

hello students welcome to the third lecture of chemical equilibrium we started with the concept of your equilibrium constant equilibrium constant the way we defined equilibrium constant is suppose we take a reaction $a + b \rightleftharpoons c + d$ this reaction tells you that a mole of a reacts with b mole of b to give you c mole of c plus d mole of t then equilibrium constant was defined as concentration of c raised to power this c small c into concentration of d raised to power d divided by reactant a power a a reactant b power b

so this is the first concept which we introduced in the your chemical equilibrium the importance of k is importance of k

so suppose i take a reaction $m g + 2 Cu \rightleftharpoons m g + 2 Cu$

so value of k of this reaction is 10^{-9} and i take another reaction which is $Fe + 2 Cu \rightleftharpoons Fe + 2 Cu$

so there are two reactions first and second for the value of this k is your k for this reaction is 10^{-3}

so in the first case your mg reacts with copper 2 plus to give you copper whereas in the second case iron reacts with copper 2 plus to give you copper now what does this value suggest now you can see the value of k is different for the two reactions in this reaction your k is quite greater than suppose i take this as a k one and this is k two

so k one is quite greater than k two what does that mean is the amount of reaction are the amount of copper formed in these two case is going to be different since k1 and k2 is different this can also tell you in which reaction copper is formed in the greater amount now you can clearly see that k1 is quite greater than k2 this only means that copper will be formed in greater amount for reaction one

so value of k value of k will tell you how much a reaction can proceed or how much a product can form product will be formed in the greater amount if your k value is large then we introduce the concept of reaction quotient before that i will again explain another thing that if suppose if we are given two reactions two reactions for example if i takes $CoO(s) + S_2(g) \rightleftharpoons Co(s) + S_2O(g)$ and the another equation is $CoO(s) + CO(g) \rightleftharpoons Co(s) + CO_2(g)$

so these are the two reactions and if i know the equilibrium constant suppose this is k one this is k two we can calculate the k we can know the value of k if a reaction is given which can be expressed in terms of one and two for example we can take $CO_2(g) + S_2(g) \rightleftharpoons CO(g) + S_2O(g)$

so k for this reaction can be expressed in terms of k1 and k2 since your this reaction can be expressed in terms of these two reactions now let us see whether we can do it or not see this what is reactant in this case there are two reactants CO_2 and S_2 if you see in the first and second reaction suppose this is one this is two now CO_2 is product in this case where S_2 is reactant in this case

so if i take the reaction one and subtract the reaction two i will get this reaction and thus the axon third which is this one can be expressed in terms of reaction one and reaction two and thus k can be expressed in terms of k one and k two lets see how we can do it

so lets write the reaction one which is $CO_2(s) + S_2(g) \rightleftharpoons CO(s) + H_2O(g)$

so this is reaction one and then i take the reaction two which is $CO_2(s) + CO(g) \rightleftharpoons CO(s) + CO_2(g)$ this is the second reaction now k for this reaction is k one will be $\frac{CO_2}{CO \cdot S_2}$

so solid we do not take this

so we can just simply write $S_2O(g)$ divided by $S_2O(g)$ where for this one we can simply write K_2 is equal to $C_{O_2}(g)$ divided by $C_{CO}(g)$ now if we take the one minus two what we are going to get is your CO

so you take minus this minus and this is your this is CO

so this will be minus and you are going to get CO_2 just $C_{CO_2}(g)$ this side $CO_2(g)$ plus $S_2(g)$ giving you your this is minus CO

so C_{CO} will come this side $CO(g)$ plus $S_2(g)$ ok

so if you subtract reaction 1 and 2 this is the reaction which you will get for which we want to calculate the value of K now you can see this this K will be $C_{CO}(g) S_2(g) H_2O(g)$ divided by your is to $H_2(g)$ into $CO_2(g)$ $CO_2(g)$ and this is nothing but your K_1 divided by K_2 K_1 divided by Q_2 now you can see here K_1 divided by K_2

