Electrochemical Technology in Pollution Control
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Lecture – 15
Potentiometry 6

Greetings to you, we will continue our discussion on the Potentiometric titrations. Earlier, we had discussed how the potential measurements can give you equivalence point at the sharp equivalence point for acid base titrations and precipitation titration; redox titrations also can be done very easily.

And, I had told you in my last class that reactions involving complexation, exhibit slightly more complicated titrations curves; because of the different ionic species that are formed in the chemical reaction; best example is silver. Silver will react with silver cyanide to give you a precipitate, if you add more cyanide it will dissolve. The precipitate will redissolve and then the you will get silver cyanide AgCN twice minus complex.

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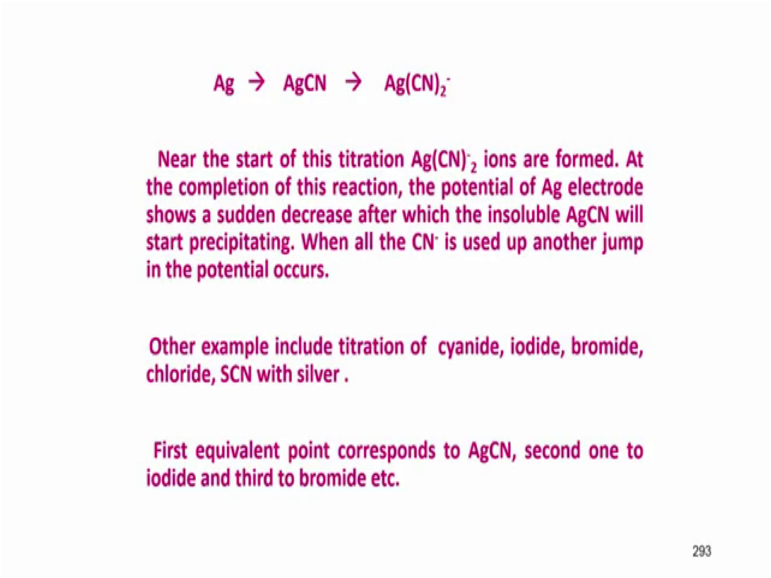

$Ag \rightarrow AgCN \rightarrow Ag(CN)_2^-$

Near the start of this titration $Ag(CN)^-_2$ ions are formed. At the completion of this reaction, the potential of Ag electrode shows a sudden decrease after which the insoluble AgCN will start precipitating. When all the CN^- is used up another jump in the potential occurs.

Other example include titration of cyanide, iodide, bromide, chloride, SCN with silver .

First equivalent point corresponds to AgCN, second one to iodide and third to bromide etc.

So, near the start of this titration; silver cyanide ions are formed, why? Because, we are taking cyanide in the beaker, and we are going to add silver from the top; you understand. Normally, we do the silver cyanide titration taking cyanide in the beaker, in the bottom conical flask and adding silver from the top so, that we do not waste silver solution. Silver is costly metal.

So, near the start of the titration, I have only cyanide solution at the in my conical flask, there I am going to add a few drops of silver. So, cyanide will be more and silver will be less. So, silver cyanide will be forming a complex instead of a precipitate. So, at silver; initially, silver cyanide AgCN 2 minus ions will be formed and AgCN 2 minus ions are soluble.

Now, you will not see a precipitate as you keep on adding more and more silver, the ratio of cyanide and silver will keep on changing. So, once it changes and silver will keep on increasing, cyanide will keep on coming down, when they become equal concentration of silver and cyanide will be same at that time precipitation will start. So, that is the basic chemistry of the system.

So, at the completion of the reaction, potential of silver chloride silver electrodes shows a sudden decrease after which the insoluble silver cyanide will start precipitating. So, when all the cyanide is used up, another jump in the potential will occur because the silver ions will be more. So, PAG will keep on increasing. So, other examples of complexation titrations include you can do silvers cyanide, silver iodide, silver bromide, silver chloride, silver thiocyanate and many any other precipitation reaction you can do, but most of them be sparingly soluble salt.

So, first equivalence point in this reaction silver cyanide, silvers cyanide will correspond to that species for which the solubility product will be lowest or highest it will be highest, ok. Solubility product is higher and that will precipitate first. And then it will react with bromo iodide, because the next solubility product next higher would be iodide slightly lower than cyanide, third will be bromide, forth will be silver chloride which will be minimum solublel, ok.

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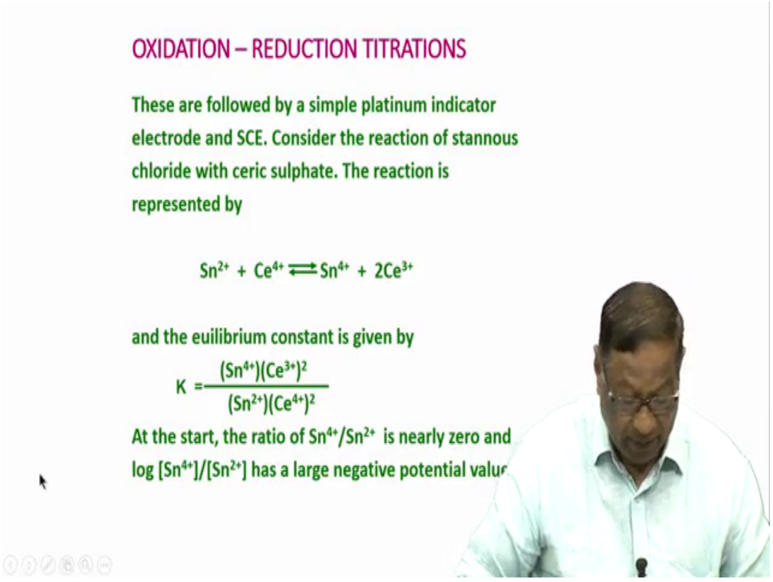

