

Electrochemical Technology in Pollution Control
Dr. J. R. Mudakavi
Department of Chemical Engineering
Indian Institute of Science, Bangalore

Lecture - 19
Voltametry & Polarography 4

In my last class I had discussed about the polarographic halfway potential.

(Refer Slide Time: 00:40)

$$i = \frac{nFk}{1 + e^{-\frac{nF}{RT}(E - E^0)}}$$

when $i = i_d / 2$,

$$E = E_{1/2} = E^0 + \frac{RT}{nF} \ln \frac{i_d/2}{i_d/2} = E^0 \text{ and at } 25^\circ\text{C}$$

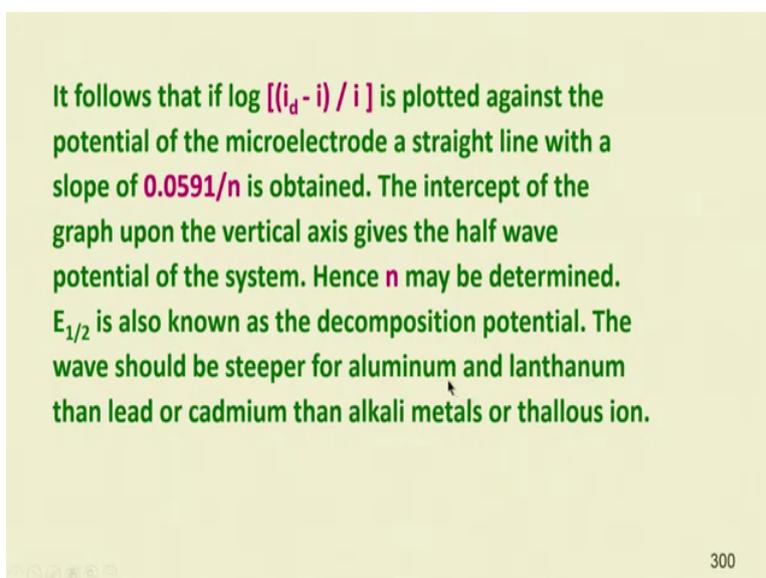
$$E = E_{1/2} + \frac{0.0591}{n} \log \left(\frac{i_d - i}{i} \right)$$

Curve $\log i_d - i$ Vs E gives a straight line with slope $0.0591/n$
 and intercept E^0 = half wave potential. This equation is

And I told you that the emf or current would emf can be expressed in the form of current; that is E is equal to $E_{1/2}$ plus 0.0591 divided by n log of i_d minus i by i when i is equal to i_d by 2 , then we have $E_{1/2}$ is equal to you know $E_{1/2}$ dash.

(Refer Slide Time: 01:01)

It follows that if $\log [(i_d - i) / i]$ is plotted against the potential of the microelectrode a straight line with a slope of $0.0591/n$ is obtained. The intercept of the graph upon the vertical axis gives the half wave potential of the system. Hence n may be determined. $E_{1/2}$ is also known as the decomposition potential. The wave should be steeper for aluminum and lanthanum than lead or cadmium than alkali metals or thallos ion.



So, it follows that $i_d - i$ by i if i plot it against the potential of the microelectrode a straight line with a slope of $0.0591/n$ is obtained; where n is the number of electrons involved in the reaction reduction. So, the intercept of the graph upon the vertical axis gives the half wave potential of the system. So, that can be recorded and it has been recorded for many elements including organic species which can be reduced or oxidized.

So, n can be determined simply by the slope of the curve 1 calibration curve. $E_{1/2}$ is also known as decomposition potential, the wave should be steeper for aluminum and lanthanum than lead or cadmium then alkali metals or thallos ion.

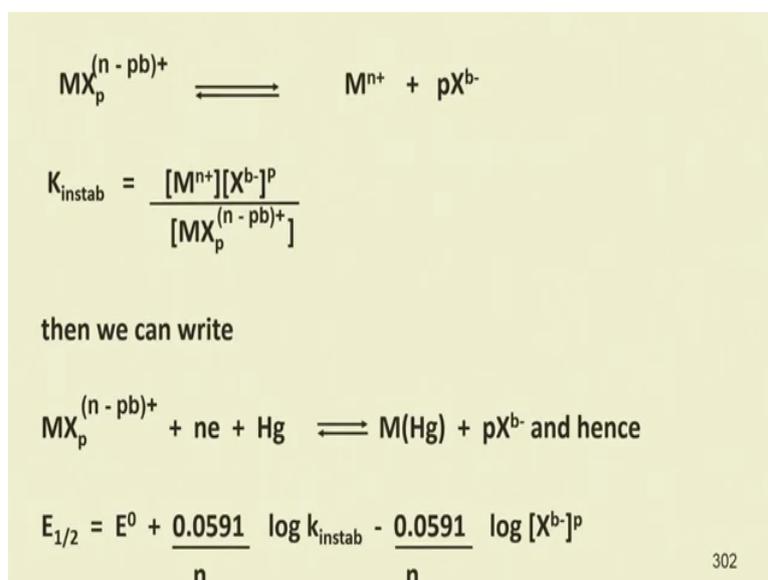
(Refer Slide Time: 02:06)

