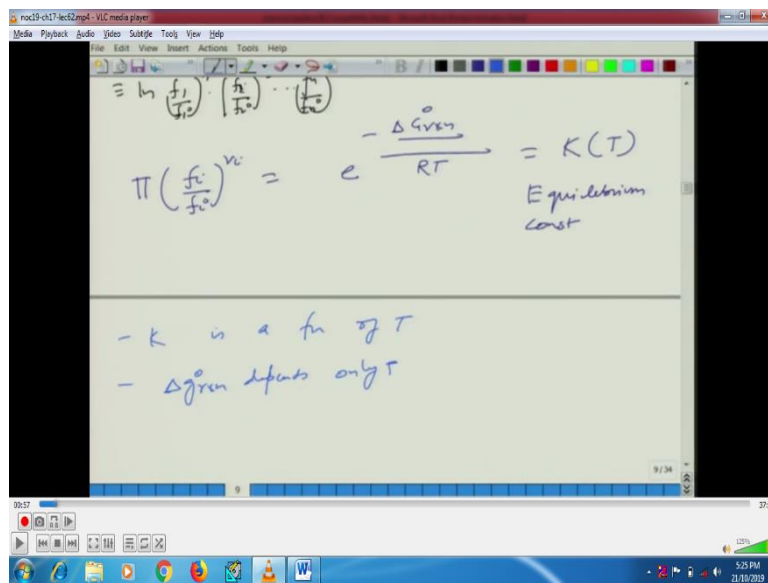


Chemical Engineering Thermodynamics
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Lecture 62
Chemical Reaction Equilibria 3

Welcome back so we just concluded last, in the last lecture that the equilibrium constraint is something which is related to the exponential of minus of Gibbs free energy at the standard condition divided by RT .

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The screenshot shows a VLC media player window with a whiteboard background. The whiteboard contains the following content:

$$\prod \left(\frac{f_i}{f_i^0} \right)^{\nu_i} = e^{\frac{-\Delta G_{rxn}^0}{RT}} = K(T)$$

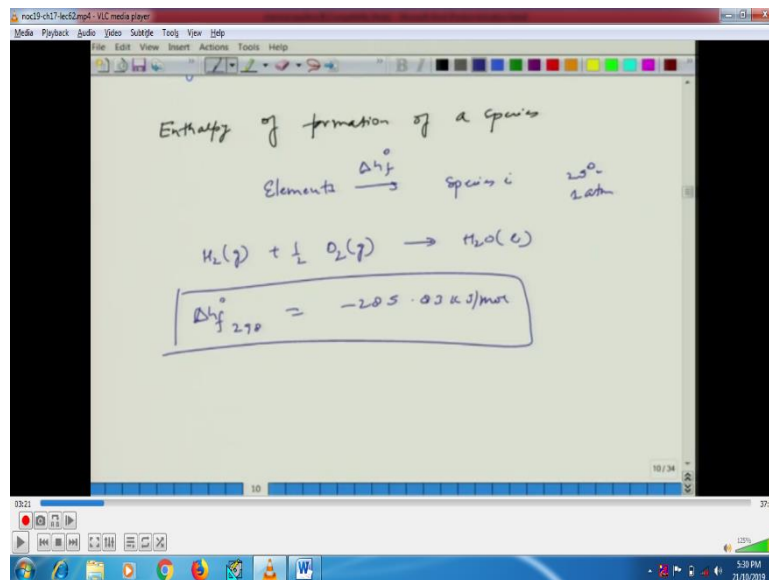
Equilibrium
const

- K is a fn of T
- ΔG_{rxn}^0 depends only T

The VLC player interface includes a menu bar (Media, Playback, Audio, Video, Subtitle, Tools, View, Help), a toolbar, and a status bar at the bottom showing the time 5:25 PM on 21/10/2019.

And this particular expression is connected to the fugacity ok is where f_i^0 is the reference fugacity which usually we consider 1 bar okay but we just kept it here like a f_i^0 . Now so we need to understand how to relate this expression finally to the composition but before we go and do that let me recall few things which you have done this earlier and if not, this will help us to come to the same page.

