Fundamentals Of Combustion (Part 1)
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Lecture – 17
Equilibrium constants and Le chatlier principle

Let us start this lecture with a third process if the life in this beautiful earth will be extinct in future; as expected by the research due to excess exploitation of nature resources by modern man then mother nature will try to restore her equilibrium.

So, in the last lecture we had basically discussing about chemical equilibrium right and we also derived relationship considering the Gibbs free energy how to relates this K p with the Gibbs free energy and temperature and also the universal gas constant. And also we express the equilibrium constant in terms of partial pressure and also the mole fractions right.

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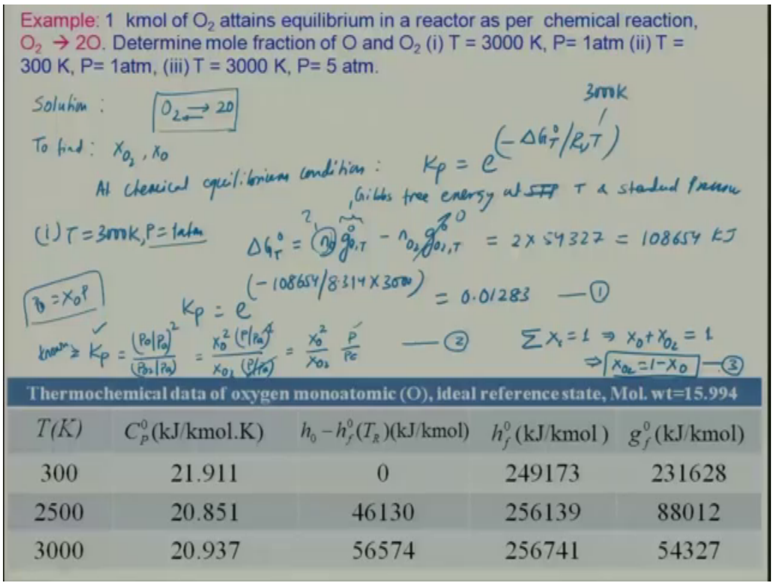

Example: 1 kmol of O_2 attains equilibrium in a reactor as per chemical reaction, $O_2 \rightarrow 2O$. Determine mole fraction of O and O_2 (i) T = 3000 K, P= 1atm (ii) T = 300 K, P= 1atm, (iii) T = 3000 K, P= 5 atm.

Solution : $\boxed{O_2 \rightleftarrows 2O}$

To find : X_{O_2}, X_O

At chemical equilibrium condition : $K_p = e^{\left(-\Delta G_T^0 / R_u \overset{3000K}{T}\right)}$

Gibbs free energy at STP T & standard pressure

(i) T = 3000K, P = 1atm

$$\Delta G_T^0 = \overset{2}{n_O}\, g^0_{O,T} - n_{O_2}\, \overset{0}{g^0_{O_2,T}} = 2 \times 54327 = 108654 \text{ kJ}$$

$$K_p = e^{(-108654/8.314 \times 3000)} = 0.01283 \quad \text{—①}$$

$\boxed{p_O = X_O P}$

$$\text{known} \geq K_p = \frac{(p_O/p_0)^2}{(p_{O_2}/p_0)} = \frac{X_O^2 (P/p_0)^2}{X_{O_2}(P/p_0)} = \frac{X_O^2}{X_{O_2}}\frac{P}{p_0} \quad \text{—②}$$

$$\Sigma X_i = 1 \Rightarrow X_O + X_{O_2} = 1$$

$$\Rightarrow \boxed{X_{O_2} = 1 - X_O} \quad \text{—③}$$

Thermochemical data of oxygen monoatomic (O), ideal reference state, Mol. wt=15.994

$T(K)$	C_p^0(kJ/kmol.K)	$h_0 - h_f^0(T_R)$(kJ/kmol)	h_f^0(kJ/kmol)	g_f^0(kJ/kmol)
300	21.911	0	249173	231628
2500	20.851	46130	256139	88012
3000	20.937	56574	256741	54327

And today we will take some example how to apply those thing to calculate the equilibrium. So, let us consider this example that is 1 kilo mole of oxygen attains equilibrium in a reactor as per chemical reaction O 2 going to the 2 O and we will have to determine the mole fraction of O and O 2 at 3 different cases have consider one is 3000 Kelvin pressure is one atmospheric pressure next is 300 Kelvin and pressure one atmospheric pressure and the third one is 3000 Kelvin and pressure 5 atmospheric what I am doing here? I am basically changing the temperature and changing the pressure that is the ideal.

