**Electrochemical Technology in Pollution Control**

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**Lecture – 16**
**Voltametry & Polarography 1**

We are going to discuss Oxidation Reduction Titrations. We had already discussed it a little bit in my last class that is I had shown you this tin and ceric reaction.

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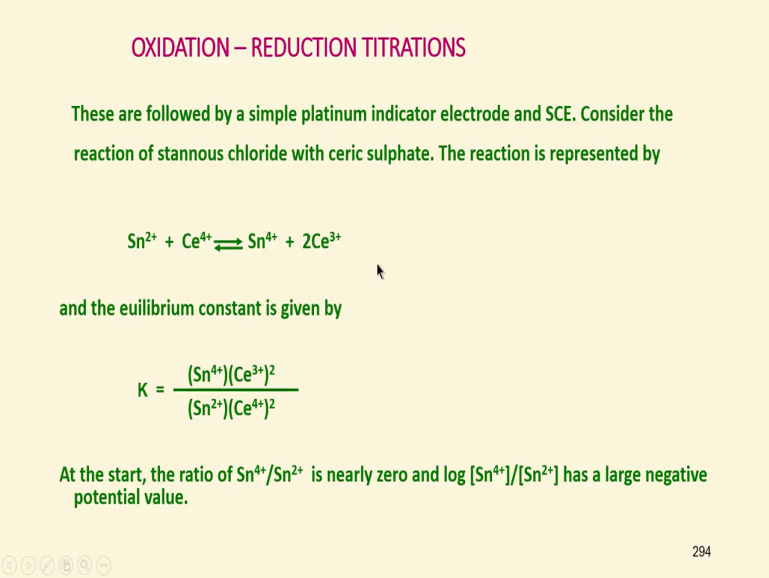


So, stannous and ceric will give you stannic and cerous and the equilibrium constant is given by the products divided by the reactants. So, here I have 2 Ce's. So, it will become square here. So, at the start the stannous to stannic to stannous is nearly 0 because we have not added anything. And S large Sn 4 Sn 2 plus will have a large negative value.

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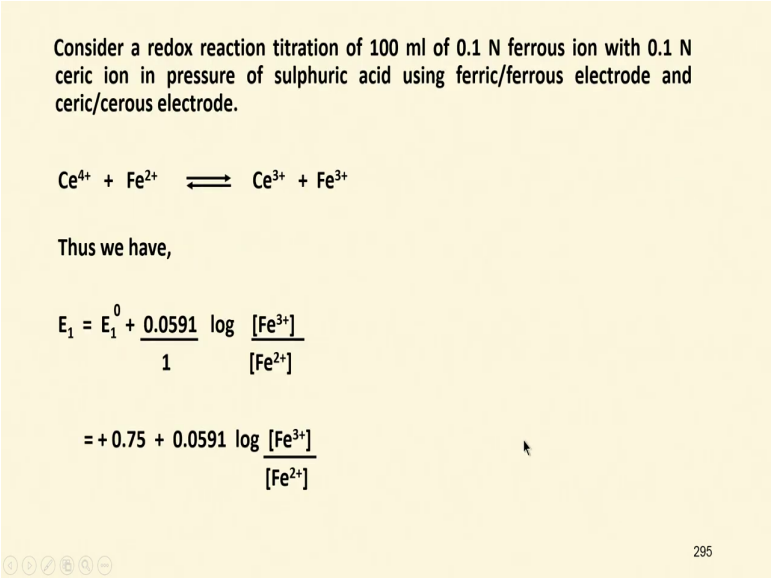


So, if we consider this reaction titration, with 100 ml of 0.1 normal ferrous sulphate and 0.1 normal ceric ion in presence of sulphuric acid using ferric ferrous electrode and ceric cerous electrode. So, we have two equivalent reactions; one for cells, one is ferric ferrous and another is ceric cerous.

So, we can write E 1 is equal to E 1 naught 501 point 0.0591 logarithm of the oxidant divided by the reductant that is ferric ferrous. So, this number works out to something like this. 0.75, this data we get it from the database of the E naught.

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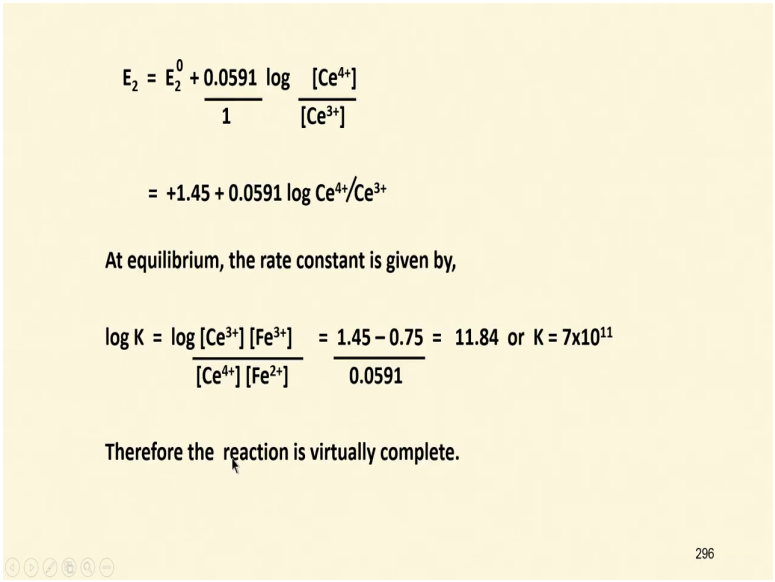


And another cell reaction is ceric cerous and here also it is oxidant divided by reductant and E 2 naught and the reduct standard reduction potential for ceric cerous is 1.45 and this is 0.0591 and divided by 1 only because it is a single electron transfer reaction.

So, at equilibrium, the rate constant is given by logarithm of K is equal to log of Ce 3 plus Fe 3 plus divided by Ce 4 plus into Fe 2 plus. So, the in terms of potential, I have 1.45 minus 0.75 divided by 0.0591 that it works out to 11.84. I take anti log of that I will get K is equal to 7 into 10 raise to 11. This is a very large number. So, I can conclude that the reaction would be virtually complete if the; I carry out this reaction.