so $S_2O(g)$ $CO(g)$ will be at the numerator and $H_2(g)$ and $CO_2(g)$ will be in denominator

so if i can express a reaction in terms of two different reaction for which K value is known then i can express the value of the third reaction the unknown reaction now let us take the second case suppose we have given a reaction which is $2SO_2(g) + O_2(g)$ giving you $2SO_3(g)$ and suppose this this has some equilibrium constant K_1 which is known known now question is can i calculate the equilibrium constant for this reaction now you see this reaction nothing but reverse of this reaction and if suppose this i take K_{dash}

so K_{dash} is equal to your partial pressure of SO_2 square partial pressure of O_2 a square if i take K_p suppose partial pressure of O_2 divided by partial pressure of SO_3 square and that we can just simply write one divided by pressure of SO_3 square and then divided by P_{SO_2} square into P_{O_2} now you see this this is nothing but your K of this reaction equilibrium constant of this reaction

so K_p dash is simply K_p dash is simply one by K now again you saw that this reaction can be written or is related to this one and

so we are able to relate equilibrium constant of the first equation and the second equation i will take same reaction

so $2SO_2(g) + O_2(g)$ $2SO_3(g)$ and i told you that suppose equilibrium constant is K_p now suppose i take this is two equivalent $SO_2(g) + \frac{1}{2}O_2(g)$ giving you

so three gas

so three gas now you see only thing change is now i am saying one mole of SO_2 is reacting with half mole of CO_2 to give you SO_3 reaction is same stoichiometry has changed now you have you will have a different value of K how this K_p and K_p dash is related you can simply calculate by using the formula of equilibrium constant

so K_p dash is what partial pressure of SO_3 into partial pressure of SO_2 $SO_2(g)$ and partial pressure of your O_2 power half this is nothing but a square root of partial pressure of

so three square divided by partial pressure of SO_2 square into partial pressure of CO_2 and this is nothing but this whole thing in bracket is your equilibrium constant of this thing

so it is simply written like $K_p^{1/2}$

so we can express we can express equilibrium constant of a related reaction related reaction if the equilibrium constant of first reaction is known

so if i take a reaction $A + B$ going to $C + D$ $C + D$ and then i take a reaction $C + D$ going to $A + B$ this is a reverse reaction

so k_1 and k_2 is related by this equation k_1 is equal to k_2 if suppose i take a reaction $a + b \rightarrow c + d$ and if i take this as k_1 if i know this and suppose i take $\frac{1}{2}a + \frac{1}{2}b \rightarrow \frac{1}{2}c + \frac{1}{2}d$ and if i take a rate constant is k_1 then your k_1 is equal to your k_2 power

so if reaction is multiplied by half time then your equilibrium constant will be your just k_1 power half if this is multiplied by two times

so $2a + 2b \rightarrow 2c + 2d$ then this will be your square this will be a square and now if he takes suppose $a + b \rightarrow c + d$ and suppose i take $c + d \rightarrow e + f$

so these are consecutive reaction $c + d \rightarrow e + f$ and then product is $e + f$ and suppose the equilibrium constant for this one is k_1 this is k_2 i know the equilibrium constant for k_1 k_2 then what i need to do is simply add this $a + b \rightarrow c + d$ in that case equilibrium constant for this reaction will be $k_1 \times k_2$ and suppose i get a reaction like this $a + b \rightarrow c$ and we also know that $e + f \rightarrow c$ then i can again calculate the equilibrium constant k_1 k_2 then i can know what will be the equilibrium constant for this equilibrium constant for reaction $a + b \rightarrow e + f$ and this i can do by just subtracting this

so if i get a reaction from the subtraction then i can simply write k is equal to $k_1 \times k_2$ now this is regarding your equilibrium constant now let us take the case of reaction quotient

so there is a difference between reaction quotient equilibrium constant equilibrium constant the difference is

so for example if i take $a + b \rightarrow c + d$ differences difference is difference is due to the concentration which concentration this concentration is basically your equilibrium concentration

