pressure at STP is 1 atmosphere. So, if I consider this as one then this become nothing but equal to  $\ln P$ , right.

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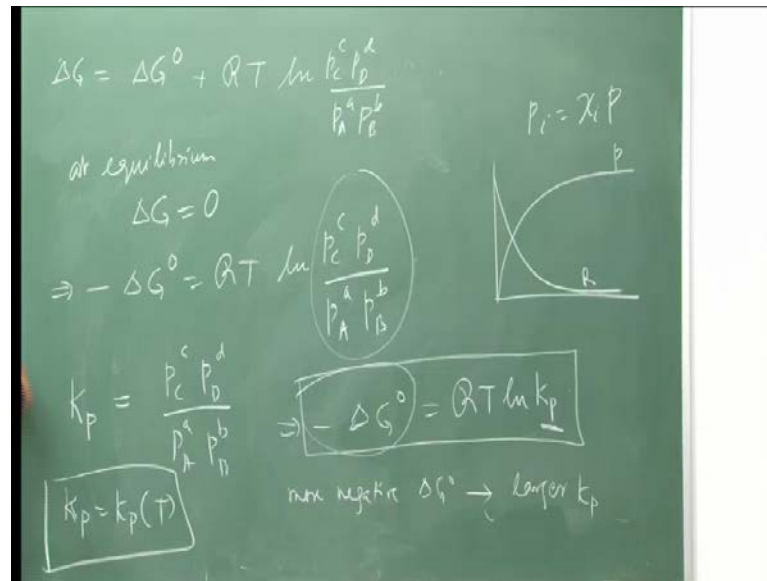


So, therefore, we get  $G$  is equal to; so Gibbs free energy at any pressure  $G$  if  $P$  equal to  $G^\circ$  naught that is Gibbs free energy at the standard pressure plus  $n R T \ln P$ , right. So, this is our expression for Gibbs free energy for any species. Now, if I go to the system chemically reacting system where I have  $i$  species; for every species  $i$ , I can define its Gibbs free energy. So, that is equal to then I write  $G_i$  equal to  $G_i^\circ$  plus  $n_i R T \ln P_i$ . Where,  $P_i$  is the partial pressure of that particular species,  $n_i$  I can take it inside. So, I can write this as plus  $R T \ln P_i$  to the power  $n_i$ . So, this is first species  $i$  in the system this is my expression for Gibbs free energy at any given pressure  $P$ .

Now, let us consider a chemical reaction; let say this is my chemical reaction  $a$  plus  $b$  giving  $c$  plus  $d$ . Some  $n_a$  mole of  $A$  reacting with  $b$  moles of  $B$  giving  $c$  moles of  $C$  and  $d$  moles of  $D$ . So, for this  $\Delta G$  which is the change in Gibbs free energy is nothing but Gibbs free energy of the products minus Gibbs free energy of the reactants, right. So, now this is equal to  $G_C$  plus  $G_D$  minus  $G_A$  plus  $G_B$ , where see  $G_C$  is the Gibbs free energy of the species  $C$ . Similarly, this is for  $D$ , this is for  $A$ , this is for  $B$ .

Now, what I do is; I use this expression here. So, what I will get is  $G_C^\circ$  plus  $G_D^\circ$  naught minus  $G_A^\circ$  plus  $G_B^\circ$  plus  $R T \ln$  of  $P_C$  to the power  $C$ ,  $P_D$  to the power  $d$  by  $P_A$  to the power  $a$ ,  $P_B$  to the power  $b$ , right. I just combined this 2 I get this. Now, what is this is the Gibbs free energy of  $C$  at the standard pressure plus that of  $D$  minus. So, this is the total Gibbs free energy of the products at the standard state minus Gibbs free energy of the reactants at the standard pressure.

