Modern Instrumental Methods of Analysis

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Lecture No. # 35

Introduction to Nuclear Magnetic Resonance Spectroscopy

In the last class, we had discussed about the NMR spectrum and chemical shifts etcetera. I had, I was dealing with the 19 F and 31 P interactions with the protons; that causes spin-spin splitting.

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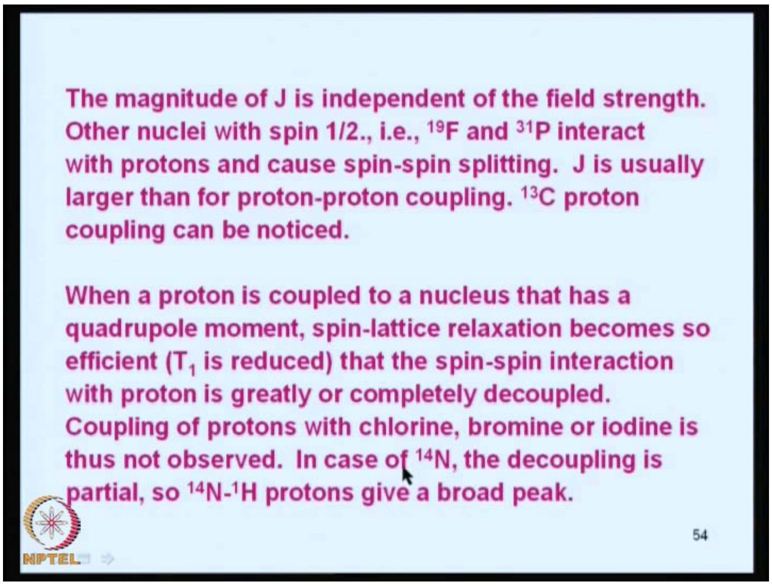

The magnitude of J is independent of the field strength. Other nuclei with spin 1/2., i.e., ^{19}F and ^{31}P interact with protons and cause spin-spin splitting. J is usually larger than for proton-proton coupling. ^{13}C proton coupling can be noticed.

When a proton is coupled to a nucleus that has a quadrupole moment, spin-lattice relaxation becomes so efficient (T_1 is reduced) that the spin-spin interaction with proton is greatly or completely decoupled. Coupling of protons with chlorine, bromine or iodine is thus not observed. In case of ^{14}N, the decoupling is partial, so ^{14}N-^{1}H protons give a broad peak.

So, we were discussing that coupling of protons with chlorine, bromine or iodine is usually not observed, but in case of 14 N, the decoupling is partial. So, 14 N, 2 1 H protons give a broad speaks.

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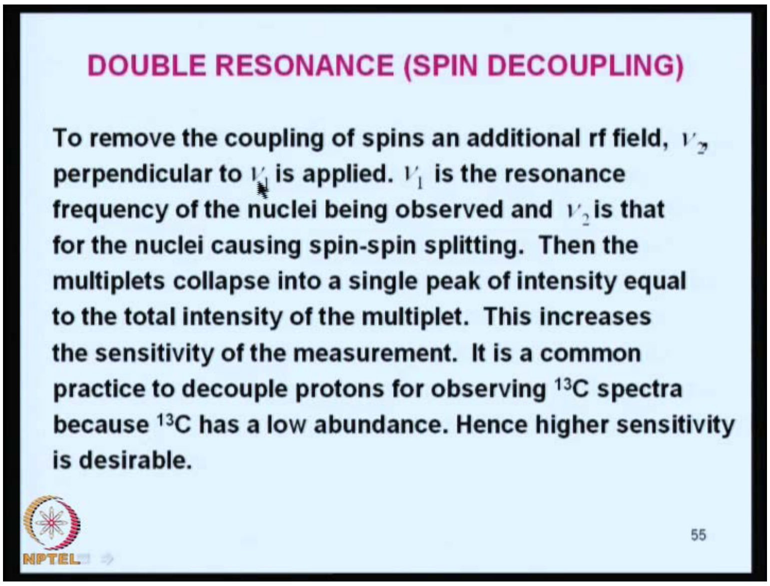

