Chemical Engineering Thermodynamics

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Lecture - 40

Chemical Reaction Equilibria

Hello and welcome back, we were talking about Chemical Reaction Equilibria in the previous video. What we will do today is, continue our discussion and see how we can obtain the criteria for chemical equilibrium and then from there determine what would be the extent of a reaction or the reaction coordinate at equilibrium in case of a chemical reaction.

So, if you recall in the previous video we talked about reaction coordinate or epsilon which serves as a single measure of the extent of chemical reaction, irrespective of what species we are talking about epsilon is constant for a chemical reaction; as the reaction progresses, this reaction coordinate is going to be a single number that identifies how far the reaction has proceeded alright.

We are going to use this concept of reaction coordinate to determine the criteria for chemical reaction equilibrium. Now if you recall when we discussed about liquid-liquid equilibrium and instability, we said that in case of an irreversible process the total change in the Gibbs free energy or I should say the change in the total Gibbs free energy are G t or in time in terms of molar quantities n G.

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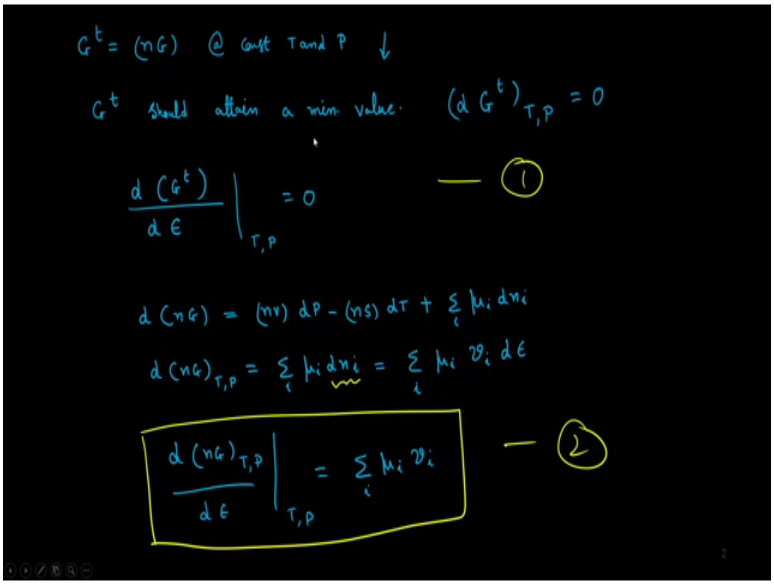

$G^t = (nG)$ @ const T and P ↓

G^t should attain a min. value. $(dG^t)_{T,P} = 0$

$$\left.\frac{d(G^t)}{d\epsilon}\right|_{T,P} = 0 \quad — ①$$

$$d(nG) = (nV)\,dP - (nS)\,dT + \sum_i \mu_i\, dn_i$$

$$d(nG)_{T,P} = \sum_i \mu_i\, dn_i = \sum_i \mu_i \nu_i\, d\epsilon$$

$$\boxed{\left.\frac{d(nG)_{T,P}}{d\epsilon}\right|_{T,P} = \sum_i \mu_i \nu_i} \quad — ②$$

The change in this quantity at constant temperature and pressure should be such that it decreases in a irreversible process. This is a requirement and in case of a process where which is moving towards equilibrium the criteria should be such that G t should attain a minima or should attain a minimum value in terms of derivatives. I can write it as the derivative of the total Gibbs free energy at constant temperature and pressure should equal 0 at the equilibrium right.

Now, this is true in general, what happens is in case of a chemical reaction when there is a mixture of species undergoing a chemical reaction this change in the total Gibbs free energy occurs, because of the progress in the reaction, remember that the temperature and pressure are constant. So, the only way the Gibbs free energy is going to change is, if the mole fraction of the constituent mixture changes or if the reaction progresses forward.

So, the other way of writing this particular criteria for a chemical reaction is that the derivative of the total Gibbs free energy with respect to the reaction coordinate, which like we said identifies the extent of our reaction at constant temperature and pressure should be equal to 0 and that determines the equilibrium for our chemical reaction.

