Modern Instrumental Methods of Analysis
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Lecture No. # 38
Polarography-1 Introduction

I had almost finished our discussions on the potentiometric titration. I had discussed about the acid based titrations then we had discussed about precipitation reactions and then the redox reaction complexsation reactions and then we had discussed about the change of pFe from 4.3 to 7.2 to 10 within a volume change of 99.9 to 100.1 ml.

So, these values are important for the choice of the indicators for the titration also. Usually, we end our discussion on this on this note by impressing that within a very small change of volume there is a big change in the potential. Especially, in all these reactions what we have studied so far. So, the apparatus as such is not very difficult, but it is a very simple potentiometer, what we had used in our previous discussions.

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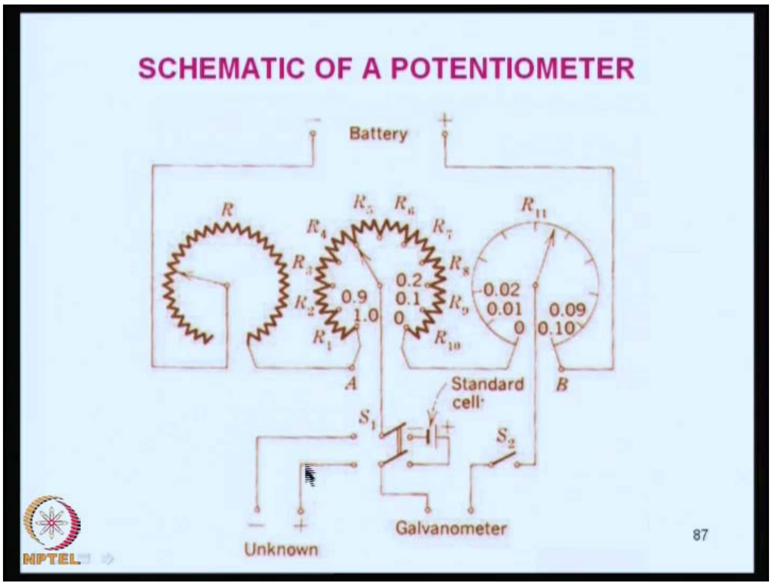

SCHEMATIC OF A POTENTIOMETER

This slide will show you a simple potentiometer, the resistances are adjusted to measure the slide wire and then the battery is a source of supply battery and the solution are kept here, and this is a basically a galvanometer and currents are measured as usual. now, we will close our discussion on the potentiometer and continue our discussions on the polarography.

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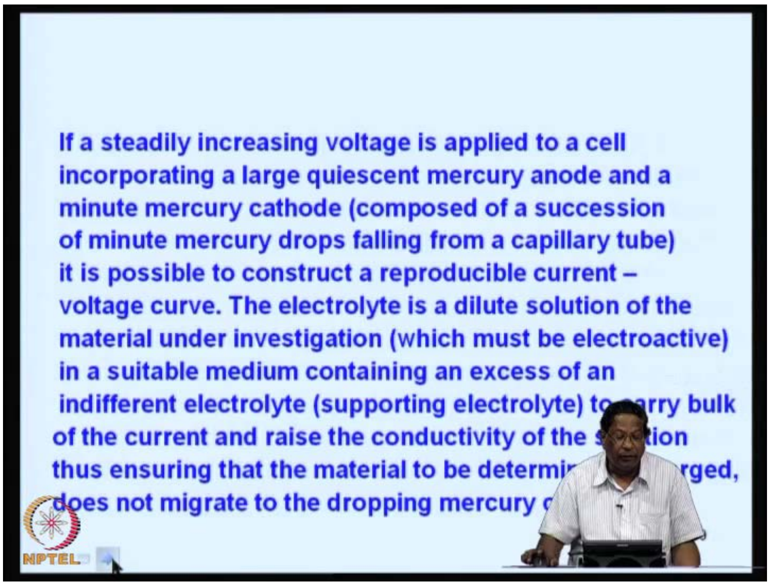

If a steadily increasing voltage is applied to a cell
incorporating a large quiescent mercury anode and a
minute mercury cathode (composed of a succession
of minute mercury drops falling from a capillary tube)
it is possible to construct a reproducible current –
voltage curve. The electrolyte is a dilute solution of the
material under investigation (which must be electroactive)
in a suitable medium containing an excess of an
indifferent electrolyte (supporting electrolyte) to carry bulk
of the current and raise the conductivity of the s tion
thus ensuring that the material to be determi rged,
does not migrate to the dropping mercury c

Now, polarography is a technique use to measure the current when an applied potential is impressed on a solution in which a mercury drop is used falling from a capillary. so, if a steadily increasing voltage is applied to a cell incorporating a large quiescent mercury anode and a minute mercury cathode it consist of a succession of minute mercury drops falling from a capillary under the gravity that is the system we are going to describe now. That is, I have a solution and in the solution I have a cathode and anode; the anode is a big mercury pool to which an electrical wire is connected and the cathode is a small capillary through which mercury is falling drop by drop.

In such a system the electrolyte is a dilute solution of the material under investigation; that means, it must be a contain a species which is electro active and then as the mercury drops fall down, the reaction is taking place and the when the mercury drops fall down there is no contact and between the anode and the cathode. So, the voltage drops to 0 and the electrolyte is a dilute solution of a material under investigation in a suitable medium that is must be a aqueous solution or a non-aqueous solution depending upon the choice and it must contain an excess of indifferent electrolyte; that means, an electrolyte which does not get reduced, the either at the anode or the cathode; that means, the electrolyte components cations and anions do not get reduced and the only reducible species is in the solution.

So, we call it supporting electrolyte and this supporting electrolyte carries the bulk of the current and raises the conductivity of the solution thus ensuring that the material to be determined if charged does not migrate to the dropping mercury electrode.

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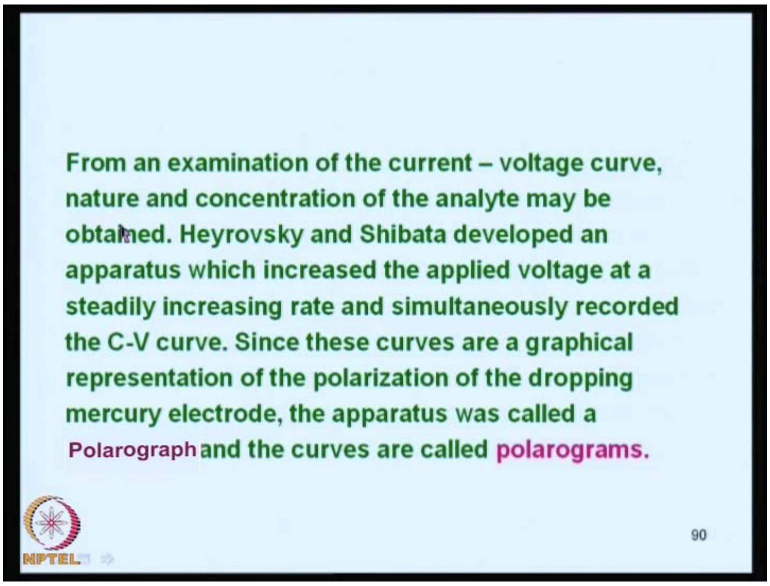

From an examination of the current – voltage curve, nature and concentration of the analyte may be obtained. Heyrovsky and Shibata developed an apparatus which increased the applied voltage at a steadily increasing rate and simultaneously recorded the C-V curve. Since these curves are a graphical representation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

So, if we look at the slide we can see that, we can examine the current voltage curves and the nature and the concentration of the analytic maybe obtained. Now, all this is in the system, what I had describe to you earlier; that is a steadily increasing voltage is applied to a cell incorporating a large quiescent mercury anode and a minute mercury cathode it is possible to construct a reproducible current, voltage curve. So, when we do this we can examine the current, voltage curves and then deduce information about the nature and concentration of the analyte.

So, Heyrovsky and shibata developed an apparatus which contains this quiescent mercury pool and a dropping mercury electrode and in which they increased the applied voltage at a steadily increasing rate. And simultaneously recorded the current, voltage curve; since these curves are a graphical representation of the polarization of the dropping mercury electrode, the apparatus was called a polarography and the curves are called as polarograms.

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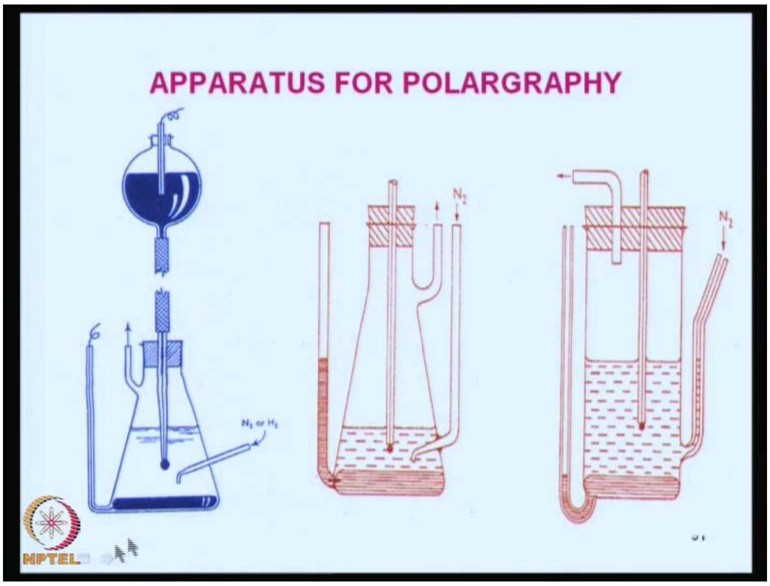

APPARATUS FOR POLARGRAPHY

That means current, voltage curves are known as polarogramTs. This is the simple apparatus for polarography here, I have a solution and then in the solution there is a capillary dipped inside that and the mercury drop is falling at the bottom I have a mercury solution which acts as the anode from here. I take the electrical current and mercury drop is falling from here, this is all mercury blue color and that mercury is connected to another electrode. So, this is cathode, this is anode.