So, if you look at solution this is basically the reaction is O 2 going to 2 O and also if it is equilibrium; that means, it can 2 O can combine may be coming back to O 2 right. So, if you look at we are basically interested to find out to find if you look at X O 2 and X O the mole fraction of the O and O 2 right. So, what will have to do will have to use the same thing right that is K p; if you look at the at chemical equilibrium condition, we know that K p is equal to e minus delta g T 0 divided by R U T right and we will have to also determine well.

What is delta g at temperature for example, we are considering the case of 1 only right this is T is equal to 3000 Kelvin and P is equal to 1 atmospheric pressure right; that means, this T this T is what 3000 Kelvin right, this will be 3 thousand Kelvin, and R u is your universal gas constant. So, how we will calculate this delta G T naught how I will do if you look at this is n o g I T I o actually, this is not o right and at the standard condition what is the standard condition 1 atmospheric pressure right, minus n o 2 g o 2 T standard condition.

And e we need to and these are what is that Gibbs free energy or Gibbs functions at standard condition right, Gibbs free energy at STP right at standard temperature, and pressure. Now from where I will get this values is it at standard temperature and pressure no this g naught right, will be function of temperature also right this will be not standard temperature right it will be at t and standard pressure is it yes or no right at different temperature, it will be different values therefore, the T is given here otherwise it could have been 298 Kelvin are you getting, now these from where I will get I will have to go to the table right, let us look at the table here in the table generally C P values will be given h h f for reference will be given h f naught will be given right, and this is g f right values at various temperature keep in mind that 3000, 3000 Kelvin it will be 54327 right kilo joule per kilo mole.

Right and it is 300 Kelvin it will be higher values, and O 2 being stable species therefore, it will be z 0 right. So, in this case what it would be 2 the number of moles is what this one is, this is your 2 moles 2 into 54327 is equal to 108654 kilo joule right. So, we will have to find out what is this K p K p will be e minus 108 654, and this is basically kilo joule, and R u is 8.314 kilo joule right what Kelvin into 3000, I will get this is 0.01283 right.

So, this is basically you can say that this is your equation 1 right, and for this above chemical reaction this is my chemical reactions, what I am using for this to valuate the equilibrium composition that is what will be K p, then K p will be p naught by p reference special reference special is atmospheric pressure.

So, I am just writing p a why I am changing, now p a because this o is there you may get confused therefore, I am changing to P a square divided by P o 2 P a right yes or no yes or no right. So, that is equal to if you look at P o P o is equal to X o into p yes or no this, I know this is o naught naught o. So, I can write down X o square P divided by P a whole square into X o 2 P by P a. So, that is coming x o square divided by X o 2, this will cancel it out. So, P by P a right this is let us say equation 2. Now keep in mind that K p value we know

this is the K p value; that means, this equation this is known this is known right, and that is equal to something for this case you know 0.0 0.01283 this is known right, this is known. Now this X o is known this is not known X o 2 is not known P is known, in this case what is P this P is 1 atmospheric pressure right, the case is this 1 nah P is 1 atmospheric pressure. So, this is p a so it can be cancel it out, but we will be keeping in general, because we will have to look at also effect of pressure ok. Now 2 unknown are there 1 equation how we will solve for that, what we will do we will have to use this summation of X i is equal to 1 that is nothing, but X o plus X o 2 is equal to 1 right; that means, X o 2 is equal to 1 minus X o, this is equation 3. Now we will combine equation 2 and 3 and try to solve it ok.

