Course on Analytical Chemistry
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Module 9
Lecture No 44
Electrochemical Methods – I (Contd.)

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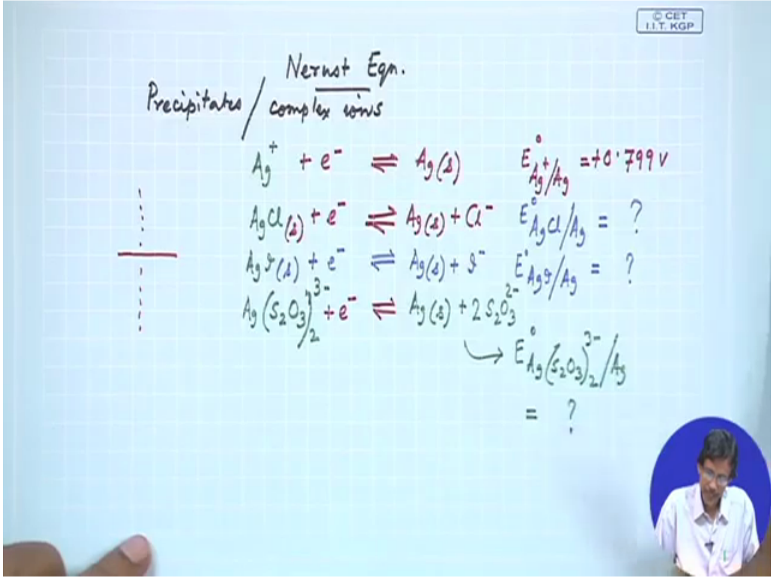

Nernst Eqn.

Precipitates / complex ions

$Ag^{+} + e^{-} \rightleftharpoons Ag(s) \quad E^{\circ}_{Ag^{+}/Ag} = +0.799\ V$

$AgCl(s) + e^{-} \rightleftharpoons Ag(s) + Cl^{-} \quad E^{\circ}_{AgCl/Ag} = ?$

$AgI(s) + e^{-} \rightleftharpoons Ag(s) + I^{-} \quad E^{\circ}_{AgI/Ag} = ?$

$Ag(S_2O_3)_2^{3-} + e^{-} \rightleftharpoons Ag(s) + 2S_2O_3^{2-}$

$\hookrightarrow E^{\circ}_{Ag(S_2O_3)_2^{3-}/Ag} = ?$

Hello welcome back to the class where we are talking about your Nernst equation, how the Nernst equation can also be useful for the derivation of different E0 values and the E values rather. So will be talking something in terms of the precipitation reaction what we have just now seen in our previous class that means the precipitates and the complex ion formation will see. So complex ion if they are developed or generated into the medium, so we will take we will see again without complex hash making complications for different other species we will stick on the same species which is silver ion because we also know by this time that what are the different values of these potentials.

So the silver electrode because we will be looking for and we are approaching towards in that situation where we get that hash corresponding colouration of the silver electrode, the different types of silver electrode we can have, so the species what is being involved can be silver ion itself, silver chloride, then silver iodide and we will take the help of some as she is for this complex ions what can be formed as we all know that this can be with thiosulfate anion S2O32 minus.

So the charges 2 minus for the thiosulfate anion, so overall charge will be 3 minus for the silver ion in the plus 1 oxidation step. So when this we have so when it accepts one electron, we get that silver as the solid separating out from the medium and we also know the corresponding standard electrode potential value for that which is E0 for Ag plus Ag is equal to 0.799 volt.

So close 2.84 for that corresponding reduction in shall of silver ion and we all know that this particular silver hash this is silver ion which is excepting electrons so is a very good oxidising agent because the positive values of the potential we do with respect to the standard hydrogen electrode, we can measure this and it is the corresponding oxidising agent which will be above the corresponding level from what we know that is about your hydrogen and below we have the reducing agents.

Then just now what we have seen solid silver chloride is accepting electron giving rise to your silver as solid and the chloride ions, so this we can have and E0 for this will be written as a corresponding silver chloride silver but this how do we know should be the value of this as a have seen this value is known at some manipulation of this particular equilibrium will you are getting something that means instead of this handling something where silver solid can react with the chloride and giving you silver chloride and electrode in a different way that silver chloride solid is reacting with electron from the electrode for its reduction to solid silver and the chloride and so how do we know this particular magnitude of E0 value.

