Analytical Chemistry
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Module 11
Lecture No 53
Electrochemical Methods 3(Contd)

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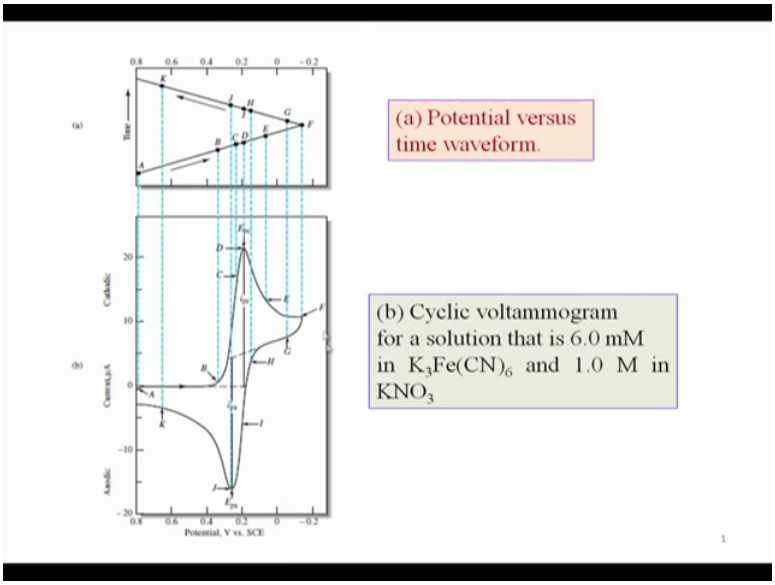

Hello, good morning everybody so we are talking about a process which you can consider as a cyclic one, where we are considering this as cyclic voltammetric analysis. So how this particular electric chemical methods can be helpful in identifying the nature of the analyte and its electron transfer properties. So what we have seen so far this is your thing that how you can draw the things so this one is your corresponding peak but we get that is labelled as EPC so what we are discussing in our last class that when we consider this and when it is moving and crossing the maximum through D that means this is the corresponding sweep for the potential what we are getting that the potential versus time waveform and the cyclic voltammogram.

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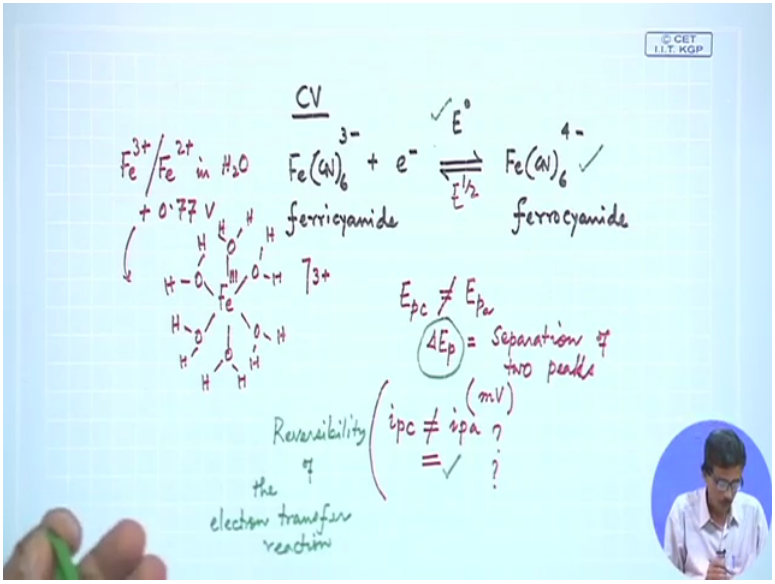

So now you have to analyse this particular thing that means how you can analyse this voltammogram so this is your typical cyclic voltammogram for a solution containing potassium salt of ferricyanide. So ferricyanide is definitely then electroactive on the electrode surface and once we know the corresponding E 0 or E hub value for this ferrocyanide or ferricyanide couple, so we start from the corresponding ferric state that means the ferric ion we are starting. So if you have FeCN whole 6 since it is ferric that means it will accept one electron and the corresponding electron transfer equilibrium will be FeCN whole 6 4 – , so this is ferricyanide and this is ferrocyanide, so what we want to look now is the corresponding E 0 value.