OXIDATION – REDUCTION TITRATIONS

These are followed by a simple platinum indicator electrode and SCE. Consider the reaction of stannous chloride with ceric sulphate. The reaction is represented by

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

and the euilibrium constant is given by

$$K = \frac{(Sn^{4+})(Ce^{3+})^2}{(Sn^{2+})(Ce^{4+})^2}$$

At the start, the ratio of Sn^{4+}/Sn^{2+} is nearly zero and log $[Sn^{4+}]/[Sn^{2+}]$ has a large negative potential valu

So, if you remember all those things one can really plan for the transfer of the silver, cyanide, bromide, iodide, complexes etcetera. Now, we will consider a little bit about the oxidation redox reactions. So, redox reactions are also followed by a simple platinum indicator electrode and SCE that is Saturated Calomel Electrode.

Consider a reaction of stannous chloride ceric sulphate. So, I can write the reaction something like this, stannous S n 2 plus E stannous will react with ceric ions to give you stannic ions and cerous ions, ok. So, the, I have two cells, one stannous stannic another cerous series, ok. So, it is like a concentration cell now, because I do not have a tin electrode I do not have a cerium electrode, both of them would be platinum electrodes, ok

So, in the platinum electrodes, I have two beakers one is stannous and see another is ceric cerous system or I can take in one beaker add ceric solution in that. So, the equilibrium constant for this reaction is given by K is equal to S n 4 products divided by reactants that is a equilibrium constant. So, I write S n 4 plus C e 3 plus whole square divided by S n 2 plus multiplied by C e plus 4; C e 4 plus whole square, ok. So, at the start of the reaction, the ratio of stannic to stannous is nearly 0, is not it; because I am taking stannous, I have not added anything. So, most of it is in stannous so, stannic will be 0.

So, S n 4 plus 0 divided by anything is 0 only. So, at the at the start before I add anything S n 4 plus S by S n 2 plus ratio is nearly 0 and log of S n 4 plus by S n logarithm of this entity has a large negative potential, it is not easily determined at all some very high number, ok.

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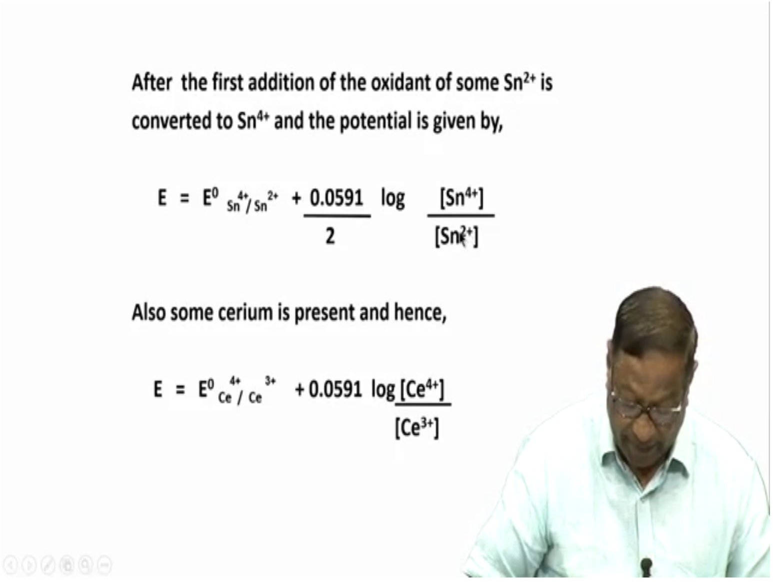

After the first addition of the oxidant of some Sn^{2+} is converted to Sn^{4+} and the potential is given by,

$$E = E^0_{Sn^{4+}/Sn^{2+}} + \frac{0.0591}{2} \log \frac{[Sn^{4+}]}{[Sn^{2+}]}$$

Also some cerium is present and hence,

$$E = E^0_{Ce^{4+}/Ce^{3+}} + 0.0591 \log \frac{[Ce^{4+}]}{[Ce^{3+}]}$$

Then after the first addition of the oxidant that is ceric some stannous is converted into stannic and the potential is given by the half cell potential E is equal to E naught of stannic to stannous that is standard reduction potential of tin system available from database plus 0.0591, it is a two reaction system. So, 0.0591 divided by 2, then logarithm of stannic to stannous; products divided by reactants.

See here, the product is S n 4 by S n 2; remember we are considering only stannic stannous system, not ceric cerous. So, for the half cell corresponding to stannic stannous we write this reaction, then after some cerium is present, we add a little bit and then what do we have? We also have another system, where ceric cerous also will be present. Because, we have added ceric ion that is used up for the reduction for the oxidation of stannous.