Similarly the solid silver iodide know that is the corresponding analytical test for the silver ion when we add chloride or when we add iodide it is getting precipitated as the corresponding silver iodide as the salt. So in the same fashion it can also give that silver solid and the iodide ion and here this E0 value also is for silver iodide and silver electrode means you have the saturated of this and the (())(4:57) give rise to the corresponding half-cell but this also we should know for calculating it out.

Similarly this when accepts electrons what we get over there, so that the reduction reaction again because the formation of this silver, metallic silver means solid silver from the silver ion is so vast that it can directly get from the corresponding silver ion or we can get it from the corresponding hash silver chloride concentration in the solid form and we get that as the corresponding thiosulfate ion as the corresponding species, what is being generated as again solid silver and the release of the corresponding to number of thiosulfate anion S2O3 2 minus and we have therefore the corresponding E values for E0 of this silver S2O3 whole 2, 3 minus against silver we should know this value also.

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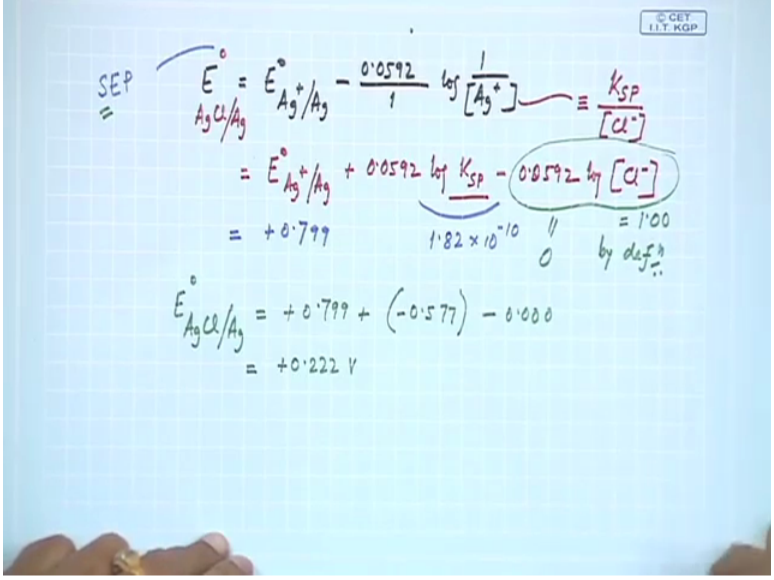

SEP

$$E^{\circ}_{AgCl/Ag} = E^{\circ}_{Ag^+/Ag} - \frac{0.0592}{1}\log\frac{1}{[Ag^+]} \qquad [Ag^+] \equiv \frac{K_{SP}}{[Cl^-]}$$

$$= \underbrace{E^{\circ}_{Ag^+/Ag}}_{=\,+0.799} + 0.0592\log \underbrace{K_{SP}}_{1.82\times10^{-10}} - \underbrace{0.0592\log[Cl^-]}_{0}$$

$[Cl^-] = 1.00$ by defn.

$$E^{\circ}_{AgCl/Ag} = +0.799 + (-0.577) - 0.000$$

$$= +0.222\ V$$

So how do we calculate how do we find out all these values that is important and what we find that in this particular case that manipulating all these values for situation, we should take the use of the corresponding E values again. So this particular case if we consider the corresponding E0 values for silver ion to silver thing, then as we have seen earlier that is 0.0592 divided by one and log of one by the corresponding silver ion concentration. So if we move from there that means the reduction of silver ion to silver formation gives us to that particular value but when it is giving you the responding silver chloride precipitation at means what are looking for, we are looking for the corresponding E0 value for silver chloride and silver electrode it is different.

So what are the things can be introduced or this is therefore at we have 2 use this particular silver ion but we should get that silver ion concentration in terms of the corresponding precipitated form of silver chloride that means this will be equivalent to that of your solubility product constant value, the KSP value. We all know that the KSP value is nothing but your product of the concentration of the silver ion and that of your chloride ion concentration.

So this silver ion concentration will be able to your PSP value divided by the concentration of your chloride ion, so what we get the corresponding E0 value for this will be equal to therefore your E0 for silver ion to silver which is all these cases are same, then if we change the corresponding sign of these that means it will be plus of 0.0592 then log of KSP that means your this value so your thing will go like this that means the log of KSP value.

So lot of KSP value minus 0.0592 of log of Cl minus concentration. So that basically gives us the corresponding thing that you have this that means silver ion concentration will be equal to the silver that KSP divided by this thing so your sign is changing to hash means the plus value of this so what we get now is that you or KSP value if you use, so this KSP value is known for your silver chloride formation.