DOUBLE RESONANCE (SPIN DECOUPLING)

To remove the coupling of spins an additional rf field, ν_2 perpendicular to ν_1 is applied. ν_1 is the resonance frequency of the nuclei being observed and ν_2 is that for the nuclei causing spin-spin splitting. Then the multiplets collapse into a single peak of intensity equal to the total intensity of the multiplet. This increases the sensitivity of the measurement. It is a common practice to decouple protons for observing ^{13}C spectra because ^{13}C has a low abundance. Hence higher sensitivity is desirable.

So, in spin decoupling, to remove the coupling of spins an additional rf field, v2, perpendicular to v1 is applied. And where v1 is the resonance frequency of the nuclei being observed and two would be that for the nuclei causing spin-spin splitting. Then the multiples collapse into a single peak as usual of intensity equal to the total intensity of the multiplet. This increases the sensitivity of the measurement. It is a common practice usually to decouple the protons for observing 13 C spectra, because 13 C has a very low abundance. Therefore, higher sensitivity is always desirable.

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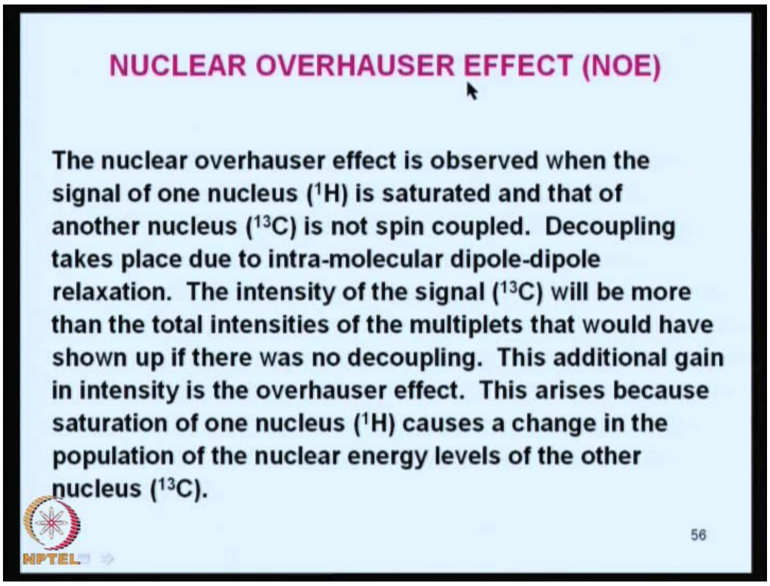

NUCLEAR OVERHAUSER EFFECT (NOE)

The nuclear overhauser effect is observed when the signal of one nucleus (^1H) is saturated and that of another nucleus (^{13}C) is not spin coupled. Decoupling takes place due to intra-molecular dipole-dipole relaxation. The intensity of the signal (^{13}C) will be more than the total intensities of the multiplets that would have shown up if there was no decoupling. This additional gain in intensity is the overhauser effect. This arises because saturation of one nucleus (^1H) causes a change in the population of the nuclear energy levels of the other nucleus (^{13}C).

Now, this is the one last, but one slide that is nuclear overhauser effect; this effect is observed when the signal of the nucleus is saturated and that of the other nucleus is not spin couple that is 13 C. Decoupling usually takes place due to intra molecular dipole-dipole relaxations. And the intensity of the signal will be more than the total intensity of the multiplet that would have shown up if there was no decoupling this additional gain in intensity is known as the overhauled effect.

This arises because saturation of one nucleus that is corresponding to one hydrogen causes a change in the population of the nuclear energy levels of the other nucleus. So, with this much of information. I would like to tell you only additional information for your for your reference that magnetic resonance imaging which is based on similar technique has gained wide popularity in the field of medicine also.

