Chemical and Biological Thermodynamics: Principles to Applications
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Lecture - 28
Effect of pressure on equilibrium constant and equilibrium composition

In this lecture we will discuss the effect of pressure on equilibrium constant and equilibrium composition. However, before I discuss the effect of external disturbances on equilibrium constant, let us be first clear about the difference between thermodynamic equilibrium constant and practical equilibrium constant. Usually we call thermodynamic equilibrium constant which is the ratio of activities that means.

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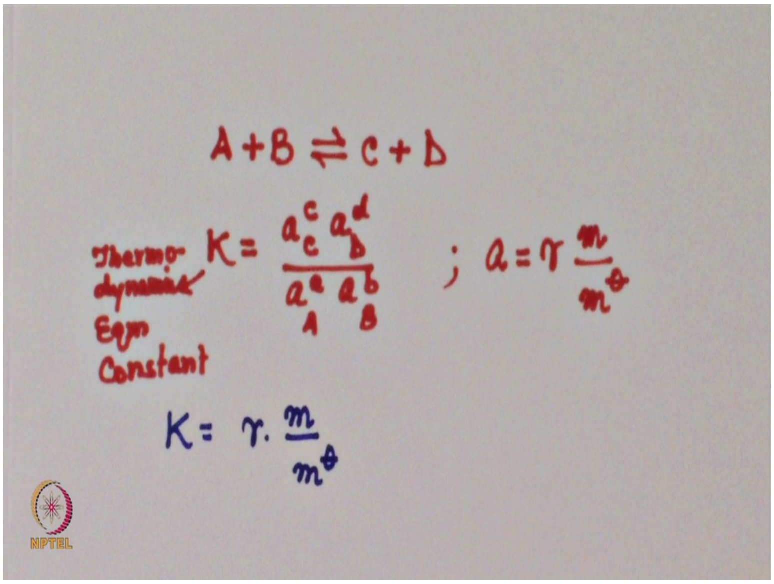

$$A + B \rightleftharpoons C + D$$

Thermo-dynamic Eqm Constant $K = \frac{a_C^c \, a_D^d}{a_A^a \, a_B^b}$; $a = \gamma \frac{m}{m^\ominus}$

$$K = \gamma . \frac{m}{m^\ominus}$$

If I consider A plus B is in equilibrium with C plus D, then thermodynamic equilibrium constant K I will write as activity of c raise to the power c into activity of d raise to the power d over activity of a raise to the power a activity of b raise to the power b; and this I will call thermo dynamic equilibrium constant and how do we measure the value of equilibrium constant in laboratory. Even if I take the same example that A plus B is reacting to form C plus D, in laboratory how will you determine the value of equilibrium constant.

In the laboratory we do not directly determine the activities, we usually when you prepared solutions you usually prepare solutions in terms of molality or molarity or mol fraction. And we know that molarity or molality or mol fraction can be connected to activity and the connector is activity coefficient. So, if activity let us say we write activity is equal to activity coefficient in to m by m naught, this is how we have defined earlier activities; that activity is connected to molality through a connector which is activity coefficient m by m naught, m naught is introduced to get read of the units.

Now let us substitute over here what I have now is K if I put instead of a gamma times m and m naught because m naught in any in any case here c d a b are 1. So, therefore, what we need to do is activity gamma times m by m naught.

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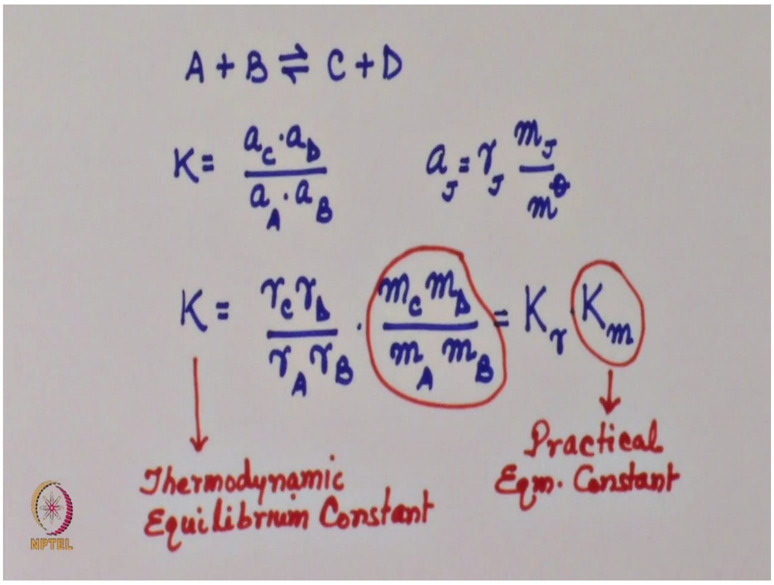

