Fundamentals Of Combustion (Part 1)

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Lecture – 15
Introduction to chemical equilibrium

Let us start this lecture with the thought process explore and experience the very essence of human life. It is very difficult to get human life as per our scripture right, but we do waste our, the time for you know behaving like an animal. So, therefore, we need to experience that a sense of humour what animal cannot, we will now we recall what we have learnt in the last lecture.

In the last lecture if you look at, we basically looked at how to determine the adiabatic flame temperature. In that case what we did we basically we are knowing that what will be the product composition right. Of course, reactants would be known to you, what will be the, how much, how many number of moles of fuel, how many numbers of oxidizer right that will be given to you, but product you would not be knowing right. But here we are assuming oh it is going to the stoichiometricaly or it is going to the lean and leap product is known; that means, number of moles of each constituent of the product are known to you, but in real situation it would not be right are you getting.

For that, what we will have to do? We will have to look at you know equilibrium compositions. Now, question arises we need to calculate equilibrium compositions right, and if you do not know the equilibrium combustion you cannot calculate the accurately the adiabatic temperature flame temperature right. And if you do not know the adiabatic flame temperature you cannot really calculate the equilibrium composition right. So, we will see as we go along let us now look at basically chemical equilibrium.

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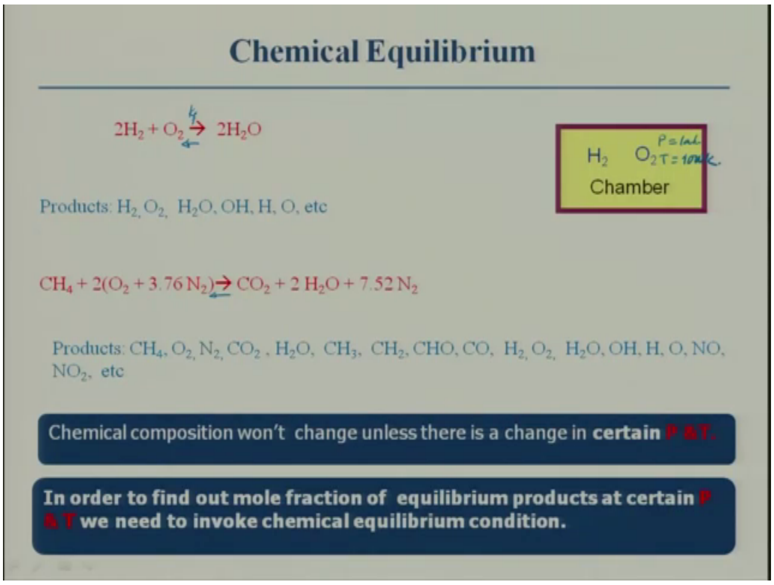

We will consider a chamber right which contains hydrogen and oxygen right it will be at a certain mixture certain what you call ratio fuel air ratio hydrogen is fuel oxygen is your oxidizer.

Now, if it is there let us say at 298 Kelvin what will be happening is it some reaction will be going on or not, is it some reaction will be. For example, this room you know imagine right that contains hydrogen and oxygen and mixed properly with certain let us say stoichiometric ratio; that means, where combustion can take place right, but it is at 298 Kelvin what will happen. There will be some reaction or not, but there might be. Because the molecules might be getting what you call bombarded they will be colliding each other, they might be breaking, they might be coming they may done it, but that is not really very much.

But if you raise the temperature let us say 2000 Kelvin what will happen there will be some reaction which will be taking; that means, hydrogen will be reacting with oxygen and we are saying it will go to the water right. Let us say 2 moles of hydrogen reacting with one mole of oxygen it is going to the 2 moles of water, but is it really will be occurring this way. Need not to be, it can also happen, right. The water will be decompose into oxygen and hydrogen right it can also take in the reverse process right. One we can say forward reaction if I say forward reaction right k f I am saying right, k f means basically a reaction rate constant you can say and backward reaction this is arrow in the opposite direction will be taking.