So what should be the corresponding E 0 or E hub value as one point of time we had discussed that we are considering something while talking about the corresponding potential or the potentiometric measurements that the corresponding half cell potential for Fe3 + to Fe2 + in water rather aqua solution was + 0.77 volt. And we have seen there also because already we know the corresponding values or the magnitude of the potential that how it is going if you have instead of this in water means water molecules surrounding your; you have 6 iron oxygen bonds so these are the water molecules bound to your ferric iron say and these will all be replaced by cyanide group so how this particular oxidation state which is the trivalent state can be stabilised or destabilise that we can see from this cyclic voltammetric measurements.

So when we get there so definitely this one basically then we start from the ferric ion so what you expect that we definitely go for the first the corresponding half cycle for the reduction, so

this is your reduction wave. Since it is reduction wave we get the maximum of this plot as the EPC so when we reach from A to F your everything on the electrode surface as the corresponding ferricyanide ion will be reduced back to your ferrocyanide ion as we have seen. So now we will just switch from F this is your point F, so now we switch the direction of the scan again from some potential which is around say – 0.1 to 0.8 volt again back.

So we will go back to the starting point so that means when you scan it back what is happening that particular direction of scanning is not going in this direction, so it is going in the opposite direction so it will come back over here so it is basically the corresponding thing that means this on this axis everything is current in microamperes so it is you see this is the 0 scale and this is 20 and this is also the negative direction that means the corresponding EPA and the current is IPA the anodic peak current. So we will have this will go and again the corresponding thing that means the corresponding mirror image of the plot what we got earlier is basically replicated over here and we again get some maximum over here and we ultimately reach 2 point K through K to again the potential which we scan first that means the corresponding potential was 0.84.

So if we get a typical cyclic process what does it mean then we can have 4 points basically very important one is D another one is the point J and the corresponding current height. So when you scan in this direction from left to right we get this maxima that means EPC which is your peak potential for cathodic reaction that means the corresponding reduction reaction EPC is the Cathodic peak potential so EPC is your Cathodic peak potential we get over here, so this cathodic peak potential we know so some magnitude of this EPC we will have and that magnitude can give rise something that when we move from here that means from B basically there is a sharp increase in the current high because the current you see the Cathodic current is almost 20 or above 20.

So above 20 microamperes current will be seen and then it will decay. So this from the baseline is extrapolated line for this horizontal baseline to that particular peak point will also give another quantity which is your IPC which is the corresponding current that means the peak current for cathodic scan. So this will be your cathodic scan that means we are looking for the reduction of the corresponding ferricyanide ion which is attached on the electrode surface is basically the available concentration of the ferric ion in form of the ferricyanide ion on the electrode surface is getting reduced.

So when we move then and when we turn on that means in the opposite direction, so this is your corresponding cathodic scan so cathode is responsible for your reduction and then we go for your corresponding anodic scan. So whatever amount of samples because everything is on start condition we have not start the solution so everything on start solution so whatever sample was there on the electrode surface will now be ready for its oxidation. So again we get that particular amount of current and we get some potential again EPA the anodic peak current as EPA and then we go back and we have some residual current obviously, it is not matching again 2 0. So this residual current we have (())(7:59) because of the condition and the corresponding nature of the electron transfer reaction on the electrode surface.

So what basically here also we again will get 2 quantities like the peak potential as well as the corresponding current which is your peak current for anodic scan and which is IPA. So how do we know these things that means how we can co-relate because this EPC is not equal to EPA. So whatever we got there this particular one that means EPC and EPA which is not equal to EPA, so when we scan in the forward direction then we go for the backward direction we get something which is a giving you some delta that means we must have another quantity is your delta EP which is your separation of 2 peaks. So this separation of 2 peaks sometimes we report not in terms of volts but we report in terms of millivolts. And also we see that the corresponding current EPC and EPA.