$$A + B \rightleftharpoons C + D$$

$$K = \frac{a_C \cdot a_D}{a_A \cdot a_B} \qquad a_J = \gamma_J \frac{m_J}{m^\ominus}$$

$$\underset{\downarrow}{K} = \frac{\gamma_C \gamma_D}{\gamma_A \gamma_B} \cdot \boxed{\frac{m_C m_D}{m_A m_B}} = K_\gamma \underset{\downarrow}{\boxed{K_m}}$$

Thermodynamic Equilibrium Constant

Practical Eqm. Constant

Let us take an example of a reaction of the type A plus B is in equilibrium with C plus D. The thermodynamic equilibrium constant has to be in terms of activities activity of C into activity of D over activity of C into activity of B right. Now in the laboratory we do not directly determine activities, when we prepare solutions in laboratory we usually prepare solutions and we express the concentration of a solution or we express the molality or we express in terms of mol fraction.

So, therefore, when we determine the value of equilibrium constant in the laboratory, we usually express that equilibrium constant in terms of the ratio of molalities or ratio of molarities or ratio of mol fractions. What I am saying is activity of any species J is equal to activity coefficient of that species J into molality of species J divided by m naught; m naught is one mole per kg m naught as we discussed earlier is introduced to get rid of the units.

Now, if I substitute these activities over here, I can write K as gamma times C gamma times D over gamma times A gamma times B into m C m D molality of A molality of B; m naught will get cancelled because there are same numbers of products and reactance in the numerator and denominator. So, therefore, I am not writing m naught what I have done is instead of activity I have put gamma times m and then separated the gamma terms and separated the m terms and if I write this as K gamma into K m. So, in the laboratory usually we determine K m which is this ratio of molalities of products and reactants, this is thermodynamic equilibrium constant and this is practical equilibrium constant and the K that is used in delta G naught is equal to minus R T log K is actually thermodynamic equilibrium constant.

So, the question is how to recover this thermodynamic equilibrium constant from practical equilibrium constant, and that can be recovered from practical equilibrium constant or converted from practical equilibrium constant if we know this ratio of activity coefficients. So, therefore, practical equilibrium constant can be converted to thermodynamic equilibrium constant, if we know the ratio of activities or if we know the activity coefficients of the products and reactants at equilibrium composition. How do we get the activity coefficients there are methods to get the values of activity coefficient we are not discussing over here, but the point is that even if we have a method to calculate the activity coefficient, according to this relation we must know the equilibrium composition in advance. So, therefore, the things start becoming complicated.

So, how actually it is done? In elementary chemistry you might have seen that in elementary books the K p or K c kind of things are discussed, and there the units are mentioned. Actually I would call those as practical equilibrium constant for example, if I express K m in terms of molality and if the strikomatric numbers on both sides are not same eventually K m will come up with the unit, but since we are getting rid of unit by introducing m naught and expressing, in terms of activity the overall value of K is dimensionless quantity. And in elementary chemistry K gamma is taken as 1; that means, we take the ratio of activity coefficient as 1 or we treat the solutions to be almost ideal or the gases to be almost perfect where gamma is standing to one or gamma is one.

So, therefore, the equilibrium constant that is measured in laboratory in terms of molality molarity or mol fraction or fugacitys is actually not true thermodynamic equilibrium constant, we need the values of activity coefficients and this activity coefficients are actually not very very serious for the very very dilute solutions of non electrolytes, but for the electrolytes even the activity coefficients deviate from unity for electrolytes solutions. For more details you need to go through the debye huckel theory, the debye huckel limiting law can be used to calculate the mean ionic activity coefficients for electrolytic solution, and by using that one can appreciate that for electrolytes even for very dilute solutions we cannot ignore the value of activity coefficients.

So, therefore, one needs to be careful when one is approximating practical equilibrium constant to be equal to the thermodynamic equilibrium constant.

