Chemical and Biological Thermodynamics: Principles to Applications
Prof. Nand Kishore
Department of Chemistry and Biochemistry
Indian Institute of Technology, Bombay

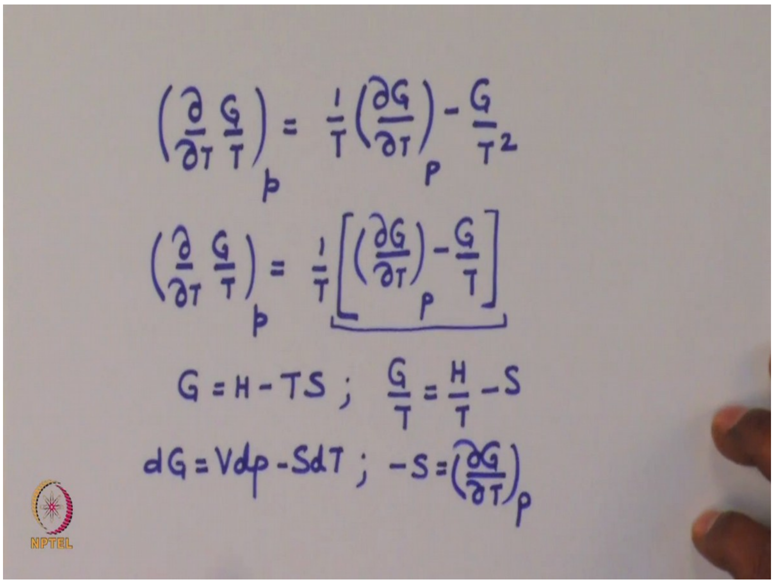
Lecture - 29
Effect of temperature on equilibria

We have been discussing the effect of external disturbances on equilibrium and in the previous lecture we discuss the effect of pressure on equilibrium. We also discuss that catalyst does not affect the equilibrium constant; the effect of catalyst that we discussed was is to only reduce the activation energy. We discussed that if we change the pressure at which the equilibrium is arrived at it does not change the equilibrium constant however, depending upon the stoichiometry of the reactants and products the equilibrium composition may change.

Today we will discuss the effect of temperature on equilibrium; the reactions can be exothermic reactions can be endothermic. Exothermic reactions are the one in which heat is released and endothermic reactions are the one in which the heat is absorbed. The equilibrium constant will change in a different manner when the reaction under consideration is exothermic or endothermic in accordance with Le Chatelier Principle and we will discuss these issues in details in today’s lecture.

We want to discuss the effect of temperature on equilibrium constant and we need to look for a relation which should connect the temperature, the enthalpy and equilibrium constant let us see how to approach this. I will begin with a relation which I have discussed earlier, but it is important to revisit that here again which is.

(Refer Slide Time: 03:12)



$$\left(\frac{\partial}{\partial T}\frac{G}{T}\right)_p = \frac{1}{T}\left(\frac{\partial G}{\partial T}\right)_p - \frac{G}{T^2}$$

$$\left(\frac{\partial}{\partial T}\frac{G}{T}\right)_p = \frac{1}{T}\underbrace{\left[\left(\frac{\partial G}{\partial T}\right)_p - \frac{G}{T}\right]}$$

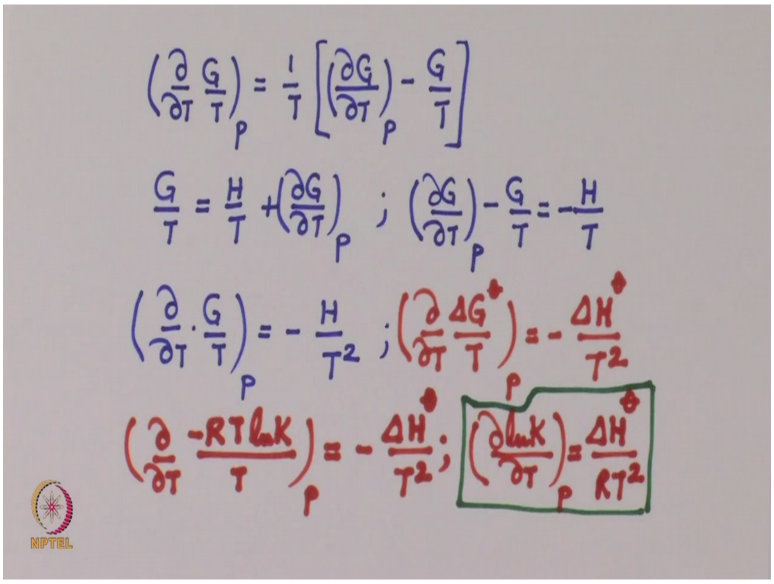
$$G = H - TS \; ; \quad \frac{G}{T} = \frac{H}{T} - S$$

