Chemical and Biological Thermodynamics: Principles to Applications

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Lecture - 31
Tutorial-1
equilibrium constant

In this lecture we will discuss numerical problems based on equilibrium constant and equilibria in various processes. As I have repeatedly emphasized on the significance of equilibrium constant, it is importance in academics as well as in industry and therefore, it becomes very, very important to see how to deal with different situations when it comes to optimization of the processes, and deciding the conditions which are most suitable for getting a maximum yield.

So, let us discuss a variety of numerical problems in this lecture as an example.

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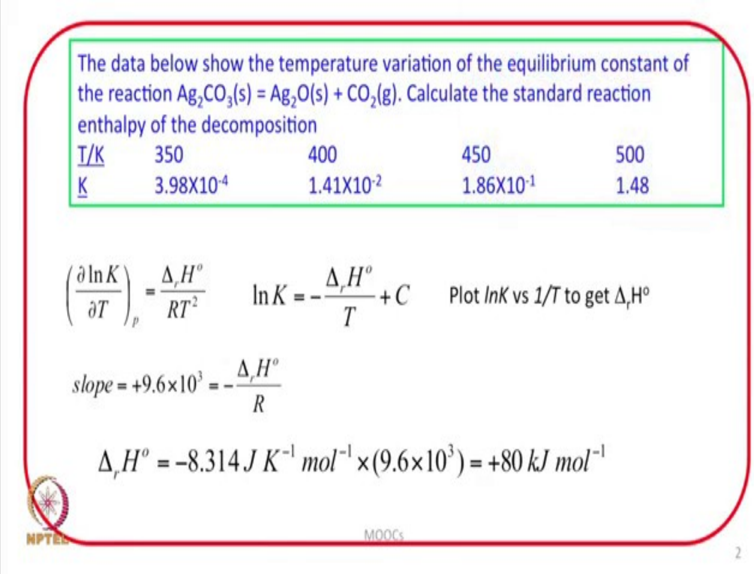

The data below show the temperature variation of the equilibrium constant of the reaction $Ag_2CO_3(s) = Ag_2O(s) + CO_2(g)$. Calculate the standard reaction enthalpy of the decomposition

T/K	350	400	450	500
K	$3.98\text{X}10^{-4}$	$1.41\text{X}10^{-2}$	$1.86\text{X}10^{-1}$	1.48

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

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

$$slope = +9.6\times10^3 = -\frac{\Delta_r H^o}{R}$$

$$\Delta_r H^o = -8.314\,J\,K^{-1}\,mol^{-1}\times(9.6\times10^3) = +80\,kJ\,mol^{-1}$$

The first one is the data shown below the data below show the temperature variation of the equilibrium constant of the reaction silver carbonate solid forming silver oxide plus carbon dioxide. Calculate the standard reaction enthalpy of the decomposition. Temperature in Kelvin is given. And the value of equilibrium constant at these temperatures is also given.

Let us carefully look at the information given. The given reaction is this decomposition reaction of silver carbonate. And we have the information on temperature dependence of equilibrium constant. We have been asked to calculate the standard reaction enthalpy. So, immediately we should think of some relation which connects the temperature dependence of equilibrium constant with enthalpy. And this equation is the well known Vant Hoff equation.

Let us see; what is Vant Hoff equation.

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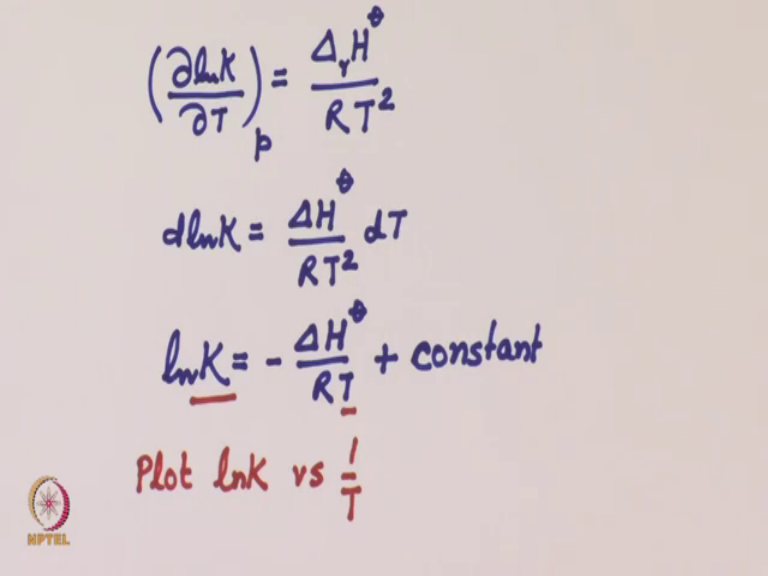

$$\left(\frac{\partial \ln K}{\partial T}\right)_p = \frac{\Delta_r H^\ominus}{RT^2}$$