So if we measure because the reverse current is basically is not exactly is the typical horizontal plot when we go for the reverse scan but it has a slope. So we extrapolate this particular slope through these 3 dotted points or dotted lines so and from there we get up to this point J we get the corresponding current. So how much this current and how much that current we will then compare and sometimes we know that whether this is equal or is not equal. So 2 things can happen so depending upon again the nature of the electron transfer reaction and since the process is a cyclic process so we will have some idea over here the corresponding species which is present in the surface and which is reduced first and then re-oxidised back that is your reversibility of the electron transfer reaction.

So you both of them are same that means IPC is equal to IPA, we will have a reversible electron transfer reaction and very small magnitude of Delta EP will also tell the corresponding nature of the reversibility. So next we will see that once we define these things and if we see that the electro generated species which is your the corresponding reduced form of the ferrous, or the ferricyanide ion.

If this is not stable within the time limit of your rescan that means the cycle back scan then you would not get the corresponding response for the reoxidisation of the ferrocyanide ion to the ferricyanide ion that we will see how we can co-relate this thing and this will all be related to not only the potential the thermodynamic potential what we are looking for the E 0 and the E hub values but also we will be looking for the electron transfer kinetics on the electrode surface

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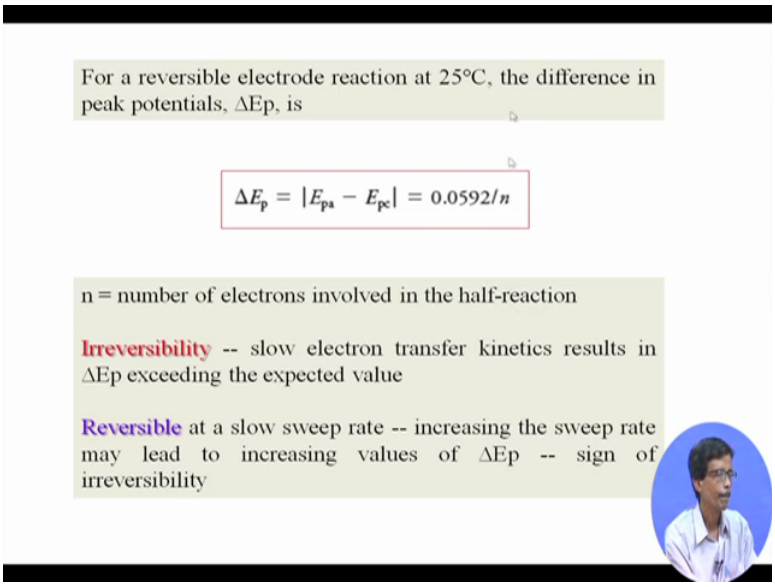

So for thus a reversible electrode reaction as a typical definition at 25 degree centigrade, the difference in peak potential what we just now seen is your Delta EP so Delta EP is your difference in peak potential on the separation of the 2 peaks what I have seen that particular one for your plot. So this Delta EP will therefore be your this separation that means your corresponding either the EPC – EPA or EPA – this, this is taken as the mode depending upon in which direction you go for the corresponding scan. So it will be equal to some magnitude because if we see that is again typically that constant what we get it for the last equation is 0.0592 by n because this n is quite significant.

This n is telling us that number of electrons involved in the half cell reaction or the half reaction. So in case of ferricyanide ferrocyanide reduction reaction what we see that n value is equal to 0 so what we expect? We expect basically a separation of 60 millivolt, so for a reversible criteria for the reversibility or this type of electron transfer is that Delta EP should be around 60 millivolt. So if we get a corresponding magnitude of this Delta EP which is 60 millivolt, we consider this as the corresponding reversible electron transfer reaction.