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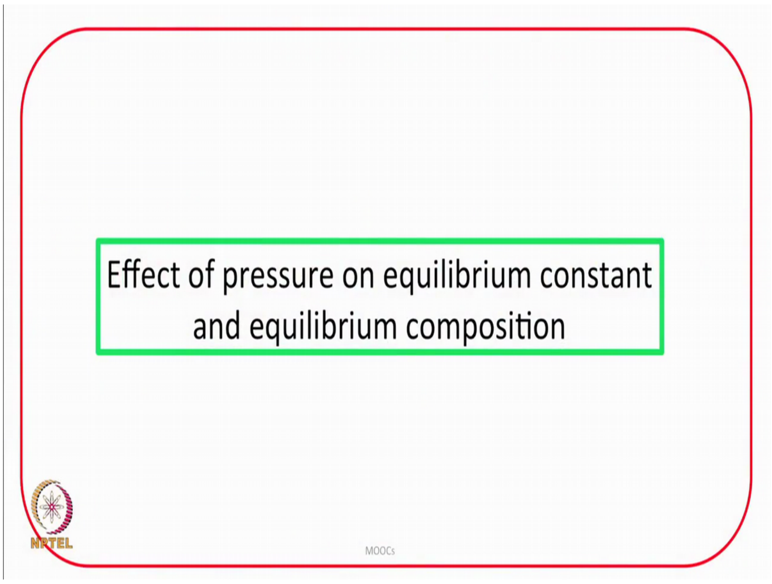

Effect of pressure on equilibrium constant and equilibrium composition

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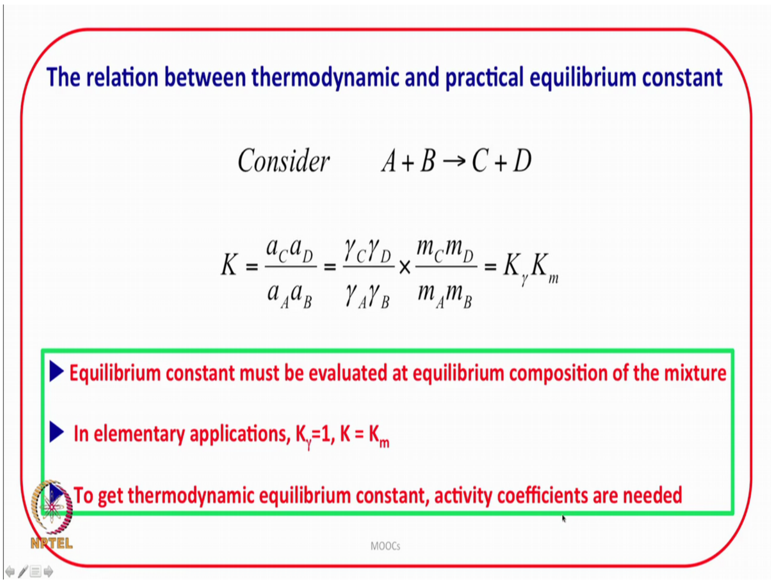

The relation between thermodynamic and practical equilibrium constant

Consider $A + B \rightarrow C + D$

$$K = \frac{a_C a_D}{a_A a_B} = \frac{\gamma_C \gamma_D}{\gamma_A \gamma_B} \times \frac{m_C m_D}{m_A m_B} = K_\gamma K_m$$

- Equilibrium constant must be evaluated at equilibrium composition of the mixture
- In elementary applications, K_γ=1, K = K_m
- To get thermodynamic equilibrium constant, activity coefficients are needed

Now, let us discuss the effect of pressure on equilibrium constant and equilibrium composition. So, once again quickly going through the thermodynamic and practical equilibrium constant, I have already discussed the derivation of this relation, but highlighting some fact that equilibrium constant must be evaluated at equilibrium composition of the mixture; that means, evaluation of equilibrium constant will require knowledge on the values of activity coefficient at equilibrium composition of the mixture, and in elementary applications we put K gamma is equal to 1 and to get thermodynamic equilibrium constant activity coefficient are definitely needed.

We can very briefly talked about the effect of a catalyst because in industry usually the catalyst are used to get a good amount of yield, but does catalyst affect the value of equilibrium constant. Catalyst does not affect the value of equilibrium constant, the role of catalyst is only to reduce the reduce the value of activation energy to make the process happen faster; whether it is a solid catalyst or whether it is an enzyme catalyst the function is same, it does not affect the equilibrium constant. However, it does affect the value of activation energy now let us talk about effect of pressure.