$$dG = Vdp - SdT \; ; \quad -S = \left(\frac{\partial G}{\partial T}\right)_p$$

If I consider the temperature derivative of G by T at constant pressure, this is equal to 1 by T into derivative of G with respect to T at constant pressure minus G by T square or if I write again in a simpler form G by T at constant pressure is equal to 1 by T and here I have this expression.

Now, we need to look for this what is this equal to. G is equal to H minus T S and at from this equation I can write G by T is equal to H by T minus S, and from d G is equal to V d p minus s d T we have minus s is equal to dou G by dou T at constant pressure from this we have discussed earlier. So, what I will do now is.

(Refer Slide Time: 05:16)



$$\left(\frac{\partial}{\partial T}\frac{G}{T}\right)_P = \frac{1}{T}\left[\left(\frac{\partial G}{\partial T}\right)_P - \frac{G}{T}\right]$$

$$\frac{G}{T} = \frac{H}{T} + \left(\frac{\partial G}{\partial T}\right)_P ; \quad \left(\frac{\partial G}{\partial T}\right)_P - \frac{G}{T} = -\frac{H}{T}$$

$$\left(\frac{\partial}{\partial T}\cdot\frac{G}{T}\right)_P = -\frac{H}{T^2} ; \quad \left(\frac{\partial}{\partial T}\frac{\Delta G^{\ominus}}{T}\right)_P = -\frac{\Delta H^{\ominus}}{T^2}$$

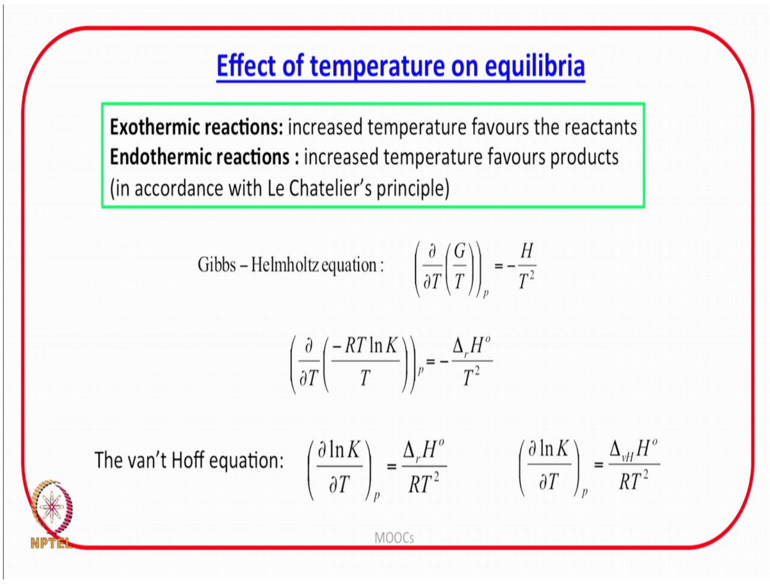
$$\left(\frac{\partial}{\partial T}\frac{-RT\ln K}{T}\right)_P = -\frac{\Delta H^{\ominus}}{T^2} ; \quad \boxed{\left(\frac{\partial \ln K}{\partial T}\right)_P = \frac{\Delta H^{\ominus}}{RT^2}}$$

I have this expression temperature derivative of G by T at constant pressure is equal to 1 by T variation of Gibbs energy with temperature at constant pressure minus G by T ok.

So, we have this expression and further we got that G by T is equal to H by T, and for minus s we have got dou G by dou T at constant pressure. And from this I can write that derivative of G with respect to T at constant pressure minus G by T is equal to minus H by T. Now this can be substituted over here and what I have now is this expression, this was this is Gibbs Helmholtz equation, and if I apply to the changes let us I applied to the reactions then I have temperature derivative of delta G let me put the standard state condition by T at constant pressure is equal to minus delta H naught by T square.

