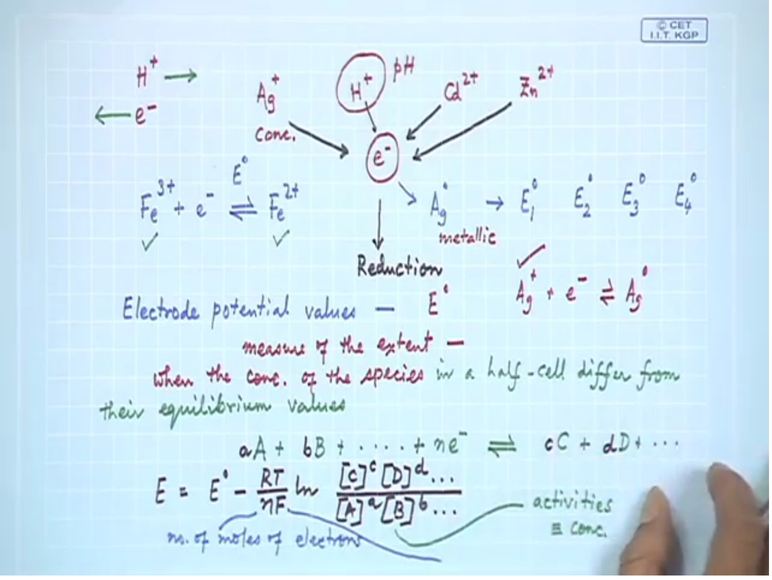
Course on Analytical Chemistry
Professor Debashis Ray
Department of Chemistry
Indian Institute of Technology Kharagpur
Module 9
Lecture No 43
Electrochemical Methods – I (Contd.)

(Refer Slide Time: 0:32)



$Fe^{3+} + e^- \overset{E^0}{\rightleftharpoons} Fe^{2+}$

$Ag^+ + e^- \rightleftharpoons Ag^0$

Electrode potential values — E^0

measure of the extent —

when the conc. of the species in a half-cell differ from their equilibrium values

$$aA + bB + \dots + ne^- \rightleftharpoons cC + dD + \dots$$

$$E = E^0 - \frac{RT}{nF} \ln \frac{[C]^c [D]^d \dots}{[A]^a [B]^b \dots}$$

n. of moles of electrons

activities ≡ Conc.

Good morning and welcome you all where we are talking about the corresponding electrochemical methods and we are looking at in our previous class what we have seen that several species such as silver ion, proton then the dicationic metal ion like cadmium and zinc 2 plus, we were comparing their affinity for electrons, so that is the most important thing. What we are looking for is the corresponding reduction of all these species and whether they are related strength and very for their electron accepting behaviour.

So if they accept electron so if this can accept electron, this can accept electron, this can accept electron and this can accept electron. So what we see, we see a typical ionic reaction or a half cell reaction for a reduction. So whenever we find that some reduction reaction is going on then at the same time what we can find that due to that reduction reaction some other species which is related to these half-cell reaction is that some oxidation is also taking place because this electron is coming from that particular one which is getting oxidised.

So in terms of the corresponding oxidising agent behaviour, behaviour for electron acceptance if we compare, then we can have some value basically for the half- cell reaction because this is the typical reaction when silver ion is accepting one electron going to AG0. So if we compare this together with one electron so that would be your half-cell reaction and for that particular half-cell reaction we should have some values that means the corresponding potential value that means the electrode potential value if this can function as an electrode.

So we have the corresponding electrode potential value, so if for the first species it is E1 for the second species if it is E20, for the third species if it is E30 and for the fourth one if it is E40 and we can compare all these species for a particular type of electron transfer even for the biological electron transfer also and also we know that or the metallurgical processes, the metal ion can also be produced from corresponding ions that means if we reduce the zinc ion by 2 electron or the cadmium ion by 2 electron we can get the corresponding metallic zinc as well as the cadmium zinc species.