So, ceric cerous also will be complimentarily available the moment you add the first drop of the ceric cerous solution. So, I can write equally another reaction that is ceric 4 plus E naught ceric cerous plus 0.0591 logarithm of C e 4 plus by C e 3 plus. Now, what do I have here? The problem is it is a single electron transfer system ceric to 4 to 3. So, I have to divide this by only 1 unit 0.0591 divided by 1. So, I do not choose not to write 1, ok. So, this ceric cerous system is given by this equation, ok.

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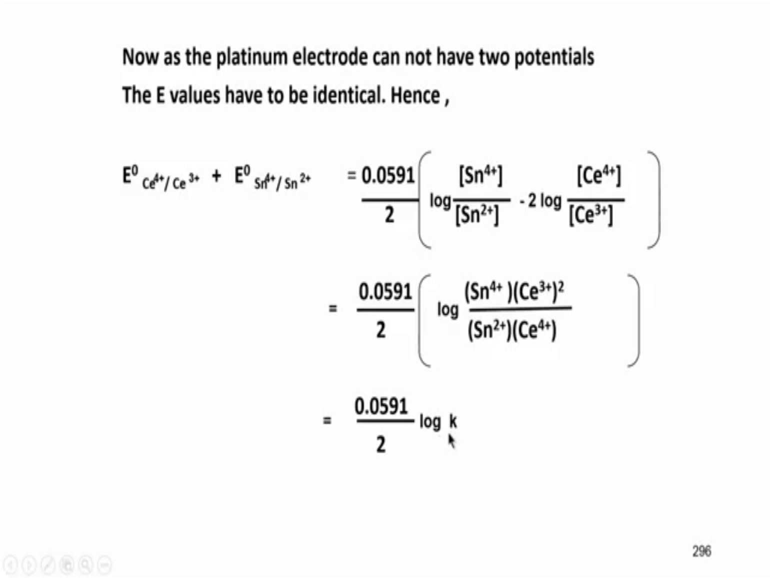

Now as the platinum electrode can not have two potentials
The E values have to be identical. Hence ,

$$E^0_{Ce^{4+}/Ce^{3+}} + E^0_{Sn^{4+}/Sn^{2+}} = \frac{0.0591}{2}\left(\log\frac{[Sn^{4+}]}{[Sn^{2+}]} - 2\log\frac{[Ce^{4+}]}{[Ce^{3+}]}\right)$$

$$= \frac{0.0591}{2}\left(\log\frac{(Sn^{4+})(Ce^{3+})^2}{(Sn^{2+})(Ce^{4+})}\right)$$

$$= \frac{0.0591}{2}\log k$$

Now, as we it is a concentration cell both of them are in solution, I have the only one of them is platinum electrode, another is it may be another platinum electrode or it can be reference electrode. Now, as the platinum electrode cannot have 2 potentials, the E value has to be identical whether it is ceric cerous or stannous stannic; stannic stannous. The potential for the single electrode has to be same, because all of them are where it shows 1 potential, it does not say first I will show you stannic stannous, then I will show you ceric cerous; no, no, no nothing it will not work like that.

The all species are there for all the species that is the emf value you get that is same for stannic stannous you can take it for ceric cerous also. So, what I have here, the E values they have to be identical. So, I can write E naught ceric cerous plus E naught stannic stannous would be equal to 0.0, I can combine; actually I am combining the previous two equations. These, this equation previous these two equations, I write 0.0591 by 2 logarithm of stannic by stannous minus E a minus E b, this is what I have taught you in the beginning.

So, the cell voltage would be the sum of the difference between the two; that is sum of the reduction potential or sum of the oxidation potential, 1 would be minus anyway. So, 1 would be reduced, 1 would be oxidized. So, I can write a reaction something like this, S n 4 plus by S n 2 plus minus 2 times log of ceric to cerous. Why this 2 here? Again it is a single cell reaction, but requires double the concentration, this is because stannic stannous there is a change of 2 valence state here it is a change of once valence state. So, it has to be twice the stoichiometry.

So, I can write this equation can be rewritten like this for 0.0591 divided by 2 logarithm of stannic by stannous into cerous by ceric both of them should be whole square. It should be 2 here, in the ceric also there is an error here. I will take a look at it later and correct it, but for the time being this is consider it as please make in your notes correction, 2 here and this expressions stannic stannous multiplied by cerous ceric whole square is nothing, but the stability constant log k.

So, I can write 0 point; the difference of the emf should correspond to 0.0591 by 2 multiplied by logarithm of k that is equivalence point; equilibrium constant.

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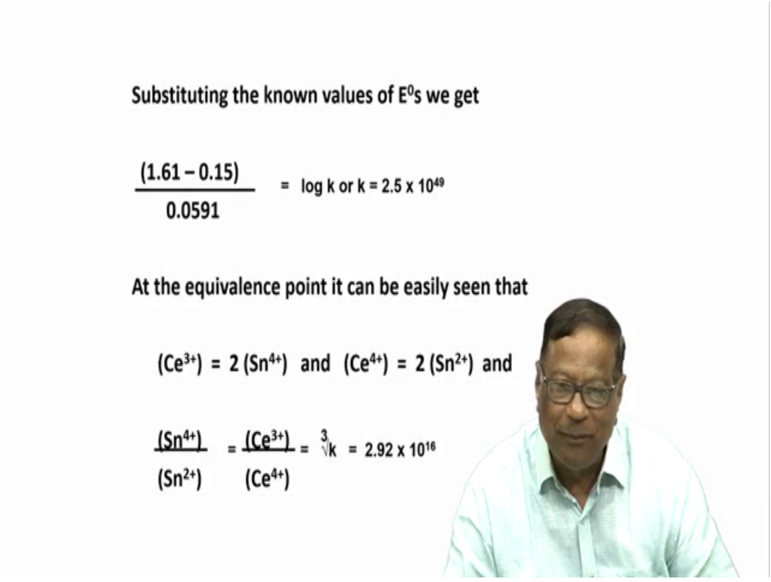