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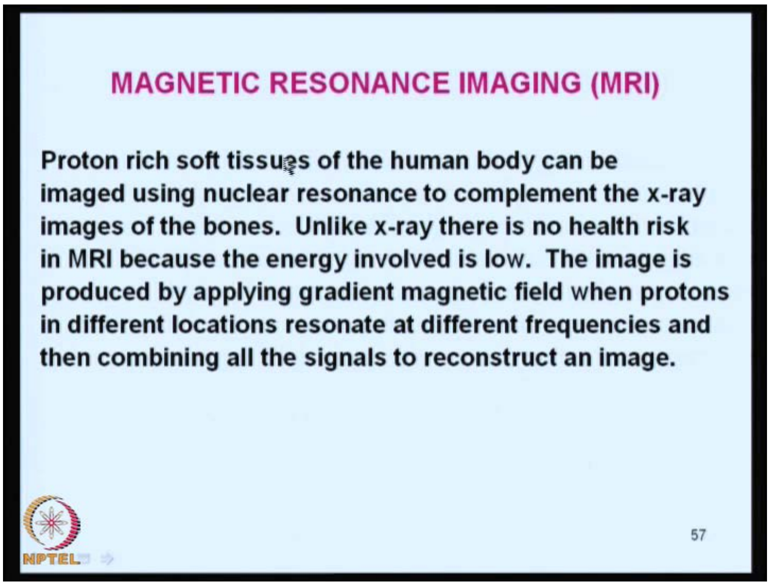

MAGNETIC RESONANCE IMAGING (MRI)

Proton rich soft tissues of the human body can be imaged using nuclear resonance to complement the x-ray images of the bones. Unlike x-ray there is no health risk in MRI because the energy involved is low. The image is produced by applying gradient magnetic field when protons in different locations resonate at different frequencies and then combining all the signals to reconstruct an image.

Usually, proton soft tissues in our human body they are all reach in hydrogen. So, proton reach tissues of the human body can be imaged using nuclear resonance to complement the x-ray images of the bones. Unlike x-ray there is no health risk here in magnetic resonance imaging. Because, the energy involved is low the image is produced by applying the gradient magnetic field when protons in different locations resonate at different frequencies and then we combine all these signals to reconstruct an image.

So, with this introduction to MRI would like to end our discussion, on nuclear magnetic resonance and we will move on to the electrometric techniques electrometric techniques.

In general have certain advantages over other types of chemical analysis basically the electrometric techniques involve the measurement of voltage, current or resistance or some other property; which is related to the chemical species. So, the electro analytical measurements what sort of advantages they give in the analytical science.

First of all, the measurements we have to understand that are specific to the oxidation state of the element ;that is the element may be in plus one oxidation state, plus two some are in plus three chromium is, plus seven like that different oxidation states of the elements respond differently to the electrochemical measurements and the instrumentation is very very inexpensive as compared to petrochemical methods. And you can set up the electro chemical instrumentation in your own laboratory using very simple available components in the market.

And then they provide information about the activities of the ions and chemical species rather than the concentrations. We have to make a distinction here regarding the activity and concentration. So, the information what you get is based on the activity rather than the concentrations.

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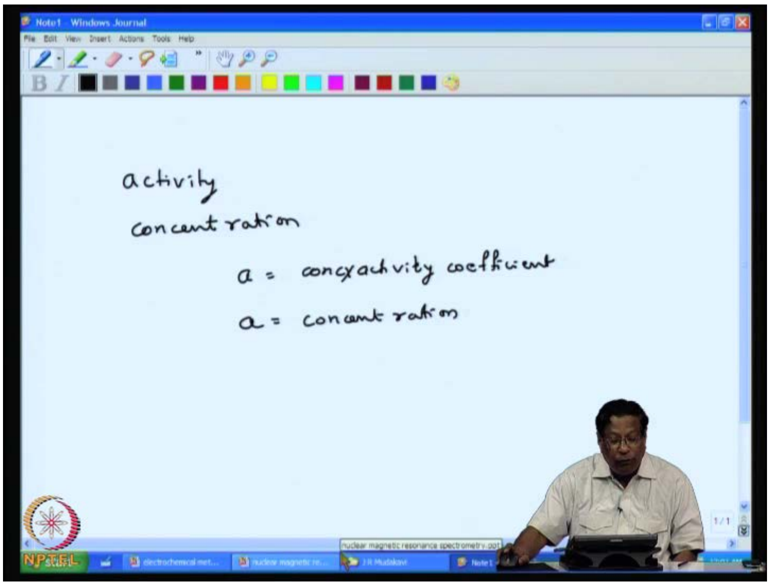
activity