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

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

Plot $\ln K$ vs $\frac{1}{T}$

It is d log K by d T at constant pressure is equal to reaction enthalpy by R T square and since we have been given information on the temperature dependence of equilibrium constant. And we have been given at least 4 temperatures. So therefore, what I will do is I will write this equation in this form d log K is equal to delta H naught by R T square T dT and perform an integration. What I will have is log K is minus delta H naught by R T plus a constant. As we have discussed during the lecture this equation we have discussed during the lecture. Now what we have been given is the value of K at different temperature.

So, what we will do is we will plot log K against 1 by T and; obviously, when you plot log K against 1 by T minus delta H naught by R is the slope. One thing to be remembered while we are solving this type of question is that we have to know whether the reaction enthalpy depends upon temperature or not. Usually when the temperature range is small we safely assume that the reaction enthalpy is independent of temperature.

Now, let us look at the equation that we derived over here, when I integrated this equation I assumed here that delta H naught does not depend upon temperature. Now let us go to the slide and recognize the significance importance of this famous this very important equation, Vant Hoff equation. And as I just discussed and integrated form of Vant Hoff equation can be written as log K is equal to minus delta H naught by T plus constant. And we plot log K versus 1 by T to get delta H naught as I just discussed that if I plot log K versus 1 by T there has to be R over here.

So, the slope is going to be minus delta R H naught by R. Please note down there is R here in the denominator. And now you rearrange and substitute the value of R as 8.314 joules per Kelvin per mole the overall value comes out to be plus 80 kilojoules per mole. The standard reaction enthalpy is coming out to be plus 80 kilo joules per mole.

Let us comment on this plus, plus means reaction is endothermic if the reaction is endothermic, then according to le chatelier principal. If we increase the temperature the value of equilibrium constant should also increase. And let us see whether the given data is in accordance with this. What we see here is when the temperature is changed from 350 to 500 Kelvin; the value of equilibrium constant increases from 3.98 into 10 is to power minus 4 to 1.48. So, this is an accordance with le chatelier principal. Since the K value is increasing with temperature therefore, the reaction must be endothermic and that is what we found out.

Now let us discuss another type of question.

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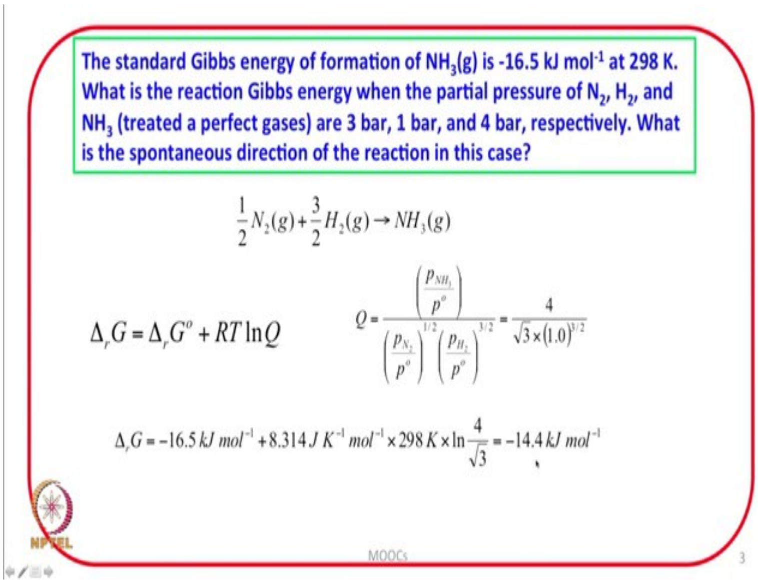

