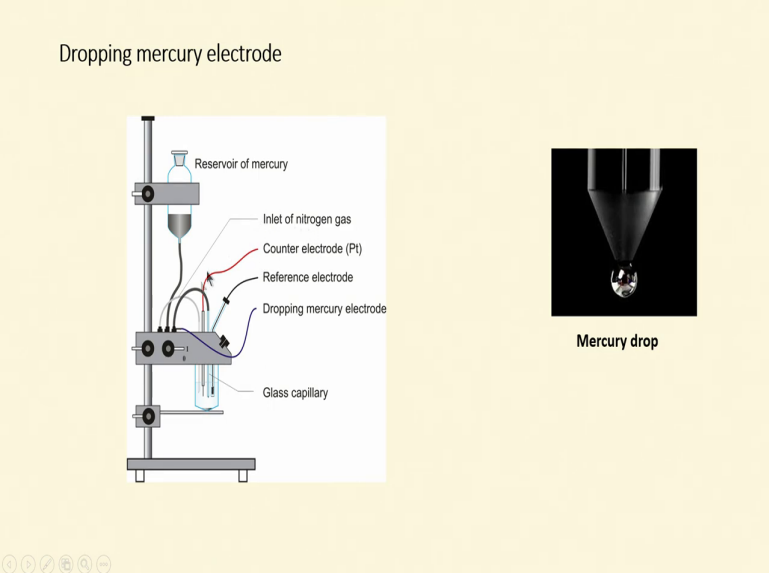
Electrochemical Technology in Pollution Control
Dr. J. R. Mudakavi
Department of Chemical Engineering
Indian Institute of Science, Bangalore

Lecture – 17
Voltametry and Polarography 2

Greetings to you, welcome to my next class on Polarography this is almost the last of the analytical techniques I will be teaching you. And in the last class I had explained to you that if I take a sample which is not polarizable and which gets reduced at the electrode in presence of a strong inert electrolyte. And I have a large mercury drop a small mercury drop as a falling electrode and a large mercury crescent system as anode I have a dropping mercury electrode.

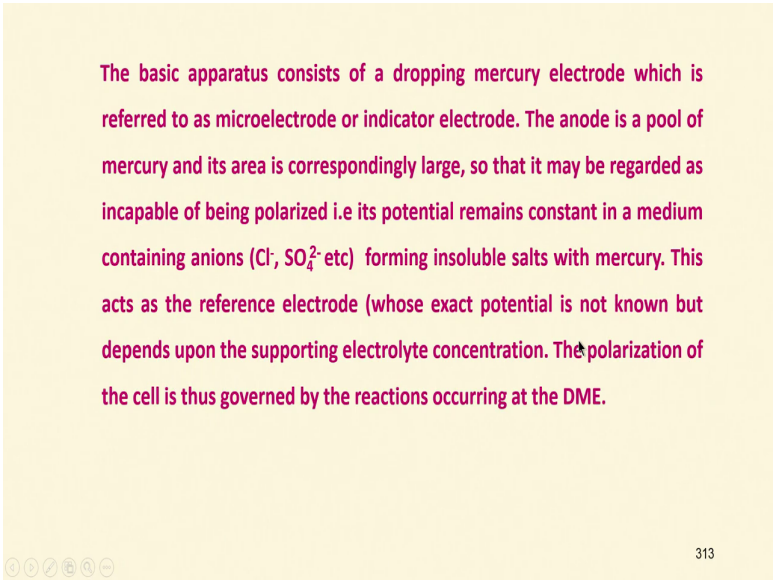
(Refer Slide Time: 01:20)



So, I had shown you this picture of the system, this is a beaker containing the analyte there is a mercury pool at the bottom and the mercury. I can also have some sort of counter electrode,

but dropping mercury electrode is the important one here. And I have a I can have a reference electrode or mercury anode etcetera in inlet of nitrogen gas and all this is the dropping mercury electrode, what I had shown you in the last class.

(Refer Slide Time: 01:49)

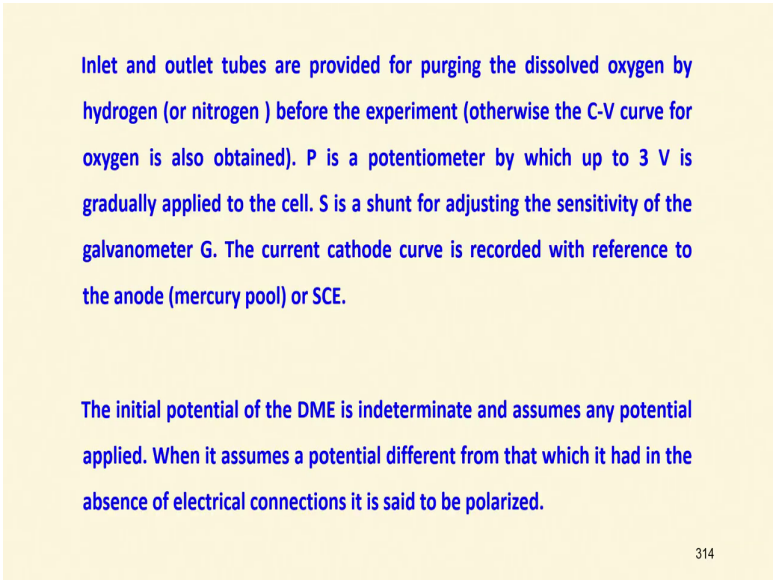


So, the basic apparatus consists of a dropping mercury electrode, which is referred to as microelectrode or indicator electrode. So, the anode is a pool of mercury as I have already told you a number of times and its area is correspondingly large. So, that it may be regarded as in capable of being polarized; that means, its potential remains constant in a medium containing anions.