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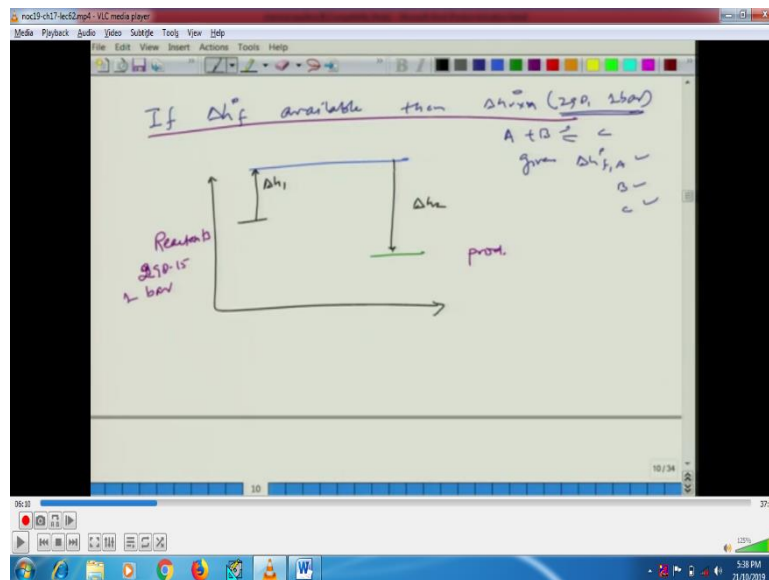


Now the first thing which I would like to focus on is enthalpy of formation of a species from is elemental or from its elements which are naturally present. So, for example, we can write schematic kind of descriptive or we can write this in a way which is more general, so let us say some elements goes to some species okay at 25 degree Celsius and one atmosphere. So such a condition where a specific species is formed through is element is often the change in the enthalpy or the enthalpy of formation of this is often written in this phase delta H, delta is H OF okay.

Now enthalpy of formation of elements are 0, because they are naturally available and hence is this is considered as a reference. So to give you an example let us say H₂ gas plus half of O₂ g this goes to H₂O which is a liquid, okay. So essentially delta H_f is going to be the enthalpy of formation of this minus enthalpy of formation of this minus half of enthalpy formation of this but enthalpy of formation of this and the H₂ NO₂ is basically 0. So essentially H₂O enthalpy formation is nothing but change in the enthalpy of the reaction.

So if you calculate that this is something which is often available to us okay, 298 would be minus 20, minus 285.83 kilo joules per mole. In other word, the change in the enthalpy here in this reaction is nothing but the enthalpy of formation that is what we consider because we consider the these two references to be 0 and this is often tubulised in kind of some of the books you will find it in appendix A table having the enthalpy of formation of various different spaces okay. So it is also there in our text book. Now if delta H_f 0 at 298 is available you can extract delta H_f at a different formation at a different temperature also.

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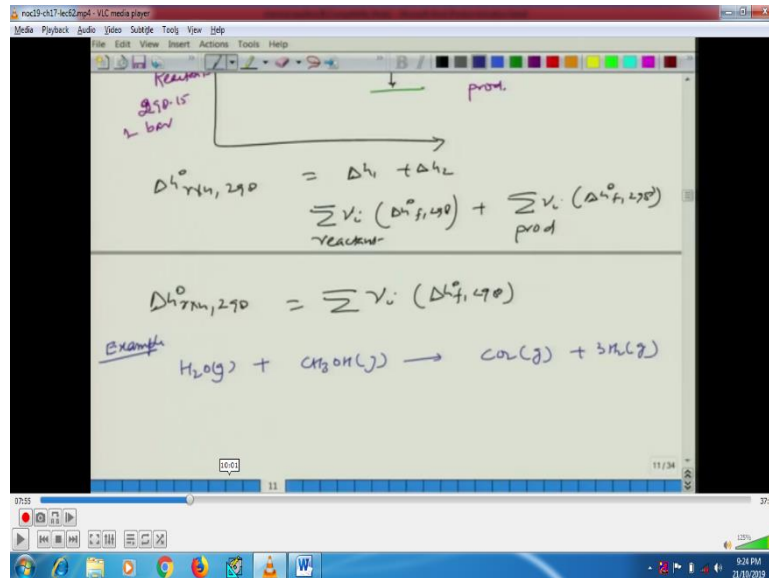
So let me schematically show that, so if ΔH_f^0 is available then straightforward to calculate then ΔH reaction is straightforward at a given temperature okay. So let us say that if you plotting enthalpy okay here and so this is your let us say elemental form this is your product okay this is your reactant okay.

So if ΔH_f is available for the species okay then essentially for a given reaction the way it is done is the following. Now we will talk about at different temperature at this point we are just talking about ΔH_f for different species which is available, so this is let us say reactant it to 298.15 per okay. So the ΔH_f for different reactants are available a similarly this is product okay again at 298.15 at bar one bar, so what we are looking at is if it is available then what would be your ΔH_f , H of the reaction? Okay.

So what we are looking at is nothing but the ΔH_f of reaction okay at that 298 on one bar okay. so I am not talking about different temperatures the same condition but enough of the reaction. So this could be let us say species A plus B goes to species C well then how do you find out the ΔH of reaction? Okay at this condition given ΔH_f for A is available, similarly for B, similarly for C is available okay. So given this you can simply use this elemental form as a reference.