so k is simply $\frac{[c]_{eq} [d]_{eq}}{[a]_{eq} [b]_{eq}}$ well q is your concentration of here all the concentration is same but this is concentration at any time any time and

so q decides the direction of reaction you decides direction and last class i told you that q is equal to k when your reaction is at equilibrium equilibrium if q is less than k reaction will proceed in reaction well

so proceed in forward direction whereas q is greater than k then reverse reaction will take place reverse reaction will take place now k and q are k and q are related to related to your ΔG we know that ΔG which is change in free energy tells you about a spontaneity of the reaction and k and q can also tell you about the spontaneity of reaction or whether forward reaction is taking place or backward reaction is taking place

so there is a relationship between q and k and the relationship is ΔG is equal to $\Delta G^\circ + RT \ln q$

so this is q reaction quotient this is a reaction quotient

so ΔG is equal to $\Delta G^\circ + RT \ln q$ and we know that ΔG is equal to zero at equilibrium at equilibrium

so ΔG is equal to zero

so if i put it here zero is equal to $\Delta G^\circ + RT \ln q$ and you see q at equilibrium is equal to k and

so i can write k here q at equilibrium this is basically q at equilibrium equally k and

so ΔG° is equal to $-RT \ln k$

so what did we told is ΔG is equal to $\Delta G^\circ + RT \ln q$ and

ΔG° is equal to $-RT \ln K$ and

so ΔG is equal to if I suppose put this value here I will get $-RT \ln K + RT \ln Q$ and if I take RT common I take \log I can simply write this is Q by K now you can see here if Q is equal to K I will get this $\log 1$ $\ln 1$ one is nothing but zero

so at equilibrium

so let us see ΔG is equal to $RT \ln Q/K$ at equilibrium you have Q is equal to K and

so ΔG is equal to simply zero because $\ln 1$ is zero when Q is less than K when Q is less than K what does that mean that ΔG will be $RT \ln$ and this quantity Q/K is going to be less than one since Q is less than K and it means $\log Q/K$ will be negative $\log Q/K$ will be negative

so ΔG is negative and that is why your forward reaction is taking place when Q is greater than K

so ΔG is equal to $RT \ln K/Q$ by K in this case this is greater than one and

so this is positive

so forward reaction will not take place what will happen is reverse reaction will take place since ΔG is positive now let us go to a very important concept in chemical equilibria which is your Le Chatelier principle this is very important from the point of view is that it tells you under what condition under what condition we can get we can get maximum weight under hard condition I mean if I increase or decrease the pressure increase or decrease the temperature ok

so what does this Le Chatelier's principle tells you Le Chatelier's principle tells you tells what this Le Chatelier principle does this tells you the factor if we alter the alter the condition condition pressure temperature of volume ok we can change the we can change the the equilibrium and it also tells you not it does not only tell you that it will change the equilibrium it will change also the direction of equilibrium the equilibrium will shift to equilibrium equilibrium will shift to that direction that direction which tends to minimize the change this tends to minimize the change ok

so what are the things we can change first is concentration second is pressure or volume and third is your third is your temperature temperature in some cases temperature and pressure

so increase in pressure can increase the product but in other cases increase in pressure will decrease the product decrease the product similarly in some cases increase in temperature will increase the product and in some cases in other cases your increase in temperature will lead to decrease in pressure or decreasing product now let us take this reaction $N_2 + 3H_2 \rightleftharpoons 2NH_3$ yes all three are in gases all three are in gases now what the Le Chatelier principle tells you that if suppose I remove ammonia from the vessel the reaction will shift to ammonia side

so that minimize the effect or minimize the effect of decrease in concentration if I suppose take into out from the solution reaction will shift towards your left hand side where more into will be formed if suppose I put nitrogen gas inside the vessel reaction will shift towards your ammonia side forward direction

so that N_2 amount of into will be minimized and that is quite clear from this K because we know that K is $\frac{p_{NH_3}^2}{p_{N_2} p_{H_2}^3}$ now you must remain ah remember this that K is a constant quantity K is a constant quantity so suppose I increase suppose I increase the amount of ammonia