What are the anions? Chloride, sulphate, etcetera very simple systems. So, the these anions form insoluble salts with mercury. So, this acts as a reference electrode that is the mercury pool their exact potential is not known, but it depends on 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, why? Because at the anode nothing happens basically.

(Refer Slide Time: 03:14)



So, I have two systems what one inlet and outlet tubes provided for purging the dissolved oxygen by hydrogen or nitrogen before the experiment. Sometimes what happens you know, the oxygen dissolved in the sample that also gets reduced. So, we have to remove all the oxygen present in the solution. Normally, in a sample solution, the concentration of dissolved oxygen is about 6 milligrams per litre that is quite high from polarographic analysis standards. So, the here in polarography we are determining about ppm level of the pollutants. Whereas, if it is in milligrams that will be milligrams in about 10 ml or 15 ml of the substance that will be concentration will be at least about 1000 or 10000 ppm.

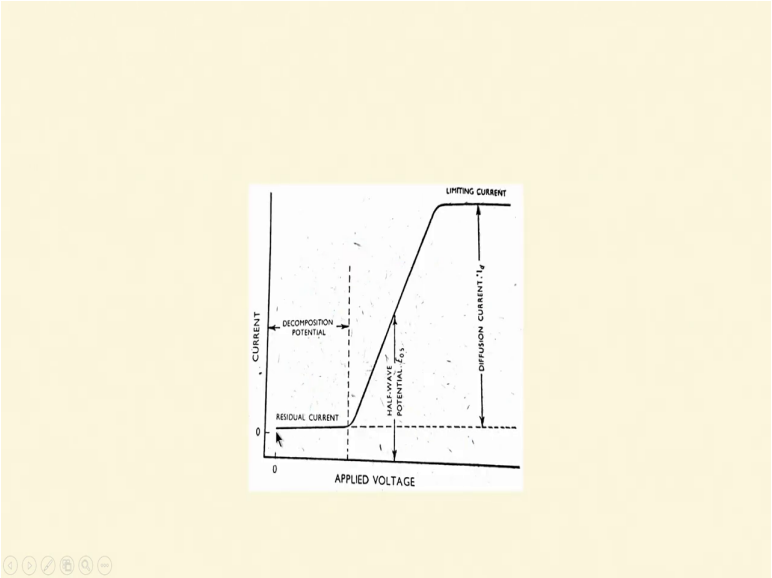
So, if oxygen is there in the system, the oxygen will get reduced and the you will not see much of the current voltage curve corresponding to the analyte ion therefore, it is very important for us to remove the oxygen from the system. This we do it very simply you pass hydrogen gas which is having lower solubility and keep on bubbling through the given solution or you can pass nitrogen also.

So, I can after doing that I have a I need a potentiometer which can give me reduction potential or it can give me I can increase the potential from 0 to 3 volts. We do not need more than that because most of the standard reduction potentials of all metals and ions are less than 3 volts.

So, 0 to 3 volts should be fine for routine analysis and it is gradually applied to the cell. So, I can also increase the shunt, shunting capability that is adjusting the sensitivity of the galvanometer. So, the current cathode curve is recorded with reference to the anode or that is anode is mercury pool. Otherwise, you can use a standard calomel saturated calomel electrode also you can record. The current voltage curve that is not important what is important is reduction at the dropping mercury electrode that is most important the anode can be anything the other reference electrode.

So, the initial potential of the dropping mercury electrode is indeterminate because nothing is happening there. So, we cannot determine what is the actual voltage there. So, it assumes any potential we apply, you must understand this point initial potential of the dropping mercury electrode is indeterminate. And it assumes any potential that is applied to the system. When it assumes a potential different from what it had been in the absence of electrical connections, it is said to be polarized this I have explained to you earlier number of times.

(Refer Slide Time: 07:12)



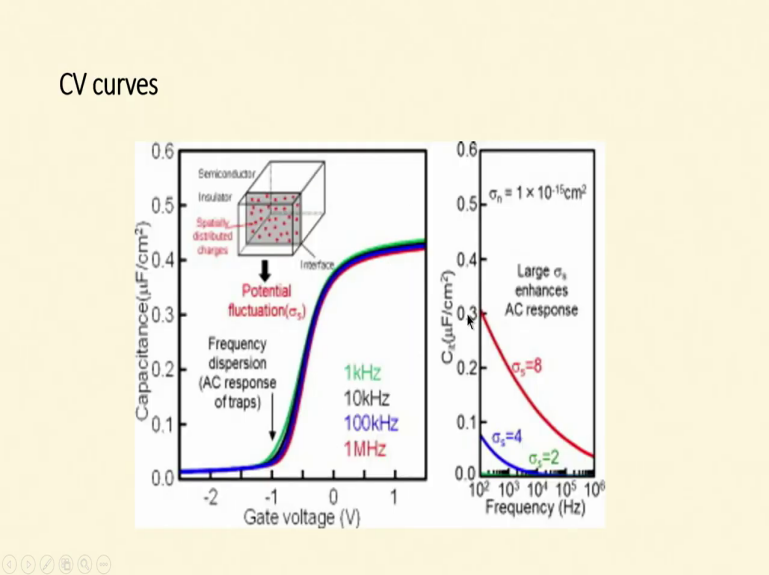
So, this is the current voltage curve. So, here what I have I measure the current and here I increase the voltage, here I have some system a let us call this a, let us call this b, let us call this c and let us call this d. So, here what I have initially I keep on increasing the voltage, but current will not increase because bulk of the current is being carried by the supporting electrolyte, but supporting electrolyte is not getting reduced, at any of the voltage we apply that is not within our range. So, at some stage I will reach the decomposition potential of the analyte element.