So if all the reactants we can take a thermodynamic path, so it is like this and then you take from the elemental to the to the product that will be H_2 , okay. So it is like you know you are taking the reactant to the elemental form and using this elemental form as a reference which is nothing but 0 as a ΔH_f^0 and from there you get to the product okay, using this change in the enthalpy of ΔH_2 .

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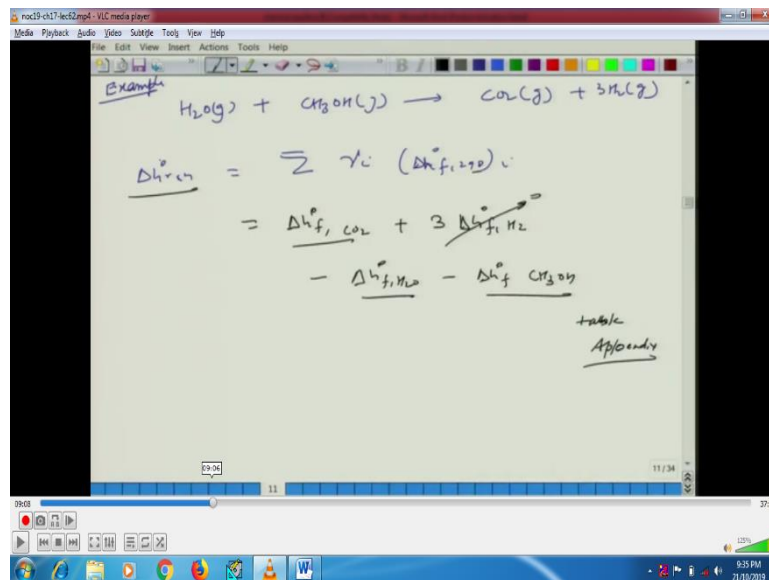
$$\Delta h_{rxn,298}^{\circ} = \Delta h_1 + \Delta h_2 = \sum_{\text{reactant}} \nu_i (\Delta h_{f,i,298}^{\circ}) + \sum_{\text{prod}} \nu_i (\Delta h_{f,i,298}^{\circ})$$

$$\Delta h_{rxn,298}^{\circ} = \sum \nu_i (\Delta h_{f,i,298}^{\circ})$$

So the reaction 298, at 298 Kelvin is going to be delta H1 plus delta H2, okay which is nothing but Nu i delta H ref 298 plus summation Nu, so this is Nu i reactant, okay. This is product, only product delta H 0 F 298 okay, so this is something which we can write because delta Hf is for this particular reaction going reactant going to the elemental form will be simply this okay, remember that Nu i for the reactance is negative and Nu i for the product is positive.

Now given those this two relation which clearly you can generalize this that Delta H of reaction 298 is nothing but summation Nu i delta Hf 298, okay. So this is something which you can generalize okay. So here we are not specifying it to be reactant or a product okay, so this is just to recall that these exercises we have done in our engineering thermodynamics also. So this now we can extent to an example, so let us consider an example so water in the gas phase CH3 OH in the gas phase goes to CO 2 plus 3 H2 gas phase.

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Okay and so been asked that well what is your delta H reaction, so this is going to be a molar enthalpy of the reaction, this is going to be in kJ mol^{-1} for all the component okay, so this means that I am going to consider delta H of CO_2 and let us not bother anymore 298 because at 298 plus 3 delta H of H_2 minus delta H of H_2O minus delta H of CH_3OH , okay.

Now this is a elemental component here, so this is going to be 0 by definition and then this values you can take it in from tables which is available in the back of the textbook or in the usually in appendix okay, some appendix you will find it and you can use this information to calculate delta H reaction at 298 Kelvin, okay. Now this exercise is something which can you can extend to the Gibbs free energy

I was just recalling this thing just to make sure that you understand that the similar exercises can be done for the Gibbs free energy as well, okay and most common thermodynamic data just like the way the most common heat of formation data is available at 298 one bar similarly most common heat of formations of you know for the heat of formation for the species is available at 25 degree Celsius in one bar okay.

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$$= \Delta H_f, CO_2 + 3 \Delta H_f, H_2 - \Delta H_f, H_2O - \Delta H_f, CH_3OH$$

Most common thermo chem data available in the form of ΔG_f° (25°C, 1 bar)

Equal to the Gibbs energy of rxn when the species is formed from its pure elemental constituent as found in nature

So this is usually available in the form of ΔG_f° which is basically 25 degrees Celsius and 1 bar okay. So this is the most common thermo chemical data available. Now the same way as we have defined it for ΔH_f° as standard condition this would mean that ΔG_f° means that this is equal to the Gibbs energy of reaction when the species is formed from its pure elemental composition or constituent as found in nature okay.