So when we compare all these thing we can have the corresponding electrode potential values, so electrode potential values if you want to compare those electron potential values because these electron potential values if you compare the very simple one from the very beginning we are taking that reference that the silver ion is reducing to silver 0. So what we find that, depending upon this and this is the corresponding metallic species, we cannot talk in terms of its corresponding activities or the concentration but we should know the corresponding concentration of these things.

So if we have a concentration gradient for supporting this electron transfer reaction, what we find at this particular case when we are talking in terms of the corresponding electrical energy what we can gather from a galvanic cell that we can draw some electricity from the cell or the electrical current or the electrical energy from the cell. When this concentration is way away from its equilibrium situation because if you have the equilibrium situation what we get that silver ion plus electron.

If we write in the equilibrium sign that will be the corresponding equilibrium concentration which is being reached for a half cell reaction or a complete electrochemical cell reaction then reaching that particular electron the equilibrium concentration will no longer give you the corresponding electrical energy if we connect the e of the left cell and e of the right cell. So this particular electrode potential basically can give rise to the measure of the extent, measure of the extent that means how far it is away from the equilibrium situation.

When the concentration of the different species in a half cell differ, when the concentration of the species that means in this particular case is the concentration of the species of silver ion but if we take another example like that of the reduction of ferric ion which is very important not only for metallurgical processes for iron recovery for getting the iron from the ore material but also in the biochemical electron transfer and electron transfer what is occurring in the biological system like that of our cytochromes and all.

Cytochromes are only we know as electron transfer mediators in the biological system or electron transfer at a particular potential value. So we know that it has a corresponding E0 value for its reduction to the ferrous ion, so both the 2 species that means when the concentration of these 2 species that means the concentration of the ferric ion as well as the concentration of the ferrous ion is dependent in a half cell that means this can combine for a half cell differ that means they are different, differ from their equilibrium values.

So if they basically different from their equilibrium value we should be able to get some E0 for that particular situation. So now we see that if some molecule, some ion or some metallic species A as well as some amount of B is there in the solution and some more can also be there when it reacts with some end number of electrons and ultimately the reaction will reach to the equilibrium condition producing number of Cs and number of Ds in the reaction plus is some more also there and the number of moles will be important.

So the number of moles like the small a, the small b can react with each other using these things, producing c moles of capital C and d moles of capital D where A, B, C, D the capital A, B, C, D are the corresponding molecules the ions or some electro active species. So if we get that so what is that particular electrode potential, so this can be related for some equation and that equation will get over here as E that means the potential what we are looking for then the E0 minus RT by nF natural logarithm and then by the product, product of these products that means C and D.

So capital C to the power C into capital D to the power or the color D and some more divided by the species A powered by the number of moles then species B powered by the number of moles of b and if some more are there. So what we are talking here is in terms of the corresponding concentrations of this species that we are looking for the silver ion concentration as well as the ferrous and ferric ion concentration.

How this E values that means the E0 values for 1, 2, 3, 4 et cetera are dependent on the corresponding concentration of the species which we are looking or the typical ionic species as you see that is a very important one when we talk in terms of the pH values, the negative logarithm of the hydrogen ion activity, so in terms of that pH so that means this will have some correlation with that of electron transfer.