The standard Gibbs energy of formation of $NH_3(g)$ is -16.5 kJ mol^{-1} at 298 K. What is the reaction Gibbs energy when the partial pressure of N_2, H_2, and NH_3 (treated a perfect gases) are 3 bar, 1 bar, and 4 bar, respectively. What is the spontaneous direction of the reaction in this case?

$$\frac{1}{2}N_2(g)+\frac{3}{2}H_2(g)\rightarrow NH_3(g)$$

$$\Delta_r G=\Delta_r G^o+RT\ln Q \qquad Q=\frac{\left(\frac{p_{NH_3}}{p^o}\right)}{\left(\frac{p_{N_2}}{p^o}\right)^{1/2}\left(\frac{p_{H_2}}{p^o}\right)^{3/2}}=\frac{4}{\sqrt{3}\times(1.0)^{3/2}}$$

$$\Delta_r G=-16.5\,kJ\,mol^{-1}+8.314\,J\,K^{-1}\,mol^{-1}\times 298\,K\times\ln\frac{4}{\sqrt{3}}=-14.4\,kJ\,mol^{-1}$$

The question is the standard Gibbs energy of formation of Ammonia is minus 16.5 kilo joules per mole at 298 Kelvin. What is the reaction Gibbs energy when the partial pressure of nitrogen, hydrogen and ammonia treated as perfect gases are 3 bar 1 bar and 4 bar respectively. What is the spontaneous direction of the reaction in this case?

Once again let us see what is the given information. The given information is that we are given the standard Gibbs energy of formation of Ammonia, which is minus 16 kilo joules per mole. And we are also given the partial pressures of nitrogen hydrogen and ammonia and we have been asked that treat these gases as perfect gases. The partial pressures of nitrogen hydrogen and ammonia are 3 1 and 4 bar respectively.

So, at this composition we have to find out whether the reaction will be spontaneous or not. This spontaneous nature of a process will be predicted by the value of reaction Gibbs energy. If the reaction Gibbs energy or delta G at constant pressure and temperature turns out to be negative, then there action is spontaneous in the forward direction.

In the context of given question, let us see what information do we have. And how do we uses it. Formation of Ammonia can be written As half nitrogen gas plus 3 by 2 hydrogen gas forms NH 3.

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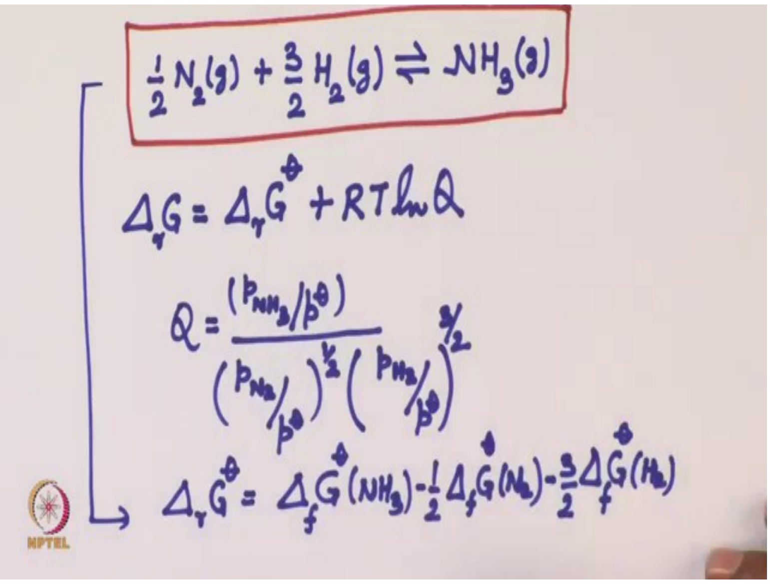

$$\boxed{\frac{1}{2}N_2(g) + \frac{3}{2}H_2(g) \rightleftharpoons NH_3(g)}$$

$$\Delta_r G = \Delta_r G^{\ominus} + RT\ln Q$$

$$Q = \frac{(p_{NH_3}/p^{\ominus})}{(p_{N_2}/p^{\ominus})^{1/2}(p_{H_2}/p^{\ominus})^{3/2}}$$

$$\Delta_r G^{\ominus} = \Delta_f G^{\ominus}(NH_3) - \frac{1}{2}\Delta_f G^{\ominus}(N_2) - \frac{3}{2}\Delta_f G^{\ominus}(H_2)$$

For this reaction I can write reaction Gibbs energy is equal to delta R G naught plus R T log Q. And Q will be equal to partial pressure of NH 3 by P naught divided by partial pressure of nitrogen by P naught raise to the power 1 by 2 into partial pressure of hydrogen by P naught raise to the power 3 by 2.