If the reaction at the indicator electrode involves complexation, satisfactory polarographs can be obtained only if the dissociation of the complex ion is very rapid as compared with the diffusion rate so that the concentration of the sample ion is maintained constant at the electrode interface.

301

So, if the reaction at the indicator electrode involves complexation, then satisfactory polarographs can be obtained only if the dissociation of the complex ion is very rapid compared to the diffusion rate. So, that the concentration of the sample ion is maintained constant at the electrode interface.

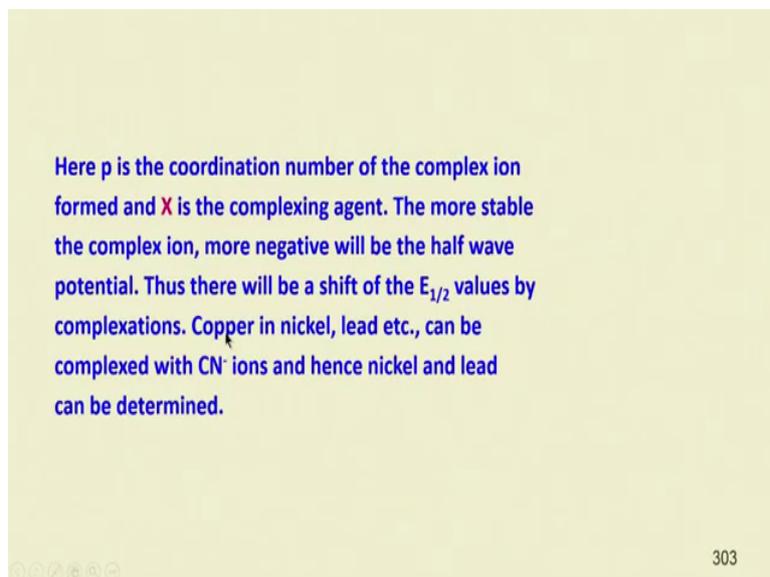
(Refer Slide Time: 02:34)



So, if for example, if I take a complex metal ion like this, $M X_p$ raised to the n minus $p b$ and then this can dissociate to give you metal ion followed by the ligand and this we have already discussed. So, it is only sort of recapitulation for you then we can calculate K instability or instability constant using this expression and M^{n+} into X^{b-} whole raised to P that is the products divided by reactants. So, we can write a reduction potential something like this $M X_p$ raise to n minus $p b$ plus plus n number of electrons with in presence of mercury it will form metal amalgam and the ligand will be freed.

And so, I can write $E_{1/2}$ is equal to E^0 minus 0.0591 by n and \log of k instability minus of 0.0591 by n \log of X^{b-} raised to b minus and that is raised to p .

(Refer Slide Time: 03:59)



Here p is the coordination number of the complex ion formed and X is the complexing agent. The more stable the complex ion, more negative will be the half wave potential. Thus there will be a shift of the $E_{1/2}$ values by complexations. Copper in nickel, lead etc., can be complexed with CN^- ions and hence nickel and lead can be determined.

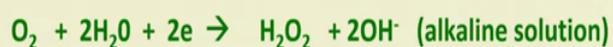
303

So, p is the coordination number of the complex ion formed and that also can be determined and here X is the complexing agent. So, the more stable the complex ion more negative will be the halfway potential; that means, it is more difficult to decompose. So, there will be a shift of the E half values by complexation. Copper in the nickel lead etcetera can be complexed with cyanide ions and then nickel and lead etcetera also can be determined in this way.

(Refer Slide Time: 04:39)

of the analyte is 10^{-4} - 10^{-3} molar and the volume of the solution is between 2 and 25 ml. However it is not uncommon to come across 10^{-2} M and as low as 10^{-8} M concentrations using volumes less than 1ml. The reproducibility of duplicate analysis may be $\pm 2\%$.

