Electrochemical Technology in Pollution Control

Dr. J. R. Mudakavi
Department of Chemical Engineering
Indian Institute of Science, Bangalore

Lecture – 10
Potentiometry Electrolytic cells 1

Hello greeting to all of you, we are going to start our discussion on the Electrochemical methods on a Potentiometry now. Earlier we had done for electrogravimetry and conductometry; third technique is potentiometry. So, what do we have in potentiometry? Here we measure the potential.

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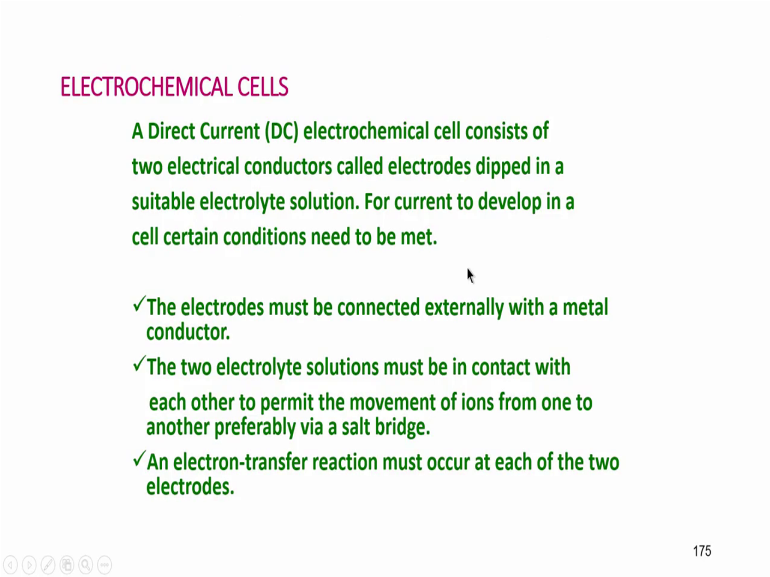

ELECTROCHEMICAL CELLS

A Direct Current (DC) electrochemical cell consists of two electrical conductors called electrodes dipped in a suitable electrolyte solution. For current to develop in a cell certain conditions need to be met.

- ✓The electrodes must be connected externally with a metal conductor.
- ✓The two electrolyte solutions must be in contact with each other to permit the movement of ions from one to another preferably via a salt bridge.
- ✓An electron-transfer reaction must occur at each of the two electrodes.

I think all of you remember Ohm’s law now, that is potential current and a resistance are the voltage, basically potential means voltage, so we are going to measure the voltage. Before that I would like to describe couple of things for you and then we will discuss about the potentiometry in detail. These are all sort of support to potentiometry only, without these input you may not be able to understand completely the ethos of potentiometry.

So, I am going to define a couple of things like this; for example, on your slide now, I am going to define what is an electrochemical cell. An electrochemical cell consists of two electrical conductors called as electrodes; they are dipped in a solution, just like what we had seen in conductometry and the solution could is called as electrolyte. For current to develop in a cell certain conditions need to be met, ok.

So, the electrodes must be connected externally with the metal conductor; that is like any wire, this also you are familiar now. The electrolytes could be in different beakers, ok. Electrolytes should be in could be in different beakers, but they must be connected electrically. So, they must be in contact with each other to permit the movement of the ions from one to another preferably via a salt bridge, I will describe to you what is salt bridge later.

So, salt bridge is an equipment that permits conduction of the ions without being in solution, external connection; but ions can be converted conducted from one beaker to another beaker. So, we also need a sort of an electron transfer reaction; that is oxidation, reduction or something like that. It must occur at each of the two electrodes; both electrodes there must be some sort of electron transfer from the solution, from the ions to the electrode or from the electrode to the solution also, that is also one of the it could be one of the requirement that happens in several techniques which we are going to learn in this course, ok.

So, electrochemical analytical measurements has certain advantages over other types of chemical analysis. What are they? One is measurement of measurements are specific to the oxidation state of the element that are the cation or anion, ok. So, it could be plus 1, plus 2, plus 3, plus 7 depends, ok.

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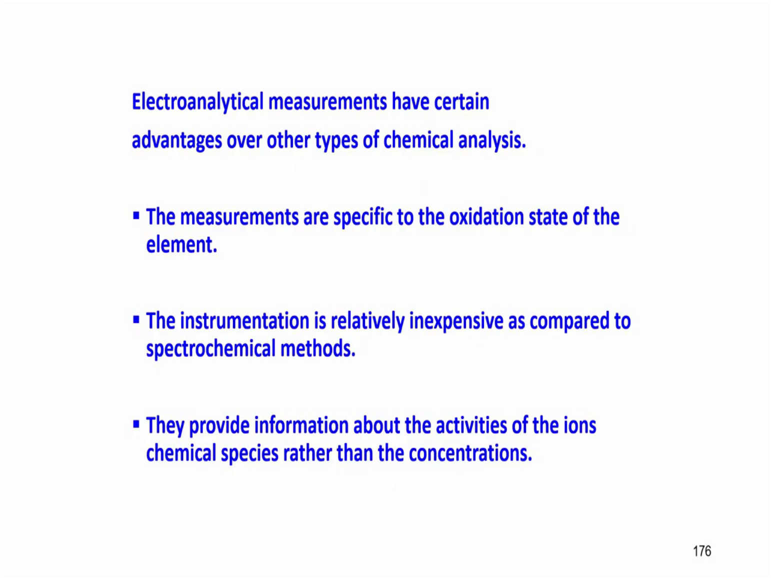

Electroanalytical measurements have certain advantages over other types of chemical analysis.

- The measurements are specific to the oxidation state of the element.
- The instrumentation is relatively inexpensive as compared to spectrochemical methods.
- They provide information about the activities of the ions chemical species rather than the concentrations.

So, measurements are I can find out what is the oxidation state of a particular species in a solution that is important. This is one advantage, no other chemical technique normally can tell me what is the oxidation state of the ion metal ion of interest; it may be in the quite often we express the metal ion concentrations in a different composition altogether.