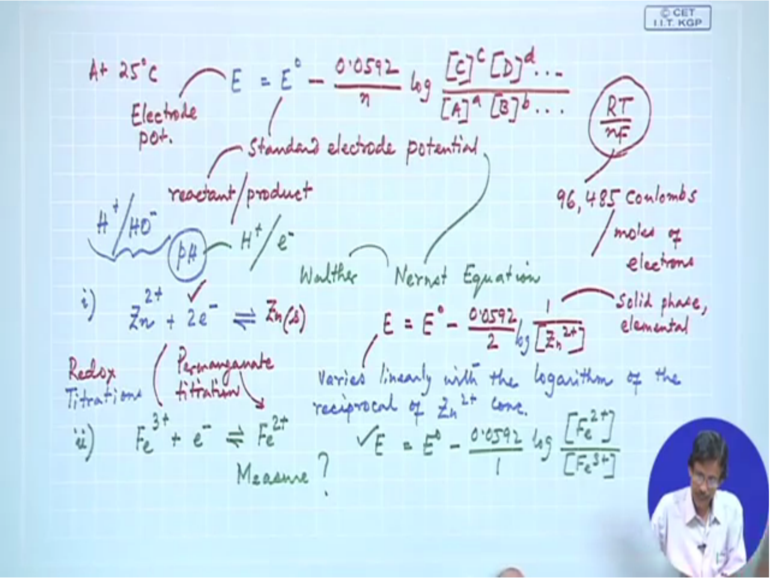
So starting from the different biological systems and all what we see that we can have these 2 things together that means the proton as well as the electron and the direction of these things will be the difference so together we consider it as the corresponding hydrogen atom but in the proton transfer can take place in a particular way so the electron transfer will take place in the reverse way.

So what we get that this particular values that means these are surely speaking the corresponding activities but in real sense when we used occasionally (())(10:36) little bit depending upon the temperature and another conditions, we consider that, that we just take the corresponding concentration or the molecule concentration of all those species or evaluating out this particular ratio of the ionic species on the left to that of your right.

Then what we find here is also very important that R we know is the universal gas constant and T is the temperature of the measurement, n is the bonding number of moles of electrons that means it is the number of moles of electrons. So n value is there so when we have this that means for a molar concentration of you ferric and ferrous the one mole of electron you require not a single electron, when you talk in terms of the one ferric ion and one ferrous ion formation.

But when we consider in terms of the corresponding concentration in the molar unit so that will get the corresponding number of moles of electrons and F is the Faraday, so F is your Faraday and that Faraday is giving you the corresponding charge. So this if you put all together will get some relationship where he is the corresponding electrode potential and E0 is your corresponding standard electrode potential.

(Refer Slide Time: 12:11)



© CET I.I.T. KGP

At 25°C

$$E = E^{\circ} - \frac{0.0592}{n} \log \frac{[C]^c [D]^d \ldots}{[A]^a [B]^b \ldots}$$

Electrode pot.

Standard electrode potential

reactant/product

$\frac{RT}{nF}$

96,485 Coulombs / moles of electrons

H^+/HO^-

pH

H^+/e^-

Walther Nernst Equation

i) $Zn^{2+} + 2e^- \rightleftharpoons Zn(s)$ ✓

$$E = E^{\circ} - \frac{0.0592}{2} \log \frac{1}{[Zn^{2+}]}$$

Solid phase, elemental

Redox Titrations (Permanganate titration)

Varies linearly with the logarithm of the reciprocal of Zn^{2+} conc.

ii) $Fe^{3+} + e^- \rightleftharpoons Fe^{2+}$

Measure ?

$$✓ E = E^{\circ} - \frac{0.0592}{1} \log \frac{[Fe^{2+}]}{[Fe^{3+}]}$$

So if we get that that means the relationship between E and E0, where your E0 is the standard electrode potential, is the standard electrode potential and E is basically that electrode what we are forming so that electrode potential and this standard electrode potential basically independent of number of moles of reactant and products. It is independent of the number of moles what is shown in the balanced equation that particular half-cell reaction.

So if it is independent of the number of moles of reactant and product, we can write in the original way and what we get therefore that E is equal to E0 minus putting on the values of your RT by nF, F is your Faraday which is 96485 coulombs is carried by the number of moles of electrons. So when electron charge is multiplied by (())(13:45) we get this number of coulombs for this particular constant what we can use it over here.

So conversion of this at 25 degree centigrade will give rise to the corresponding value as 0.0592 by n which is important then conversion to that log that means the corresponding 2.303 is also accounted over here. So C to the power c, D the power d and some more and A powered a and B powered b some more will give you some relationship and that is a very famous relationship what we know that this particular relationship is known as Nernst equation.