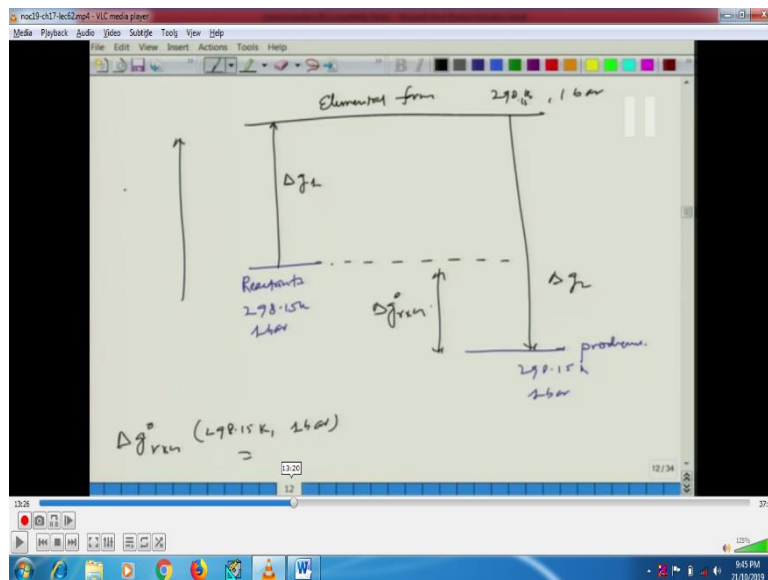
So this is akin to what we have done for the ΔH_f° , so ΔH_f° is also equal to the enthalpy change of reaction when the species is formed from its pure elemental constituents and as found in the nature. So we extending that understanding to the free energy, Gibbs free energy okay.

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from its pure elemental constituent as found in nature

Given ΔG_f° To find ΔG_{rxn}° (25°C, 1 bar)

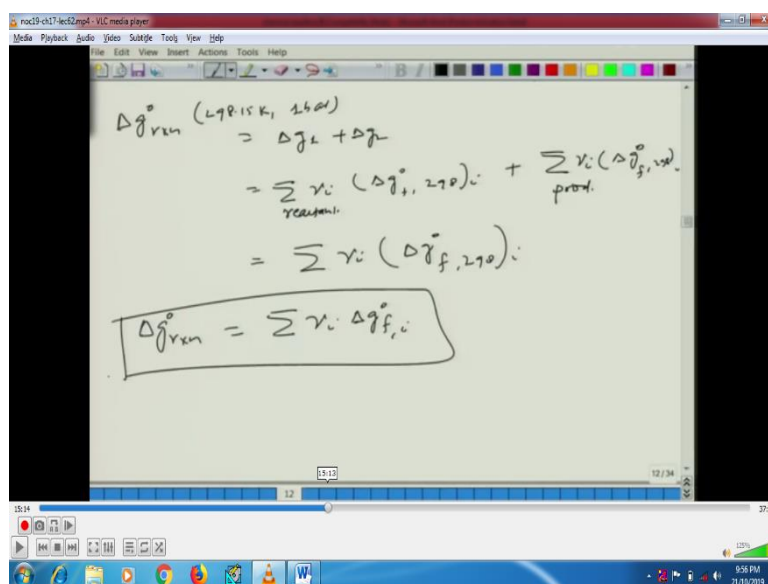
Elemental form 25°C, 1 bar



Okay, so let us look at it again the same way as we have done, so if you have some reactant so given ΔG_f° we can find out, to find $\Delta G^\circ_{\text{reaction}}$ okay which essentially means nothing but 298 Kelvin and 1 bar ok we will do the same exercise as we have done for ΔH_f° , so let us see that this is a that is the elemental form which is a 298 Kelvin and 1 bar means to be very precise is 298.15 Kelvin okay again we are going to consider this as an axis of increasing the Gibbs free energy.

This is my, this is the reactant let us say which is at 298.15 Kelvin and 1 bar this is the product again at 298.15 Kelvin and 1 bar ok for the sake of correctness I will write this as 1.15 okay, so now what would be your $\Delta G_{\text{reaction}}$ at 298.15 Kelvin 1 bar? This is going to be if we consider here again this is your ΔG_1 this is your ΔG_2 , so in a sense this difference is nothing but your $\Delta G^\circ_{\text{reaction}}$ okay.