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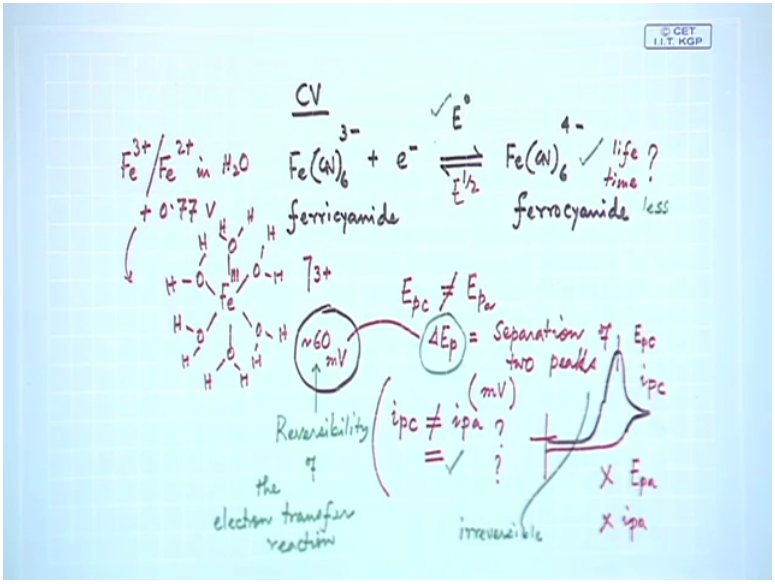

So this reversible electron transfer reaction is very important to understand or very important to know and this particular one we see that if we get this so when we start scanning this and we get up to certain magnitude of this and then again it comes back and then when we go for this so this is basically up to this point so this is for the corresponding scan for your reaction for this reduction, ferric is going to the ferrous state then the ferrous state is again reoxidised so what I am taking about this the corresponding stability or the life the lifetime. Where that lifetime?

The lifetime on the electrode surface, if the lifetime on the electrode surface is not much what we see that is instead of getting the whole cyclic process your voltammogram can go and see it like this, so this is your corresponding starting potential. So if this one is a reversible one and here only we get that corresponding one that EPC the Cathodic peak and the corresponding current IPC but we do not get on the other side the EPA or IPA are not available because on the reverse scan we do not get the corresponding speed because the lifetime of this is less or is negligible. So immediately whatever thing is that is either decomposing or going away from the electrode surface, so this is a typical example for a irreversible process.

So between these 2 extreme that means one can you have 60 millivolt and in another case it is almost nil nothing is there, but in between what you can have, you can have some time we get a very small peak over here because the current is less because this is the extrapolated line and we get the current over here and sometime if the life is more we get the plot like this. So

these all are quasi reversible processes. So we have the reversible process we have the quasi irreversible process and we have the typical irreversible process.

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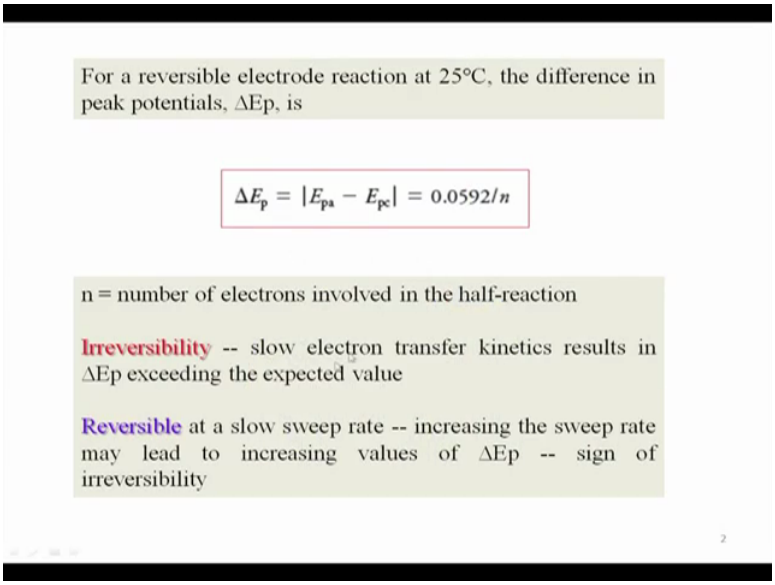

So when we see that this is we have two cases thus that how we find a cyclic voltammogram having a reversible signature and an irreversible signature so irreversibility is such that slow electron transfer kinetic results in Delta EP exceeding the expected value that means the electron transfer kinetics results in Delta EP exceeding the expected value, the expected value is your 60 millivolts so if it is beyond 60 millivolts sometimes it can be 120 millivolt even 180 millivolt or 240 millivolt, so these are the ranges what we get basically. So we consider that electron transfer is there but is irreversible electron transfer because only it can go for only oxidation or only reduction.

