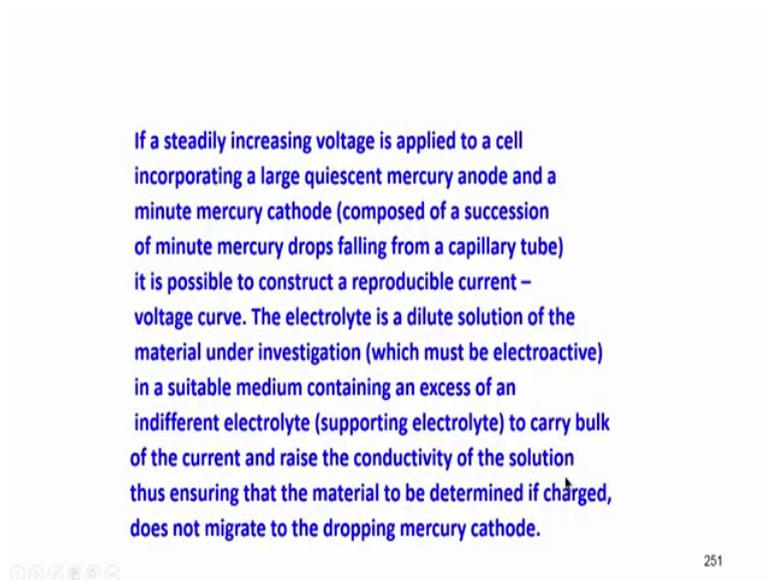


**Electrochemical Technology in Pollution Control**  
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**Lecture – 18**  
**Voltametry and Polarography- 3**

Greetings, we will continue our discussion on Polarography and yesterday, I had taught you about the basic equipment for polarography.

(Refer Slide Time: 00:47)



And I had told you that if a steadily increasing voltage is applied to a cell incorporating a large quiescent mercury like anode and a minute mercury cathode which is nothing but a dropping mercury electrode. It is possible to construct a reproducible current voltage curve because the drop will be falling as well as forming again.

So, the electrolyte is a dilute solution of the material under investigation and in a suitable medium it should contain an excess of an indifferent electrolyte to carry bulk of the current and raise the conductivity of the solution. So, it ensures that the material to be determined if charged does not migrate to the dropping mercury electrode.

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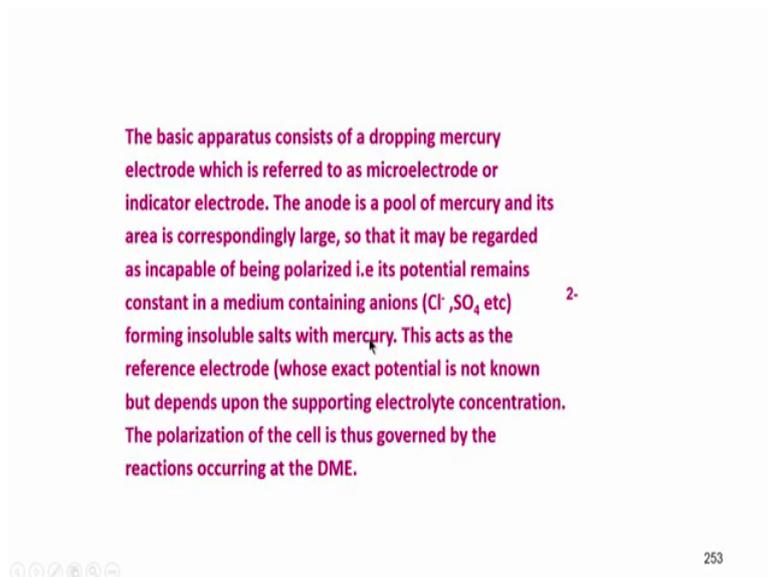
From an examination of the current – voltage curve, nature and concentration of the analyte may be obtained. Heyrovsky and Shibata developed an apparatus which increased the applied voltage at a steadily increasing rate and simultaneously recorded the C-V curve. Since these curves are a graphical representation of the polarization of the dropping mercury electrode, the apparatus was called a **polarograph** and the curves are called **polarograms**.

252

And from an examination of the current voltage curve we can also determine the nature and concentration of the analyte including the speciation.

So, Heyrovsky and Shibata have developed this technique for which they were awarded Nobel Prize, and then we are going to study such a system containing C-V curve they are known as polarograph and polarograms.

(Refer Slide Time: 01:59)



And the basic operators consists of a dropping mercury electrode, which is referred to as a micro electrode and the other one is a reference electrode.

It can be calomel electrode or it can be a mercury anode and it is incapable of being polarized that we should remember; that means, it will show only what is their potential applied to that and then it is the polarization of the cell is governed by the reactions occurring at the DME.

(Refer Slide Time: 02:42)

Inlet and outlet tubes are provided for purging the dissolved oxygen by hydrogen (or nitrogen ) before the experiment (otherwise the C-V curve for oxygen is also obtained). P is a potentiometer by which up to 3 V is gradually applied to the cell. S is a shunt for adjusting the sensitivity of the galvanometer G. The current cathode curve is recorded with reference to the anode (mercury pool) or SCE.