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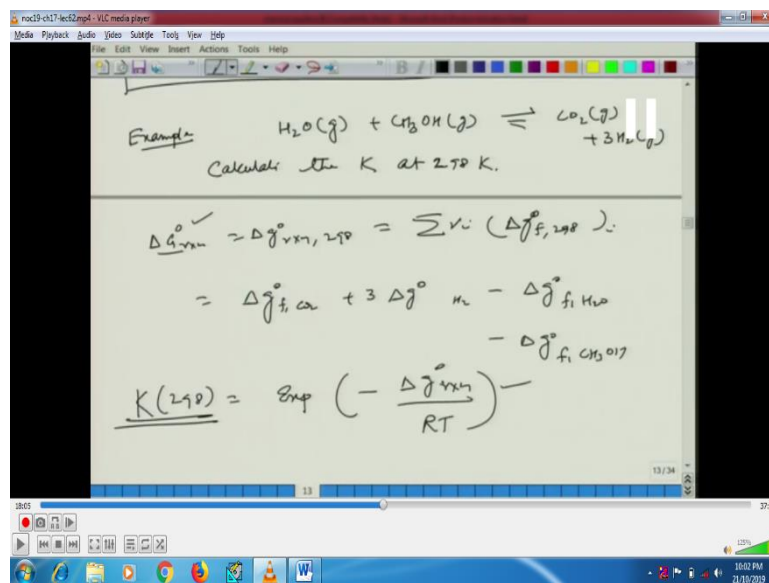
So this is going to be your ΔG_1 plus ΔG_2 okay remember that the arrow indicates that we are taking reactant to the elemental form okay and then this is from the elemental form to the ΔG_2 and that is why I $\Delta G_{\text{reaction}}$ is the sum of these two components.

This I can now express this in terms of $\sum \nu_i \Delta g_{f,i}^0$ at 298 K for reactant plus $\sum \nu_i \Delta g_{f,i}^0$ at 298 K for product, so this is for the product okay.

$$\begin{aligned} \Delta g_{rxn}^0(298.15 \text{ K}, 1 \text{ bar}) &= \Delta g_1 + \Delta g_2 = \sum_{\text{reactant}} \nu_i (\Delta g_{f,i}^0) + \sum_{\text{prod}} \nu_i (\Delta g_{f,i}^0) \\ &= \sum \nu_i (\Delta g_{f,i}^0) \\ \Delta g_{rxn}^0 &= \sum \nu_i \Delta g_{f,i}^0 \end{aligned}$$

So now this can be, this clearly can be expressed as $\sum \nu_i \Delta g_{f,i}^0$ okay and ν_i okay, so at so that is why now so let me just summarize this because we have done this rigorous exercise now okay. So let me summarize and then we can take up an example so Δg reaction can be (relate) can be written as summation of ν_i and Δg of formation for each species as a part of the reaction. So let us take this, use this expression by considering an example.

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So the example could be again a simple one. Let us say you have been asked to find out the first Δg and once you find out Δg reaction at a standard condition then the second question could be that can you now calculate K which is an equilibrium constant. So let us take an example of H_2O plus CH_3OH formation it gives you the CO_2 plus 3 H_2 gas phase, so this is all gas phase as far as the reaction is concerned but now we are talking about 298.

So let us say we the main question is that calculate the K at 298 Kelvin okay, so the first thing we have to do is we must get the Δg reaction because if you recall the K is nothing but is exponential of this minus of Δg molar Δg of the reaction at the standard condition

divided by RT . So we can now calculate ΔG reaction given that the thermodynamic data for H_2O gas and basically all for all of them is available at 298 Kelvin.

So we can get this ΔG reaction or ΔG reaction at 298 Kelvin is summation of $\sum \nu_i \Delta G_f^\circ$ okay ΔG of formation at 298 for all the species and this essentially means ΔG of CO_2 plus 3 times ΔG of 298 H_2 of course this is going to be a 0 minus ΔG of H_2O minus ΔG of CH_3OH okay. Now this is at 298 but note that this is in a hypothetical gas state further for the water but this information is available in the appendix. So using this information once we calculate this I can calculate then K at 298 as exponential minus ΔG of this reaction at 298 by RT .

So once I have this information I can obtain is this directly and obtain the equilibrium constant K okay, okay so but note that we have not yet come to the point where we can connect this K to the to the compositions we will come to that point soon. But let me first focus on that how do you calculate K at a different temperature? Because most of the reactions occur at a temperature other than that 25 degree Celsius.

So, it is valuable for us too also find out a means to obtain K at a different temperature okay. And the other important thing is often thermodynamic data is at a 298 degree or 298 Kelvin or 25 degree Celsius and 1 bar. So essentially you need to calculate K at 25 degree Celsius 1 bar and then you use that as a reference to obtain K at a different temperature, so let us look at that.

