Course on Analytical Chemistry
Professor Debashis Ray
Department of Chemistry
Indian Institute of Technology Kharagpur
Module No 03
Lecture 14: Chemical Equilibria (Contd.)

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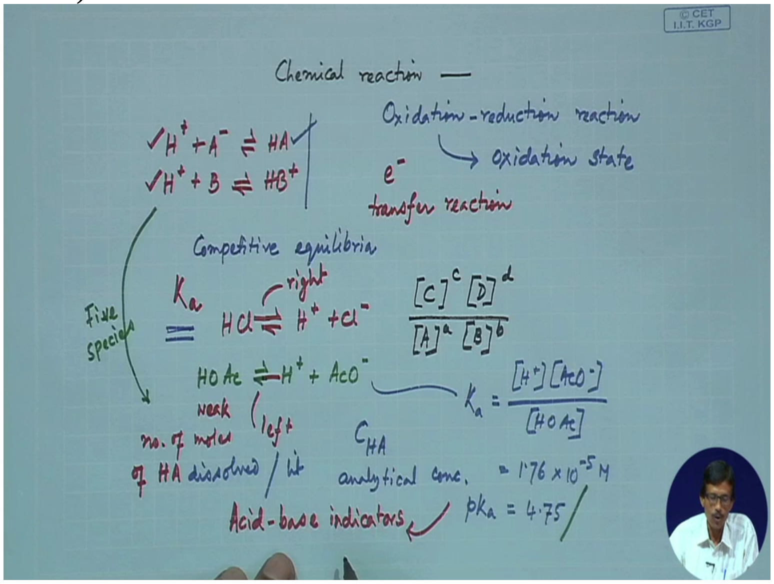

Hello, welcome back to this class and we are talking about the determination of KA values and what we are talking in terms of the corresponding concentration. So if we have a concentration like C power C multiplied by D power D the number of moles, so how we quantitatively determine the concentrations of the different species present over there? So this we have seen that this A powered A and B powered B. So what are the species you can have in a particular reaction like this?

So that we will see that if we have a reaction like this where we can have the species HA, the species HB and HA minus and B, so all of them, that means concentration of these, these, these 2 and so we have 5 species together. So the their individual concentrations are therefore important to undermine the corresponding KA value. So if we have simple acetic acid dissociation, we know that this is a weak acid and this dissociation is very important because we will be talking something related to not only the dissociation of acid but also the corresponding fate of the corresponding anion which is produced in the reaction.

Because since this is a weak acid, dissociation is not much, K value is less, so if this particular acid is weak, its conjugate base will be strong enough. So how this particular strong Uhh this particular anion can function and can control the corresponding equilibrium. So what we see that the number of moles because this C, D, A and B so we are talking and the power thing for the corresponding concentration we are powered by the corresponding strength.

So if we consider that that we are, how far this equilibrium is going from left to right if it is weak that equilibrium lies far to the left. So equilibrium is only going towards the left. So this will be a long arrow. The other one is a very short arrow. So it is going to the left. And the concentration what we are talking or we are thinking about is the number of moles of this acid, that means the HA. If we consider that this is your HA so the number of moles of this HA so what is that?

This HA dissolve per litre of the solution is dissolved per of the solution. So we will get at some point that the CHA which is nothing but your analytical concentration which we are interested to determine. So this analytical concentration that how we determine this particular one, so this one compared to your hydrochloric acid, as I told you in our previous class which is completely dissociated so if we have HCl so this HCl can give rise to your H plus plus Cl minus.

And this is going more on the right-hand side so it is staying or lies far to the right. This particular equilibrium is staying on the left and this particular equilibrium is going to the right. So the concentration of the individual species (())(4:40) in a particular equilibrium process or equilibrium reaction is different. So that way we what we get, this particular reaction, that means the same KA value, the KA value for the species A, B, C, D what we are discussing so far in this particular concentration for the acid, so the acid dissociation constant A stands for acid is for the corresponding H plus concentration, corresponding acetate ion concentration and the concentration of the undissociated acetic acid.

So all will be there and this particular value is less basically, is 1 dollar 76 into 10 to the power minus 5 molar. So this particular one if we consider, that also give rise to we, how we determine or how we record or how we tabulate or represent the value in terms of this PK value like that of your pH. So its PK value is 4 dollar 75. so this is an interesting parameter for acetic acid giving a value of 4 dollar 75 so which is related to the corresponding acid dissociation constant of your acetic acid.