So, I have nitrogen or hydrogen passing through this in a solution and there is a means for escaping the dissolve excess gases, this is the basic apparatus for polarography similar other designs are like this essentially same, but more useful conveniently for convenience and there is not much difference except that the functions are essentially same this is a conical flask, this is cylindrical flask, etcetera. And the nitrogen is being bubbled here and here it is going through out of from the space in which the gas is held here, it is passing out, gas is passing out through the solution itself and from here also it is going out from the available space.

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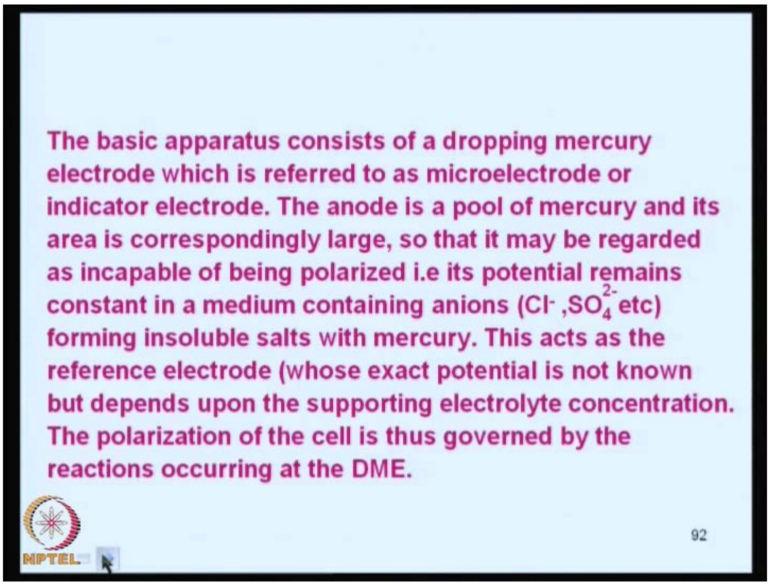

The basic apparatus consists of a dropping mercury electrode which is referred to as microelectrode or indicator electrode. The anode is a pool of mercury and its area is correspondingly large, so that it may be regarded as incapable of being polarized i.e its potential remains constant in a medium containing anions (Cl^- ,SO_4^{2-} etc) forming insoluble salts with mercury. This acts as the reference electrode (whose exact potential is not known but depends upon the supporting electrolyte concentration. The polarization of the cell is thus governed by the reactions occurring at the DME.

So, the basic apparatus consist of a dropping mercury electrode which is referred to as the micro electrode or indicator electrode, the anode is a pool of mercury and its area is correspondingly vary large. So, that it may be regarded as incapable of being polarized that is their potential remains constant in a medium containing anions such as chloride, sulphate, etcetera and it forms an insoluble salts with mercury.

This acts as the reference electrode; that means, the anode acts as the reference electrode whose exact potential is not known. But, because it is because it is acting as a quiescent mercury pool and things are not getting reduced there oxidized as well and. So, this acts as a reference electrode, but whose exact potential is not known, but it depends upon the supporting electrolyte concentration.

So, the polarization of the cell is thus governed by the reactions occurring only at the dropping mercury electrode that is DME in inlet and outlet tubes as you have seen in the previous figure.

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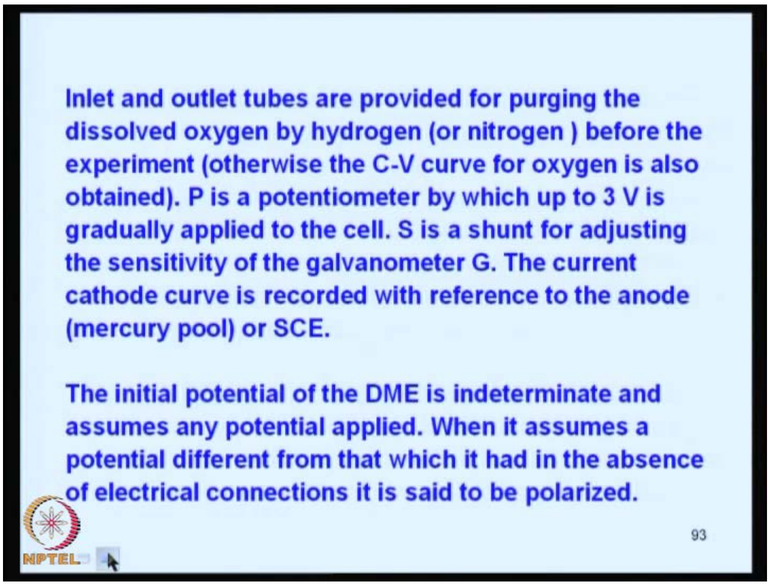

Inlet and outlet tubes are provided for purging the dissolved oxygen by hydrogen (or nitrogen) before the experiment (otherwise the C-V curve for oxygen is also obtained). P is a potentiometer by which up to 3 V is gradually applied to the cell. S is a shunt for adjusting the sensitivity of the galvanometer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

These figures are provided for inlet and outlet tubes and these are provided for purging the dissolved oxygen by hydrogen or nitrogen before the experiment, otherwise the current, voltage curves for oxygen are also obtained dissolved oxygen, because many of these solutions contain some amount of dissolved oxygen, the oxygen gets reduced in such situations. So, dissolved oxygen we do not want in the system.

So, other systems will remain the same; that means, we have a potentiometer by which up to 3 volts can be applied to the cell. So, I will have a shunt for adjusting the sensitivity of the galvanometer that is G. The current, voltage cathode, the current cathode curve is recorded with reference to the anode either mercury pool or with another reference electrode such as saturated calomel electrode. The initial potential of the dropping mercury electrode is indeterminate; that means, when you are not passing the voltage the voltage of the dropping mercury electrode is in determine; that means, you cannot determine and it can assume any potential that you apply.

When it assumes a potential different from that which it had in the absence of electrical connections it is said to be polarized this we have discussed earlier, what is polarization? Etcetera. And now, I want you to consider a simple example that is consider a cadmium solution along with sodium chloride in an oxygen free medium; that means, the supporting electrolyte is sodium chloride and the species to be reduced is cadmium and I have already passed a nitrogen through the solution and that is it does not have any dissolved oxygen. so, when an external EMF is applied to such a system two phenomenon occur.

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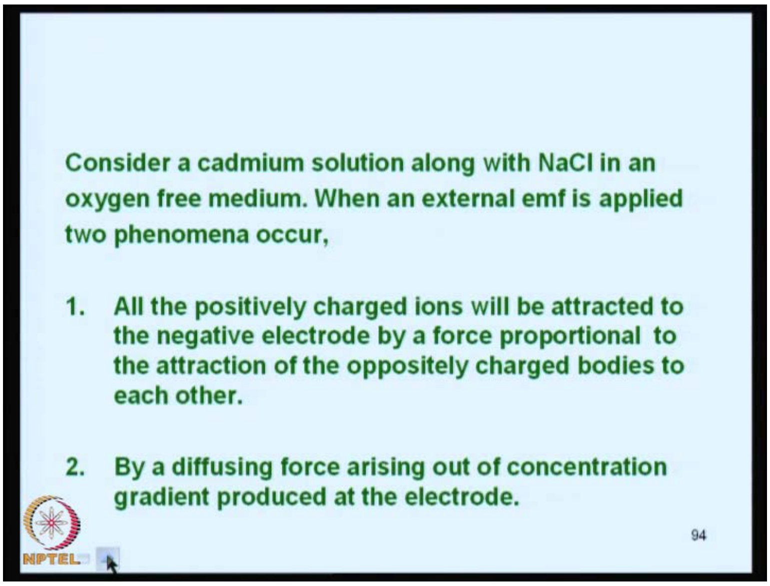

Consider a cadmium solution along with NaCl in an oxygen free medium. When an external emf is applied two phenomena occur,

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.

I have written down both the phenomenon's in this slide; one is all the positively charged ions will be attracted to the negative electrode by force proportional to the attraction of the oppositely charged bodies to each other it is a very natural phenomena all the positive ions will travel towards the negative electrode and negative ions will be travelling towards the positive electrode.

So, this phenomenon is a very simple phenomenon to understand and the second phenomena that occurs is a diffusing force operates arising out the concentration gradient produced at the electrode; that means, because it is irreversible the reactions will not be taking place at the electrode until the only reducible species cadmium reaches the electrode and because the electrodes, because cations and anions are not reduced they remain near the electrode forming a sheath of a resisting force a concentration through which cadmium has to migrate to the electrode to reach the electrode and get reduced.

So, a diffusing force is operative in for the with respect to cadmium. So, the diffusion force arises out of concentration gradient produced at the electrode. So, the total current passing through the cell can be regarded as the sum of these two factors one is electrically oppositely charged particles another is current due to diffusing force arising where the electrode where the electro active species will be passing through where the electro active species will be passing through a concentration gradient until it reaches the electrode. So, the total current is the sum of these two factors and a typical current, voltage curve, I am going to show you in this slide.