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Need to calculate K of any rxn
at any T from one set of Gibbs
energy data (usually at $25^\circ C$, 1 bar)

$$\ln K = -\frac{\Delta G^\circ}{RT}$$
$$\frac{d \ln K}{dT} = -\frac{1}{\Delta G^\circ / RT^2}$$

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

$$\frac{d \ln K}{dT} = - \frac{d}{dT} \left(\frac{\Delta G_{rxn}^0}{RT} \right)$$

$$= \frac{\Delta G_{rxn}^0}{RT^2} - \frac{1}{RT} \frac{d \Delta G_{rxn}^0}{dT}$$

At const P
 $dg = -s dT + v dp$
 $dg/dT|_P = -s$

So the question is need to calculate K of any reaction at any temperature from one set of Gibbs energy data which usually is at usually at 25 degrees Celsius one bar, okay. Okay so to calculate that thermodynamic dependence of K we are going to use some thermodynamic relation. Now based on our definition Ln K is nothing but minus delta g 0 by RT so we can take D Ln K by dt this is minus of d by dt delta g reaction by R T okay.

This I cannot differentiate by parts this will be Delta g0 by RT square minus 1 by RT delta g by dt okay. So this gives you the differential change in the log of K with respect to temperature now let us consider the case because we are interested in the thermodynamic we interested in the temperature dependence of K then at a constant pressure we can come up with some approximation or some simplification rather the approximation some simplification, so for that we can start with this dg, dg is nothing but minus s dT plus v dP okay.

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At const P
 $dg = -s dT + v dp$
 $dg/dT|_P = -s$

At const P $\frac{d(\Delta G)}{dT}|_P = -\Delta S$

$\therefore \frac{d \ln K}{dT} = \frac{\Delta G_{rxn}^0}{RT^2} + \frac{1}{RT} \Delta S_{rxn}$

$\Delta G_{rxn}^0 = \Delta H_{rxn}^0 - T \Delta S_{rxn}$

$\frac{d \ln K}{dT} = \frac{\Delta H_{rxn}^0}{RT^2} - \frac{\Delta S_{rxn}^0}{RT} + \frac{\Delta S_{rxn}^0}{RT}$

The image shows a whiteboard with the following handwritten equations:

$$\frac{d \ln K}{dT} = \frac{\Delta H_{rxn}^{\circ}}{RT^2} - \frac{\Delta S_{rxn}^{\circ}}{RT} + \frac{\Delta S_{rxn}^{\circ}}{RT}$$

$$\boxed{\frac{d \ln K}{dT} = \frac{\Delta H_{rxn}^{\circ}}{RT^2}} \quad \text{where} \quad \Delta H_{rxn}^{\circ} = \sum \nu_i (h_{f,i}^{\circ})$$

So at constant temperature dg by dt at a constant P is nothing but minus s okay which essentially means that if I am considering at constant pressure then essentially my d of ΔG by dt at a constant pressure this can be written as minus ΔS . So therefore, I can write now $d \ln K$ by dt as ΔG is 0 okay RT^2 plus 1 by RT and this is now written as in ΔS standard condition okay of course reaction here.

So this is at constant pressure remember that okay. Now you can further simplify by considering the fact that ΔG_{rxn} is ΔH_{rxn} minus $T \Delta S_{rxn}$ right, so this we can write, now with this we can replace this expression So we get $\ln K$ by dt and this becomes ΔH_{rxn} okay by RT^2 minus ΔS_{rxn} by RT plus of course ΔS_{rxn} by RT .

So this cancels out so what you have now is an expression which is $d \ln K$ by dt is ΔH_{rxn} by RT^2 okay, where ΔH_{rxn} is nothing but summation $\sum \nu_i H_{f,i}^{\circ}$ of individual species okay, okay so yeah so this is something which we can now write it, okay so it relates the equilibrium constant is now clearly related to the enthalpy change at standard condition of the reaction okay.

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Exothermic $\Delta H_{rxn}^{\circ} < 0$
 $\Rightarrow K$ decrease with T

Endothermic $\Delta H_{rxn}^{\circ} > 0$
 $\Rightarrow K \uparrow$ with T

for a small T range
 consider $\Delta H_{rxn}^{\circ} \approx \text{const}$

for a small T range
 consider $\Delta H_{rxn}^{\circ} \approx \text{const}$

$$\int d \ln K = \int \frac{\Delta H_{rxn}^{\circ}}{R} \frac{dT}{T^2}$$

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

So we can consider couple of two examples or two particular cases, first is exothermic. We know for exothermic ΔH is less than 0 which essentially means that K will decrease with temperature because RT^2 is positive. Now for the case of endothermic reaction ΔH is greater than 0 which implies that K will increase with temperature. Now we can try to integrate this also in such a case we can consider for example for a small T range, temperature range if we consider ΔH to be so for a small temperature range let us say consider ΔH reaction to be approximately constant.

