hello students my name is shashankdeep and i am associate professor at department of chemistry iit delhi today i am going to talk about equilibrium generally this is a very important topic in a chemistry since suppose we are taking a reaction ammonia formation or pcl5 dissociation or any reaction which you can think of we need to know that under what condition we can get maximum concentration of the product

so in that case we will apply concept of equilibrium

so in this chapter we are going to discuss about first what is equilibrium when we can say that a reaction is in equilibrium then we look for the reason why equilibrium exist then we can discuss about type of equilibrium and then we will discuss about homogeneous and heterogeneous equilibrium what do we mean by homogeneous or heterogeneous equilibrium then we will discuss how to get equilibrium constant and what is the significance of this

so we will calculate k c which is equilibrium constant using equilibrium concentrations then we will also discuss the relationship between initial concentration and kc value types of equilibrium constant relationship between k c k p k x a reaction quotient

so we will calculate k c if initial concentration is given we can also go in opposite direction if kc is given we can calculate what can be the concentration at equilibrium what is the concentration attitude

so let us first discuss about what is equilibrium what do we mean by equilibrium equilibrium what do we mean by equilibrium for that i will use this picture equilibrium is basically a state of balance between opposite forces or action a state of balance you must remember this is called a state of balance and there are two opposing forces

so if we take a case of seesaw seesaw here you see on the both side there is a person sitting and

so they are exerting force

so this person exerting force in this direction and this person exerting force in this direction they will get a balance only when the force is equal here balance between two opposing forces and we can get equilibrium suppose we have a reaction we can take any reaction for example a to b a to b now suppose i start with pure a suppose i start with pure a

so there are suppose six molecule of a if i leave a alone in a container what will happen that a will go to b a to b a is a spontaneous reaction a is going to be after some time what we will see is the number of mole of a decreasing a number of mole of b increasing

so suppose we have four molecule of a left and two molecule of b is formed now suppose i look at the container after sometime i see more changes in the number of molecules of a and number of molecules of b

so suppose now only three molecule of reactants is there and three molecules of b is found now again wait for some hour and then look at the container now what i see is there is no more changes in a and no more changes in b

so just look at if suppose i give this a state 1 state two state three state four

so we see that from one to two there is change in number of molecules of reactant and product if i go from a state 2 to a state 3 again there is a change of your number of reactant and number of product but after this we are seeing there is no change there is no change we can wait for more hour if we do not see any change that means equilibrium state is achieved ah equilibrium s t t s j

so three and four gives you equilibrium state equilibrium state now take the reverse reaction b two a what will happen again b two a is also spontaneous

so what does that mean delta g for this process will be less than zero

so suppose i start with b

so only b molecules are in container and we leave it for some time what i will see is b is going to a and suppose again two molecule of b goes to a now leave for some more time you will see that your more a is converting to b and we will go to the state where three molecules of b and three molecules of a is present and then we will see no change you will see no change again three molecules of a and three molecules of b as in case of your forward process

so in reverse process we start with six molecule of b and then we see that again we are going and getting three molecules of a and three molecules of b and if we leave it for more time there is no change in the number of molecules of a and b and then this state is called equilibrium mistake

so suppose if i plot amount of a and b a and b with extent of reaction extent of reaction what you will see is there is a decrease of a thats what we expect and there is a increase of b with time and finally there will be a plateau and concentration of a

so this is your a this is your b a decreases with time and there is a plateau after that concentration of a does not change the increase of b and after sometime there is no change in the concentration of b

so concentration of a and b does not change with change with time at this plateau at this plateau and then we say that reaction has achieved equilibrium on the other hand if we start with b and look at extent of reaction an amount of a and b then b will first decrease and then its concentration does not change after some time a will increase and at this time the concentration of a will not change

so after this time when concentration of a and b are not changing not changing we say that equilibrium equilibrium estate is achieved equilibrium has been established ok

so now think of another reaction a plus b giving you c again you will say same thing initially a and b will decrease a and b will decrease and c will increase c will increase with time with time and after some time after some time your concentration of a and b a b and c will not change it means equilibrium state is achieved