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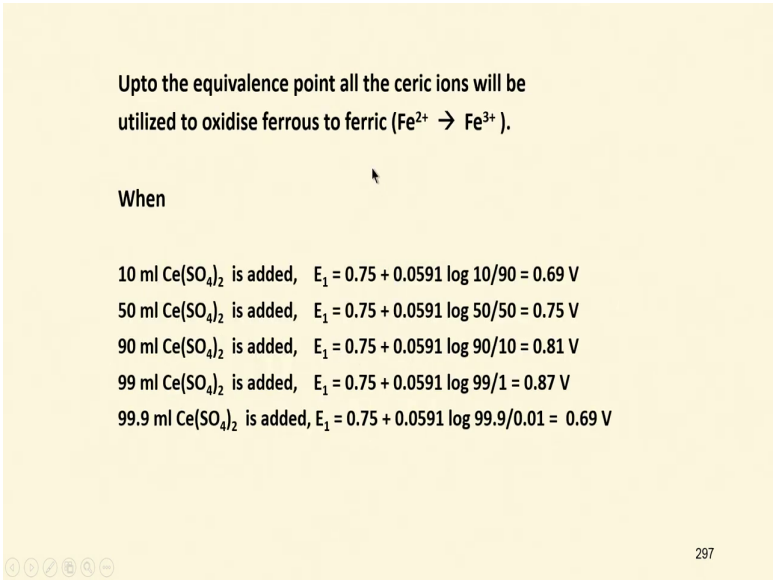


Now, up to the equivalence point, all the ceric ions will be utilized to oxidize ferrous to ferric ok. So, after the equivalence point, there won't be any reaction further. So, ceric sulphate will be accumulating. So, when 10 ml of this ceric sulphate is added to a 100 ml solution, I can say that E 1 is equal to the EMF of the cell would be it would have reacted with 10 percent of ferrous sulphate and if I write the product I can say that this is the ferric E naught and 10 percent is converted, 90 percent is unconverted and I get 0.69.

Here, I am neglecting the dilution. So, actually it cannot be 10 90 because I would have added taken 100 ml and added 10 ml, but for the time being I am I am reducing the sort of neglecting the dilution effect. That is why we take 10 raised to 10 times concentration of ceric compared to 100 ml of 0.01 that is ferrous and I need 100 ml of the 0.01 ferric , but I am taking only 0.1 normal that is 10 times more concentrated.

So, anyway so, I can I am justified in neglecting the dilution effect. So, when I 50 ml of this is added, nearly 50 percent of ferrous is oxidized and 50 percent is not oxidized. So, if I put it in this equation E 1 is equal to 0.75 or plus 0.0591 log of 50, this is 1. So, it becomes 0.75 only. This becomes log of 1 is 0. So, when I add 90 ml, I get 90 percent conversion, 10 percent not conversion and the value will be 0.751 0.81. 99, I get 0.87; 99.9, I get 0.69.

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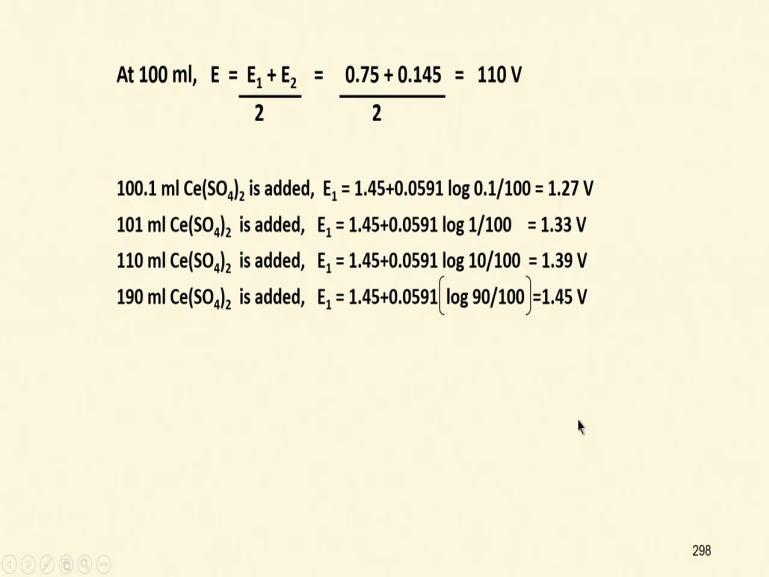


So, at 100 ml, I there is nothing more to be organized and reaction is complete. So, the EMF should be the average of these two that is E 1 plus E 2 by 2 that would be 110 volts. Now, if I add 0.1 ml extra ceric sulphate, the reaction will be governed by ceric ceric cerous concentrations rather than ferric ferrous now. Because all the ferric has been all the ferrous has been oxidized to ferric now so, only ceric cerous ratio will change compared to ferric ferrous all right.

So, even should give you give me the 1.45 plus 0.0591, I would I am not writing 1 because it is a single electron system here now. So, log of 0.1 that is added extra and 100 I am neglecting the dilution now. So, that gives me 1.27 and when I add 101 ml, I get 1 percent conversion, 100 percent of cerous. So, 1 percent is extra; 100 percent remains same that is cerous and then when I get 1.33.

Similarly, if I take 110 ml, I have 10 percent extra here, 100 percent of cerous and conversion will be the potential value will be 1.39. So, 190, I get 90 by 100 that is one 0.145.