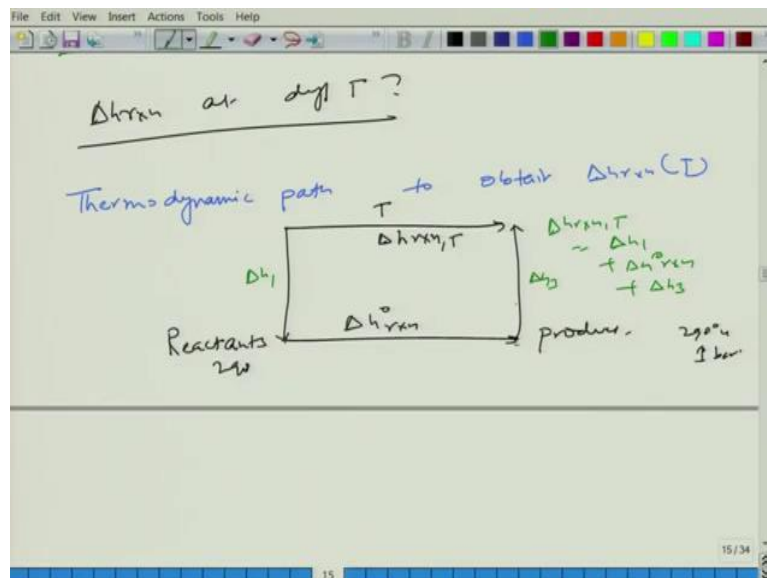
And if you do that then I can integrate this expression so I can write $d \ln K$ by dt I can write this as ΔH of reaction by R okay and then you have this dt by T^2 okay. So if you integrate this I get $\ln K_2$ by K_1 and this becomes minus of ΔH reaction by R and this is $\frac{1}{T_2} - \frac{1}{T_1}$ okay. Now as I said that most of the thermodynamic data or thermo chemical data is available at 298 Kelvin and 1 bar.

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The image shows a digital whiteboard with a toolbar at the top. The main content consists of two equations. The first equation is $\ln \frac{K_2}{K_1} = -\frac{\Delta_r H^\circ}{R} \left(\frac{1}{T_2} - \frac{1}{T_1} \right)$. The term $\frac{1}{T_1}$ is circled in red, and an arrow points from it to the word "ref" written below. The second equation is $\ln \frac{K_2}{K_{298}} = -\frac{\Delta_r H^\circ}{R} \left(\frac{1}{T_2} - \frac{1}{298} \right)$, which is enclosed in a green rectangular box. The number "298" is written above the second term in the parentheses of the second equation. At the bottom of the whiteboard, there is a blue bar with the number "15" and a page indicator "15/34".

So this T_2 would be your or the reference temperature let say K here can be a reference temperature or data which is available is at 298 Kelvin, so if I say so then I can write this expression as K_2 by K at 298 and this becomes minus delta H reaction okay again at 298 1 by T_2 minus 298 okay. So this is the expression which we can make use of it in order to obtain the equilibrium constant at temperature other than 298 okay. Okay so let us try to also obtain this Delta H reaction okay which is here of course I have kept to be constant around this range of temperature but you may ask the question that of course the delta h reaction can be at a different temperature also.

(Refer Slide Time: 27:04)



So in general ΔH reaction we may be interested okay at different temperature okay. So how do we find that so ΔH of reaction at different temperature we will be using again the similar kind of a thermodynamic path which we have been doing that so because in general ΔH reaction which we are interested in could be at a temperature other than 298.

So we need to find out a way to also find if the sense if the heat capacities are given of the species then we should be able to find the ΔH reaction at a different temperature so we use this thermodynamic path to obtain ΔH of reaction at temperature let say T . So let us consider again our reactant to product okay and this is let us say at you know 298 1 bar and this is what we usually refer as ΔH^0 reaction okay now we are interested to find ΔH at a temperature let say T .

So the way we are going to do that is the following okay we will be using ΔH reaction at temperature T okay so which is this right so essentially this something which we can write is the following that we can take because we are interested from here the reactant and the product here so we are interested to obtain this difference from here to here okay. So we can take path 1 which is the reactant at temperature t to the reactant at a temperature 298 okay then this ΔH reaction at 298 and then bringing the temperature of the product to our temperature T .

So this will be your company this will be your ΔH reaction at temperature T so in other word ΔH reaction at temperature T is nothing but ΔH_1 plus this part plus ΔH_3 okay which brings the temperature of the product from 298 to the temperature T okay. So now these two parts are basically sensible heat, so we can simply use these two in order to get these two terms in terms of heat capacity.

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The image shows a digital whiteboard with the following handwritten content:

$$C_{p,i} = A_i + B_i T + C_i T^2 + D_i T^{-1} + E_i T^{-2}$$

$$\Delta h_1 = - \int_T^{298} \sum_{\text{reactant } i} \nu_i R C_{p,i} dT = \int_{298}^T R \sum_{\text{reactant } i} \nu_i C_{p,i} dT$$

$$\Delta h_3 = \int_{298}^T R \sum_{\text{prod}} \nu_i C_{p,i} dT$$

$$\Delta h_{rxn,T} = \Delta h_{rxn,298}^{\circ} + \int_{298}^T R \sum \nu_i C_{p,i} dT$$

So let us assume that the heat capacities are given in this following form okay. So this is a of course common terms which are part of many tables where A, B and C and D and these are available for species in numerous books textbook in our textbook also or the reference book which we are considering you will find this in the table. So you can find out delta h1 by simply considering the following $R \sum \nu_i C_{p,i} dt$ okay. So this is your basically R and since this is a product here, so ν_i is negative so we have to make sure this is negative here this is from temperature T to 298 okay.

