Electrochemical Technology in Pollution Control

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Lecture – 07
Electrogravimetry

Greetings to you, we are going to start the next session of our course on Electrochemical Techniques on Pollution monitoring.

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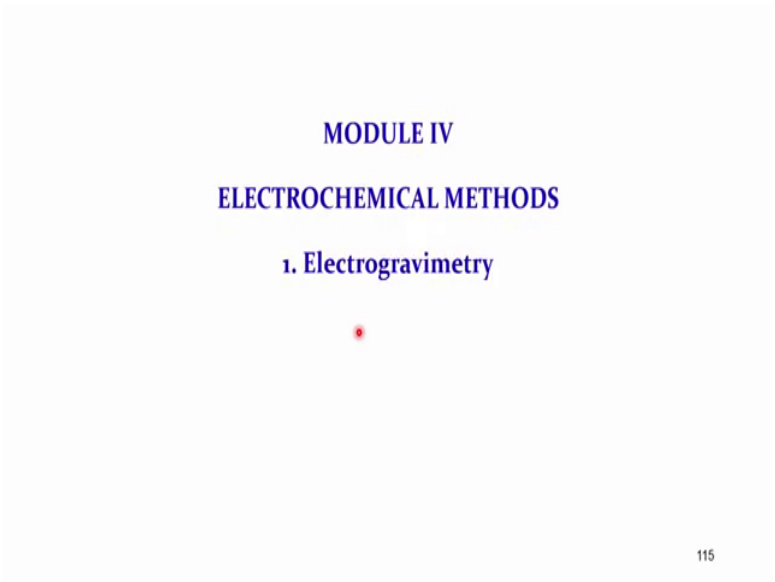

And that will be module 4, in this module we are going to study several electrochemical analytical techniques. So, they include Electrogravimetry, conductivity, polarography, potentiometry and several other electric analytical techniques which will help us in the day to day monitoring of the effluents especially for pollution control.

And unless we understand the basic principles of the techniques, we will not be in a position to interpret the results that is why our approach in this module would be to understand the basic theory. And then instrumentation and then applications as and when possible. So, after some time what we are going to do is we are going to solve some problems to make you more familiar with the concepts that you have already learnt ok.

So, let us start with the an electrochemical techniques that is first thing what I want to talk to you is about the electrogravimetry. So, electrogravimetry is nothing, but the same gravimetry what you have been what you have learnt in your college as a gravimetric analysis. You would have done, many of you would have done in your pre-university or college level the gravimetric determination of metals that is used for the determination of milligram quantities.

Let us say you want to determine aluminum and you have to precipitate aluminum in such a way that it is quantitatively removed from the solution by carrying out a chemical reaction which will produce a salt of sparingly soluble characteristics. And, then you filter it and wait that is the normal gravimetry. In electrogravimetry what we are going to do is we are going to carry out the same reaction, but we are going to remove the analyte that is the metal of inter metal ion of interest from the solution by electric applying electric impulse.

And, the metal ions will be reduced to metals and the metal ions at such reactions take place at the cathode. And the once it is reduced, it is it sticks to the cathode. So, in electro gravimetry the metal ion will be moving towards the cathode, at the cathode there will be a reaction reducing the metal ion to metal and the metal will be deposited on the cathode. So, the weight of the cathode will increase and the difference in the weights of the cathode should be proportional to the quantity of the ion present in the solution that is the basic fundamental principle.

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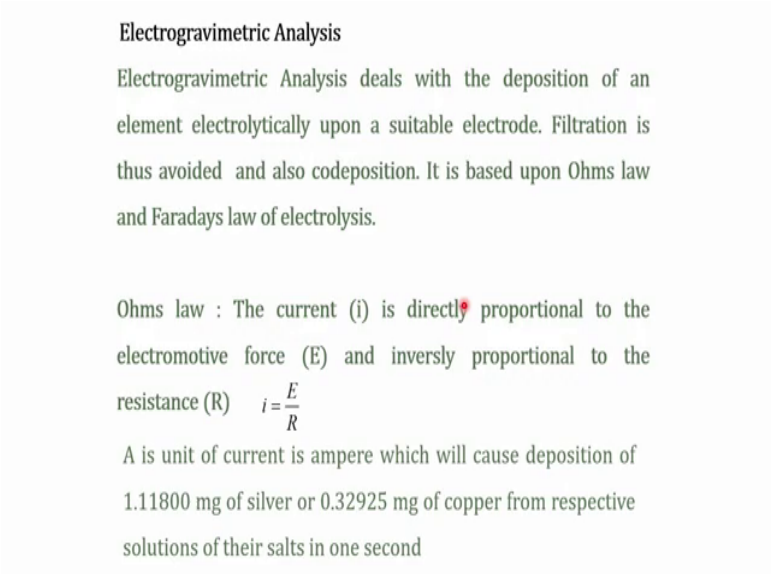