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So, therefore this difference is nothing, but total change in the Gibbs free energy at the standard pressure, right. So, I can write this as then that total change in Gibbs free energy is equal to change in Gibbs free energy at the standard pressure plus universal gas constant times T, then ln of p C to the power c, p D to the power d by p A to the power a, p B to the power b, ok. Now, at the beginning what we said is that; we are interested in chemical equilibrium, right. I am talking about equilibrium thermodynamics. So, how much will be the change in Gibbs free energy at equilibrium? It will not change. So, at equilibrium total change in Gibbs free energy is 0.

So, delta G is 0, which essentially means that minus delta G naught is equal to R T ln p C to the power c, p D to the power d by p A to the power a, p B to the power b ok. Now, by definition this ratio, what is this ratio? This is defined as K P, this is equilibrium constant K P. So, this is defined as p C to the power c, p D to the power d by p A to the power a, p B to the power b. Here all these things P A P B P C P D are partial pressure of different species. So, then this is a defined property therefore, we get minus delta G naught is equal to R T ln K P ok.

So, now what does this relationship give us? This relationship gives us the relation between the standard free energy change and the equilibrium constant at any arbitrary pressure and temperature, right. So, as you can see here temperature is present here, and K P will include pressure, because the partial pressure includes the, partial pressure is



mole fraction of species  $i$  times the total pressure, right. So, that is how partial pressure is defined. So, therefore this total pressure information of the system is already included in the definition of  $K_P$  and temperature is there. So, now we have both pressure and temperature; that is the deviation from what we have been talked about adiabatic flame temperature. Where we said it was not standard temperature. We were completely silent about pressure, but now we are bringing in pressure term as well.

So, here now that is how pressure comes in into the reaction. So, coming back to this then let us look at it little more closely.  $K_P$  here first of all is the equilibrium constant is known to be a function of temperature. So,  $K_P$  is a function of temperature that is unknown thermodynamic property. So, now if we know the Gibbs free energy at standard condition minus  $\Delta G^\circ$  then we can estimate  $K_P$  for some other temperature or pressure and based on that then we can estimate the mole fraction also as you can see here. Otherwise if  $K_P$  is known, we can get this. So, both of them can be estimated.

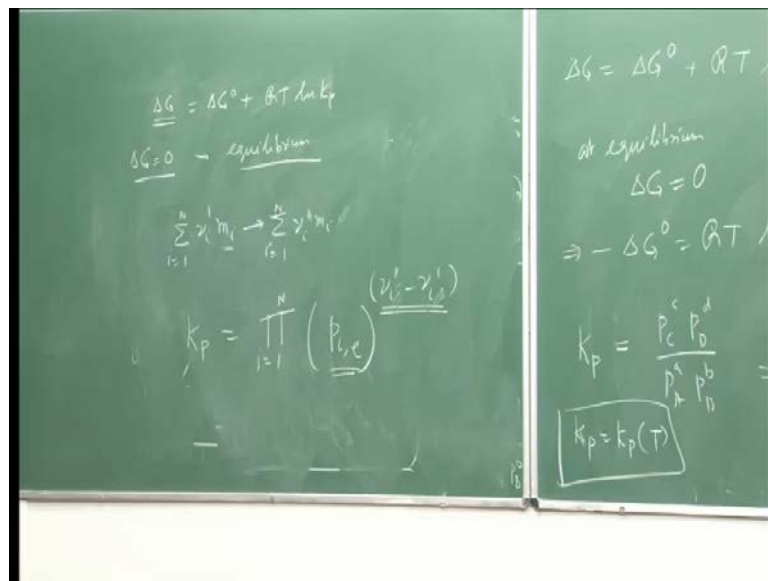
Now, I like to point out few properties of this  $K_P$  and  $\Delta G^\circ$ . If I look at  $\Delta G^\circ$ , what is this? This is the standard Gibbs free energy, right. So, it is at standard pressure at standard temperature as well, temperature we have not talked about, but the standard temperature as well. So, this can be actually related to the standard free energy of formation ok. Now, in general if I look at this term  $\Delta G^\circ$ ; more negative the values of  $\Delta G^\circ$  is right. So,  $\Delta G^\circ$  if  $\Delta G^\circ$  is negative then this becomes positive so  $K_P$  is positive. More negative the value of  $\Delta G^\circ$  is  $K_P$  is more positive. So, we have larger value of  $K_P$ . So, I can say that more negative  $\Delta G^\circ$  we get larger  $K_P$ .