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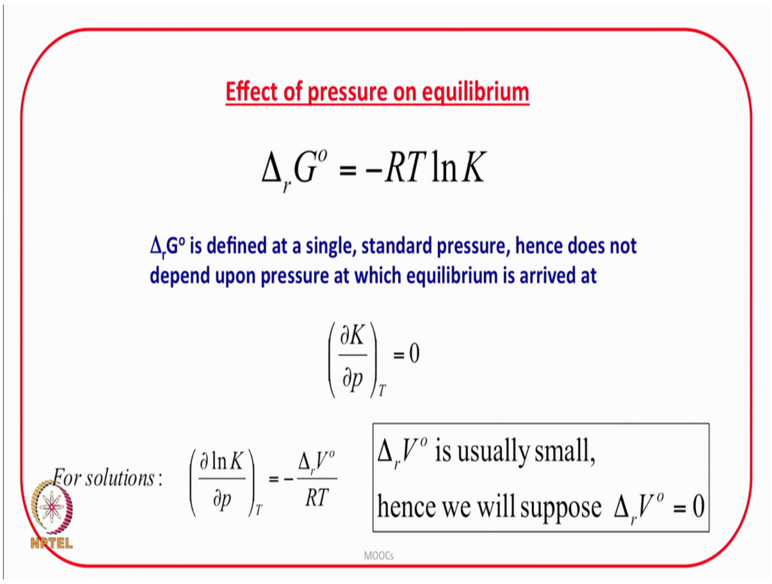

Effect of pressure on equilibrium

$$\Delta_r G^o = -RT\ln K$$

$\Delta_r G^o$ is defined at a single, standard pressure, hence does not depend upon pressure at which equilibrium is arrived at

$$\left(\frac{\partial K}{\partial p}\right)_T = 0$$

For solutions: $\left(\frac{\partial \ln K}{\partial p}\right)_T = -\frac{\Delta_r V^o}{RT}$

$\Delta_r V^o$ is usually small, hence we will suppose $\Delta_r V^o = 0$

We can appreciate the effect of pressure on the value of equilibrium constant by looking at an expression or relationship between delta G naught and K let us take a look at this, this slide. Delta G naught is equal to minus R T log K, the left hand side of the equation is delta r G naught. Naught means it is a standard state quantity defined at one bar pressure; that means, the left hand side quantity is defined only at one bar pressure irrespective of the pressure where at which the equilibrium has been arrived at.

And since the left hand side of the equation is independent of pressure at which the equilibrium is arrived at the right hand side must also be independent of the pressure at equilibrium and that is why it is commented over here that delta r G naught is defined at single standard pressure and hence does not depend on pressure at which equilibrium is arrived at and therefore, I can very very comfortably ride that that dou K by dou P at constant temperature is equal to 0, this setting up of this derivative equal to 0 means K does not depend upon pressure as long as the temperature is held constant.

But is it always true; for solutions it can be shown that d log K by d p at constant t is minus delta r V naught by R T; where delta r V naught is the standard reaction volume; that means, the change in standard volume of products and reactance at equilibrium. Usually for solutions this valley is very very small, and can be conveniently neglected therefore, in our discussion we will suppose that delta r V naught is equal to zero and in general we will suppose that the equilibrium constant of for gases it does not depend the equilibrium constant is independent of pressure. To discuss a little more how can we increase the pressure.

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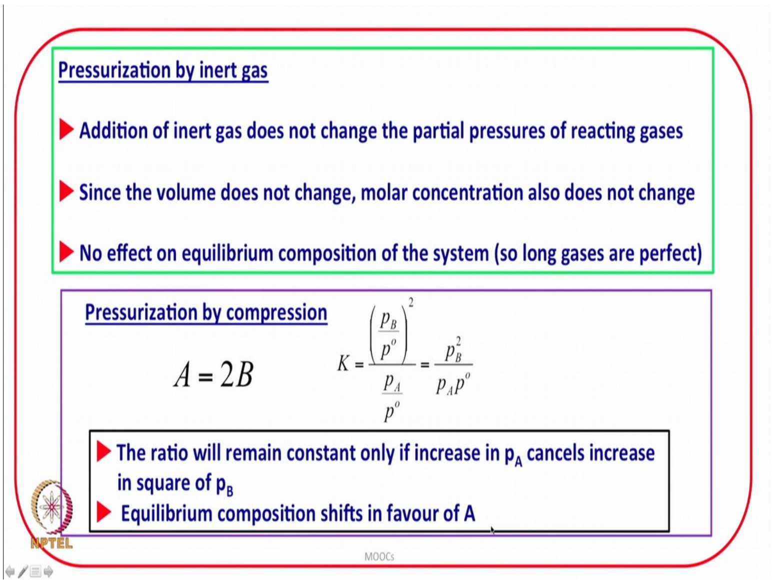