Since we are given the information that you treat these gases are ideal gases therefore, I am using the pressures instead of a gas it is. And now we have been given the partial pressures of ammonia we have been given the partial pressure values of nitrogen and hydrogen, which we can substitute in this and find out whether delta R G turns out to be positive or negative.

Let us see what do we get we go back to the slide. This is the given reaction half nitrogen plus 3 by 2 hydrogen forming ammonia, and we have discussed that the Q the value of Q is going to decide the value of delta R G. Because delta R G naught at a given temperature is constant. That information is given we are given that we have been given that delta R G naught. In fact, if you look at the given information is standard Gibbs energy of formation, and from the standard given energy a given standard Gibbs energy of formation for this reaction, I can write delta R G naught is equal to free energy of formation of NH 3 minus half free energy of formation of nitrogen minus 3 by 2 free energy of formation of hydrogen. Nitrogen and hydrogen being elements their free energy of formation is zero.

Therefore the standard reaction Gibbs energy is equal to the Gibbs energy of formation of Ammonia. And that information we can substitute in the slide over here. We define Q as P by P naught of ammonia divided by P by P naught of nitrogen raise to the power 1 by 2 into P by P naught of hydrogen raise to power 3 by 2. We substitute the numbers the given partial pressures are 4 ammonia it is 4 for nitrogen it is 1 and for hydrogen for nitrogen it is 3 and for hydrogen it is 1. Once you substitute you have the value of Q.

Now, I will substitute the values of delta R G naught and Q into this equation delta is delta G is equal to delta G naught plus R T log Q. The value comes out to be minus 14.4 kilo joules per mole. See delta R G R G reaction Gibbs energy is turning out to be negative. Reaction Gibbs energy is actually the slope of Gibbs energy against the extent of reaction and if the slope if the slope is negative; that means, the reaction in the forward direction is spontaneous.

So therefore, since we are talking about this particular reaction, then under the given conditions the reaction will move towards the right hand side; that means, more ammonia will be formed. And that is what is commented upon in this slide let us take a look at.

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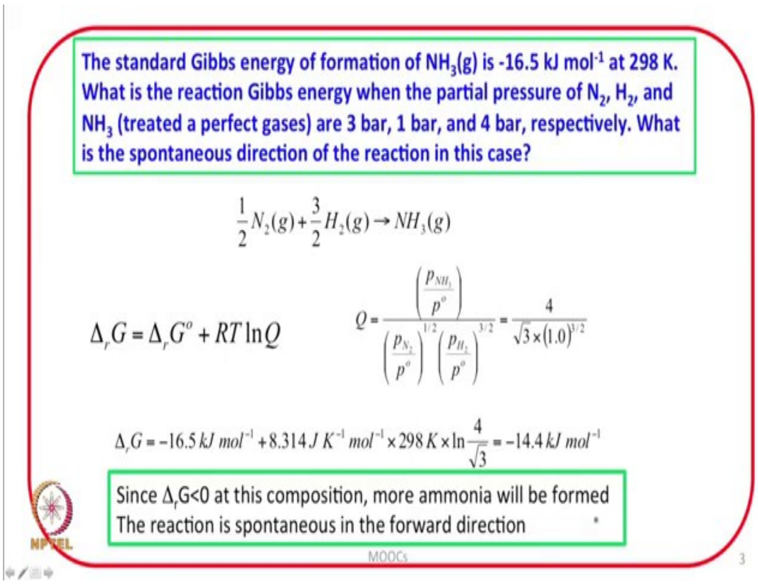

The standard Gibbs energy of formation of $NH_3(g)$ is -16.5 kJ mol^{-1} at 298 K. What is the reaction Gibbs energy when the partial pressure of N_2, H_2, and NH_3 (treated a perfect gases) are 3 bar, 1 bar, and 4 bar, respectively. What is the spontaneous direction of the reaction in this case?