And now what I will do is in place of delta G naught, I will write minus R T log K because delta G naught is minus R T log K by T at constant pressure is equal to minus delta H naught by T square T and T cancel and I can bring r on this side the resulting equation is delta log K by d T or dou T at constant pressure is equal to delta H naught by R T square and I want to discuss this particular equation in details.

(Refer Slide Time: 08:22)



Effect of temperature on equilibria

Exothermic reactions: increased temperature favours the reactants
Endothermic reactions : increased temperature favours products
(in accordance with Le Chatelier's principle)

Gibbs – Helmholtz equation : $\left(\frac{\partial}{\partial T}\left(\frac{G}{T}\right)\right)_p = -\frac{H}{T^2}$

$$\left(\frac{\partial}{\partial T}\left(\frac{-RT\ln K}{T}\right)\right)_p = -\frac{\Delta_r H^o}{T^2}$$

The van't Hoff equation: $\left(\frac{\partial \ln K}{\partial T}\right)_p = \frac{\Delta_r H^o}{RT^2}$ $\left(\frac{\partial \ln K}{\partial T}\right)_p = \frac{\Delta_{vH} H^o}{RT^2}$

MOOCs

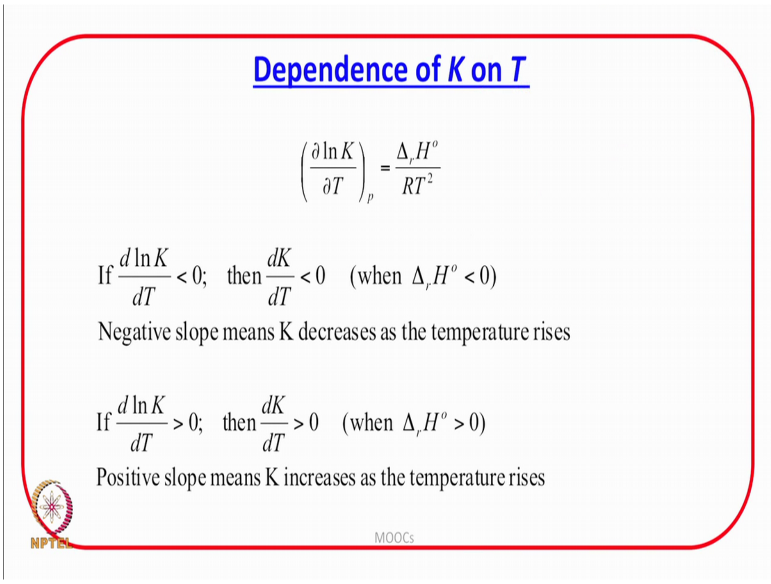
Let us go to the slides now, Le Chatelier principal suggest that for exothermic reactions increased temperature should favour the reactants, and endothermic reaction increased temperature should favour the products that is what is experimentally observed. Because if a given reaction produces lot of heat, then when you increase the temperature according to Le Chatelier principal the equilibrium should shift in such a direction so as to undo the effect of external disturbance.

So, equilibrium constant decreases, I will mathematically prove based upon this Van't Hoff equation what we did was we took Gibbs Helmholtz equation and we converted this two changes for the reaction and came up with this equation and finally, we derive this equation dou log K by dou T at constant pressure is delta H naught by R T square, this is called Van't Hoff equation, this is a very important equation very important result and if you look into research articles then they instead of reaction enthalpy many journals you will find the right this as Van't Hoff enthalpy; because this is enthalpy which is calculated from the temperature dependence of equilibrium constant.

So, this Van't Hoff enthalpy highlights another interesting feature that we need not determine enthalpy of a reaction just by using calorimeters or from the heats, we can actually determine the value of enthalpy of a reaction if we know how the equilibrium constant depends upon temperature. Take a look at this Van't Hoff equation in this slide; according to this equation if I know how log K varies with temperature I can evaluate the value of enthalpy of reaction the question is how do you determine the value of equilibrium constant. Equilibrium constant determination is a different matter because what you need is you need the activities or concentrations or molalities of the products and reactance at equilibrium, how you determine those concentrations on molality is a different matter, because it depends on the properties of the material, one can use spectroscopic method to get and value of equilibrium constant, one can get H p l c to get a value of equilibrium constant, but there are several methods we can get the value of equilibrium constant.

The point is that if we can determine equilibrium constant at different temperatures, we can get enthalpy by using Van’t Hoff equation.