Now, let say at 1000 Kelvin it is being raised now some reaction is occurring then the products are being formed. And as you goes on you know measuring this hydrogen, oxygen and water let us say for example, right then what will be happening. After certain time that the; concentration of hydrogen oxygen and water if you are measuring will be remaining constant is not it. They would not be change after certain time right. Then we call it as a richer equilibrium right.

But question arises is it at the equilibrium only water, hydrogen, oxygen will be there or only water will be there.

Student: All 3 (Refer Time: 05:00).

All 3 will be there, but is there apart from that is there any other species will be there likely to occur right.

Student: Yes, sir.

So, what are those species one can think of. Any idea ?

Student: (Refer Time: 05:15).

OH, maybe O right H all those things can be there right. So, the product if you look at it will be hydrogen, oxygen, water, OH, H, O and some other things as well like.

Now, question arises is it like the equilibrium when you say it is basically reaction is going on or not, or reaction is stopped.

Student: (Refer Time: 05:44).

It will be going on right. In this case what will be happening like if you will consider I will go back to the simple example of let us say 2 moles of hydrogen react to make them 1 mole of oxygen going to the 2 moles of water. That means, there will be forward reaction and also there will be backward reaction even at equilibrium, but the forward reaction rate will be same as that of the backward reaction rate, yes or no right. So, then we call it as the equilibrium right. That means, it is statically equilibrium or dynamically it is basically dynamically, it is all is going on only is the forward reaction is same as the backward reactions right. So, that will be given.

Let us take an example like methane 1 mole of methane is reacting with 2 moles of air and going to the product of carbon dioxide, 1 mole of carbon dioxide, 2 moles of water and of course, 7.52 moles of nitrogen right. And of course, these are the things what we generally right, but however, we can say that backward it also will be reacting and let product will be converted into the reactants right in a backward direction also.

So, apart from this stable species like a carbon dioxide, water and nitrogen are stable species there will be also other species which will be there. What are those, any idea? If you look at it will be CO right, hydrogen, it can be C S 3, C S 2, CH O, CO, oxygen, OH, H, O, NO, NO 2 and several other species which I have not listed you know like it will be several species right.

And keep in mind that at equilibrium we need to find out what are this you know mole fractions or the mass fraction of this species at the equilibrium. For example, methane air system if you are handling is a very small. I have only jotted down few of them you know, it maybe some more number space is very difficult right.

Now, what I had told you earlier that that this is occurring you know basically when the pressure and temperature is not changing right. That means, the chemical composition will remain same provided the temperature and pressure in this case let us say P you know I can say one atmosphere pressure temperature is 1000 Kelvin right, that is not (Refer Time: 08:38) If I change right that either temperature or the pressure then what will happen to the equilibrium composition ? Will it equilibrium maintain? Equilibrium will be changing right; that means, any change in this either one of them will have a change in the composition right. So, that is very important you should keep in mind.

In order to find the mole fraction of equilibrium products at certain pressure we need to invoke chemical equilibrium condition. So, what are those conditions we need to look at it?

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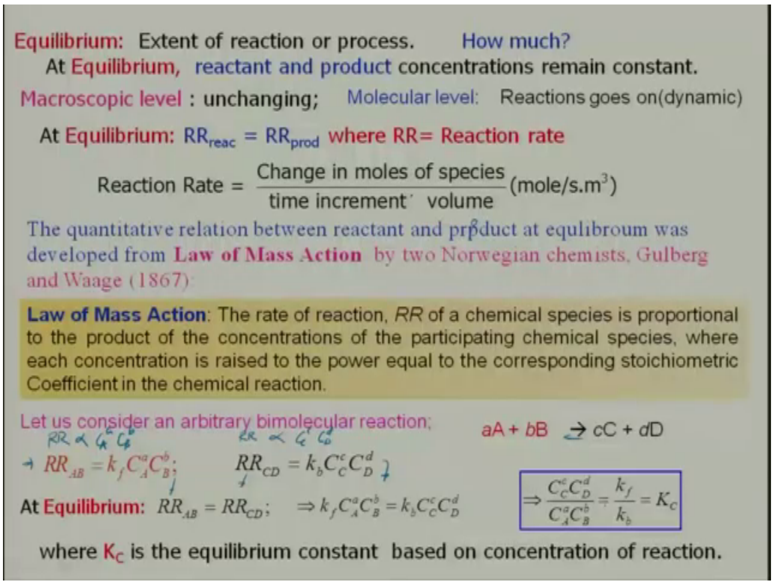