For example if you want to estimate express iron concentration in a ore, we do not write iron; we write iron as a Fe2O3 and aluminum as A l 2 O 3, calcium as calcium carbonate like that. But that will tell me actual analysis is done in the form of ions, but expressed as some component. In this case I can express it as ferric 2 plus, sorry ferric 3 plus or ferrous 2 plus, chromium 7 plus like that I should be able to measure the specific oxidation state of the element.

Second is instrumentation is very very inexpensive, we have already seen that the instrumentation in conductivity measurements is very simple; the equipment can be bought in for about 600 or 800 rupees or 1000 rupees within that you can do a lot of research, that can be done.

And then we can also say that, the they provide information about the activities of the ions and the chemical species rather than the concentrations. You remember our discussion about the activity, ok. So, we get information about the activity rather than the concentration; that is another important aspect that is very important for us to consider in almost all electo analytical measurements.

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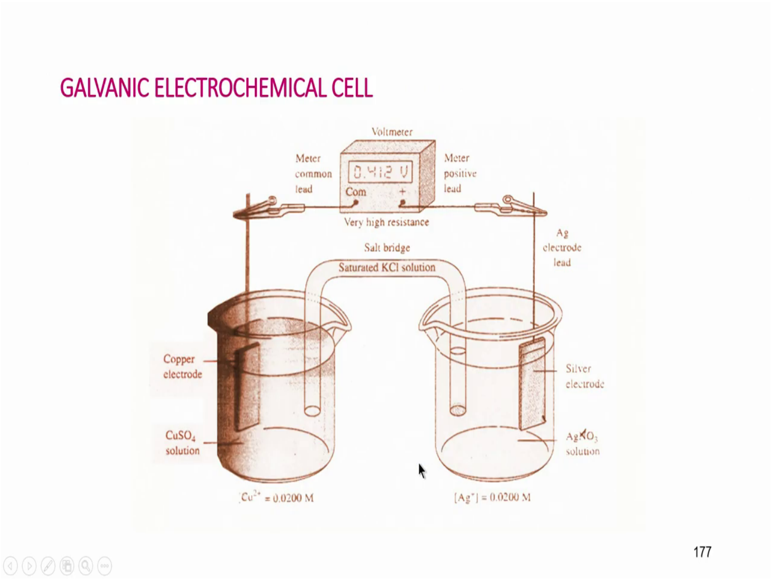

GALVANIC ELECTROCHEMICAL CELL

So, here I am showing you a galvanic electrochemical cell, here I have an electrode dipped in a beak in this beaker containing a solution; one electrode is here, another electrode is here, ok.

So, both the cathode and anode are separated from each other; they are not only separated from each other in different beakers and this solution is not mixing with this solution that is the beauty and it is connected from outside two wires.

Here it is a copper electrode, here it is copper sulfate solution of 0.0200 molar 0.02 molar; here it is silver solution also of 0.2 molar, here I have a silver electrode connected with a conducting wire that could be copper or aluminum or yeah mostly copper and it is connected to a volt meter, this is what we measure voltage. And both these beakers are connected with a saturated solution of KCL mixed with some sort of a gum that is gelatin. So, what we is, we take a glass unit bent in a u shape and then take potassium chloride solution, add gelatin and heat them, pour it in this and allow it to settle like this.

So, this contains a paste of potassium chloride solution and gelatin. So, this is known as a bridge and because it contains salt, this is known as salt bridge. So, this salt bridge has got potassium chloride; that means, chloride ions are there; it will the gel is not very settling, it is fairly well settled, but it can conduct allow electrons ions to move from this point to from this beaker to this beaker. So, here it is silver nitrate solution and here it is copper nitrate solution; copper sulfate, copper nitrate solution.

So, if I make a solution of one of the ions which is common to both; then the electrical contact can be established using a salt bridge that is salt bridge for you, and use of salt bridges are quite common in all electrochemical potentiometric techniques, ok. So, this is a typical system.

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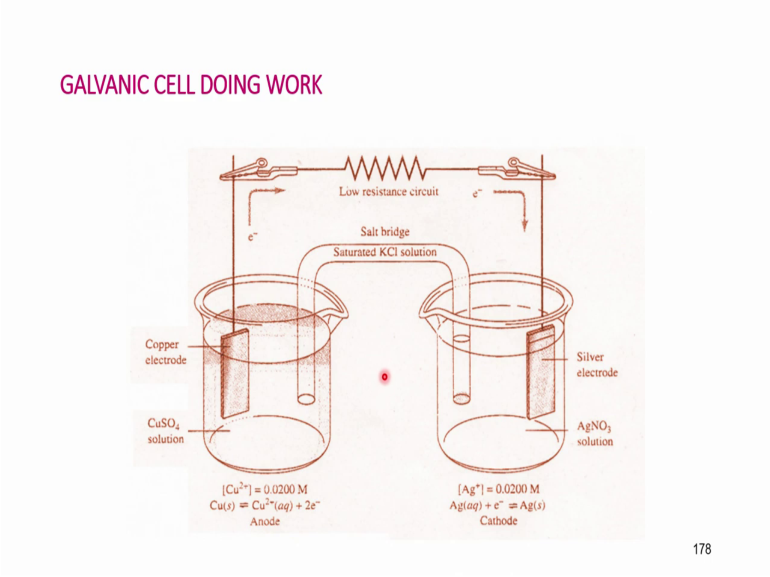

GALVANIC CELL DOING WORK

Another system is something like this. Here this is galvanic electrochemical cell and this is how the galvanic electro chemical cell will work. Here what happens? When I pass electric current, electrons will be moving from here to anode and this is cathode and the copper ions; this is in equilibrium with copper ions and the electrons will be released, this is silver ions and in equilibrium with the aqueous solutions, so it is solid. So, here the reaction is silver ions will combine with electrode to give you silver that is a solid, that will be deposited on the silver electrode.

Here copper solid, this will dissociate to give you C u 2 plus and 2 e minus; these electrons will be conducted from my external circuits to this and the electric current will be flowing. In the outside part there is only electronic moment and in the inside of the beakers and the salt bridge, there will be ionic moment that is that you should understand clearly, ok.

So this is how a galvanic cell is doing the work. What work it is doing? It is allowing silver ions to deposit on a cathode. Now, this cathode can be your key chain, it may be a jewelry item. So, if I allow take copper, allow silver ions to sit on that; it will be like electroplating. So, chemical work is being done by the electrical energy and that is deposition of silver ions on copper or silver electrode etcetera. Similarly for gold plating; gold ions can be deposited on copper or gold or silver or any other metal brass something like that. So, this is galvanic cell doing the work, ok.