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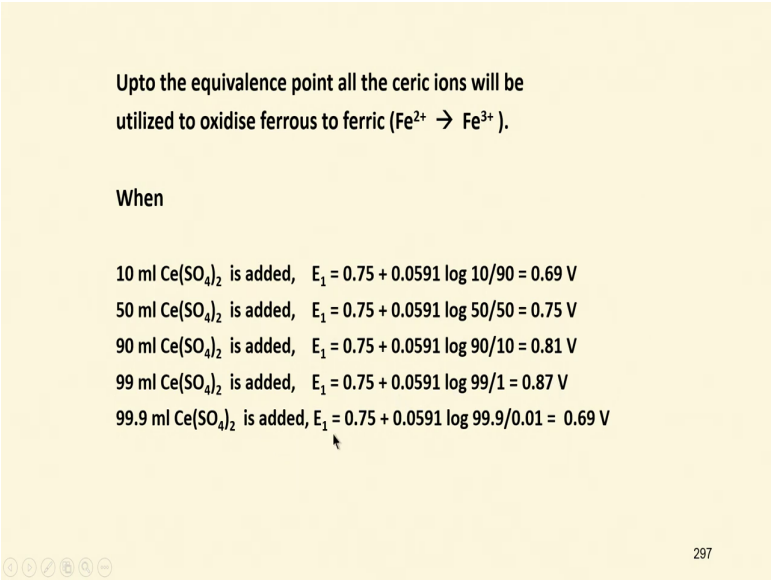


Now, look at the numbers here, I am going back now with between 99, it is 87; 99.9, it is 0.69 and 100, it is 110 volts and 100.1, it is 1.27; 101, it is 1.33; afterwards it is almost unchanged

here. So, the drastic change that occurs is only between 99.9 and 100.1. 99.9, 100, and 100.1, there is a sudden change in the curve or slope of the curve and I get my end point.

So, it is very simple and straightforward with a huge change in the; at the equivalence point and I should be able to complete my titration without any problem at all.

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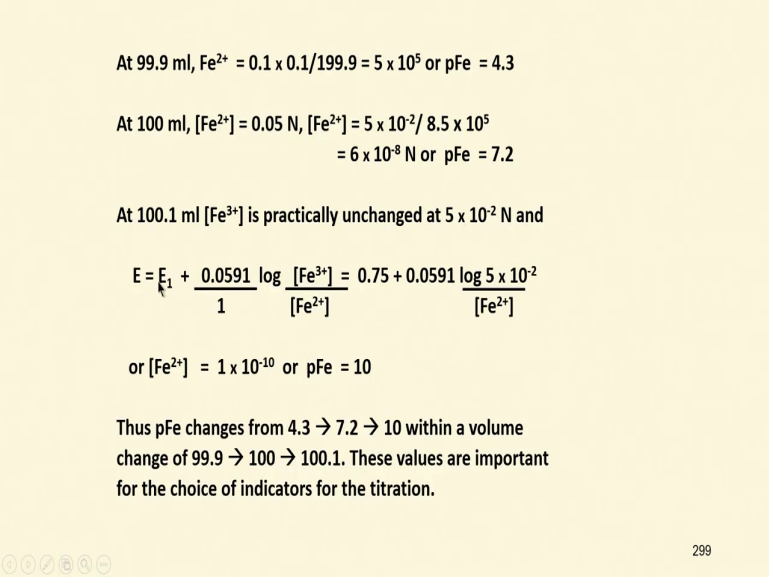


So, at 99.9, let us calculate what is the concentration of ferrous. Now, I know that 0.1 percent is not converted and this ratio is 0.1 by 199. Now, I am taking the dilution factor um. This equation if I solve, I get 5 into 10 raised to 5 or pFe would be 4.3 just like pH.

So, at 99.9, pFe is 4.3; at 100, it is 7.2. It is at 100, it is 7.2 and at 100.1 ml, it is practically unchanged at 5.5 into 10 raised to minus 2 normal and the pFe would be 10. So, from 4.3 to 7.2 to 10, it happens within 3 drops 99.9, 100, and 100.1.

So, the pFe changes within a volume of volume change of this, these values are important for the choice of indicators if you want to do it with indicators also. So, the indicator also should have a potential change or color change with this EMF change.

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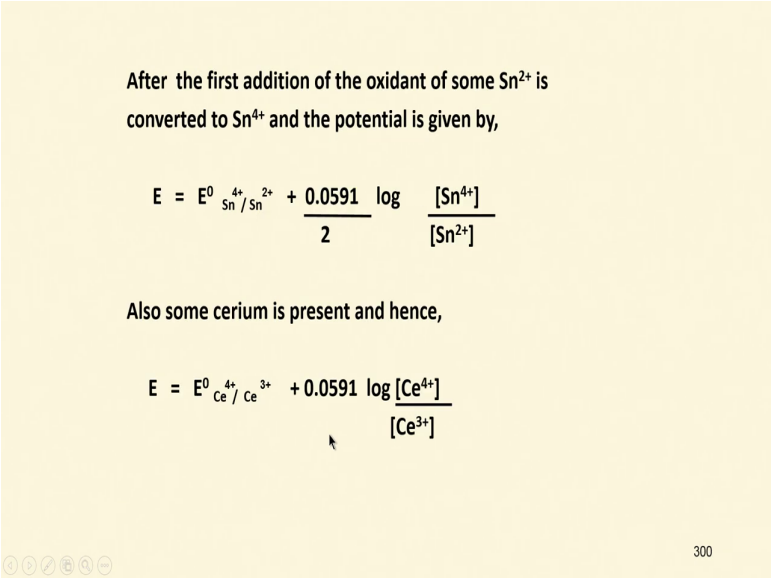


So, that is what we are aiming at. Now, what do we want to do now is we will let us calculate what is the concentration. I have after the first addition of the oxidant, some of the stannous is converted to stannic and the potential is given by Sn 4 plus by Sn 2 plus and cerium is after some cerium is present, it is log of ceric by cerous.