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$$\Delta_r G=-16.5\,kJ\,mol^{-1}+8.314\,J\,K^{-1}\,mol^{-1}\times 298\,K\times\ln\frac{4}{\sqrt{3}}=-14.4\,kJ\,mol^{-1}$$

Since $\Delta_r G<0$ at this composition, more ammonia will be formed
The reaction is spontaneous in the forward direction

Since delta G is less than 0 at this composition more ammonia will be formed; that means, the reaction is spontaneous in the forward direction.

Now let us take a look at another question.

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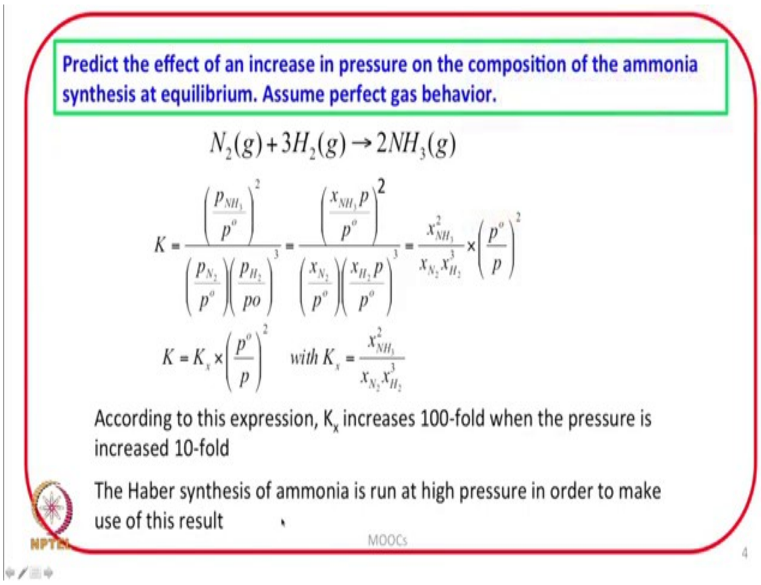

Predict the effect of an increase in pressure on the composition of the ammonia synthesis at equilibrium. Assume perfect gas behavior.

$$N_2(g)+3H_2(g)\rightarrow 2NH_3(g)$$

$$K=\frac{\left(\frac{p_{NH_3}}{p^o}\right)^2}{\left(\frac{p_{N_2}}{p^o}\right)\left(\frac{p_{H_2}}{po}\right)^3}=\frac{\left(\frac{x_{NH_3}p}{p^o}\right)^2}{\left(\frac{x_{N_2}}{p^o}\right)\left(\frac{x_{H_2}p}{p^o}\right)^3}=\frac{x_{NH_3}^2}{x_{N_2}x_{H_2}^3}\times\left(\frac{p^o}{p}\right)^2$$

$$K=K_x\times\left(\frac{p^o}{p}\right)^2 \quad with\ K_x=\frac{x_{NH_3}^2}{x_{N_2}x_{H_2}^3}$$

According to this expression, K_x increases 100-fold when the pressure is increased 10-fold

The Haber synthesis of ammonia is run at high pressure in order to make use of this result

Predict the effect of an increase in pressure on the composition of the ammonia synthesis at equilibrium. Assume perfect gas behavior. Synthesis of ammonia is very important industrially. Well known habers process is used. And in this question we have been asked to predict what will be the effect on the composition of Ammonia synthesis when the pressure is increased.

So, in order to discuss the effect of pressure on the composition, first I will write the equation.