So, as I told that equilibrium basically we will tell you the extent of reaction or a process whatever is taking place right. And at equilibrium right and it will be telling basically how much it would not be telling you the rate of reaction right, it will be telling extent of the reaction is taking place or the process how far it can go to attend the equilibrium.

So, as I told that that at equilibrium reactant and product concentration remain constant right, it will not change unless otherwise that is change in temperature or the pressure right or there might be also some change whenever suppose some reactant it being increase, suppose some reaction is going on. Let us hydrogen oxygen you have added little more hydrogen ok, let us say in a chamber it is a reaction is going in a equilibrium something then you add more hydrogen; that means, concentration you have changed there will be also change in the composition right. Even you change the volume right then also it will be changing the equilibrium composition right.

So, at the macroscopic level what is happening? It is remaining unchanged, means what, at equilibrium composition is not changing at the macroscopic level. But if you look at microscopic level what is happening? Is it changing or not? Something is happening or not, right? That means, reaction goes on it is basically known as dynamic equilibrium right. But however, how then it is happening the macroscopic level is not changing because the rate of forward reaction is same as the rate of backward reaction; that means, the reaction rate of the reactants is equal to reaction rate of the products at equilibrium, are you getting. So, that is the very important thing you should keep in mind.

Now, rate of reaction means what? Basically change in moles of species per unit time pr unit volume that is moles per second metre cube right. Now, when you talk these thing, but you know we will have to evaluate this reaction rate quantitatively right then for that we will have to use basically the law of mass action which was given by two Norwegian chemists, Gulberg and Waage in 1867 right, because we are interested to find out right a quantitative relationship between the reactant and product for that we need to invoke the reaction rate. So, therefore, we will have to find out right.

So, law of mass action states that that reaction rate of a chemical species is proportional to, to the product of concentration of the participating chemical species right, where each concentration right is raised to the power of to the corresponding stoichiometric coefficient in a chemical reaction right. And this you must have studied in your plus 2 level right, we are using it again. And again I will be invoking law of mass action in whenever we are dealing with chemical kinetics. This is very important one which we need to understand and keep in mind.

So, let us consider an arbitrary bimolecular reactions, right for example, like a moles of species a A means capital right is reacting with b moles of species capital B going to the c moles of species C and d moles of species D right.

Now, I want to you know right down this law of mass action for this. What it would be then? Any idea? This will be reaction rate is basically of a b if I take is proportional to c a concentration a power to the small a concentration of b power to the small b and these proportionality constant what you call basically k f that is forward reaction constant. You can, if you look at according to law of mass action right RR is proportional to C A a and C B b right and then this is equal to basically (Refer Time: 14:34). This k f is the forward reaction rate constant or the specific reaction rate constant people say that.

And similarly reaction rate of C d like when it is getting to backward direction then RR is proportional to C C c and C D d right and k b is backward reaction rate constant right. So, at equilibrium what is that RR AB is equal to RR CD right. So, therefore, we can say basically from here right I can say k f and using this relationship here right k f C A a, C B b is equal to k b C c and C d coefficient basically d small d right.