Substituting the known values of E^0s we get

$$\frac{(1.61-0.15)}{0.0591} = \log k \text{ or } k = 2.5 \times 10^{49}$$

At the equivalence point it can be easily seen that

$(Ce^{3+}) = 2\,(Sn^{4+})$ and $(Ce^{4+}) = 2\,(Sn^{2+})$ and

$$\frac{(Sn^{4+})}{(Sn^{2+})} = \frac{(Ce^{3+})}{(Ce^{4+})} = \sqrt[3]{k} = 2.92 \times 10^{16}$$

So, I know the values of these stannic stannous and ceric cerous here I am writing E a minus E b, that is both the cells emf I know ah. So, 1.61 that is for ceric cerous and 0.15 is stannic stannous and 0.0591 that is equal to log k. So, or k is equal to antilog of this number that will be 2.5 into 10 raised to 49. So, what do you deduce from this value k is equal to 2.5 into 10 raised to 49, equilibrium constant for the reaction stannic to stannous plus ceric to cerous is 10 raised to 49.

2.5 into 10 raised to 49 what do you deduce, what does it tell you? I will give you 3 seconds think about it, ok. If you have got it right, you are a good chemist, you have understood the principles, if you did not get it, here is the answer. An equilibrium constant of very high value approximately more than 10 raised to 2, 1 raised to 3 anything above that indicates that the reaction is totally complete virtually complete. So, that you should remember, Any equilibrium constant if it is high; that means, the reaction is proceeding towards the right whichever way you write the equation, ok.

So, the we understand that the value of 2.5 into 10 raised to 49 means all the stannous is converted into stannic using ceric ions, that is a redox reaction percentage more than 100 percent, not more than 100 percent, but it will be almost 100 percent. So, at the equivalence point I can say that the concentration of cerous C e 3 plus should be twice that of stannic, because it is a 2 system 2 electron system.

1 molecule of C e 3 plus will react with 2 molecules of stannous sorry, other way around 2 molecules of ceric 3 plus will be reacting with ceric 4 plus will be reacting with 1 molecule of stannic, to give you 2 molecules of stannous stannic and the quantity of cerous should be equal to twice that of stannic concentrations. So, C e 4 plus also should be twice that of stannous this is oxidant this is reductant reduced species. So, this should be like this and stannic to stannous would be the total number of ions would be 2 of ceric and 1 of stannous stannic. So, 3 molecules are there.

So, the ratio of stannic to stannous should be equal to ceric to cerous to ceric this is oxidation this is reduction. So, I write the reduced species on the numerator and oxidized species on the denominator. So, stannic to stannous ratio should be equal to cerous to ceric. So, the equilibrium constant for this reaction is given not by square root, but by cube root 3, 3 species are there. So, so the k value we know is 2.5 into 10 raised to 49 here, ok; I take the cube root; that means, how much I am getting? 2.92 into 10 raised to 16, what does it tell us again, I will give you 3 seconds pause.

May be 5 seconds pause you must consider this reaction and find out tell me what does it mean, ok if you are guessed it well and good. Otherwise, here is the answer that is the ratio of stannic to stannous is same as ceric cerous to ceric that is number 1 point number 2 the ratio is 2.9; 2 into 10 raised to 16 for any of this.

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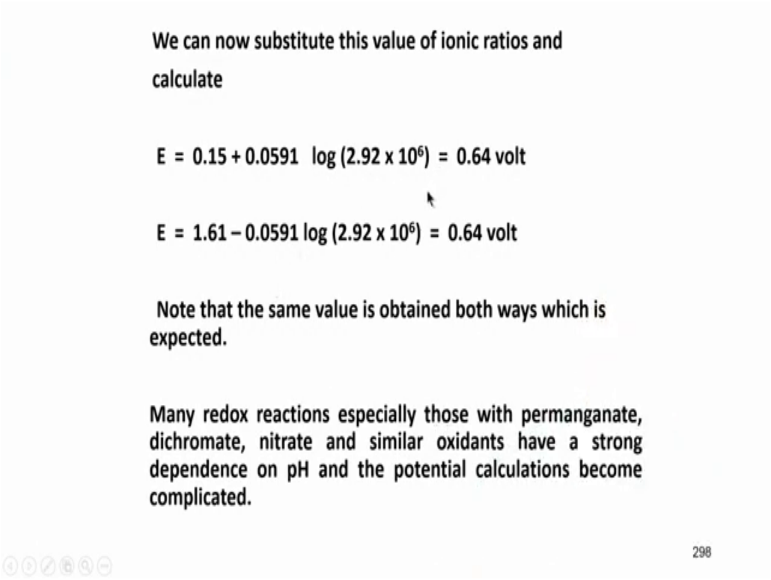

We can now substitute this value of ionic ratios and calculate

$E = 0.15 + 0.0591 \log (2.92 \times 10^6) = 0.64$ volt

$E = 1.61 - 0.0591 \log (2.92 \times 10^6) = 0.64$ volt

Note that the same value is obtained both ways which is expected.