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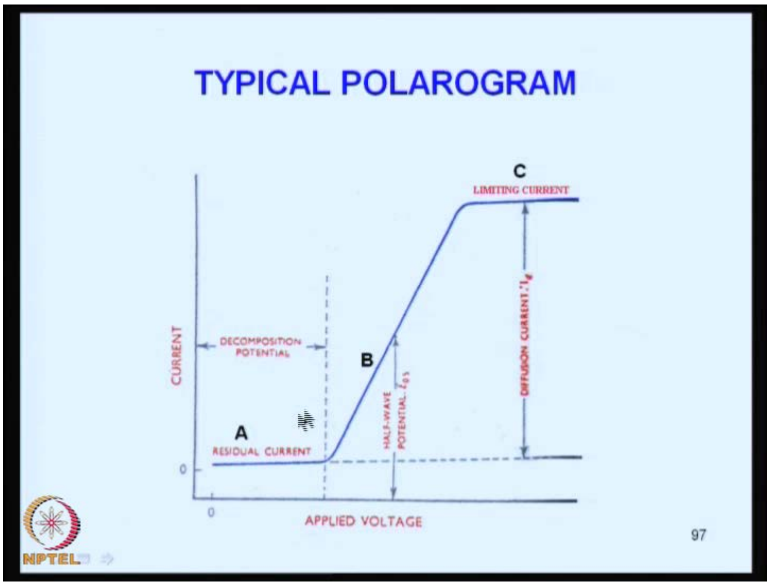

TYPICAL POLAROGRAM

This is the typical current and voltage curve. So, you can see, I have plotted current here versus applied voltage and you can see 3 different parts of the curve that is A, B and C. In A, I have written as residual current, in B it is the half wave potential and it is rising and in the portion C the current remains largely unaltered.

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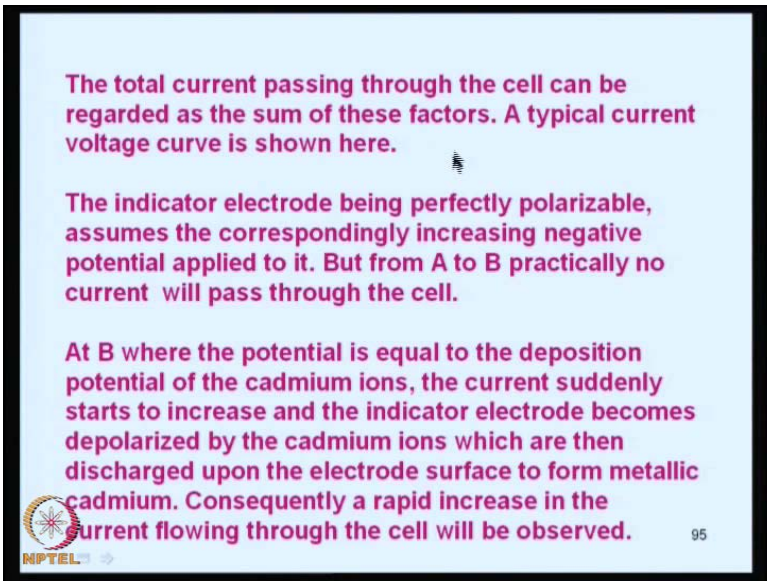

The total current passing through the cell can be regarded as the sum of these factors. A typical current voltage curve is shown here.

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, this is the known as decomposition potential. So, the curve at B from A to B there is practically no current that is, what we called residual current? And then from the point B the potential is equal to the decompose deposition potential of the cadmium ions; that is in this range the cadmium ions will be depositing and the when they reach the electrode cadmium ions will be discharged upon the electrode surface to form metallic cadmium and the metallic cadmium will react with mercury to form amalgam and then this amalgam will defuse into the electrode that is in the dropping mercury electrode, mercury mass of the drop and then it will fall down .

So, consequently as the electrode as the electro chemical species reaches the electrode, a rapid increase in the current flowing through the cell will be observed that is, what you are observing here, a rapid increase in the region B.

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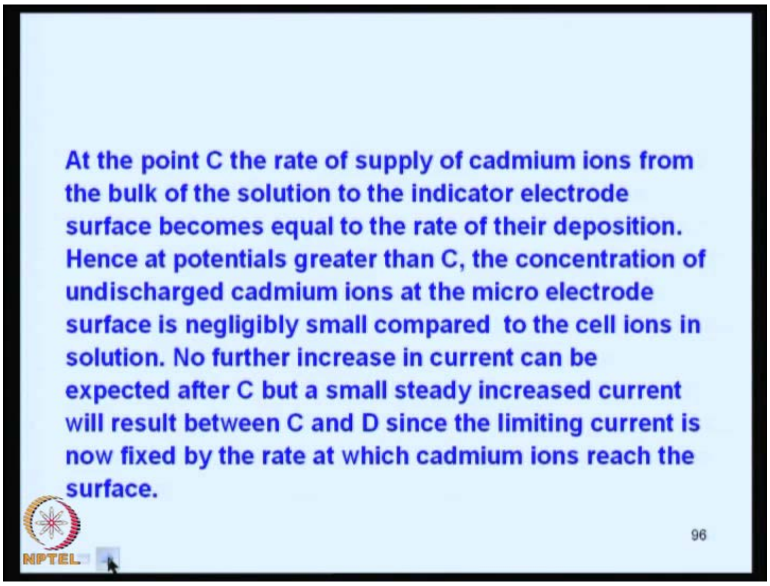

At the point C the rate of supply of cadmium ions from the bulk of the solution to the indicator electrode surface becomes equal to the rate of their deposition. Hence at potentials greater than C, the concentration of undischarged cadmium ions at the micro electrode surface is negligibly small compared 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.

So, at the point C please look at the slide again at the point C, I have a flat region; So, in this flat region from 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; that means, as the there is no more diffusing force operating the ions of cadmium are capable of reaching the electrode in a with a sufficiently faster rate and getting reduced also at the same rate.

So, the rate becomes equal to the rate of their deposition. So, at potentials greater than C the concentration of the undischarged cadmium ions at the microelectrode surface is negligibly small compared to the cell ions in the solution. No, further increase in current can be expected after C, because the rate of deposition and rate of travel are all the same. So, with the result that between C and D the limiting current is now fixed by the rate at which cadmium ions reach the electrode.

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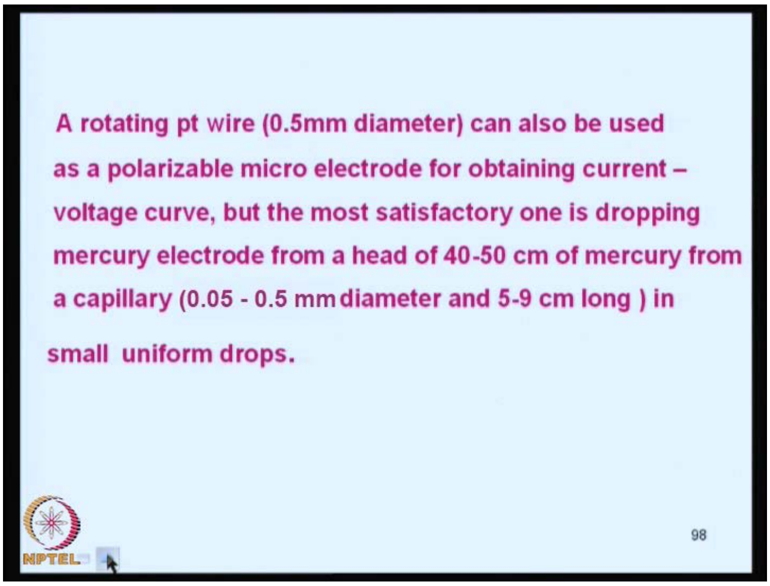

A rotating pt wire (0.5mm diameter) can also be used as a polarizable micro electrode for obtaining current – voltage curve, but the most satisfactory one is dropping mercury electrode from a head of 40-50 cm of mercury from a capillary (0.05 - 0.5 mm diameter and 5-9 cm long) in small uniform drops.

So, we can this is the basic apparatus for the polarography and electro reducible species is usually cadmium or any other ion if you can replace it by another ions which can be electrolytic ally reduced. And instead of mercury pool you can use a rotating platinum wire also as a polarizable microelectrode you can just use a platinum wire which is rotating that is to disturb the ionic shield around it, but the most satisfactory one is the dropping mercury electrode from a head of about 40-50 centimeter of mercury you should remember this figure that is the height of this figure, in this figure from this point to this point is about 40-50 centimeter. And the idea of taking large quantity of mercury is to see that there is no apparent decrease in the height of this column, due to the falling mercury drops that is why you should have a big head of 40-50 centimeter of mercury from a capillary and usually the capillary size is 0.05-0.5 diameter and about 5-9 centimeter long, in mercury should be dropping in small small droplets.

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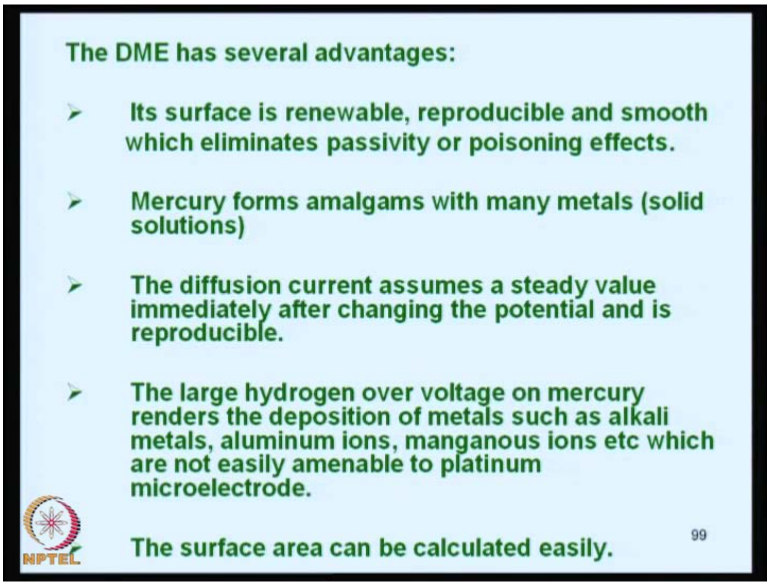

The DME has several advantages:

- 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.

So, this DME has got several advantages, its surface is renewable, it should be reproducible, it should be smooth and which eliminates the passivity or poisoning effects. Mercury forms amalgams with many metals that is another advantage, because any of the electro active species, what you take? They must get reduced at the mercury they must form amalgams and diffused into the mercury drop also. And then the diffusion current assumes a steady value immediately after changing the potential; that means, I am physically changing the applied potential and determining the current.