so when concentration of reactant of products are not changing with time then we say that equilibrium state is achieved similarly we can start from c c will again go to a plus b if we have a only c in the container it will go to a plus b till a b and c does not change when the change is 0 there is no change happening we see that equilibrium is achieved

so what is importance of equilibrium that in equilibrium all measurable property all measurable property properties of the system of the system remain constant and what is the balancing force here balancing force is rate of forward reaction when rate of forward reaction becomes rate of reverse reaction or backward reaction we say that equilibrium is achieved equilibrium is h equilibrium is achieved now let us talk about why equilibrium happens region for equilibrium

so suppose we are talking about this reaction a gas to b gas from thermodynamics we know that this reaction is spontaneous spontaneous only when delta g is less than zero what does that mean gb is or less than ga gb is less than ga

so when gb is less than ga reaction is spontaneous now question is if g b is less than g a y reaction does not go to completion the second question is if g b is less than g a y reverse reaction happens if we start from start from pure b for this let us again think about reaction a gas to b gas

so we started from puree puree and then we are going to pure b we are going to pure b in between you have a states where there is a mixture of a and b

so sum of a exist as a and sum of a has gone to b so this is your first state second state and this is third we know that free energy of this state is g a this is gb this is per mole of ah g free energy per mole of a this is free energy per mole of b and then you have g of g of the state two now how will we calculate g of state two will be given by this we can calculate by ah looking at this equation

so suppose a gas going to b gas we start with one mole this is zero mole and at time t this is extent of reaction is e and in that case left a is one minus e mole and this is e mole per liter

so g of state 2 will be equal to g of this state 2 will be equal to 1 minus e multiplied by g of a since there are 1 minus e mole of a in the mixture

so we can just simply multiply g a by 1 minus e and plus now in mixture we have e molecule of b

so we have e into g

so g two is equal to one minus e into g a plus e into g b

so delta g for the process will be equal to delta g will be equal to 1 minus e g a plus e into gb and since we started with one mole of a

so minus one into g a and

so this is g a minus e g a plus e g b minus g a this g a g a cancels out

so what we are left with is e g b minus g and we know that b is g b is less than g a

so this is always going to be negative

so what does that mean is if we plot g versus g versus extent of reaction we will get equation like this and that is quite clear from here that when we have e is equal to 0 then you are left with only g a

so e is equal to 0 at this point then your g is equal to g a when e is equal to 1 this term goes to 0 and we have g 2 is equal to zb g2 is equal to gb

so this is ga and gb and if i just write down this g a minus e g a plus e g b

so you can see that your g 2 is equal to simply ga plus e gb minus ga gb minus ga

so this is a equation of a straight line if you plot g two versus e slope will be gb minus ga and intercept will be g

so thats what you are getting here

so slope is your g b minus g slope is your gb minus j

so what we expected since gb is equal to gb ah delta g is equal to negative at each point

so what we expect that reactions should go to compression however we know that reaction does not go to completion

so what is the things which stops reactions to go to completion

so let us again think about the process we started with pure a and we went to pure b we went to pure b now think of what is happening in this process you start with puree and you end with pure b in between there are states which are both a and b which has both a and b if these are separate then the delta g which you calculated will be the way we got it

so delta g will be equal to egb minus ga however being in mixed state has contribution to entropy has contribution to entropy

so mixed state always have higher entropy compared to the pure steel

so just if you look at the mixing process and try to understand about entropy then in this first process where we are going from pure reactant to mixed state delta s will be greater than zero however when we go from this state state 2 to a state 3 delta s is less than 0.