Many redox reactions especially those with permanganate, dichromate, nitrate and similar oxidants have a strong dependence on pH and the potential calculations become complicated.

You can now substitute the value of these ionic ratios in the equation Nernst equation this is for stannic stannous E is equal to 0.015 this is E naught S n 4 plus by S n 2 plus 0.0591 divided by 1 log of oxidant divided by reductant.

But, we know that stannic to stannous ratio is 2.92 into 10 raised to 16, it should be 16 yeah, again there is an error here, I should correct it. So, log of 2.92 into 10 raised to 16 multiplied by 0.0591 and add 0.15 this reads to 0.64 and because the emf cannot show one value for stannic stannous and another value for ceric cerous. We should get the same value for ceric cerous also whether I calculate it for stannic stannous or ceric cerous I will I should get the same value.

Now, you check this the E naught value for ceric cerous is 0.61 and here I am writing minus 0.0591; find out why I write minus here and plus here, ok; that is an exercise for you. And this minus this into log of 2.92, 10 into 10 into 10 raised to 16 that is understood, that also would give you the value of 0.64 this is a thumping corroboration of the theory what you have been talking about, ok. So, either way whether it is stannic stannous or ceric cerous, we get the same potential that is what we want any way that is what we expect.

So, the same value is obtained with both ways which is expected. So, many redox reactions especially those with permanganate, dichromate and nitrate and other similar oxidants have a strong dependence on the p H and the potential calculations become slightly complex, what does it mean again? Again, I will give you 3 seconds pause to try ask you and ask you to digest this in for this information on this paragraph. Many redox reactions; especially, those with potassium permanganate, potassium dichromate nitrate and similar oxidants have a strong dependence on the p H.

So, what does it mean? That means, the equation what you have written here E is equal to E naught plus rt by n f log of some concentration of the oxidant divided by reduced species. This number will be influenced by the p H, that is whether you carry out the reaction in acidic medium or basic medium or what should be the p H? If it is 4, you will get some value; if it is p H is 5 you will get some other value like that. So, there is no clear indication to calculate what is the expected emf for a reaction which is p H dependent, ok.

So, you can listen to this lecture again and again and find out what exactly I have said just now. So, in general it is it should be good for you to understand that the reactions would be fairly comfortable, if you understand that the p H interactions are important. They can affect the ratio of the oxidant to redoxed species and we cannot write the actual equations involving the standard reduction potential as obtained from Google or Nernst data other database. So, will have to actually carry out the reaction at different p H and then determine the emf what we get, ok.

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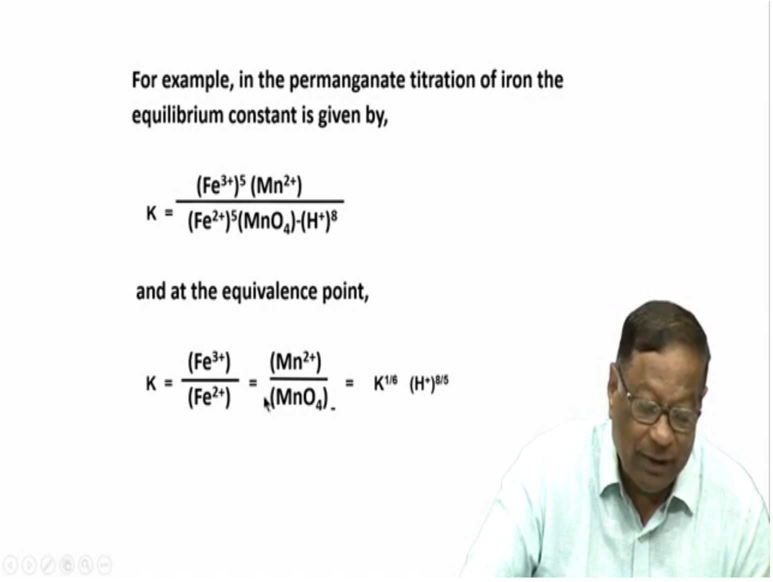

For example, in the permanganate titration of iron the equilibrium constant is given by,

$$K = \frac{(Fe^{3+})^5\,(Mn^{2+})}{(Fe^{2+})^5(MnO_4)\text{-}(H^+)^8}$$

and at the equivalence point,

$$K = \frac{(Fe^{3+})}{(Fe^{2+})} = \frac{(Mn^{2+})}{(MnO_4)_-} = K^{1/6}\ (H^+)^{8/5}$$

So, for example, in the permanganate titration of iron, the equilibrium constant is given by this expression, look at this K is equal to F e 3 plus raised to 5 and M n 2 plus that is the reaction concentrations of the products divided by ferrous raised to 5, MNO 4 minus raised to 1 and H plus raised to 8; that means, the reaction is very very highly dependent upon acidic medium. This reaction will go that is oxidation of ferrous to ferric using potassium permanganate; will go only if these reaction is strong reaction media is strongly acidic; otherwise, it will not go it will be very slow. So, the emf also be different.