Now, in electro gravimetric analysis what we are dealing with, it is the deposition of an element electrolytically on a suitable electrode. So, we are practically avoiding most of the filtration and also co deposition. In normal gravimetry there is always certain amount of mechanical drudgery involved because you have to precipitate, you have to make sure that everything is settled. And, first you remove their clear solution and then filter it and then collected that on the filter paper.

Burn the filter paper, remove the make it almost ash less and you take the difference between the weights. And, it is a sort of mechanical tragedy, it is no it does not happen easily. But, it has got its own utility also for example, if you want to determine how much of a metal ion, metal is there in an ore; there is no other reliable method unless you separate specifically separate the metal ion of interest from the ores that is containing all the other elements and

silica and other muck etcetera. So, it has got its own use, but in electro gravimetry we are avoiding the filtration because, we are going to deposit it on the cathode.

So, that electrode cannot be a general electrode, it has to be a suitable electrode; that means, the metal ion should be capable of getting deposited and stored safely until you are ready to weight. And, in normal gravimetry there will always be certain amount of co deposition and then some other metal elements may deposit. And, sometimes coagulation may take place, sometimes co-precipitation may take place. Several other complications are essential evils associated with gravimetry.

So, one has to learn a lot of chemistry to do the gravimetric analysis. Here what we do? We are avoiding filtration, we are avoiding co-deposition. Why co-deposition is avoided? You should think about it, I will give you a 2 second pause, 5 second pause after I asked such questions. So, if you have got the answers like what I am going to tell you; that means, you are an intelligent person alright.

So, co-deposition is the deposition of other elements under the given conditions. So, when one element is being deposited at a particular voltage or current, then the any other element that can deposit at the same voltage only can precipitate such conditions are very rare in the electro gravimetry. Therefore, essentially what you are going to do is almost specific a determination of the metals. So, this is one of the greatest advantages of electro gravimetry.

So, an electro gravimetric technique gives you the specificity that is very important because, no other metal ion will be precipitating under the given conditions with the same amount of voltage. Because, for every element deposition voltage and current are different for each element; so, it is almost specific now. So, this is it is a characteristic of the element that we want to determine, it is there therefore, the electro gravimetric analysis is based upon Ohms law and Faradays laws of electrolysis.

So, what is Ohms law and what is Faradays laws of electrolysis we will try to understand now. Now, Ohms law states that the current i, the current designated as i is directly proportional to the electro motive force, that is potential also known as potential emf and

inversely proportional to the resistance. So, I can write i is proportional to E by R or I can say i is equal to E by R.

So, A is a unit of current in amperes, A is the symbol for amperes current which will cause deposition of 1.11. What is 1 ampere? We are going to define the ampere now. So, 1 ampere of current will cause deposition of 1.11800 milligrams of silver or 0.32925 milligram 0.3259 32925 milligram of copper from respective solutions of their salts in one second. So, that is the definition of ampere; so, the current i, this is the unit for i ok.

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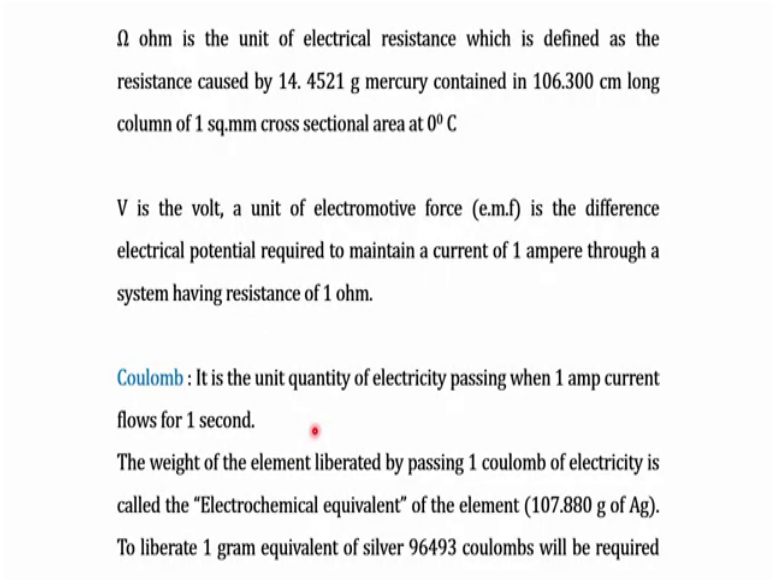