Pressurization by inert gas

- Addition of inert gas does not change the partial pressures of reacting gases
- Since the volume does not change, molar concentration also does not change
- No effect on equilibrium composition of the system (so long gases are perfect)

Pressurization by compression

$$A = 2B \qquad K = \frac{\left(\frac{p_B}{p^o}\right)^2}{\frac{p_A}{p^o}} = \frac{p_B^2}{p_A p^o}$$

- The ratio will remain constant only if increase in p_A cancels increase in square of p_B
- Equilibrium composition shifts in favour of A

Let us assume we have two reacting gases in a container, there are two ways of increasing the pressure one of the ways is that we inject an inert gas; when we inject an inert gas the total pressure is increasing and do not allow the volume to change. Let us say the volume is not changing and the gases all gases are perfect.

Since the volume is not changing the total pressure is changing, the mol fractions are accordingly modified so that the partial pressure of each reacting gas does not change. If the partial pressure of each reacting gas does not change, that means, the equilibrium composition is not going to change one point I want to make clear over here. We have discussed that the equilibrium constant is independent of the pressure at which the equilibrium is arrived at, but that does not mean that the equilibrium composition is independent of pressure.

When we increase the pressure the equilibrium composition may have to re adjust to keep the value of equilibrium constant same, and this will depend upon the stoichiometry of the reaction. I will take an example and demonstrate; now as I said that if we pressurized by in inert gas the partial pressures of individual gases which are reacting is not changing and therefore, it does not affect the equilibrium composition the concentration is not changing. Another way of pressurizing the gases is that you reduce the volume you pressurize you reduce the volume, if the volume is reduced then you know n by v the concentration is affected concentration is changed and partial pressures are modified. Now what is the effect? Now equilibrium composition is going to change.

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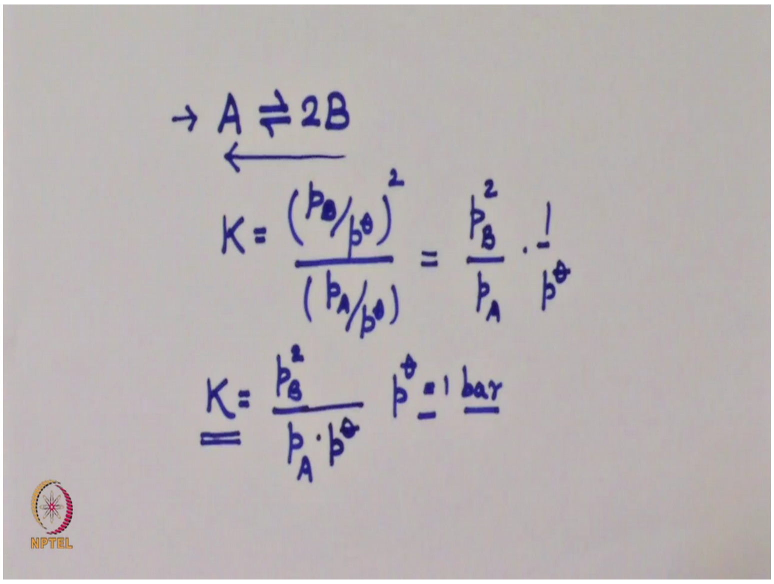

$$\rightarrow A \rightleftharpoons 2B$$

$$\longleftarrow$$

$$K = \frac{\left(p_B/p^{\ominus}\right)^2}{\left(p_A/p^{\ominus}\right)} = \frac{p_B^2}{p_A} \cdot \frac{1}{p^{\ominus}}$$

$$\underline{\underline{K}} = \frac{p_B^2}{p_A \cdot p^{\ominus}} \qquad \underline{p^{\ominus} = 1\ \text{bar}}$$

We will take an example of A in equilibrium with 2B these are gas phase we are talking about gas phase only it is a dissociation kind of reaction, then how do I write K if I since I am assuming perfect gases, then I will write P B by P naught whole square divided by P A P naught. Since P naught is equal to one bar, I will write P B square over P A, P naught I am putting as 1 bar. We are discussing an alternate way of increase of pressure that is by reducing the volume you reduce the volume increase the pressure by reducing the volume. Equilibrium constant will remain same we discussed it is not going to be affected; that means, if we are talking about this kind of reaction then even if there is a small change or increase in P B there has to be large increase in P A so that the effect of this square is taken care of the ratio remains constant. I repeat a small change in P B lets say there is a small increase in P B, there is a square of that that has to be compensated that how it will be compensated there will be steep increase in p A. So, that this ratio remains constant and that means, the shift of composition towards left; that means, more molecules of A will be produced.

