Analytical Chemistry
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Module 10
Lecture No 47
Electrochemical Methods 2 (Contd)

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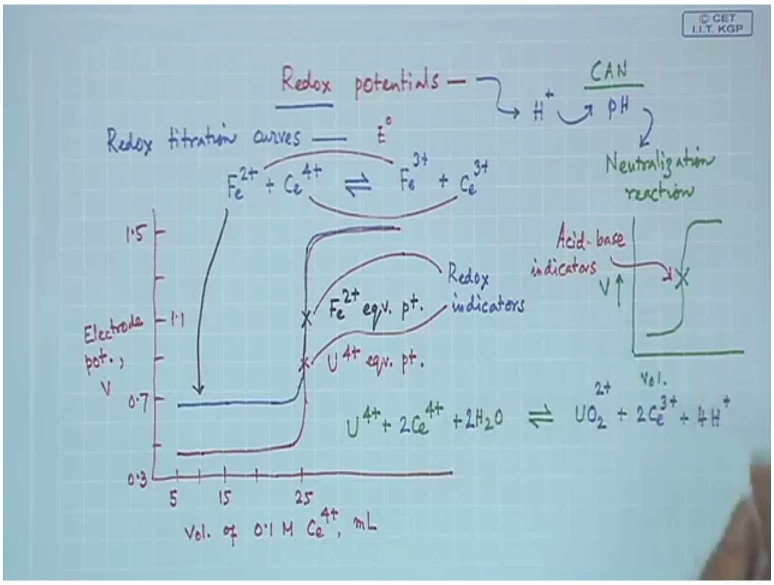

Good evening everybody, so we are still with the electrochemical methods of analysis and where we are talking about the corresponding redox potentials and how we can measure all these potentials that we have seen. And interestingly we were able to correlate these things that means the measurements of these redox potentials in terms of the combining of two hub cells and the cell potential has also been utilised to monitor the change in hydrogen ion concentration in terms of its pH and we have utilized that particular measurement of pH in terms of potentiometric titrations for any kind of neutralization reactions neutralization reaction.

And there also we know the most important shape of the plot and we see these are the corresponding plots and we will get somewhere the end point that means the volume of titrant we add and the potential electrode potential we measure. So the same thing whether you will be able to use for other types of reactions as I told earlier that we can use this for precipitation reaction, also we can use the same thing for complex formation reactions and also we can use this for oxidation reduction reactions.

So this determination of redox potentials by potentiometric way or potentiometric method can useful for redox titration curves, so we will see that what sort of this plot will get when the two components are responsible like that of our neutralization reaction is for the oxidation of one particular species say ferrous ions. If we want to determine the corresponding concentration of ferrous ions by a solution of oxidation agent which is the ceric ion as we all know that the ferrous ion present in more salt can also be analysed in terms of other oxidization agents such as potassium permanganate the oxo-anionic species or the potassium dichromate

So similarly, if we have a standard solution of the ceric ion which can be used for the oxidation of ferrous ion what sort of potential we can use because this is the corresponding oxidizing agent, so it will have a higher redox potential value compared to the corresponding other couples so ceric ion will be reduced to ferrous ion, ferrium 3 + so these 2 have someone potential for oxidation and we also know the very well known and very standard potential for the ferrous ferric system.

So this we can utilize for this analysis and also we will take the example of another little bit complex reaction which is the corresponding reaction with uranium 4 + and that is also we are utilizing with the ceric ion solution that means the standard ceric ion solution which is your oxidation agent can be your ceric ammonium nitrate, can be your ceric ammonium sulphate even ceric hydroxide that means CEOH whole 4 can also be useful and also be fine for this sort of analysis.