Saturated solutions of oxygen at ambient temperature (2.5×10^{-4} M) give two waves according to the reactions,



304

So, normally, the analyte should be of the order of about 10^{-4} to 10^{-3} molar and the volume of the solution is between 2 and 25 ml. However, it's not uncommon to come across 10^{-2} molar as well as to 10^{-8} molar solutions.

So, reproducibility of the duplicate analysis may be plus or minus 2 percent. So, saturated solutions of oxygen at ambient temperature due to waves corresponding according to the reactions $\text{O}_2 + 2\text{H}_2\text{O} + 2\text{e} \rightarrow \text{H}_2\text{O}_2 + 2\text{OH}^-$ the other one is $\text{O}_2 + 2\text{H}^+ + 2\text{e} \rightarrow \text{H}_2\text{O}$ going to water that is in acidic solutions.

(Refer Slide Time: 05:42)

The second wave is

$$\text{H}_2\text{O}_2 + 2\text{e} \rightarrow 2\text{OH}^- \text{ (alkaline solution)}$$
$$\text{H}_2\text{O}_2 + 2\text{H}^+ + 2\text{e} \rightarrow 2\text{H}_2\text{O}$$

Therefore oxygen needs to be removed by passing nitrogen through the analyte. Further a 0.005% gelatin should be added to remove the appearance of maxima.

305

So, the second wave is H_2O_2 plus 2 electrons that goes to alkaline solution and then H_2O_2 plus 2 H plus 2 e goes to $2\text{H}_2\text{O}$. So, oxygen needs to be removed by passing nitrogen through the analyte its a must further 0.005 percent gelatin should be added to remove the appearance of the maxima.

(Refer Slide Time: 06:09)

If the $E_{1/2}$ differ by at least 0.4 volts (for univalent ions) and by 0.2 V for divalent ions, they can be easily determined. For $E_{1/2}$ which overlap each other, complexation can be employed to displace them to more negative potentials. Precipitation, electrolytic deposition etc., can be employed to advantage if complex analysis has to be carried out.

Nickel, zinc in pure copper salt can be dissolved in ammoniacal solutions (NH_4Cl) and electrolysed at about -0.7 volt vs SCE. Then determine zinc and nickel. As less as 0.00001 % nickel can be determined in this way.

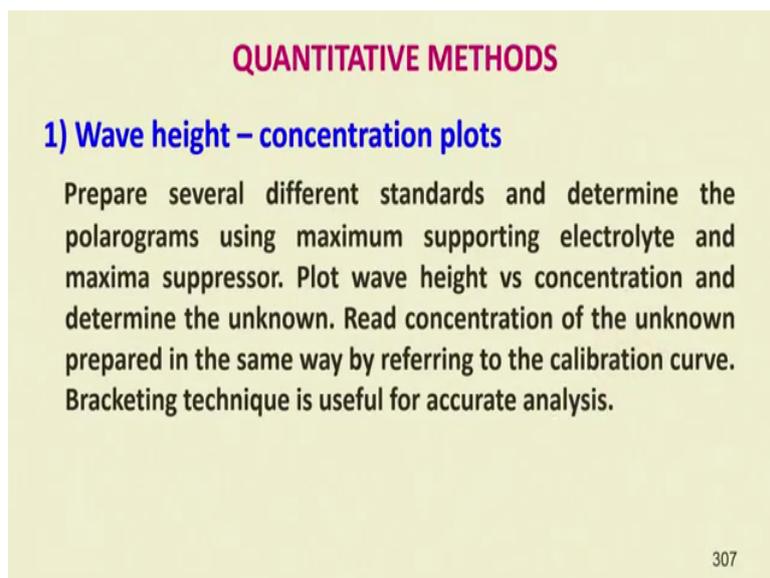
306

So, if the $E_{1/2}$ differ by at least 0.4 units we can determine number of elements whose $E_{1/2}$ differ by 0.4 units. If it is a univalent ion the sodium lithium potassium etcetera thallium copper cuprous all those univalent ions. But if it is a divalent ion then the $E_{1/2}$ should at least differ by 0.2 volts and they can such things can be easily determined.