So, once the decomposition potential is reached, then that analyte will be able to reach the microelectrode and get reduced the moment it gets reduced, there will be the potential will become instead of indeterminate it becomes determinate. So, it I can start measuring. So, there will be a certain amount of current passing through depending upon the concentration of the metal ion that is getting reduced and then it keeps on increasing. And then at some stage all of

it is converted and there is no more metal to be reduced. So, current will virtually stop increasing and it will assume a constant value.

So, here I have I have marked a different areas, one is a decomposition potential and here it is known as residual current a little bit of current will still be flowing. And this is a midpoint of this steep curve that is known as half wave potential E naughts and this is known as the difference between the initial residual current and the limiting current is known as diffusion current ok.

(Refer Slide Time: 09:32)

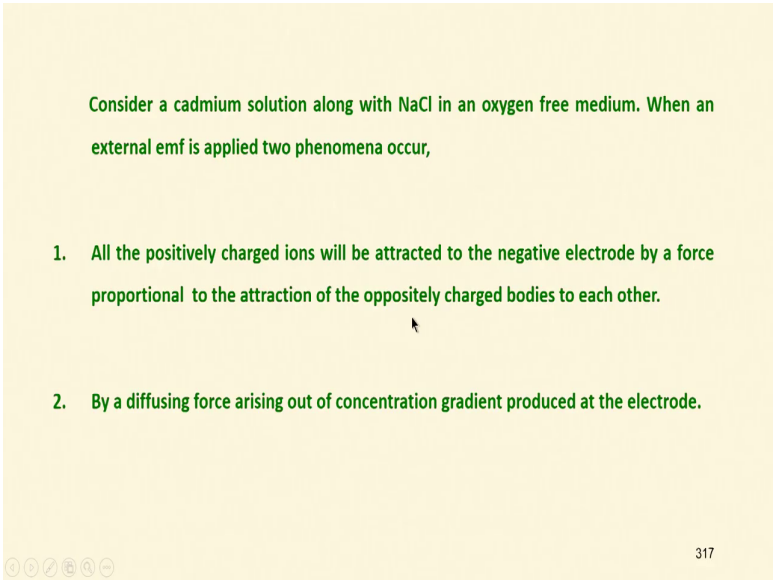


So, this is the basic arrangement of current voltage curve under the system. Here I have a semiconductor insulator and then distributed charges are there. And I can start the voltage from this point that is capacitance almost 0 0 and then slowly it will increase and then it will go up and it will reach a standard saturated value.

So, I can increase the gate voltage and the frequency also. Frequency I can increase from 1 kilo Hertz to 10 kilo Hertz 100 kilo Hertz and 1 million kilo Hertz also I can increase. And the concentration frequency curve what I get it will be something like this sigma s is equal to 4 and this is 2 this will be 8 and this is where it enhances the AC response.

So, this is slightly more of the electronic side not to worry, but the basic theory remains the same. That is initially there will not be any increase in the current how you give the voltage and current is your this thing you can either use a capacitor or through a an applied voltage through instrument.

(Refer Slide Time: 11:14)



So, let us consider a cadmium solution along with sodium chloride in an oxygen free medium ok. Assume that I have passed all the air removed all the oxygen. So, when I now what I have? I have 2 solutions; one is sodium chloride another is cadmium solution. And sodium

chloride is an indifferent electrolyte that is it does not take part in any chemical reaction it does not get reduced it does not get oxidized. And the other one cadmium solution can get reduced to cadmium metal at the appropriate voltage, that is its standard reduction potential ok.

So, when I apply an external emf two phenomena occur. So, what are the two phenomena? One is 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 positive will go to negative, negative will go to positive that is what I have written here ok. So, all the you positively charged ions will be attracted to negative by force proportional to the attraction of the oppositely charged bodies. And there will be another diffusive force arising out of concentration gradient produced at the electrode.

This is what I was trying to tell you. So, I have large quantity of NaCL; everything is moving all the sodium ions are moving towards electrode. Cathode all the sodium chloride ions are moving towards anode, where the cadmium will go? Cadmium will be moving towards cathode, but none of these things are able to get reduced at the cathode. So, how will the cadmium reach the electrode? I will give a pause about 3 seconds; you just have to think that the large number of sodium ions are moving towards cathode and very small number of cadmium ions also moving towards cathode.

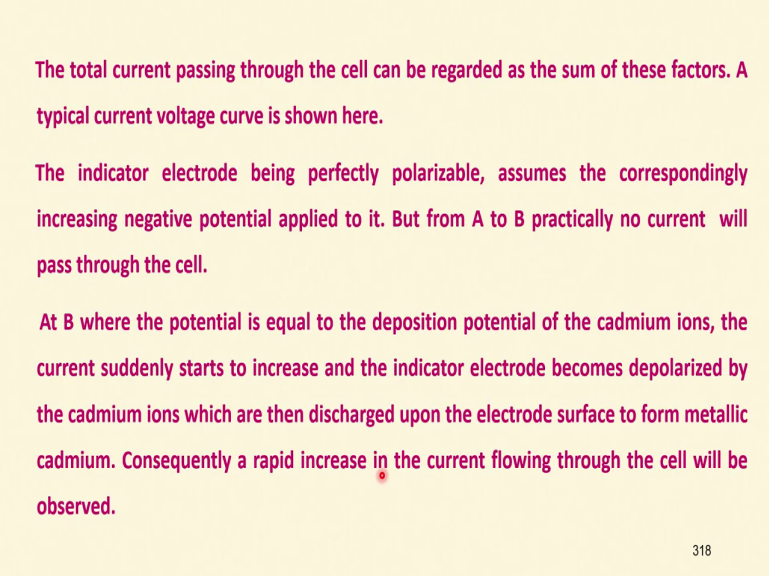
How will the cathode cadmium ions reach the electrode? At the applied voltage they are not reaching, but how will the cadmium ions will feel, they feel like a minority, their majority of the people are sodium ions cadmium ions are a minority they want to reach the other side they have to struggle among the large number of people who are gathered in the middle they are not doing anything.