Now similarly delta h3 is going to be 298 by T again it is going to be (normally) this is for all the species of the reactant, so it should be summation of that okay again we have to say this kind of a reactant and this is going to be product and this is going to be R summation $\nu_i C_{p,i}$ of i dt okay, so that means the h reaction at t is nothing but delta h reaction at 298 plus 298 T okay now if I can also write this expression as 298T I can get rid of a negative sign and this is going to be our $\nu_i C_{p,i} dt$ further reactant okay.

So these two now can be generalized, so you can add it up and then you can get rid of reactor in the product and for all the species I can write R summation $\nu_i C_{p,i} dt$ okay so this becomes my expression to find out the delta h reaction at a given temperature using the delta h reaction as a standard condition plus the sensible heat okay which takes all the species from 298 to a temperature T with appropriate you know ν_i and this terms which are inserted here okay, so this becomes a very straight forward exercise for us mathematically if you have the information.

Now the last part which I want to connect is basically the K relation to the concentration of the reacting species okay, so now we have the information of K to the you know at a different temperature based on the delta h reactions also we can connect to a different temperature, now k are again related to the fugacity so this is something which we need to come up with this.

(Refer Slide Time 33:48)

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K relation with concⁿ of reacting species

Gas phase rxn

$$K = \prod \left(\frac{f_i}{f_i^0} \right)^{\nu_i}$$

$$K = \prod (y_i \phi_i P(\text{bar}))^{\nu_i}$$

$f_i^0 = 1 \text{ bar}$

$f_i = y_i \phi_i P(\text{bar})$

16/34

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$$K = \prod \left(\frac{f_i}{f_i^0} \right)^{\nu_i}$$

$$K = \prod (y_i \phi_i P(\text{bar}))^{\nu_i}$$

a) $\phi_i = \phi_{i, \text{pure}}$

b) $\phi_i = 1$ ideal gas

a) $K = \prod (y_i)^{\nu_i} \prod (\phi_{i, \text{pure}})^{\nu_i} \prod (P^{\nu_i})$

b) $K = \prod (y_i)^{\nu_i} P^{\nu}$ ideal gas

17/34

So now what we are interested is to get this K relation with concentration of reacting species okay because we have done the analysis now what remains is to find out how to relate K to the concentration. So let us consider a standard fugacity at one bar so remember that K is also a function of concentration, so if I consider f_i^0 to be 1 bar okay and for let us say we are considering the only gas phase reaction. Then in that case f_i can be treated as $y_i \phi_i P$ right and since the reference is one bar P has to be in bar.

So I have now $\prod y_i \phi_i P$ at bar $\sum \nu_i$ okay, so that is the K, so usually you need rigorous kind of iterative approach but we can do some approximation okay. For example, I can consider Lewis fugacity rule and consider a for a ϕ_i to be $\phi_{i, \text{pure}}$ okay another one we can consider is that this is ideal gas that ϕ_i is equal to 1 which means this ideal gas, okay.

So that mean I can make use of this expression, so in the case of a I have $K = \prod y_i^{\nu_i} \prod \phi_{i, \text{pure}}^{\nu_i} P^{\sum \nu_i}$ pure $\sum \nu_i$ and $\prod y_i^{\nu_i} P^{\sum \nu_i}$ okay which is nothing but $P^{\sum \nu_i}$, okay. The rest of course remains same but this could be because $\prod \phi_{i, \text{pure}}^{\nu_i} P^{\sum \nu_i}$ is nothing but $P^{\sum \nu_i}$ and B is K is $\prod y_i^{\nu_i} P^{\sum \nu_i}$, okay so this is your ideal gas, okay. So these are the two expression which we can consider as approximation.

Now the other aspect is that we can do the same thing for the gas phase, so for the (gas) for the liquid phase or gaseous phase because we just have to relate ϕ_i (sorry) we just have to relate f_i , f_i for the liquid phase would be related to $X_i \gamma_i f_i^{\text{reference}}$, so something which I will come back to come back to that but let me stop here okay and then I will take up an example to illustrate some what we have just learned to obtain ΔH reactions, to obtain K and then making use of this information to obtain extent of reaction. So let me make use of an example to illustrate what we have learned in last two lectures okay, so for now I will stop here I will see you in the next lecture.