Sometimes $E_{1/2}$ overlap each other then complexation can be employed to displace them to more negative potential that is the use of complexation. So, precipitation electrolytic deposition etcetera many other chemical techniques can be used to advantage if complex analysis has to be carried out. Nickel, zinc etc in pure copper salt can be resolved in ammonia solutions that is you can even resolve it in NH_4Cl etcetera and electrolyzed at about minus 0.7 volts versus SCE. So, then we can determine zinc and nickel.

So, as less as 0.00001 percent nickel, can be determined in this way. So, the beauty of polarography is in the lower limit of the detection limit. Here I have shown you only for nickel, but for many other elements also they will be in the similar range.

(Refer Slide Time: 08:03)



QUANTITATIVE METHODS

1) Wave height – concentration plots

Prepare several different standards and determine the polarograms using maximum supporting electrolyte and maxima suppressor. Plot wave height vs concentration and determine the unknown. Read concentration of the unknown prepared in the same way by referring to the calibration curve. Bracketing technique is useful for accurate analysis.

307

So, what we how do we go about the quantitative analysis? Very simple, basically all you have to do is draw i_d minus i_b by i_c curve keep on adding your increasing the voltage at some stage it will start decomposing and then you start measuring the current. So, the current versus voltage curve will give you the curve which will tell you the concentrations.

So, the i_d i_b versus concentration should give you a calibration plot just like in spectrophotometry or something. So, whatever is the current generated would give you the concentration of the unknown. So, there are two or three methods that can be used for

quantitative analysis and some of them are very standard. Here I am showing you wave height concentration plot.

So, here what we do? We prepare different standards and determine the polarograms using maximum supporting electrolyte and maxima suppressor. Then all you got to do is plot the wave height versus concentration and also run a an unknown sample that is your analyte. And you can treat the concentration of the unknown prepared in the same way by referring to the calibration curve very simple technique and we can also use bracketing techniques.

So, what is the bracketing technique? A bracketing technique is you concentrate you choose particular concentration work only in that concentration. So, if the your sample is where having very high, concentration of the analyte you dilute it and then do the analysis. If it is dilute you will have to find ways and means of concentrating the solution. So, this is one method that is wave height versus concentration plot.

(Refer Slide Time: 10:27)

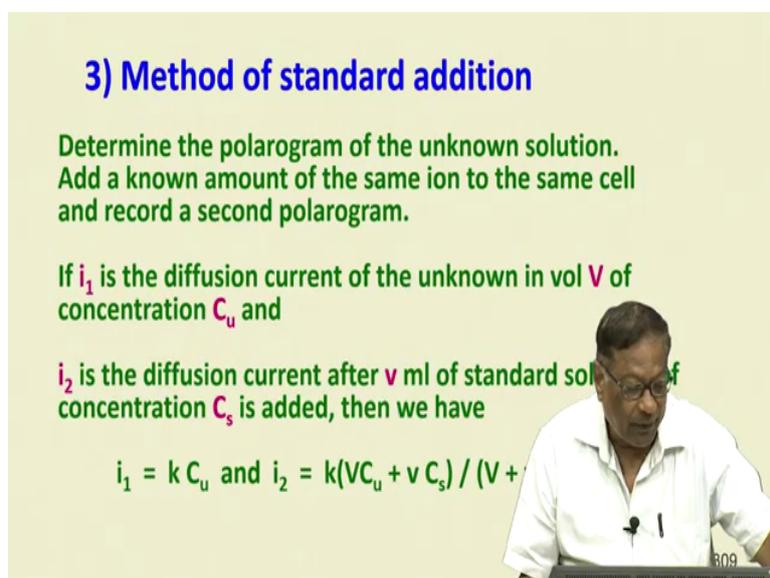
2) Pilot ion method

The relative diffusion currents of ions in the same supporting electrolyte are independent of the characteristics of the capillary electrode and temperature. Determine the relative wave height of the unknown and with some standard or pilot ion added in known amounts and compare these with the ratio for known amounts of same two ions. This procedure is limited to applications with minimum 0.2 V difference for the ions under investigation.

308

And then we can have a pilot ion method. Here what we do is the relative diffusion current of the ions in the same supporting electrolyte usually they are independent of the characteristics of capillary and the electrode and temperature. So, we determine the relative wave height of the unknown and some standard or pilot ion known to us is added in known amounts. And we compare the ratio for known amounts of same two ions this procedure is limited to applications with minimum 0.2 volts difference for the ions under investigation. So, this is also fairly simple method.

(Refer Slide Time: 11:26)



3) Method of standard addition

Determine the polarogram of the unknown solution.
Add a known amount of the same ion to the same cell and record a second polarogram.