Imagine, an accident place where large number of people are gathering and another 1 or 2 people are trying to find out what is happening at the accident spot, they are not able to reach because there are large number of people.

So, the cadmium ions will move to by diffusion, not through physical movement, but through a slowly diffusing, diffusing, diffusing movement. So, there are two ways; one is direct

movement another is diffusion movement. So, the diffusion force arising out of the concentration gradient is produced around the electrode.

(Refer Slide Time: 15:24)



So, the total current passing through the cell, can be regarded as the sum of these factors. The total current whatever I get little here in this residual current area whatever I am getting is the sum of the electrostatic attractive force some diffusive force. So, both of them together producing only this much of current ok.

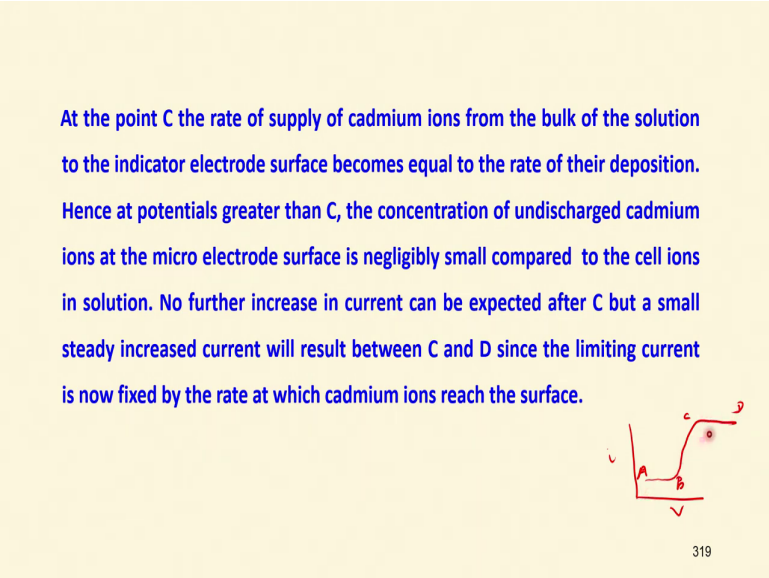
So, the indicator electrode is perfectly polarizable; that means, it assumes the correspondingly increasing negative potential applied to it. But from A to B first portion of the previous cell, this one there is practically no current moving slight increase is there, but very less negligible, is not it? So, the indicator electrode is all we say it is polarizable it assumes the voltage, but

not the current. So, from the first portion practically no current will be passing through the cell.

Then at the point B, again I should go back and show you that figure here, at the this is the point B I have not written here, but this is their point a b c and d at the point B what happens? Potential is equal to the deposition potential of cadmium ions ok. Now, sodium ions are no more capable of reaching the electrode, but cadmium ions are not able to reach through standard attractive force, but they are reaching the electrode through a diffusive force. And these cadmium ions are capable of getting reduced; that means, they have reached the we have already reached the deposition potential of the cadmium ions.

So, the current starts to increase why? Because they are able to break through the cauldron of sodium ions and reach the electrode now ok. So, the current the moment it reaches the electrode it will get reduced electron transfer will take place as usual. And the mercury is there and cadmium is there, cadmium and mercury will form some sort of amalgam it will go into the drop mercury drop and what happens to the current? Current will increase by that amount. So, the cadmium ions are discharged upon the electrode surface from the metallic cadmium. And then consequently rapid increase in the current flowing through the cell will be observed. That is what you we have seen here correct.

(Refer Slide Time: 19:14)

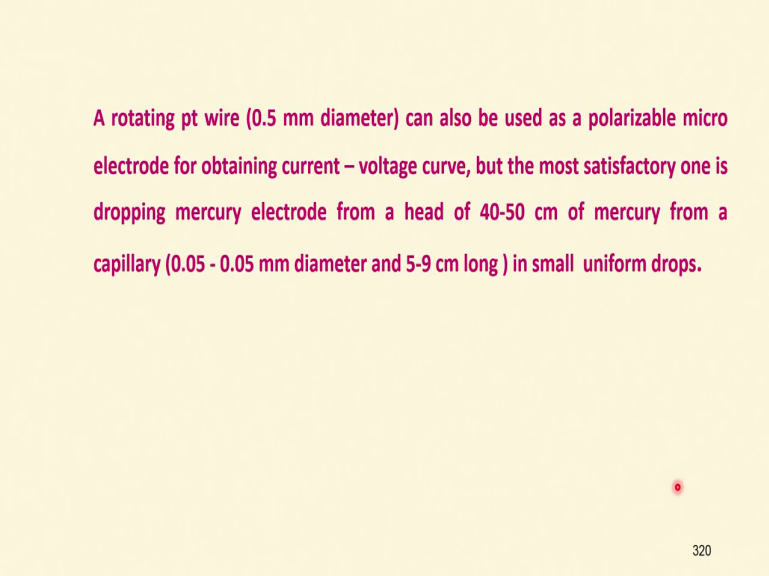


Now, here rapidly increasing current, will come here after that what happens? At the point c that is at the top of the curve, I can I will draw a figure here this is B this is A this is C this is D. So, at the point C, the rate of supply of cadmium ions forms the bulk of the solution to the indicator electrode surface become equal to the rate of deposition here it is voltage here it is current i. So, from here the cadmium ions will start reaching the electrode and getting radiance current will keep on increasing.