So, what is Ohm? Here we have written resistance R, that is E emf, this is current. So, we do not call it amperes and this thing, but now we also define a unit called as ohm by defined by this symbol. We write the ohm as this symbol, this symbol is the unit of electrical resistance. I have given you the current designation as A and ohm is the unit of electrical resistance which

is defined as the resistance caused by 14.4521 gram of mercury contained in 106.300 centimeter long column of 1 square centimeter cross sectional area at 0 degree centigrade.

This is also sort of definition and very useful for day to day purposes, we say resistance of any system can be so many ohms. Means you must understand that it is the electrical resistance, that is defined as they cause resistance caused by 14.4521 gram of mercury. Or, contained in 106.300 centimeter long column of 1 square centimeter cross sectional area. How these two, these numbers have come is they there is certain requirement which have which is described in the text books; I recommend you to read it.

And, I am not going to explain to you, but this is a very practical unit of the ampere, I certainly recommend you to read how this definition has been arrived at. And, V is the voltage that is emf a unit of electro motive force. And what is the V? It is the difference one we call it volt; what is 1 volt or 10 volts, 440 volts you are all familiar with the voltage. Most of our households run on 220 volts, that is the electro motive force that is entering our house through the electrical wires etcetera. Sometimes we use 110 volts in foreign countries and in India and other countries we use 200 volts.

And, 4 400 volts and 440 volts are also in use for high electric current movement ok. So, the volt is also very useful quantity and it is the difference electrical of the electric potential required to maintain a current of 1 ampere through a system having resist of resistance of 1 ohm. What does it mean actually? We say it is you cannot see them, you see ohm, resistance you cannot see. And, then ohms you cannot say, we cannot see and the current amperes you will not be able to see them.

They are all electromagnetic forces so, we have to depend upon the sort of definitions and some other alternate measuring techniques to determine all these numbers; whatever we are talking about, I said 220 volts. So, where is 220 volt? Nobody writes 220 volts, is not it? So, 220 volts means you must understand like the definition now, it must generate a current of to 1 volt should generate a current of 1 ampere. So, 220 volts should generate a current of 220 amperes through a system having resistance of only 1 ohm.

It was like that we are we should we are able to visualize what is 220 volts, what is 110 volts etcetera. So, we also define another term that is Coulomb, it is the unit quantity of electricity passing when 1 ampere current flows through for 1 second. So, whenever I pass a current of 1 ampere current for 1 second, I say 1 Coulomb of electricity has been passed through that wire ok. So, that is a another definition you should remember, it is the unit quantity of electricity passing through when 1 ampere current is flowing for 1 second.

So, the weight of the element it is what is the job of the current? The job of the current is to reduce the metal, isn't it? So, how much of the element is reduced? So, if I know I can if I can calculate how many Coulomb's are there, Coulomb's of currents I am passing through. So, the weight of the elementary liberated when I am passing 1 Coulomb of electricity is called the electro chemical equivalent of the element, that is 107.880 gram of silver. This is a choice made by made by the scientists and very much in use.

So, to that what does it mean? To liberate 1 gram equivalent of these silver that is one, what is 1 gram what is the equivalent weight of silver? It is 107.880. So, if I want to liberate 107.880 gram of silver, I would say that I am liberating 1 gram equivalent of silver. Now, to liberate 107.880 gram of silver, I had to pass 96493 Coulomb's will be required, I had to pass that much of the current in Coulomb's 96493 and that is what it means.