(Refer Slide Time: 12:07)



Dependence of K on T

$$\left(\frac{\partial \ln K}{\partial T}\right)_p = \frac{\Delta_r H^o}{RT^2}$$

$$\text{If } \frac{d\ln K}{dT} < 0; \quad \text{then} \frac{dK}{dT} < 0 \quad (\text{when } \Delta_r H^o < 0)$$

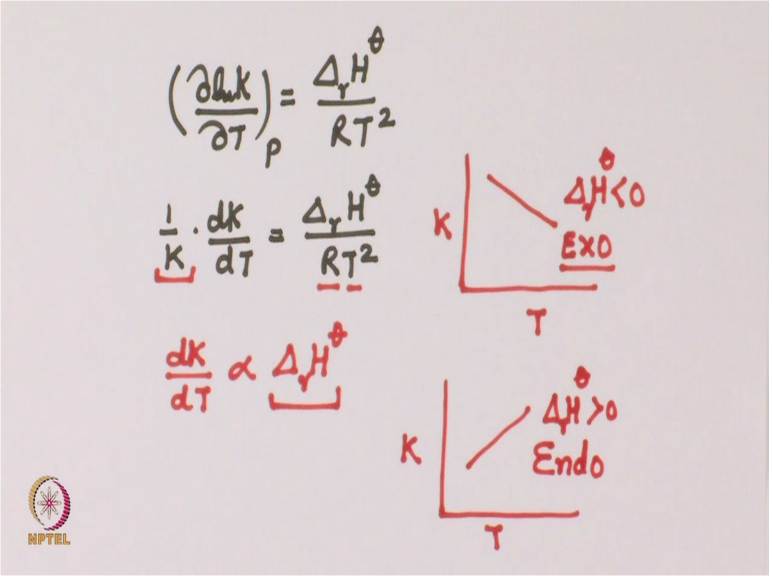
Negative slope means K decreases as the temperature rises

$$\text{If } \frac{d\ln K}{dT} > 0; \quad \text{then} \frac{dK}{dT} > 0 \quad (\text{when } \Delta_r H^o > 0)$$

Positive slope means K increases as the temperature rises

Let us continue our discussion on equilibrium constant dependence on temperature; we have just derived this equation Van’t Hoff equation. So, let me rewrite Van’t Hoff equation over here.

(Refer Slide Time: 12:37)



$$\left(\frac{\partial \ln K}{\partial T}\right)_p = \frac{\Delta_r H^\ominus}{RT^2}$$

$$\underbrace{\frac{1}{K}}_{}\cdot\frac{dK}{dT} = \frac{\Delta_r H^\ominus}{\underline{RT^2}}$$

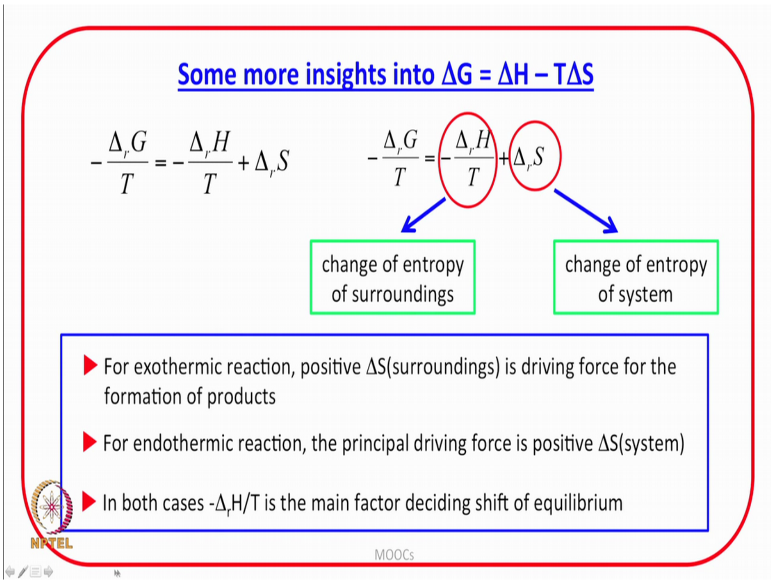
$$\frac{dK}{dT} \propto \underbrace{\Delta_r H^\ominus}_{}$$

According to Van’t Hoff equation derivative of log K with respect to T at constant pressure is delta r H naught by R T square. I can write this as 1 by K d K by d T at constant pressure of course, will be equal to delta r H naught by R T square.