At this point C the rate at which cadmium comes and gets deposited, gets reduced is equal to the cadmium that is moving into the microelectrodes surface. So, no further increase in current can be expected after C; but a small steady increase in current will result between c here also there will be a slight increase. Since the limiting current is now fixed by the rate at which

cadmium ions reach the surface. So, there will be some slight increase as between A and B and C and D, but the sharp increase will be there between B and C.

(Refer Slide Time: 21:03)

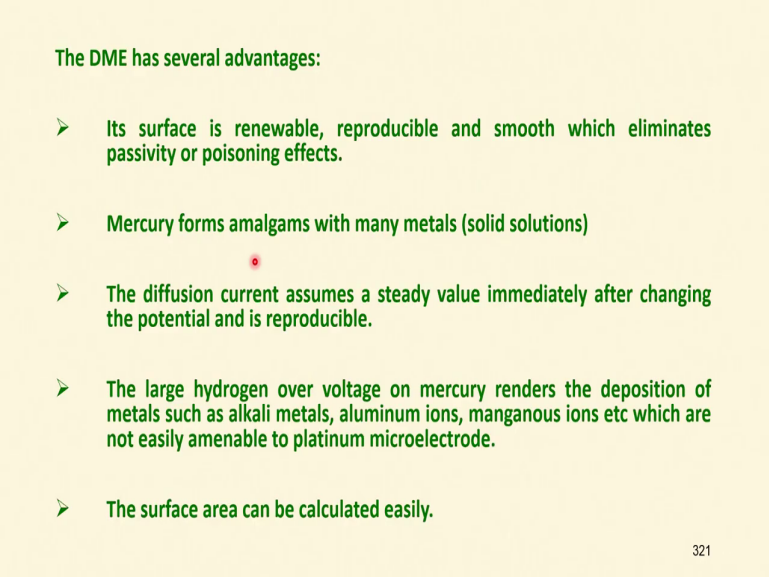


So, a rotating platinum wire also I can use as a polarizable microelectrode for obtaining the current voltage curve. But the most satisfactory one is dropping mercury electrode from a head of about 40 to 50 centimeter of mercury from a capillary of 0.05 mm dia and 5 to 9 centimeter long in small uniform drops. So, what I am trying to say to you is this reaction cadmium reduction can be carried out by a rotating platinum wire electrode and a polarizable microelectrode. Or I can use the dropping mercury electrode itself, I can replace dropping mercury electrode with a rotating platinum wire electrode.

The platinum wire electrode is should be approximately 0.5 mm dia and dropping mercury electrode should fall from 40 to 50 centimeter height. And then the capillary should be having

a diameter of about 0.5 to 0.05 approximately this can be 0.1 also and it should be 5 to 9 centimeter long capillary through which mercury will be falling continuously. Here it can I can increase it till 05 to 05 is not correct it should be 0.07, 0.1 something like that.

(Refer Slide Time: 22:53)



So, why dropping mercury electrode at all? There is a requirement of producing a reproducible dropping mercury and mercury has got advantages. So, when a drop is forming from the capillary, the surface gets renewed every time there is no chance of poisoning of the electrode fresh surface is available every time. It is renewable, it is reproducible, it is smooth and it eliminates passivity or poisoning effects of the normal electrodes what we come across in day to day life.

Normally, in any laboratory you buy any equipment containing electrodes, after sometime the response becomes sluggish and then after sometime it may corrode. So, none of those things

will happen, if I have a mercury dropping from an electrode from a hanging mercury drop through a capillary; because once the drop is gone no more poisoning can take place that is number 1 advantage.

Number 2 mercury has got a great capacity, to react with many metals. So, they form solid solutions they can form amalgams, mercury amalgam is known since 100 of years and used in myriad problems. And then the third one is the diffusion current assumes a steady value immediately after changing the potential and is reproducible what is the point if I change the voltage I keep on increasing the voltage, but it does not take there is a delay. So, what is the point? So, I have to wait until that takes place.

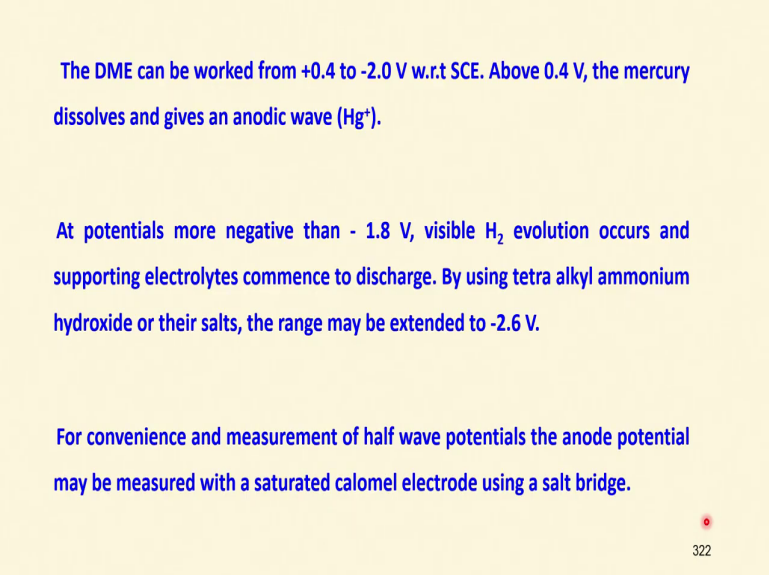
Instead of that, mercury dropping mercury electrode assumes a steady value immediately after changing the potential from 0.1 I do 0.12; it changes to 0.12 I make it 0.15 it will change to 0.15 like that any change that is introduced into the circuit. If I have a mercury electrode, that change will be automatically registered and assumes a steady value immediately that is one more advantage. And then there is a hydrogen voltage large hydrogen overvoltage on mercury it renders the deposition of metals. Such as alkali metals aluminium ions manganous ions etcetera which are not easily amenable for platinum electrode.