Now, what does the larger  $K_P$  represent?  $K_P$  is higher,  $K_P$  is more. What does that mean? Either this is large or this is small or both. So, therefore what it says essentially is that  $P_C$  by  $P_D$  this product is more than this product which essentially means that the partial pressure typically for the products is more than that of the reactants. So, essentially what it means is that we have more products in the final equilibrium mixture than the reactants, which essentially means that this is the spontaneous direction of reaction, right. Because if you recall in chemical equilibrium thermodynamics we have said that all the reactions will have the opposing reaction as well, right.

In equilibrium actually the way we have defined in the previous courses; at equilibrium what we have is that we have a forward reaction, and we have a backward reaction. There is certain rate of this forward reaction given by a say  $k_f$  or not say  $k_f$   $\omega_f$  and there is certain rate of this backward reaction given  $\omega_b$ . At equilibrium; we say that the rate of forward reaction is equal to the rate of backward reaction. That is what chemical equilibrium is. But now what we are saying is that if  $K_P$  is positive and more positive then the extent at which we get this equilibrium it will have more products than the reactors.

So, the spontaneous direction is this, not this. So, this is favored, this is not favored if you have higher value of  $K_P$ . So, that is what is essentially the definition of chemical equilibrium is. And now we show that if we have higher value of  $K_P$  then we get more of the products and rest of the reactants will remain at equilibrium. And therefore if I plot the variation let us say of concentration of  $c$  initially it will be 0, it goes like this where as a concentration of  $a$  it goes like this. So, this is the equilibrium. So, at equilibrium we see that we have more of the products and rest of the reactants, just because that will be possible if  $\Delta G$  is negative and more negative. So, this is something that comes out from this discussion. Now, one more thing I like to point out. Here, this discussion we have is primarily based on  $\Delta G^\circ$  which is standard Gibbs free energy.

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Now, in general we have this term  $\Delta G$ , which is equal to  $\Delta G^\circ + RT \ln K_p$ , that is why change in Gibbs free energy for a particular system at any arbitrary pressure and temperature. Now, when this term is zero, when  $\Delta G$  is zero which means that the Gibbs free energy for the product total Gibbs free energy for the product is equal to the total Gibbs free energy for the reactants. In that case, the reaction will now will not have any tendency to proceed in any direction, right. So, reaction actually takes an equilibrium position and that is why we say that at equilibrium this is because of the fact that this Gibbs free energy is the major of the tendency of a reaction to proceed into particular direction. So, therefore when this is zero then it has reached equilibrium; if it will not have spontaneous tendency to proceed in any preferred direction, ok.

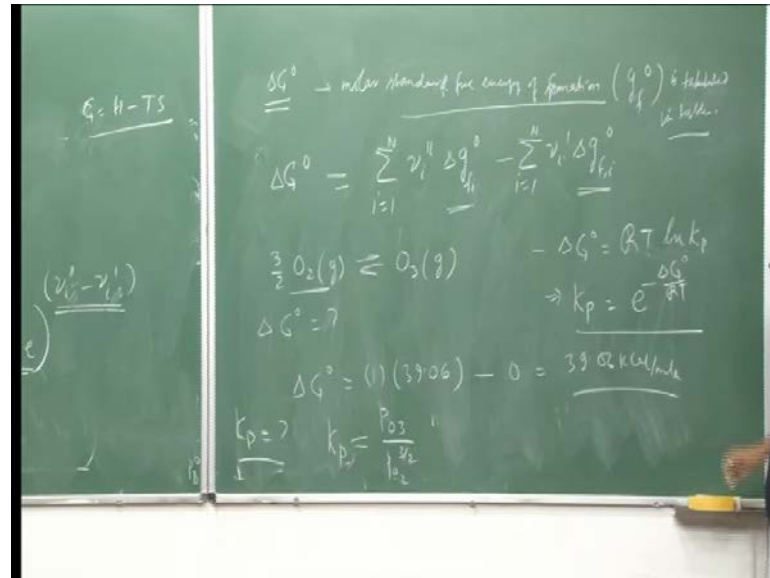
Now, let us consider the general chemical reaction we have been talking about so far in this course; this is how we have been represented as general chemical reaction, right. Where we have  $N$  species and represented by  $m_i$  this is reactants says the stoichiometric coefficient for the reactants, stoichiometric coefficient for the products. So, this is our general chemical reaction that we have been describing so far. So, for this general chemical reaction now, how do we represent  $K_p$ ? So,  $K_p$  will be equal to we have represented it for a particular reaction  $a A + b B \rightleftharpoons c C + d D$ . Now, if I look at this reaction then this will be equal to the product  $p_i$  equal to 1 to  $n$ .