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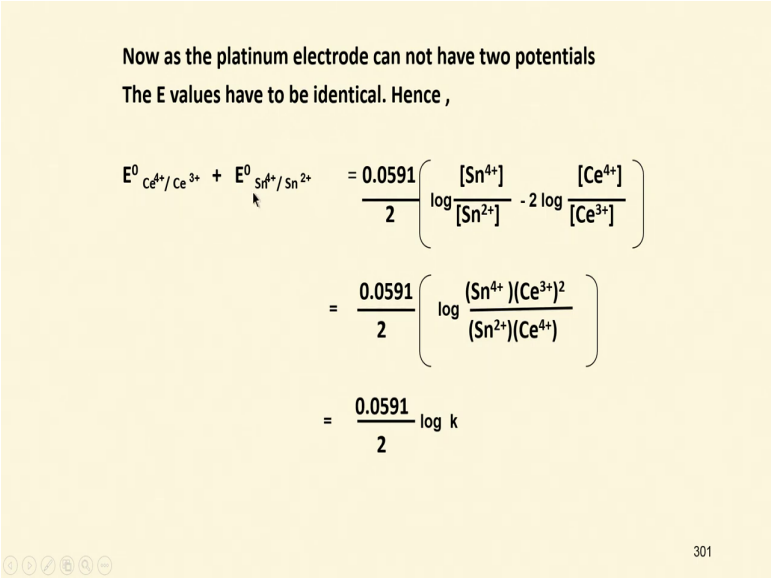


And this value should be now I am talking about stannous stannic reaction. So, in the stannous stannic reaction, E naught ceric cerous plus E naught stannic stannous is nothing but the difference between the concentrations of these two systems.

So, 0.0591, it is a two-electron system and this would be twice up to two times ceric volume molarity volume of the ceric solution is required. Because it is ceric cerous is a single electron system; this is two electron system. So, if I write K equivalent constant log K, I will get 0.0591 by 2.

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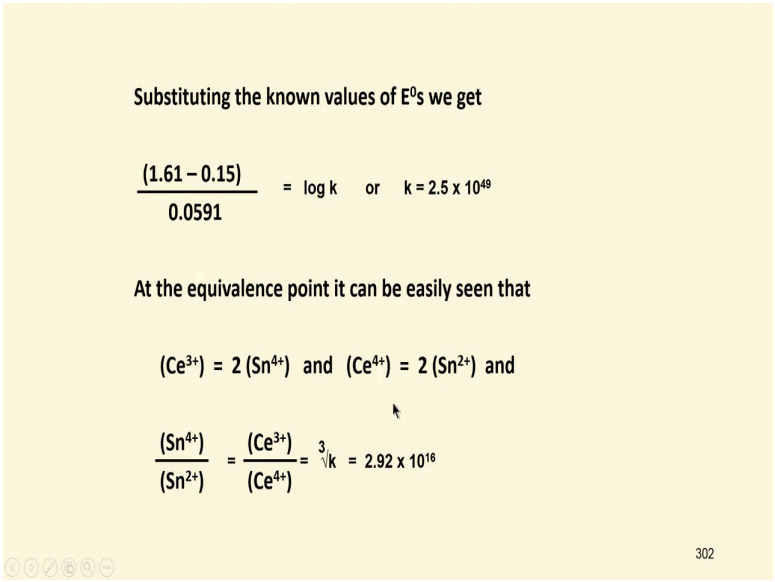


And substituting the known values of E naught, we get log K is equal to 2.5 into 10 raised to 49. So, for this reaction also we can say that K is equal to its a large value and the reaction virtually goes to completion and at the equivalence point if Ce 3 plus would be twice the concentration of Sn 4 plus. Just think a little bit about it and you will get it and Ce 4 plus also would be equal to 2 times the stannic stannous.

So, I can write stannous stannic to stannous and the ratio of cerous to ceric is 3 times; this is 2 times concentration, this is 1 time concentration. So, in the equivalence point equilibrium this thing this will become raised to 2 2 plus 1 is 3. So, the square root of equilibrium constant tells me that 2.2 2.92 into 10 raised to 16; just cube root of this 10 raised to 49.

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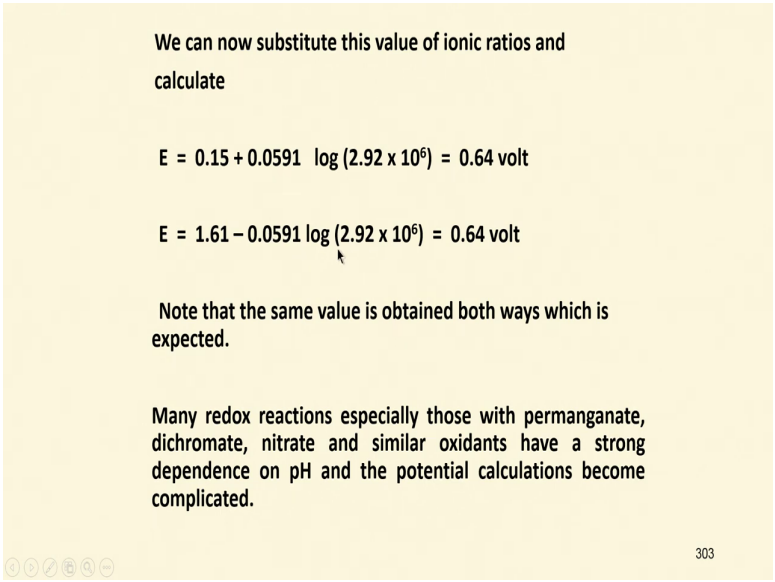


Cube root of k it works out to this value and we can now substitute the value of this ionic ratios and calculate e is equal to 0.15 that is a stannic stannous and 0.0591, this is ceric cerous. So, 0.15 and 0.0591 log of 2.92 into 10 raise to 6 that works out to 0.64. Even if I take twice that value, this would be same value will be obtained, if I take the other one with 1.61 and minus this. So, same value is obtained both ways which is always expected.

So, there are many types of reactions, redox reactions especially those involving redox reactions such as permanganate, very strong oxidizing agent; potassium dichromate is a very strong oxidizing agent; nitrite is also a strong oxidizing agent. Such oxidizing agents can reduce many substances in normal chemical reactions. But they have a strong dependence on the pH.