The initial potential of the DME is indeterminate and assumes any potential applied. When it assumes a potential different from that which it had in the absence of electrical connections it is said to be polarized.

254

And I had yesterday again told you that described you the equipment along with a figure.

(Refer Slide Time: 02:51)

Consider a cadmium solution along with NaCl in an oxygen free medium. When an external emf is applied two phenomena occur,

1. All the positively charged ions will be attracted to the negative electrode by a force proportional to the attraction of the oppositely charged bodies to each other.
2. By a diffusing force arising out of concentration gradient produced at the electrode.

255

And now, we consider a cadmium solution with sodium chloride in oxygen free medium.

When an external emf is applied all the positively charged ions will move towards the cathode including the cadmium, but it cannot be determined. Because, they do not have the required potential to reach the cathode and get reduced and, but there is also another force that stops cadmium from reaching the cathode that is a diffusive force arising out of concentration gradient produced at the electrode.

(Refer Slide Time: 03:29)

The total current passing through the cell can be regarded as the sum of these factors. A typical current voltage curve is shown here.

The indicator electrode being perfectly polarizable, assumes the correspondingly increasing negative potential applied to it. But from A to B practically no current will pass through the cell.

At B where the potential is equal to the deposition potential of the cadmium ions, the current suddenly starts to increase and the indicator electrode becomes depolarized by the cadmium ions which are then discharged upon the electrode surface to form metallic cadmium. Consequently a rapid increase in the current flowing through the cell will be observed.



So, the total current passing through the cell can be regarded as a sum of these two factors and typical current voltage. We had shown you I had shown you yesterday. So, the indicator electrode being perfectly polarizable assumes the correspondingly increasing negative charge potential, but from A to B there is no current passing through the cell at some point it will reach the diffusion voltage where decomposition voltage where the electron where the cadmium can reach the cathode and get reduced to the cadmium metal.

The moment it gets reduced it gets converted to mercury amalgam and then from there on it will diffuse into the mercury drop and then again when the mercury drop falls again we have a fresh mercury drop that is coming in I have to form the next this thing next reduction.

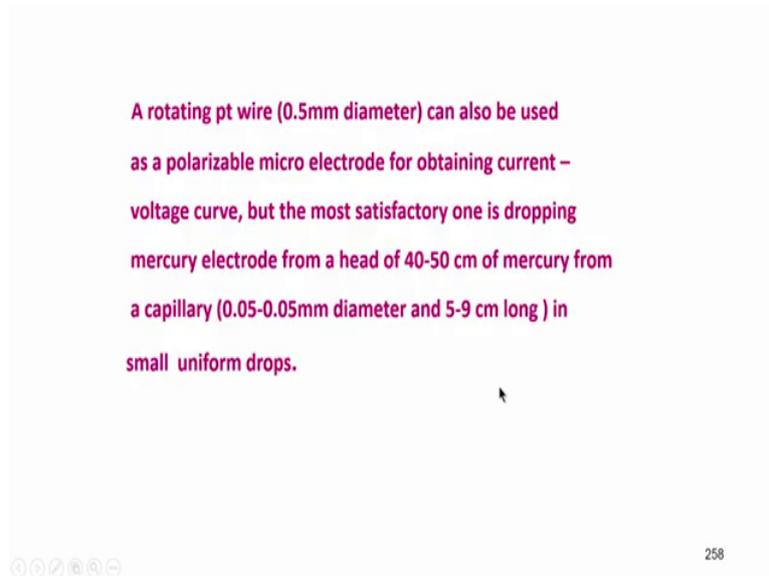
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At the point C the rate of supply of cadmium ions from the bulk of the solution to the indicator electrode surface becomes equal to the rate of their deposition. Hence at potentials greater than C, the concentration of undischarged cadmium ions at the micro electrode surface is negligibly small compared to the cell ions in solution. No further increase in current can be expected after C but a small steady increased current will result between C and D since the limiting current is now fixed by the rate at which cadmium ions reach the surface.

257

So, at point C, the supply of cadmium ions from the bulk solution becomes equal to the rate of deposition. So, again we will have a steady current flowing from the micro electrode and the surface since the surface is negligibly small to the cell ions in the solution no further increase in current can be expected after the point C, but a small steady increasing current will result.

(Refer Slide Time: 05:05)



So, a rotating platinum wire also can be used as a polarizable micro electrode, but it does not have the same advantage like mercury amalgam.

(Refer Slide Time: 05:18)

The DME has several advantages:

- Its surface is renewable, reproducible and smooth which eliminates passivity or poisoning effects.
- Mercury forms amalgams with many metals (solid solutions)
- The diffusion current assumes a steady value immediately after changing the potential and is reproducible.
- The large hydrogen over voltage on mercury renders the deposition of metals such as alkali metals, aluminum ions, manganous ions etc which are not easily amenable to platinum microelectrode.
- The surface area can be calculated easily.