Now, K is a positive quantity it cannot be negative quantity, R is a constant and T, T square will depend upon what temperature is given. So, at a constant temperature at a given temperature T square will be a constant. So, therefore, d K by d T is proportional to the value of the enthalpy of reaction and if the value of enthalpy of reaction is negative; that means, the slope of a plot of K verses T will be negative for example, if I plot K verses T and I get a behaviour like this, this is a negative slope; that means, in this case delta r H naught is less than 0 it is an exothermic reaction; and on the other hand if delta r H naught is positive endothermic reaction, in that case this are just the approximate plots K verses T if the variation is like this the slope is positive; that means, I have delta r H naught which is positive and this is endothermic reaction.

Let us go to the slide, this is what I discussed that if d log K by d T or d K by T d T whatever way you want to consider is less than 0 or d K by d T less than zero; that means, this is true for exothermic reaction as you can see from this negative slope means K decreases as the temperature rises. And on the other side on the other hand if the plot of d K by d T gives a positive slope. That means, the reaction is endothermic and positive slope means K increases has the temperature rises, and that is what I discussed in the beginning that these observations are in accordance with the Le Chatelier Principle.

(Refer Slide Time: 16:00)



Some more insights into $\Delta G = \Delta H - T\Delta S$

$$-\frac{\Delta_r G}{T} = -\frac{\Delta_r H}{T} + \Delta_r S$$

$$-\frac{\Delta_r G}{T} = -\frac{\Delta_r H}{T} + \Delta_r S$$

change of entropy of surroundings

change of entropy of system

- For exothermic reaction, positive ΔS(surroundings) is driving force for the formation of products
- For endothermic reaction, the principal driving force is positive ΔS(system)
- In both cases $-\Delta_r H/T$ is the main factor deciding shift of equilibrium

Let us get some more insights into delta G delta H and T delta S. Let me write this equation delta G equal to delta H minus T delta s as minus delta G by T is equal to minus delta H by T plus delta S, I have just rearranged this equation into this form. Now what are these this delta S is the entropy change for the system, and if there is a thermal equilibrium between system and surrounding and delta H is the enthalpy change for the system for the surrounding it is going to be minus delta H, because any change for the system will be equal to minus of that change for the surrounding as long as there is a thermal equilibrium.

So, therefore, let us go to slide if this is identified as change of entropy of the system this is identified as change of entropy of the surroundings; that means, in one sense this minus delta r G by T represents the global entropy change that means, entropy change of the system plus entropy change of the surrounding. So, there is a lot of hidden meaning into this equation we can discuss the effect of temperature based upon this equation also, but in a qualitative manner.

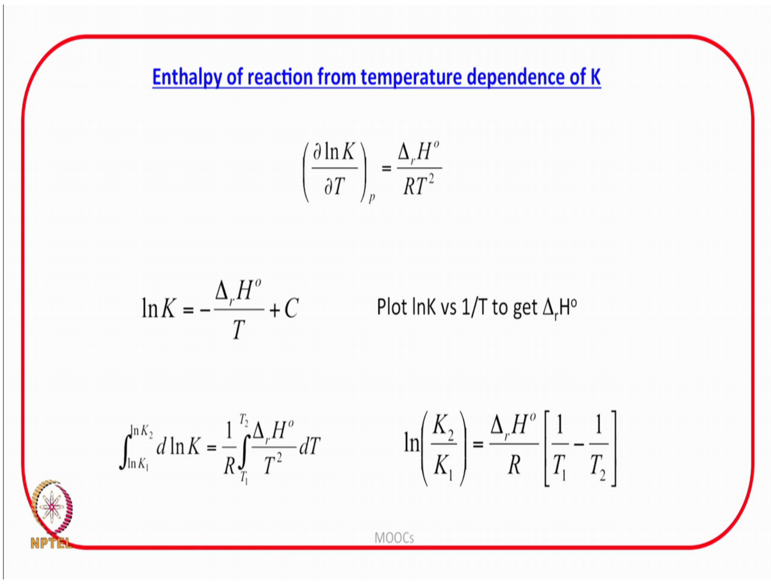
Let us first considered an exothermic reaction; when a reaction is exothermic the heat is given out, if the heat is given out that means, entropy of the system decreases and if the entropy of the system decreases we have many times discuss that the entropy of surroundings must be must increase and also if we look at in the slide that minus delta r H by T term if reaction is exothermic delta H is going to be negative and overall value is going to be positive, and that is what is commented over here for exothermic reaction positive delta s surrounding is the driving force for the formation of products right.