So, this kind of asymmetric reaction when the pressure is increased the equilibrium is shifted towards the direction in which there are lesser number of moles of the gaseous species, this kind of effect was actually generalized by Le Chatelier. According to Le Chatelier, principal whenever equilibrium is disturbed by any external factor the equilibrium composition or equilibrium will adjust in such a matter in such a manner to undo the effect of external equilibrium.

Let us go to slides now pressurization by inert gas we have discussed that addition of inert gas does not change the partial pressure of reacting gases and since the volume does not change molar concentration also do not change and there is no effect on equilibrium composition so long gases are perfect; then we discussed an alternate method and that was by compression, you pressurized by compression and we came up with this expression and then discuss that the ratio has to remain constant and that will remain constant only if increase in P A cancels the increasing square of P B.

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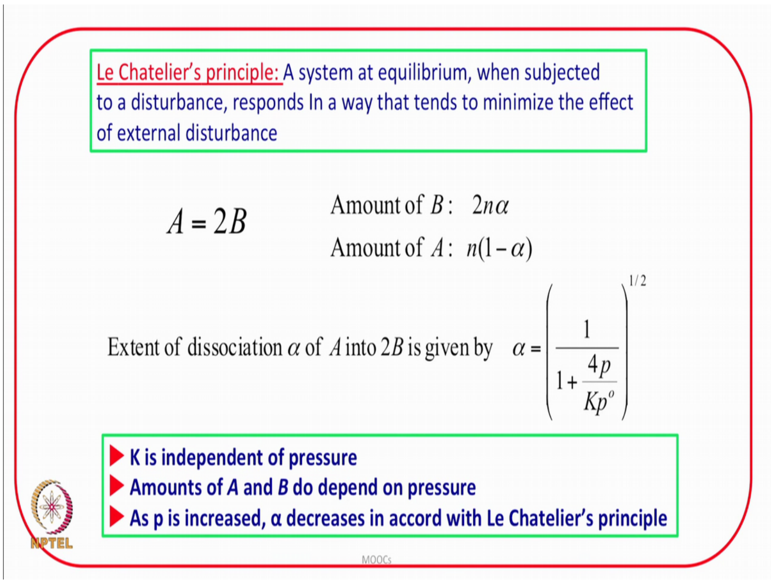

Le Chatelier's principle: A system at equilibrium, when subjected to a disturbance, responds In a way that tends to minimize the effect of external disturbance

$$A = 2B$$

Amount of B: $2n\alpha$

Amount of A: $n(1-\alpha)$

Extent of dissociation α of A into $2B$ is given by $\alpha = \left(\frac{1}{1+\frac{4p}{Kp^{o}}}\right)^{1/2}$

- K is independent of pressure
- Amounts of *A* and *B* do depend on pressure
- As p is increased, α decreases in accord with Le Chatelier's principle

So, equilibrium composition shifts in favour of a and then we generalized this in terms of Le Chatelier Principle, that is a system at equilibrium when subjected to disturbance response in a way that tends to minimise the effect of external disturbance. And we will see throughout the discussion on equilibrium and equilibrium constant how Le Chatelier Principle is obeyed.

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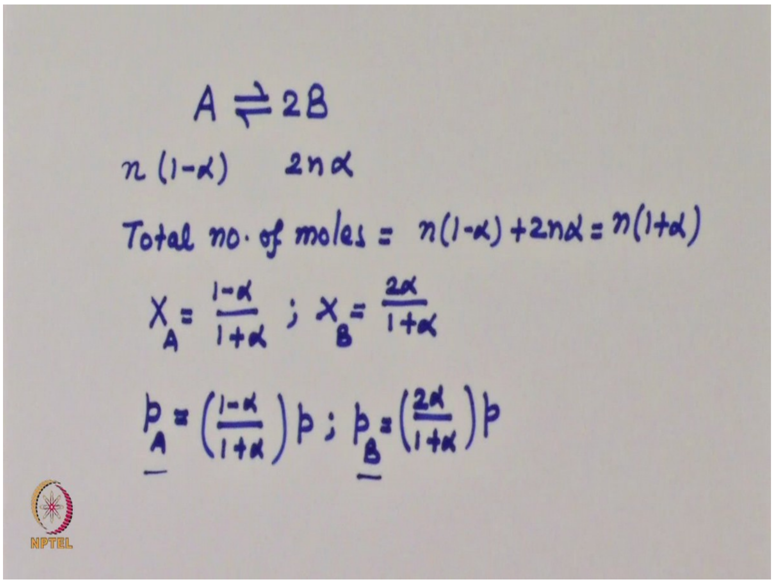