So is a situation tending towards equilibrium which can be governed by the typical Nernst equation and is due to the person who is Walter Nernst is a German so that Walter Nernst is the person who gave us the particular idea for this particular relationship in honour of him we name this particular equation as the Nernst equation. So if we find now for the real example so this is the most generalise reaction, you can have 2 components reacting each other and the corresponding activity and concentration if we consider.

Then we take 2 or 3 examples over here which will be very useful to understand that if we consider the corresponding reduction of zinc 2 plus by a situation where electron transfer number is 2 and those electron transfer can give rise to the corresponding solid zinc or the metallic zinc which we will consider as s or Zn0. So what should be the corresponding E value for this to color reaction will be he is equal to E0 that means the electrode potential how this dependent on something else that we will see now.

Then minus 0.0592 by 2, 2 is your electron transfer number then one by because we are talking this that means the product that means the reduced form divided by the product which is being reduced so one by the corresponding activity of bivalent zinc ion, so this one is corresponding to the solid zinc which is the corresponding solid phase of zinc, so solid phase of zinc which is elemental in nature.

So that is why the magnitude of this activity of zinc solid is one. So what we find that the corresponding E value that means the electrode potential value varies linearly with the logarithm of the reciprocal, which is in the denominator, so the reciprocal of the zinc 2 plus concentration, so it is dependent on a logarithmic function. Sorry this is there the log is there. It is okay you just do some mistake then you will find out you will realize what is missing.

So in a logarithmic function so the electrode potential therefore E therefore varies linearly with the logarithm of the reciprocal of Zn 2 plus concentration. So this gives us some information which is very important in this particular time that the overall E value, so we can change the electrode potential value by manipulating some of the parameters which are interrelated by the electron transfer reaction that means if the E value is dependent on the zinc concentration present for the half cell.

So we can change the corresponding E value because we cannot change this particular one the standard electrode potential because the standard electrode potential is the fixed value for this particular zinc reduction in a standard condition. So it will not vary but we can vary this particular potential for this particular reaction, so once we know theoretically this particular Nernst equation and its use but how we can use it for this particular manipulation and all.

So one such example or use the experimental or the practical use of or utility of this Nernst equation is the corresponding reaction or the titration what we earlier discussed again if I find time I will discuss it for the corresponding reaction which is responsible for the electron transfer to the ferric ion giving you the ferrous ion that means we know that this we can do for a corresponding titration that means any oxidising agent and give rise to a corresponding determination of the concentration of the ferrous ion.

Such is your permanganate titration we know, so permanganate titration we know, so when we try to oxidise it by potassium permanganate in solution we know that some endpoint we get so using the classical titration technique, the burette prepare technique but what we are looking for there that we are looking for some redox reactions that means the redox titration and now we should know that how the different E0 is contributing to find out the corresponding potential values and how these E0 values are changing for the different redox titration.

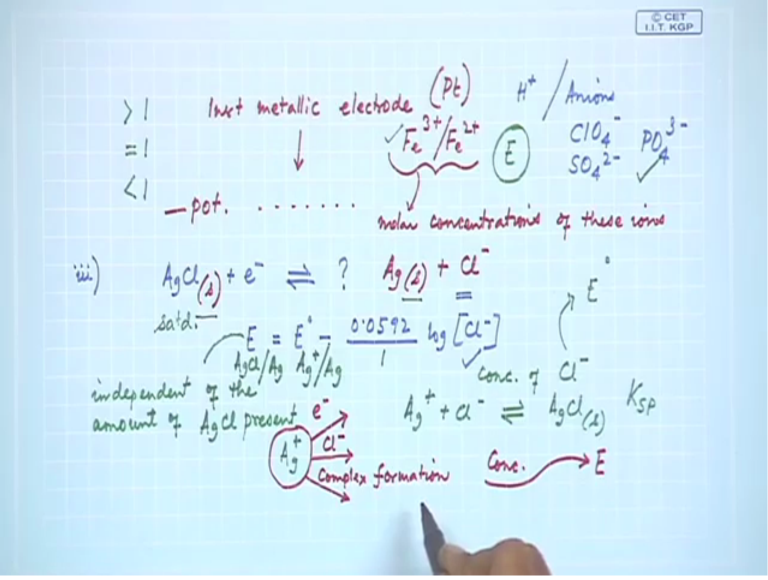
So that is the typical vacation and what you should know from all these theoretical explanation, justification and the derivation for the Nernst equation and its application likewise what we have seen or our neutralisation reaction for the determination of H plus or HO minus for those determinations we know that it is the pH, so pH we can monitor and pH we can find out or this particular category or the titration but how the pH because just now I told you that this particular pH is nothing but the corresponding transfer or the presence of hydrogen ion in a solution.

