Introduction to Chemical Thermodynamics and Kinetics
Dr. Arijit Kumar De
Department of Chemistry
Indian Institute of Science and Education Research, Mohali

Lecture – 24
Chemical Equilibrium – Part 4

We will now discuss the effect of external variables like say, if we vary pressure or temperature what happens to the equilibrium constant and that is connected to a principle which you already studied in your high school, which is known as le chatelier principle which is named after the French scientist Henry Louis Le Chatelier.

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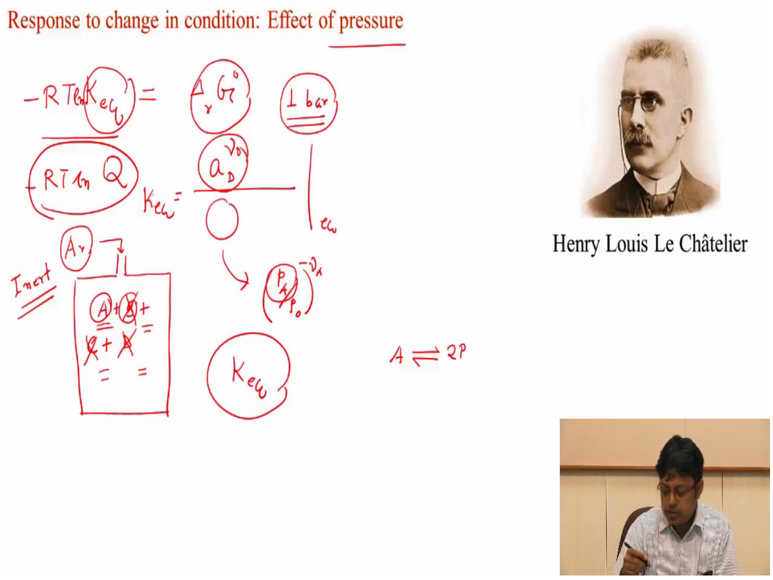

Response to change in condition: Effect of pressure

Henry Louis Le Châtelier

So, what it says is that? If you want to make a change in the system, the system will try to counteract the effect, by shifting the equilibrium towards the more favorable position and that ways the system will counteract the effect on the external effect.

Now, what we are going to discuss is the effect of pressure in on the chemical equilibrium or equilibrium constant. Now remember that, equilibrium constant it was connected to the reaction Gibbs free energy. Because, it was minus R T ln K equilibrium that is what we called as reaction free I mean the equilibrium constant. Now this equilibrium constant, which means if it is connected to delta G0 what is delta? G0 it is basically, the standard reaction Gibbs free energy by standard we means actually the pressure was fixed it at one bar. So, already it is defined or it is a well-defined quantity that, K equilibrium will be equal to not equal to it is connected to change in Gibbs free energy, that was carried out that basically corresponds to one bar pressure.

Which means actually, the pressure is well defined in the definition itself. So, even if we change the pressure, there will be no change in K equilibrium, there should not be any change; however, R T ln Q can change of course. The reaction quotient can change, because that is not connected to pressure, but the equilibrium constant will not change. Now, when I say the equilibrium constant will not change, it does not mean at equilibrium the this amount of say, a b and c d those numbers will not change, that does not no I mean that these things will not change, this may change and we will try to devise a formula how it changes. But the total equilibrium constant which it is dependent on at equilibrium, that will not change.

So, that is the meaning of the response to the conditions particularly the pressure. Now the question is, how you will increase the pressure of a mixture? Say in the mixture I have abcd everything, and then one way to increase the pressure is that, you insert some inert gas, say we insert are going here, now what will happen the pressure will increase; however, this increase in pressure will cause nothing to the partial pressure of a b c and d, because I can write the activities in terms of Prussian pressure, by the divided by the standard step pressure which is the one atmosphere pressure and raised to the stoichiometric.

Now, if you think in this way. So, this is basically the expression for a, which I just used does not matter it is for any constituent we can write it, but the point here is that what is pa, pa is partial pressure. Now what do mean by partial pressure? It is the pressure of the gas, if the same amount of the gas of the sent gas would have failed to enter container, like if I do not have b c and d. So, the pressure of the a in the same container will be equal to it is partial pressure, now which means actually it does not matter if I introduce argon or some other gas, which are we are by the way introducing inert gas to make sure that, there is no reaction happens between the it does not interfere with the abcd system. So, it should not react all by itself if it reacts then it is a different story.