Then I can write down this you know we can right down C C power to the c, C D power to the small d divided by C A power to the a and C B power to be it will k f by k b is nothing, but K C. And this K C is what? Equilibrium constant right, this is the constant based on the concentration of the species right.

So, now we will have to see how we will handle it and what are the things right; about this equilibrium constant. If I know these values right K C, if I know this C A and C B then I can find out basically C C and C D that is the you know requirement what we need to estimate right. Because we have basically interested to find out what will be the product right concentrations and at the equilibrium what will have to find out.

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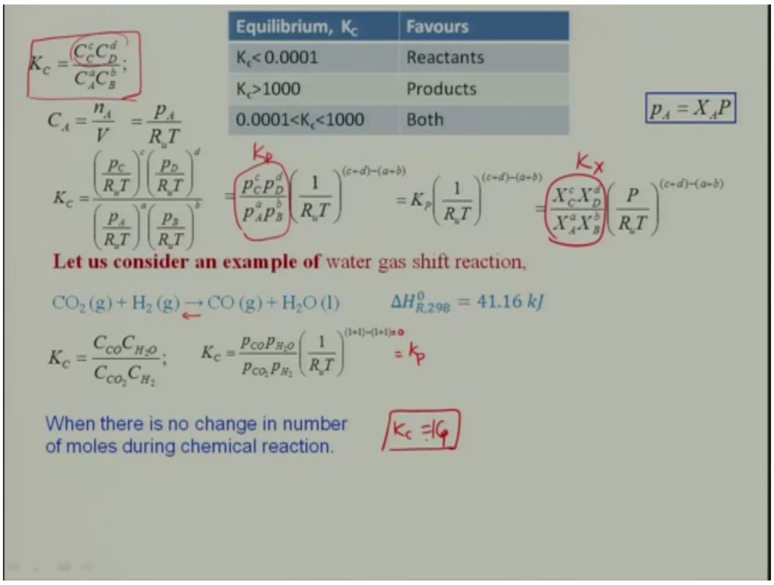

So, we know that K C is basically this term right, and if you look at K C is let us say very very less right, if it is a very small number ; what does it mean ? That means, basically the more reactants are favoured; that means, the reactants in the in the equilibrium product will be more as compared to the actually the products species right. But if K C is very very large right ; that means, ; that means, this will be this portion the product portion will be much large than that of the reactant.

So, therefore, products are favoured. But if it is in between; that means, reactant and you know products will be kind of thing will be there so, that we will take an example maybe to see that little later on.

But now let us look at basically concentration means the number of moles per unit volume right. And I can write down this by for the an ideal gas because keep in mind that we will be using ideal gas for our combustion calculation, for all the practical purposes right. So, then that is nothing, but your partial pressure away divided by R u T, R u is a universal gas constant, T is the temperature right.

Now, what I will do? I will instead of this concentration I can express in terms of partial pressure, right. So, then K C would be basically P C by R u T power to the C P D divided by R u T power to d right and that is in the numerator for the K C and denominator will be P A, R u T power to the a and P B, R u T power to the b right. I can you know segregate; that means, right down this partial pressure of east species separately and temperature separately. So, that would be basically you know this time constant picture and this we call it as a basically known as K p right equilibrium constant based on partial pressure right. And R u T (Refer Time: 19:27) c plus d minus a plus b right and that you can say.

Now, we will be more interested to basically find out in terms of mole fraction right. So, what we will do? We will a now convert this into mole fraction right. So, we know very well that right mole fraction is p A X A P, P is the pressure of the mixture p A, small p A is partial pressure of species a right. Summation of partial pressure of small species will be equal to the total pressure right.

So, then we can write down basically here in this place I can right down P C then X C c and X D d divided by X A a and X B b of course, this P will come into picture in the same term. So, this I call it as a K X. That means if you know one of them you can convert into other forms right, equilibrium constant, 3 equilibrium constants being used right. Let us consider an example of water gas shift reaction right, reaction which is being for producing hydrogen right because if you use in a reverse way right you can carbon monoxide reacting with the water going to the hydrogen and carbon dioxide right you can really and get that, and other way around you want to produce the carbon monoxide you can use that.