concentration

a = conc $\times$ activity coefficient

a = concentration

So, what is the relation between activity and concentration? We have defined two terms; one is activity and another is concentration. In normal circumstances activity and concentration are almost uniform they mean the same thing, but actually activity is a term defined as concentration multiplied by activity coefficient. So, when the activity coefficient is one then activity would be equal to concentration this situation applies when the for dilute solutions. So, when we are talking of activities and concentrations we have to understand that we are dealing with the thermo dynamic quantity rather than chemical quantity.

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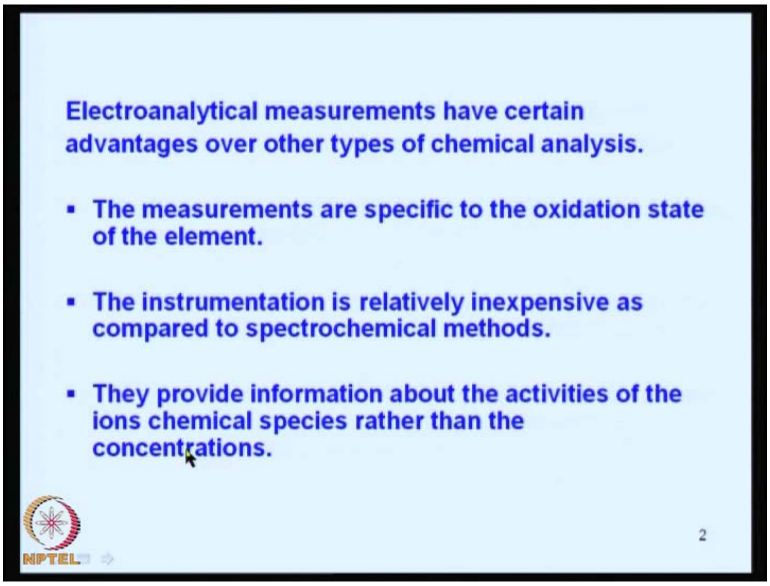

Electroanalytical measurements have certain advantages over other types of chemical analysis.

- 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, the information what we get in terms of electrometric measurements is about, the activities rather than the concentrations. Now, almost all the measurements in electrochemical techniques are done in electrochemical cells.

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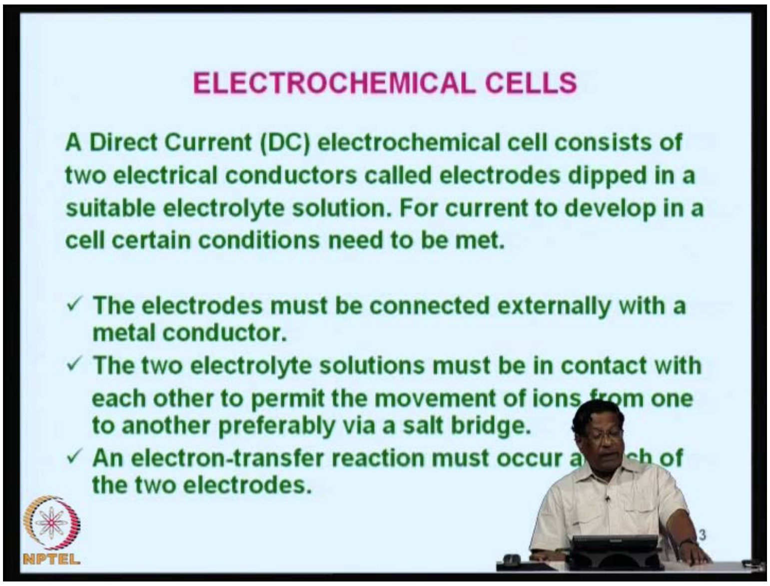

ELECTROCHEMICAL CELLS

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 a [illegible] ch of the two electrodes.