So, we are just increasing the pressure. So, if we introduce the argon gas here, the partial pressure of all this component does not change. Because by definition partial pressure is that amount of the constituent which basically, if the same amount actually fills the entire container the pressure will be equal to it is partial pressure. So, by definition that should not change, if I introduce anything else. So, the partial pressure remains constant, which means they for each constituent partial pressure remains constant. So, that K equilibrium also does not change; however, think about a slightly different situation.

Suppose, we are introducing say a suppose we let us say some kind of dissociation reaction, say we have a going into say for example, to b. So, this kind of reactions are called dissociation reaction let me use a new page. So, A is dissociating into say 2 molecules of B, that is what we are saying at dissociation.

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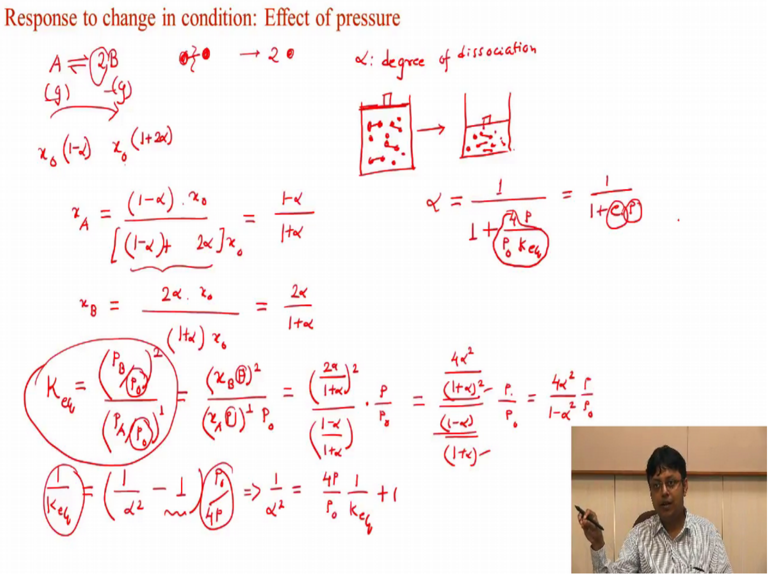

Response to change in condition: Effect of pressure

$$A_{(g)} \rightleftharpoons 2B_{(g)} \qquad \rightarrow 2$$

$$x_0(1-\alpha) \quad x_0(1+2\alpha)$$

α: degree of dissociation

$$x_A = \frac{(1-\alpha)\cdot x_0}{[\underbrace{(1-\alpha)+2\alpha}]x_0} = \frac{1-\alpha}{1+\alpha}$$

$$\alpha = \frac{1}{1+\frac{4P}{P_0 K_{eq}}} = \frac{1}{1+cP}$$

$$x_B = \frac{2\alpha\cdot x_0}{(1+\alpha)x_0} = \frac{2\alpha}{1+\alpha}$$

$$K_{eq} = \frac{\left(\frac{P_B}{P_0}\right)^2}{\left(\frac{P_A}{P_0}\right)^1} = \frac{(x_B P)^2}{(x_A P)^1 P_0} = \frac{\left(\frac{2\alpha}{1+\alpha}\right)^2}{\left(\frac{1-\alpha}{1+\alpha}\right)}\cdot\frac{P}{P_0} = \frac{\frac{4\alpha^2}{(1+\alpha)^2}}{\frac{(1-\alpha)}{(1+\alpha)}}\frac{P}{P_0} = \frac{4\alpha^2}{1-\alpha^2}\frac{P}{P_0}$$

$$\frac{1}{K_{eq}} = \left(\frac{1}{\alpha^2} - 1\right)\frac{P_0}{4P} \Rightarrow \frac{1}{\alpha^2} = \frac{4P}{P_0}\frac{1}{K_{eq}} + 1$$

Now, we had some kind of a say, we can denote it like this and then we are breaking this bond. These are not actually necessarily atom it may be a fragment and this is also another fragment, and that we are dissociating to get 2 times of these fragments, that is the reaction and reverse reaction is known as association reaction.