So experimentally we can determine also for this particular parameter for some other species where we find that this particular species can be useful to determine or level particular compound, organic compound which can be again a weak acid like that of our acetic acid. So we will see that some point of time we will again bring this thing. That means there are several acid base indicators we all know like that of our phenolphthalene, that of our methyl orange and also the methyl red.

So if they are like acetic acid, a weak acid, weak organic acid, so you can determine the corresponding PK value for this and this is basically levelled which is a characteristic property for all these indicators where we all know that PKA for this and we will also see why this particular PK is so important because these PK values will be directly related to the corresponding colour change range for all these indicators okay?

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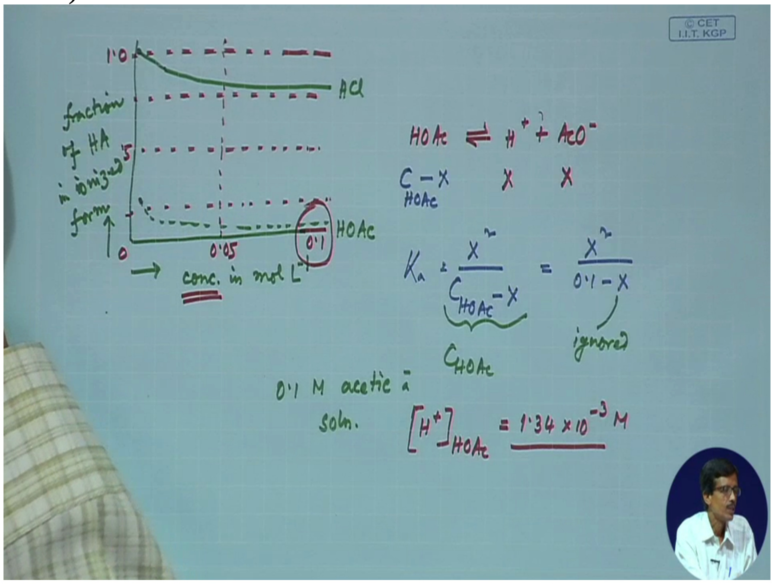

$HOAc \rightleftharpoons H^+ + AcO^-$

$C_{HOAc} - x \quad x \quad x$

$K_a = \frac{x^2}{\underbrace{C_{HOAc} - x}_{C_{HOAc}}} = \frac{x^2}{0.1 - x}$

ignored

0·1 M acetic a soln.

$[H^+]_{HOAc} = 1.34 \times 10^{-3}$ M

So what we see therefore that how this particular PK value is important and if we consider the corresponding dissociation, we try to plot the corresponding dissociation of these, that means how far the equilibrium is lying towards the left towards the right. So if we plot the fraction of the corresponding acid, the fraction of the corresponding HA in ionised form with respect to that of our concentration in moles per litre, so we have defined or we have considered two such acids, so if we can have this particular acid, for this reaction, so if we have, this is 0 dollar 5, then we have 0 dollar 75, then we have 1 and this is 0 dollar 25 starting the value at 0 and this vertical line is also at the midpoint giving 0 dollar 05 molar concentration and 0 dollar 1 molar because in most of the cases we are handling a deci molar solution.

That means the final concentration is 0 dollar 1 molar solution we are talking about. So for this particular case, that means when we have the hydrochloric acid, so if we have hydrochloric acid so when we have hydrochloric acid, the corresponding curve for this fraction of this dissociation can be like this. So you see that at a very low concentration, when concentration is approaching 0, you have almost 100 percent dissociation, so this fraction is almost 1.

So this is for the corresponding dissociation of HCl. So at the lower concentration range, this particular range, your hydrochloric acid is fully dissociated. But what about this corresponding acetic acid? Acetic acid by definition we all know that this is the corresponding weak acid. So it is going like this and this is your acetic acid. So extent of dissociation thus in this particular case is dependent strongly on the concentration.

It is dependent on the concentration. So this dissociation, so it is going say to up to 0 dollar 25 and above 0 dollar 25 fraction is say therefore 25 percent. So we see 25 percent dissociation of acetic acid only at the lower range. So upto this range only. Otherwise it is decreasing towards the higher concentration range. So this particular range of this concentration is therefore important.