259

What are the advantages of mercury amalgam? It forms amalgams with many metals, surface is renewable, division current assumes a steady value immediately after applying the potential and large hydrogen over voltage on mercury renders deposition of the metal such as alkaline metals, aluminum metal, manganous etcetera which are not easily amenable to platinum microelectrode. The surface area also can be calculated very exactly.

(Refer Slide Time: 05:44)

The DME can be worked from +0.4 to -2.0 V w.r.t SCE. Above 0.4 V, the mercury dissolves and gives an anodic wave ( $\text{Hg}^+$ ).

At potentials more negative than -1.8 V, visible  $\text{H}_2$  evolution occurs and supporting electrolytes commence to discharge. By using tetra alkyl ammonium hydroxide or their salts, the range may be extended to -2.6 V.

For convenience and measurement of half wave potentials the anode potential may be measured with a saturated calomel electrode using a salt bridge.

260

So, the DME you can work from 0.4 to minus 0.2 volts with respect to SCE and above 0.4 volts mercury dissolves and gives an anodic wave.

So, at potentials more negative than that 1.8 volts visible hydrogen evolution occurs and supporting electrolyte commences to discharge. So, by using tetra alkyl methyl tetra alkyl ammonium hydroxide or their salts the range may be extended to minus 2.6, but at no point should we exceed 0.3 volts or 0.4 volts.

(Refer Slide Time: 06:34)

**THEORETICAL PRINCIPLES**

**Residual current**

Mercury is unique in remaining electrically uncharged when it is dropping freely into a solution containing an indifferent electrolyte such as KCl or KNO<sub>3</sub>. But even in such cases a small current will flow before the decomposition of the analyte. This current increases linearly with increased voltage, but it is observed even when extremely pure solutions are used. Therefore it cannot be due to any impurities but it is residual non faradic current or condenser current. This is due to the electrical double layer of positively and negatively charged ions. The capacity of double layer varies depending upon the (metal e.g. mercury) and the potential applied.

261

So, for convenience and measurement half wave potentials of the anode potential may be measured with a saturated calomel electrode using a salt bridge. Then we discussed about the residual current and the residual current is one which is a steadily increasing current, but no apparent reaction occurs.

(Refer Slide Time: 06:47)

In practice traces of impurities present in the indifferent electrolyte do cause small and imperceptible currents superimposed upon the condenser current. All these are called 'residual current' and in practical work, this current is automatically subtracted from the total observed current by proper extrapolation.



Residual Current

262

So, in practice traces of whatever impurities are there it may cause small and imperceptible currents, but in spite of all that residual current cannot be eliminated. So, what we do is we will draw a tangent and then we draw a tangent like this and this is the residual current.

So, this kind of residual current we can subtract from the given system as a blank value.

(Refer Slide Time: 07:36)

**Migration current**

Electro active material reaches the surface of the electrode largely by two processes:

(i) Migration of charged particles in the electric field caused by the potential difference existing between the electrode and the solution and by diffusion of ions. Migration current can be made negligible by the addition of large quantity of indifferent electrolyte ( $> 100$  times of the analyte).

Under such conditions practically all the current will be transported by the  $K^+$  and  $Cl^-$  ions and the analyte can reach the electrode only by diffusion. But they will not reach at the electrode.

263

So, we have to extrapolate it and do that and then we can we were discussing about the migration current and we I had to stopped here and today we are going to start from micro migration current. So, basically electro active material reaches the surface of the electrode largely by two processes; one is migration of the charged particles in the electric field caused by the potential difference that exists between electrode and the solution and by diffusion of ions.

These are the two forces we had already covered yesterday, but migration current can be made negligible by the addition of large quantity of the electrolyte, approximately 100 times. Under such conditions all the practically all the current will be transported by indifferent electrolyte that is potassium and chloride ions and the analyte can reach the electrode only by diffusion,

but they will not reach the electrode because the decomposition potential has not being reached.

(Refer Slide Time: 08:43)

**Diffusion current**

Under these conditions the potential gradient is compressed very close to the electrode surface but it cannot permit the transport of cadmium ions. Therefore the limiting current is solely due to diffusion current.

264

So, diffusion current the potential gradient keeps on compressing and after some time when the potential gradient is no more existing or minimum the limiting current is solely due to diffusion current.

(Refer Slide Time: 09:01)

D. Ilkovich (1934) examined the various factors governing the diffusion current and deduced the equation,

$$i_d = 607 n C D^{1/2} m^{2/3} t^{1/6}$$

where  $i_d$  = diffusion current,  $\mu\text{A}$

$n$  = number of electrons involved in the reduction

$C$  = concentration of reducible substance, mM/lit

$D$  = diffusion coefficient of the reducible substance  $\text{cm}^2/\text{sec}$

$m$  = mass of the mercury flowing through the capillary, mg/s

$t$  = drop time in seconds

265

So, Ilkovich examined the various factors governing the diffusion current and deduced this equation  $i_d$  is equal to  $607 n C D$  raise to half  $m$  raise to 2 by 3 and  $t$  raise to 1 by 6. Where  $i_d$  is the diffusion current,  $n$  is the number of electrons involved,  $C$  is the concentration of the reducible substance and  $D$  is the diffusion coefficient of the reducible substance that units are in centimeter square per second  $m$  is the mass of the mercury following through the capillary,  $t$  is the drop time in seconds.