So, the moment I change the potential the mercury will be the potential will take the potential what I apply immediately without any time lag and it is reproducible. So, the another advantage of the dropping mercury electrode is that the large hydrogen over voltage on mercury renders the deposition of metals such as alkali metals, aluminum ions, manganese ions, etcetera which are not easily amenable to platinum microelectrode.

For example, if you want to determine aluminum ions and manganese ions etcetera; it is not easy to determine with a rotating platinum microelectrode, but it is easy to determine with the dropping mercury electrode and the another advantage is the surface area of the mercury drop can be calculated very easily all you got to do is assume take 10 drops of mercury in a bicker. And then wait and then assume that each mercury drop is almost spherical and then calculate how much each drop weighs? And then you can determine the surface area very easily with simple arithmetic.

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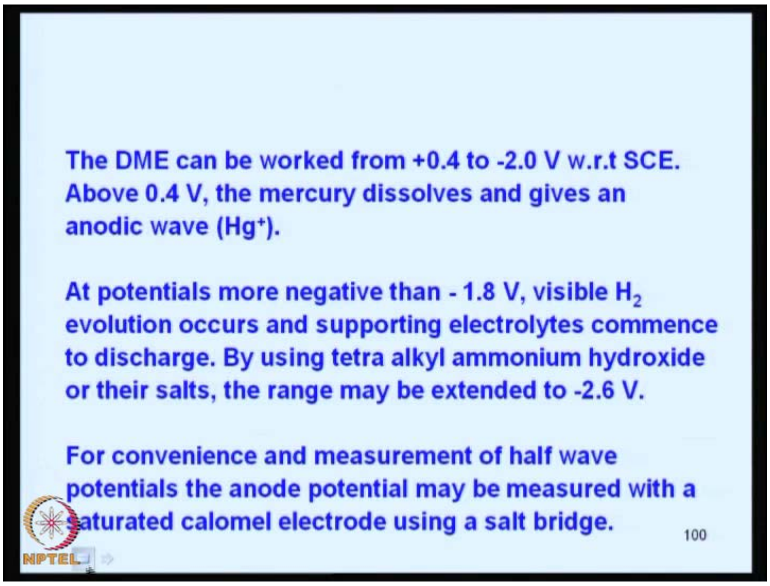

The DME can be worked from +0.4 to -2.0 V w.r.t SCE. Above 0.4 V, the mercury dissolves and gives an anodic wave (Hg^+).

At potentials more negative than - 1.8 V, visible 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.

So, these are the advantages of DME and that is why? Polarography has become one of the most popular technique for the determination of metals and metallic other non-metals also to some extent. And then reducible species we can do the speciation study that is in what oxidation state metals are present you can determine and then the advantage of DME is it can be work from plus 4 to minus 2 volts, with respect to saturated calomel electrode.

Above 0.4 volts it is not usually done, because the mercury starts dissolving and starts giving you an anodic wave; that means, it will give a separate wave for mercury and at potentials more negative than minus 1.8 volts visible hydrogen evolution takes place that is hydrogen bubbles will start appearing if the solution is acidic. So, that is also not very advisable. So, by supporting electrolyte also sometimes commences to discharge by using tetra alkyl ammonium hydroxide or their salts the range may be extended up to minus 2.6 instead of usual alkyl metal salts.

For convenience and measurement of the half wave potentials, the anode potential maybe measured with a saturated calomel electrode using a salt bridge one can use salt bridge also. So, early polarography use to work only with a salt bridge and then saturated calomel electrode has a reference electrode. So, let us look at the theoretical principles of polarograph now, that we have seen how a polarograph is looking and what is happening at the polarograph? And at the electrodes and anodes you know you know the working range of the polarograph polarograph. Yes.

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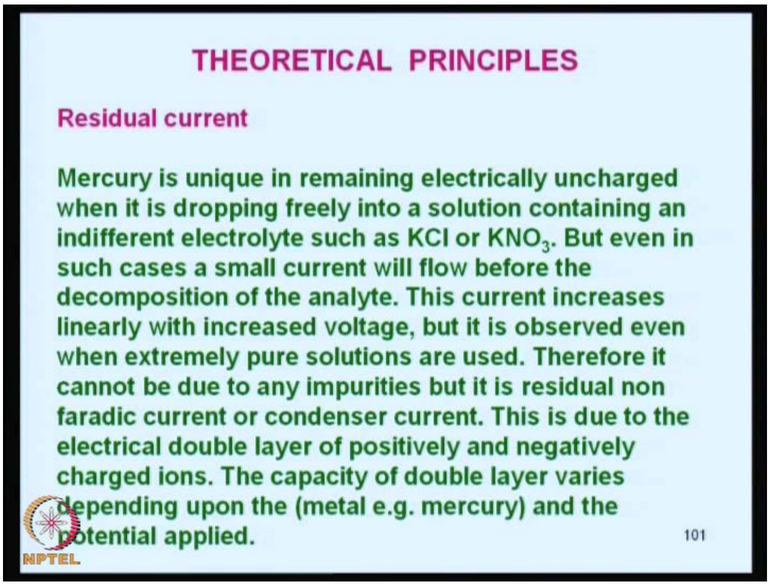

THEORETICAL PRINCIPLES

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_3. 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.

Then let us look at the theoretical principles, one thing you should understand is what we mean by residual current. Mercury is unique in remaining electrical uncharged when it is dropping freely into a solution containing an indifferent electrolyte, you have you know that we can use potassium chloride and potassium nitrate, sodium chloride etcetera; these are called indifferent electrolytes; that means, they do not get reduced at the electrodes. But, even in such cases a small amount of current will flow before the decomposition occurs, that is why? You will see, a small rise in the current in the range A to B that is if you permit me to go back this residual currents there is a slight increase; it is not exactly horizontal, but it is slightly increasing.

So, this current increases linearly with increased voltage, but it is observed even when extremely pure solutions are used; that means, it is not necessarily arising out of the out of the use indifferent electrolyte, but suppose you use very pure solutions even then you would see a small increase in the current as you increase the potential therefore, it cannot be due to any impurities, because we have we even you will the same thing when you use very highly pure chemicals, but it is the residual non faradic current; that means, it is it does not result in the reduction at the electrode, but it is a non-faradic current that is why it is known as non-faradic current or condenser current.

This is due to the electrical double layer of positively and negatively charged ions surrounding the electrode, but not getting reduced at the electrode and the capacity of this double layer varies upon the metal. And the potential we apply, metal means usually mercury and in practice traces of impurities present in the indifferent electrolyte do cause certain amount of small and imperceptible currents super imposed upon this condenser current.

So, all these are called as put together as residual current and in practical work this current is automatically subtracted from the total observed current by proper extrapolation, you just have to extrapolate and then subtract from the limiting current to get the decomposition potential. Then you will also see, the migration current; that is the migration of the charged particles in the electric field caused by the potential difference existing between the electrode and the solution and by diffusion of the ions that is migration of the charged particles in the electric field caused by the potential difference; and the potential difference exist between the electrode and the solution and also there is diffusion. Migration current can be made negligible by the addition of large quantity of indifferent electrolyte; that means let the indifferent electrolyte carry maximum current and migration current should be a very small part of the total current that is being carried.

Under such conditions practically all the current will be transported by the indifferent electrolytes like potassium and chloride ions, if you use potassium chloride or sodium chloride ions; if you use sodium chloride as the supporting electrolyte and under, but they do not get reduced. So, they go and hang around the electrode in a forming a sheath of the positive ions at the negative electrode and sheath of negative ions at the positive electrode.

So, under these conditions, the reducible species that is cadmium what we had discussed earlier or any other species, can reach the electrode only by diffusing through that sheath of the ions that is by diffusion, but they will not reach the electrode until a particular value is reached; that means, they must have enough force to bridge through the wall of the indifferent cations hanging around the electrode.

So, we have, what you call once these conditions; under these conditions, the potential gradient is compressed as you keep on increasing the potential the potential gradient keeps on getting compressed around the electrode, surface. But, it cannot permit the transport of the cadmium ions that is the analyte in which we are interested. So, the limiting current is solely due to the diffusion current, because the electrolyte does not carry any current.

So, whatever current you see, you observe could only be due to the diffusion of the analyte through the electrical layers. So, this is known as diffusion current ilcovich examined various factors governing this diffusion current and he deduced an equation like this.

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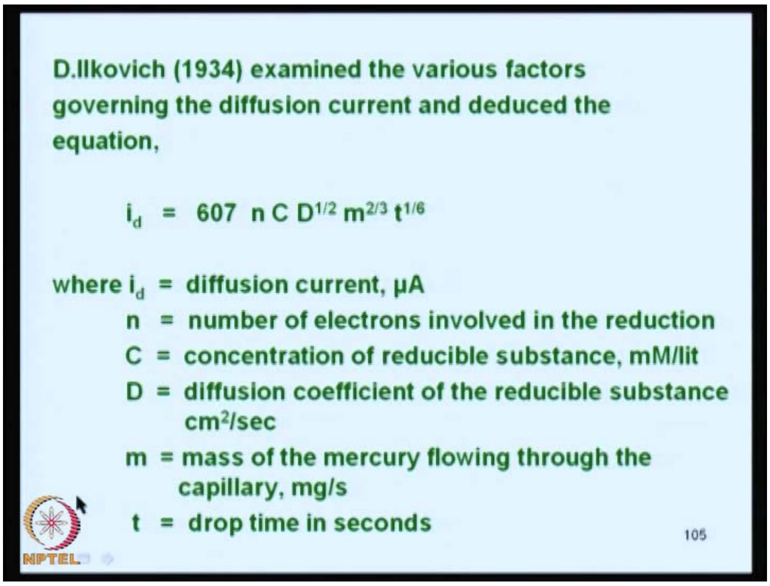

D.Ilkovich (1934) examined the various factors governing the diffusion current and deduced the equation,

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

where i_d = diffusion current, μA
n = number of electrons involved in the reduction
C = concentration of reducible substance, mM/lit
D = diffusion coefficient of the reducible substance cm^2/sec
m = mass of the mercury flowing through the capillary, mg/s
t = drop time in seconds

That is id is equal to 607 n C D raise to half, m raise to 2 by 3 and t raise to 1 by 6. So, this is the practical equation actually it should be 7 naught 4, but due to changes in the temperature and other factors 7 naught 4 gets changed to 6 naught 7.