And the reverse when that means whether you get a reversible at slow sweep rate because it has something that means as I told you that the lifetime in terms of some seconds or maybe second it should have some idea about the stability of the oxidised or the reduced the species after electron transfer reaction on the electrode surface if we can see that at slow sweep rate increasing the sweep rate mainly to increasing values of Delta EP. That means if we sweep the first-rate but your electron transfer kinetics is not matching with that electron transfer process so your Delta EP is also increasing so we get a sign of the reversibility.

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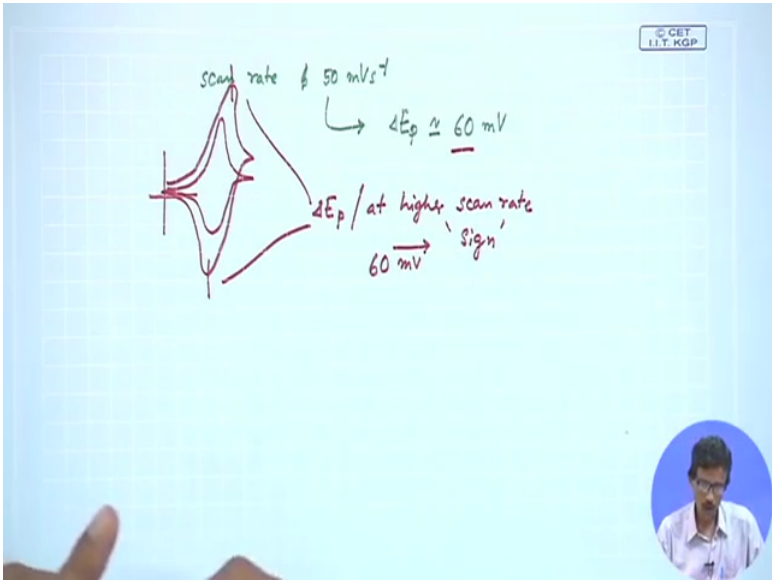

So it lowers scan rate your Delta EP can be less but at high risk and rate your Delta EP would be higher. But to get a standard Delta EP value what we are talking here as 59.2 millivolt or roughly 60 millivolt, we consider this as for a scan rate of 50 millivolt per second. So if you have a scan rate of 50 millivolt per second we expect a corresponding Delta EP value of 60 millivolt so this is basically a rule of thumb you can also add here, get the corresponding idea by looking at the corresponding electron transfer process because what we see that we get the Delta EP values very less when you have a scan rate of this type.

But when the scan rate is higher your current is increasing but it is moving like this and is going like this and is going like this so this and this will tell you the corresponding Delta EP value at higher scan rate and is going beyond that magnitude of 60 millivolt so it is when the corresponding sign of the reversibility or quasi reversibility. So it is basically giving the corresponding sign so looking at only the Delta EP values what we find that the Delta EP values will immediately give us that idea that we will have a reversible situation or irreversible situation for your electron transfer reaction.

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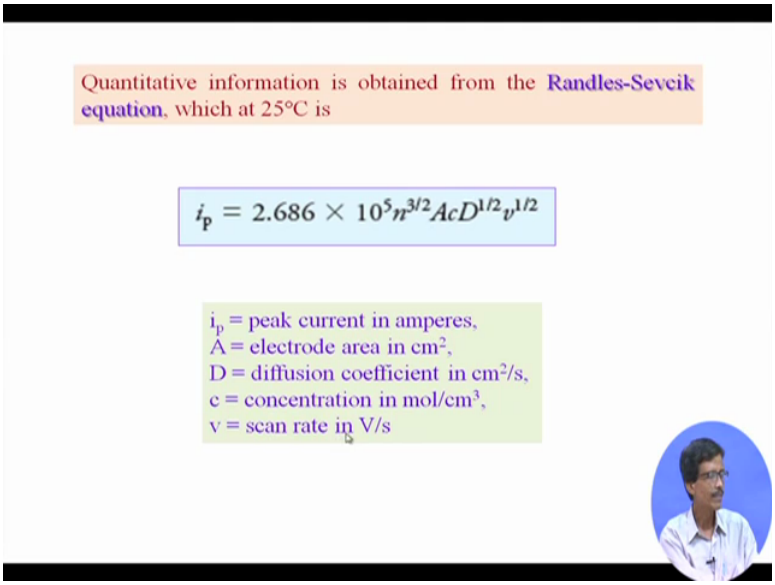