So, at the equivalence point K is equal to ferric by ferrous should that also should be equal to oxidant by reductant. So, what is the other system? M n 2 plus divided by M n O 4 minus, ok. So, this comes here, the total species is 5 here, 1 here. So, it should be 6. So, the for any species the concentration equilibrium concentration ratio of the oxidant redox should be one sixth of the equilibrium constant total 6 ions.

So, K raised to 1 by 6 into H plus raised to 8 that is the chemical reaction and then 5 electrons system. So, divided by 5; 8 by 5. So, the equilibrium constant K is that value then take one sixth and then multiply it by H plus raised to 8 by 5, you will get the ratio of ferric to ferrous.

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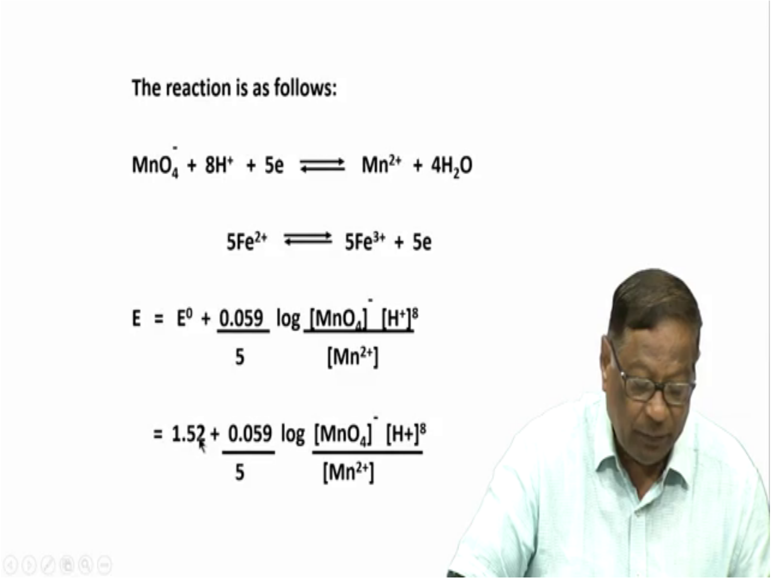

The reaction is as follows:

$$MnO_4^- + 8H^+ + 5e \rightleftharpoons Mn^{2+} + 4H_2O$$

$$5Fe^{2+} \rightleftharpoons 5Fe^{3+} + 5e$$

$$E = E^0 + \frac{0.059}{5} \log \frac{[MnO_4^-]\,[H^+]^8}{[Mn^{2+}]}$$

$$= 1.52 + \frac{0.059}{5} \log \frac{[MnO_4^-]\,[H+]^8}{[Mn^{2+}]}$$

Now, look at it what is the reaction basically, I have M n O 4 minus plus 8 H plus that is a highly acidic reaction plus 5 electrons that will lead to M n 2 plus 4 H 2 O and 5 F e 2 plus this other half cell reaction goes to 5 F e 3 plus 5 electrons, ok.

So, E is equal to E naught plus 0.0591 divided by 5, 5 electron system logarithm of M n O 4 minus into H plus raised to 8 divided by M n 2 plus,. This should be equal to the redox potential of the system E naught 1.52 remaining concentrations etcetera will remain the same.

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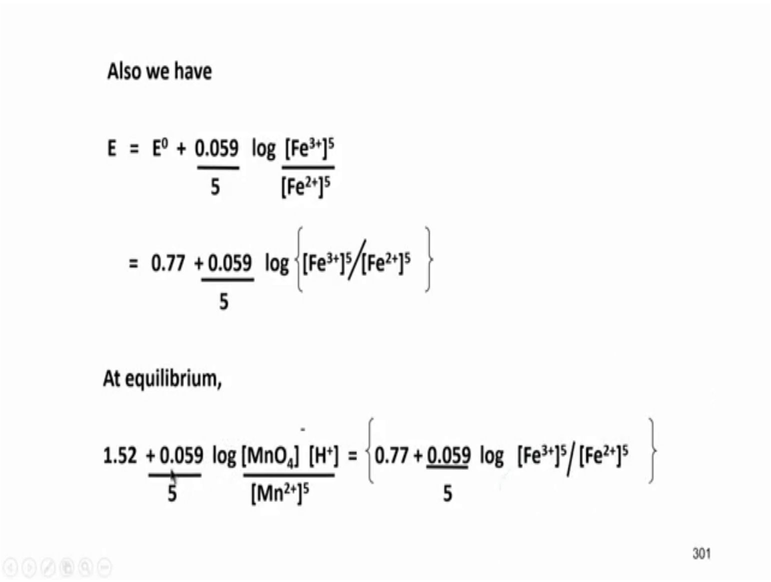

Also we have

$$E = E^0 + \frac{0.059}{5} \log \frac{[Fe^{3+}]^5}{[Fe^{2+}]^5}$$

$$= 0.77 + \frac{0.059}{5} \log \left\{ [Fe^{3+}]^5 / [Fe^{2+}]^5 \right\}$$

At equilibrium,

$$1.52 + \frac{0.059}{5} \log \frac{[MnO_4]^{-} [H^+]}{[Mn^{2+}]^5} = \left\{ 0.77 + \frac{0.059}{5} \log [Fe^{3+}]^5 / [Fe^{2+}]^5 \right\}$$

And we also have another system that is one previous one was for M n O 4 and M n O 2 plus. And now another system that is prevalent in the same beaker is ferric ferrous. So, I write E is equal to E naught plus 0.0599 for 059 divided by 5 logarithm of ferric by ferrous raised to 5.