Now, recall that the fundamental property relation for Gibbs free energy reads the derivative of the total Gibbs free energy G t or n G, n being the number of moles equals nv dP minus ns dT plus sigma over all the chemical species mu i dn i. This is the fundamental property relation for the Gibbs free energy. Now, at constant if we impose the criteria of constant temperature and pressure for this particular relation then at constant T and P the first two terms drop out and this will simply be equal to sigma of mu i dn i. In addition to this if there is a chemical reaction that is occurring then like we said dn i can be written in terms of the reaction coordinate and stoichiometric number; this will equal sigma over i mu i mu i times d epsilon or the reaction coordinate.

So, the stoichiometric number multiplied with the differential change in the reaction coordinate would give me the differential change in the number of moles of that particular species d and i right. So, this is going to be the change in the total Gibbs free energy or in other words if I were to write from this equation if I were to write the derivative of the total Gibbs free energy with respect to the reaction coordinate at constant temperature and pressure then that would simply be sigma mu i nu i.

So, for a chemical reaction this derivative we are interested in will equal sigma mu i the chemical potential times mu i the stoichiometric number that summation goes over all the chemical species that are present right. And, like we said from equation 1 and equation 2 at equilibrium it is obvious that then this summation we are talking about sigma mu i nu i needs to go to 0 at equilibrium right.

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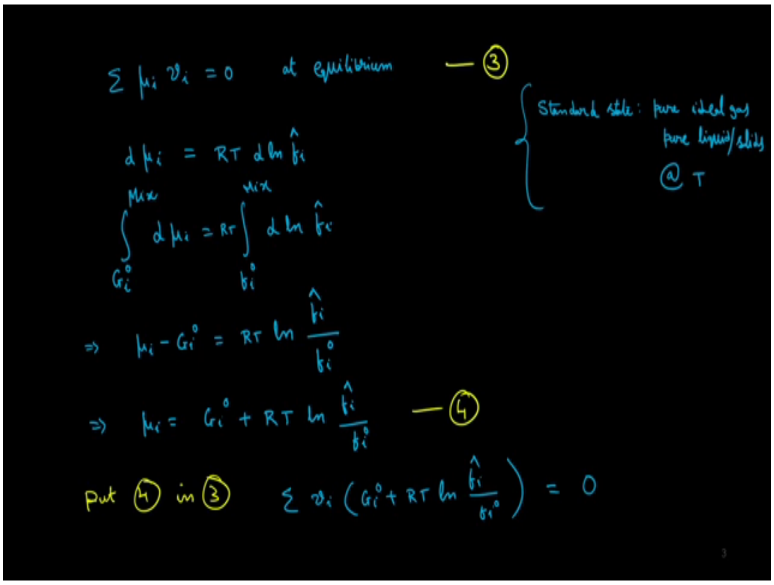

$\sum \mu_i \nu_i = 0$ at equilibrium — ③

Standard state: pure ideal gas
pure liquid/solids
@ T

$d\mu_i = RT\, d\ln \hat{f}_i$

$\int_{G_i^0}^{mix} d\mu_i = RT \int_{f_i^0}^{mix} d\ln \hat{f}_i$

$\Rightarrow \mu_i - G_i^0 = RT \ln \frac{\hat{f}_i}{f_i^0}$

$\Rightarrow \mu_i = G_i^0 + RT \ln \frac{\hat{f}_i}{f_i^0}$ — ④

put ④ in ③ $\sum \nu_i \left(G_i^0 + RT \ln \frac{\hat{f}_i}{f_i^0} \right) = 0$

From equation 1; let us go back to the previous slide from equation 1 the derivative of the total Gibbs free energy G t or n G should equal 0. And, from the second equation this derivative turns out to be sigma mu i nu i or in other words at equilibrium sigma mu i nu i needs to go to 0. So, this is the criteria for equilibrium in case of a chemical reaction.

Now, like we said it is much easier to work with fugacity rather than the chemical potentials. So, what we will do is rewrite this particular equation in terms of fugacity. If you recall, let us give this equation a number to begin with, let us call this as equation 3, this is the criteria for equilibrium in case of a chemical reaction. Now, let us try to rewrite this equation in terms of fugacities d mu i the change, differential change in the chemical potential is RT d ln f i hat or it is related to the fugacity of the species i that is present in the mixture right.