And the id is known as diffusion current; id is the diffusion current measured in micro amperes and n is the number of electrons involved in the reduction that is its cadmium, if it is a cadmium ion 2 electrons are involved. So, n would be 2, if it is lithium ion it could be n is equal to 1, because that is only 1 reduced species and in case of aluminum etcetera n would be 3. And the C is the concentration of the reducible species that is in micro moles per liter in general and D is the diffusion coefficient of the reducible substance, the units are centimeters square per second and m is the mass of the mercury flowing through the capillary that is. So, many milligrams per second and t is the drop time.

So, we have the exponentials the diffusion current is raise to 1 by 2; that is square root of the diffusion current and mass of the mercury is raise to 2 by 3 and drop time that is the amount of time taken for the mercury to form and fall down that time duration is t and its raise to 1 by 6, we will not go into the derivation of this, but we will try to use this expression for the remaining discussion.

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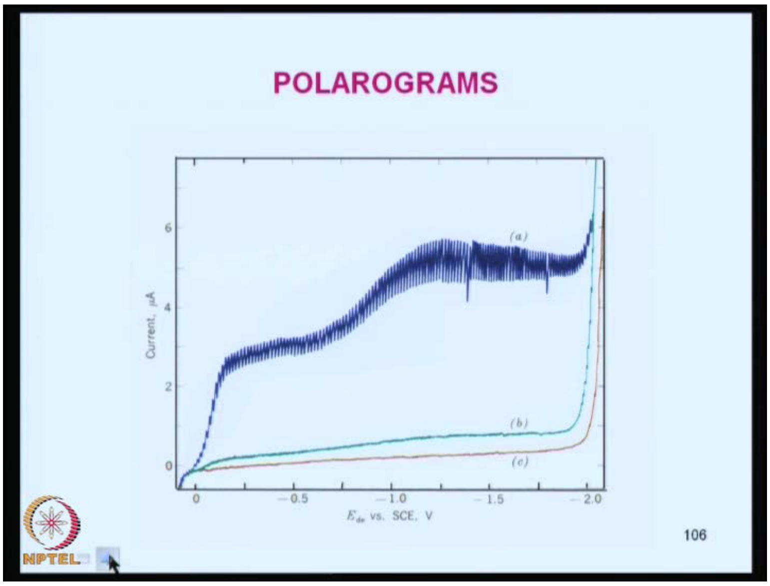

POLAROGRAMS

Now, you can see a polarogram here and here the residual current is like this and then another residual current is like this and then the polarogram is like this. So, the you can see there is one species is getting reduced here another species is getting reduced in this range and again it will reach the limiting current somewhere here and there is one more species that is getting reduced in this range. So, there are 3 species getting reduced what we have plotted means current versus, the potential versus measured against time saturated calomel electrode.

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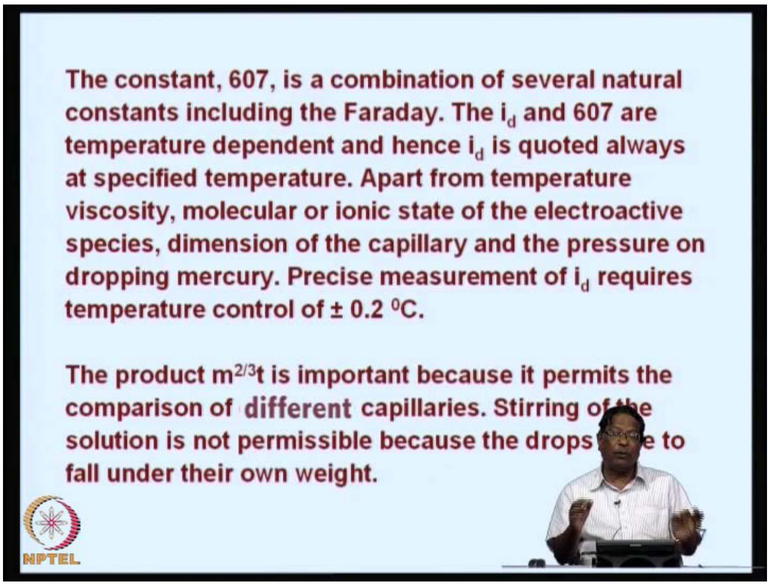

The constant, 607, is a combination of several natural constants including the Faraday. The i_d and 607 are temperature dependent and hence i_d is quoted always at specified temperature. Apart from temperature viscosity, molecular or ionic state of the electroactive species, dimension of the capillary and the pressure on dropping mercury. Precise measurement of i_d requires temperature control of ± 0.2 ^{0}C.

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

So, the constant 607 is a combination of several natural constants including the faraday, the id and 607 are temperature dependent and therefore, id is coated always at specified temperature let us say 25 degree centigrade 30 degree centigrade like that, apart from temperature the other factors are viscosity molecular and ionic state of the electro active species dimension of the capillary and pressure on the dropping mercury etcetera.

So, precise measurement of id requires temperature control of plus or minus 0.2 degree centigrade, the product m raise to 2 by 3 into t is important, because it permits the comparison of different capillary suppose you change the capillary from one specific diameter to another diameter then the product is important. So, that it will govern the actual diffusion current.

So, stirring of the solution is not permissible during the measurement, because the drops have to fall under their own weight. So, if you stir the solution drops will be drop time will be different. And now, I want to introduce you to a another concept known as polarographic maxima, sometimes current and voltage curves of the dropping mercury electrode exhibit pronounced maxima which are reproducible.

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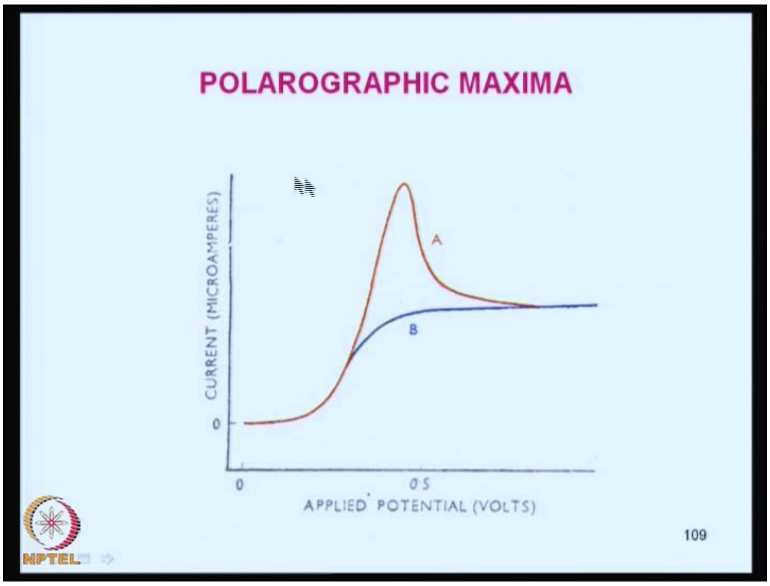

POLAROGRAPHIC MAXIMA

I do not know, whether I have a figure? Yes. Here, in this figure we can see that the normal residual current is like this sometimes in applied it is not actually a residual current, it is a polarogram, but you are seeing a sudden jump in the case of A compare to B this is unnatural, because the actual polarogram is B not A.

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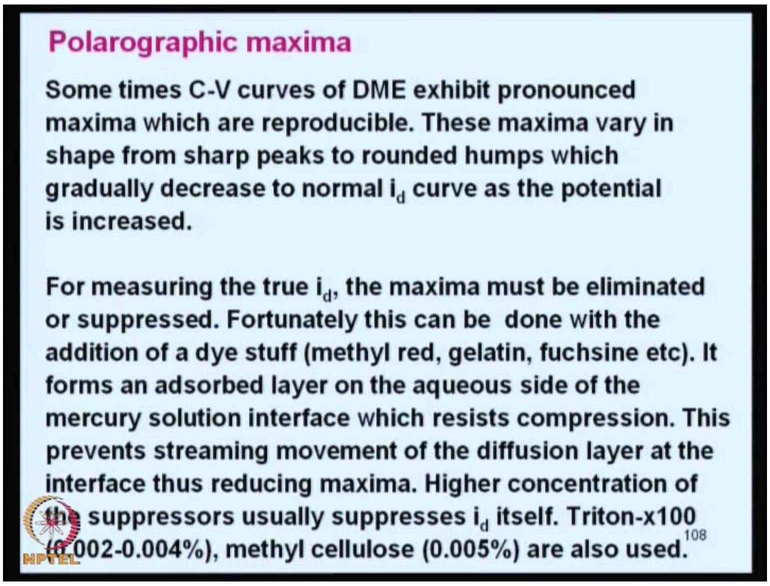

Polarographic maxima

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.

So, these sudden maxima sometimes they vary in shape from sharp peaks to broad rounded humps which gradually decrease to normal id curves as the potential increases. So, you may be misled that, there could be another reducible species which we do not know actually it is not. So, it is just a spurious maximum so far, measuring the true id the maxima must be eliminated or suppressed it should not be there in general.

So, fortunately we can do this, with the solution of a using a small amount of dye stuff, methyl red and then fuchsine etcetera. We can we can even use gelatin solution for that meter and what it does? Is it forms an absorbed layer on the aqueous side of the mercury solution interface which resist compression this prevents streaming movement of the diffusion layer at the interface thus reduce in the maxima.