So, if I have again E naught value is known 0.77 and 0.59 by 5 this remains the same at equilibrium I can write the left hand side manganous manganite is once the half cell, the potential should be equal to ferric ferrous that potential. So, for manganous manganous react; manganous manganic reaction; the E naught is 1.52 plus, this and I can write equivalent ion system and if you take a look at this system. You can separate the numerical terms 1.52 and point double 7 on this side, this part you can transfer on the other side and rewrite this equation.

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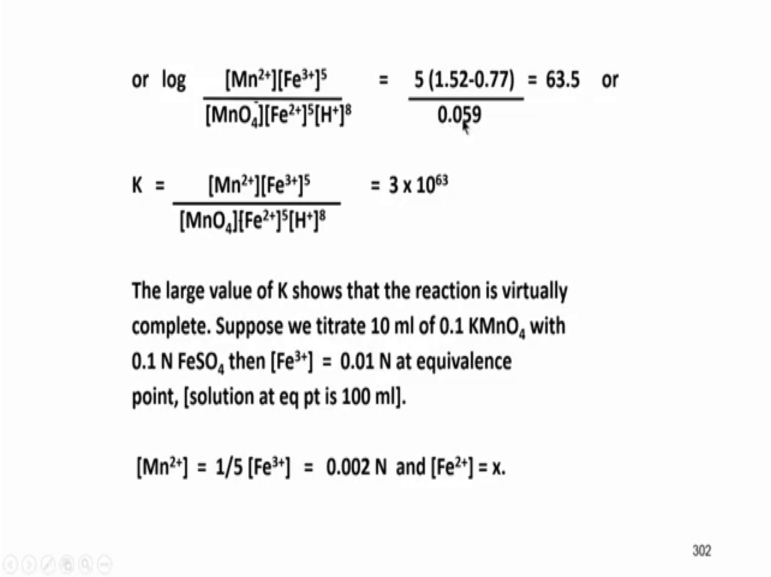

$$\text{or } \log \frac{[Mn^{2+}][Fe^{3+}]^5}{[MnO_4][Fe^{2+}]^5[H^+]^8} = \frac{5\,(1.52-0.77)}{0.059} = 63.5 \text{ or}$$

$$K = \frac{[Mn^{2+}][Fe^{3+}]^5}{[MnO_4][Fe^{2+}]^5[H^+]^8} = 3 \times 10^{63}$$

The large value of K shows that the reaction is virtually complete. Suppose we titrate 10 ml of 0.1 $KMnO_4$ with 0.1 N $FeSO_4$ then $[Fe^{3+}]$ = 0.01 N at equivalence point, [solution at eq pt is 100 ml].

$[Mn^{2+}]$ = 1/5 $[Fe^{3+}]$ = 0.002 N and $[Fe^{2+}]$ = x.

So, what do I have? Logarithm of M n 2 plus and F e 3 plus raised to 5 divided by this M n O 4 minus into F e 2 plus raised to 5 into H plus raised to 8 should be equal to 5 into 1.52 minus point double 7. This is the E naught values ok, there is no magic left divided by 0.0591; 591, ok. So, that will be 63.5 that value. So, K is equal to this value divided by this value. So, how many species are there? Again 3; because M n O 4 and F e 3 plus F e 2 plus 1 oxidant, 1 reductant and H plus. So, there are 3 species complicated reaction.

So, the again K value; what is the K value? K value is 3 into 10 raised to 63 you just solve, this equation you will get the 63.5 convert it into logarithms antilogs. So, K is equal to 3 into 10 raised to 63, this large value shows that the reaction is virtually complete; that means, in presence of acid you can reduce all the hydrogen; sorry, all the iron ferrous to ferric and what is the oxidant here? Potassium permanganate so, from the equation large value of K we can try to decide how to do the titration.

I can take 10 ml of 0.1 molar potassium permanganate and 0.1 molar mole of ferrous sulphate. So, then F e 3 plus would be 0.01 normal at the equivalence point and assume that we are using only 100 ml. So, M n 2 plus would be 1 over 5 F e 3 plus that is equal 0.002 normal and F e 2 plus would be x that is unknown. Why? Because whenever I am trying to remove ferrous as ferric and the reaction is almost complete virtually complete with a K value of 63.5.

The reduced species would be very low in, very negligible that is why we are writing F e 2 plus as negligible. It is a small quantity x we are writing like this, but M n 2 plus, I know what is the concentration, ferric I know what is a concentration, ferrous I do not know the concentration how much is unreacted because the reaction is virtually complete. So, very small quantity we cannot determine that, ok.