Similarly this can also be directly coupled to the electron transfer, so how the electrochemical method can also be useful for this pH metric titrations or the neutralisation titrations that we will see also but right now what we see the corresponding deduction and the application of this Nernst equation. So Nernst equation for this electron transfer on the ferric ion will also give you the same type of relationship.

Directly we should write that like 0.0592 by 1, now one electron transfer do not miss the mob now, so log of now you cannot know like one of the solid zinc is now the corresponding ferrous ion the reduced form and the ferric ion, so here we give you the opportunity or the manipulation of all these 2 concentration so if they are having some unit activity we get the corresponding value that means this will be cancelled out so log one is equal to 0.

So we get the E0 value for the corresponding potential which we know that close to 0.77 volt for this oxidation for the reduction of the ferrous ion. So this particular thing how we can measure also that is the challenge, how will you measure this particular potential. So far we know that how to construct the cell and now we will see that how we measure in the advantage of the use of this particular Nernst question.

(Refer Slide Time: 22:56)



So any couple or this particular couple that means the ferrous ferric couple can be measured with an inert metallic electrode it can take hand in this particular inert metallic electrode for monitoring ferric and the ferrous ion which should not, the solution of the ferric ion or the ferrous ion should not react with this particular in art metallic electrode, so what we get there that means the potential of this can be measured immersed in a solution containing both these ionic species.

So this inert metallic electrode you put in this particular electrode such as we all know that inert metallic electrode can be a platinum electrode. So here also now the ratio of these 2 that means if you try to change or if you try to manipulate the corresponding ratios of these 2, what we find that the corresponding ratio and change because the potential now, the electrode potential now depends again on the logarithm of the ratios of what the molecule concentrations, the molar concentration of these ions.

So now we see that if we have this and the corresponding reactivity for these with some protons or some corresponding anions. So how we maintain some acidity such as that of very strong acidic condition if we measure the corresponding potential for these system will find whether that is way away from your corresponding E0 value that means the standard electrode potential or not.

So if this H plus is there and if it is reacting with these or if it is giving or changing the corresponding active concentration of these species or the anions like say when you use perchloric acid we have the perchloric anion, when you use sulphuric acid we have SO42 minus and when we use phosphoric acid we use phosphate ion and when we go for the corresponding oxidation of the ferrous ion to the ferric ion so this is there and if we produce that whatever concentration of ferrous ion you have all will be oxidise to the ferric concentration.

But if these anions are there and they have different binding affinity for the ferric ion because we know that the ferric ion is very tightly bound by the corresponding phosphate because it has also 3 negative charge which is exactly matching with the ferrous ion and we all know the ferric phosphate has a poor solubility. So in presence of the phosphoric acid we definitely expect that your E value that means the electrode potential value must change. Why?

Because we are changing the corresponding ratios of these 2 concentrations and on these 2 concentrations this shows your electrode potential is dependent so in this phosphate environment your Fe3 plus is binding that means the ratio is changing because these ratio when it is one we do not know and it can be less than 1 or it can be above 1. So these are the things that means the manipulation what we are talking or thinking about is the corresponding manipulation of the relative concentration of these 2 species are very important.

So if we now make another example which is also very interesting to know that we will be talking in terms of the corresponding silver ion which can except one electron giving rise to some product we all know but instead of taking the typical silver ion we take the silver salt that means the salt of that particular ion that means silver chloride which will also react with that of your electron, so what is happening then?