So, maxima can be reduced either by using this methyl red or gelatin or fuchsine etcetera these are dyes actually organic dyes and they can reduce the maxima and you can do your normal operation of the polarogram determination. And higher concentration of the suppresser, suppose you use very high concentration then what happens is usually suppresses the id itself. So, it should not be too high and sometimes we use triton X 100 that is a surfactant in the concentration of 0.002-0.004 percent or you can use even methyl cellulose in 0.005 percent.

So, we now these polarographic maxima are basically spurious ones and they can be eliminated by using small quantities of the surfactants like triton accelerate or methyl red or fuchsine or gelatin itself etcetera. And you should not use very high concentration, because the diffusion current itself will get suppressed; that is not very ideal, because we want to determine the concentration of the unknown substance.

So, what is there to know more about polarogram, what is left is half wave potential since the solution studied polagraphically are very dilute. We can assume that the activity of the cation does not differ from its concentration in the bulk; that means; its activity could be most probably one, because the solutions are very dilute that statement we have made when the concentrations are very low activity is equal to concentration; because activity coefficient would be one.

So, we assume that the concentration of of the reducible species, even in the mercury drop is very low and its activity remains one. So, that we can talk about concentrations in general. So, polarography is basically concerned with the electrode reactions at the indicator electrode that is DME involving electron transfer, it has to have an electron transfer between the electrode and the analyte. During the reduction of the oxide electrons leave the cathode reacting the solution with the formation of the equivalent amount of the reluctant. Similarly, during the oxidation of a reluctant at the anode surface electrons pass from solution to the electrode and form equivalent of the oxidant.

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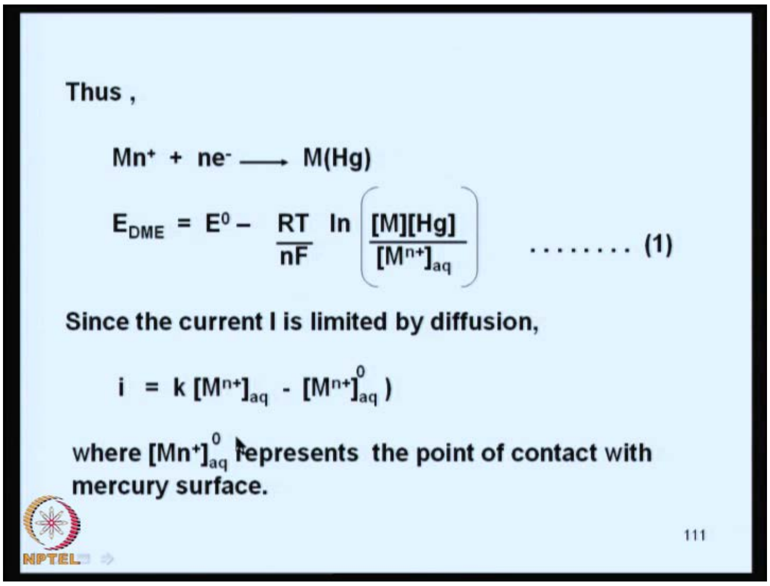

Thus ,

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

$$E_{DME} = E^{0} - \frac{RT}{nF} \ln \left(\frac{[M][Hg]}{[M^{n+}]_{aq}} \right) \quad \text{........ (1)}$$

Since the current I is limited by diffusion,

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

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

So, look at this reaction, I am going to write a very simple reaction Mn plus plus ne minus going to M Hg that is a metal ion with M plus that is in the oxidation state going to reacting with electrons to form and to get reduced; and that reduced metal is in contact with mercury here that is what I am going to write in this equation.

So, I can write an expression known as E DME that is potential at the dropping mercury electrode is nothing but, the standard reduction potential E naught minus RT by nf ln metal into mercury concentration divided by the and reduced species that is Mn plus. Since, the current i is limited by the diffusion, I can write an expression like this that i is equal to k into Mn plus aqueous minus Mn plus with a subscript 0 aqueous; that means, this is that the electrode. So, the actual concentration between the reduced species and at the reduced at the mercury electrode would be a product of a proportional p constant and the current the current is the proportional t constant of multiplied by the difference between these two. So, where Mn 0 aqueous represents the point of contact with the mercury surface.

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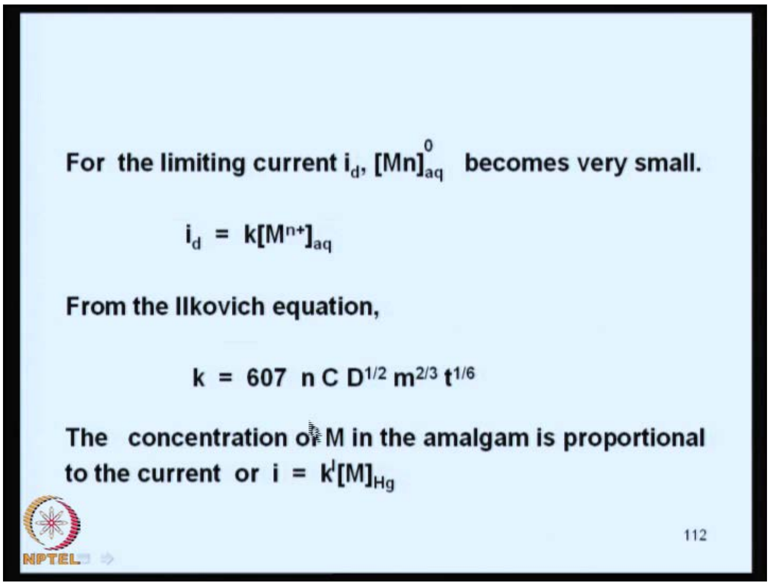

For the limiting current i_d, $[Mn]^0_{aq}$ becomes very small.

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

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 $i = k^{I}[M]_{Hg}$

Similarly, for the limiting current the concentration of mercury at the point of contact becomes very small; that means, it is almost negligible. So, in this equation in the previous equation, I am going to neglect this and then write only the remaining part here id is equal to M k into Mn raise to, m raise to n plus aqueous, because other part I am going to neglect, from the ilkovich equation k is equal to this is a very standard expression the concentration of m in the amalgam is proportional to the current i.

Or now, I am going to talk about, the concentration of the metal in the amalgam that is proportional to the current i is equal to K dash, I am going to, I am not going to write k here, but I am going to write K dash into metal on mercury that is what I have written here.

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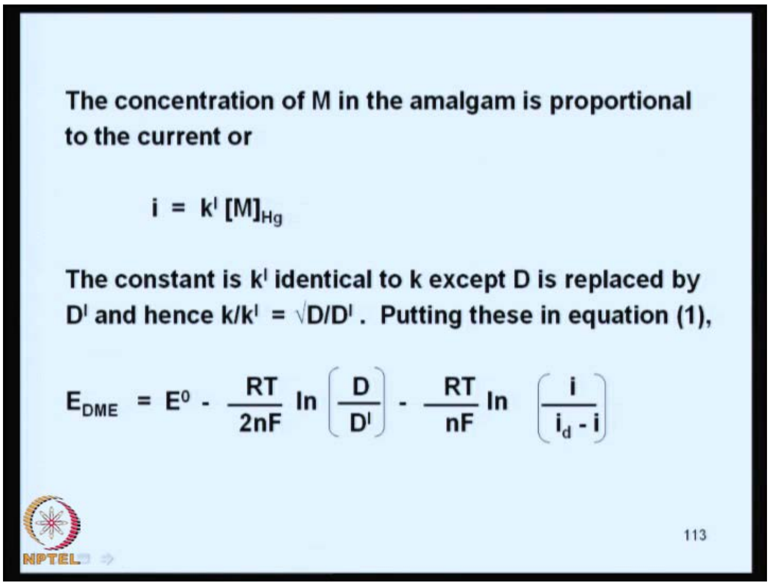

The concentration of M in the amalgam is proportional to the current or

$$i = k^{I} [M]_{Hg}$$

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

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

So, the concentration of m in the amalgam is also proportional to similar expression K dash into M Hg. The constant K dash is identical to k except D is diffusion coefficient is replaced by D dash and K by K dash would be you can show it by simple derivation that K by K dash is equal to square root of D by D dash; these equations I am going to put it in equation number one that is in this equation E is equal to E naught minus RT by nF.

And what I have is E DME is equal to E naught minus RT by nF, because it is cadmium it is 2. RT by nF ln the we known because it is square root it is the I have taken it here 2, and then ln D by D dash, I am going to separate the diffusion terms here and then instead of the concentration I am going to write this i and id minus i, RT by nF ln i upon id minus i.

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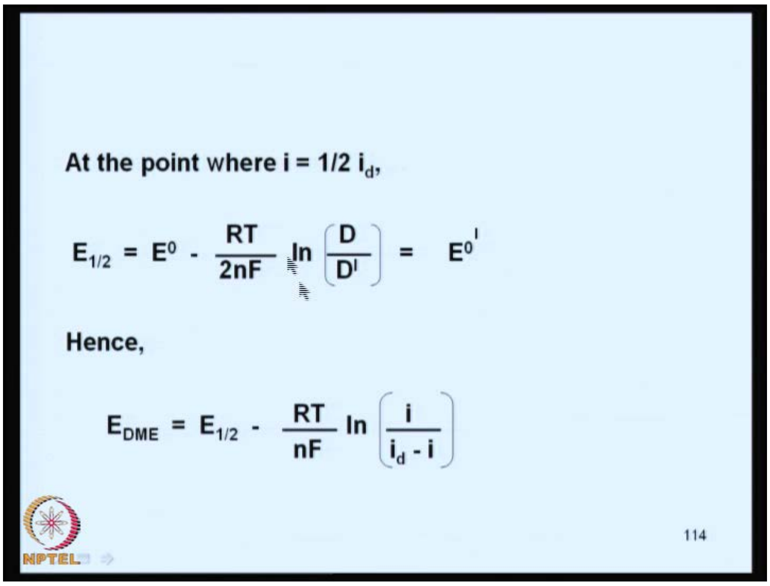

At the point where $i = 1/2\ i_d$,

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

Hence,

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

So, if we process this equation further at the point, where i is equal to id by 2, go back to this equation i is equal to id by 2; that means, your id here, I am going to write id by 2 that is id minus id by 2, here id by 2, id minus id by 2 is id by 2 and here it is id by 2; that means, it log of 1 it becomes 0.