If i_1 is the diffusion current of the unknown in vol V of concentration C_u and

i_2 is the diffusion current after v ml of standard solution of concentration C_s is added, then we have

$$i_1 = k C_u \text{ and } i_2 = k(V C_u + v C_s) / (V + v)$$

But, there is one more technique that is more accurate that is known as method of standard deviation standard addition not deviation. So, here what we do is, I determine the polarogram of the unknown solution and then I add a known amount of the same ion to the same cell and recording record a second polarogram. I take the sample and then add one more some more of the known analyte record the polarogram then record the polarograms of the unknown also.

So, now, I have two curves two values that is unknown if there is a diffusion current of i_1 in volume V of the solution of concentration C_u . And for the standard solution I get another current some other value that is i_2 that is the diffusion current after v ml of standard solution of concentration C_s is added. And then basically what we do is we take the unknown run a polarogram then take the same quantity of unknown in another set add a known volume of a standard to the unknown matrix and then run the polarogram.

So, it has to be actually higher than the previous one standard the analyte alone but, we do not know, what is the analyte concentration. So, but they we have the total unknown plus known concentration is added that current value we have. So, I can write the you look at the last equation here, I can write i_1 is equal to k into C_u where k is the proportionality constant. And what would be i_2 ? i_2 would be the sum of the currents corresponding to known volume of the unknown volume we know concentration we do not know plus I am adding a v volume of the unknown.

So, the total volume would be small v plus v here I have written it at the denominator here. So, the i_2 current diffusion current is a is in direct proportion to the concentrations of the unknown and the standard in a volume of V plus v capital V and small v . So, just like that I can write $k i_2$ is equal to k into capital V into C_u that is unknown and then small v into C_s that is known, but there is we are taking here the dilution factors that is V plus v . So, the actual concentration would be not the same as what we have taken alone, but as a mixture. So, here I write i_2 is equal to k into $V C_u$ plus v small $v C_s$ divided by V plus v that is the concentration total volume.

(Refer Slide Time: 15:21)

Thus $k = i_2 (V + v) / (VC_u + v C_s)$ and

$$C_u = \frac{i_1 v C_s}{(i_2 - i_1) (V + v) + i_1 v}$$

The accuracy of the method depends upon the precision with which the two volumes of the solution and corresponding i_d s are measured. Here the assumption is made that the wave height is a linear function of the concentration in the range of concentration employed. Best results are obtained when wave height is approximately doubled by the standard addition.

310

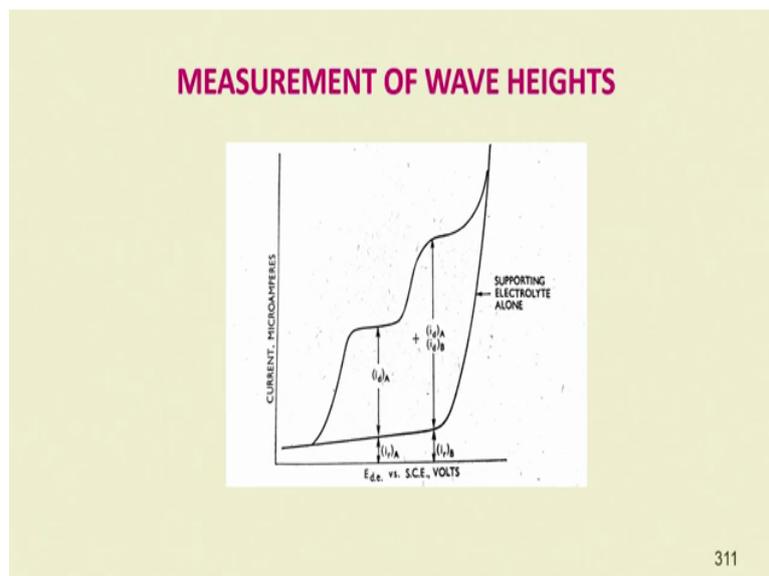
So, $k = i_2 (V + v) / (VC_u + v C_s)$ and I can write $k = i_1 v C_s / ((i_2 - i_1) (V + v) + i_1 v)$. And I can calculate what is C_u using this expression that is $i_1 v C_s$ divided by $i_2 - i_1$ multiplied by capital V and small v total volume plus $i_1 v$. This is a very simple derivation though you do not have to worry too much about the equation, but it is described in most of the textbooks.