So basically if we just analyse like we all know for the electron transfer reaction for polarographic type or polarographic electron transfer reactions can be analysed with a very famous equation what we consider as the the corresponding ilkovic equation so that ilkovic equation type of thing can also be used for your cyclic voltammetric measurement which is Randles Seveik Equation, so Randles Seveik Equation at 25 degree tells us that is IP is equal to some constant 2.686 10 to the power 5 + some values of n AcD and your v small v so that is the thing what we are talking about just now is the scan rate.

And we are talking about the scan rate of millivolt per second that can be converted to volt per second and so we get the corresponding current this is the peak current height whether you have a IPA or IPC. So this particular equation basically tells us a relationship between your IPC or IPA with respect to your scan rate, so when scan rate is increasing just now what we have seen that your scan rate is increasing so this is for the first one is for say is is for your 50 millivolt and this one is for more than 50 it is say 200 millivolt per second and in both these cases compared to this current this other current is increasing so your peak current IP increases.

So that basically is being quantified for this case as with that of your Randles Seveik Equation. So IP is your peak current in amperes, so 2 things we are considering here in this equation that peak currents are not in milliamperes or microamperes, it will be in amperes and v is the scan rate, c is definitely the concentration what concentration you are using because depending upon the concentration of the ferricyanide what you are using for your

cyclic voltammetry measurement has a role to play on the corresponding current because we can sometimes find from directly from the current height that what is the concentration of the species is everything a standardised and we have the corresponding calibration card.

And A is the corresponding electrode area, so definitely if you have disk type of electrode and the electrode surface area is also important in centimetre square for your work and D is the diffusion coefficient in centimetre square per second possesses the diffusion where the bulk solution from the bulk solution is transferring the electroactive species on the electrode surface. So from this and if we analyse or simulate everything very nicely what we can see that one important cost and what we know is the solution electrochemistry that this diffusion coefficient so that diffusion coefficient can be found out from this particular equation and the cyclic voltammetric measurements.

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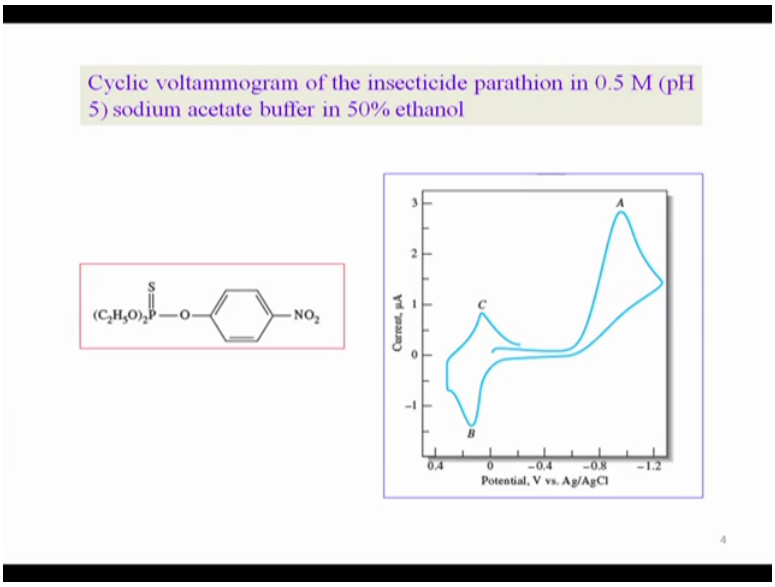

So now we will see some interesting information related to some insecticide analysis because this one is very important, so as we have electroactive analyte and this particular electroactive analyte we all know that most of the biological compounds it can be drug molecule, it can be of pharmaceutical molecule, it can be now insecticide that pesticides or herbicide also. So one such example is a very important molecule is that insecticide parathion. Parathion is that para is some positioning of that and the trade name basically all you do not know one of the things parathion is the general terminology for this molecule. And this parathion is straight name basically that our company is knowing is the corresponding molecule is known as the Folidol in the market is available as name as Folidol.