So the magnitude of this KSP value if we put that particular value and the value for this also. This is known to us which is plus 0.799 volt and we put this value also as 1.82 into 10 to the power minus then, so these are the requirements or calculating this to you. So this will basically give rise to the corresponding KSP value at means you should know about this things.

So if this is your unknown quantity and you can find out the solubility product so because has some direct relationship or the concentration of silver ion for its corresponding solubility product and you all know that all this (())(10:15) soluble salts and they are undergoing some electron transfer reaction from these salts, we get this as an interconnecting thing for your PSP value and the chloride concentration.

So this particular one will give you the corresponding chloride and concentration but on standard condition because we are looking for, this is standard electrode potential or your silver chloride silver situation, so what should be the corresponding chloride ion concentration, the chloride ion concentration is nothing but by definition than the standard condition is activity should be equal to 1.00.

So it is by definition for your standard situation or the standard condition is so for the standard condition you have here Cl value is one so that will because this particular magnitude will be therefore equal to 0. We put this KSP value and when we put this particular value and multiply with this we get some value which will be equal to your E0 for silver chloride silver case is equal to plus 0.799 volt minus 0.577 minus is 0.000.

So in a standard situation what we get this particular standard situation we have this so that means this is the correction what we get by moving from an electrode which is silver ion to silver electrode to silver chloride to silver electrode, what we get is therefore that is basically this particular amount of change so it will be equal to 0.222 volt.

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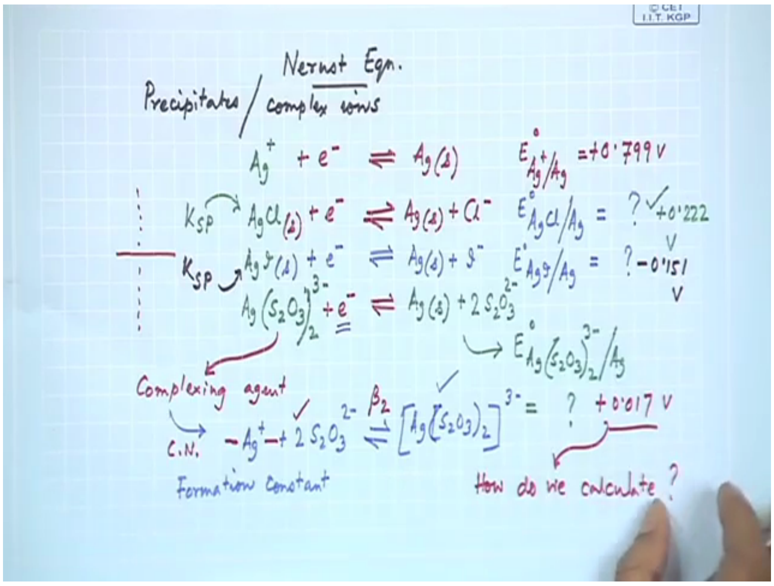

Nernst Eqn.

Precipitates / complex ions

$Ag^+ + e^- \rightleftharpoons Ag(s)$ $E^\circ_{Ag^+/Ag} = +0.799\ V$

K_{SP} $AgCl_{(s)} + e^- \rightleftharpoons Ag(s) + Cl^-$ $E^\circ_{AgCl/Ag} = ?\ \checkmark +0.222\ V$

K_{SP} $AgI(s) + e^- \rightleftharpoons Ag(s) + I^-$ $E^\circ_{AgI/Ag} = ?\ -0.151\ V$

$Ag(S_2O_3)_2^{3-} + e^- \rightleftharpoons Ag(s) + 2S_2O_3^{2-}$ $\rightarrow E^\circ_{Ag(S_2O_3)_2^{3-}/Ag}$

Complexing agent

C.N.

$Ag^+ + 2S_2O_3^{2-} \overset{\beta_2}{\rightleftharpoons} [Ag(S_2O_3)_2]^{3-} = ?\ +0.017\ V$

Formation Constant

How do we calculate ?

So what we were talking earlier in our previous transparency or the slide what we see that this is now known to us that means it will be plus 0.222 volt. So from here we can go there that we can calculate it out similarly now you know that what you should know as we are looking for the corresponding KSP value of silver chloride which is there so we introduce in the Nernst equation the parameter what we are introducing is your KSP value.

Similarly another KSP value which is different from that of your silver chloride will be used for this but how? So that after getting all these values calculation is we get is value so we should know the value and the value is quite different which will be minus 0.151 volt. So you see the situation is because the variation from this so you have the value which is pretty high to 0.8 volt then we go down and we go down further your silver iodide concentration and its solubility product.