(Refer Slide Time: 09:40)

The constant, 607, is a combination of several natural constants including the Faraday. The  $i_d$  and 607 are temperature dependent and hence  $i_d$  is quoted always at specified temperature. Apart from temperature viscosity, molecular or ionic state of the electroactive species, dimension of the capillary and the pressure on dropping mercury. Precise measurement of  $i_d$  requires temperature control of  $\pm 0.2$  °C.

The product  $m^{2/3}t$  is important because it permits the comparison of difference capillaries. Stirring of the solution is not permissible because the drops have to fall under their own weight.

266

So, the constant 607 is a combination of several natural constants and it is temperature dependent also. Apart from temperature viscosity, molecular or ionic state or speciation of the electroactive species is the an important factor.

And dimension of the capillary and pressure on the dropping mercury also is an important factor, but precise measurements of  $i_d$  requires plus or minus 0.2 degree centigrade control over the system.

(Refer Slide Time: 10:21)

**Polarographic maxima**

Some times C-V curves of DME exhibit pronounced maxima which are reproducible. These maxima vary in shape from sharp peaks to rounded humps which gradually decrease to normal  $i_d$  curve as the potential is increased.

For measuring the true  $i_d$ , the maxima must be eliminated or suppressed. Fortunately this can be done with the addition of a dye stuff (methyl red, gelatin, fuchsine etc). It forms an adsorbed layer on the aqueous side of the mercury solution interface which resists compression. This prevents streaming movement of the diffusion layer at the interface thus reducing maxima. Higher concentration of the suppressors usually suppresses  $i_d$  itself. Triton-x100 (0.002-0.004%), methyl cellulose (0.005%) are also used.



267

So, the product  $m$  raised to 2 by 3  $t$  is important because it permits us to compare different capillaries. So, if you want to I told you that yesterday that its impossible to reproduce capillaries of the same size.

So, different if somebody is using different capillaries  $m$  raised to 2 by 3 and  $t$  raised to 1 by 6 is going to change. So, that permits us to compare different capillaries that will also tell us the diffusion current what it will be approximately if we put those numbers in the Ilkovich equation. Sometimes C-V curves of a dropping mercury electrode exhibit pronounced maxima which are reproducible.

These maxima vary in shape and from sharp peaks to rounded humps something like this; this is our standard curve, but suddenly you will see a maxima or something like as if there is

something some element is here some which is getting reduced, but actually this is not this is a polarographic maxima.

As if some impurity is there which is getting reduced, but actually this is not an impurity. So, these maxima vary in shape from very sharp peaks to broad peaks also to rounded humps and which gradually decrease to normal  $i_d$  curve that is the residual current curve and until the potential is increased. For measuring the true  $i_d$  the maxima must be eliminated or suppressed the actually there are ways of doing this and fortunately we can do this with the addition of a dye stuff something like methyl red, gelatin, fuchsine etcetera.

It forms an absorbed layer on the aqueous side of the mercury solution interface which resists compression. So, this prevents the streaming movement of the diffusion layer at the interface. So, maxima gets reduced higher concentration of this suppressors usually suppress  $i_d$  itself. So, we should be very careful because if the higher concentration suppressed this diffusion; this diffusion then we would not have a reaction.

So, I must use the suppressant maxima suppressant in judiciously taking care that this diffusion current should not be affected. So, we have to be slightly careful with respect to such things and usually we use Triton X-100 that is a non ionic surfactant to be used in polarographic solutions, but what is the concentration? It should be approximately 0.002 to 0.004 percent. So, I can use methyl cellulose also and gelatin and several other solutions can be used for polarographic experiments.

(Refer Slide Time: 14:15)

**HALF WAVE POTENTIALS**

Since solutions studied polarographically are very dilute, we can assume that the activity of the cation does not differ from its concentration in the bulk as well as in the amalgam. Polarography is concerned with electrode reaction at the indicator electrode involving electron transfer between the electrode and analyst. During the reduction of an oxide electrons leave the cathode, react in solution with the formation of the equivalent amount of the reductant.

Similarly during the oxidation of a reductant at the anode electrons pass from the solution to the electrode and form equivalent of the oxidant.

268

So, now we talk about half wave potential. Since, the solutions studied polarographically are very dilute, usually it is in ppm level which we will be doing the experiments and we can assume that the activity of the cation does not differ from its concentration. Because, earlier I have taught you that if the solution is very dilute, then the activity and concentration would be almost same because activity coefficient approaches unity in very dilute solutions. So, polarography is concerned with electrode reaction at the indicator electrode involving electron transfer between the electrode and the analyst.