What I can do is integrate this from a standard state condition. Remember for us standard state, the typical standard states we use are pure ideal gases or pure liquids or solids right; depending on the state we are looking at, its either the pure ideal gas or pure liquids and gases add the temperature of interest which is T in this case that is the standard state typically we use. So, what we will do is, we will integrate this particular equation for chemical potential in terms of fugacities from the standard state condition to the condition in the reactor or the reaction mixture.

When we do that integral of the standard state for pure i is G i naught, because it is pure, there is no chemical potential or chemical potential and Gibbs free energy are the same, because it is a standard state we use the superscript naught for species i. I am using the subscript i to the condition in the mixture d mu i this will be equal to integral. Again at the standard state condition, the pure component fugacity I can write it as fi naught i for species i naught for the standard state and to the one in the mixture RT is constant d ln fi hat. It is at the same temperature as that of the mixture that is the standard state condition. So, that T can come out and it will simply be integral of d ln fi hat

Or, if I rewrite as it will be mu i that is the condition in the mixture minus G i naught that is the condition at the standard state will equal RT ln f i hat in the mixture over f i naught at the standard state right. What I can do is rewrite the chemical potential from this equation which turns out to be in terms of standard state conditions G i naught plus RT ln fi hat over fi naught. This is the expression for chemical potential in terms of the Gibbs free energy at the standard state and the fugacities right.

So, now what we will do is take this equation 4 and put it back in equation 3 so, that I can change the criteria for equilibrium from chemical potentials to the fugacities. When I do that I will write that here we will put 4 in 3 right to get sigma nu i G i naught plus RT ln f i hat over f i naught equals 0 that is the criteria for equilibrium in terms of fugacities in a chemical reaction. What we will do from here is make some mathematical manipulations. So, that for special cases it is easier to handle this particular equation right.

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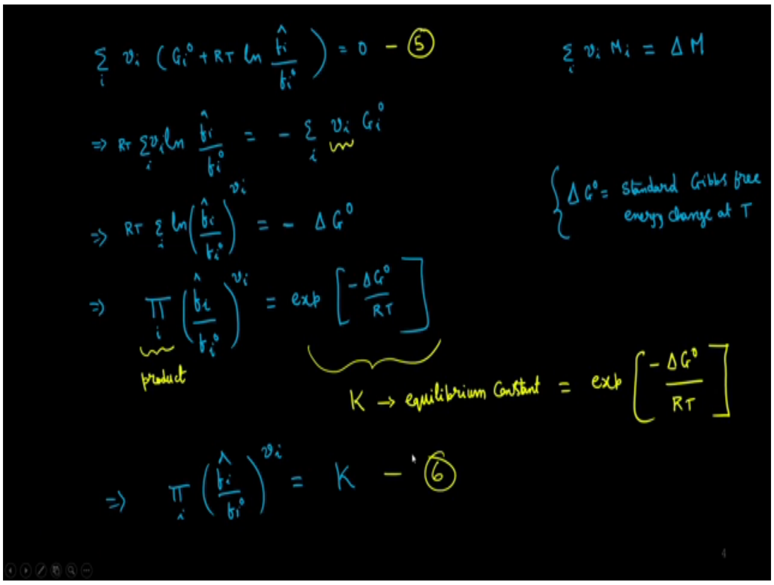

$$\sum_i \nu_i \left(G_i^0 + RT \ln \frac{\hat{f}_i}{f_i^0} \right) = 0 \quad - ⑤$$

$$\sum_i \nu_i M_i = \Delta M$$

$$\Rightarrow RT \sum_i \nu_i \ln \frac{\hat{f}_i}{f_i^0} = - \sum_i \underbrace{\nu_i G_i^0}$$

$$\Rightarrow RT \sum_i \ln \left(\frac{\hat{f}_i}{f_i^0} \right)^{\nu_i} = - \Delta G^0$$

$\left\{ \Delta G^0 = \right.$ Standard Gibbs free energy change at T

$$\Rightarrow \underbrace{\prod_i}_{\text{product}} \left(\frac{\hat{f}_i}{f_i^0} \right)^{\nu_i} = \underbrace{\exp \left[\frac{-\Delta G^0}{RT} \right]}$$

$$K \rightarrow \text{equilibrium Constant} = \exp \left[\frac{-\Delta G^0}{RT} \right]$$

$$\Rightarrow \prod_i \left(\frac{\hat{f}_i}{f_i^0} \right)^{\nu_i} = K \quad - ⑥$$

So, let us rewrite that equation again nu i G i naught plus RT ln f i hat over f i naught this needs to be equal to 0 at equilibrium right. Let us call this as equation 5 continuing our numbering from the previous slide and this is of course, summation over all i's right. And, if I do this sigma of i RT ln of f i hat over f i naught nu i will be equal to summation over i negative of that nu i G i naught right.