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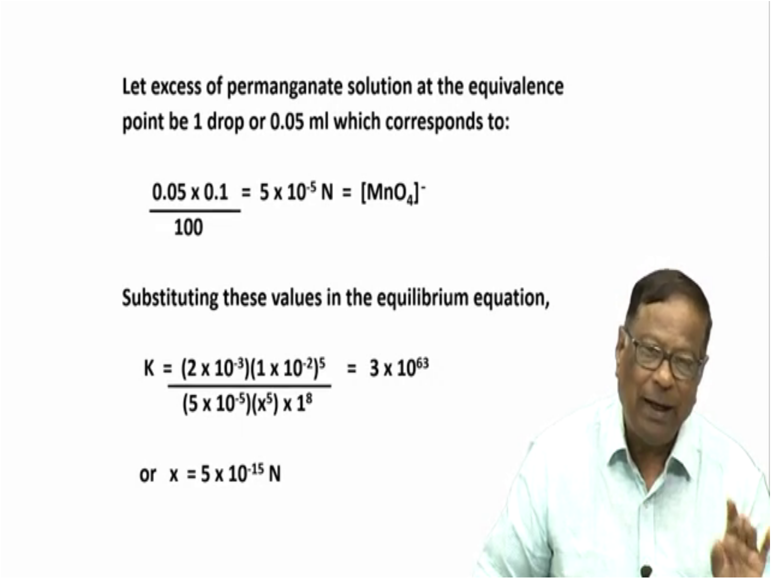

Let excess of permanganate solution at the equivalence point be 1 drop or 0.05 ml which corresponds to:

$$\frac{0.05 \times 0.1}{100} = 5 \times 10^{-5}\ \mathrm{N} = [\mathrm{MnO_4}]^-$$

Substituting these values in the equilibrium equation,

$$K = \frac{(2 \times 10^{-3})(1 \times 10^{-2})^5}{(5 \times 10^{-5})(x^5) \times 1^8} = 3 \times 10^{63}$$

$$\text{or} \quad x = 5 \times 10^{-15}\ \mathrm{N}$$

So, let excess of permanganate solution at the equivalence point be 1 drop, ok. So, 0.05 ml 1 drop or 0.05 ml; 1 drop in a beurate from a beurate corresponds to 0.05 normal ml. So, I can write 0.05 ml and then 0.1 is the concentration, total volume is 100 m l the concentration of ferrous would be 5 into 10 raised to minus 5 normal for that 1 drop excess and that is also should be equal to manganous permanganate iron M n O 4 permanganate.

So, ferrous would be equal to manganite ion, because all the permanganate has been used up in the oxidation, very less of the oxidant will remain at the end of the reaction when you add stoichiometric quantities. So, using the same analogy ferrous to ferric manganous to manganic whatever is ferrous should be equal to oxidant of the other system and whatever is reduced system should be equivalent oxidant of reduced species of the other system.

So, we submit the values, in this equation K is equal to 2 into 10 raised to minus 3 multiplied by 1 into 10 raised to minus 2 this is for ferrous and this is for the M n O 4 minus x raised to 5 into H plus 1 molar acid 1 raised to 8. So, this works out to 5 into 10 raised to 63 and x would be 5 into 10 raised to 15 minus 15; that means, the reaction is again virtually complete there is no more ferrous to be reacted, that is why whenever we want to oxidize ferrous ion we take potassium permanganate and oxidize it.

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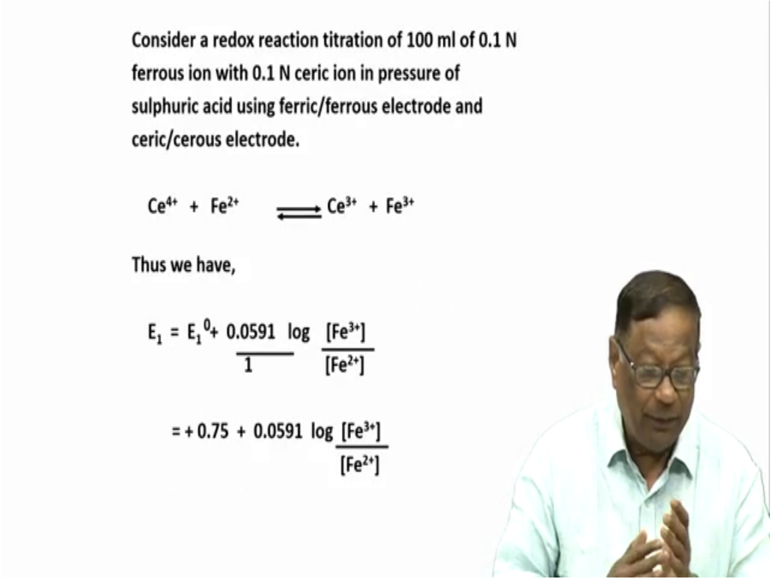

Consider a redox reaction titration of 100 ml of 0.1 N ferrous ion with 0.1 N ceric ion in pressure of sulphuric acid using ferric/ferrous electrode and ceric/cerous electrode.

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

Thus we have,

$$E_1 = E_1^0 + \frac{0.0591}{1} \log \frac{[Fe^{3+}]}{[Fe^{2+}]}$$

$$= +0.75 + 0.0591 \log \frac{[Fe^{3+}]}{[Fe^{2+}]}$$

So, we are going to consider a redox reaction of titration of 100 ml of 0.1 normal ferrous ion with 0.1 normal ceric ion in presence of sulphuric acid using ferric ferrous electrode and ceric cerous electrode. We will study this reaction the actual reaction can be represented like C e 4 plus and F e 2 plus goes to ceric and ferrous, this is a very standard reaction, ok. So, we will continue studying this reaction in the next class and then move on to paleography after that.

So, thank you very much, we will meet again.