Analyte actually it should be it cannot be analyst it has to be analyte please correct that during the reduction of the of an oxide, electrons leave the cathode react in solution with the formation of the equivalent amount of the reductant. Similarly, during oxidation of a reductant

at the anode electrons pass from the solution to the electrode and from equivalent form equivalent of the oxidant.

(Refer Slide Time: 15:40)

Thus ,

$$Mn^{n+} + ne^{-} \longrightarrow M(Hg)$$

$$E_{DME} = E^{\circ} - \frac{RT}{nF} \ln \left( \frac{[M] [Hg]}{[M^{n+}]_{aq}} \right) \dots\dots\dots (1)$$

Since the current I is limited by diffusion,

$$i = k [M^{n+}]_{aq} - [M^{n+}]_{aq}^0$$

where  $[M^{n+}]_{aq}^0$  represents the point of contact with mercury surface.

269

So, the half wave potential what we are discussing is at 50 percent of the reduction of the metal we have what is known as half wave potential. So, if I write an equation something like this  $Mn^{n+} + ne^{-} \longrightarrow M(Hg)$  plus this n plus refers to the valence plus n electrons, it must react to give you M plus metal and the metal will be absorbed on to the mercury at the electrode at the dropping mercury electrode I can write E is equal to  $E^{\circ} - \frac{RT}{nF} \ln \frac{[M] [Hg]}{[M^{n+}]_{aq}}$  products divided by the reactants.

So, in the products I have metal and mercury and the anion that is the reactant that is  $Mn^{n+}$  plus it is not anion it is cation. Since, the current I is limited by diffusion I can say that I is proportional to the difference between the concentrations of  $Mn^{n+}$  plus and  $Mn^{n+}$  naught, both in

aqueous solutions. Here,  $M^{n+}$  aqueous represents the point of contact with the mercury surface that is why we write  $M^{n+}$ . Otherwise, there is no way we can differentiate because the moment the electrode reaches the DME it immediately forms the amalgam.

So, to denote that fact we normally write  $M^{n+}$ ; that means, metal it has been reduced to metal and formed amalgam.

(Refer Slide Time: 17:41)

0

For the limiting current  $i_d$ ,  $[M^{n+}]_{aq}$  becomes very small.

$$i_d = k[M^{n+}]_{aq}$$

From the Ilkovich equation,

$$k = 607 n C D^{1/2} m^{2/3} t^{1/6}$$

The concentration of M in the amalgam is proportional to the current or  $i = k[M]_{Hg}$

270

So, for the limiting current I can write  $i_d$  limiting current  $i_d$ , I can write  $M^{n+}$  aqueous becomes very small and  $i_d$  would be equal to  $k$  into  $M^{n+}$  aqueous solution.

From the Ilkovich equation, I can say that  $k$  is equal to  $607$  into  $n C D$  raise to half. The concentration of M in the amalgam is proportional to the concentration of the metal.

(Refer Slide Time: 18:36)

The concentration of M in the amalgam is proportional to the current or

$$i = k' [M]_{Hg}$$

The constant is  $k'$  identical to  $k$  except  $D$  is replaced by  $D'$  and hence  $k/k' = \sqrt{D/D'}$ . Putting these in equation (1),

$$E_{DME} = E^0 - \frac{RT}{2nF} \ln \left( \frac{D}{D'} \right) - \frac{RT}{nF} \ln \left( \frac{i}{i_d - i} \right)$$



271

So, the current would be proportional to  $k M_{Hg}$  that is, metal and the mercury. So, I have two sets of equations; one is  $k M_{n+}$  plus aqueous and  $k M_{n+}$  plus mercury. So, the concentration of M in the amalgam is this.

We can say that  $i$  is equal to  $k'$  into  $M_{Hg}$  in the reduced state. So, the constant  $k'$  is identical to  $k$  except  $D$  is replaced by  $D'$  here,  $D$  is and hence  $k$  by  $k'$  would be equal to square root of  $D$  by  $D'$  where,  $D$  is the diffusion current diffusivity of the medium. So, putting these in equation I can write  $E_{DME}$  is equal to  $E^0$  minus  $\frac{RT}{2nF} \ln \frac{D}{D'}$  and then  $\frac{RT}{nF} \ln \frac{i}{i_d - i}$ .

So, this is a constant for a given medium  $D$  by  $D$  dash and the  $E$  naught dash is fixed. So, this also is a constant. So, I can write  $E$  naught minus this would be something like  $E$  naught dash another constant.

(Refer Slide Time: 19:44)

At the point where  $i = 1/2 i_d$ ,

$$E_{1/2} = E^0 - \frac{RT}{2nF} \ln \left( \frac{D}{D'} \right) = E^0$$

Hence,

$$E_{DME} = E_{1/2} - \frac{RT}{nF} \ln \left( \frac{i}{i_d - i} \right)$$

272

So, at a point when  $i$  is equal to  $1/2$  of  $i_d$  then this expression; this expression  $i_d$  by  $2$  minus  $i$  this will be  $i_d$  by  $2$  and this will become  $1$  and this becomes  $0$ . So,  $E_{DME}$  would be the difference between  $E$  naught dash and the viscosity the diffusivity of the sample. So,  $E$  naught dash minus  $RT$  by  $nF$   $\ln D$  by  $D$  dash is equivalent to  $E$  naught dash.