So, what we have discussed is for an exothermic reaction, the increase in entropy of the surrounding is one of the major driving force for the formation of product. And now if you lets go back to again slide if we look at this surroundings part the temperature comes in the denominator and therefore, when you increase the temperature the favourable contribution increase in entropy of the surrounding is a favourable contribution that goes down, the positive delta s surroundings which we identified as the major driving force for the formation of products as temperature is increased since temperature comes in the denominator this contribution goes down and therefore, the equilibrium should shift in the opposite direction; that means, the value of equilibrium constant must go down.

Now, let us discuss for endothermic reaction; endothermic reaction means is heat is absorbed and if heat is absorbed obviously, the entropy of the system will increase the delta s for the system will be positive and that is what is commented over here that is for endothermic reaction the principal driving force is positive delta s of the system. And in the same way if we now look at the surroundings part if delta H is positive, then minus this minus delta H by T term is negative once again if delta H is positive then minus delta H by T is negative quantity; that means, there is an unfavourable contribution from entropy change in the surrounding; and as temperature is increased this unfavourable contribution goes down and that drives the formation of products more products.

So, we found that in case of exothermic reaction delta s surrounding is the major driving force, in case of endothermic reaction delta s surrounding is an unfavourable contribution and this unfavourable contribution goes down when the temperature is increased therefore, as commented in the next sentence in both the cases minus delta r H by T is the main factor deciding the shift in equilibrium. So, qualitatively we have discussed that how the entropy change in the system and entropy change in the surroundings are linked with the equilibrium or equilibrium constant, and how the temperature effect can be explained.

(Refer Slide Time: 22:52)



Enthalpy of reaction from temperature dependence of K

$$\left(\frac{\partial \ln K}{\partial T}\right)_p = \frac{\Delta_r H^o}{RT^2}$$

$$\ln K = -\frac{\Delta_r H^o}{T} + C$$

Plot lnK vs 1/T to get $\Delta_r H^o$

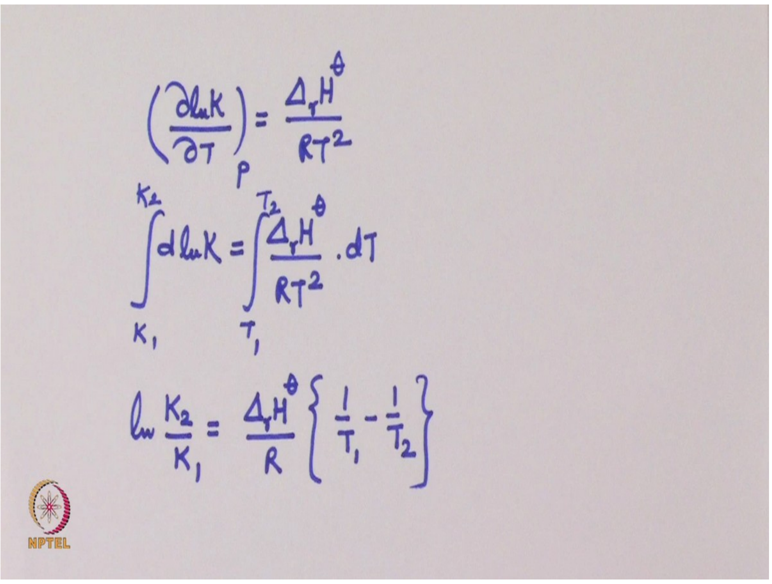
$$\int_{\ln K_1}^{\ln K_2} d\ln K = \frac{1}{R}\int_{T_1}^{T_2} \frac{\Delta_r H^o}{T^2} dT$$

$$\ln\left(\frac{K_2}{K_1}\right) = \frac{\Delta_r H^o}{R}\left[\frac{1}{T_1} - \frac{1}{T_2}\right]$$

MOOCs

Let us discuss more about the enthalpy of reaction from temperature dependence of K and Van’t Hoff equation we just discuss that we can determine enthalpy from temperature dependence of K a little more detail we can discuss, what we have is variation of K with temperature at constant pressure is equal to delta r H naught by R T square.