So, the reaction will be faster sometimes in acidic medium, sometimes in alkaline medium. For example, H2 O2 you know the redox reactions can proceed both in acidic and alkaline conditions. And potassium dichromate and permanganate etcetera, they reaction is very fast in acidic solutions. Sometimes the reactions proceed very fast when the reactive substances are in solid state that is a dry state; when they are in liquid, the reactions are also equally fast; but not all the reactions.

So, the pH has a strong effect on the potential especially when they are redox reactions, we cannot ignore. Just look at these example. We have a chemical reaction involving oxidation of ferric to with manganese manganic potassium permanganate.

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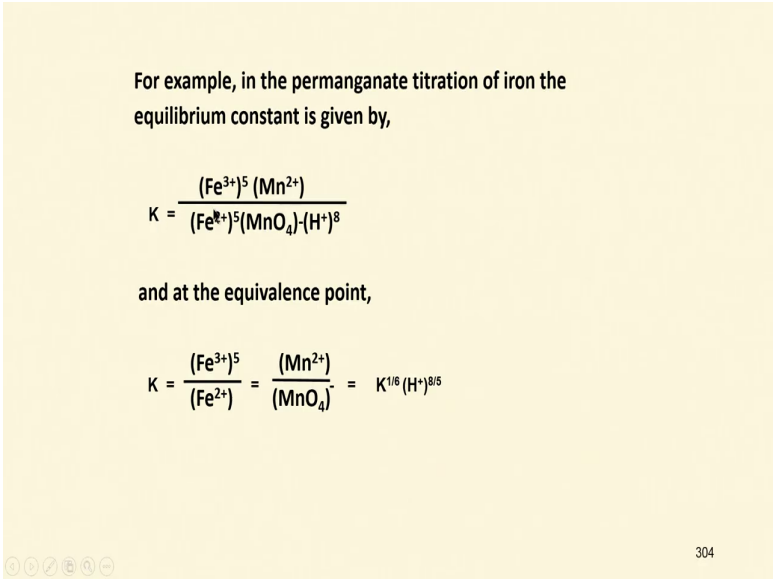


So, for this reaction, I can write equilibrium constant K is equal to Fe 3 raise to 5 and it is a five electron transfer system. Manganese 2 and Fe 2 plus raise to 5 into Mn O4 and then, I

have a term that is H plus raised to 8. This is Mn O4 minus. This minus should not have been here, it should have been here. Please remember that and that means; if the acidity is very high, then the reaction goes to completion.

So, I at the equivalence point what do I have here? Ferric raise to 5 divided by ferrous raised to 5 is equal to Mn 2 plus Mn of 4 minus. Here, also it should have been 5 and K is equal to one-sixth of this because 5 electrons here and 1 here. So, it is one-sixth total species is 6 and H plus is 8 by 5.

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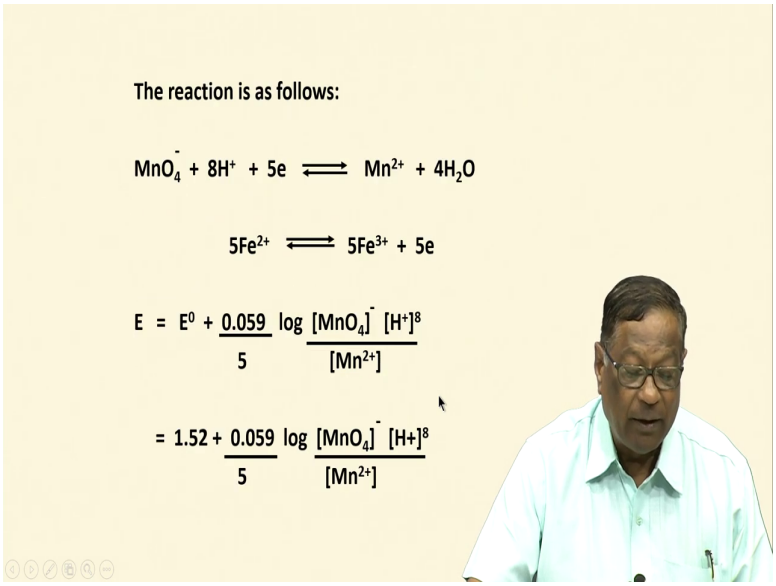


5 electron system, this is the reaction basically. Mn O4 plus 8 H plus 5 e goes to Mn 2 plus 4H2O. For this reaction, I have already written the equations like this.

So, here 5 Fe 2 plus goes to 5 Fe 3 and 5 electrons are there. This is 8 hydrogen that is acidic very high acidic medium approximately 0.1 molar and E is equal to E naught plus 0.059 divided by 5 electron system 5 and log of Mn O4 minus into H plus 8 raised to divided by Mn 2 plus H plus raise to 8 is there. So, if I put 1.52 here, I can write the correct value.

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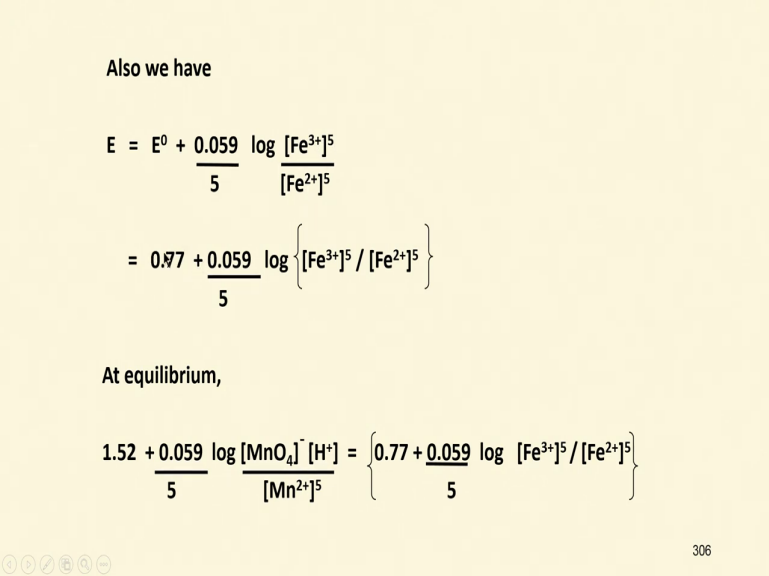


And we also have another reaction that is log of Fe 3 by Fe 2 plus whole raise to 5 that is 0.77 that is the standard reduction potential for ferric ferrous and 0.059 divided by 5 and as usual we write the products divided oxidant divided by reductant with a plus sign. Otherwise, you have to write minus sign with Fe 2 plus a reductant at the top and oxidant at the bottom. So, that is all simple mathematics, I do not have to explain to you.