If I use platinum electrode, I cannot use alkali metals why? Sodium hydroxide will attack the aluminium it will dissolve. So, very standard chemical reaction and aluminium ions I cannot use and manganous ions I cannot use. So, these are not easily amenable to platinum mercury electrode they will get attracted and poison the electrode; whereas with mercury there is no chance for poisoning. And another thing is if I know the capillary and if I know the weight of the mercury assuming that the cap from the capillary a spherical drop falls down I can calculate the surface area of the dropping mercury very easily.

I know the weight I know it is circular. So, what would be the 4 by 3 pi r cube or something like that is there now. So, that is a very standard reaction I can know the exact value of the surface. So, these are the advantages of dropping mercury electrode; its surface is renewable, reproducible, smooth which eliminates the passivity or poisoning is not there.

And then mercury forms amalgam with many metals which is known and its an advantage here. And diffusion assumes steady value immediately after I change the voltage and large hydrogen overvoltage on mercury renders the deposition of metals such as alkali aluminium and manganese. They are not amenable for polarography that is platinum microelectrode and surface area can be calculated very easily five advantages all the five are really good.

(Refer Slide Time: 28:23)

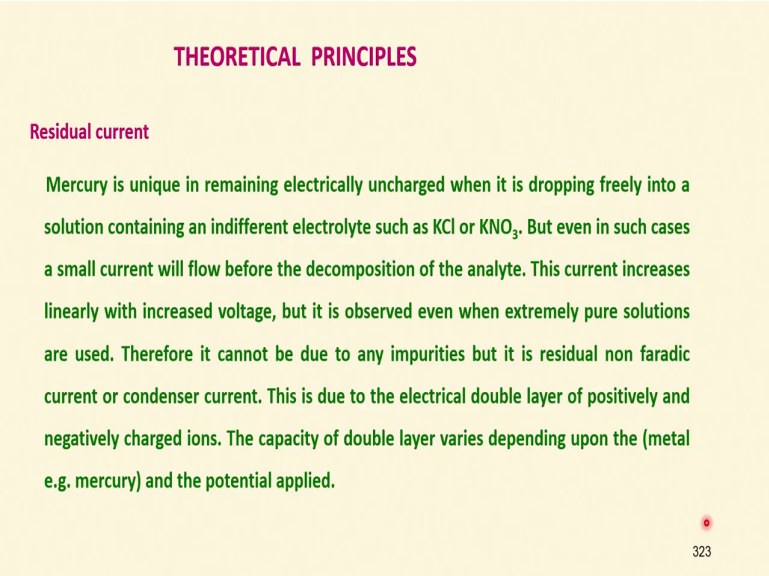


And the DME can be worked from plus 4 to minus 2 volts with respect to SCE Saturated Calomel Electrode. Above 0.4 volts mercury starts dissolving and it gives an anodic wave. So, that is another technique anodic stripping voltammetry, but that is not within our scope right now, but let me see whether I can introduce a little bit about anodic stripping voltammetry, it is also a very special technique. So, at potentials more negative than 1.8 volts, visible

hydrogen evolution occurs we do not want that; because water can decompose and start giving you hydrogen and oxygen again that will take over the polarization system.

So, the supporting electrolyte commence start commence to discharge we do not like that. By using I can use tetra alkyl ammonium hydroxide restandard chemical all their salts the range may be extended up to minus 2.6, but beyond that again I have the same problem. So, for convenience and measurement of half wave potentials, the anodic potential must be measured with a saturated calomel electrode using a salt bridge that I can use ok.

(Refer Slide Time: 30:04)



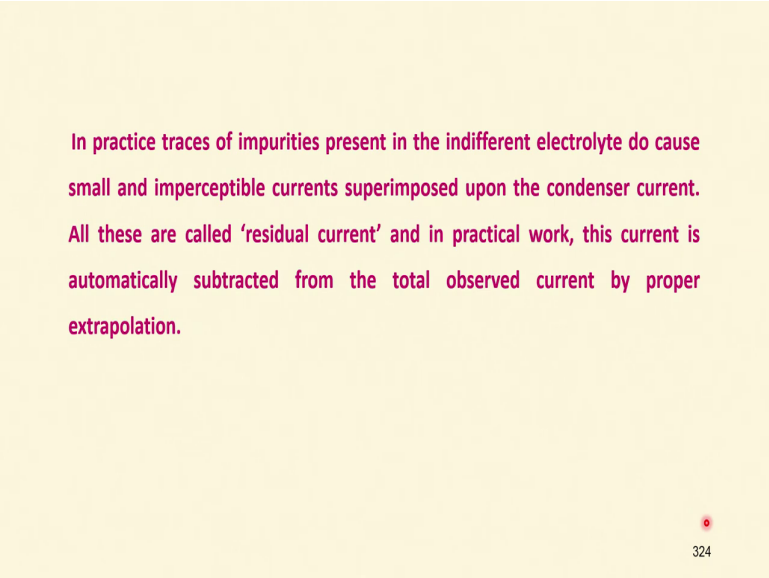
So, let us discuss a little bit about the theoretical principles of the polarograph. First of all I had told you that it is in I had shown you that the current voltage curve will have 4 parts a, b, c, d; one is straight part another is increasing part another is steady part.