And, remember summation over i nu i any property M i these i's are occurring in the chemical reaction is what we called as delta M right or the change in the property due to the chemical reaction. Here I have sigma over nu i G i naught. So, G i naught is weighted with the stochiometric number for that species occurring in the chemical reaction. So, we can safely call the right hand side quantity as delta G naught; this will be negative of delta G naught.

So, this delta G naught is the standard implying that this is the change at the standard state conditions, Gibbs free energy change at the temperature of interest or there the temperature of the standard state in this case it is T. So, this delta G naught is the Gibbs free energy change upon reaction at the standard state condition at a temperature of T and the standard state condition being the typical pure gas, pure ideal gas.

Then the left hand side of this equation will read RT sigma over i; I will take that nu i to the power since it is a logarithm to the power nu i. I can bring RT to the other side and take a exponential so, then it becomes pi the product for I am getting rid of the logarithm. So, this left hand side becomes product of these terms f i naught over f i hat. I am getting rid of the logarithm so, the left hand side becomes product of these terms f i hat over fi naught raised to the power nu i that would equal exponential of minus delta G naught over RT. This pi i here indicates the product just like sigma indicates the summation pi i here is the product of all these terms for different i's.

So, this is the criteria for chemical reaction equilibrium. The right hand side is typically what we call as the K or the equilibrium constant for the chemical reaction. Although, we say it is a constant it is actually dependent on the temperature as the temperature changes this constant K value of course, is going to change. So, and this will equal exponential e to the power minus delta G naught the standard. Gibbs free energy change over here upon the reaction over RT right. So, in other words the criteria for equilibrium I can write it as the product of the terms f i hat over f i naught raised to the power nu i equals K.

We can call this equation, let us give it a number. We can call this as equation 6. What we will do is we will try to simplify the left hand side of this particular equation a little bit.

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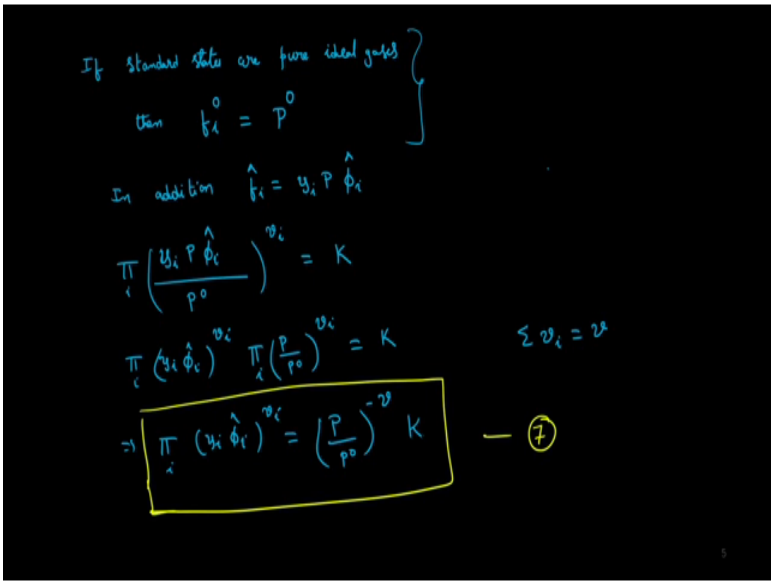

If standard state are pure ideal gases then $f_i^0 = P^0$

In addition $\hat{f}_i = y_i P \hat{\phi}_i$

$$\prod_i \left(\frac{y_i P \hat{\phi}_i}{P^0}\right)^{\nu_i} = K$$

$$\prod_i \left(y_i \hat{\phi}_i\right)^{\nu_i} \prod_i \left(\frac{P}{P^0}\right)^{\nu_i} = K \qquad \sum \nu_i = \nu$$

$$\Rightarrow \boxed{\prod_i \left(y_i \hat{\phi}_i\right)^{\nu_i} = \left(\frac{P}{P^0}\right)^{-\nu} K} \quad — ⑦$$

Now, if we consider the standard state to be the typical pure ideal gas like standard states then the fugacity at the standard state condition f i naught will be equal to the pressure of the standard state let us say which is P naught. In addition the fugacity f i hat in the mixture can be expressed in terms of the fugacity coefficients as y i P times phi i hat right.