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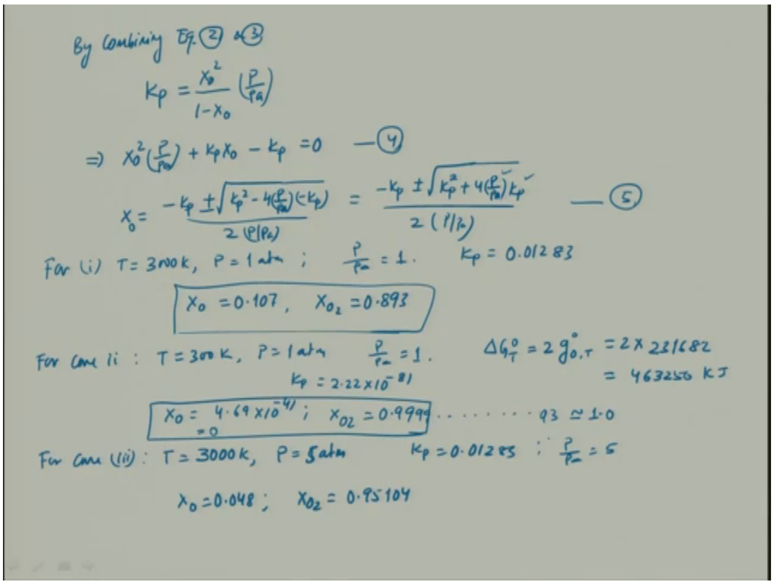

By combining Eq. ② & ③

$$K_p = \frac{X_o^2}{1-X_o}\left(\frac{P}{P_a}\right)$$

$$\Rightarrow X_o^2\left(\frac{P}{P_a}\right) + K_p X_o - K_p = 0 \quad — ④$$

$$X_o = \frac{-K_p \pm \sqrt{K_p^2 - 4\left(\frac{P}{P_a}\right)(-K_p)}}{2(P/P_a)} = \frac{-K_p \pm \sqrt{K_p^2 + 4\left(\frac{P}{P_a}\right)K_p}}{2(P/P_a)} \quad — ⑤$$

For (i) $T = 3000\,K$, $P = 1$ atm ; $\frac{P}{P_a} = 1.$ $K_p = 0.01283$

$$\boxed{X_o = 0.107, \quad X_{O_2} = 0.893}$$

For case ii : $T = 300\,K$, $P = 1$ atm $\frac{P}{P_a} = 1.$ $\Delta G_T^0 = 2\, g^{\circ}_{O,T} = 2 \times 231682$

$= 463250$ kJ

$K_p = 2.22 \times 10^{-81}$

$$\boxed{X_o = \underset{= 0}{4.69 \times 10^{-41}} ; \quad X_{O_2} = 0.9999} \cdots\cdots 93 \simeq 1.0$$

For case (iii) : $T = 3000\,K$, $P = 5$ atm $K_p = 0.01283$; $\because \frac{P}{P_a} = 5$

$X_o = 0.048$; $X_{O_2} = 0.95104$

So, by combining equation 2 and 3 right, am I right 2 and 4, so what I will get, I will get basically K p is equal to x naught square into 1 minus X naught right in place of X o 2 I am putting one minus X p by P a right, is not it is it right. So, what we will do I can write down this as X naught square P by P a right, plus plus K p X naught minus K p is equal to 0 yes or no. Let us say this is equation basically 4, and this equation we can solve because it is a quadratic equation we know the solution, what is that that will be X is equal to X naught X naught means X o not naught o, and minus you know what is that it would be minus ah.

Student: (Refer Time: 12:19).

K p is it minus K p right minus K p plus minus K p square 4 P by P naught into minus K p right. So, divided by 2 into P by P naught yes or no so I will get basically minus K p plus minus root over K p square plus 4 P by P naught K p divided by 2 P by P naught. So, in this equation if you look at all are known K p is known right, this is known P by P a naught is known. So, you can do very easily if I will substitute those values for case ok, I can write down this is 5 for substituting values for case, for i right i is what T is equal to 3000 Kelvin, and P is equal to 1 atmospheric pressure.