So these in presence of water basically because this gives a very useful reaction because uranium we all know that when we oxidize it can go to uranium 5 + or uranium 6 + so what sort of species we can have once it is oxidized by ceric ions. So simple ceric ion starting from your organic chemistry or any other chemistry where we can use the very useful oxidization agent and we call some species as CAN which is the aggregated form of ceric ammonium nitrate, ceric ammonium nitrate can give rise to so many useful reactions, one such is that of your oxidation of your uranium4 + and uranium4 + because we have taken water so that also gives you some indications that whatever species you will be forming over there is the oxo bearing species that means the oxide bearing species

So when it goes for higher oxidation state it has the typical affinity for forming the corresponding uranyl ion, so UO2 + is forming this is coming from your water + for the reactions stoichiometry because there you have uranium 4 + is going to uranium 6 + so it is 2 electron transfer reaction. So you have 2C3 + and the protons which are coming out from the water molecules, so you require 2 of this water molecules.

So the transfer of these O2 – from the water molecules can go to your uranium centre, but this is a typical redox reaction and we want to follow this by means of your redox titration and what sort of redox titration curve we can have. One example we have seen earlier that in the case of this that you have the corresponding potential for these two and the potential for these two so the E0 value we should know so these E0 values are also useful to identify the corresponding titration curve.

So we see the corresponding curve and value we can have and say it is 5, 10, 15, 20 and 25, so 5 15 20 25 which is nothing but the volume of 0.1 molar ceric ion solution in millilitres so that gives that particular access and you have the electrode potential in volt starting from 0.3 then 5 then 7 then 9 then 1.1, 1.3 and 1.5, this is 1.1.

So if we get that and if we have some idea because this particular potential what we have these ferrous ferric system we know standard condition in some 1 molar sulphuric acid condition, it is around 0.77 +, 0.774. So ceric having more higher are bigger higher potential of this can oxidize it, so the potential for this that means the ferrous ferric system can change and this can go from here basically, so its start from here and it goes, so this we get for the corresponding values for your Fe 2 + this reaction

But for the other one what how it looks like so you get at some point, midpoint of this is your end point that means whatever amount of ferrous ion was there present in the unknown solution we can determine by means of the corresponding oxidation by ceric ion so it would be your Fe 2 + equivalent point what we can determine. So this particular thing and also the corresponding uranium one and this particular potential is less so it will above 0.3 volt and it also goes like this and you have the corresponding values like this and it goes like this.

So here basically also you get a potential value for this, obviously you have the corresponding concentration in the same range such that the in the same volume range you get the end point, so it will be your uranium 4 + equivalent point. So these things are there that if you have any titration like uranium 4 + or iron 2 + we can determine and the corresponding redox titration curves will very much similar to that of your neutralization curve. And we will be able to get this particular reaction for your titration and we get this corresponding end point because this end point will be very much useful and where you have this change in because you see that sudden change so it change from 0.5 basically here from 0.5 to 1.4.

So sudden shoot up of the E value when we reach the corresponding end point so it is in the midway you have the corresponding equivalence point but this whole range is for changing the corresponding potential of the cell from say 0. 4 to 1.4 volt. So how can we detect those things because here we have seen that in potentiometric titration we can determine this particular one in terms of the corresponding acid base indicators.

We have used acid based indictors to detect the corresponding end point which is your end point for your neutralization reaction, so how we detect this end point or this end point so these we can also detect from that of our indicators so in this particular case we have the corresponding indictors known as your redox indicators, so redox indicators will be utilised in a similar way. So your cell, your electrode and your corresponding reactions can give rise to this particular type of reaction where we can have that redox indicators.

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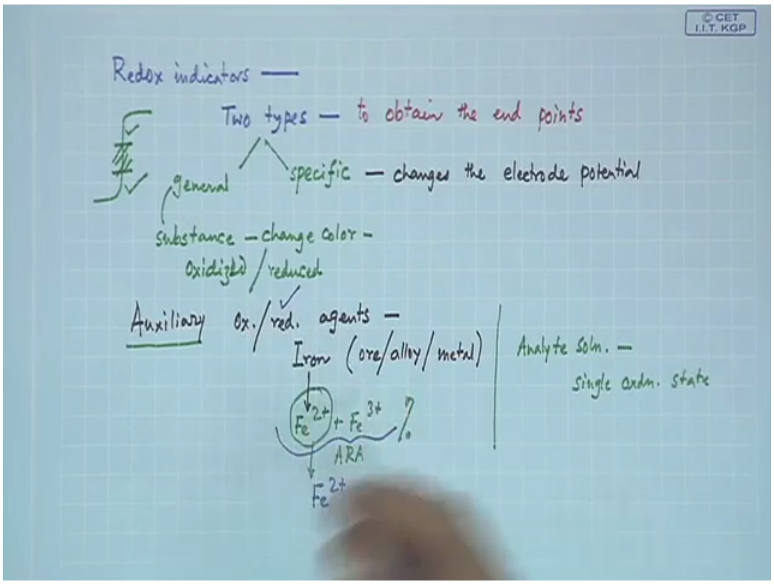