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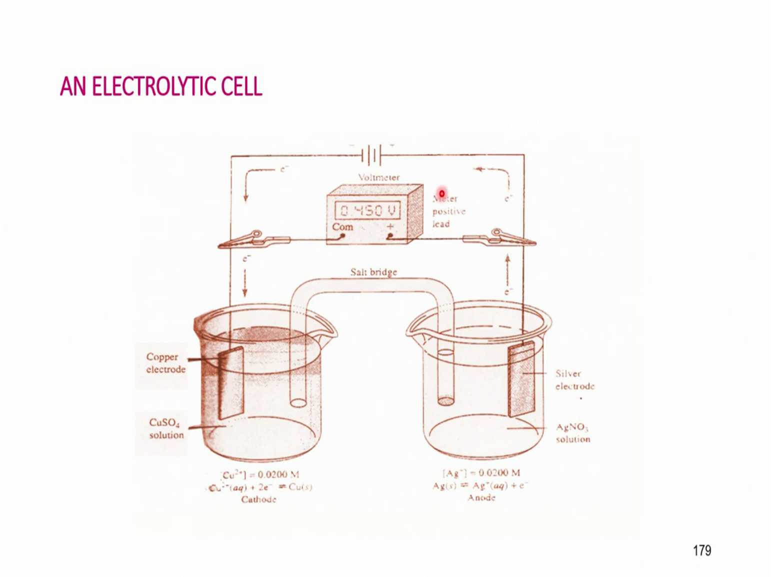

AN ELECTROLYTIC CELL

This is an electrical electrolytic cell, I am going to define what it is; essentially same thing two beakers are there, there is salt bridge, there are two electrodes and silver is here and here it is copper, ok.

Here the reaction will be from chemical energy to electrical energy, it will be converted. So, we are going to generate electricity, you are you must be familiar with lot of systems like this in your day to day life; most of the torch cells what you come across and your lithium cells in your watches and in cameras and several other things they convert chemical energy into electrical energy, batteries basically. So, this is known as an electrical cell that converts chemical energy into electrical energy; and a galvanic cell will convert electrical energy into chemical energy.

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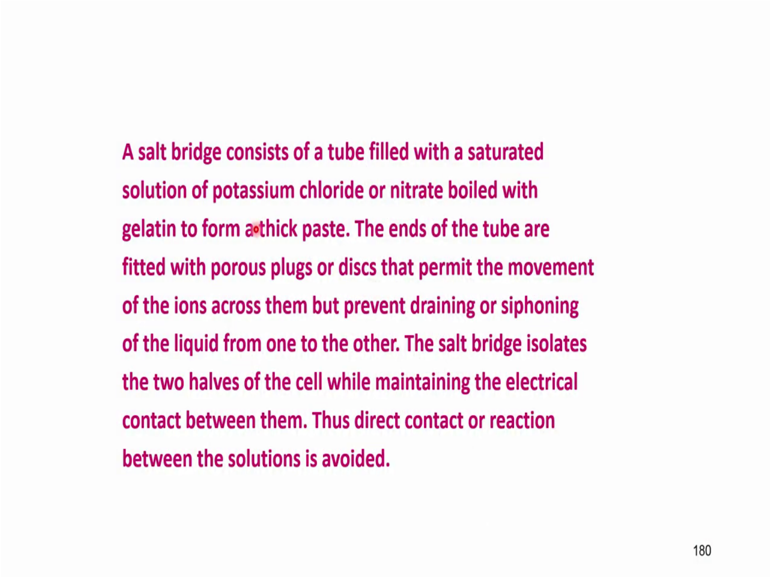

A salt bridge consists of a tube filled with a saturated solution of potassium chloride or nitrate boiled with gelatin to form a thick paste. The ends of the tube are fitted with porous plugs or discs that permit the movement of the ions across them but prevent draining or siphoning of the liquid from one to the other. The salt bridge isolates the two halves of the cell while maintaining the electrical contact between them. Thus direct contact or reaction between the solutions is avoided.

So, this salt bridge consists of a tube filled with a saturated solution of potassium chloride or nitrite boiled with gelatin to form a thick paste. Ends of the tube are fitted with porous plugs, so that the solution paste does not run away from the; because it is dipped upside down. If you remember it is dipped upside down, so it should not run away from the salt bridge into the solution by virtue of gravity.

So, we plug them, but prevent draining or siphoning of the liquid from one to another. Salt bridge isolates the two halves of the cell while maintaining the electrical contact between them, and then direct contact or reaction between the solutions is avoided, ok.

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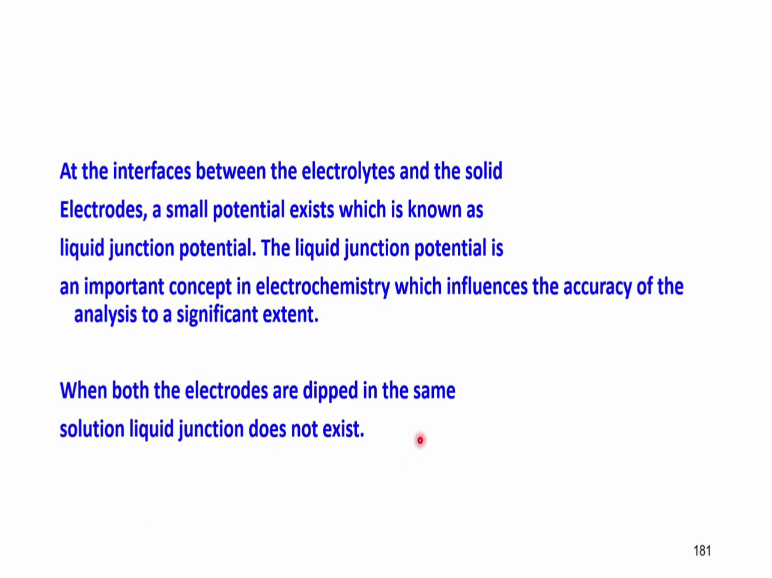

At the interfaces between the electrolytes and the solid Electrodes, a small potential exists which is known as liquid junction potential. The liquid junction potential is an important concept in electrochemistry which influences the accuracy of the analysis to a significant extent.