Some other constant, but this is not exactly same as the reduction standard reduction potentials slightly different. So, I can write  $E_{DME}$  is equal to  $E_{1/2}$  minus  $RT$  by  $nF$   $\ln I$  by  $i_d$  minus  $i$ .

(Refer Slide Time: 20:49)

The potential at  $E_{1/2}$  is termed the half wave potential and  $E_{1/2}$  is the characteristic constant of any red-ox system and its value is independent of the concentration of the oxidant [OX], in the bulk of the solution.

The theoretical treatment of anodic waves is similar to that of the cathodic wave outlined above.

273

So, the potential at  $E_{1/2}$  is termed as the half wave potential and  $E_{1/2}$  is characteristic constants of any red-ox system in polarography and its value is independent of the concentration of the oxidant in the bulk of the solution.

So, if you can see here there is no concentration term here at all when I put  $i$  is equal to  $i_d$  by 2. So, this is  $i_d$  by 2 and  $i_d$  by 2 here  $i_d$  by 2 will remain. So, there is no where is the concentration term; that means,  $E_{1/2}$  is a characteristic of any reducible species that is what we have written here, its value is independent of the concentration of the oxidant in the bulk of the solution.

The theoretical treatment of anodic waves, suppose you are doing the analysis of anion then it will go to it will go to anode. So, I can have anodic wave also instead of cathodic wave I can have anodic wave and the treatment of anodic wave was also essentially same as the cationic

system. What does it mean? It is at E half potential at the potential where the  $i_d$  is equal to  $i_d$  by 2 for the anodic species again it is independent of the concentration of the anionic species. So, it is a characteristic of the reduction potential of the anion.

(Refer Slide Time: 22:46)

The same result can be obtained as follows:

$$\text{Ox} + ne \rightleftharpoons \text{Red}$$

$$E = E^0 + \frac{RT}{nF} \ln \frac{a_{\text{ox}}}{a_{\text{red}}} \quad \text{or} \quad (1)$$

$$E = E^0 + \frac{RT}{nF} \ln \frac{[\text{ox}]_0}{[\text{Red}]_0} \quad (2)$$

where 0 refers to the concentration at the electrode surface and E refers to the value during the life of a mercury drop.

274

So, the same result we can obtain something like this and the slightly another treatment I can write oxidant plus ne electron n number of electrons goes to reductant and E is equal to E naught plus RT by nF ln a oxidant divided by a reductant. Or I can write ox naught and reduction reduce species naught. Here, again it represents to the concentration of the analyte at the electrode surface and E refers to the value during the life of a mercury drop.

(Refer Slide Time: 23:30)

The same result can be obtained as follows:

$$\text{Ox} + ne \rightleftharpoons \text{Red}$$
$$E = E^0 + \frac{RT}{nF} \ln \frac{a_{\text{ox}}}{a_{\text{red}}} \quad \text{or} \quad (1)$$
$$E = E^0 + \frac{RT}{nF} \ln \frac{[\text{ox}]_0}{[\text{Red}]_0} \quad (2)$$

where 0 refers to the concentration at the electrode surface and E refers to the value during the life of a mercury drop.

274

So, if I by combining these equations the current at any point on the wave is determined by the rate of diffusion of the oxidant from the bulk of the solution to the electrode surface under a concentration gradient from oxidant to oxidant concentration of 0 that is at their mercury electrode.

So, from the normal concentration what you have started till the oxidize oxide component is reduced, and then it touches the mercury and then it gets absorbed onto the mercury forming an amalgam the concentration gradient exists.

So, the concentration gradient gives rise to the diffusion current I is equal to K into ox minus ox naught. So, I can since the concentration of the ox oxidant is almost negligible because it is getting reduced now it getting reduced to metal. So, this will be neglected.

So, it will be a function of  $K_{ox}$  only  $ox_{naught}$  will be 0. Concentration of the oxidant on the mercury surface will be zero because it will diffuse immediately. So,  $I$  is equal to  $K_{ox}$  this is the concentration term that is equal to  $i_d$ . So, when  $ox_{naught}$  is equal to 0 this one; when  $ox_{naught}$  is equal to 0  $i_d$  would be equal to diffusion current and that is known as Ilkovich current  $K$ . So, I put the value of  $ox_{naught}$  in this equation  $ox_{naught}$  is equal to  $i_d$  minus  $i$  divided by  $K$  the same expression what we have drawn earlier.

(Refer Slide Time: 25:39)

The concentration of the reductant  $[Red]_0$ , on the surface at any value of  $i$  will be proportional to the rate of the diffusion of the reductant from the surface of the electrode into the mercury drop. Hence,

$$i = k [Red]_0 \text{ substituting this in equation (3)}$$

$$E = E^0 + \frac{RT}{nF} \ln \frac{K}{k} + \frac{RT}{nF} \ln \left( \frac{i_d - i}{i} \right)$$

$$= E^0 + \frac{RT}{nF} \ln \left( \frac{i_d - i}{i} \right)$$

276

So, the concentration of the reductant also we should know and on the surface at any value of  $i$ . It will be proportional to the rate of the diffusion of the reductant from the surface of the electrode into the mercury drop. So, now we had separated the oxidant and reductant ok.