So the magnitude of dissociation, that means which particular strengths or which particular concentration we are handling for this particular titration or any other reaction we see that a particular dissociation of HOAC between H plus and acetate ion and if we consider that the fraction of the dissociation we all know that the fraction of this dissociation is X, so XH plus and X acetate ion is also forming, and if we have the original analytical concentration of acetic acid, is basically CHOAC, is the original acid strength or the concentration which is present before dissociation.

So after dissociation, it is C minus X. So as we define KA, so KA will be X square, this multiplication of these two X and C of HOAC minus X is equal to nothing but your X square -0 dollar 1 minus X because we have taken and we are considering the corresponding acetic acid in this particular range of concentration. So how this dissociation and all these things can be there.

If the dissociation is very less, if it the magnitude of X is very small, it can be ignored and this can be equivalent to CHOAC, the original acid concentration what we are considering.

So this we have we can find out the corresponding concentration of H plus which is produced in the reaction medium, that means in a 0 dollar 1 molar acetic acid solution, if we have this is the acid, so if we have a 0 dollar 1 molar acetic acid solution, we should be able to tell about the corresponding H plus which is coming out, the amount of H plus which is coming out from HOAC considering the corresponding KA value, the dissociation constant value we all know. So it will be 1 dollar 34 into 10 to the power minus 3 molar concentration.

So we can have some good idea about the concentration of all these acids what is forming at that particular point. So this guide, this guidance for this particular concentration is very important, very much important in terms of the corresponding equilibrium process because we will be seeing that this particular thermodynamic quantity what we are handling for this analytical processes is the corresponding identification of any of these species, either this acid we will be considering for your acid-base titration or the something which will be related or tagged to the corresponding acetate ion form.

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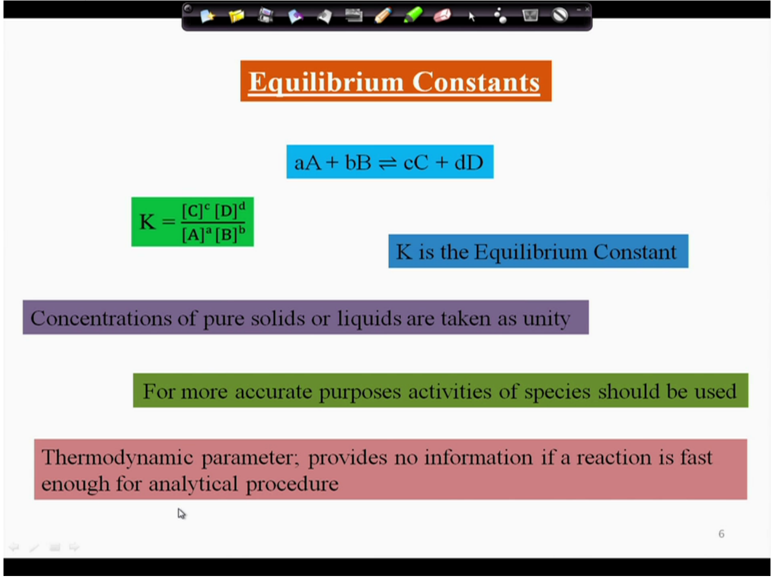

Equilibrium Constants

$aA + bB \rightleftharpoons cC + dD$

$K = \frac{[C]^c[D]^d}{[A]^a[B]^b}$

K is the Equilibrium Constant

Concentrations of pure solids or liquids are taken as unity

For more accurate purposes activities of species should be used

Thermodynamic parameter; provides no information if a reaction is fast enough for analytical procedure

So that we just slowly considering for the equilibrium constant. So so far we have seen that that corresponding species how we know but the equilibrium constant what we are talking about is the corresponding thermodynamic parameter but it has no relationship to the rate of reaction because the rate of the reaction what we are talking in terms of the corresponding titration reaction, titration is also a reaction where the analyte is getting titrated by the reagent.

So if the reaction is very fast enough, we have to have some procedure where very quickly we can determine the product of that particular analytical reaction. So that is independent of that of your K Uhh value or the corresponding equilibrium constant.