So therefore, P by P naught is equal to 1 and K p, if you look at we got 0.01283. So, for that case what you will get you will get X naught is equal to 0.107 and X naught 2, 0.893

right, this values you are getting. Now if you look at decomposition of o 2 is very very less even 3000 Kelvin are you getting 3000 Kelvin.

Temperature you will get now I will consider the case 2 right for case 2 what is that T is equal to 300 Kelvin. So, for that right delta and pressure of course, 1 atmospheric pressure, then similarly P by P naught will be 1, and delta G naught if you look at delta G T temperature at 300 Kelvin that we are calculating what it would be this will be basically 2 into g o T naught at 300 Kelvin.

So, that happens to be this values 231682 ok. So, we will just use that values is equal to 2 into 231682 is equal to 46 3256, and if I know this values that you know K p you will be getting what will be the K p values, and you will find that X naught K p values you will get for this, this you will get K p values 2 into 22 into 10 power minus 81, and you will get X will be 4.69 10 power T minus 41, and X o 2 will be 0.99.

So, these values you are getting what does it mean, that means at 300 Kelvin that is no dissociation at all this approximately equal to 0 this approximately equal to 9 9 9 9 9 may be dot dot dot goes on you know what it call 6 9 let us say 7 9 3 something it goes you know further what; that means, this is approximately equal to 1, no decomposition 298 Kelvin nothing will happen you know if we can assume that, but still why I am saying this still there will be little decomposition that is you cannot measure. So, it is negligible small are you getting. So, now we will consider for case 3 temperature 3000 Kelvin, and pressure 1 atmospheric no this is.

Student: 5 atmospheric.

5 atmospheric pressure right. Now if you look at we have already done that, right K p values we know K p will be same right. So, K p values.

Student: (Refer Time: 17:46).

Will be 0.01283, and what will be X naught X naught will be 0.048, and X naught 2 will be 0.95104 right. So, what is happening when you compare; that means, this X o was higher at 1 atmospheric pressure, and it is lower at this and vice versa; that means, x o 2 is higher at higher pressure right.

Student: Sir P upon P a will be 1 upon 5.

Yes P by I think P by P a will be 5, because P is 5 and this is this thing right ok. Now let us summarize these things.

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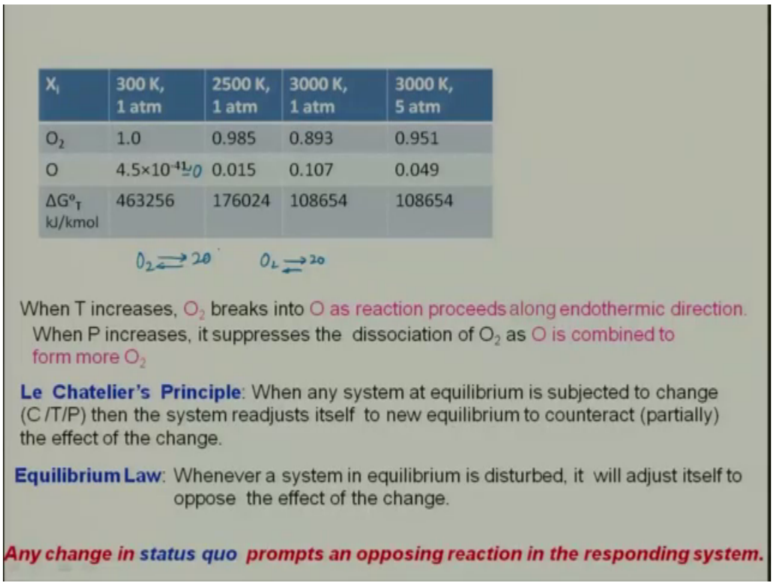

X_i	300 K, 1 atm	2500 K, 1 atm	3000 K, 1 atm	3000 K, 5 atm
O_2	1.0	0.985	0.893	0.951
O	$4.5\times10^{-41} \simeq 0$	0.015	0.107	0.049
ΔG°_T kJ/kmol	463256	176024	108654	108654

$O_2 \rightleftarrows 2O$ $O_2 \rightleftarrows 2O$

When T increases, O_2 breaks into O as reaction proceeds along endothermic direction.
When P increases, it suppresses the dissociation of O_2 as O is combined to form more O_2

Le Chatelier's Principle: When any system at equilibrium is subjected to change (C /T/P) then the system readjusts itself to new equilibrium to counteract (partially) the effect of the change.