So these are of two types and these redox indicators are utilized for the detection of the end point so to obtain the end points like that of your acid base indicators so one of this category is of general type, general redox indicator so which can change its colour on being oxidized or reduced how it is this you have a indicator material or substance that change colour when it change colour because we know like that of your methyl red or methyl orange it changes its colour due to the proton loss or proton gain.

Similarly here also whether the species is oxidized that means oxidized form or the reduced form and if these two forms have different colour then you can have the corresponding indicator and we get a broad range basically a band so when you have this corresponding change we get a corresponding band. So at this particular point you have the corresponding reduced colour and at this point you have the corresponding oxidized form and we all know that we get the corresponding window for its colour change.

But for the corresponding one which can be termed as the specific redox indicator, so that specific redox indicator depend on the changes in the electro potential. So specifically it can detect the changes in the electrode potential here also we are locating what is a brown type or a band off of the corresponding change of colour, so here the specific one changes the or detect the corresponding changes in the electrode potential. So those we can think and we can use those things so in some of these reactions what we can see that we can also use auxiliary, oxidizing or reducing agents because this particular thing when you have the corresponding analyte which is in the single oxidation state.

So if you have iron say when you dissolve it that means iron in some ore or in some alloy or some metal so what happens then when iron is dissolved we get a mixture of Fe 2 + + Fe 3 +, so how to use and what is the corresponding auxiliary part so auxiliary part so if you have this so auxiliary reducing agent we call ARA. So if we use that auxiliary reducing agent and the analyte solution what you have because just now what we have seen that iron means you require the whole solution as Fe 2 + then only you can oxidize it by potassium permanganate, potassium dichromate or ceric iron solution.

So this analyte solution should have a single oxidation state so we require a single oxidation state otherwise depending upon the percentages of the individual oxidation stage that means what percentage of ferrous iron is present or the corresponding amount of ferric iron is present, we cannot detect because these particular reactions can only oxidise because the ferric iron can oxide only the corresponding presence of the ferrous iron, so what we do, we use some auxiliary reducing agent which can be able to convert the whole thing the mixture of the ferrous and ferric ion to only 2Fe2 + as we all know from the laboratory method or the titrimetric method we use in acidic conditions stannous chloride reduction for this ferric ion reduction.

So stannous chloride reduction can have you have the corresponding choice for this particular reaction and that particular reaction can also be utilised for your reduction that means auxiliary reducing agent can be useful so how the different other types of auxiliary reducing agent we are talking first the auxiliary reducing agent then we will come to the corresponding oxidizing agent also.

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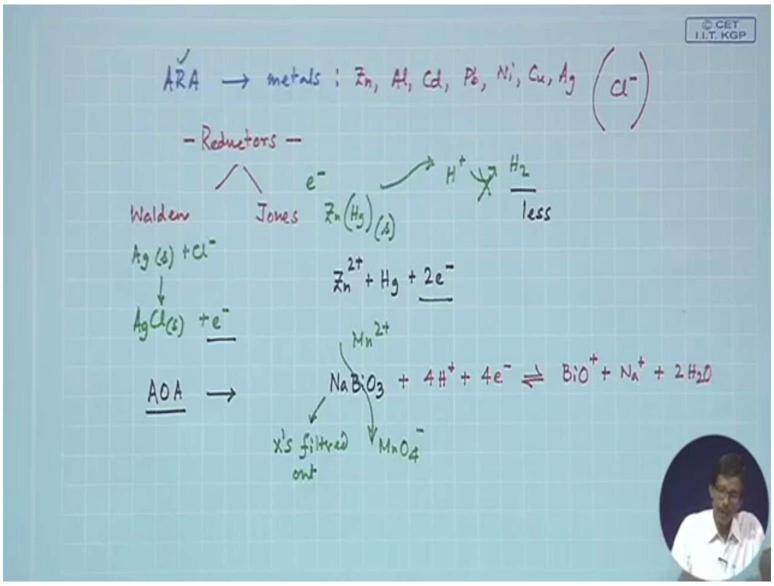