So, we can have direct current electrochemical cell which can consist of two electrical conductors called as electrodes. You need two metal plates; metal wires something like that to carry the electrode to the current these electrodes are dipped in a suitable electrolyte solution. And the solution must be having ions to carry the currents. So far, current to develop in a cell certain conditions need to be met, what are these conditions? The electrodes must be externally connected through a wire like copper wire or something it is known as metallic conductor. And then the two electrolyte solutions must be in contact with each other to permit the movement of the ions from one to another preferably via a salt bridge.

We will see, what is salt bridge? In a moment and then another condition is an electron transfer reaction must occur at each of the electrodes; that means, a chemical reaction must be taking place, an electron transfer must be taking place in separate sense and then they should be connected in the solution through the ions and externally through the metal wire which can carry the electrons.

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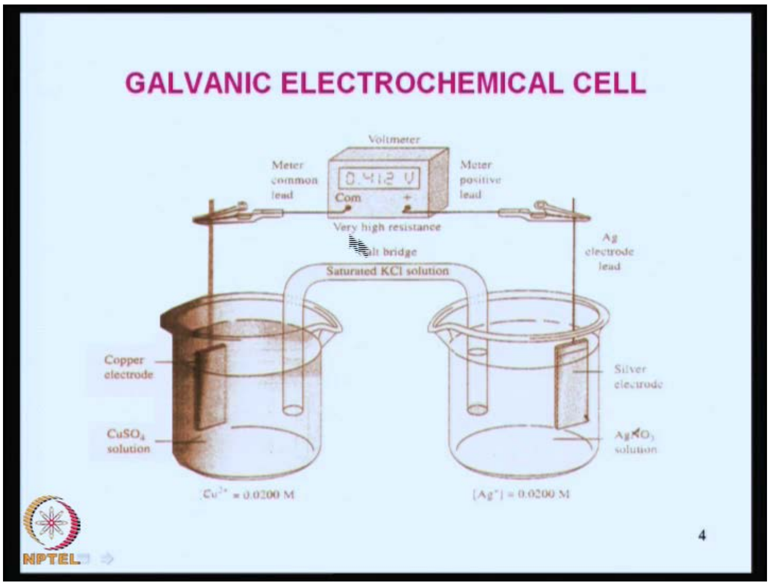

GALVANIC ELECTROCHEMICAL CELL

So, this is what we mean by an electrochemical cell; this is known as galvanic electro chemical cell. Here, I have an electrode this is a copper electrode and here, I have a silver electrode and this is connected through an external power supply; this is volt meter and this beaker contains copper sulphate solution and this beaker contain silver nitrate solution and there is a salt bridge, a glass bridge containing saturated potassium, chloride solution and one end is dipping in one beaker another end is dipping in another beaker. So, this is what a constitutes an electro chemical cell a galvanic electro chemical cell.