When both the electrodes are dipped in the same solution liquid junction does not exist.

At the interfaces between the electrolytes and the solid electrodes, a small potential exists which is known as liquid junction potential. This is very important, earlier I had referred to that in our my previous class also. So, liquid junction potential is an important concept in electrochemistry which influences the accuracy of the analysis to a significant extent.

We must know about the liquid junction potential if you want to be called as an electro chemist. When both the electrodes are dipped in the same solution, liquid junction does not exist, this you must understand; if the electrodes are both in the same solution, there is no liquid junction.

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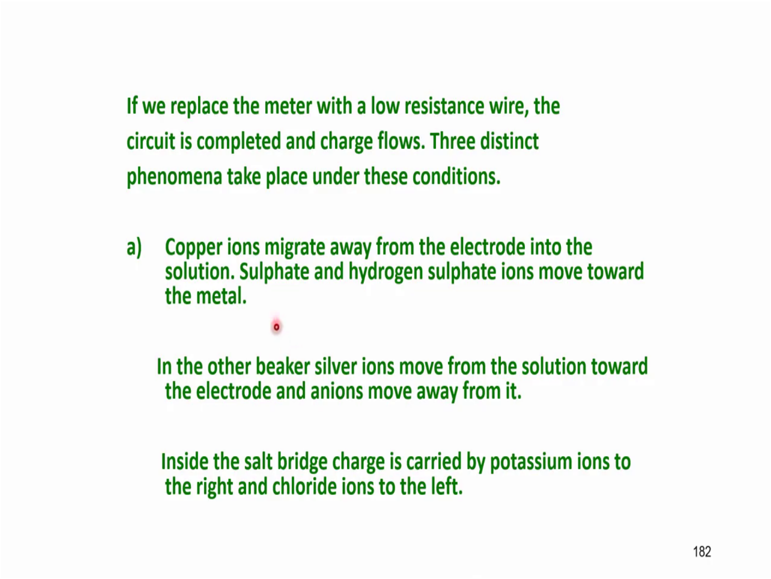

If we replace the meter with a low resistance wire, the circuit is completed and charge flows. Three distinct phenomena take place under these conditions.

a) Copper ions migrate away from the electrode into the solution. Sulphate and hydrogen sulphate ions move toward the metal.

In the other beaker silver ions move from the solution toward the electrode and anions move away from it.

Inside the salt bridge charge is carried by potassium ions to the right and chloride ions to the left.

So if we replace the meter with a low resistance wire, the circuit is completed and the charge flows. Three distinct phenomena take place under the conditions; copper ions migrate away from the electrode into the solution. Sulfate and hydrogen sulfate ion move towards the metal.

In the other beaker silver ions move from the solution, this I am referring to the previous figures what I had shown you; towards the electrode and anions move away from it. Inside the salt bridge charge is carried by potassium ions to the right and chloride ions to the left; if I use make a potassium chloride salt bridge, ok.

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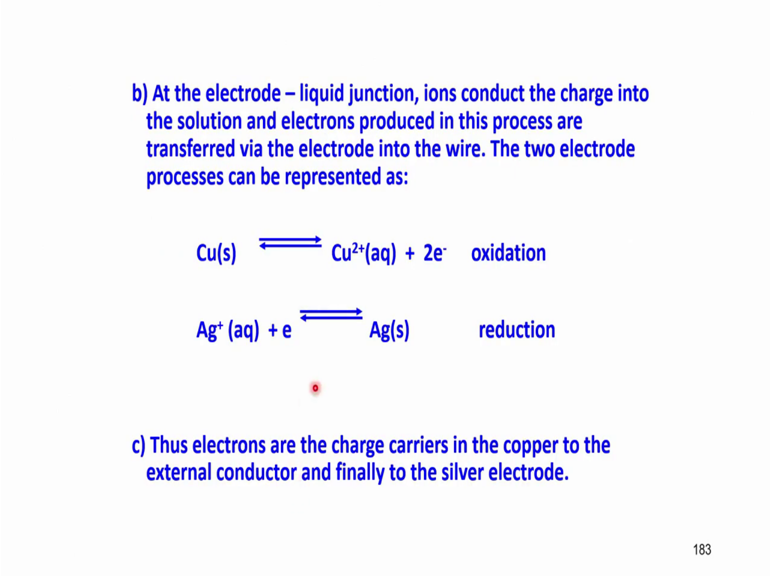

b) At the electrode – liquid junction, ions conduct the charge into the solution and electrons produced in this process are transferred via the electrode into the wire. The two electrode processes can be represented as:

$Cu(s) \rightleftharpoons Cu^{2+}(aq) + 2e^-$ oxidation

$Ag^+(aq) + e \rightleftharpoons Ag(s)$ reduction

c) Thus electrons are the charge carriers in the copper to the external conductor and finally to the silver electrode.

So, at the electrode; electrode and liquid you see that is liquid junction. So, at the electrode liquid junction, ions conduct the charge into the solution from the metal and the electrons produced in this process are transferred via the electrode into the external wire, ok.

So, the there are two electrode processes; one is the electrons are released into the external wire from the cathode wire from the cathode, and electrons enter the anode from the external wire in the other beaker. So, what is happening? In one case copper as a solid that is the electrode, it is dissolving to give you copper ions; and in the other, silver is depositing in the on the electrode.

So, both of them can be equilibrium reactions so long as there is no current, and the equilibrium reaction is represented as copper sulfate, copper solid. We are not writing the anion reaction, anion part, ok. So, if I write copper S here, it is copper solid and it solid copper is going to be producing cupric ions C u 2 plus ions; and as I had explained to you earlier, it will be surrounded by water molecules in my previous lecture and so we write aqueous.

So, plus 2 it is going to release two electrons, this is known as oxidation. Why? Electrons are released the removal of electrons is oxidation, I had explained to you in the concepts of chemistry part when in the beginning of this course. And in the other on the other electrode, silver ions in the aqueous phase pick up the electron and form silver solid silver particles which will deposit on the cathode anode.