so this will be greater and for that to keep this constant this needs to be

greater

so when this will be greater when reaction will shift towards this direction all right

so that pressure of nitrogen will increase pressure of hydrogen will increase and this is whole thing will increase and the ratio of these two terms will remain constant suppose somehow i increase the pressure of nitrogen reaction will shift in that direction in which you see ammonia amount of ammonia will increase

so pressure of ammonia will increase such that K remains constant if i remove one of them if i remove suppose one of them for example i remove ammonia this will be a smaller term this has to be a smaller term and that will only happen and reaction will go to forward direction reaction will go to forward direction

so suppose i remove this suppose i remove ammonia then in that case your equilibrium is disturbed and Q is your $\frac{p_N^3}{p_N^2 \cdot p_S}$ now i have removed ammonia and p_N^3 is small

so Q will be less than K cube will be less than this quantity since numerator is now small and we know that when Q is less than K what happens what happens reaction will go towards forward direction reaction will go towards forward direction now effect of pressure change ok effect of pressure effect of pressure chain ok or you can say volume chain suppose i have taken a gas in this cylinder ok now if i increase the volume increase the volume

so $V_1 < V_2$ in this case V_1 is less than V_2

so what we expect that pressure in a vessel initial vessel will be greater

so $p_1 > p_2$

so what happens when we do that how does reaction gets affected how does equilibrium gets affected now you can take any reaction a suppose a mole of a plus b mole of b giving you c mole of c plus d in this case what will happen suppose all are in gases for ok

so K_p will be $\frac{p_c^c \cdot p_d^d}{p_a^a \cdot p_b^b}$ and now you see that what we did is we either increase the pressure suppose we increase the pressure

so what will happen

so we know that this is simply $K_p = \frac{x_c^c \cdot x_d^d}{x_a^a \cdot x_b^b}$ and this quantities when i take this out they will give you $K_p \cdot (p)^{\Delta n}$

so this is simply $K_p \cdot (p)^{\Delta n}$ and that is Δn is simply $c + d - a - b$

so just look at this if this is positive what does that mean this means this term will be greater if i increase the pressure this term will be higher but K_p is constant

so what needs to change $K_p \cdot (p)^{\Delta n}$ will change if Δn is positive this must decrease and when this will decrease when product will go to your reactant then only your K_p value will decrease on the other hand if Δn is negative then $K_p \cdot (p)^{\Delta n}$ should increase since K_p needs to be constant and $K_p \cdot (p)^{\Delta n}$ will only increase when product is formed in greater amount

so reaction will shift

so suppose i take two examples one is $2SO_2 + O_2 \rightleftharpoons 2SO_3$ giving you $2SO_3$ gas now in this case K_p is equal to your $K_p \cdot (p)^{-1}$ and for $2SO_2$ for oxygen one

so $2 - 2 + 1 = -1$

so is equal to $K_p \cdot (p)^{-1}$ now if suppose i increase the

pressure if i increase the pressure what will happen to k x if we increase the pressure we need to increase the k x am i right

so this is your k x by p this is k x by p

so i if i increase the pressure k a x should increase

so that k p remains constant when k x will increase k x will increase

so increase the p pressure k x will increase increase in k x and this means that your reaction will be forward reaction forward reaction will be failure forward reaction will be favored now take the second case p c l five your gaseous form going to p c l three gas plus c l two gas ok now your k p in this case will be k x into p you see in product side one p c l three one one c l two plus one now reactant minus one

so this is simply k x into p

so suppose i increase p the value of p if i increase the pressure what will happen if i increase the pressure your k x should decrease to keep k k p constant k x should decrease to keep k p constant and that means that reaction will proceed in in reverse direction reaction will proceed in a reverse direction

so there are two ways in which we can increase the pressure one is by just compressing and another by your just expanding it just by sorry ah by compressing by you can increase the pressure by expanding you can decrease the pressure