Then what about this because this will be the typical complex ion formation so what is this? This is your complexing agent, so how we use this particular complexing agent which is complexing this and you have the concentration that means this particular one, so how strongly like that of your this insoluble precipitate this is not your insoluble precipitate but you add some complexing agent.

Sometimes we consider this complexing agent as the ligands. So when you add this complexing agent from the silver ion is a relative concentration of this species are different from that of your free silver ion. So that we should know and how you know this E0 value, in this particular one it is still further less with respect to but in the positive direction it is plus 0.017 volt.

So how do we calculate it out? How do we calculate this particular value of 0.017 that we will see because already we know the trick you have to use something that where it is directly related to the corresponding concentration or if it is there that means the corresponding titration of these things that is related to your silver ion concentration and this thing because this is for this electron transfer we are getting there is but otherwise the direct complexation reaction what is different from that where the silver ion is are available which is reacting with 2 of the thiosulfate ion giving rise to the corresponding complex species Ag hash S2O3 whole 2 3 minus.

So this is the corresponding complexation reaction silver ion because all these cases you are looking for silver ion whether it is present as a free silver ion or it is present as silver chloride or it is present with silver iodide or it is in the complex form. So this concentration we should know so this is during the complex formation so this complexation we get that as the corresponding formation constant, formation of the complex.

So the corresponding formation constant what we have in our hand and that particular formation constant is nothing but the ratio of the concentration of the complex form and the free ion form that means the product of the concentration of the silver ion as well as the product of the complexing agent. So all these things can give rise and if we consider the 2 of these are attaching to the silver ion so it is not in a very straight way fashion.

So if we consider at the corresponding silver chloride we have this and silver we all know and it can have a low coordination number that means coordination number of 2. So if we are trying to fulfil coordination number of 2 and if we see that the silver is binding this one first there in the second step you get a corresponding second one. The first one is binding to silver from this side and the second one is binding to this particular silver from the other side.

So what we get that corresponding formation constant and the overall formation constant is considered as the beta 2. If we have a step K1 for the first attachment and K2 for the second attachment, we should get this as a corresponding beta 2 is overall formation constant or the complex ion what is being formed.

So this particular one so beta 2 is nothing but ratio of this divided by the product of the concentration of the silver ion and the thiosulfate ion. So like the use of your KSP value we now used the corresponding beta 2 value now during the complexation formation to evaluate out this particular magnitude of the potential which is 0.017 volt. So like this we have utilise this was the calculation in case of your silver chloride thing so now we will see how directly we get that particular value for your complex formation.

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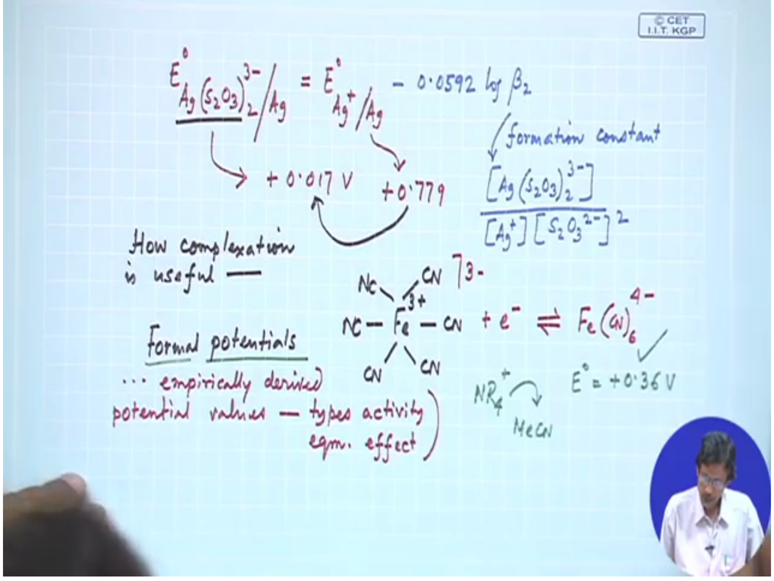

So what we get we get the corresponding E0 value definitely in the standard condition for the complex species is your Ag S2O3 whole 2 3 minus and the silver 0 is equal to your E0 Ag plus Ag. All the cases we consider the corresponding standard electrode potential or the standard condition because we are talking all in terms of the corresponding silver ion concentration whether it is in the free state or in the complex state.