So, reduction, this is known as the reduction; addition of electrons is known as reduction. But forget about deposition, because this is an electric equivalent, it is a an equilibrium reaction I am trying to show, ok. So, the electrons are the charge carriers in the copper to the external conductor and finally to the silver electrode, this I had explained to you earlier, ok.

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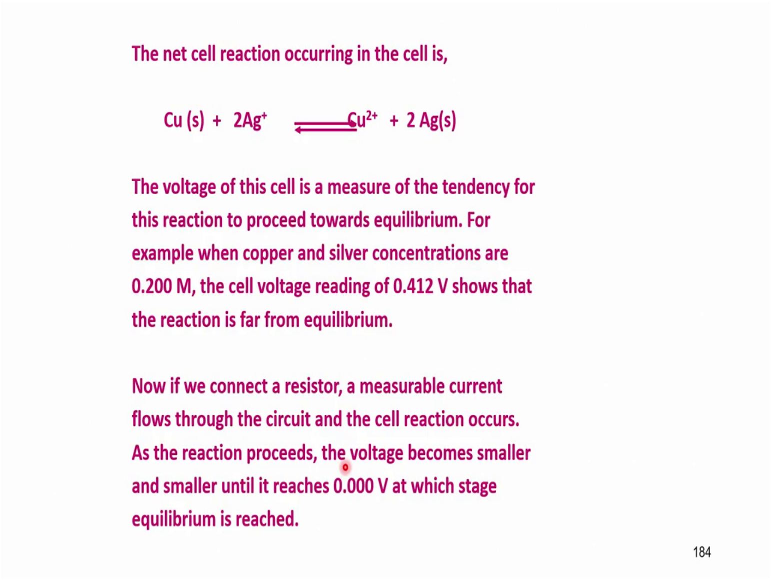

The net cell reaction occurring in the cell is,

$$\text{Cu (s)} + 2\text{Ag}^{+} \rightleftharpoons \text{Cu}^{2+} + 2\,\text{Ag(s)}$$

The voltage of this cell is a measure of the tendency for this reaction to proceed towards equilibrium. For example when copper and silver concentrations are 0.200 M, the cell voltage reading of 0.412 V shows that the reaction is far from equilibrium.

Now if we connect a resistor, a measurable current flows through the circuit and the cell reaction occurs. As the reaction proceeds, the voltage becomes smaller and smaller until it reaches 0.000 V at which stage equilibrium is reached.

Now, you listen to this carefully. So, the net cell reaction occurring in the cell is given by C u solid copper solid plus 2 silver ions, I am writing the stoichiometry now; because silver ion requires only one electron to be reduced to silver metal, but copper solid when it dissolves, it is going to give two electrons. So, one copper ion, it can react with two silver ions to react with copper 2 to give you a copper 2 plug one copper 2 plus ion and 2 silver element as a solid reduced to silver form.

So, that is the stoichiometric reaction, the voltage of this cell is a measure of the tendency for this reaction to proceed towards equilibrium. So, what happens? The voltage of such a reaction is that tells us whether it can proceed towards equilibrium, that is towards the right or left. For example, when copper and silver concentrations are 0.2 molar and cell voltage was reading 0.412 in the previous slide, it shows that the reaction is far from equilibrium.

If it is in equilibrium, what would have been the voltage? It should be zero; there should not be any current flowing, because whatever is going in the right hand side is coming back on the left hand side that is reduction oxidation reduction reactions will be taking place on their opposite side.

Now, if I connect a resistor and a measurable current flows through the circuit, the cell reaction occurs. As the reaction proceeds, voltage becomes smaller and smaller; and from 0.412, it will reach almost 0.000 volts at which stage we will say, no more copper is depositing, no more copper is dissociating to give you copper 2 plus ions, nor silver is being formed at that stage and it is a it has reached the equilibrium position. So, at equilibrium position, the voltage of the substance of the system would be zero.

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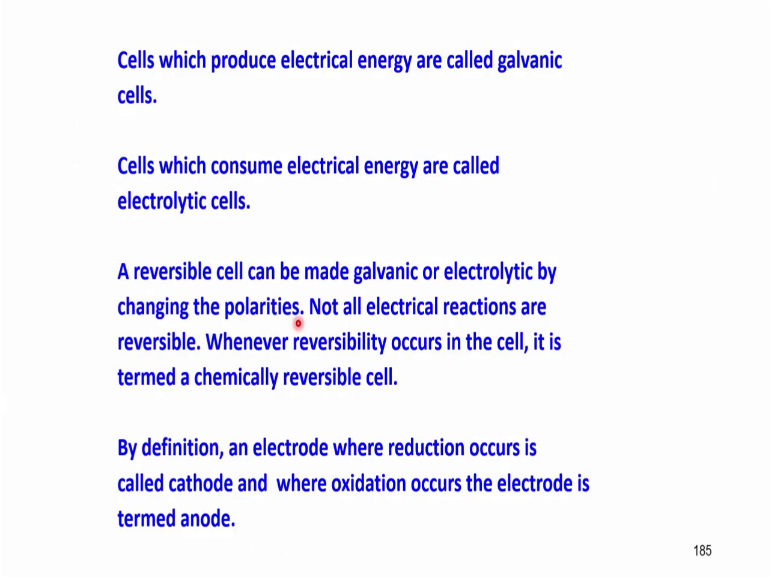

Cells which produce electrical energy are called galvanic cells.

Cells which consume electrical energy are called electrolytic cells.

A reversible cell can be made galvanic or electrolytic by changing the polarities. Not all electrical reactions are reversible. Whenever reversibility occurs in the cell, it is termed a chemically reversible cell.

By definition, an electrode where reduction occurs is called cathode and where oxidation occurs the electrode is termed anode.

So, cells which produce electrical energy are called galvanic cells. Very simple try to remember this expression cells, and then I am writing one more sentence which cells which consume electricity are called electrolytic cells. So, the battery cell, what you put in your torch or watch or camera or anywhere else is producing electrical energy whenever you want. So, it is a galvanic cell. So, electrical energy which are which consume electrical energy are called electrolytic cells. So, all electroplating systems are electrolytic cells.