Partial pressure at equilibrium of species  $i$  given by  $p_i^e$  and then the differencing stoichiometric coefficients, right. So, the differencing stoichiometric coefficients given like this. This is the partial pressure at equilibrium of species  $i$  the product of that gives us the value of  $K_p$ . Once again you will see that when we are in the product side  $\mu_i^{\text{double prime}}$  is greater than  $\mu_i^{\text{prime}}$  in the product. So, therefore that comes into the numerator, where as in the reactant  $\mu_i^{\text{double prime}}$  is less than  $\mu_i^{\text{prime}}$ . So, that is negative therefore that comes in the denominator. So, it is exactly same as the definition that we have given here. So, this is how we defined  $K_p$  for the generic chemical reaction we have been discussing so far.

So, now this is our definition of  $K_p$ , by the way we have taken one approach to prove these things using some other thermodynamic approach also we can prove that, so that I am not going to the details of that various things. We can use even the entropy valence

and all. Now, let me point out here one more thing. How do we get this value, minus delta G n G naught for chemical reaction? We want to estimate the change in standard Gibbs free energy for a given chemical reaction delta G naught, how do we get this?

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Actually the molar standard free energy of formation which is designated by  $G_f^\circ$  is tabulated typically in tables, in thermo chemical tables. Now, first of all; what is our standard free energy of formation? This is similar to our standard heat of formation. So, when we say standard it means that the formation reaction is from its elements in their standard state at standard temperature and pressure. So, standard free energy of formation is the free energy change for a given chemical reaction, when a particular molecule is formed from its elements at their standard state at standard temperature and pressure.

Now, we have already incorporated the standard pressure here  $P^\circ$  is already there and  $T^\circ$  is the standard temperature. We cannot we can assume that the reaction occurs at the standard temperature that is how we have been working out this details, right. So, if we consider the reaction isothermal reaction is as standard temperature then this definition applicable to this case as well. So, therefore we can get now for a given reaction  $\Delta G^\circ$ . Now, this reaction actually involves  $i$  species, right. So, every species has its own standard free energy of formation. So, we can estimate the total

standard free energy of formation for a given chemical reaction by looking at the standard free energy formation for this reaction.