Let us say this is a heat of reaction for this reaction of course. Now, K C if I want to write down for these reactions it will be p C right this is a 1 mole. So, therefore, the like index is 1 and P water divided by P CO 2 and p hydrogen and 1 by R u T and keep in mind that this is all are 1 moles. So, therefore, this will be equal to 0 right yes or no right.

And then right is equal to basically K P K C is equal to K P, K. that means, it says when there is no change in number of moles during chemical reaction then K C is equal to K P. Only for this condition otherwise it will be different, K C is not same as the K P, are you getting.

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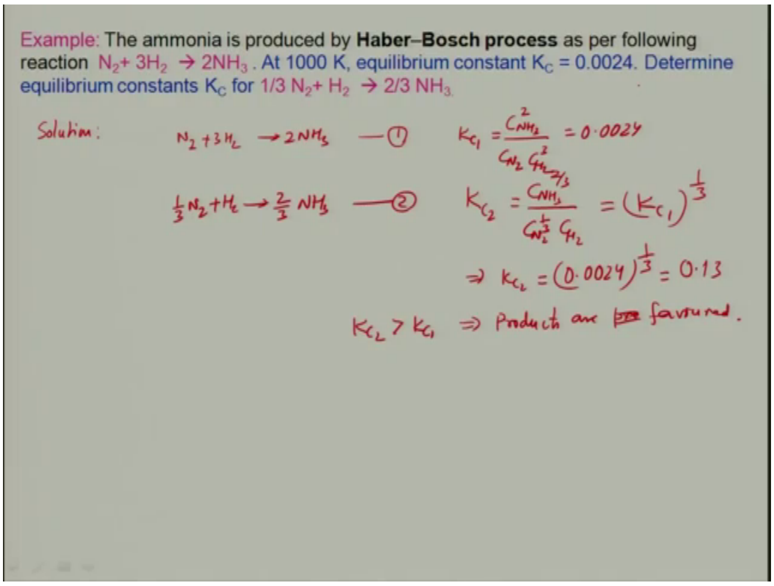

So, let us take an example right and in this example basically ammonia is produced by Haber Bosch process as per the following reaction, one moles of nitrogen react in 3 moles of hydrogen getting into 2 moles of ammonia. You might be knowing this ammonia you know is being used for the first time by this people, like you being produced by Haber and Bosch separately and right. So, at 1000 Kelvin equilibrium constant is K C 0.0024 right is given.

Now, we need to determine equilibrium constant K C for this reaction right. Like one-third mole of nitrogen react with one mole of hydrogen getting into product two-third moles of ammonia right.

So, if you look at the reaction you know you know that N 2 plus 3 s 2 into 2 NH 3 right, and this is let us say reaction 1, I can write down K C 1 as C NH 3 2 divided by C N 2 CH 2 3 is equal to 0.0024. And for reaction, second reaction right that is one-third N 2 plus H 2 two-third NH 3, what will be K C 2 ? Will be C NH 3 2 by 3 divided by N 2 one by third 3 and C H 2 right.

If you look at right this is nothing, but K C 1 power to the one-third is not it. So, that will happens to be; that means, K C 2 is equal to 0.0024 power to the one-third is equal to 0.13.

In this case if you look at we can calculate very easily from the if I know one of them other thing, but what is the implication of this example is that K C 2 is greater than K C 1, yes or no, is not it. Because this is 0.0024 this is 0.13, so this is greater. That means, in this case what will be preferred? It is the products right, products are preferred or favoured right.

Now, we will learn more about you know how to handle this you know equilibrium constants and how to calculate because in this example it is given K C, but now how I will know that that will have to see in the next lecture. We will stop over here.

Thank you very much.