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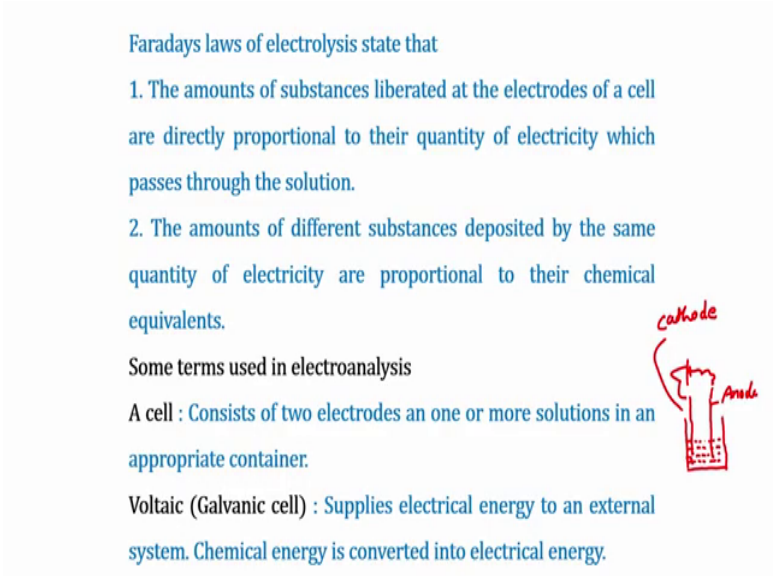

Now, you will be surprised to know that the same 96493 Coulomb's will be required to precipitate any element, any element in its equivalent weight in grams. So, suppose you want to liberate sodium, what is the atomic weight of sodium? 23. So, 96493 Coulomb's are required to liberate 23 grams of sodium and if you say copper 1 gram equivalent of copper you should know.

So, to determine that we need to pass 96493 Coulomb's. So, it is a very simple straightforward law that is definition of Coulomb. Now, I we are going to talk about Faradays laws of electrolysis and there are two laws. One is it states that the amount of substance is liberated at the electrodes of a cell are directly proportional to the quantity of electricity which passes through the solution.

So, this is a sort of one's observation and intuition, if I say I pass more current, more will be liberated correct. So, if I pass less current less quantity of the substance will be liberated at the cathode and the cathode weight will increase. So, it is a general observation, but verified scientifically since last 200 years, that this is exactly what is happening in the in an electrochemical system.

So, the amount of substance that is liberated at the electrodes of a cell is directly proportional to the quantity of electricity. Suppose, you pass 96473 493 Coulomb's 1 gram equivalent will be deposited. Suppose, you pass half of that that is approximately 48246 Coulomb's, you will be getting 107.880 divided by 2 that will be approximately 53.44 gram of silver. Suppose, you still reduce say at the current you will get still less silver deposited.

So, that is one thing and second thing is the amount of different substances deposited by the same quantity of electricity are proportional to their electrochemical equivalence. There what does it mean? The amount of different substances deposited by the same quantity of electricity are proportional to their chemical equivalents. That means, you do not have to pass all the time 96493 Coulomb's to find out, you can find to find out the how much of material is deposited, you can calculate.

Now, only thing is you should know the atomic weight of these substance. Now, atomic weight and this quantity that is 1 Coulomb are closely related because 1 96493 Coulomb's will deposit 1 gram equivalent of the substance. And, 1 gram equivalent of the substance is nothing, but the atomic weight of the substance, any element. We are talking mostly of the metal determination in electro gravimetric 99 percent of the time.

So, there are certain terms, technical terms used in electrochemical cells. What are those technical terms? You should be familiar with here are they, here they are. So, a cell we define what is a cell; a cell is nothing, but a beaker something like this. I have a beaker here glass beaker, I have two electrodes dipped in a solution. And, this is connected through a battery and a resistor at that completes the say electrical circuit. So, I pass current from battery to the anode, this is known as anode, this is known as cathode ok.

So, this arrangement is called as a cell. So, what does a cell consists of? It consists of two electrodes in one or more solutions, I can have one electrode in one beaker and another electrode in another beaker both of them connected externally through a wire and a battery system and arrangement to pass electrical current ok. So, the definition says it you requires two electrodes and both electrodes may be in only one solution or each electrode may be in different beakers, but connected from outside by external wiring. Now, we define what is known as voltaic cell.

What is the voltaic cell? Voltaic cell or it is also known as galvanic cell. So, both of them are the names of the scientist Volta and Galvane, galvanic cell yes it says the cell supplies electrical energy to the external system. So, that is a voltaic cell or galvanic cell; that means, this cell will generate current and up come here and put it in the battery. So, the current will be generated by a chemical reaction going on in this beaker and then it will come here, from here electrons will be generated and electrons will be moving here. The energy will be stored in the battery such systems are called as voltaic cell or galvanic cell.