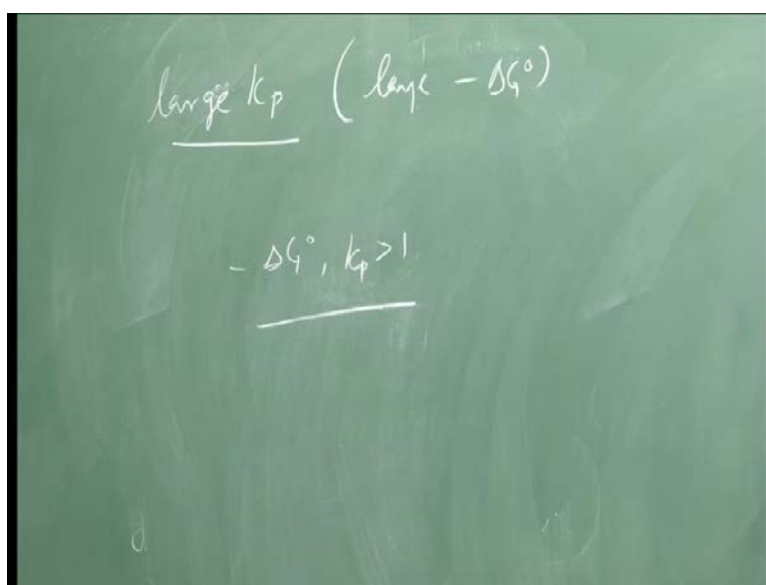
So, then that will be equal to  $\sum_{i=1}^N$  the total free energy standard free energy of formation for the reactants sorry, products minus the total free energy of formation standard free energy of formation for the reactants, right. So, once again I have to rewrite to write the point that these values are typically tabulated. And we can stack a step forward and say that  $G$  is equal to  $H$  minus  $T S$  right, this is how it is defined. This is the standard energy of formation can be tabulated, this is the standard temperature, this is the entropy of formation. So, entropy change from the absolute zero temperature is also tabulated. So, we can use this also to estimate that or directly we can look at the tables and get this. So, this is the way we get the standard free energy of formation for any sorry, the standard free energy change in any chemical reaction.

Let us take an example to explain this little more. Let us consider a reaction where, oxygen which is of course, in gaseous state converts to ozone in gaseous state, and this is the equilibrium reaction. That is why I have given it this sign equilibrium sign. So, first this reaction we have to find  $\Delta G$  naught is what? So, we can get  $\Delta G$  naught by using this equation our product is ozone. We can look up at the tables and get the molar free energy of formation of ozone this is 39.06 kilocalorie per mole, and that of the oxygen. Now what will be the free energy of formation for oxygen? 0, right. So, this is 0. So, this comes out to be equal to 39.06 kilocalorie per mole, ok. So, that is the value of  $\Delta G$  which we can get by looking at thermo chemical tables.

We can stack a step further and estimate the  $K P$  for this also. So, we can say what is the  $K P$  for this reaction? For that let us first define  $K P$ .  $K P$  is equal to the partial pressure of oxygen divided by partial pressure of sorry, partial pressure of ozone divided by partial pressure of oxygen. And from that definition of  $K P$  from here since; we are talking at equilibrium, so this term is 0, right. So, we can get minus  $\Delta G$  naught equal to  $R T \ln K P$ . Therefore,  $K P$  is equal to  $e$  to the power minus  $\Delta G$  naught by  $R T$ , right. So, from here  $\Delta G$  naught I have estimated,  $R$  is the universal gas constant, which is known for this unit is 1.982,  $T$  is the temperature in kelvin. So, the temperature we are talking about is standard temperature. So, this is 298 kelvin. So, I put all these values.