Now, if I make these two substitutions into the previous equation we had equation 6 then it becomes the product of the terms f i hat now is y i P phi i hat over P naught to the power nu i will equal K right or what I can do now is separate the first term out into two different terms. The product of the terms y i times phi i hat to the power nu i and the product of the terms P over P naught to the power nu i will equal K. Or, the product of the terms y i times phi i hat to the power nu i and because, P over P naught for all i's is same you can combine all the nu i's. And, if you recall we said sigma nu i is nu then this equation will reduce to P over P naught to the power negative nu if I bring it to the other side multiplied with K.

So, this is the criteria for chemical equilibrium if the standard state is a pure ideal gas. What we have done is rewritten the expression in terms instead of fugacities we have rewritten in terms of the fugacity coefficient phi i hat right. Let us call this as equation 7; we can do one additional manipulation to simplify this equation if the gas phase is ideal right.

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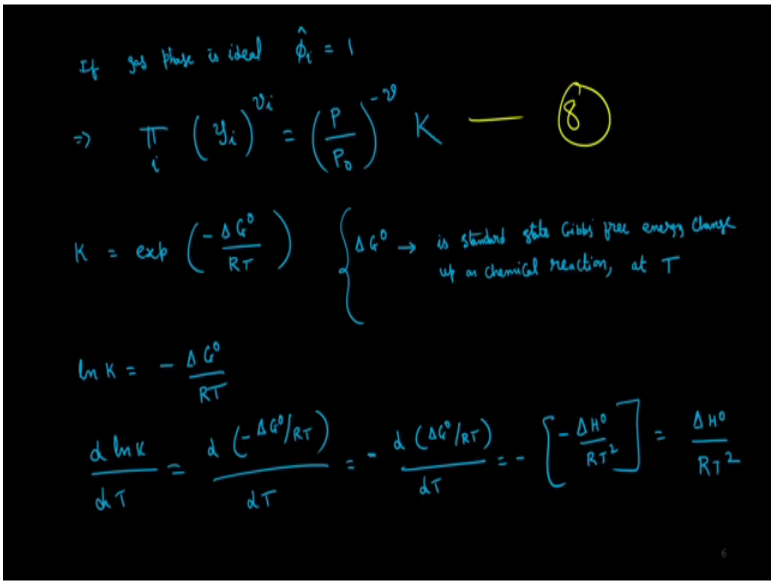

If gas phase is ideal $\hat{\phi}_i = 1$

$$\Rightarrow \prod_i (y_i)^{\nu_i} = \left(\frac{P}{P_0}\right)^{-\nu} K$$ — ⑧

$$K = \exp\left(-\frac{\Delta G^0}{RT}\right)$$

$\Big\{ \Delta G^0 \rightarrow$ is standard state Gibbs free energy change of a chemical reaction, at T

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

$$\frac{d \ln K}{dT} = \frac{d\left(-\Delta G^0/RT\right)}{dT} = -\frac{d\left(\Delta G^0/RT\right)}{dT} = -\left[-\frac{\Delta H^0}{RT^2}\right] = \frac{\Delta H^0}{RT^2}$$

If the gas phase is ideal or its ideal gas like then phi i hat or the fugacity coefficient in the mixture will be equal to 1. And, that equation reduces to the product of the terms y i times nu i will be equal to P over P naught to the power negative nu times the equilibrium constant K and let us call this as equation 8 right. So, we have looked at several forms of these criteria for reaction equilibrium. Let us quickly run through all of them one more time. Equation 3 is written in terms of the chemical potential mu i and the stochiometry coefficient nu i. We have converted it into the equation we see below 4 here. Let us this equation is another way of writing the equilibrium criteria this time in terms of the standard state Gibbs free energy and the fugacity values we call that as equation 5.