But this is the convention right plus and oxidized state at the top numerator and reduced state at the denominator. So, at equilibrium, I can write the potential at the manganese manganic

should be equal to potential at the ferrous ferric ok. So, I can write 1.52 into plus 0.059 divided by 5 logarithm of this equilibrium reaction of the system should be equal to this.

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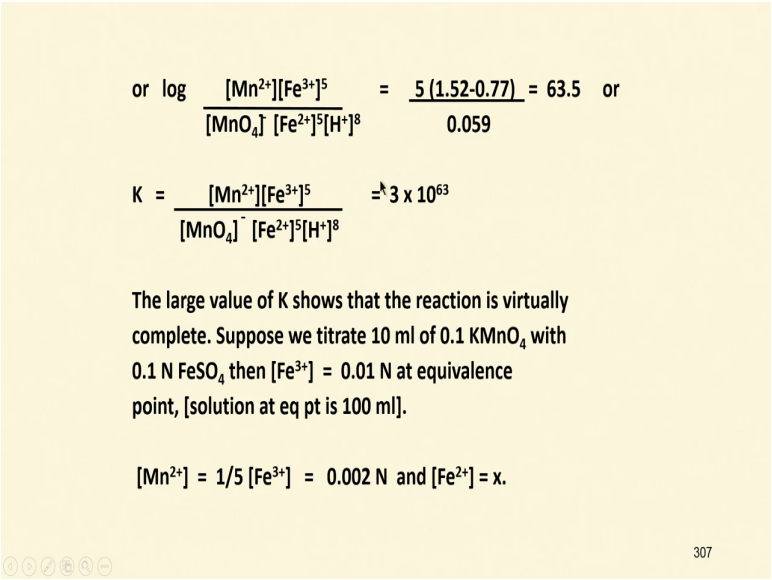


And I get log of this should be I can put the numbers here and I get 63.5 or I get K is equal to take the antilog and that gives me 3 into 10 raise to 63. So, again, the large value of K shows that the reaction is virtually complete. So, anytime you want to see whether a reaction is complete or not, all you have to do is look at the value of K. If it is more than 10 raise to 3, simply say that the reaction is very fast.

Suppose, we titrate 10 ml of 0.1 molar KMnO4 now, with 0.1 normal FeSO4, then the Fe 3 plus would be 0.01 normal at the equivalence point and the solution at equivalence point is at 100 ml. So, I can write Mn2 plus should be equal to one-fifth of that that is 0.002 normal and Fe 2 plus would be almost not existent. So, we will say it is x.

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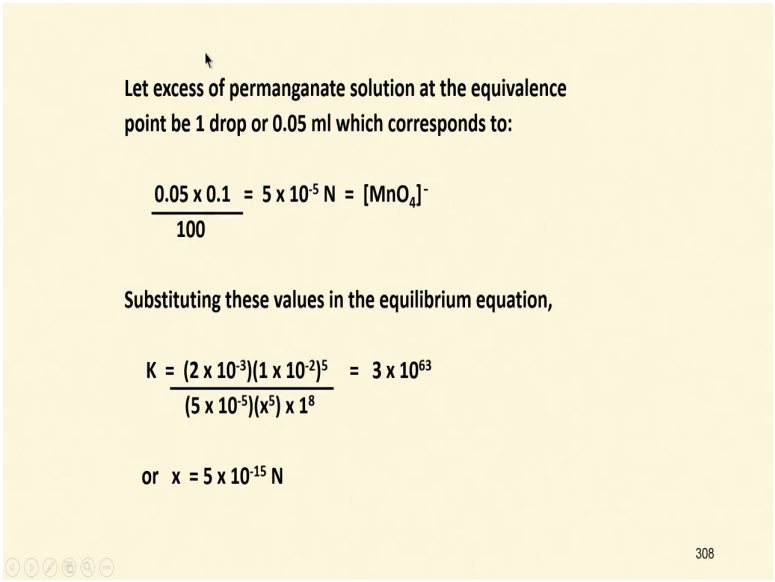


So, a little excess of the potassium permanganate solution, at the equivalence point one drop let us say 0.05 ml we add, then that 0.05 ml gets diluted to 100 ml and that is the normality. So, what I get concentration is 5 into 10 raise to minus 5 normal MnO4 minus. So, substituting these values, I get 2 into 10 raise to 3 that is go back and here manganese 2 plus is 2 into 10 raise to minus 3 and this is 1 into 10 raise to minus 2 raise to 5 that is ferrous ferric manganese ferrous to ferric, yes.

So, this is ferrous and K if this would be manganese, this would be x raise to 5 the because ferrous, we do not know yet in to 1 raise to 8 at that is the reaction being carried out at pH 1. So, how much do I get? 3 into 10 raise to 63 or x should be 5 into 10 raise to minus 15 normal; that means, the concentration of x that is Fe 2 plus would be 5 into 10 raise to minus

15 normal, you are getting at the end of the reaction; that means, the reaction is virtually complete.

So, like that a knowledge of the standard reduction potential along with the concentrations tells us whether a reaction is complete or not. So, that completes our studies on potentiometry.