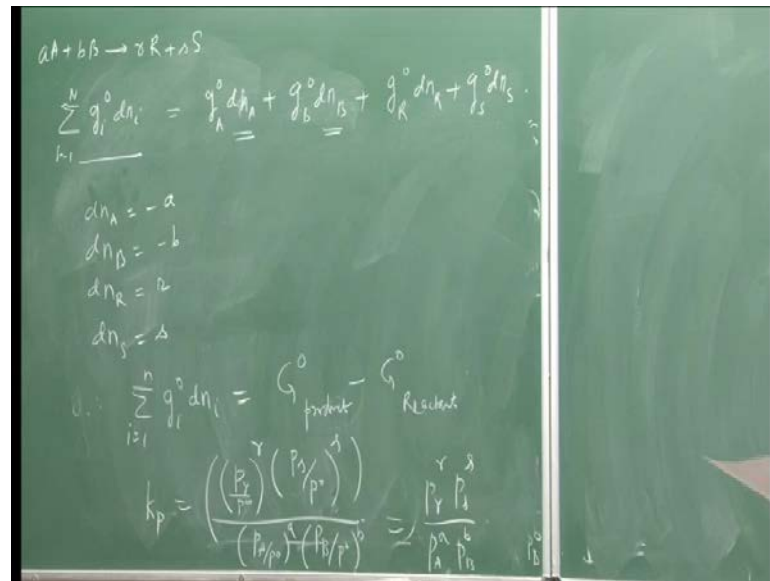
So, I will write it here  $K_p$  is equal to  $e$  to the power minus  $\Delta G^\circ$  which is equal to 39.06 kilocalorie per mole divided by 39.06 kilocalorie  $10^3$  divided by 1.982 sorry, 987 that is the value of universal gas constant in FPS unit times 298, right. So, this gives me the value of  $K_p$  to be equal to 2.25  $10^3$  that is the value of  $K_p$ . So, if the value of  $K_p$  were given; we can estimate what is  $\Delta G^\circ$  also, right. So, this is the example we wanted to talk about. Once again let us go back to our discussion on large values of  $\Delta G^\circ$ . As we have said that if we have large negative values of  $\Delta G^\circ$  then  $K_p$  is large.

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Now, what does large  $K_p$  means or large  $K_p$  represents, large  $K_p$  which is when large negative  $\Delta G^\circ$ . In that case for this conditions when the value of  $K_p$  is large once the reaction starts the conversion of the reactants to products in their standard state of course will be quite complete at equilibrium. So, essentially we have mostly products in the final state and very little reactants. In general for any values of  $\Delta G^\circ$   $K_p$  is typically greater than 1. So, for this cases when  $\Delta G^\circ$  is like this very large values  $K_p$  is typically greater than 1, ok. Now, let us now continue with this discussion and look at so far we have defined  $K_p$ , but what we wanted to do first to get the additional equation that we are looking for. Someone let us continue with this discussion, and try and see that how we get those additional equations, because that was our initial objective.

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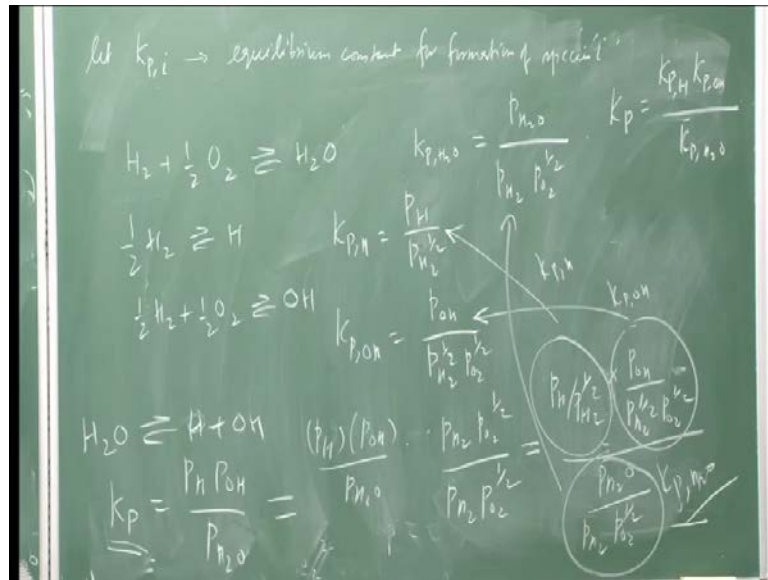
So, for that once again let us look at general chemical reaction; first of all let us say that what we have is a chemical reaction, after if I look at the product final product. Let us say that the final product is given as; this is the total change in the Gibbs free energy at standard state right where, this at any species  $i$ . So, we are looking at the general equation. So, this is the total change in Gibbs free energy. Now, this is equal to the essentially change in the gibbs free energy of the every species, right. So, this is nothing but equal to let us consider first of all the reaction that we are considering let us say that we are considering this reaction. So, this will be  $R$  minus  $g$   $S$  naught  $d n$   $S$ .