The next thing we have done is rewritten the equation in terms of the Gibbs free energy and the fugacity is instead of the chemical potentials which is equation 5, we see here. Then we have used the idea of equilibrium constant which is exponential of negative delta G naught over RT we call that as equilibrium constant K right. And, equation 6 is the criteria for chemical reaction equilibrium in terms of the equilibrium constant rather than the standard Gibbs free energy of reaction, but we still have fugacities on the left hand side. For an ideal gas standard state we can rewrite the fugacities in terms of fugacity coefficient and at the standard state it is simply P naught f i naught will be P naught and we get equation 7 as a consequence of that.

And finally, if the gas phase itself is ideal than phi i hat or the fugacity coefficient for all species will be equal to 1 and that equation for chemical reaction equilibrium further simplifies to equation 8 we see here. So, in all these formulations if you look at it on the left hand side we have the mole fraction for each of the species and stoichiometric numbers etcetera. On the right hand side we have the reaction conditions, be it the pressure or the equilibrium constant K which is in terms of the temperature and the standard Gibbs free energy.

So, if I want to know how far a chemical reaction will proceed then all I need to do is solve equation 8. If I know the temperature and pressure I know everything on the right hand side of the equation, I can solve this equation 8 to get the left hand side or the unknown quantities which is in this case essentially the composition at a equilibrium right. We will see how we do that when we get there, but essentially equation 8 is the criteria for chemical reaction equilibrium. Now, there is one other thing that is left to be handled before we can actually solve the problems that is we said K the equilibrium constant is going to depend on the temperature. So, if the temperature changes K will change and we want to account for that change. How do we account for that change? If you recall K is exponential of negative delta G naught over RT.

If I know the temperature I can calculate this except with one catch. I need to know delta G naught; recall the delta G naught is standard state Gibbs free energy change upon chemical reaction. And, when we say standard state it is at the standard state conditions and the temperature for this standard state condition needs to be at the same T we are talking about whatever T at whatever T the reaction occurs right.

Now, if you recall our discussion in one of the previous videos we said usually these Gibbs free energy changes upon chemical reaction or enthalpy changes upon chemical reaction are going to be tabulated at a certain temperature be it 298 Kelvin, which is most commonly the case or at any other convenient temperature. We do not have the information on delta G naught across a range of temperature; we will probably have it at one or two temperatures available to us, but to be able to calculate K we need it at the temperature T of interest. So, how do we get K? Well, to answer that question we first need to look at how K changes with temperature.

We resort to the fundamental property relations, we derived earlier essentially K is the somehow related to the Gibbs free energy change upon reaction right. What I can do is write this equation as ln K is negative delta G naught over RT. If I want to know how this changes with temperature d ln K over dT will be equal to the derivative of delta G naught over RT with respect to T. Recall that the Gibbs free energy over RT or change in Gibbs free energy over RT with respect to T is H over RT square.

In this case it will be negative of d delta G naught over RT by dT. So, that negative sign stays there and the derivative we are looking at is essentially delta H naught by RT square. If you recall the fundamental property relation for G in terms of v and H this derivative with respect to T is negative delta A; negative H by RT square. In this case it will be negative delta H naught over RT square or this will be delta H naught over RT square.

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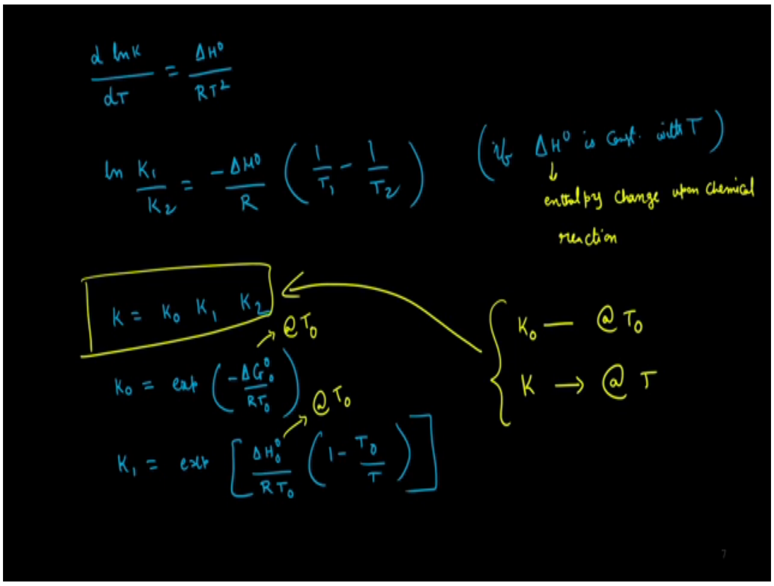

$$\frac{d\ln K}{dT} = \frac{\Delta H^0}{RT^2}$$

$$\ln\frac{K_1}{K_2} = \frac{-\Delta H^0}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)$$