When these 2 fragments actually join together to give the apparent molecule. Now, suppose these are this is happening in equilibrium and now what we have is that, and let us also assume that, the degree of dissociation is alpha. So, the alpha is the degree of dissociation, which you can actually connect it to your advancement of reaction, degree of dissociation is alpha. Now suppose initially, I had some mole fraction let us say xA to begin with and say xB to begin with some mole fraction. So, the if the alpha is that dissociation, if when the reaction starts and if alpha is the extent or the degree of dissociation. So, the amount of xA that or amount or the mole fraction that will be present, it will be nothing but xA times 1 minus alpha, for B it will be nothing but xB times 1 plus 2 alpha. Because, if alpha is the degree of dissociation it will be minus alpha for A, but that one molecule is giving rise to 2 molecules.

So, it will be plus 2 alpha for P and we are just using a generalized notation in the sense that, initially it was xA xB and suppose you have, at some time we have this much amount of degree of dissociation. So, we can actually write the mole fraction in this way. So, if we write it in say this fashion xA, we can actually write the initial ones as say x0 or something. We can write it as xA0, similarly for xB we can write it as xB0 or something like that. So, xA will be nothing but, now look at it carefully what will be xA? It will be nothing but 1 minus alpha times, it will be the divided by the total thing, now if we if you think in terms of the mole fraction.

Let us say that the total number of moles were instead of writing it as xA0 and xB0. We can just write it as the total number of moles was say x0. So, then it will be easy for us to understand because, what I am saying is that in the mole fractions total number of moles actually where x0. So now, the mole fraction will be xA by xA0, whichever way you want to calculate. So, xA by x0 that will be nothing but 1 minus alpha, divided by the total number of moles which is 1 minus alpha into 1 plus 2 alpha. So, this is the total number of basically moles which is proportional of course, you have to multiply it by x here. So, you can actually write it in this way times x0 and times x0. So, that will be nothing but, the numerator I am getting 1 minus alpha and, in the denominator, let us see what we have? We have actually 1 minus alpha plus, we have not 1 plus 2 alpha it will be just 2 alpha.

So, we will have 1 plus alpha here and then the x0 cancels. So, that is why I just took it as a total number of moles or something like that. So, this will be the mole fraction of A similarly the mole fraction of B that, we are getting will be 2 alpha times x0 and denominator will be the same, 1 plus alpha into x0. So, that will be nothing but 2 alpha by 1 plus alpha. Now, what you can do is that, you can just write the equilibrium constant in terms of partial pressures or the mole fractions whatever you want to write. So, let me write it as a first is a partial pressure, it is basically Pb by P0 and let us write it and as this.

Now, it should be squared because, actually have in the stoichiometry 2 and divided by why we are dividing? Because it is minus 1 and Pa by P0, but that raised to one only. So, we can just now expand it. So, we it is nothing but, this is basically partial pressure and we know the partial pressure is mole fraction into total pressure. So, you can just write it. So, the mole fraction is xP into total pressure say, is P that squared and divide it by similarly xA into PA that squared. Now look at the P0 terms, we have 1 over P0 square 1 over P0. So, there will be one extra P0 sorry this one B squared is just raised to 1.

Now, what is xB into P xB? Already we calculated it is basically 2 alpha, divided by 1 plus alpha that squared and xA it is raised to 1 only. So, it will be 1 minus alpha divided by 1 plus alpha. So, just like P0, will have the total pressure. So, this will be total pressure, it is P square here and it is P here. So, there will be a P over all. So, will have something like u times P by P0. So, that will always P there. So, let us just expand it. So, it is 2 alpha by 1 plus alpha square. So, it is 4 alpha square divided by 1 plus alpha squared divided by 1 minus alpha, divided by 1 plus alpha. So, this one 1 plus alpha will cancel it another 1 plus alpha. So, giving rise to something like you can write here. So, it will be nothing, but 4 alpha square divided by I will have 1 plus alpha remaining and that will get multiplied with this 1 minus alpha.