So, for oxidant we have done the we have done the treatment as if oxidant is there in the aqueous phase as well as oxidant is there in the mercury drop. At the mercury drop

concentration of the reductant that is cadmium in our case is almost 0. So, we have drawn we have done an expression we have obtained an expression for the oxidant species. Now if I want to write a nernst equation you should remember that  $E$  is equal to  $E^\circ$  plus  $\frac{RT}{nF} \ln$  oxidant divided by reductant.

Now, I know their numerator I should now determine the denominator. So, in the denominator again I am going to do the same treatment here  $I$  is equal to  $K$  into reductant. Here,  $0$  again represents the reduced species at the mercury surface. So, I can write  $E$  is equal to  $E^\circ$  plus  $\frac{RT}{nF} \ln \frac{K}{k}$ .

And then  $\frac{RT}{nF}$  this is another constant small  $k$  I have written here plus  $\frac{RT}{nF} \ln \frac{d}{i}$  minus  $i$  by  $i$ . So, again I combine these two  $\frac{RT}{nF} \ln \frac{K}{k}$  plus  $\frac{RT}{nF} \ln \frac{d}{i}$  minus  $i$  by  $i$  and  $E^\circ$ . then I write  $E^\circ$  here plus  $\frac{RT}{nF} \ln \frac{d}{i}$  minus  $i$  by  $i$ . So, now, I have concentration of the reductant in terms of the emf and earlier I had drawn the I have derived the concentration of the cation oxide that is oxidant.

(Refer Slide Time: 28:08)

where  $E^0 = E^{\text{d}} - k$  and  $k = \frac{RT}{nF} \ln \frac{K}{k}$

when  $i = i_d / 2$ ,

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

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

Curve  $\log i_d - i$  Vs  $E$  gives a straight line with slope  $0.0591/n$  and intercept  $E^{\text{d}}$  = half wave potential. This equation is termed as the equation of the polarographic wave.

277

So, an  $E_{1/2}$  is equal to where  $E^{\text{d}}$  minus  $k$  and  $k$  would be  $\frac{RT}{nF} \ln \frac{K}{k}$ . So, when  $i$  is equal to  $i_d / 2$  again  $E_{1/2}$  would be  $E^{\text{d}}$  plus  $\frac{RT}{nF} \ln \frac{i_d/2}{i_d/2}$  and this is 0,  $\ln 1 = 0$  and  $E_{1/2}$  should be equal to  $E^{\text{d}}$ .

So,  $E_{1/2} = E^{\text{d}} + \frac{0.0591}{n} \log \left( \frac{i_d - i}{i} \right)$ . So, what does it tell me? It tells me that the curve  $\log \left( \frac{i_d - i}{i} \right)$  versus  $E$  gives a straight line with slope  $\frac{0.0591}{n}$  and the intercept  $E^{\text{d}}$  gives me the half wave potential.

Why this is the intercept  $y$  is equal to  $mx + c$  something like that. So, this gives me  $c$  this equation is termed as the equation of the polarographic wave. So, so far what we have done is to consider a system in which I have a reducing species and then the reducing species is

moving towards cathode. So, I have a system I have a system where the metal is getting reduced in aqueous solution and then it is reaching the mercury surface and diffusing inside.

So, from the concentration change in the oxidation state I can write the nernst equation  $E$  is equal to  $E^{\circ}$  plus  $\log$  of  $\frac{RT}{nF} \ln \frac{\text{oxidant}}{\text{reductant}}$  for oxidant I have got an expression in terms of the diffusion current that is  $i_d - i$ . Similarly, I do the treatment for reductant again in aqueous phase as well as in the mercury surface.

So, I combine those two equations and then I got the curve nernst equation I can write and this represents everything in terms of the current that is being produced. So, this half wave potential is nothing, but the polarographic wave.

(Refer Slide Time: 30:58)

It follows that if  $\log \left[ \frac{(i_d - i)}{i} \right]$  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 thalious ion.

278

So, what I do is it follows that  $\log$  of  $i_d$  minus  $i$  by  $i$ . If I plot against the potential of the mercury electrode I with, I get a straight line with a slope of  $0.591/n$  where  $n$  is the number of electrons involved in the red-ox reaction.

So, the intercept of the graph upon the vertical axis gives the half wave potential of the system. So,  $n$  may be determined very easily. So,  $E_{1/2}$  is also known as the decomposition potential and the wave should be steeper for aluminum and lanthanum than lead or cadmium because the lead and cadmium are two electron systems aluminum and lanthanum are three electron system and alkali metals or thallos ion would be single electron system for as far as red-ox reactions are concerned.

(Refer Slide Time: 32:04)

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.