So, E DME is equal to this and when i is equal to id by 2, the potential at E half is actually E naught dash. Here, it is E half is equal to E naught minus RT by 2 nF ln D by D dash that should be something similar to standard reduction potential except modified by the contribution from these terms. So, E DME is nothing but, E half minus RT by RF ln of id by minus id by id minus i.

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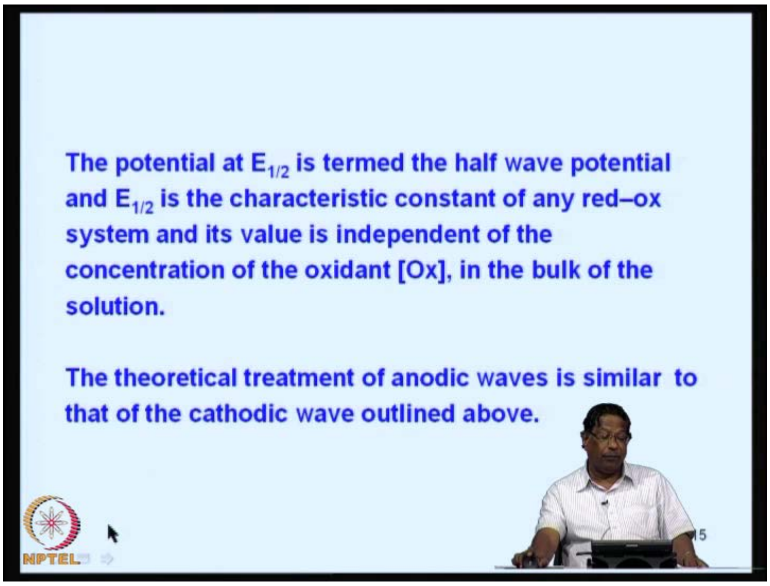

The potential at $E_{1/2}$ is termed the half wave potential and $E_{1/2}$ is the characteristic constant of any red–ox system and its value is independent of the concentration of the oxidant [Ox], in the bulk of the solution.

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

The potential at E half is termed as the half wave potential and E half is the characteristic constant of any red-ox system; that is it could be an cadmium ion to cadmium metal or nickel ion to nickel metal or any of the reduction standard reduction systems what we have studied in our electro chemical series and its value is independent of the concentration of the oxidant in the bulk of the solution, the theoretical treatment so far, what we had that is for cathodic treatment. Now, let us consider the anodic wave where mercury is also getting reduced and you can prove that a similar theoretical treatment works in the case of cathodic wave.

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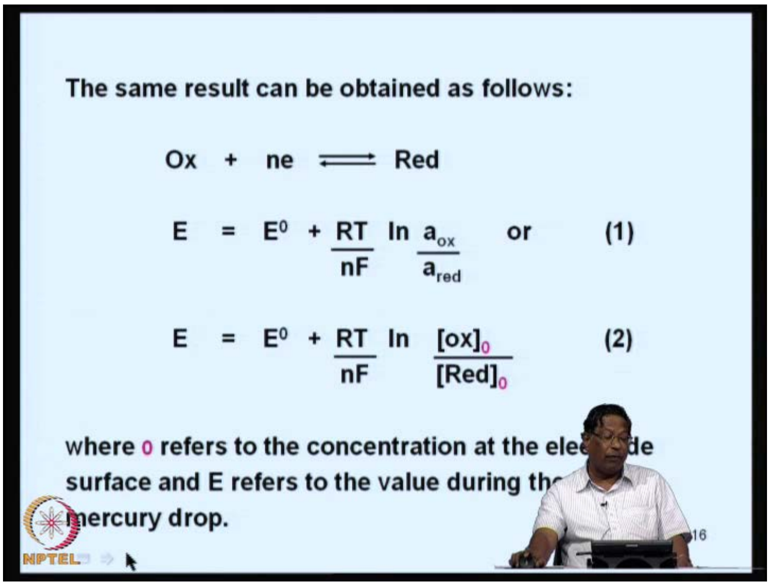

The same result can be obtained as follows:

$$Ox + ne \rightleftharpoons Red$$

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

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

where 0 refers to the concentration at the ele de surface and E refers to the value during th ercury drop.

So, the same result we can write it like this Ox the same derivation, I am going to do it in a slightly different fashion now that is Ox plus ne is equal to reductant oxidant plus n number of electrons that gets n electrons goes to reduced species. E is equal to E naught plus RT by nF a oxidant this is the form in which we are more familiar, a oxidant by a reductant and E is equal to E naught plus RT by nF ln oxidant divided by the reductant. Where 0 refers to the concentration at the electrode surface and E refers to the value during the life of a mercury drop.

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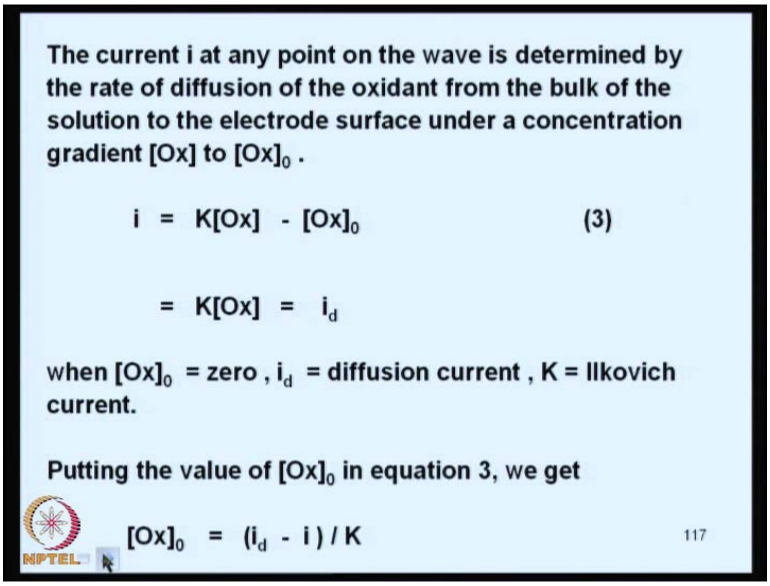

The current i at any point on the wave is determined by the rate of diffusion of the oxidant from the bulk of the solution to the electrode surface under a concentration gradient $[Ox]$ to $[Ox]_0$.

$$i = K[Ox] - [Ox]_0 \qquad (3)$$

$$= K[Ox] = i_d$$

when $[Ox]_0$ = zero , i_d = diffusion current , K = Ilkovich current.

Putting the value of $[Ox]_0$ in equation 3, we get

$$[Ox]_0 = (i_d - i) / K$$

So, the current i 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 and under a concentration gradient of Ox to Ox naught. So, as usual we can ignore the contribution from Ox naught that is on the mercury surface and you can write K Ox is equal to id; id is equal to K Ox and when Ox naught is 0, id is simply diffusion current and K is the ilkovich current putting this value of Ox naught in the equation three, what you get is Ox naught is equal to id minus I divided by K.

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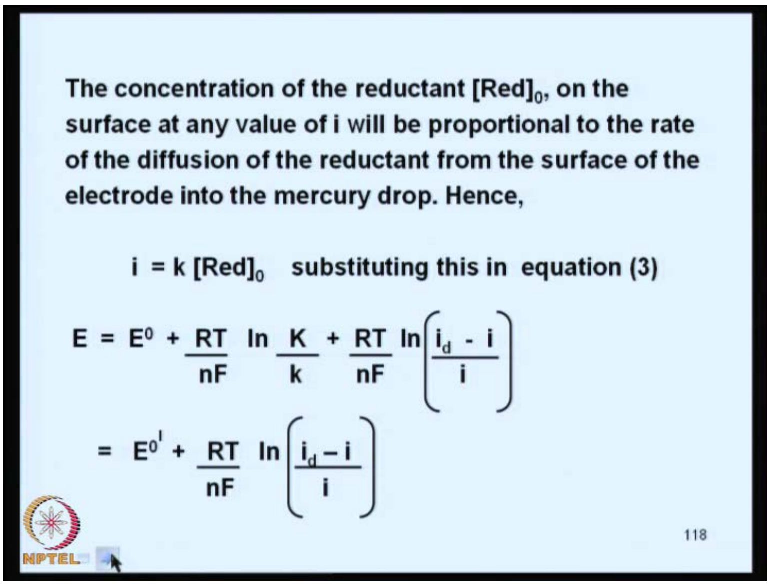

The concentration of the reductant $[Red]_0$, on the surface at any value of i will be proportional to the rate of the diffusion of the reductant from the surface of the electrode into the mercury drop. Hence,

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

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

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

Very simple derivations I am going to give you now, the concentration of the reductant we can also also we can consider now on the surface at any value of i should be proportional to the rate of the diffusion of the reductant from the surface of the electrode E to the mercury drop.

So, I can write i is equal to k into reductant at the mercury surface. So, E, I can write now, I have reduced species and oxidize species in the previous slide. So, I am going to put these values now in the same equation. So, E naught plus RT by nF ln K by k that is one is capital and another is small just to differentiate between the reduction reduced species and oxidized species plus RT by nF ln of id minus i up on i.

So, if you you can again as usual you can combine this ln K dash k capital K by small k it is only a numerical constant which will effect only the E naught dash value. So, I am going to write it as E naught dash which includes this number now, plus RT by nF ln of id minus i up on i.