$$A \rightleftharpoons 2B$$

$$n(1-\alpha) \quad 2n\alpha$$

$$\text{Total no. of moles} = n(1-\alpha) + 2n\alpha = n(1+\alpha)$$

$$X_A = \frac{1-\alpha}{1+\alpha} \; ; \; X_B = \frac{2\alpha}{1+\alpha}$$

$$\underline{p_A} = \left(\frac{1-\alpha}{1+\alpha}\right)p \; ; \; \underline{p_B} = \left(\frac{2\alpha}{1+\alpha}\right)p$$

Let us extend the discussion on the dissociation reaction which is under discussion, we are talking about A dissociating to 2B and let us say we had n moles in the beginning and extent of dissociation or degree of dissociation is alpha. So, at equilibrium we have 2 n alpha moles of B and n into 1 minus alpha moles of A.

So, total number of moles will be equal to n into 1 minus alpha plus 2 n alpha which is equal to n into 1plus alpha you will find out this turns out to be n into 1 plus alpha. So, mole fraction of a will be equal to this divided by the total number of moles is going to be 1 minus alpha over 1 plus alpha and mole fraction of B is going to be this divided by the total number of moles which is going to be 2 alpha over 1 plus alpha.

Therefore partial pressure of A will be equal to by Dalton’s law of partial pressure one minus alpha over 1 plus alpha into total pressure, p is a total pressure and partial pressure of b is going to be 2 alpha over 1 plus alpha into the total pressure. So, once we have the expression for the partial pressure of A and partial pressure of B we can substitute these into an expression for equilibrium constant let us see what it comes to let us take a look at slide we have discussed for this dissociation reaction amount of B is 2 n alpha amount of a n into 1 minus alpha I have just discussed and for this reaction I will again take this slide back and extend not to cancel P naught.

So, it will be P B square by P A into 1 by P naught; that means, I will put P naught over here. So, I will use this result now what I have is K is equal to P B square over P A into p naught and I will substitute the mole fractions.

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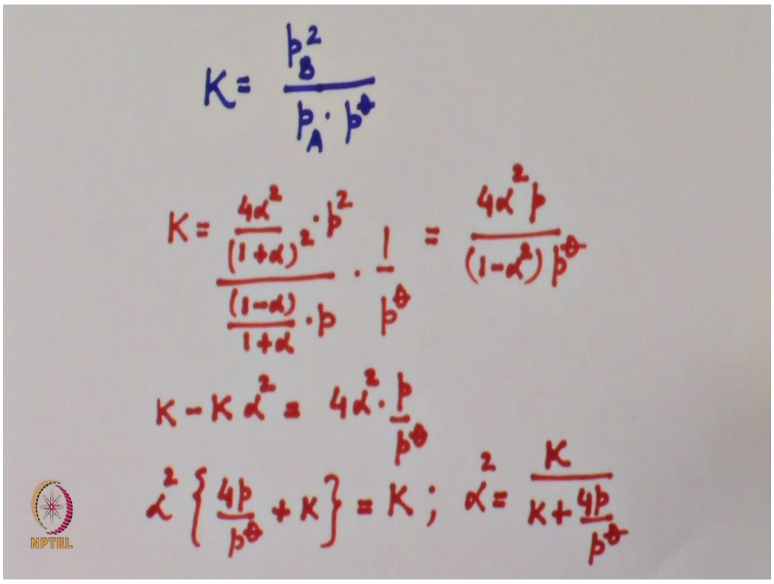

$$K = \frac{p_B^2}{p_A \cdot p^{\ominus}}$$

$$K = \frac{\frac{4\alpha^2}{(1+\alpha)^2} \cdot p^2}{\frac{(1-\alpha)}{1+\alpha} \cdot p} \cdot \frac{1}{p^{\ominus}} = \frac{4\alpha^2 p}{(1-\alpha^2)\, p^{\ominus}}$$

$$K - K\alpha^2 = 4\alpha^2 \cdot \frac{p}{p^{\ominus}}$$

$$\alpha^2 \left\{ \frac{4p}{p^{\ominus}} + K \right\} = K ; \quad \alpha^2 = \frac{K}{K + \frac{4p}{p^{\ominus}}}$$