(Refer Slide Time: 23:21)



$$\left(\frac{\partial \ln K}{\partial T}\right)_P = \frac{\Delta_r H^\ominus}{RT^2}$$

$$\int_{K_1}^{K_2} d\ln K = \int_{T_1}^{T_2} \frac{\Delta_r H^\ominus}{RT^2} . dT$$

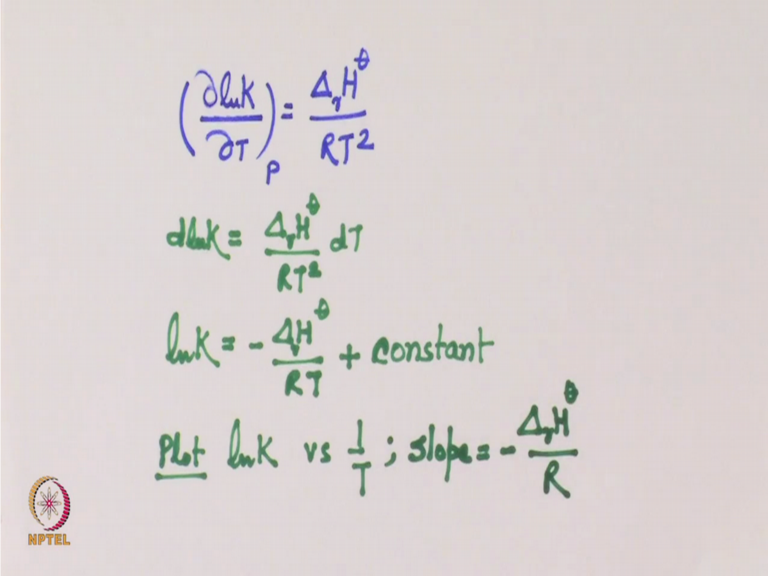
$$\ln \frac{K_2}{K_1} = \frac{\Delta_r H^\ominus}{R} \left\{ \frac{1}{T_1} - \frac{1}{T_2} \right\}$$

And if you permit me to write like this d log K is equal to delta r H naught by R T square into d T, and then I integrate from the limits let us say here from K 1 to K 2 and T 1 to T

2 then what will I get, I will get log K 2 by K 1 is equal to delta r H naught by r into 1 over T 1 minus 1 over T 2 after you solve the integral and substitute the values of T 1 and T 2. This is one way here we are assuming that enthalpy of reaction is independent of temperature. So, we are taking it out otherwise we cannot ignore the heat capacity terms and those things we will take up while solving the numerical problems.

However, if the enthalpy does not change over a small temperature range we can use this equation, if we know the value of equilibrium constant at two temperatures we can calculate the value of delta H naught this is one way.

(Refer Slide Time: 25:30)



$$\left(\frac{\partial \ln K}{\partial T}\right)_P = \frac{\Delta_r H^\ominus}{RT^2}$$

$$d\ln K = \frac{\Delta_r H^\ominus}{RT^2}\, dT$$

$$\ln K = -\frac{\Delta H^\ominus}{RT} + \text{constant}$$

Plot $\ln K$ vs $\frac{1}{T}$; slope $= -\frac{\Delta_r H^\ominus}{R}$

Then I again go back to Van’t Hoff equation, which is d log K by d T at constant pressure is equal to delta r H naught by R T square and d log K is equal to delta r H naught by R T square d T or if I just integrate is minus delta H naught by R T plus a constant. So, what we need to do is plot log K verses 1 by T. Once you plot log K verses 1 by T then you will have slope will be equal to minus delta r H naught by R this is what you are going to get.

Let us go back to the slides this is one method that I discuss that you plot log K verses 1 by T and what we will get is from the slope we can get delta H naught and similarly you can do and integration within the limits and get a value of delta H naught from here. So, one is from log K is equal to minus delta r H naught divided by R T then it should be r over here, and second is if the enthalpy it does not depend upon temperature for a short range you can take it out of integral and use the two values of k.

So, what we discussed in this lecture is how temperature affects the equilibrium. In accordance with the Le chattier principal for exothermic reaction increased temperature favours reactance, for endothermic reaction increased temperature favours products; that means, the equilibrium constant will accordingly increase or decrease depending upon whether the reaction is endothermic or exothermic. We also discussed in a qualitative manner that what could be the possible reasons for this increase and decrease, and this we could connect with the entropy changes in the system and entropy changes in the surrounding; then we derive the Van't Hoff equation which is a very important result, because it allows evaluation of enthalpy of a reaction from the knowledge of equilibrium constant.

We will discuss several numerical problems based upon the temperature and pressure dependence of equilibrium constant in the tutorial session.

Thank you very much.