So, mercury is unique in remaining electrically uncharged. When dropping mercury, when is the mercury is dropping freely into a solution containing an indifferent electrolyte. What is an indifferent electrolyte? It can be sodium chloride, it can be potassium chloride, it may be potassium nitrate or any such salt. But even in such surfaces a small current I already I told you that if small current keeps on coming at it increases a slowly. The current increases linearly with increased voltage, but it is observed when extremely pure solutions are used which observed then also.

Sometimes people think that if I am getting some current, it may be having some impurity. So, people thought let us try pure solutions. So, the you distill water once, distill twice, distill 10 times and then still used still there is increase in current. So, this kind of residual current is there whatever is your purity, it has nothing to do with the purity of the solutions.

So, then what it could be? What it could be we can tell, but what it cannot be I can tell. So, it cannot be due to any impurities present in the solution correct. But it is residual current, it is non faradic current and it maybe condenser current. This is due to the electrical double layer that varies depending upon the metal and the potential applied. I have already taught you the about the electrical double layer and how it can be handled.

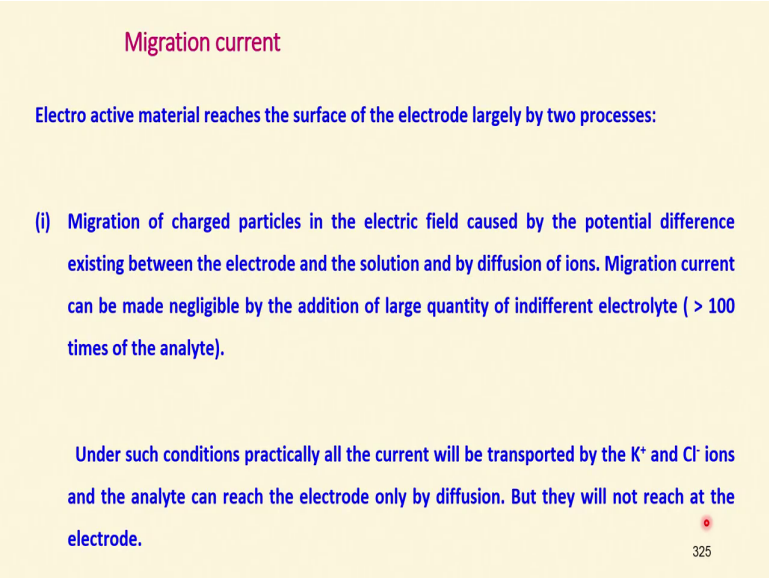
(Refer Slide Time: 32:43)



So, this residual current is due to the electrical double layer not due to the purity. So, in practice, traces of impurities present in indifferent electrolyte do cause small and imperceptible current generated or superimposed upon the condenser current. So, all these things put together are called residual current and in practical work, this current is automatically subtracted from the total current that is obtained by proper evaluation.

So, extra not evaluation, but it is extrapolation. So, it is not a disadvantage, but it is a nuisance anyway the residual current has no analytical value and it is a necessary evil; however, much you purify there is a residual current. And usually we subtract it as a noise, it cannot be treated as a signal. So, then we talk of another system; we talk of another system that is migration current.

(Refer Slide Time: 34:17)

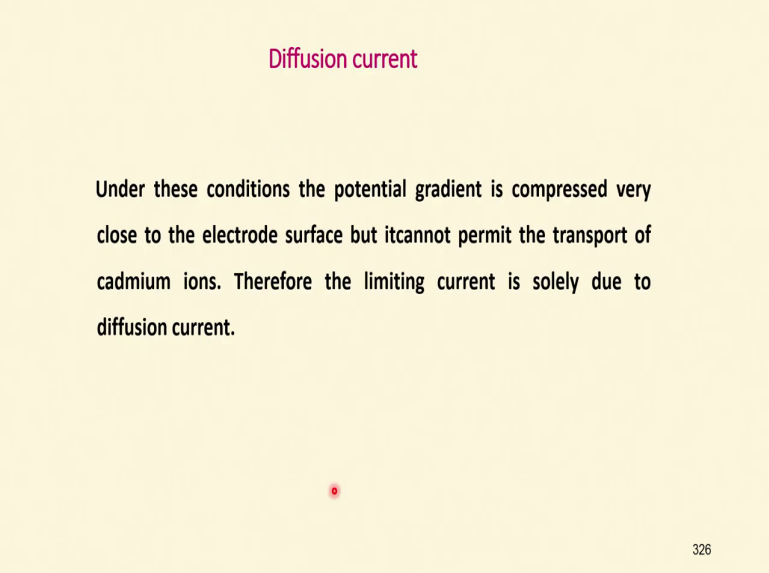


In the migration current, I have electroactive material reaching the surface of the electrode largely by two processes; this I have already explained to you. Migration of the charged particles in the electrical field caused by the potential difference existing between the electrode and the solution and by diffusion of ions that is second process.

First process is potential difference that attracts the cations towards the cathode and the second one is by diffusion also they can reach. So, migration currents can be made negligible by the addition of large quantity of indifferent electrolyte. Usually, we take about 100 times the quantity of the analyte minimum. So, under such conditions practically all the current will be transported by the indifferent electrolyte that is potassium chloride and the analyte can be can reach the electrode only by diffusion ok. But, they will not reach the electrode.

Maximum current is carried by the supporting electrolyte and that is the both cations and anions. And the analyte can reach the electrode by diffusion, but it will not reach the electrode and no reaction.