Basically, what happens is in all such systems chemical energy is converted into electrical energy. There these are all basic terminology you should remember in all our future discussions because, I will simply say that it will be it is the voltaic cell, it is a galvanic cell, it is a normal cell. Like that I will be talking about and I will not be elaborating on such systems, but if you understand this; you should be able to immediately visualize what I am talking about ok.

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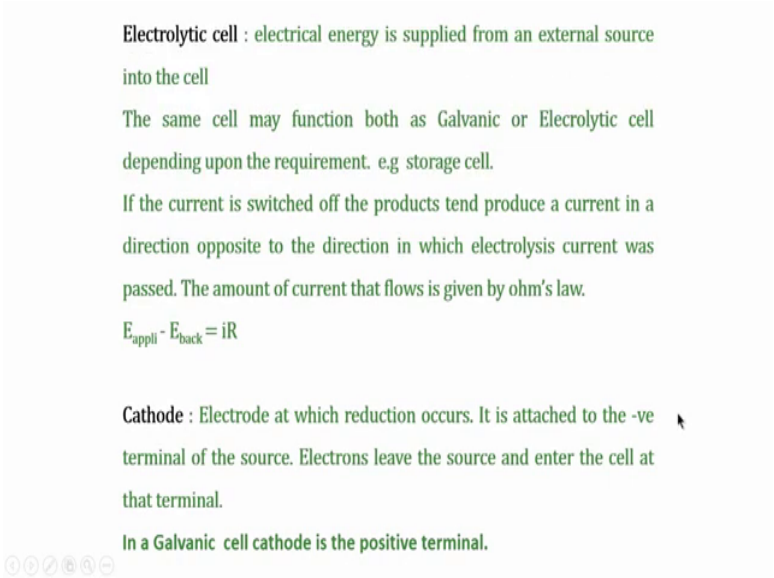

Then I can define an electrolytic cell; so, an electrolytic cell works when electricity is supplied from the battery to the from an external source into the cell. You remember here remember this figure, in this figure the battery will let out of the current and a chemical reaction will take place, that is an electrolytic cell. In galvanic cell the chemical reaction will generate electrons and that will be stored in the battery or a cell. So, basically you are very familiar with batteries in cars and you are also familiar with batteries in watches and torch cells etcetera.

We are talking about the same thing, they all supply certain amount of current approximately 1.2 volts, 1.6 volts like that; different quantity. And, that battery is the receiver of energy, if it is a galvanic cell and it is a giver of energy if it is a electrolytic cell. So, the same cell I can have the same cell functioning both ways, sometimes I can use it to collect electricity into the

battery or some other time I can use the stored energy again to let out, to carry out certain chemical reactions here. So, both of them are possible, both types of uses are possible.

So, this is statement is true, the same cell may function both as galvanic cell or an electrolytic cell depending upon your requirement that is for example, a storage cell. A storage cell is what you go and buy in a shop, in the storage cell you go there and say give me 1.5 volt battery Eveready battery or any power battery. There are so many battery manufacturers around and you can buy that or you can buy a battery for your scooter, car and many other things. They are slightly heavier and bigger, they supply more electrical energy.

We are going to talk about the batteries later in another unit, in the same course, but for the time being that is known as storage cell; that means, it can store electro motive force, electrical energy emf in a given battery which can be tapped to take out the current; whenever we want. And, when the battery completely gives out all the storage stored energy, I can make it a galvanic system in which electricity will be put into the same cell.

So, reusable alkaline batteries you must have heard, they are in the market. So, such things are capable of functioning as galvanic cell as well as electrolytic cell. So, if the current is switched off what happens the products tend to produce the current in the direction opposite to the direction in which electrolysis current was passed ok. Now, imagine a system like this, system like this it is going on and I switch off the current stop the reaction.

So, then what happens? If the current is switched off, the products tend to produce a current in a direction opposite in the opposite direction. So, the amount of current that flows again is given by Ohms law. So, E applied that is emf applied minus emf coming backwards is probably qual to iR. So, this expression holds good. So, we define what is known as cathode and what is known as anode. So, a cathode is one thing, it is an electrode.