Equilibrium Law: Whenever a system in equilibrium is disturbed, it will adjust itself to oppose the effect of the change.

Any change in status quo prompts an opposing reaction in the responding system.

Let us and see whether we can you know observe anything in this. So, let us consider the you know I have taken another case also, 2500 Kelvin and, 1 atmospheric pressure right at 300 Kelvin 1 atmospheric pressure what is happening to O, O is almost what we call 1, and this is approximately 0 ok. And when I increasing to 2500 Kelvin, keeping the pressure 1 atmospheric 0.985, and 0.15, and when I increase further the O 2 again reduce, because it is decompose into the O 0.107, right what is the interpretation you can do; that means, when temperature increases O 2 breaks into O, because the reaction is endothermic you know right.

And the reaction proceeds in endothermic direction, endothermic means basically O 2 is going to 2 O right. So, this is the direction in which it is going that does not mean no reaction is occurring in opposite direction it is occurring, but this side is more. So, therefore, you are getting what you call decomposition of the species right that means, O is more right.

Now let us look at consider these case these 2 cases like, 1 atmospheric pressure, and 5 atmospheric pressure right, let us say that what we are observing like here, if it is pressure is increase this is what do you call this is decrease O 2 is decomposes less right, it is not dissociated that much right, O 2 remain not dissociated to that extent what is occurring at 1 atmospheric pressure right and of course, similarly the O is reduced with increase.

In pressure right now when P increases it surfaces the dissociation right, in other words of O 2 as O is combine to form that means, the reaction if you look at in this way it is, but it is predominant in this direction 2 O is going to the O 2 right is more predominant at the pressure right.

So, can you really observe anything; that means, it is whenever the temperature increases the reaction proceed, in this, this you know reaction in a forward direction predominantly as compared to the backward direction, and when pressure increases the opposite way. And if I change the concentration right ok, at the equilibrium what will happen it will also change right. And if I summarize this thing what do you observe are you observing something.

Student: When you disturb the equilibrium it tries to regain.

It tries to regain, and as I told in the my opening remarks from you know this thing that mother nature will try to get back the equilibrium what it was right. So, that this observation was made, and stated by a scientist known as le chatelier right, and his principle is when whenever any system at equilibrium is subjected to change of either concentration, or the volume, or the temperature, or the pressure, any one of them right.

Then system re adjust itself to a new equilibrium to contract partially the effect of them it is not the total effect right for example, you might be knowing when we are inverted, right by the let us say may be Greek, or the Muslim, or the Hun, then we try to resist in the beginning we might have lost the equilibrium, but later on we reestablished the equilibrium yes on no.

But unfortunately today there is a cultural invasion, or culture is not been spoil by the all invaders keep in time, we have kept in time, but today without a knowledge there is a cultural invasion to this country to the market process, but we are not aware. If we are aware then we will try to regain our equilibrium.

So, I would aware upon you people to look at these things this is of course, chemical equilibrium, but you should also look at right; that means, whenever a system in equilibrium disturb it will adjust itself to oppose the effect of change right, and that we call it as a equilibrium nature. As an, this is the physical laws, and we are all subjected to physical laws. So, also our mind right.

So, therefore we need to reestablish our equilibrium by opposing the cultural invasion which is spoiling our country at this moment so; that means, any change in status quo prompts an opposing reaction in responding to heat right. So, therefore, we need to do and in the next lecture, I will find out how we can carry out these analysis of finding out equilibrium composition in a systematic manner right, and then I will take an example ok.

Thank you very much we will stop over here.