so if mixture is compressed pressure increased and your reverse reaction will happen on the other hand we can think of if i decrease the pressure what will happen if i decrease the pressure then reaction will proceed in forward direction now pressure can be increased in another way pressure can be increased in another way the way is your by introduction of introduction of anode gas

so now what i am doing i am not just we have taken a gas and then

so suppose volume is v and now what we can do is we can just introduce some inert gas

so pressure increased increased ok introduce some minor gas

so that pressure increase

so at if i increase if i if i increase the pressure by just adding another gas what will happen what should happen ok

so initially what we

so showed is if i change the pressure by changing the volume i did

so it will depend on which kind of reaction we are talking about ok which kind of reaction we are talking about if delta n is positive but we did see that if i increase the pressure if i increase the pressure reaction will go to reverse direction if i decrease the pressure reaction will go to forward direction if delta n is negative then just reverse is the case but now we are increasing pressure not by changing volume by just introducing your just introducing your inert gas in that case what will happen

so let us take this case p c l five gas going to p c l three gas plus c l two gas ok and i did told you that k p is equal to pressure of p c l three multiplied by pressure of c l two divided by pressure of p c l five pressure of p c alpha ok and we can also write in terms of mole fraction

so x p c l three into p p is the total pressure x p c l three into your sorry c l two into p divided by x p c l five into p ok now you can think of this this is what n p c l three p c l three by your sigma n where sigma n is total number of moles total number of moles that will include not only mole of p c l phi p c l three c l two but also moles of inert gas ok

so this is into p into p

so let us take p outside

so i will just first write your number of moles

so number of moles of PCl_2 divided by σ_n and then a number of moles of PCl_5 divided by σ_n and this is one p cancels out this is p and so this is simply your n_{PCl_5} into n_{PCl_2} divided by n sorry this is n_{PCl_3} n_{PCl_3} this is n_{PCl_5} into σ_n

so one σ_n one σ_n cancels out

so σ_n is left into p now you see when i am trying to increase the pressure by just adding inert gas and i keep volume constant what happens is we have this term p by σ_n okay p by σ_n and since pressure is changed by introducing n and we know p by n is constant p by n is constant at constant volume and temperature

so this p by n σ_n is simply constant and

so there is no effect of addition of inert gas on equilibria if pressure is increased by keeping volume constant pressure is increased by adding inert gas but keeping volume constant equilibria will be affected if i add inert gas pressure is constant but volume is not constant ok

so lets see the effect of inert gas effect of inert gas on equilibrium effect of inert gas on equilibrium your PCl_5 gas 2PCl_3 gas plus Cl_2 gas ok and we know that K_p is equal to $p_{\text{PCl}_3}^2 p_{\text{PCl}_5}$ and this is your n_{PCl_3} by σ_n into p_{Cl_2} by σ_n into p_a^2 for first p for this PCl_3 and the second one for p_{PCl_5} and this is n_{PCl_5} by σ_n into p

so what does that mean is your again we can write n_{PCl_3} into n_{Cl_2} by your n_{PCl_5} into σ_n into p now see i told you that now what i am trying to do is i am trying to introduce in not gas keeping pressure constant

so pressure is constant but σ_n has increased

so we have added inert gas such that σ_n has increased

so what is effect of inert gas when pressure is constant you can just see σ_n

so this is your σ_n has increased

so what need to decrease

so that K_p is constant you can see this needs to decrease

so if i add inert gas reaction will proceed from this direction to this

so to the left σ_n increase will increase this sorry σ_n increase will increase this

so p_{Cl_2}

so basically your forward reaction will be forward reaction is going to be favored if σ_n decrease then your reverse reaction will be favored

so let us make a conclusion

so effect of increase in effect of increase in pressure your Δn is Δn is equal to your positive then your forward reaction will a reverse reaction well reverse reaction will be favored in favor Δn is negative then forward reaction will be favored with increase in pressure this is with increase in pressure ok i will stop here in the next class we will discuss the effect of temperature foreign