What is an electrode? Again I give you a 5 second pause, I have been talking about electrodes, cathodes etcetera and what is an electrode. What do you visualize when I say it is an electrode? So, you should remember that whenever I am talking about an electrode, I am talking about a wire. This is a wire, this is cathode, it is a metaled wire and anode is also a

metaled wire it, but it need not be wires alone. You know it need not we have very thin section, it can be a plate, it can be an object like your coffee cup or something like that. It can be a metal plate, it can be cylindrical, it can be circular, it can be squarish, it can be anything.

But, it is a metal piece that receives the electrons from the solution or gives out electrons into their solution; so, that is a cathode ok. So, electrode at which, what is a cathode? It is a metal wire dipped in a solution at which reduction takes place, you at the cathode reduction takes place; that means, wherever reduction is taking place on a metal surface in an electrolytic cell we call it cathode.

So, the there lot of people have confusion regarding anode and cathode; what happens at anode, what happens at cathode; are electrons release from the anode or from the cathode. So, there it is important for us to understand that what exactly happens. Now, if you remember cathode is the positive terminal, negative terminal in a given system and there the reduction occurs.

Now, if what is reduction? If a metal ion becomes metaled metal ion means it is charged, if the charge is removed; that means, reduction is occurred. If the charge becomes less then it becomes a metal ion. So, that process is known as reduction. So, iron ion is Fe 2 plus, if the 2 plus is removed if I; that means, if I put 2 electrons in that iron Fe 2 plus will become electron is minus.

So, 2 minus I am adding so, Fe 0 represents iron metal ok. So, an electrode is one at which reduction occurs, it is attached to the negative terminal of the source, there by that way also you can identify what is an electrode. And, electrons leave the source and enter the cell at that terminal. So, in a galvanic cell cathode is the positive terminal, galvanic cell, but in the electrolytic cell it will be the other way around.

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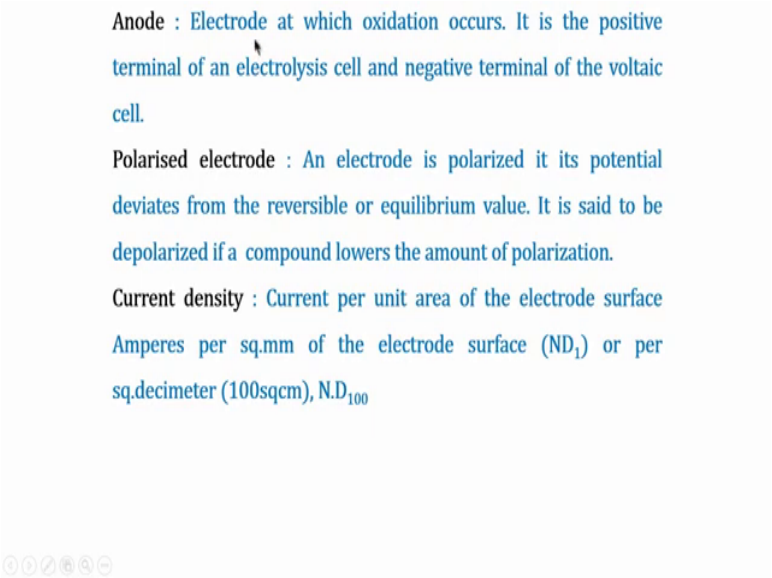

So, what is an anode? Anode is also an electrode that is a metal piece, it may be of any shape, cylindrical, wire, round, circle, plate etcetera at which oxidation occurs. So, it is the positive terminal of the electrolysis cell and negative terminal of the voltaic cell, this I have already explained to you. So, when oxidation takes place at the anode simultaneously a similar reaction reduction must take place at the cathode.

So, both these processes occur simultaneously, they cannot occur independent of each other ok. It is like a coin having both sides, head and tail. So, we also define another term known as polarized electrode. A polarized electrode is one when its potential deviates from the reversible or equilibrium value. What is equally reversible or equilibrium value? Again I give you a 5 second pause, try to think of the definition.

So, equilibrium value or reversible value is what is a calculated value of the sub electrode. So, if the calculated value is different from actually what you measure then we have a if they are not same, then we call it polarized electrode ok. It is said to be depolarized if a compound lowers the amount of polarization.

So, fully we have learnt what is cathode, what is anode, what is electrolytic cell this thing etcetera, electrolytic cell, what is galvanic cell. We only have to learn about the current density, that is current per unit area of the electrodes surface in amperes per square millimeter of the electrode surface or per square decimeter, we can do it either way. This current density also we are going to talk quite a lot in our discussions. We will continue our discussion in the next class.

Thank you very much.