Now, we will go to the go to another technique equally exciting and currently one of the best technique for the determination of many metals at microgram and nanogram and picogram also; that is voltammetry and more popularly known as polarography. Basic technique is voltammetry and there are lot of variations, I am going to teach you about polarography.

But there are other techniques like cyclic voltammetry and there are simple voltammetry and then, polarography; all these things are there. We will discuss about these things now and I have to tell you at this stage that the polarography as we are going to discuss today is one of the best technique that is available not only for the determination of the metals, but also for the speciation.

So, what is speciation? Speciation is that branch of science which tells us in what actual chemical form, a particular substance is there in the finished product. So, it is very important sometimes if I take iron tablet, I may be taking ferrous or ferric and I want to know how much of ferric ferrous is there; how much of ferric is there?.

Similarly, there are many substances which are in different chemical forms, but present all the way all the same. So, this kind of speciation has gained a lot of recognition over the last 50 years and everybody would like to you know exactly what kind of chemical is there in a particular matrix. So, polarography is one of those special techniques which tells us in what form a chemical species is there; whether it is plus one state, plus two state, complex form, neutral form, as a solid, as a liquid like that there are lot of things.

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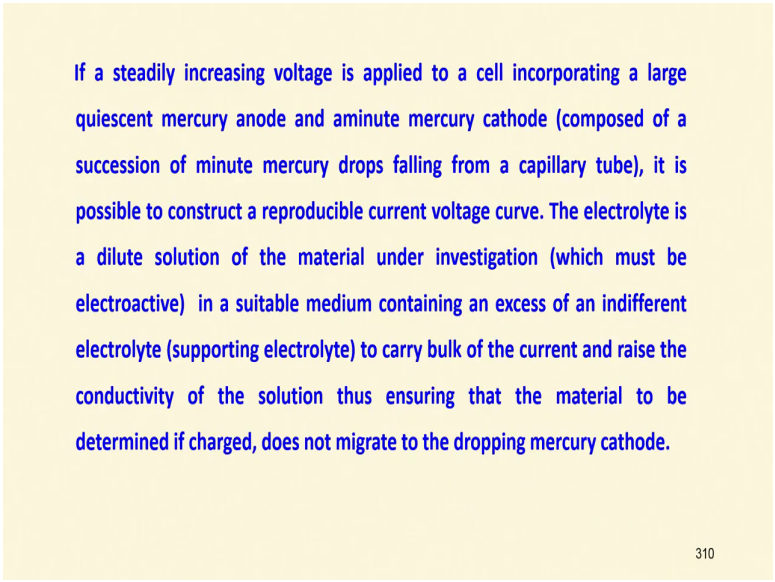


So, here in polarography what I do normally is I take a substance to be reduced normally most of the chemical reactions involving polarography are redox reactions ok. So, the redox reactions most of the metals will undergo anyway. So, it is I increase the voltage of a cell incorporating large quantity of anode that does not take part until a particular stage is reached.

Then what happens? The ions will migrate towards the cathode. Metal ions will migrate towards the cathode and the anions will migrate towards the anode, but the reaction does not go through. So, they will be hanging there.

And then, the ions if I increase the voltage there will be certain resistance for the metal ion to reach the electrode and get reduced there is certain voltage you know for every piece, for every metal there is a voltage at which it will get reduced. So, if I start from 0 or almost negative value, then slowly I keep on increasing deposition will not take place; but ions will

migrate all the same. So, as I keep on increasing, there will be a stage when the ions will start migrating through the solution and be able to reach the cathode at a particular voltage that is standard reduction potential.

So, the, but this potential does not happen, does not satisfy the standard potential. It is not a match; it is not the same as a standard reduction potential. What you have been talking about, but it will be a combination of factors of the standard reduction potential and there is a diffusion because all ions have come to the cathode; but only a few are reaching the cathode.

So, they have to fight their way through the sample matrix to reach the electrode. So, there is a diffusion term that gets added up and the EMF potential, the voltage will be slightly different from the standard reduction potential that includes the diffusion term.

So,, but still it is a great technique. So, let us see what my text tells you regarding the standard reduction potential. Now, just look at this slide now I have written exactly the same thing what I had told you. If a steadily increasing voltage is applied to a cell incorporating a large quiescent mercury anode. What is a large quiescent mercury anode? It is a mercury pool connected electrically to anode and it us so large that there is no change in its appearance or in the behavior as if it is a stagnant pool ok.

So, I have a stagnant pool of mercury anode which is connected to anode and a minute mercury cathode ok; minute mercury cathode and a large pool of mercury solution which does not get disturbed; but connected to anode. I have two electrodes; one is dropping mercury cathode and another is mercury anode, both of them are something like concentration cells only and the cathode has got a special property that is it is composed of a succession of small minute mercury drop falling from a capillary tube.

So, what I am doing is I am going to put mercury in a beaker, connect a capillary, allow the mercury to fall drop by drop, drop by drop into the solution in which my analytical sample is there. So, I have a system containing dropping mercury electrode and then, the migrant ion migration will take place and I have an anode of mercury only.

But that is not a drop mercury, but it is a large surface area maybe about 10 centimeter; whereas, from a capillary you can imagine how much would be the size of the mercury drop that would be almost of the order of about 10 raise to minus 2 or minus 3 grams that is all. So, a few milligrams. But this will be in grams.

So, the electrolyte; then, electrolyte is the substance which will contain the material under investigation. But the capillary is something special here; is not it? Why? Because the capillary reacts, I have a capillary from where the drops are falling; slowly the drop will form, form bigger, bigger, bigger, bigger, I will have a drop and then suddenly because of its own way, it will fall down from the capillary and then, the moment it falls down it will reach the mercury anode and then, I have one more drop forming simultaneously at the tip of the mercury electrode mercury capillary. That is the cathode.

So, the dropping mercury, it is known as dropping mercury electrode or it is a nothing very special a small capillary on which is fitted to a large pool of mercury on the top and mercury is allowed to a drop, drop by drop into the solution that contains the analyte.