So if you have the corresponding metal ions that means auxiliary reducing agent where we can use you can have several metals and those metals if we can have say as per example we can have zinc, we can have aluminium, we can have cadmium, we can have lead, nickel, copper and silver and say all of them are present in presence of the chloride ion.

Suppose we have use the hydrochloric acid for the acid dissolution so if we use this that means the corresponding reduction reaction then you can have the two reductors we can use, these reductors are useful that means in C2 or some solid support we reduced all of them or this reductors can be Walden reductor because it has historical importance in terms of the corresponding introduction by those scientists or the Jones syndicate reductor. So the Jones reductor is there and this particular one we can have the corresponding electrons that means we require these electrons because you are talking about auxiliary reducing agent supplying the number of electrons to the species such that it can be reduced to one particular oxidation state like that of your ferric ion.

So Walden reductor is based on silver solid and Cl – the reaction which is following forming AgCl solid + electron similarly the Jones one can be utilized because the Jones reductor is nothing but the corresponding one as zinc amalgam we call zinc hg is a zinc amalgam which is solid in nature, so this can be useful because this can also have the tendency to reduce H +

to H2, but we have to minimize this particular step of reduction of proton to hydrogen formation.

So hydrogen production should be less and we use this because the zinc what is present over there in presence of mercury and you have electrons so the zinc amalgam which is formed this amalgam formed and this will give you this electron or this electron can be utilized for functioning as a auxiliary reducing agent . Similarly as a counterpart we can have auxiliary oxidizing agent, so these are auxiliary oxidizing agent and this can also be very much useful if we take we all know that one such is NaBiO3, NaBiO3 is sodium bismuthate and this sodium bismuthate is useful for the oxidation of some metal ion from lower to a higher oxidation state and this basically undergoes reduction. So sodium bismuthate undergoes reduction reaction with a four electron, four proton transfer giving you BiO + so is a oxo species of bismuth, bismuth3 + trivalent bismuth then Na + is also formed and water.

So what for we basically use we use these for the conversion of your Mn2 + so Mn2 + can be oxidized by sodium bismuthate to MnO4 –. So the determination of manganese 2 + it can also be achieved by its conversion to permanganate and iron and that permanganate iron can be titrated with a excess addition of Mohr's salt or the ferrous ion and then again we can titrate back to this solution with that of our standard potassium permanganate solution. So we take these as a solid which is a powdered one and we boil it out in presence of these manganese 2 + and all of the manganese is being converted so you have the excess NaBiO3, so excess we can filtered out to get a clear solution of MnO4 –.

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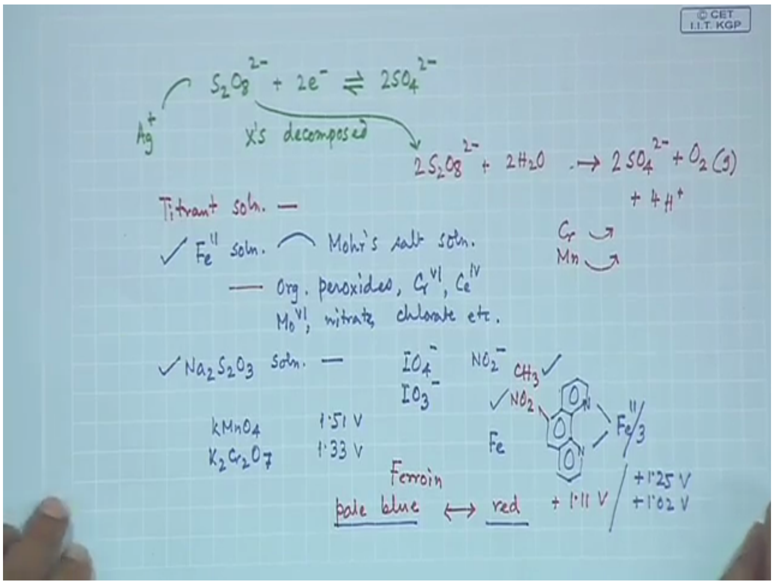