So, I can you can look it up in case you get confused while listening to this standard addition method, but it is widely practiced everywhere. Here one advantage is the matrix the standard what you add is going to be added to the same matrix that the known is. So, standard is also subjected to the same kind of interference from the other matrix components. So, the accuracy of the method depends upon the precision with which the two volumes of the solutions and

corresponding i_d 's are measured. So, here we make the assumption that the wave height is a linear function of the concentration in the range of concentration what we are measuring.

So, we do not say it will be linear in every concentration range, but we should be careful. So, best results are obtained when wave height is approximately doubled by the standard addition. So, its a fairly simple technique and standard addition, I suggest you go through some textbooks and other things there is nothing much to add except that if you understand the terms capital V small v V C u etcetera, the derivation of the unknown is also a very simple process.

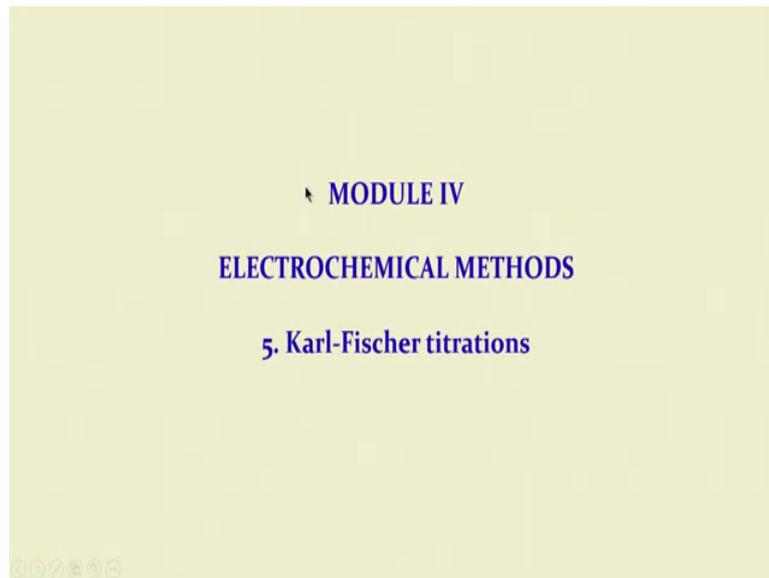
(Refer Slide Time: 17:50)



So, this is how we do the wave height measurement. Suppose I have a polarogram here; polarogram here this is the residual current and then wave height here it goes and then I draw a tangent here and tangent here. So, this is first ion, this is first ion plus second ion. So, this is

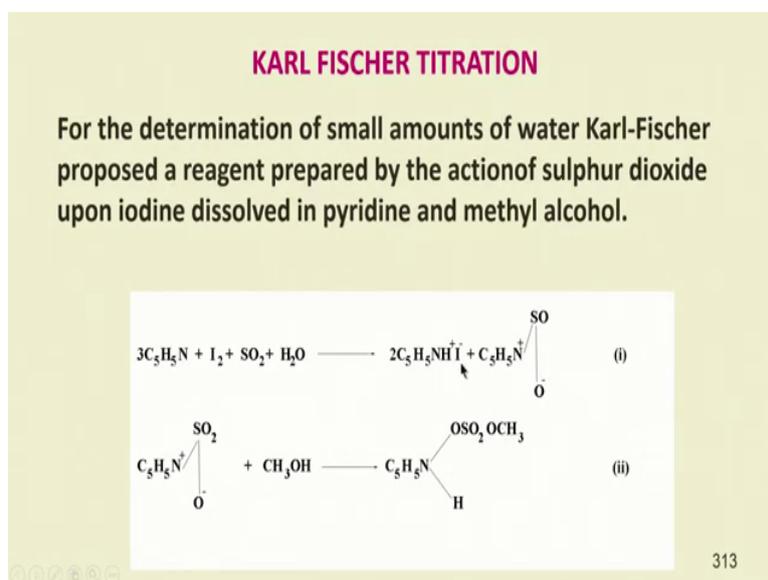
for the supporting electron that is the normal this thing. So, I this is the decomposition potential versus S C E Standard Saturated Calomel Electrode and it can be easily carried out the analysis of unknown. There are electro chemical laboratories which who do polarography on a large scale day in and day out. So, its not very uncommon for people to work on polarography.

(Refer Slide Time: 18:52)



So, that completes our discussion on polarography. But we will continue our discussion now on Karl Fischer titration. This is a very interesting behavior very interesting analysis that permits the determination of water in a given compound.