this is just because of mixing

so i am talking about effect of mixing and this has contribution to delta g and what we will write here is delta g mixture now we know that delta g mixture delta g is equal to delta h minus t delta s if mixing is ideal then we take this equal to zero

so basically delta g mixing is equal to minus t delta s mixing and we know that for first step delta x mixing is greater than 0 and

so this will be your delta g mixing will have your negative component it will have negative component but when you go from mixed state to pure b delta s is less than 0 delta s is a negative quantity and

so this will have positive contribution

so your delta g is total delta g is we know that this is your this has negative contribution since gb is less than ga delta g mix has both type of contribution if you take process this it has a negative contribution if you take this stage it has positive contribution when you are working with this state delta positive there will be a time when this factor outweighs the negative part and in that case delta g becomes positive

so if we plot g versus e again g versus e again if you do not consider mixing then you you should get graph like this but if we consider your if we consider mixing then there will be minus t delta s initially it will make the process more spontaneous but after certain time when delta g is greater than zero you will get this kind of thing this kind of waste and

so this is because of this change in entropy due to mixing that a reaction does not go to completion a reaction does not go to completion if there is no effect of there is no effect of mixing then we should expect that delta g should be less than always delta g should be less than zero but it is because of mixing you have two different design in one regime delta g is less than zero delta g is less than zero and other regime delta j is greater than zero and this is the point when delta g is equal to zero and this is your equilibrium point this is your equilibrium point this is your equilibrium point and again we can answer the second question also that if we start from pure b y reaction happens although g b is greater than g

so if there is no mixing then reactions should not have happen but due to mixing entropy increases and that gives you negative contribution to g and

so reaction takes place

so in entropy of mixing entropy of mixing is responsible for reaction not going to completion reaction not going to compress

so we discussed first about equilibrium what is equilibrium suppose we start with a and just leave it in a container for some time there will be a time when a and b the concentration of a and b ratio of concentration of a and b will become constant a will not change b will not change and during that state no physical property will change in that case you tell ok equilibrium is achieved reason for equilibrium is although g of b may be less than g of a when b is getting form a and b will mix and there will be a time when this mixing will be will decrease delta g to such an extent that conversion further conversion of a to b is not possible similarly if you start from b we will get converted into a since b is getting mixed with a entropy of mixing entropy of mixing is increasing entropy of mixing is increasing

so now we discussed about what is equilibrium and why that happens now let us go and discuss about types of equilibrium types of equilibrium there are two types of equilibrium one is your physical equilibrium and chemical equilibrium physical equilibrium and chemical equilibrium

so physical equilibrium is when equilibrium is established in a physical process physical process while chemical equilibrium is when equilibrium is established in a chemical reaction chemical reaction

so let us discuss first about what is a physical equilibrium

so lets see this is the condition which i am going to discuss is your your melting of ice are freezing of water so freezing of water

so this is the case when s two o liquid at zero degree celsius and one atmosphere converge to solid zero degree celsius at one atmosphere now reverse process is melting when s2 is solid at 0 degree celsius and 1 atmosphere converge to s2o liquid at 0 degree celsius and 1 atmosphere you can think about this case suppose you take a beaker you have water and then you put ice here this is ice ok this is water and if we put at 0 degree then either water will go to ice or ice will melt depending on concentration of water and ice

so at zero degree celsius and one atmosphere your concentration of water divided by concentration of ice is going to be constant similarly we can start from ah ice cube and just leave it at zero degree celsius and one atmosphere what you will see is that water ice is getting converted into water

so a small amount of ice will go to water you can go in other way start with water put at zero degree celsius one atmosphere you will see some freezing of water into ice

so melting and freezing of melting of ice or freezing of liquid water is a reversible process is a reversible process and equilibrium exist between your water ice and water liquid now next thing you can think of is boiling boiling of water molecule ok

so suppose i take water and put at 100 degree celsius what will happen that some molecule of water will get converted into water vapor not all molecule will go to your water vapor similarly if i take water vapor and put at 100 degree celsius it will some of the amount of water vapor will go to water into the liquid form

so an equilibrium is always established whether we start from liquid form or vapor from form an equilibrium will established when there is no more conversion between liquid and vapor no more conversion between liquid and this is known as liquid vapor equilibrium there are other cases of equilibrium and for example if you are looking at solubility of solute in solution

so suppose i take water and i want to dissolve a gcl you put some amount of agcl you mix it you will see it will dissolve but if you put extra m on then you will see it is not getting dissolved only very small amount of a gcl goes into water ok

so these are the soluble form a g plus plus c l minus while you will see that lot of a g c l comes and settles down at the bottom at the bottom it means this is a reversible reaction and a g plus plus c l minus is in equilibrium with agcl solid form adcl solid form ok egcl solid form and