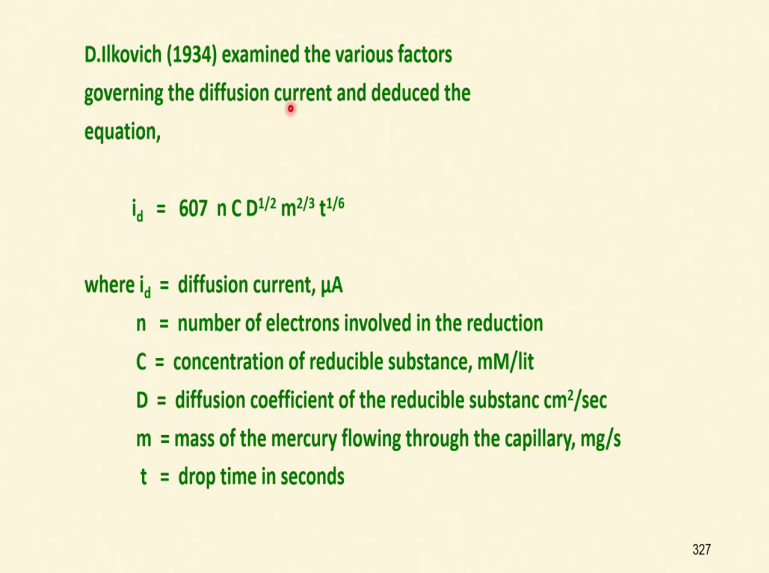
(Refer Slide Time: 36:01)



So, next thing what we discuss is about the diffusion current. So, once the these conditions are applied I keep on increasing the potential, then the electrical double layer keeps on getting smaller and smaller, smaller and smaller; after sometime it will become very negligible. So, at that time probably the electrode reduction potential standard reduction potential would be reached and the ions will be able to pass quickly from solution to the electrode surface that is the dropping mercury electrode.

So, the potential gradient is compressed very close to the electrode surface, but it cannot permit the transport. Therefore, limiting current is only due to the diffusion current, whatever you get must be due to that only.

(Refer Slide Time: 37:13)



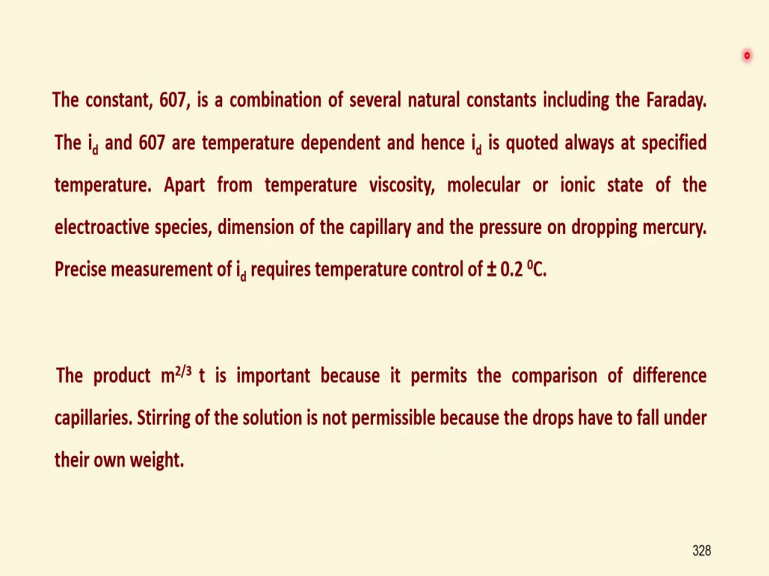
So, Ilkovich examined the various factors governing the diffusion current and the and deduced the equation i d is equal to 607 n C D raised to half and multiplied by mass of the drop dropping mercury that is to m raised to 2 by 3 and t raised to 1 by 6. Here in this equation, it is a very important equation even from the examination point of view for those who want to take examination.

Here the i d that is diffusion current is defined as 607 into n into C D raised to half raised to then m raised to 2 by 3 and t raised to 1 by 6. Where i d is nothing but diffusion current in

microamperes, n is the number of electrons involved in the reduction, C is the concentration of the reducible substance; that is in centimeter square that is in millimols or liter.

D is the diffusion coefficient of the reducible substance, the units are centimeter square per second. And m is the mass of the mercury flowing through the capillary that is milligrams per second and t is the drop time in seconds. That is how much time the mercury drop takes to form and fall from the electrode surface from the capillary.

(Refer Slide Time: 39:13)



So, the constant 607, is the combination of several natural constants including the Faraday. So, do not worry about how that number is coming, but for our practical purpose we can take 607 as a standard one, it is a combination of several natural constants and i d and 607 are temperature dependent. So, i d is quoted always at specified temperature. Apart from temperature viscosity is there, molecular or ionic state of the electro active species I talked

about speciation sometime back. And dimension of the capillary is important because we are talking about drop time t raised to 1 by 6.

So, drop time is important. And the pressure on dropping mercury, how from how much height it falls on the ground from the electrode to the anode pool. And then we also need the precise measurement of i d requires the temperature control of plus or minus 0.2 degrees, that is the requirement for the measurement of i d. And the product m raised to 2 by 3 is important into t of course, the product of mass into time because it permits the comparison of different capillaries otherwise how will you compare. I can make I cannot make the same capillary everywhere all the time with the same engineering properties.

So, there will be some slight variations and drop time will vary for drop depending upon the capillary. So, stirring of the solution is not permissible once these reaction starts because the drops we have to fall under their own weight so, that is also important. So, we cannot say let us make the drops fall uniformly by stirring the solution. Now, in dropping mercury electrode, nothing should be disturbed except the solution that is being analyzed. So, we will continue our discussion of regarding the other features of the current voltage curve, in our next class.

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