So, this is the chemical reaction we are considering. So, the total change in Gibbs free energy at standard Gibbs free energy is nothing but this, ok. Now, in this case for the particular case that we are looking at the change in number of moles of  $A$  and  $B$  are essentially negative, right. So,  $d n$   $A$  is equal to minus  $a$ ,  $d n$   $B$  is equal to minus  $b$ , but for  $R$  and  $S$  is as positive because these are the products. So, therefore in general if I generalized it, total change in the Gibbs free energy is equal to the change in Gibbs free energy for the products minus the change in Gibbs free energy for the reactants right, this is in general, ok.

Now, we have defined all of this; and now for every reaction for every reaction at equilibrium we can define  $K_p$  as  $p^r$  by  $p$  naught to the power  $r$  by  $p^s$  by  $p$  naught,  $p^a$  by  $p$  naught  $a$   $p^b$  by  $p$  naught  $b$ . we defined  $K_p$  for this reaction like this. Here,  $p$

naught is the pressure; we are considering it as standard state. So, that is for it is atmospheric pressure. So, therefore this reduces to the same expression that we had earlier seen. Now, this is applicable to any reaction at equilibrium. So, let us look at some common reactions and see what happens.

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In general, let  $K_{p,i}$  is the equilibrium constant for formation of species  $i$  that is how we are defining. So, now if we have few reactions occurring together; let us say one of them is this, other is this and other is this. These are all equilibrium reactions occurring together. Then, we get  $K_p$  from this reaction;  $K_p$  for this is the formation reaction of  $H_2O$  right. So,  $K_p$  for  $H_2O$  is equal to nothing but  $P_{H_2O}$  divided by  $P_{H_2} P_{O_2}$  to the power half, right. Similarly, this is the formation reaction for  $H$ . So, I can write  $K_{p,H}$  is equal to  $P_H$  upon  $P_{H_2}$  to the power half, and this is the formation reaction for  $OH$ . So, I can write this as ok.

Now, let us consider some other reactions for which I do not know the  $K_p$ ; let us consider another reaction, let say consider this reaction  $H_2O$  is equal to  $H$  plus  $OH$ . Now, what is the value of  $K_p$  for this? For this reaction it is  $P_H P_{OH}$  by  $P_{H_2O}$ . Let us write this as  $P_H P_{OH}$  upon  $P_{H_2O}$  times  $P_{H_2} P_{O_2}$  to the power half upon  $P_{H_2} P_{O_2}$  to the power half, I can write it like this right. This can be then for the simplified as equal to  $P_H$  upon  $P_{H_2}$  to the power half into  $P_{OH}$  upon  $P_{H_2}$  to the power half  $P_{O_2}$  to the power half divided by  $P_{H_2O}$  upon  $P_{H_2} P_{O_2}$  to the power half. Now, this term



here is this. So, this is my  $K_p$ , this term here is this  $K_p$   $H_2O$  this term here is this  $K_p$   $H_2O$ .

So, now this is no longer a formation reaction right, this is what formation reaction. What we have seen now is that from the formation reaction; we can get these values for different species. Now, when we go to a complex reaction like this a different reaction like this we can get the  $K_p$  as equal to for this example it is  $K_p$   $H_2O$  times  $K_p$   $O_2$  divided by  $K_p$   $H_2O$ , right. So, just in this expression for of  $K_p$  the partial pressure appearing here at just replaced by  $K_p$  right, and with. So, therefore for this reaction we can get the expression for  $K_p$ . So, that is an important tool which we can use to get some values.

So, I will stop here today. In the next class first what we will do is we have defined here  $K_p$  the equilibrium constant, there are some other definitions of equilibrium constant like for ad best and concentration etcetera, those are interrelated. So, first we will give some more definitions of equilibrium constant and then continue with this discussion to show how do we get finally, the product composition. And we will also solve some problems in the next class, to show how to estimate the product composition.