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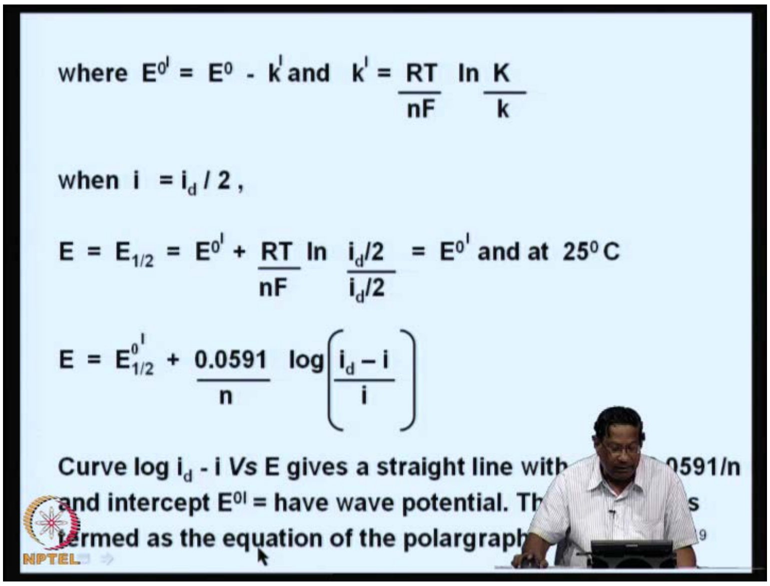

where $E^{0'} = E^0 - k'$ and $k' = \frac{RT}{nF} \ln \frac{K}{k}$

when $i = i_d / 2$,

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

$$E = E^{0'}_{1/2} + \frac{0.0591}{n} \log\left(\frac{i_d - i}{i}\right)$$

Curve log i_d - i *Vs* E gives a straight line with 0591/n and intercept $E^{0'}$ = have wave potential. Th s termed as the equation of the polargraph

So, when E naught dash is equal to E naught minus K dash and K dash would be RT by nF ln k by K dash.

So, again as usual I do the exercise when i is equal to id by 2, here I am going to get E naught dash at the this this expression reduces to 1, log of 1 is 0. So, E is equal to E naught dash. So, E is equal to E half at any other value E naught dash half plus 0.0591 up on n this expression you are very familiar now and to multiplied by log of id minus i up on i.

So, the curve log of id minus i versus E gives a straight line, if you plot id minus i versus E, you would get a straight line with a slope of 0.0591 divided by n. So, this number the intercept could give you E naught dash, where it cuts the X axis and that is the half wave potential this equation is termed as the equation of the polarographic wave.

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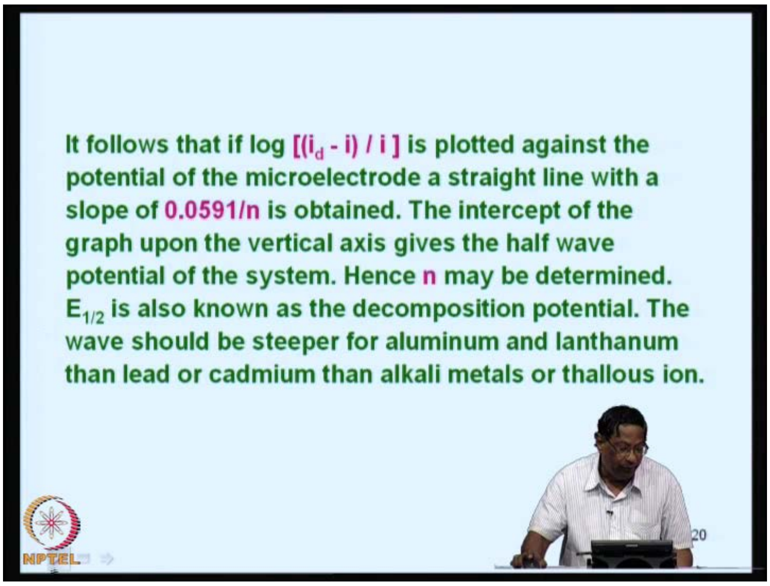

It follows that if log $[(i_d - i) / i]$ is plotted against the potential of the microelectrode a straight line with a slope of 0.0591/n is obtained. The intercept of the graph upon the vertical axis gives the half wave potential of the system. Hence n may be determined. $E_{1/2}$ is also known as the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

It follows therefore, that if log of id minus i by i is plotted against the potential of the micro electrode a straight line graph should be obtained with a slope of 0.0591 variant divided by n. The intercept of the graph upon the vertical axis gives the half wave potential, I am just repeating for your clear understanding and hence from the slope we can determine the number of electrons involved in the reduction of the species at the cathode that is ne half is also known as decomposition potential, because at that potential you can expect the material to reach the electrode easily.

The wave should be steeper for higher valance electrons, higher valance elements like aluminum because it involves one should be 3 and for lanthanum it is 3, cadmium and led or cadmium it is 2, for alkali metals are halloos ion or lithium ion etcetera it should be 1. So, the steepness of the curve is also dependent upon the number of electron.

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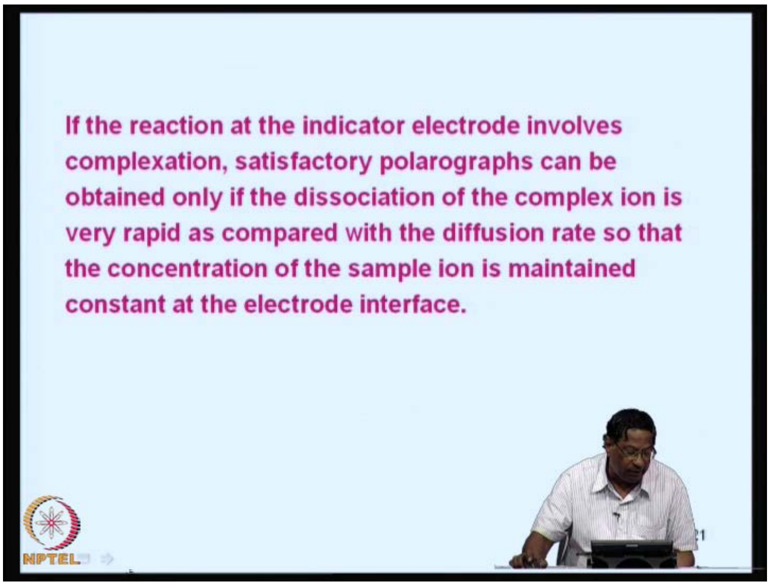

If the reaction at the indicator electrode involves complexation, satisfactory polarographs can be obtained only if the dissociation of the complex ion is very rapid as compared with the diffusion rate so that the concentration of the sample ion is maintained constant at the electrode interface.

Therefore, if the reaction at the indicator electrode involves complexsation apart from just normal reduction then satisfactory polarograms can be obtained only if, the disassociation of the complex ion is very rapid there is no compromise on that front as compare with the diffusion rate. So, that the concentration of the sample ion is maintained constant at the electrode surface that is a very important concept otherwise you will not be able to do the complex analysis.

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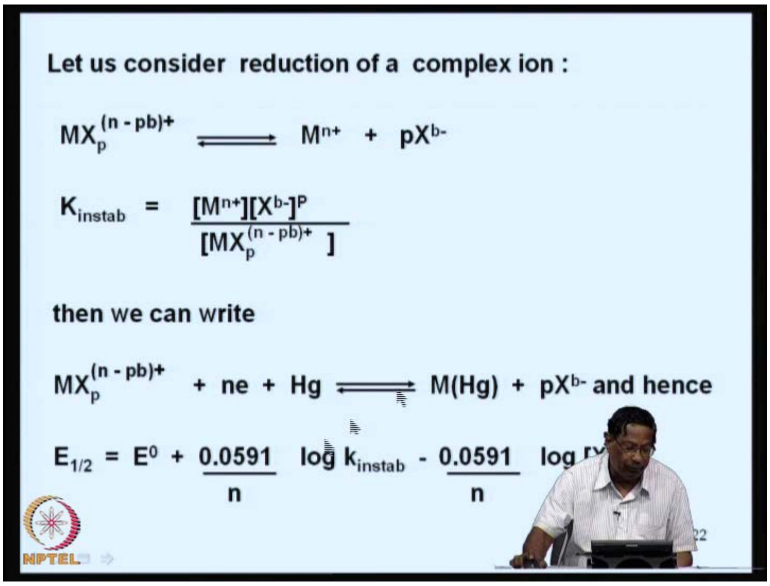

Let us consider reduction of a complex ion :

$$MX_p^{(n-pb)+} \rightleftharpoons M^{n+} + pX^{b-}$$

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

then we can write

$$MX_p^{(n-pb)+} + ne + Hg \rightleftharpoons M(Hg) + pX^{b-} \text{ and hence}$$

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

Unless the complex also gets reduced immediately and moves into the bulk of the bulk of the system bulk of mercury drop. so, for now you we can consider a complex ion then the complex ion is represented as M Xp raise to n minus pb plus going to Mn plus and p Xb minus; this p Xb minus is the ligand and p is the number of moles and m minus pb is the charge on the complex ion for this, I can write an instability constant; k instability is equal to the products on the right hand side divided by the left hand side; that is Mn plus into X raise to b minus whole raise to p divided by MXp n minus pb plus, this is the very simple expression for all chemistry students would be knowing this expression.

Then we can write the equation like MXp raise to n minus pb plus plus ne plus Hg going to metal getting reduced to the metal on mercury and releasing the legend pX raise to b pX raise to b minus and hence E half we can incorporate, as the K instability constant plus remaining part that is minus 0.0591 up on n into log of X raise to b minus whole raise to p. We will continue our discussion on the complexsation reactions in the polarography in the next class. .