Ag^+ $S_2O_8^{2-} + 2e^- \rightleftharpoons 2SO_4^{2-}$

X's decomposed

$2S_2O_8^{2-} + 2H_2O \rightarrow 2SO_4^{2-} + O_2(g) + 4H^+$

Titrant soln. —

✓ Fe^{II} soln. Mohr's salt soln.

— Org. peroxides, Cr^{VI}, Ce^{IV} Mo^{VI}, nitrate, chlorate etc.

Cr

Mn

✓ $Na_2S_2O_3$ soln. — IO_4^- IO_3^-

NO_2^- CH_3 ✓ ✓NO_2

$KMnO_4$ 1·51 V

$K_2Cr_2O_7$ 1·33 V

Fe

$Fe^{II}/3$

Ferroin

pale blue ⟷ red

+ 1·11 V / +1·25 V +1·02 V

Similarly the other one the other auxiliary oxidizing agent which is also well known is your persulfate, so the persulfate anion is S2O82 –, so this basically give us in presence of some (())(23:30) amount of silver iron which can accept 2 electrons forming 2SO42 – and this basically is going for the corresponding oxidation of the other species so you get to know that you can oxidize with persulfate of your bismuth also sodium bismuthate

So here also again the solid one which we can have or in a solution a earlier what we have seen that your sodium bismuthate was filtered out, but in this particular case that excess of that material can be decomposed, so this excess of these will be decomposed that means S2O82 – can be decomposed so twice of S2O82 – in presence of water can be decomposed back to sulphate and oxygen here so 2SO4 2 – + O2 which as gas is liberated + 4H +

So this are basically the corresponding manipulation of using all these things that means wherever we are going for handling some solution and that solution is utilized for the corresponding oxidation or the reduction reactions. So sodium bismuthate as well as persulphate can be useful for your oxidation, similarly we have seen that some reductor can be utilised for reducing the species. So if we want to know that there are certain reducing agents and the titrants, the choice for your titrant solution is that if you have this particular titrant solution so iron 2 solutions are very much useful, it can be standardized with respect to the standard potassium permanganate solution

So this particular one that means the ferrous solution we all know from other sources that you can have a Mohr’s salt solution, which is ammonium sulphate ferrous sulphate double salt, so this can be very much useful if you have a standard ferrous sulphate solution or Mohr’s salt solution to determine some of the oxidizing agents also that means if you have some alloy that means it has chromium or manganese, so this can be converted to dichromate, manganese can be converted to corresponding permanganate and addition of excess Mohr’s salt solution we can back titrate

The remaining excess of the corresponding Mohr’s salt for the determination, so such that these are formed these are corresponding oxidizing agents so we can determine organic peroxide in this fashion also. We can determine chromium 6 like that of your dichromate or chromate then we can determine cerium 4 we can determine molybdenum 6 then nitrate, chlorate et cetera. So this is one such solution then sodium thiosulphate solution Na2S2O3 solution, which is not a standard solution we have to standardize it so that sodium thiosulphate solution can be useful for the other oxidizing agent, so the sodium thiosulphate is the reducing agent.

So we can have the corresponding nitrate is for the determination of iodate or periodate IO3 – and IO4 – or nitrite, this can be very usefully determined by means of the corresponding titrations with standard solutions then as I told you that this particular one that means the corresponding use of the oxidization agent that means the KMnO4, K2Cr2O7 because they have the corresponding known potential values of 1.51 and 1.33 volt.