(Refer Slide Time: 19:19)



So, what is Karl Fischer titration? For the determination of small amounts of water Karl Fischer German scientists proposed a reagent prepared by the action of sulfur dioxide, upon iodine dissolved in pyridine and methyl alcohol. So, what I do? I dissolve the iodine in pyridine add methyl alcohol and then start the titration and determine the water content. How what is the basic chemistry involved here its very simple.

I have 3 molecules of C 5 H 5 N that is pyridine I am adding iodine I am adding SO 2 and if there is water in the sample all of them are going to give me a an inner complex C 5 H 5 N H plus I minus this is a salt and C 5 H 5 N SO 2 minus N plus SO 2 minus. This will react with methanol to give you C 5 H 5 N and OSO 2 OCH 3 this is methanol reacting with SO 2 addition compound.

And there is the hydrogen here this hydrogen comes here and OCH_3 comes here SO_2 is here. So, this one part is SO_2 and this part will become OSO_2OCH_3 . So, this oxygen will be OCH_3 will be added to this and nitro another part of the this methanol will be bonded to the nitrogen in the pyridine group. So, I have a compound like $\text{C}_5\text{H}_5\text{NHSO}_2\text{OCH}_3$.

(Refer Slide Time: 21:42)

In the first step sulphur dioxide(SO_2) is oxidized by iodine and an intermediate compound pyridine sulphur trioxide is formed. This is the inner salt of pyridine N-sulphonic acid.

The second step is the formation of pyridinium methyl sulphate which prevents the pyridine complex from reacting with another molecule of water or other hydrogen active compound. Hence one molecule of I_2 is equivalent to one molecule of water.

314

In the first step, sulfur dioxide is oxidized by iodine and an intermediate compound pyridine sulfur trioxide is formed this is SO_2 actually. So, $\text{C}_5\text{H}_5\text{N}\text{SO}_2\text{O}_3$ that is sulfur trioxide and that compound is the inner salt of pyridine and sulphonic acid. The second step is the formation of pyridinium methyl sulfate which prevents the pyridine complex from reacting with another molecule of water. See here in the previous step look at the second reaction all valances are complete.

So, there is no chance for further reaction. So, addition of pyridine pyridinium methyl sulfate prevents the pyridine complex from reacting with another molecule of water because there is no more pyridine and iodine and sulfur they are all not there at all this is on molecular level.

(Refer Slide Time: 23:16)

The original KF reagent is prepared with excess of methanol which serves as a reactant as well as a diluent. This reagent is somewhat unstable and needs frequent standardization. A more stable reagent may be prepared from ethylene glycol monomethyl ether (methyl cellosolve).

Freshly prepared reagent has a deep reddish brown colour and the spent reagent is pale yellow straw colour. So that it can be used as a direct titrant also. But the decomposed reagent also has a brownish colour and the end point detection is difficult. It is therefore preferable to add a slight excess of the reagent and titrate the excess with a standard solution of water in methanol. The end point is determined electrometrically.

315

So, the original Karl Fischer reagent; that means, the in Karl Fischer reaction I take pyridine, I take sulfur dioxide iodine and methyl alcohol. If there is water in a given sample, it will react with Karl Fischer reagent one molecule will react with one molecule of pyridinium complex and that is the basis for water analysis. So, one water molecule if it is there it will react with the pyridinium complex. So, the original Karl Fischer reagent is prepared with excess of methanol which serves as a reactant as well as a diluent methanol is also a solvent. So, that will be done and this reagent is somewhat unstable and needs frequent standardization.

So, every time you want to do a Karl Fischer titration you have to standardize it with a substance of known concentration of water. There are many several such substances like that with exact concentration of water present in the water of crystallization. So, a more stable reagent we can prepare from ethylene glycol mono methyl ether; that is also known as methyl cellosolve which is an industrial chemical and it is prepared in millions of tonnes in the industry.

So, when I prepare the reagent fresh it has a deep reddish brown color. And the one which is reacted with water and spent that is light yellow in color straw yellow color. So, you can even do the ordinary titration from deep reddish brown to straw yellow color and with experience one can determine exactly how much of water is there and that water concentration will be in ppm parts per million ok. So, that it can be used as a direct titrant also if you are comfortable with change in the color from deep brown to light yellow.

But, the decomposed reagent also has a brownish color and the endpoint detection is slightly difficult that is why I said somebody should have experience in conducting this kind of reaction. So, it is therefore, preferable to add a slight excess of the reagent and titrate the excess with a standard solution of water in methanol. I can prepare methanol also with known quantity of water because water and methanol are very easily miscible. So, the endpoint is determined normally electrochemical usually not by visual titration.