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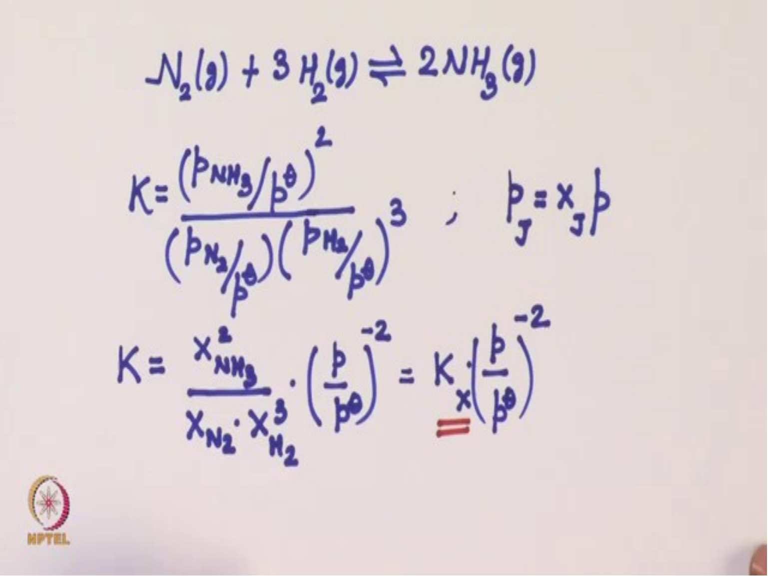

$$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$$

$$K = \frac{(p_{NH_3}/p^\theta)^2}{(p_{N_2}/p^\theta)(p_{H_2}/p^\theta)^3} \quad ; \quad p_J = x_J p$$

$$K = \frac{x_{NH_3}^2}{x_{N_2} \cdot x_{H_2}^3} \cdot \left(\frac{p}{p^\theta}\right)^{-2} = \underline{\underline{K_x}} \left(\frac{p}{p^\theta}\right)^{-2}$$

Nitrogen plus 3 hydrogen it forms 2 and H 3 gas. I can write 1 by 2 3 by 2 whatever way you write the actual or final answer is going to be same. We have to find out what is the effect of pressure. As a first step I will write an expression for K. K will be equal to partial pressure of ammonia by P naught raise to the power 2 divided by partial pressure of nitrogen by P naught, into partial pressure of hydrogen by P naught raise to the power 3, and since we have been asked to find out the effect of increasing pressure the total pressure.

Let us see which equation we can use which connects the partial pressure with the total pressure. And from elementary chemistry we remember that Dalton’s law of partial pressure can be used; that means, partial pressure of any substance J will be equal to the mole fraction of J into the total pressure. That is from Dalton’s law of partial pressure. We will use this information over here, and what we will have is once you put instead of p you put mole fraction into the total pressure, I will have mole fraction of Ammonia raise to the power 2 over mole fraction of nitrogen into mole fraction of hydrogen raise to the power 3, and pressure term is also there. So, it will be P by P naught raise to the power 2 minus 1 minus 3, that is 2 minus 4 is minus 2.

Can I write this ratio, I will write as K x. That is a ratio of the mole fractions, into total pressure divide by P naught which is 1 bar raise to the power minus 2. The effect of pressure on composition is given by K x, because K x is the ratio of mole fractions. Now let us go to the slides. We took an example of this formation of Ammonia from nitrogen and hydrogen, and we express equilibrium constant in terms of the ratio of the partial pressures, converted into the product of mole fraction and the total pressure and eventually came up with an expression that K is equal to K x into P naught by P raise to the power 2. And actually here if you look at what I showed here is K is equal to K, k x into P by P naught raise to the power minus 2, which is same as P naught by P raise to the power 2.

Now, if we look at this slide according to this equation, if I increase the pressure 10 times, since K x does not depend on pressure K x is a constant at a given temperature. P will go on the other side and it goes as a square. So, 10 times increasing pressure will increase the value of K x by 10 fold; that means, it will become 100 10 will become 100 sorry, it will become 100 fold since P become P goes when you take P to the other side it is a P squared term.

So, if you increase the pressure by 10 fold, K x will increase by 100 fold, and K x you see K x is the ratio of the mole fractions of ammonia and the reactants. So, if K x increases; that means, the production of Ammonia increases. And that is why is you see the comment over here the Haber synthesis of ammonia is run at high pressure in order to make use of this result.

So, this example very clearly demonstrates the effect of pressure on the equilibrium composition. But let us derive a general expression which explains the effect or which connects the effect of pressure on equilibrium constant, which is actually equilibrium constant is independent of pressure, but we need to talk about is K x.