And like that of your chloride thing so will directly we write now like 0.0592 and log of your beta 2 the formation constant value. So when you put this particular concentration at the concentration of these 2 values that means like your corresponding solubility product values in a tabular form we get this from the data table yet the corresponding beta 2 value for the silver thiosulfate complex.

So the formation constant the beta 2 is your formation constant which is nothing but the ratio of your silver in complex form. This is the species what is formed by this concentration of silver ion and the concentration of the thiosulfate ion 2 times. So something we are relating now not in terms of your KSP value at now we are relating something for the complex equilibria the metal ion complex equilibria.

So the methyl and complex equilibria that we all know that the formation constant in some other way we can find out this formation constant now. The analytical chemist had that particular opportunity that he or she can use this thing in a nicer way that if the potential are known and if you frame this cell by taking the help of your standard hydrogen electrode or any other electrode or you know the corresponding values for these you can find out any unknown formation constant of the complex species.

So is not that it is the thiosulfate ion so any other laggard in group can also be helpful to determine this particular value, so what we get these values what is useful for that and that particular one will then equal to plus 0.017 volt. So that gives us a very useful information that when you have this magnitude of this E0 silver ion and silver potential is equal to plus 0.779 volt.

So you see due to complex formation what is our basic intention that you try to reduce the free ion concentration that means the silver ion concentration in the (())(21:32) to a lesser extent so the complexation can reduce the corresponding potential value from 0.779 volt to 0.017 volt. So that is the good information that what we can have or knowing this thing how complexation help us for any reaction, so how complexation is useful or any titrations particularly the redox titration and all other things because one more important thing what we will now talk about in terms of another definition for discussing about the formal potentials.

We define this as what is the formal potentials but at the same time what we are looking at as silver is binding to thiosulfate and we all know the electron transfer for the ferry ion or the ferrous ion. Now we will put some other strongly bound complexing agent such as cyanide ions. So this cyanide ions are attaching to that so it is the corresponding ferrous ion (()) (23:03) FeCN whole 6 3 minus and formation of these species how they are changing?

Whether the corresponding electron transfer reaction will take place at the same potential close to that of your 0.77 volt which we know for your reduction for ferric iron to the ferrous ion or it is different and how this complexation can change or manipulate the corresponding potential value and we will see the corresponding value for this is therefore changing and this particular change is due to that corresponding complexation reaction.

So how we define this particular former potential so these are some empirical values are so this empirically derived potential values, which compensate the types of activity and compensating the equilibrium effects so the types of activity in the reaction medium that we are adding cyanide ion and the equilibrium effect. These 2 things if we consider together we can get the thing that means the corresponding reduction of these as one electron transfer for this giving rise to the ferrous cyanide ion which is FeCN whole 6 4 minus and interestingly what this particular case we will find this as the corresponding value of E0 for 0.36 volt.

So that is why it is very interesting to understand and because it is not so I that of your ferric ferrous system, so this particular value of ash this 0.36 volt will be useful to know us that this can change the value and you can get this for as a standard material because the corresponding potassium ferrous cyanide or the sodium ferrous cyanide you all know that all these the Ferro and the ferric cyanide are known but if we can consider this corresponding salts as the corresponding NR4 salt that means tetra-alkyl ammonium salt which can be soluble in some non-aqua solvent like MeCN of any other thing.

And this particular value is a very standard one experimentally we can determine by some other technique, electrochemical technique experimentally we determine that we will see in the later part of these classes of electrochemical methods of analysis which is useful for measuring the cycling voltammetric analysis. So is a standard sample for knowing the corresponding standard potential values for these cycling voltammetric measurements. So right now what we see that this particular value and how we can change or how we can manipulate the corresponding values in terms of the values what we require for electron transfer in a medium which is slightly acidic or strongly acidic.

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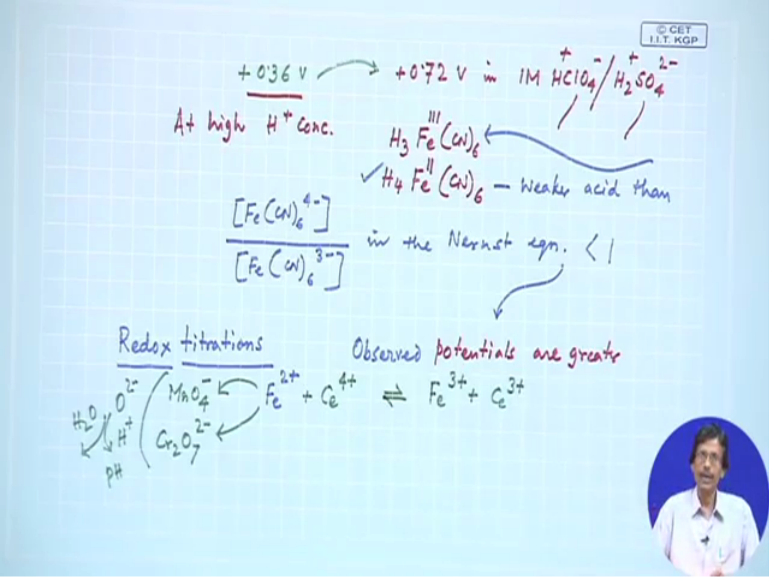