So, I can write it as 1 minus alpha square times P by P0. So, that is the overall equilibrium constant or you can write it as KP, or let us write it as K equilibrium constant. Now, what we can do we can actually solve it for alpha, just to look at what is the degree of dissociation? And how it is connected to the pressure? Or that or the total pressure how we can connect it? Now, if we insert the inert gas or in this case we can also use another way of increasing the pressure, you can think of our original I mean discussion on this cylinder with a frictionless mass less piston, and suppose we had these molecules around.

So, this is basically A and suppose this is basically B all of them are here and then all of a certain, we are doing compression and suppose, we reduce the following by say amount, but notice the volume by say, I mean make the final volume is half of the initial volume. So, the pressure will be just twice, if because pressure is proportional to following and we are keeping the temperature also constant. Now, what happens to alpha? If we want to solve it, just look at it carefully I want to solve alpha. So, the way we can solve it, it is for alpha square divided by 1 minus alpha square. So, what we can do? We can just write

1 by K equilibrium and that will be 1 by alpha 1 minus alpha square divided by 4 alpha square.

So, it will be 1 by 4 alpha square minus it will be 1 over 4, into now I will have P0 by P and then I can take the everything else on the other hand side, and write it will be basically I am just multiplying it by the 1 over K equilibrium by this term. So, and adding one 4th to it, and then let us see what happen. So, we can actually we could have actually taken the 4 to be common. So, it will be just minus 1. So, what we will have is 1 over alpha square will be nothing but, as we see here it will be 4 P by P0 into 1 over K equilibrium.

So, now we can see the degree of dissociation alpha, will be the square root of the inverse of this quantity, which will be nothing but, if we write it in this way 1 divided by and it will be class one because there is a 1 here. So, it will be 1 divided by 1 plus I will have 4 into P divided by P0 into K equilibrium. Now, you can see that all these factors are basically constant and now, the alpha actually is you can write it as something like 1 plus some constant into P. So, if I increase the pressure, what will happen? Is that the system it is basically, it is showing that if I increase the pressure alpha will decrease. Now, why alpha is decreasing here, the reason if I go from left to right.

So, the pressure is increasing, because every molecule of A is giving 2 molecules of B. And so, initially they are all in gas phase. So, the total pressure is actually increasing if I make this one make change where A is going to B. So, then actually I will I twice the pressure, now what I am doing is that I am externally applying the pressure and making it say 2, and if I make the pressure twice, then what will happen? The alpha will actually be reduced and the reduction is happening in the other way. In the sense that, now the being molecules will now do a association reaction and form more a molecules. So, in the sense that the in the equilibrium, the ratio should be constant because the K equilibrium is constant it is it is already within the constant. So, it that is also constant.

So, by if I increase the pressure my alpha will change. So, what it means is that of course, pressure does not have any effect; however, we can actually control this ratio between the reactant and the products, particularly in the gas phase reaction. And that ratio, if I change then I can control the ratio by changing the pressure and this is happening because, the equilibrium constant does not change. So, the equilibrium constant does not change; however, the pressure of the individual things has to change, in order to make that equilibrium constant same, which means the degree of dissociation will change. So, this is the very simple explanation, you could have actually easily figured that out from this particular equation, that we have pressure of say B squared divided by pressure of A raised to 1 actually. So, if I make the pressure of B double in by in ome sense, or say that if you are actually the example is slightly different, here the we are talking about the total pressure.

The example we have given it is not like, if I double that pressure of B alone then of course, the equilibrium will shift towards left and propose me by a proportionate amount, but what are we are saying right now, is the total pressure if I change the total pressure of the system then how it goes. So, if I make that this pressure as double. So, of course, it will not be it will not reduce the alpha by half amount, it will reduce the alpha by, but to some extent. And that is happening because, the equilibrium constant is independent of pressure.

So, it is constant and since this is connected to the delta 0 G and delta Z 0, which is actually independent of pressure by definition because, it is defined as the free energy change at constant pressure which is remember. So, it is it does not have should not have any effect on pressure, because it is defined in that way. So, we see that a nice demonstration, how one can actually realize? How le chatelier principal is working? And how the degree of dissociation is changing? And how it is connected to the le chatelier principle? Now, we can talk about the second effect, which is the effect of temperature.