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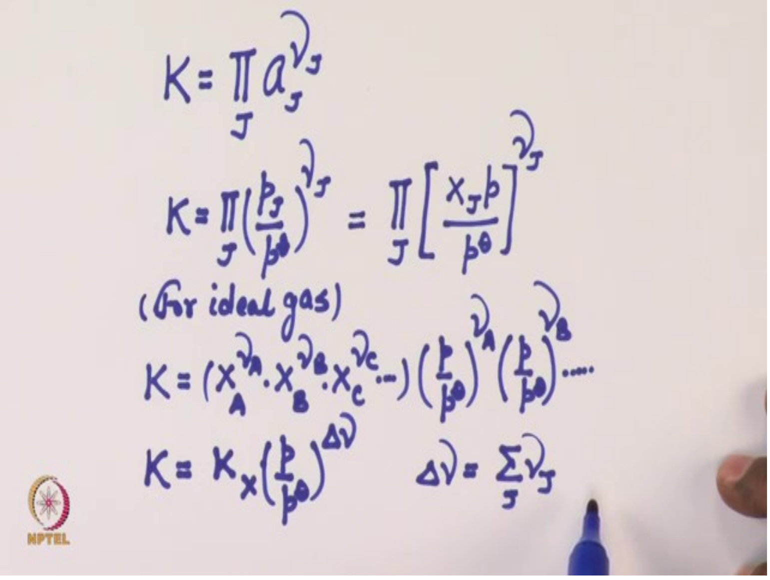

$$K = \prod_J a_J^{\nu_J}$$

$$K = \prod_J \left(\frac{p_J}{p^\ominus}\right)^{\nu_J} = \prod_J \left[\frac{x_J p}{p^\ominus}\right]^{\nu_J}$$

(for ideal gas)

$$K = (x_A^{\nu_A} . x_B^{\nu_B} . x_C^{\nu_C} ..)\left(\frac{p}{p^\ominus}\right)^{\nu_A}\left(\frac{p}{p^\ominus}\right)^{\nu_B} .....$$

$$K = K_x\left(\frac{p}{p^\ominus}\right)^{\Delta\nu} \qquad \Delta\nu = \sum_J \nu_J$$

K let me write down now general thing.

K is a product of activities, this is general definition of K. And for perfect gases I can write P J by P naught raise to the power nu J. Because we have discussed activity for a perfect gas can be replaced by P by P naught for ideal gas. And as I just discussed let me, instead of partial pressure let me write mole fraction of J into total pressure P naught raise to the power nu j.

Now, K I can write as, now when I expand this I will expand separately for mole fraction and separately for P by P naught. It will be mole fraction of A raise to the power nu A into mole fraction of B raise to the power nub into mole faction of C raise to the power nu C etcetera, in to P by P naught raise to the power nu A P by P naught raise to the power nu B etcetera. All I can write K is equal to K x in to P by P naught raise to the power delta nu. Where delta nu is equal to summation J nu J and this stoichiometric number is positive for products and negative for reactant.

So, if we carefully examine this and we put positive sign for the product, and negative sign with the stoichiometric number for the reactant it actually is the ratio, it is actually is the ratio of the mole fraction product of mole fractions of the products raise to the power by their appropriate stoichiometric number divided by the product of mole fractions of the reactant. So this actually is K x K is equal to K x into P by P naught raise to the power delta nu and since if you combine all these p by P naught these powers will be added. We have to put negative sign with the stoichiometric numbers for the reactance and positive sign for the stoichiometric number of the products, and overall sum is actually a difference between the number of moles of gaseous product and the number of moles of gaseous reactants.

So, let us now go back to the slide, we want to talk about the relation between K and K x.

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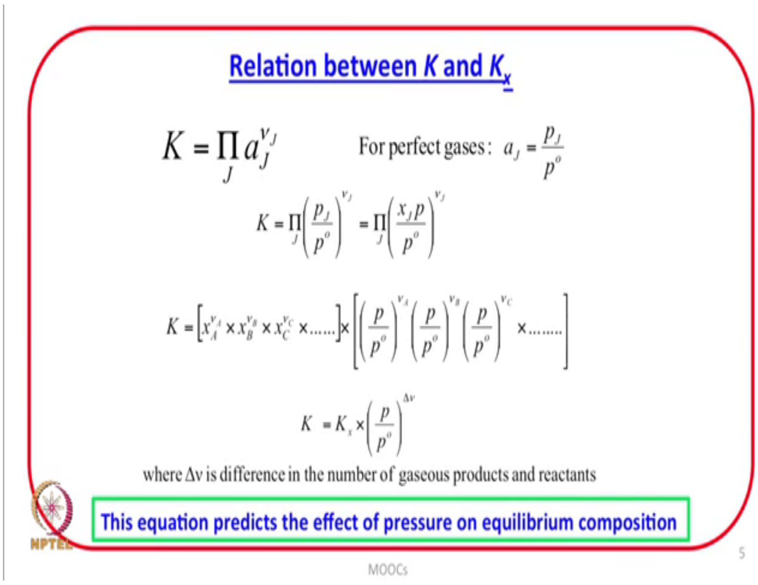