so this is a different kind of equilibria where we are looking at solubility of solute in solution now chemical equilibrium this is the till now we have discussed physical equilibrium now we can discuss chemical equilibrium chemical equilibrium you can take any chemical reaction a plus b going to c plus d for example formation of ammonia n two plus three s two giving you two n s three you can look at dissociation of p c l five v c l three plus c l two these are the cases of chemical equilibrium

so either we start with p c l five or p c l three or c l two there will be one point when reactant will stop getting converted into product

so after a time

so 100 percent conversion is not possible pcl 5 dozen goes completely into p c l three and c l two amount of p c l five will change to p c l three and c l two now equilibrium can be of different types the type of equilibrium will also depend on ah phases which kind of phases are there in the reaction

so there are two different kind of reactions first is your homogeneous reaction in homogeneous reaction all the components are in single phase what i mean by single phase is it is either in solid form or liquid or gas is formed all reactants and products

so all reactants and all component means all reactants and products and products for example if i take a reaction now you can see that a in gaseous form is going to be in gaseous form plus c in gaseous form

so all come all reactant and product a b c are in gaseous phase this kind of reaction is called homogeneous reaction now heterogeneous equilibria heterogeneous equilibrium for example if you take a solid for example calcium carbonate this is this exists in solid form and if we just dissociate it it will give me calcium oxide solid plus c o two gas now you can see that although calcium carbonate and calcium oxide are in solid phase your co two is not in solid phase

so you have two phases in the reaction solid and gaseous phase and that kind of equilibria is known as heterogeneous equilibrium heterogeneous equilibrium now what i told you about equilibrium is chemical equilibrium is the balancing force is rate of forward reaction and the other force is rate of reverse reaction when they are equal then we say that equilibrium exist

so suppose i take a reaction a molecule of a reacting with b molecule of b to give you c molecule of c and d molecule of d

so lets calculate what is the rate of forward reaction rf we know that r f is equal to k f which is the rate constant a power a b power b similarly we can calculate rate of backward reaction and that is k b c power c and d power d now at equilibrium at equilibrium since r f is equal to r reverse or r backward

so we can simply write k f a power a b power b is equal to k b c power c and d power d in that case we can simply write k f by k b is equal to c power c d power d divided by a power a and b power b and since these are constant k f and k b are constant you can write k k and this k is called equilibrium constant gram constant equilibrium constant

so you can see that if i use the condition r f is equal to r b then we get this formula where c power c d power d divided by a power a b power b will give you a constant and that constant is called equilibrium constant and since here we are taking as concentration this is also known as kc this is also known as kc

so suppose i take a reaction n 2 plus 3 s 2 giving you n s 3 two n s three ok

so in that case k will be k c will be n s three product n s three the product

so you see product s square since stoichiometry is two divided by n two this comes from here by s two and since three molecules of s two has been used

so put three here and this is how we calculate equilibrium n constant three s square divided by n two is two three

so we can calculate k c using concentration of n s three s square into divided by n two into s two q you must keep this thing in mind that this concentration is the concentration of ammonia at equilibrium not at any time ah this is the concentration of ammonia at equilibrium similarly this is the concentration of nitrogen at equilibrium this is the concentration of s2 at equilibrium if you take some another point where equilibrium is not achieved then the concentration ratio is not k c in that case it is called q which is reaction quotient

so this is different this is not equal to k c and when we write this this is n s three at any time t a square this is not at equilibrium divided by n two at any time t where equilibrium is not achieved divided by s two but suppose this at this time equilibrium is achieved it means the concentration an ns3 at that particular time is basically equilibrium concentration of ammonia similarly n 2 is equilibrium concentration of nitrogen and h 2 at time t is equilibrium concentration of hydrogen gas then in that case q becomes equal to kc now take this reaction again further n 2 plus 3 is 2 a 2 n s 3 equilibrium can also be equilibrium can also be also be expressed in terms of partial pressure of partial pressure since all these three components n 2 is in gaseous form s 2 is in gaseous form and n s 3 is in gaseous form in that case equilibrium can also be expressed in terms of partial pressure of various gases