Then ferric ion also 1.44 volt but if we try to go something for that reaction that means the corresponding redox reaction that means the metal complex like that of our iron with the corresponding one as your ortho phenanthroline, which is this particular identified ligand which can bind to your Fe2 and three such is there giving you the corresponding octahedral complex and this can have a good colour change for this two different oxidation states.

So for the determination of cerium in the solution so which is giving the corresponding indicator as your ferroin the corresponding ferrous ortho phenanthroline solution. So this ferroin is indicator so is a redox indicator and it can change its colour from pale blue, which is the oxidized form to the red one which is the reduced form with a potential value for 1.114 so we see that within this particular potential range we can use this as a indicator for some redox titration and if we can have some substitutions on it so it is 1, 2, 3, 4, 5, so this is the five position of these.

So substitutions on five positions by nitro group or methyl groups can change the corresponding potential values from 1.11 to + 1.25 volts for your nitro one and 1.2 volts which is going down due to the presence of methyl function. So within this whole range of 1.02 volt to 1.25 volt you can use this particular one for the corresponding redox titrations where we can use this as the good redox indicator because it can change its colour from pale blue to red.

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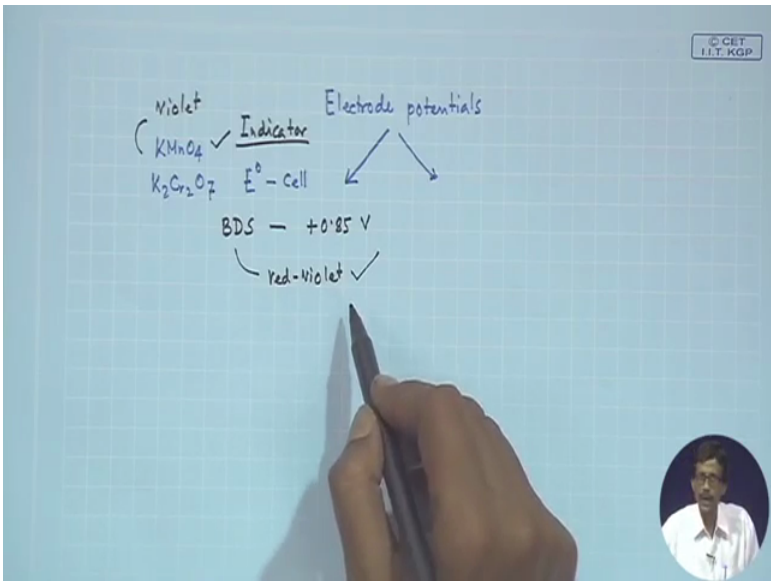

And all these things we can utilize nicely for your corresponding reactions where we come to know that this potential values are very much useful for the different electrode potentials, and the corresponding values are changing so how the corresponding E0 values for the reaction cell which is getting changed for all these reactions whether we use KMnO4 or K2Cr2O7. So this cell potential is always very much important and some of these reactions as we have just now seen that for your ferroin indicator.

But what we use for these two that means, when we use these that means whenever we use this as the oxidizing agent so your substrate can be oxidized and this will you can use and at this point we just ask yourself that whether we need any indicator or not. And since it is a traditional knowledge of permanganate titration from your school level or college level, you can immediately say that no you do not want any indicator because your potassium permanganate is self indicating that means you get something that where get the corresponding end point and this end point is known by the extra drop of potassium permanganate which is violet in colour.

So the entire solution can be coloured by this but when you go for your potassium dichromate solution and this dichromate solution is not so clearly visible like that of your potassium permanganate so we use one indicator which is abbreviated as BDS, which is barium diphenylamine sulfonate and this can be oxidized so this sulfonate diphenylamine can be oxidized and coupled together at a potential value of + 85 volts 0.85 volt and its oxidized form is red-violet in colour. So when the reducing agent is fully oxidized by your potassium dichromate finally the indicator will be oxidized and the end point is marked by the colour change from some dilute solution colour depending upon the species which are present but finally the whole solution will be red violet in colour ok, Thank you very much for this part of your course.S