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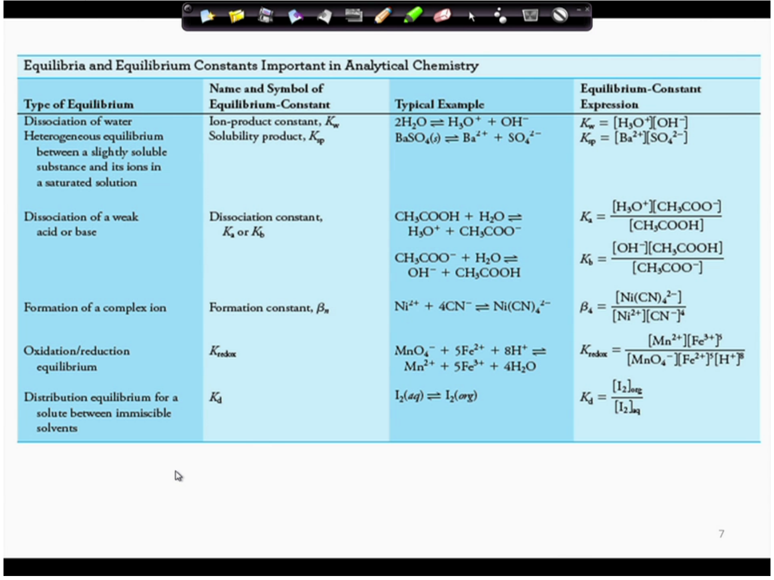

Equilibria and Equilibrium Constants Important in Analytical Chemistry

Type of Equilibrium	Name and Symbol of Equilibrium-Constant	Typical Example	Equilibrium-Constant Expression
Dissociation of water	Ion-product constant, K_w	$2H_2O \rightleftharpoons H_3O^+ + OH^-$	$K_w = [H_3O^+][OH^-]$
Heterogeneous equilibrium between a slightly soluble substance and its ions in a saturated solution	Solubility product, K_{sp}	$BaSO_4(s) \rightleftharpoons Ba^{2+} + SO_4^{2-}$	$K_{sp} = [Ba^{2+}][SO_4^{2-}]$
Dissociation of a weak acid or base	Dissociation constant, K_a or K_b	$CH_3COOH + H_2O \rightleftharpoons H_3O^+ + CH_3COO^-$ $CH_3COO^- + H_2O \rightleftharpoons OH^- + CH_3COOH$	$K_a = \frac{[H_3O^+][CH_3COO^-]}{[CH_3COOH]}$ $K_b = \frac{[OH^-][CH_3COOH]}{[CH_3COO^-]}$
Formation of a complex ion	Formation constant, β_n	$Ni^{2+} + 4CN^- \rightleftharpoons Ni(CN)_4^{2-}$	$\beta_4 = \frac{[Ni(CN)_4^{2-}]}{[Ni^{2+}][CN^-]^4}$
Oxidation/reduction equilibrium	K_{redox}	$MnO_4^- + 5Fe^{2+} + 8H^+ \rightleftharpoons Mn^{2+} + 5Fe^{3+} + 4H_2O$	$K_{redox} = \frac{[Mn^{2+}][Fe^{3+}]^5}{[MnO_4^-][Fe^{2+}]^5[H^+]^8}$
Distribution equilibrium for a solute between immiscible solvents	K_d	$I_2(aq) \rightleftharpoons I_2(org)$	$K_d = \frac{[I_2]_{org}}{[I_2]_{aq}}$

So like that of our example, this is a typical textbook table which has been taken from your Skoog’s book. So this how we can write down basically and what we are seeing so far that the corresponding reaction, that means the dissociation of acetic acid which has been abbreviated as HOAC so far, so that dissociation we are basically considering for a time of equilibrium which is known as the dissociation of a weak acid or a weak base.

So these 2 reactions, these 2 equilibrium reactions are nothing but the corresponding reactions involving their constants for the dissociation reaction. So this is basically the corresponding reaction where one is K, another is KB. So in case of the K reaction what we see that K is equal to in place of H plus, we will be writing as the corresponding hydronium ion because the in presence of water the proton forming from this acetic acid is forming H3O plus. So these 2 concentrations divided by the acetic acid concentration will give you the corresponding KA value.

Similarly for KB what we see that this is your conjugate base. Acetate iron is your conjugate base which is reacting with water. So based will accept the corresponding proton and this basically accept the proton forming hydroxide ion and the energetic acid. So kb we will be written in this particular fashion but this particular kb also you can be able to write if we have ammonia H3O plus or H plus forming ammonium ion and the corresponding water molecule.

So that also give rise to the corresponding KB value. So any equilibrium related to some reaction, that means dissociation of acid or some association with proton or the dissociation in terms of the reaction with the water with the corresponding base will give rise to this K, the equilibrium constant for acid and KB is the equilibrium constant for the base. So these things we can apply very quickly for other chemical equilibrium.