so for example in this reaction we can write k is equal to pressure of ammonia partial pressure of ammonia square divided by partial pressure of n 2 and partial pressure of s to power q and that k is called k p this k is called k p

so this is different from k c in k c we use concentration where as in k p we use partial pressure partial pressure

so we can write for example suppose we take p c l five giving you pcl 3 plus cl2 again these are in gaseous form gaseous form gas is formed

so we can express this equilibrium in two different terms k c and k p k c is basically p c l three into c l two divided by p c l five whereas k p can be written as pressure of p c l three into partial pressure of c l two divided by partial pressure of u c l five partial pressure of fish alpha now once we know that what is k p k c we can also look at the relationship between this relationship what is the relationship between k p and k c

so let us think of same reaction p c l five giving you p c l p c l three plus c l two these all are in gaseous form and just i wrote down k c k p is equal to pressure or k c is equal to concentration of p c l three into c l two by p c l phi suppose these are gases which follow your ideal gas equation in that case we can write simply p v is equal to n r t and p is equal to n by v r t and we know that n by v is c

so we can simply write c r t ok

so suppose i take k p k p is p p c l three into p c l two divided by p p c l five i can write this simply as p is equal to concentration of p c l three concentration then r t

so multiply here by r t and then c l two multiply this by r t p c l five divided by p c l five multiply this by r t one r t r t cancels out

so we can simply write that kc into rt kc into rt rt power one

so this is the way we can calculate the relationship between k p and k c lets take a general case a a going to b b ah sorry plus b b giving you c molecule of c plus d molecule of d in this case your k c will be k p will be given as pressure of c power c pressure of d power d divided by pressure of a power a and pressure of p power v power b and we know that p is equal to c r t

so we can simply write c this is the concentration of c or let us write concentration of c into r t power c concentration of d r t power d divided by concentration of a r t power a b r t power b now we can simply write c into d c power c into d power d divided by a power a b power b now what is left is r t and

so we can just write r t c plus d minus a minus b or we can simply write k c into r t delta n

so delta n is where delta n is n of product minus n of reactant

so for example in this case you can see that np is c plus d where is n r is a plus b

so this is c plus d minus a minus b

so there is a relation between k p and k c and the relation is k p is equal to k c r t delta n r c delta m for example if i take two n o two n o two gas to n two o four n two o four gas now what is the relationship between k p and k c

so k p will be k c r t delta n you see n is n in product is one minus a n in reactant is two

so it is simply k c r t minus one

so this is the relationship between k p and k c for this reaction for this reaction now suppose we take another reaction s two plus i two jar again gas is formed gives you two h i gases four now in this case k p is equal to k c r t now you see product is two minus one minus one it means this is simply zero

so this is simply
so for this reaction s two plus i two going to two h i gas your k p is basically equal to k c
so till now we have discussed cases of homogeneous equilibrium
so whether we take p c l five going to p c l three plus c l two n two plus three h two going to ammonia all components are in gaseous phase and that is why ah we can say that these reactions are homogeneous reactions and the equilibria established in these reactions are homogeneous equilibrium now lets think about if suppose i have a heterogeneous system what will happen in heterogeneous how will we express equilibrium constant in cases where system is not homogeneous system is heterogeneous there are more than one phases available for example calcium carbonate solid going to calcium oxide solid plus co2 gas co2 gas now in this case we write k c as simply concentration of c o two since concentration of solids are taken as one they are constant and taken as one and in that case kc is equal to co2 simply co2 or kp if i want to express kp i will just neglect this solid terms we i will simply write pco2
so kp is pressure of co2 kp is pressure of co2 we can again think of another equilibria like agcl going to a g plus plus c l minus a g plus plus c l minus
so this is in solid form and this is aqueous a g plus this is a quest c l minus now again agcl in solid form and
so we express k c is equal to simply a g plus plus sorry a g plus into c l minus
so this is your k and this is called solubility product k s p this equilibrium constant is called k s p and this is equal to a g plus into c l minus
so today i will stop here in the next class we will do more questions and discuss what is the effect of temperature pressure on the equilibrium constant you