So, we are going to say that a reversible cell can be made galvanic or electrolytic by changing the polarities; I can make for example, external circuit you remember, it is just wire with a connection, and this wire with connection I can change the polarity. And then I what happens, I can make galvanic cell into an electrolytic cell; if I change the wires again positive will become negative, negative will become positive, because it is an electro chemical system equilibrium system. So, reaction can go either this way or that way. So, a reversible galvanic cell can be made into a reversible electrolytic cell and vice versa.

So whenever reversibility occurs in the cell it is termed as a chemically reversible cell. By definition an electrode where reduction occurs is cathode, and oxidation occurs is anode; this I think I had told you a number of times and it is better to remember, reduction at cathode, oxidation at anode very important and you should do not get confused where happens what. So, now, I am going to talk a little bit about the electrical double layer.

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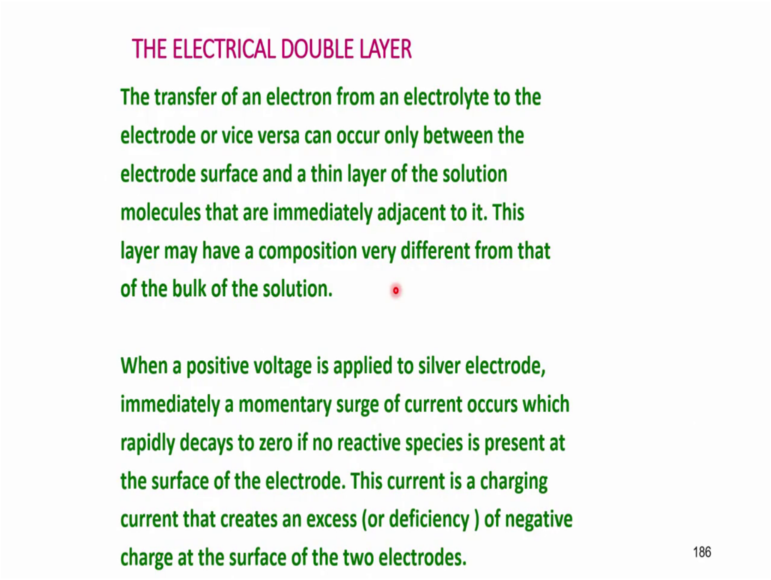

THE ELECTRICAL DOUBLE LAYER

The transfer of an electron from an electrolyte to the electrode or vice versa can occur only between the electrode surface and a thin layer of the solution molecules that are immediately adjacent to it. This layer may have a composition very different from that of the bulk of the solution.

When a positive voltage is applied to silver electrode, immediately a momentary surge of current occurs which rapidly decays to zero if no reactive species is present at the surface of the electrode. This current is a charging current that creates an excess (or deficiency) of negative charge at the surface of the two electrodes.

So, what happens in an electrical double layer? The electrical double layer forms whenever there is a contact between a liquid and solid, ok. So, the transfer of an electron from an electro light to the electrode or vice versa occurs only between the electrode surface and a thin layer of solution containing molecules that are immediately adjacent to it.

So, you can imagine, if I give you a solution containing an electrode dipped in a solution; around the electrode, you can imagine a thin portion of a thin slice of shape of the electrode containing water around it, that may be 1 mm water cell or it may be 2 mm that is the that your imagination should be of the same shape of the electrode.

A water body having the same shape as the electrode and very minute thickness maybe half a millimeter or 0.5 millimeter, 0.05 millimeter depends upon your imagination. So, that layer of water that is immediately adjacent to the electrode is the electrode junction; water electrode junction. So, this layer may have a composition very very different from that of the bulk of the solution.

Why? Let me give you a two minute pause I am sorry about three seconds pause to think about it; why it should be, it is different, around immediately adjacent to the electrode that solution part. What you are imagining maybe 0.5 mm, 0.2 mm something like that, why it is different from the bulk of the solution. Externally if you look at the bulk of the solution you may not see anything; but there is a difference between the solution part that is immediately adjacent to the electrode, whether it is anode or cathode both of them are having this liquid junction around it. Any solid surface for that matter will have a liquid junction around it. So, why it is different in electrochemical cells?

Think about it and now the two seconds are over, I have repeated and given you more than five seconds to think about it. Now, I will I would like to state that, the all the ions are traveling towards anode or cathode. So, all the cations are coming towards anode, and many of them are not capable of getting reduced at the cathode, or getting oxidized at the anode; then what happens? They are attracted towards a particular cathode or anode, but they are not reaching the cathode.

So, they are all hanging around the electrode in a small portion of the solvent, what you are imagining; that imagination section, cross section of that imagined solvent part contains all the electrons that have been the that have successfully reached the cathode, but they are not capable of reacting with the cathode. So, they form a special layer of concentrated ions around the electrode and not doing anything.

Just imagine I can give you analogy I; imagine you are going on the road there is an accident, a guy has fallen with a motorcycle or something like that, hit another motorcycle, they two are affected, they two are reacting and there is a large crowd around them. They are not doing anything they are only standing there and watching or shouting; bring somebody doctor, bring somebody police, bring somebody this thing that thing, but nobody helping them. So, these are all like bystanders, watching what is happening around it, ok. So, that is the liquid junction for you.

So, the layer may have a composition very different containing hydroxyl ions, hydrogen ions, other ions, sulfate ions, chloride ions all ions around the anode; and sodium, potassium, lithium, copper, silver, gold, iron all other cations around it, but only one ray one of them is getting reduced at the cathode.

So, when a positive voltage is applied; and now coming back to our system when a that is copper silver system, I have been talking about. Where a positive voltage is applied to silver electrode, immediately a momentary surge of the current occurs which rapidly decays to zero; if no reactive species is presented at the surface of the electrode. This current is known as charging current; the moment you switch it on, that creates an excess or deficiency of negative charge at the surface of the two electrodes, ok.

Do not get confused, do not get worried about if you do not understand this sentence; but if you look at the slide think about it, you will appreciate what I have written, ok. So, look at the slide now; when a positive voltage is applied to silver electrode, immediately a momentary surge of current occurs, this you understand. So, that rapidly decays to zero, if there is no reactive species is present; this current is a charging current that creates an excess of negative charge at the surface of the electrodes, ok.