So the importance of the analytical chemistry is that how we can follow the different equilibrium. It is not only the acid-base equilibrium but we are following this which is very basic reaction or a very simple reaction what we can follow and we can have so many applications for that, so many calculations from your school days you have studied, the determination of the pH of the medium and how much concentration you are getting for a particular strong acid or a strong base or a weak acid or a weak base.

So very 1st thing, we can also figure out from the determination of KA and KB values is the involvement of the KW which is a very important parameter which we consider as the dissociation of water because water in water, that means your solvent is water and water molecules are present. Some amount of dissociation can take place, that is why we have a pH scale of 0 to 14 where we see that the corresponding range or corresponding thing has been standardised with respect to the corresponding reaction of H2O forming H3O plus and HO minus and KW will be nothing but your product of the concentration of H3 O plus and HO minus.

Then the same thing can be applied to some solubility product constant where which is KSP and where we have a sparingly soluble substance and its ion in a saturated solution. So the formation of barium sulphate as we know all that this barium sulphate is a very important reaction what we can study in terms of the corresponding qualitative identification of sulphate ion.

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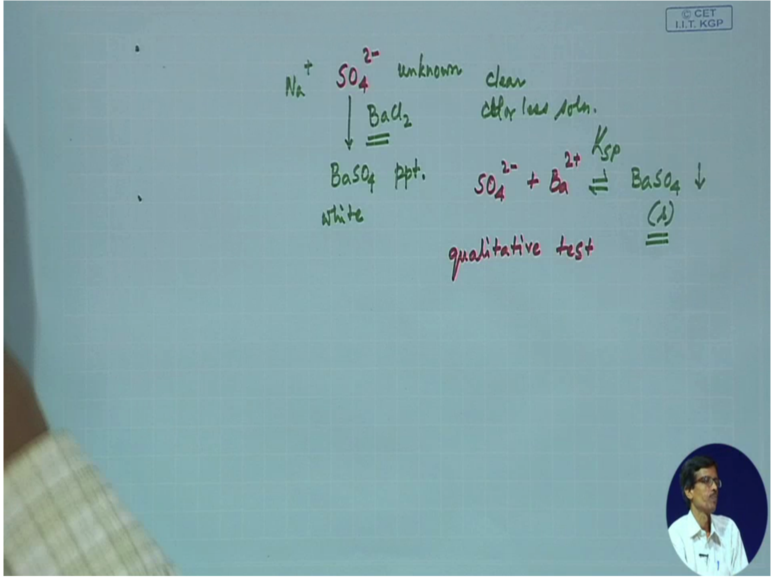

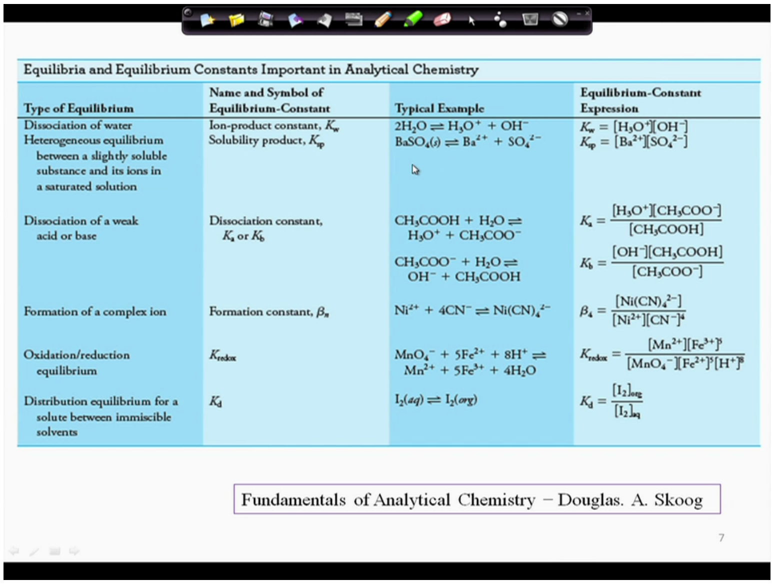

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Fundamentals of Analytical Chemistry – Douglas. A. Skoog

So if we have SO42 minus ion and we want to identify this, this we all know that is a very simple reaction we follow. We add a solution of barium chloride to an unknown solution of sulphate ion. Say the solution has been prepared from sodium sulphate. So this will give rise to the formation of barium sulphate and visually within a test-tube, we detect basically by our naked eyes through its formation of a white precipitate.