So at a concentration of 0.5 molar at pH 5 in acetate buffer in 50 percent ethanol because it is not fully soluble in water so 50 percent ethanol is fine and in a buffered medium you go for the corresponding electrochemistry of this particular compound. So this is a typical organic compound a nitro substituted because this part is your Nitrobenzene part and Nitrobenzene part attached to someone which is a phosphate ester so this phosphate ester with some oxygen and sulphur are not double oxygen and double sulphur and these are from the corresponding ethoxide unit that means it is coming from the corresponding alcohol group.

So it has the corresponding alcohol groups and all these things is not a very complicated process of making this molecule also. Now we want to see the corresponding electroactivity that means whether it can show some electron transfer reaction in terms of CV, so what should be the cyclic voltammetry for this compound and what are the corresponding electroactive species. So if you separate it out that you have a typical benzene ring and one part of that carbon on the benzene ring on one side because as I told you that is basically is a para compound a para-substituted di substituted benzene ring will have some para.

It is very easy to remember also and thion we know one of them is a sulphur bearing on phosphorus because it is a phosphorus based insecticide because this phosphorus-based compounds are always very deadly and they are and they are very bad also for our health also because they are useful for blocking acetylcholinesterase and all these things, so they can also function as non-regents we call. So chemical warfare we all know so they are also very good chemical non-regents. So if we have the substituted nitro group on this then this part so which part basically if we consider this is A part this is B part and this is C part.

Say organic molecule in your hand having A, B, C 3 parts together and we want to see the electron transfer reaction in terms of cyclic voltammetric this molecule and want to see whether A is electroactive the part A or the part B is electroactive or part C. So this is the typical response just now the ideal one we have seen and we are discussing ideal response for the standard reference material which is your potassium ferricyanide but this is not a very standard material, but with respect to that because you can put that ferricyanide solution within it also and you can scan that for your measurement so the potential on X axis is basically plotted in terms of B versus Silver, silver chloride electrode which is a very well-known and very well established standard reference electrode.

So this standard reference electrode what is in your hand can be used for your corresponding measurement and that measurement is giving you the corresponding values for your 3

electrode system within the cell. So here is your starting point, again is 0 so you start from here at point 0 and you scan again on this particular side so you have the corresponding one so you get the corresponding reduction side that means your cathodic peak potential is at A. So at A new get some cathodic peak potential for some species which is coming out from this then we scan back and while we scan back we do not get anything related to this particular A species at A species.

The reduced species is formed that means this is not getting directly reduced back to the species what originally present otherwise you have this peak in this side and the corresponding reverse peak on the other side and you get the corresponding cyclic one. But instead of that if you scan more to the positive side so when you go to the positive side, you reach at a point B. Okay fine you reach B so we can consider that A is not directly reducing back to the original compound but it is reducing back to something else so if you then switch back again and try to get in a cyclic process because you can have repeat scan for any compound like your potassium ferricyanide and if you can repeat the scan and if the compound is stable in the solution as well as on the electrode surface the reduced form, you get the overlapping cyclic process for your measurement.

But here instead of getting anything related to the corresponding reverse peak of A, we now get a reverse peak of B basically because you see these are very close by and you have a very characteristic Delta EP value for this process between this B and C so that is why we want to identify now what are the species basically what and whether A is important, B is important or C part of the molecule is important. So now we will find that this is the C part that means this nitro function is undergoing or showing the electro activity for your parathion molecule since this molecule is attaching and not that is the only nitro group and nitrobenzene can have a different mode of reactivity. And also sometimes we can find that nitrobenzene may not show this sort of electro activity or your measurement.