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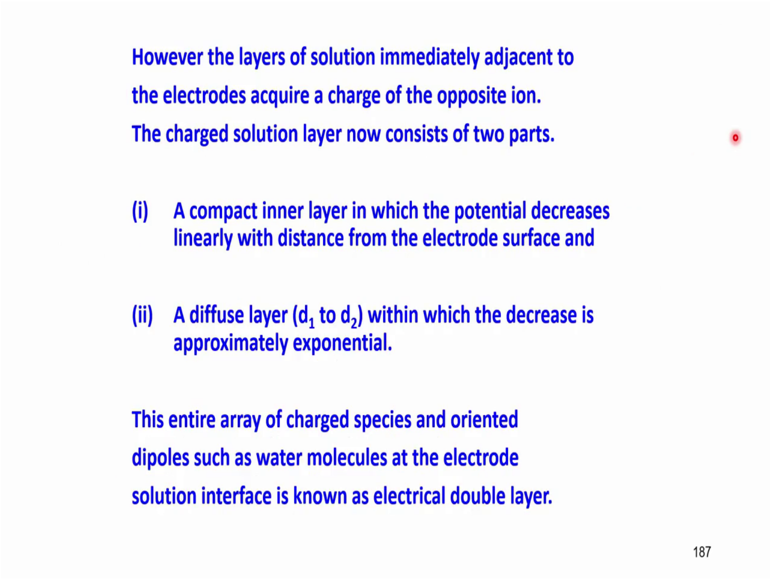

However the layers of solution immediately adjacent to the electrodes acquire a charge of the opposite ion. The charged solution layer now consists of two parts.

(i) A compact inner layer in which the potential decreases linearly with distance from the electrode surface and

(ii) A diffuse layer (d_1 to d_2) within which the decrease is approximately exponential.

This entire array of charged species and oriented dipoles such as water molecules at the electrode solution interface is known as electrical double layer.

So however, the layers of solution immediately adjacent to the electrodes acquire a charge of the opposite ion. Layers of solution, I am talking about the liquid junction know. So, imagine that layer of solution, immediately adjacent to the electrode acquires a charge of the opposite ion. The charged solution layer now consists of two parts; one is a compact inner layer in which potential decreases linearly from the electrode surface, and a diffuse layer d 1 to d 2, I will show you a figure shortly, with within which the decrease is approximately exponential, ok. That what is exponential, what is the parameter we are talking about?

We are talking about the potential. So, compact inner layer in which potential decreases linearly with distance from the electrode surface in the liquid junction what your imagining, and it has also a diffuse layer within which the decrease is a approximately exponential. This entire array of charged species and oriented dipoles such as water molecules that I have shown you that figure earlier I drew it with a red ink, at the electrode solution this interface is known as electrical double layer.

A very important concept in all electrochemical, among all electro chemical techniques technologists, scientists. And what it means is, a liquid junction has two layers; one is in which the voltage decreases linearly, another layer it decreases exponential. So, that is a electrical double layer for you, this is the best I can explain to you, this whole concept; not many people especially student level do understand these concepts very clearly.

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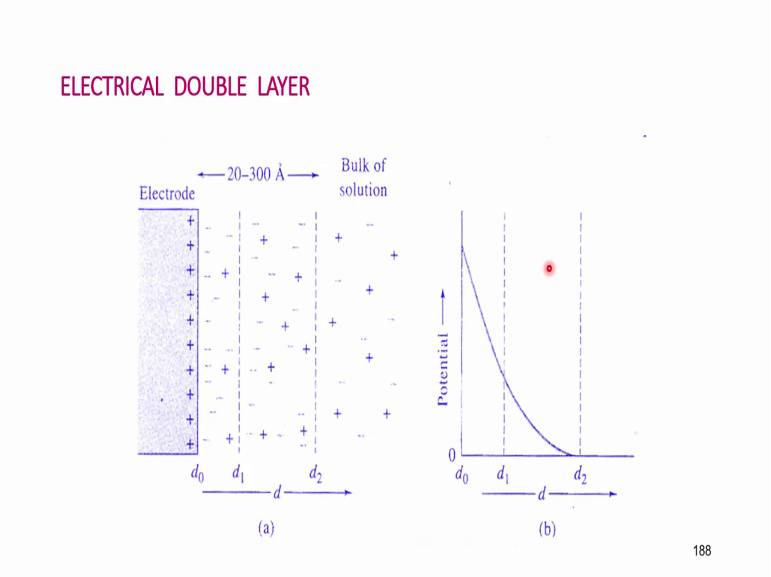

ELECTRICAL DOUBLE LAYER

Now, look at the figure I am drawing; here I have an electrode in this side plus, plus, plus, plus, plus this is all metals ok; this is the metal are there in the cations are there on the outer surface of the metal. And electrons will be hanging around that; that is fermi layer; that means, the top surface of the material will be having cations. And all the positive ions from the bulk of the solution, this is the bulk of the solution; I am imagining two layers one here, another here of the order of 20 to 300 angstrom minutes, this is the bulk of the solution.

From the bulk of the solution, the moment I add, the moment I give a charge; the cations will start moving towards the electrode ok, this cations will move towards electrode like this, this will move towards electrode like this, this will be move electrode like that all cations will be moving towards the electrode. And then this the immediately adjacent to this I can imagine two layers; one up to from 0 to 20 angstrom minutes, and 20 to 300 angstrom minutes, ok.

So, here there is no, this is the first layer ok; compact inner layer in which potential decreases linearly. I have drawn the potential from this point dashed line to d 1 to d 0, d 0 to d 1, and this in this region it is decreasing linearly almost linearly, I have drawn here. And in this region, the potential decrease; potential here will be less than this, so it is decreasing. So, I have draw from, when I draw the potential curve from here; that is from the metal surface up to 20 angstroms and up to 300 angstroms, in this region it is decreasing linearly and in this region it is decreasing exponentially, ok.