So if the addition of barium chloride to any solution which is a clear solution because this is a sodium solution say sodium plus pitches are clear, colourless solution, clear colourless solution.

And this is giving you a white precipitate. So definitely this reaction what is forming over there, is nothing but we have SO42 minus, the analyte which we are trying to detect by a qualitative test by the addition of a reagent and we are only focused our attention to the cation because we are trying to identify the anion.

So the barium we are giving, that barium as a barium chloride which is soluble in water. So this giving rise to the precipitate as barium sulphate and we write this as the the corresponding precipitate, white precipitate of barium sulphate. So what we see that this particular one so it is a solid and which is sparingly soluble. So think that this is an equilibrium process and is going from left to right, it does not mean that you have 100 percent of this barium sulphate is forming from the reaction medium.

So steel, you have some barium plus, 2 plus and SO42 minus in the medium. That we all know that the precipitating reaction is also controlled by the corresponding solubility product constant or KSP value. So if we know the KSP value, so the KSP value if it is very high, or if it is low, we know that what concentration of barium can be added to get the corresponding precipitate of barium sulphate. That means the individual concentration of these barium and the sulphates are important.

So if we know the KSP value, then the product of these 2 concentrations should exceed the KSP value of the barium sulphate. If you take it the KSP value, the product of these 2, then only you get the barium sulphate precipitation. Otherwise, you have this barium and the sulphate ion in the solution and this solid what we are getting and we are trying to (())(22:54) is that a corresponding solution which is sparingly soluble.

That means some amount of solubility is definitely there and it can provide barium ion and the sulphate ion in the solution medium. So we have this KSP value which is a solubility product K value for this equilibrium of the formation of a sparingly soluble solid which is largely very less soluble in the medium and KSP value will be the product of the individual concentrations of the barium 2 plus and sulphate 2 minus.

Then we can have a very important thing, that means the considering the corresponding beta values, the formation constants, how we can follow analytically a particular metal complex reaction, we consider at the corresponding complexation reaction. It is a different type of reaction, is not that the corresponding salt formation, that means the nickel cyanide is not forming. That means NICL2, the charge balance or the charge neutralisation reaction can give rise to NICL2 only.

But this is a complexation reaction where we find that cyanides are your ligand is and not two cyanides are very useful such that it is required for charge neutralisation but you require 4. That means on the left-hand side, you have cation and anion but on the right-hand side also a anionic metal complex is forming. And if it is coming from sodium cyanide, we get the corresponding sodium salt. If it is coming from potassium salt, you will be getting the corresponding potassium salt of this.

And like that of all other equilibrium constant value, it is written and its definition is different. That means it is abbreviated as beta not K. Now beta for beta 4 we are writing. That means it is involving 4 steps, 4 equilibrium steps it is evolving. So 1234, so you will have beta 1, beta 2, beta 3 and beta 4, that we will find out afterwards also for any other examples where they can identify that no this is not a simple acid-base type of reaction, is definitely acid-base reaction because we all know that this cation which is very much similar to your acid, so this is the acidic side.

And these ligands are the bases, corresponding bases. So this is again another form of acid-base reaction but giving rise to the corresponding complexation reaction. And the beta is therefore we are determining from that means the overall formation constants for this tetracyano nickelate complex okay? Then if we go for the redox reaction where not the proton transfer is taking place but the electron transfer can take place where the permanganate ion is reduced to manganese ion of Mn2 plus by ferrous ion.

So ferrous will be oxidised to ferric ion and manganate is permanganate is reduced to Mn2 plus and we find that the K redox value, so this particular one is also very much important because this K redox, this corresponding value, K value for this equilibrium constant is very much important for their individual species which is present and how easily you can detect that this particular reaction is going only in presence of some amount of acid.

So it is in the acid medium. Some concentration of acid is required and we can find out the corresponding redox potential value. That means the driving force for that particular reaction for the individual couple, that means the ferric ferrous couple and the permanganate manganese couple we all know and how would win from left to right, the K value we all know and from the K value, we can find the corresponding free energy change and the corresponding Uhh Uhh values or the matching values for the Delta G0 values and from there we can find out the E0 values from there.