So, if the reaction at the indicator electrode involves complexation satisfactory polarographs can also be obtained for complex ions only if the dissociation of the complex is very rapid and

it should be comparable with the diffusion rate. So, that the concentration of the sample is maintained constant at the electrode surface that is most important the reduce species must form an amalgam and then go into the mercury drop.

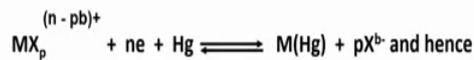
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Let us consider reduction of a complex ion :



$$K_{instab} = \frac{[M^{n+}][X^{b-}]^p}{[MX_p^{(n-pb)^+}]}$$

then we can write



$$E_{1/2} = E^0 + \frac{0.0591}{n} \log k_{instab} - \frac{0.0591}{n} \log [X^{b-}]^p$$

280

So, you for a complex reaction suppose I have a complex metal anode this is cation and this is anion ligand anion is nothing, but a ligand here and. So, many it is using something like ZnCl<sub>2</sub> HgCl<sub>4</sub>. So, p is nothing, but stoichiometric combining ratio and they have valence the of this complex ion would be n minus p b plus that is a stoichiometric including the charge.

And I can get M n plus p X b minus and then I can write K instability constant because here complex is getting destroyed. So, I can write instability constant would be again product of products divided by reductant. So, M n plus raise in multiplied by X b minus raise to p divided by MX p raise to n plus pb. So, we can write MX p raise to n minus pb do not worry too

much about this it looks threatening, but actually it is a very simple system use a  $\text{HgCl}_4$  you will find all the things very easy to understand.

I had written general equations. So, it looks a little daunting. So, anyway. So,  $\text{MX}^p$  raised to this is the valence  $\text{MX}^p$  raised to  $n$  minus  $p$  plus  $n$  plus mercury goes to mercury metal amalgam and. So, much of anion will be released.

So, I can write  $E_{1/2}$  is equal to  $E^\circ$  again  $E^\circ$  and then  $0.0591/n \log$  of  $k$  instability instead of  $D$  by  $D^\circ$ . Earlier, like what we have used. So, I can write  $D$  by  $D^\circ$  instead of that instability constant and  $0.0591/n$  by divided by  $n \log$  of  $X$  raised to  $b$  minus that is a raised to  $p$ .

Now, you can imagine that I know this concentration I can all other number all others are numbers determined by experiment. So, I can determine the instability constant of a system of a complex ion that is the beauty of polarography.

(Refer Slide Time: 35:35)

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.

281

So,  $p$  is a coordination number here as I had explained to you earlier and it is the number of the coordination number of the complex ion formed and  $X$  is the complexing agent.

So, the more stable the complex more negative will be the half wave potential thus there will be a shift of the  $E$  half values by complexations. So, I can say copper in nickel, copper, lead and all these things can be complexed with cyanide ions and hence nickel and lead can be determined very easily provided their instability constants are different.

So, it is not difficult to determine the complex ions as well as standard metal ions. Now, where do I get complex ions in a day to day life you get lot of them there will be number of occasions whenever you take a vitamin iron you get a complex iron in the form of a complex whenever

you eat some things food it is again a complex and. So, many other places we have we do not have simple metal ions in our systems all around us.

Most of the time they would be in complex the complex species and they can be determined as such using polarography, that is a beauty. So, polarographic analysis can be carried out if the concentration is of the order of about  $10^{-4}$  to  $10^{-3}$  to  $10^{-5}$  to  $10^{-6}$  also people have been doing research at the parts per billion level ppb there is one professor Rajgopal from nal who has pioneered this concept of p parts per billion analysis using polarography.

So, the volume of the solution is again a very special it can be just 2 ml, 1 ml, 0.5 ml or up or up to 25 ml. So, the beauty is whatever is the sample available, it can be subjected to polarographic analysis to get the accurate analysis. However, it is not uncommon to come across  $10^{-2}$  molar solutions and as low as  $10^{-8}$  molar solution.

That is also possible. So, such solutions even if I have 1 ml of the sample I can do a polarographic analysis that is the beauty. So, the reproducibility I can always say that it is within plus or minus 2 percent. Normally, whenever we talk of the reproducibility in spectroscopy up to 20 to 25 percent deviation from the is allowed and we still say they are fairly reproducible up to 20 to 25 percent, but in case of polarography it may be as low as plus or minus 2 percent.

(Refer Slide Time: 39:01)

Polarographic analysis can be carried out if the concentration 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 ( $2.5 \times 10^{-4}$  M) give two waves according to the reactions,



282

So, saturated solutions of oxygen at ambient temperature give two waves according to this reaction that is  $\text{O}_2$  plus  $2\text{H}_2\text{O}$  plus  $2\text{e}$  going to  $\text{H}_2\text{O}_2$  and  $2\text{OH}^-$ . And another is in acidic solution we have oxygen reacting with hydrogen ions to give  $\text{H}_2\text{O}_2$ . There are other chemical reactions that will be happening in polarography we will take a look at how to continue our investigation today with respect to such reactions and conduct the quantitative analysis in the next class.

Thank you very much.