So, we have the sample under investigation in a suitable medium, containing an excess of indifferent electrolyte indifferent electrolyte that that means, it does not get reduced. It is not taking part in the reaction that is know that is why it is known as indifferent electrolyte and we can also call it supporting electrolyte, but this electrolyte ions produced from the supporting electrolyte indifferent electrolyte.

They carry the bulk of the current and raise the conductivity of the solution. So, it ensures that the material to be determined, if it is charged it does not migrate to the dropping mercury electro cathode. So, what does this supporting electrolyte do? It will carry bulk of the current, won't allow the material to be charged and to be analyzed it should not migrate to the dropping mercury electrode or whatever it is, the sample will not reach the electrode in sufficient quantities.

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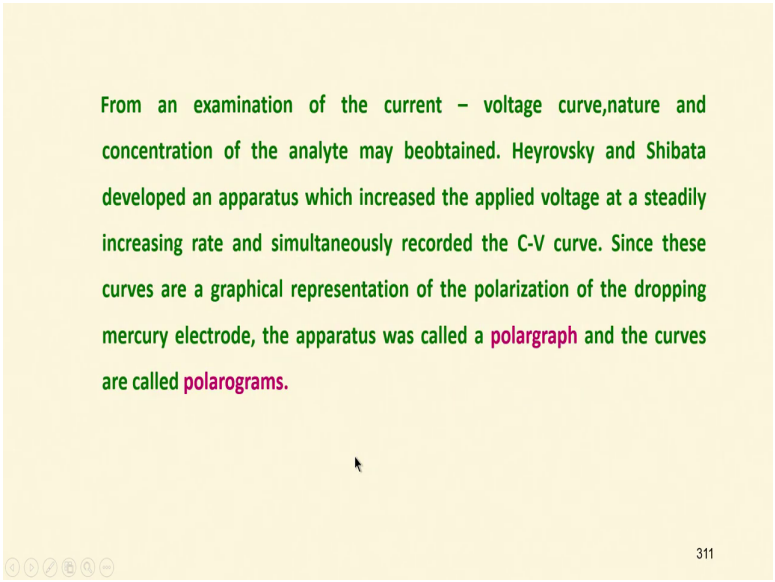


So, bulk of the current is carried by an indifferent electrode, it does not reach the electrode. Because it is indifferent to the applied voltage and then, whatever ions of the analyte reach the electrode by carrying the current it is so small that it has no effect on the overall reaction that is the basic system. So, I can then what I do is I can increase the current voltage curve; I can increase the voltage.

So, after the current voltage, the I can determine what more electrolyte will pass nearer the electrode and then more of the analyte also will form, but the again the reaction will not be completed because the reduction potential of the analyte has not yet reached. So, I keep on increasing slowly; at some stage, it will start reaching the electrode after its reduction potential is reached.

So, I can the ion will start getting reduced and I can study the curvature of the electrode potential, how it has changed or the current how it has changed; how initially current was not flowing, later on current will be flowing; but voltage I know how much I am applying and I can determine how the current is varying over a period of time until the sample starts getting reduced.

So, this is the beautiful way of analyzing a sample provided I have a material which can be electrolytically oxidized or reduced. So, then there were two Russian scientists, Heyrovsky and Shibata, they developed an apparatus which increase the applied voltage at a steadily increasing rate and simultaneously recorded the CV curve. Since these curves are a graphical representation of the polarization of the dropping mercury electrode, the apparatus was called as polarograph and the curves are called as polarograms.

So, in essence what we are saying is you take a sample, put an indifferent electrolyte in a beaker, put a put some amount of mercury in the beaker, connect it to anode and allow a capillary to be dipped in the solution and allow the mercury to drop slowly of its own weight. So, that is the system.

Externally what I need? I need a I need a system to increase the voltage applied voltage and I need a system for recording the current; very simple equipment for which the technique was based on which the technique was developed and they were awarded Nobel prize for this invention.

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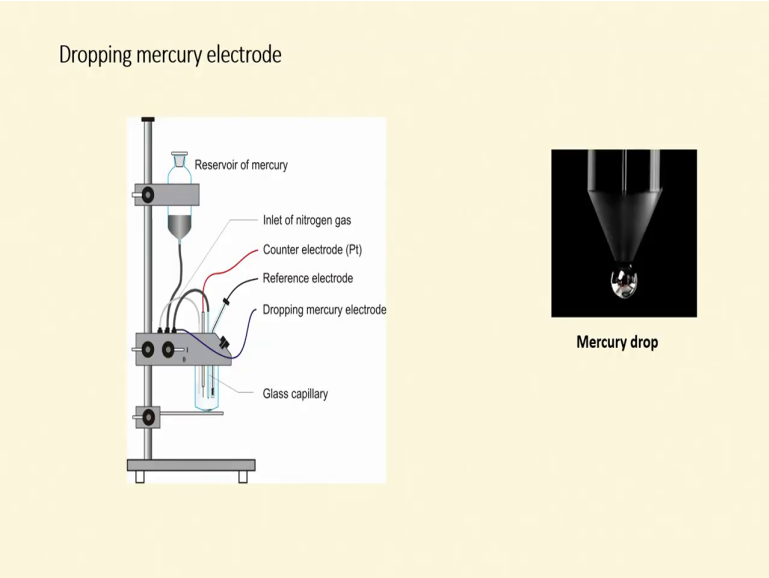


So, the here is the picture of the polarograph. So, here I have a reservoir of mercury on the top and then, I have a small capillary here and here I have some sort of inlet gas and there is a counter electrode containing the platinum and a reference electrode is there and here I have the dropping mercury electrode from the capillary and I have a glass capillary here. This one from where the electro electrolyte from where the mercury will be dropping and falling at the bottom.

So, this is the basically the arrangement of the dropping mercury electrode and this is the picture of the mercury drop that is being formed and just about to fall down. I have just put it for a curiosity.

We will continue our discussion, how to interpret the analytical data that can be generated by the reduction of the analyte element in our next class.

Thank you very much.