So from these redox things, all these things are critically very much essential to know. So you should again go back to your theory classes for the redox reactions before we can handle, we can go for the corresponding identification because from this particular reaction what we can see that you can immediately identify the species, this is your A species, this is your B species. So we can identify the nature of the permanganate ion, the nature of the ferrous ion, nature of the manganese ion and the nature of the ferric ion.

Or we can quantitatively determine the amount of unknown ferrous ion present in the medium by titrating it with a solution, standard solution of potassium permanganate okay? And lastly another thing is very much important where we can consider a particular species, particular chemical species which is getting distributed between 2 medium which is immersible such as organic and aqueous medium. If it is therefore the iodine and iodine we all know that is soluble in water medium as well as it is soluble in the aqueous medium and what should we do distribution.

So that is known as the distribution equilibrium for a solute between immersible solvents. So water and any other solvent like Uhh Uhh chloroform or dichloromethane or benzene, they are immersible with that of our water and we can have some distribution between these. And again these 2 species into medium basically, so we should be able to construct the corresponding concentration of iodine in organic medium and corresponding concentration of iodine in aqueous medium.

And that will tell us the corresponding value of KD because if we know the individual concentrations in the organic phase and the individual concentration in the aqueous phase, this has tremendous application in all other cases, some catalytic reactions verily consider the face transfer catalyst. So which particular phase we will be utilising, that is very important to tell that how we can consider that particular phase such that you do the reaction and some other phase.

And if the active ingredient such as iodine is also there, can be used there which can be transferred from one particular phase to the other phase.

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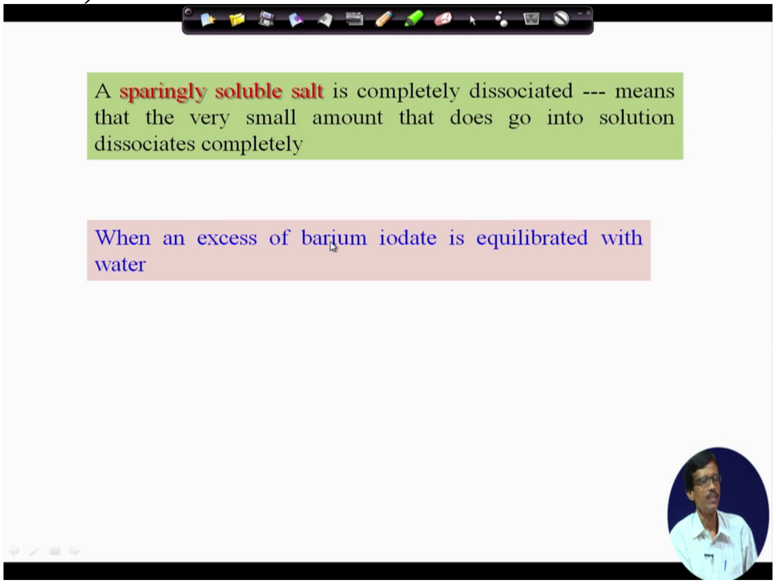

A **sparingly soluble salt** is completely dissociated --- means that the very small amount that does go into solution dissociates completely

When an excess of barium iodate is equilibrated with water

So these things and also we will be talking in terms of the corresponding salt which is sparingly soluble. Just now I told you that the precipitation of barium sulphate and when it is forming, that particular salt if we take, and if we dissolve it in water, we find that some amount of these ions are coming out from that particular salt and this is considered as the corresponding sparingly soluble salt, a very small amount is available in the solution and we can be able to detect that particular ion or the cation or the ion in that particular solution because you have certain amount of solubility in that particular medium.

So that we will just discuss and we will see in detail afterwards that if we have some amount of excess barium iodate which is equalibrated with water, so what we will consider this as the corresponding salt which is getting giving us some amount of barium concentration, some amount of iodate concentration, so which is nothing but your reverse of your barium sulphate formation, that barium sulphate is forming as a precipitate, some amount of barium plus is still that with along with the sulphate.

But in the same way we take the barium iodate and if we these solid iodate is try to do we try to dissolve with water, so equilibrium, how quickly the equilibrium is reached due to the dissolution of that particular barium iodate. So that we will discuss in detail because we slowly moving towards the corresponding reaction of the hydrolysis of some salt, that the salt hydrolysis, so how sparingly soluble salts are utilised, that we will see for during the hydrolysis of salt also. Thank you very much.