So, K is equal to P B square, P B square is 4 alpha square over 1 plus alpha square this is P B square divided by P A, P A is 1 minus alpha over 1 plus alpha and into this P square into P into 1 over P naught. So, this is equal to 4 alpha square into P divided by 1 minus alpha square into P naught and if I further write this as K minus K times alpha square is equal to 4 alpha square into P by P naught. Alpha square then I has 4 P by P naught plus K is equal to K and from this I have alpha square is equal to K over K plus 4 P by P naught.

So, let me rewrite now what I have is alpha square is equal to K over K plus 4 P by P naught.

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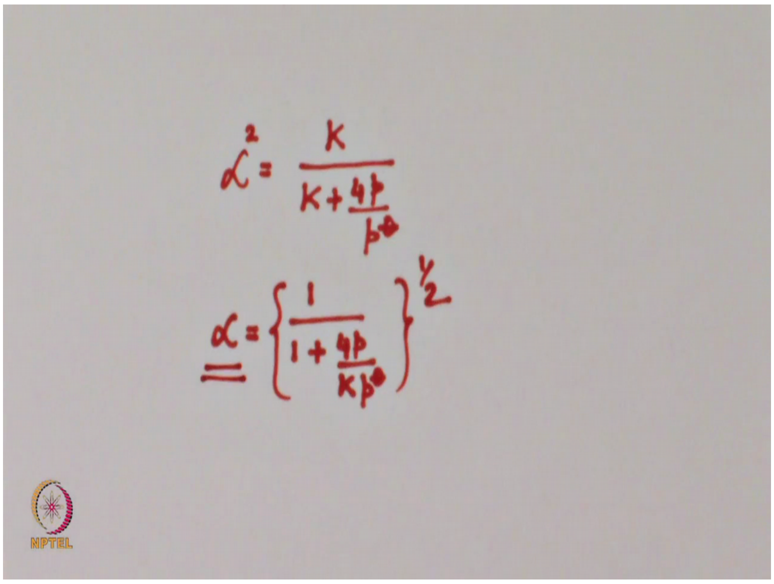

$$\alpha^2 = \frac{K}{K + \frac{4p}{p^\ominus}}$$

$$\underline{\underline{\alpha}} = \left\{\frac{1}{1 + \frac{4p}{Kp^\ominus}}\right\}^{1/2}$$

And if I rearrange alpha is equal to 1 over 1 plus 4 p over K into p naught I am dividing throughout by K. So, I end up with this relation and this alpha defines the extent of dissociation. Now let us take a look at the slide the extent of dissociation of A into 2B is given by 1 plus 1 over 1 plus 4 p by K p naught that is what we have derived. Now and this is an important result because according to this equation if pressure total p is the total pressure is increased alpha will decrease. If alpha decreases; that means, 2 n alpha amount of b will decrease and amount of a will increase this is an important result once again when pressure is increased alpha decreases, and if alpha decreases amount of B will decrease and amount of A will increase.

So, this example demonstrates because K is independent of pressure the amount of A and B do depend on pressure and this is demonstrated by the small calculation, and in accordance with Le Chatelier Principle when pressure is increased the amount of A and B are modified alpha decreases in accordance with Le Chatelier principal that is the number of molecules of a will increase and number of molecules b will decrease or the reaction will shift towards left and that is what is predicted by the Le Chatelier Principle.

So, what we have discussed in this lecture is that the catalyst does not affect the equilibrium constant, we have also discussed that for gases the inert gas does not affect the equilibrium composition, an important result that we have discussed is that equilibrium constant is independent of pressure it does not depend upon the pressure at which the equilibrium is arrived at provided the temperature is held constant that does not mean that the equilibrium composition remains same.

If the pressure is increased by compression the equilibrium composition will readjust so as to keep the value of equilibrium constant same at a given temperature, and this readjustment will depend upon the number of gaseous molecules in the product or in the reactor, and what we have shown by taking an example in which the dissociation takes place that is more number of gaseous products are formed, an increase in total pressure shifts the equilibrium towards left in accordance with Le Chatelier Principle.

There are other external factors which can affect the value of equilibrium constant, and that we will discuss in the next lecture.

Thank you very much.