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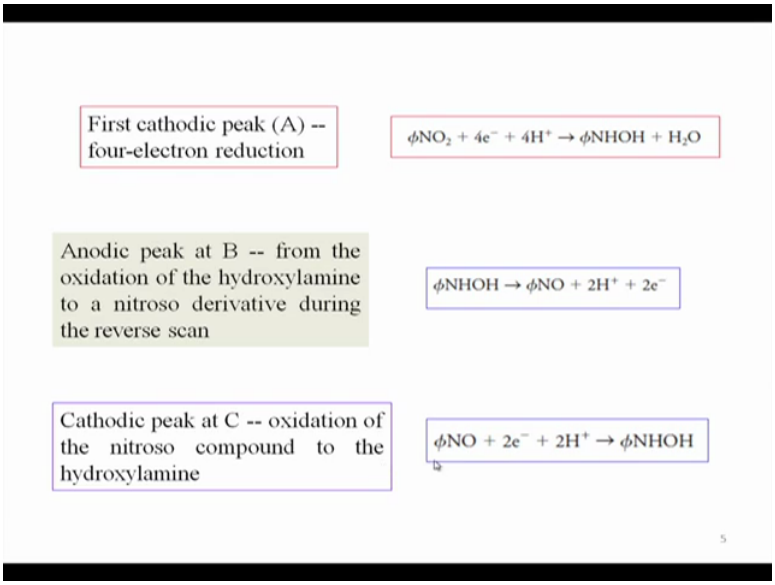

So it is this particular compound which is very specific for this parathion compound for its electro activity to show first the reduction at A then oxidation at B and again another sort of reduction at C. So what we get that the first cathodic peak what we obtain as A, so which is basically 4 electron reduction process because we have seen that the current height is big enough, is doubled to that of your B or C. So if it is a double enough current what we get, it can considered as a 4 electron transfer, 4 electron reduction reaction for the species based on your nitro function. So Phi part is as we abbreviate Phi as a typical benzene ring so this Phi part has been reserved for the other part containing benzene and the phosphate ester part.

So this nitro group on the right-hand side that means the C part of the parathion molecule is getting reduced to a form which we write as a functional group analyses as NHOH which is nothing but your hydroxylamine. So NO2 is basically reducing to your corresponding parathion not in nitro form but in hydroxylamine, so this hydroxylamine form of parathion is reduced by not only those electrons that means electrons you can put on the nitro group, nitro group can show something as a dot extra electron nitrogen, but is not there.

You will also require the transfer of hydrogen at the same time so the electron transfer on this you can put the hydrogen also so you have NO2, one of the oxygen will be removed from there and that oxygen will be converted to water and this nitrogen will also have this NH was there this NO was there that one of the O will be converted to OH and another patches attached to this making it as a corresponding hydroxylamine species. But when you go for the

reverse scan, the anodic peak B from the oxidation of the hydroxylamine is not back to your nitro compound but it will go back to the nitroso compound during the reverse scan.

So when you go for this so this NHO that mean hydroxylamine is not going back to NO2 that is why you are not getting the corresponding reverse peak of A, we are getting B somewhere else well away from your peak A so it is for your NO formation that means the corresponding nitrobenzene nitrosobenzene type of thing that means Phi NO is forming so the nitroso derivative of that parathion is formed for your oxidation now by 2 electrons only. So this is for your 2 electron oxidation and finally the Cathodic peak C that means this NO is there and this NO is you can have, so this NO is in your hand and this NO can now be oxidised that oxidation of the nitroso compound to the hydroxylamine compound.

So this B and C so somewhere you are having A here then you have the B peak and then you have the C peak and these 2 are basically closed by reversible, so whatever you have for this so you have this NO formation the NO group and you have the NHOH function. But here you have that NO2 is going to your NO formation, so once it is NO NO is formed for your nitrobenzene you cannot get back to your nitro compound but you will get back to your corresponding hydroxylamine compound so that is why the cathodic peak C is for your oxidation of nitroso compound to your hydroxylamine form.

So again it is 2 electron 2 proton transfer as we all know that whenever you have electron transfer, electron transfer if it goes in one direction your proton transfer will be on the other direction in terms of the electrode concern. So this Phi NO and this 2 electron transfer will give you back this, so if you get that, if we again cycle it back will get a reversible peak for these 2 so NO and NHOH that means nitroso benzene and the hydroxylamine for these 2 parts will be so and will be connected by same number of electron proton transfer and they are reversible in nature, so next day we will continue from here that how we can apply for these 2 things for some applications okay thank you very much.