$\left(\text{If } \underset{\substack{\downarrow \\ \text{enthalpy change upon chemical reaction}}}{\Delta H^0} \text{ is const. with } T\right)$

$$\boxed{K = K_0 K_1 K_2}$$

$$K_0 = \exp\left(\frac{-\Delta G_0^0}{RT_0}\right) \text{ @}T_0$$

$$K_1 = \exp\left[\frac{\Delta H_0^0}{RT_0}\left(1 - \frac{T_0}{T}\right)\right] \text{ @}T_0$$

$$\left\{\begin{array}{l} K_0 \text{ — @}T_0 \\ K \rightarrow \text{@}T \end{array}\right.$$

So, the logarithm of the equilibrium constant will change with temperature according to this particular equation. Let us rewrite this again d of ln K over dT will be delta H naught over RT square right. Now, if I want to calculate K at a different temperature then all I need to do is integrate this equation and this equation will give me ln K1 over K2 is going to be negative delta H naught over R 1 over T 1 minus 1 over T 2.

Of course this is assuming that delta H naught is constant with temperature. So, if delta H naught or the enthalpy change upon chemical reaction right, delta G naught was Gibbs free energy change upon chemical reaction. Delta H naught is enthalpy change upon chemical reaction. If this quantity is independent of temperature or it is constant with temperature then we can take that delta H naught out of the integral and when we integrate we get ln K 1 over K 2 is 1 over T 1 minus 1 over T 2 multiplied with negative of delta H naught over R.

So, if I know the equilibrium constant K at a particular temperature T 1 which is K 1 then I can calculate the constant K 2 at a different temperature T 2. All I need is the information of delta H naught which is usually available. But, then the catch is that it needs to be constant with temperature, if it is not constant then we have to handle it a little differently; after mathematical manipulation it turns out right, it turns out that K is usually expressed as a product of three terms K naught, K 1, and K 2 or K naught is going to be exponential of negative delta G naught over RT naught. So, this is at a temperature of T naught wherever the delta G naught is available. So, notice that I have a superscript naught for standard state condition and the subscript naught for delta G is for indicating that this standard state is at a temperature of T naught and in the denominator of course, we have RT naught.

So, let me write that out this is at a temperature of T naught that is the delta G naught at a temperature of T naught. Then, I need to account for change in temperature; the way we do it is through K 1 assuming that delta H naught is constant with temperature then this K 1 will be exponential of delta H naught naught just like delta G naught we have both subscript and superscript RT naught 1 minus T naught over T. So, this K 1 will correct the equilibrium constant from a temperature of T naught it will take it to a temperature of T, but with the rider that delta H naught is constant with T. But in reality delta H naught of course, the enthalpy is not independent of temperature. It will change with temperature.

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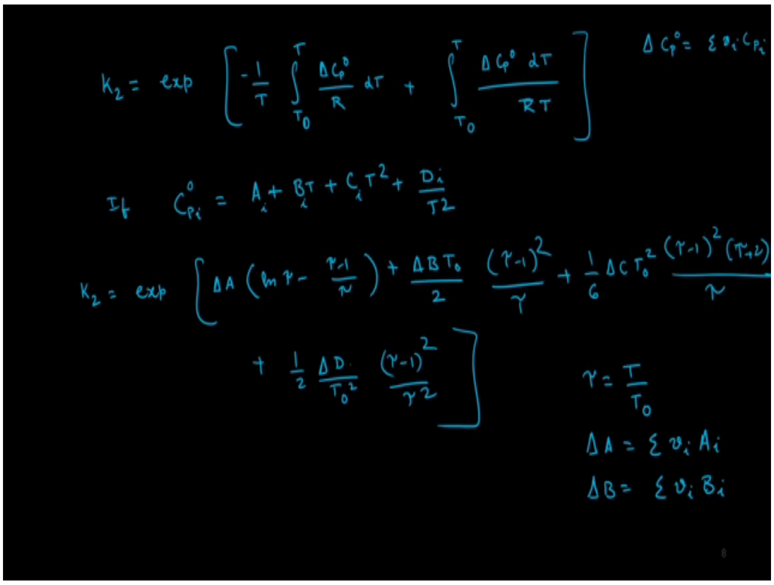