$+0.36\text{ V} \rightarrow +0.72\text{ V}$ in 1M $HClO_4^- / H_2SO_4^{2-}$

At high H^+ conc.

$H_3Fe^{III}(CN)_6$

✓ $H_4Fe^{II}(CN)_6$ – weaker acid than

$\frac{[Fe(CN)_6^{4-}]}{[Fe(CN)_6^{3-}]}$ in the Nernst eqn. < 1

Observed potentials are greater

Redox titrations

H_2O, O^{2-}, H^+, pH

MnO_4^-, $Cr_2O_7^{2-}$

$Fe^{2+} + Ce^{4+} \rightleftharpoons Fe^{3+} + Ce^{3+}$

So this value that means the potential is plus 0.36 volt and whether we can push it to a lower value or either we can push up to another value at we will see that this can be pushed to a value of plus 0.72 volt in 1 molar perchloric acid or sulphuric acid but now interestingly you can see or what you can find out is that that in this particular case you are values for all these that means your supplying H plus and ClO4 minus 2 of H plus and SO4 2 minus and earlier we are talking about the complexing capability of the percolate ion and sulphate ion to the iron side but now these values we are talking about the corresponding ferrous cyanide ferric cyanide ion.

So there is no chance of decreasing the concentration by complexation with these anions, so what we can see here now that in these cases what we get that the protonation at this values (())(28:04) the 1 molar are or the higher at high proton concentration get the corresponding protonated form of these species which is H3 Fe CN whole 6 which is ferricyanide and ferrous cyanide is H4 Fe CN whole 6 which is 2.

So this particular one then the corresponding acidity of all this is important and if they are there that means the corresponding thing is that when the charge is less than it is ferrous ion is weaker acid than your ferric counterpart. So if they are strong and weak therefore the concentration of the free ion in the solution the ratio of the species that means the 2 species involved that means your Fe CN whole 6 4 minus concentration that means this concentration divided by this is the reduced form by Fe CN whole 6 3 minus other concentration.

So if this is the thing, so that means you have the corresponding one hash that means the ratio is changing so by this that means in high concentration you have the corresponding change in the corresponding ratio of these 2, so in the Nernst equation as I told you that what we are talking about the corresponding magnitude what should be greater than 1 or less than 1. So this is less than 1 so when it is less than 1 we get something or we get the information their reactions is that the corresponding observed potential so that is why this observed potential are going up.

So due to this particular manipulation in the acidic medium the observed potentials are greater, so that way the formal potential values are useful and we can use all these things to understand something where we can see or we can know for our ultimate results will be your redox titrations and during those titrations because we all know that the titrations are the corresponding continuous process where the analyte is examined by the corresponding titrant what we add for analysing the species.

So either the oxidising agent or the reducing agent you can add to get this particular type of titration reactions and one such example and we will see that where we can titrate this as I told you earlier that this ferrous ion can be titrated nicely from your school or college days we determine that also using the corresponding solutions of permanent ion or the corresponding solutions of dichromate ion.

So these permanganate and dichromate ion concentrations were useful manipulate these things but another one is also very much interesting is the corresponding ceric ion, so ceric ion are further strong oxidising agent containing one single metal ion because these are the corresponding oxoanionic species because this has something to play because it has the very unstable O2 minus present in it.

So it will have some affinity that means the pH dependence that means it will always attract the protons and you have the formation of the corresponding water molecule out of that and definitely this will therefore the defendant C there and pH of the stability of these species but in a particular reaction concentration that you can directly study this reaction for this ferric ion that means the tetravalent cerium with that of your ferrous ion to convert it to the ferric ion as well as the corresponding ferrous iron. So in our next class we will be considering this as getting the corresponding redox titration curves and how we plot those curves to get those information related to those redox titration. Thank you very much.