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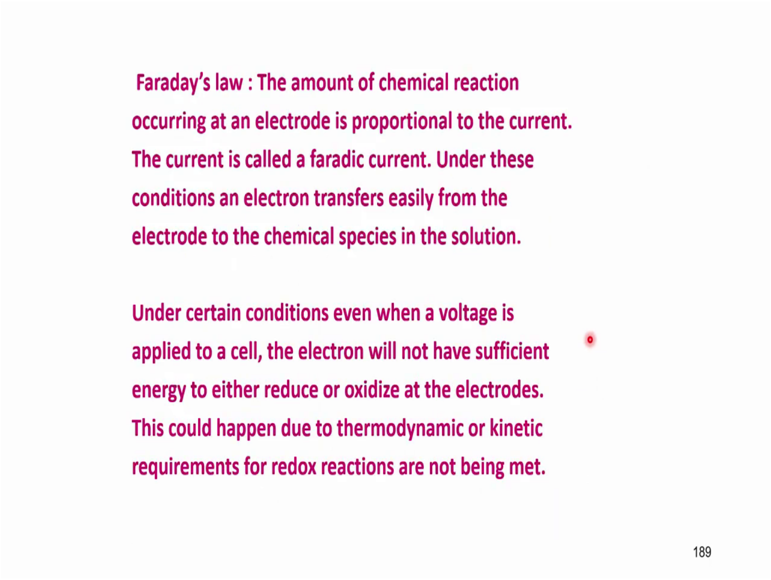

Faraday's law : The amount of chemical reaction occurring at an electrode is proportional to the current. The current is called a faradic current. Under these conditions an electron transfers easily from the electrode to the chemical species in the solution.

Under certain conditions even when a voltage is applied to a cell, the electron will not have sufficient energy to either reduce or oxidize at the electrodes. This could happen due to thermodynamic or kinetic requirements for redox reactions are not being met.

So, that is electrical double layer for you. If you understand that much, you will understand all other research papers in electro chemical technology perfectly well. If a somebody says, the electrical double layer is so thickness, so and so thickness and the voltage will change so much, so much like that, we can easily do that.

And then I want to define this Faraday's law, which I have already defined earlier; that is the amount of chemical reaction occurring at the electrode is proportional to the current, this is faradic current. Under these conditions an electron transfers easily from the electrode to chemical species. Under certain conditions even when the voltage is applied to a cell, the electron will not have sufficient energy to react at the electrode, either reduction or oxidation. This could happen due to thermodynamic region, kinetic region requirement etcetera, they are not being met.

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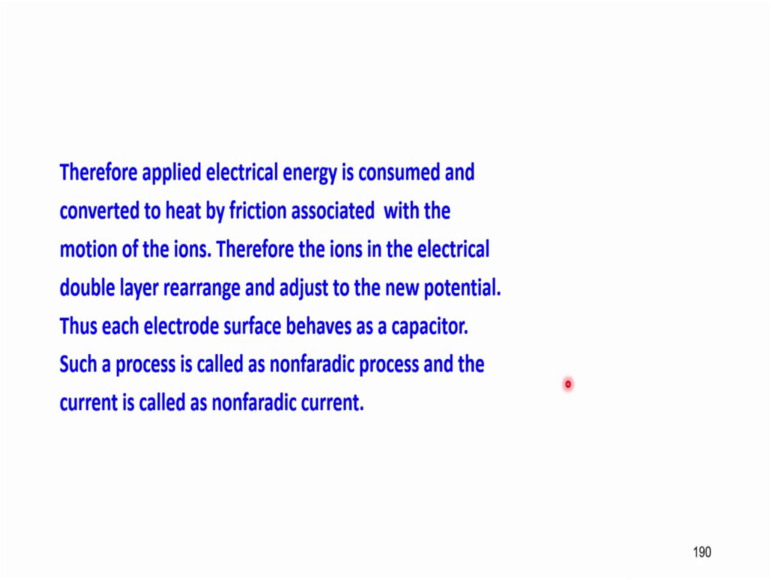

Therefore applied electrical energy is consumed and converted to heat by friction associated with the motion of the ions. Therefore the ions in the electrical double layer rearrange and adjust to the new potential. Thus each electrode surface behaves as a capacitor. Such a process is called as nonfaradic process and the current is called as nonfaradic current.

So, therefore, applied electrical energy is consumed and converted to heat by friction associated with the motion of the ions. And the electrical double layers rearranges and adjust to the new potential. So, each electrodes surface behaves as a capacitor. So, what is a capacitor? Capacitor is the, an area in which the charges are held; potential is there, but it is not being utilized. Such a process is called nonfaradic process and the current is called nonfaradic current; whatever current it can produce is known as nonfaradic current.

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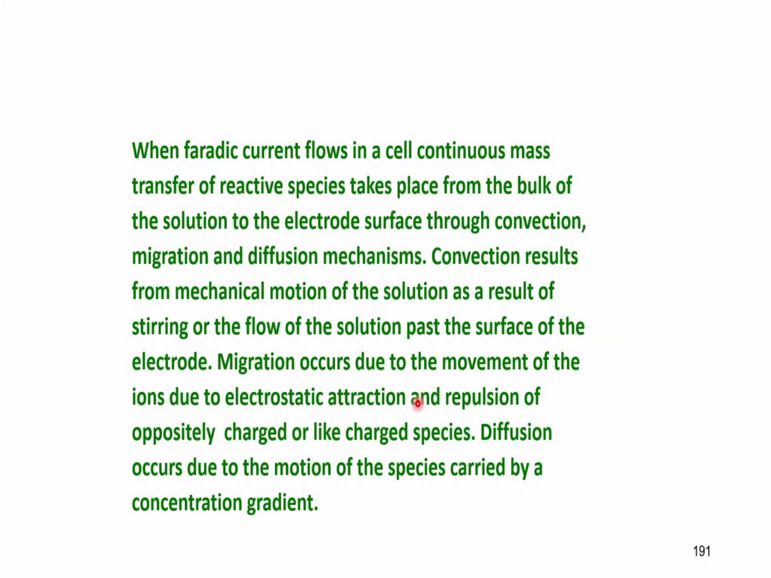

When faradic current flows in a cell continuous mass transfer of reactive species takes place from the bulk of the solution to the electrode surface through convection, migration and diffusion mechanisms. Convection results from mechanical motion of the solution as a result of stirring or the flow of the solution past the surface of the electrode. Migration occurs due to the movement of the ions due to electrostatic attraction and repulsion of oppositely charged or like charged species. Diffusion occurs due to the motion of the species carried by a concentration gradient.

So, we will stop here, and continue our discussion on faradic current and convection, migration etcetera etcetera in our next class.

Thank you very much, have a nice day.