Relation between *K* and K_x

$$K = \prod_J a_J^{\nu_J} \qquad \text{For perfect gases: } a_J = \frac{p_J}{p^o}$$

$$K = \prod_J \left(\frac{p_J}{p^o}\right)^{\nu_J} = \prod_J \left(\frac{x_J p}{p^o}\right)^{\nu_J}$$

$$K = \left[x_A^{\nu_A} \times x_B^{\nu_B} \times x_C^{\nu_C} \times \ldots\ldots\right] \times \left[\left(\frac{p}{p^o}\right)^{\nu_A} \left(\frac{p}{p^o}\right)^{\nu_B} \left(\frac{p}{p^o}\right)^{\nu_C} \times \ldots\ldots\right]$$

$$K = K_x \times \left(\frac{p}{p^o}\right)^{\Delta\nu}$$

where Δv is difference in the number of gaseous products and reactants

This equation predicts the effect of pressure on equilibrium composition

And I have just discussed this entire derivation and we came up with this expression K is equal to K x in to P by P naught delta nu, where delta nu is the difference in number of gaseous products and reactants. And this equation predicts the effect of pressure on equilibrium composition.

Elementary text books described the relationship between K P and K C.

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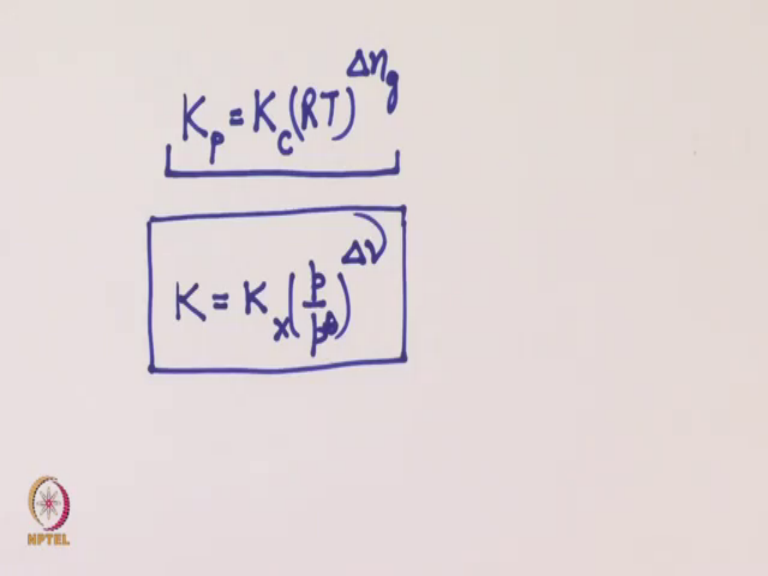

$$\underline{K_p = K_c(RT)^{\Delta n_g}}$$

$$\boxed{K = K_x\left(\frac{p}{p^{\circ}}\right)^{\Delta \nu}}$$

K P is equal to K C in to R T a raise to the power delta n G. It works out well, but you know the K P is expressed as the ratio of pressures K C is expressed as the ratio of concentrations. And this although this equation works, but if you look at the unit is on each side it runs into trouble.

Therefore this expression K is equal to K x into P by P naught raise to the power delta n G or you can put delta nu delta nu is same as delta n G, it does not run into any units problem. And this equation very clearly connects the K x with the pressure, what will be the effect of pressure on the equilibrium composition. K remains constant with pressure it is K x which changes.

So, I hope that these numerical problems have brought out the meaning of equilibrium constant and the effect of pressure on equilibrium constant in a more clearer manner. In the next tutorial we will discuss the effect of temperature and few more problems to make an understanding of equilibrium and equilibrium constant still better.

Thank you very much.