So if we are able to know this because just now what we have seen in case of your zinc electrode, the zinc is getting reduced to the corresponding zinc metallic species that means zinc 0 that means within the medium like that of your thing the electrode can be a solid one or a metallic electrode, so this particular thing at means the species which is involved in electron transfer reaction can be a solid one.

So silver ion we are talking for accepting electron and we except that here we have the corresponding generation of the solid, solid silver metallic silver or the solid silver, so this is also solid what is reacting with this and producing this is as the corresponding reduced form all we know from the silver ion less what we get now that this will come out now once is forming a solid silver ion so your chloride ion will be released.

So how you handle how your tackle this particular reaction is a very interesting reaction because we can use as a standard reference electrode or this reaction also because silver silver chloride electrode is also there like that of your standard electrode what you consider as the calomel electrode, so this is the most important reaction based on that using Nernst equation we can develop the corresponding electrode the standard electrode or the reference electron.

So now we see that the talking in terms of the 2 other species what is there, we are bringing some thing as your corresponding chloride ion into the solution, so this will be in the solution so this concentration will also be there we should consider this concentration also over there, so this E value now according to your Nernst equation will be equal to this E will be equal to E0 minus again 0.0592 by 1.

Then log of the concentration of your chloride ion concentration, so for this particular electrode what we will see if we develop or if we use or if you construct that particular electrode we should be very much careful about the corresponding concentration of your chloride ion. If you have a supporting electrolyte like potassium chloride or anything else it should maintain the corresponding concentration of Cl minus because what we have the silver silver chloride electrode.

So this particular E value because this is solid and this is also solid so this is independent on the amount of silver chloride present in the system that means it will be dependent of the amount of silver chloride present in the system. That means you have a system where you have the saturated silver chloride. The solid silver is also separating out so activities of this and activities of this is we are not considering, we are considering only the concentration of the chloride ion.

So you have a corresponding potential value for this particular system which is dependent on the concentration of your Cl minus. So this will give rise to the corresponding information and what the idea what we get for this that if we can develop the corresponding standard electrode using this particular situation and what we find that there was reaction we know that the silver the metallic silver and the action with the chloride whether it can happen not that we will also see but also at the same time the corresponding thing that means the corresponding values for the solubility product of this.

That means if we have the corresponding thing which is getting separated out of the situation that means if you have silver ion and the chloride ions. So we get the reaction of Ag plus that Cl minus we all know that you have the solid silver chloride precipitation and which is separating out and we consider this in terms of the corresponding KSP value that means the solubility product values.

So this solubility product that means the amount of silver ion because silver ion is present in your solid silver chloride, so how you take out particular one which is also dependent on the concentration of the chloride ion, so this particular concentration that means the concentration of this Cl minus and control the corresponding values of your E0 and this particular case this E0 value for the electrode what we will be talking is not the electrode cause this E0 value what will be using over here is corresponding reduction reaction or silver ion to silver.

But this one will definitely your corresponding silver chloride so E of your silver chloride and the metallic silver, so these 2 things are different so depending upon this situation and what we have now, we know what is the electrode that means the corresponding electrode potential thing into the consideration of the corresponding standard electrode potential values for the silver silver ion system we can find out this particular one also.

So not only these things that means if you have the silver ion which is getting reduced so the importance of this particular silver ion is important in this particular reaction. So whether that is accepting one single electron in a direct way or it is producing something that means it is reacting with Cl minus or producing AgCl, AgCl is giving rise to the corresponding solid silver also, so the reaction of your Cl minus then other species that means where you can get the complex formation.

So why we are talking all these things because we are talking something related to the corresponding concentration of silver ion as well as the silver chloride concentration and the chloride itself consideration, so because the concentration can have some good role to play on manipulating your E values, so in our next class what we will see how we can change this E value by monitoring or by changing corresponding chloride concentration and what other information is you can gather by constructing this half-cell and measuring this corresponding potential values in the different all these reactions. Thank you very much.