$$K_2 = \exp\left[-\frac{1}{T}\int_{T_0}^{T}\frac{\Delta C_p^0}{R}\,dT + \int_{T_0}^{T}\frac{\Delta C_p^0\,dT}{RT}\right]$$

$$\Delta C_p^0 = \Sigma\, \nu_i C_{p_i}$$

$$\text{If} \quad C_{p_i}^0 = A_i + B_i T + C_i T^2 + \frac{D_i}{T^2}$$

$$K_2 = \exp\left[\Delta A\left(\ln\tau - \frac{\tau - 1}{\tau}\right) + \frac{\Delta B T_0}{2}\frac{(\tau-1)^2}{\tau} + \frac{1}{6}\Delta C T_0^2\frac{(\tau-1)^2(\tau+2)}{\tau} + \frac{1}{2}\frac{\Delta D}{T_0^2}\frac{(\tau-1)^2}{\tau^2}\right]$$

$$\tau = \frac{T}{T_0}$$

$$\Delta A = \Sigma\, \nu_i A_i$$

$$\Delta B = \Sigma\, \nu_i B_i$$

And, if you have to bring in that functionality as well another constant K 2 that had involved the change in the enthalpy of reaction with temperature and this K 2 turns out to be exponential of negative 1 over T integral from T naught to T delta C p naught over R dT plus integral of T naught to T delta C p naught dT over RT right; and remember that this delta C p naught is sigma nu i C p i for the chemical reaction. So, just write delta H naught we have delta C p naught which is C pi's weighted with their stoichiometric numbers and the summation of all of those.

So, this is the term K 2 and if delta C p or C pi is available, let say C pi is a function of temperature as you recall it is A, it may be usually written as A plus B T plus C T square plus D over T square or I can write it as A i B i T C i T squared D i over T square. If this is the form for the standard state heat capacity at constant pressure then K 2 will boil down to exponential of delta A ln tau minus tau minus 1 by tau plus delta B T naught over 2 tau minus 1 whole square by tau plus 1 over 6 delta C T naught square tau minus 1 square tau plus 2 we are integrating 2 C p terms. And, that is where we get all of these from plus half of delta D over T naught square tau minus 1 whole square by tau square.

So, this is the lengthy expression for K 2 we are looking at where tau is of course, T over T naught we have looked at this earlier when we try to work with changes in enthalpy and entropy and delta A is essentially again sigma of nu i A i delta B is sigma of nu i B i etcetera. These are the terms for the heat capacities A i's B i's etcetera right. We weight them with these stoichiometric numbers and we get delta A for the reaction delta B for the reaction etcetera.

And, we can use these numbers and tau to calculate the term K 2; as is the case usually the effect of K 2 is much smaller as compared to the first two terms K naught and K 1. So, the product of K naught and K 1 for most part gives me a reasonably good estimate of what the equilibrium constant is of course, that is assuming that delta H naught does not change with temperature and K 2 is a small correction on top of that to account for change in enthalpy of the chemical reaction.

So, once I do this exercise then what I will get is K the equilibrium constant for my chemical reaction at any temperature T of interest. The actual Gibbs free energy change and the enthalpy change themselves are available only at a temperature of T naught. But, then using this particular expression I can correct the equilibrium constant to the temperature of interest K. So, again K naught is at T naught K is equilibrium constant at T and to make this conversion I am going to use this equation. And, then use the information available for Gibbs free energy change and enthalpy change at T naught, the heat capacity data and come up with a value for K at the temperature of interest.

So, then I know how to calculate the equilibrium constant at the temperature of my interest and I also know the criteria for chemical reaction equilibrium. For example, equation 7 over here; I know K, I know the criteria for equilibrium all I need to do then is somehow solve this equation 7 or equation 8; if it is an ideal gas and obtain y i’s. We will come back and do that in the next video.