(Refer Slide Time: 26:39)

If a small e.m.f is applied across two platinum electrodes immersed in the reaction mixture, a current will flow as long as free iodine is there to remove hydrogen and depolarize the electrode. When the last trace of iodine is removed the current will decrease to zero or very close to zero.

Conversely the technique may be combined with a direct titration of the sample with the KF reagent. In this case any excess of iodine causes the current to rise sharply. This is a more elegant method.

316

So, if a small emf is applied across two platinum electrodes, immersed in the reaction mixture a current will flow as long as free iodine is there, to remove hydrogen and depolarize the electrode. So, when the last trace of iodine is removed what happens to the current? Current becomes zero or very close to zero. Here in this reaction iodine is there. So, this iodine is usually prepared by in the presence of potassium iodide. So, the iodine iodide will be there in this.

So, long as iodide is there potassium iodide and iodine are there the current will be passing through. But once all of it is consumed there will not be any addition of there will not be any addition of water of current. Basically because $I_2 + I^-$ goes to I_3^- which is a negative ion that carries the current.

So, the second step is the formation of pyridinium methyl sulfate this I have already covered. And what I have here is I do have excess of water in methanol slight standard addition. So, the I know exactly what should be the end point with a standard methanol and then that can be checked against the accuracy then you can determine the unknown by the same way titration or measurement of the electrode.

So, the iodine when it becomes totally consumed, we have zero or very close to zero current. Conversely the technique may be combined with a direct titration of the sample with Karl Fischer reagent. In this case any excess of iodine causes the current to rise sharply. So, Karl Fischer reagent can be added excess then the current will increase.

So, initially we will have a reducing current slowly it becomes zero and then any additional excess of the reagent if you add from the burette the current will start rising because we have i_{3-} ions excess. So, that will carry the current. So, it is a very sharp end point if you do the electrical electrochemical titration. So, it is obviously a more elegant method.

(Refer Slide Time: 29:57)

The apparatus is very simple. The source is a 3 V battery (torch) , M is a microammeter, R is a 500 ohm resistor, 0.5 watt radio potentiometer. The potentiometer is set so that there is a potential drop of about 80 mV across the electrodes and does not require adjustment until the battery is exhausted.

KF reagent may be standardized with 5-6 mg water in methane or with pure disodium tartrate dihydrate. This contains 15.66% of water.

317

So, the apparatus Karl Fischer apparatus is also very simple; it has got a 3 volt battery and it has got a micrometer, 500 ohm resistor, 0.5 Watt radio potentiometer etcetera. So, the potentiometer is set so, that there is a potential drop of about approximately 80 milli volts, across the electrode and does not require adjustment until the battery is exhausted. So, Karl Fischer reagent may be standardized using 5 to 6 milligram of water in methanol or you can use pure disodium tartrate dihydrate, that is a very standard salt with a known concentration of water.

So, this salt disodium tartrate dihydrate that is two molecules of water is there it contains approximately 50 15.66 percent of water. So, if you get 15.66 percent water with potassium disodium tartrate then you can proceed with the unknown. So, what should be the value of Karl Fischer reagent? It is in terms of its in terms of accuracy, its in terms of accuracy that Karl Fischer titration can be carried out any unknown substance. You want to determine water

of crystallization or any of the water content in a given sample one has to determine such situations arise quite a lot in day to day life.

Especially in pharmaceutical industry etcetera, where tablets are being made, everybody wants to know what is the water content in that. And whether it is hygroscopic or not hygroscopic how long it can be kept in the open like that lot of information is required. So, Karl Fischer titration is a very standard technique in pharmaceutical industries. The apparatus is very simple you can buy it for about 6 to 8000 rupees with electrical endpoint detection.

(Refer Slide Time: 32:54)

The reagent may be applied to samples with the following requirements.

- **They should not react with the reagents or hydrogen iodide to yield water.**
- **They are miscible with the reagent and preferably do not cause precipitation of the pyridine complexes formed during the titration.**
- **They will conduct electric current.**

318

So, the reagent may be applied to samples with the following requirement. There are certain conditions which need to be fulfilled. And we will look at them in my next class. So, we will go ahead and see what are the conditions that need to be satisfied and also what are the interferences in Karl Fischer titration.

Thank you very much. We will continue in our discussion in the next class.