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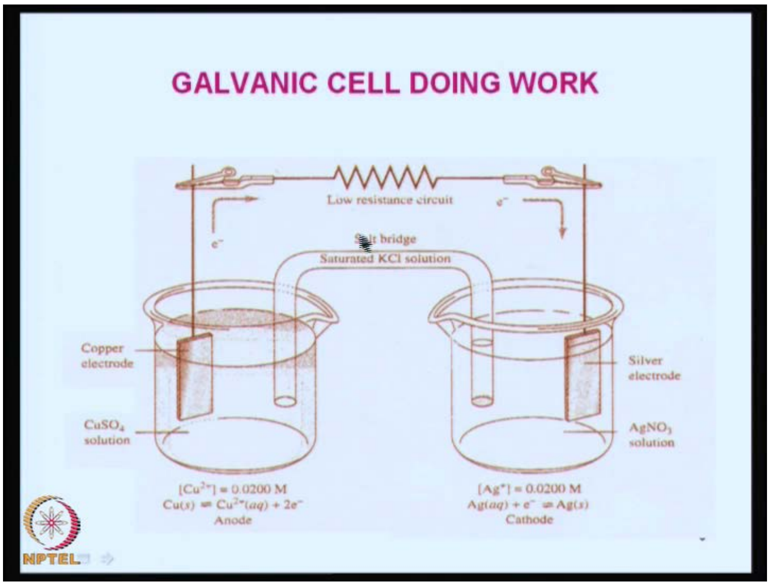

GALVANIC CELL DOING WORK

So, this is; if, I make the current pass through then I have the electro chemical electrons will be carrying from one end to the other end and then the reaction will be going on electrons will be released, ions will be passed, the current will be carried through the salt bridge into the this solution and then electrons will be released. So, this is how a galvanic cell operates.

Now, this is an electrolytic cell in which, I am supplying energy through an outside battery and again the remaining components remain the same thing that is beaker electrodes, copper electrodes, copper sulphate solution and this is the silver electrode and silver nitrate solution. So, again in this case the electrons are moving to the battery from the solution to the battery and then back into this copper sulphate solution; that means, I am supplying electrical energy to the cell to do the chemical work .

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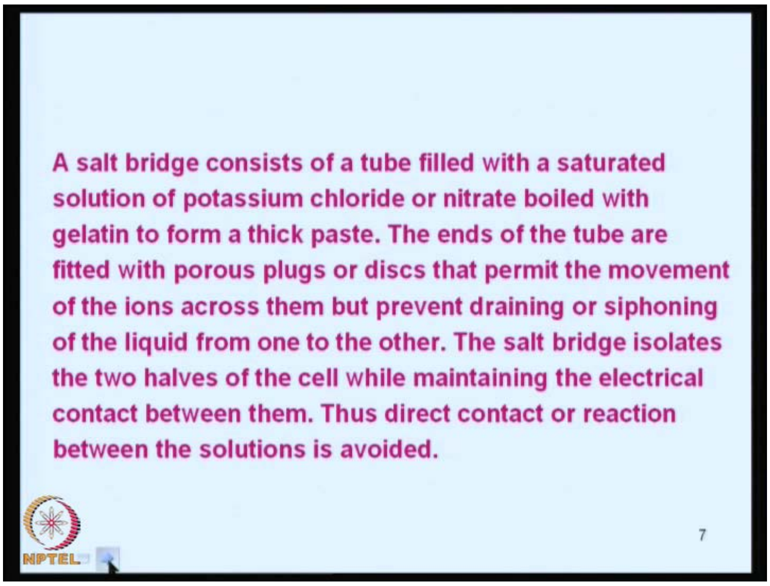

A salt bridge consists of a tube filled with a saturated solution of potassium chloride or nitrate boiled with gelatin to form a thick paste. The ends of the tube are fitted with porous plugs or discs that permit the movement of the ions across them but prevent draining or siphoning of the liquid from 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, let us discuss about, the salt bridge you have seen, what is salt bridge essentially? It is a glass, rod bent in the u shape and it is filled with potassium, saturated potassium chloride or some other suitable salt it. So, basically it consists of a tube filled with a saturated solution of a potassium chloride or nitrate and boiled with gelatin to form a thick paste.

So, when you take potassium chloride and this silver potassium chloride or potassium nitrate mix it with gelatin, heat it in a with a little bit of water it forms a thick paste you pour the solution into that. And then seal the ends with a permeable membrane or you can leave it just like that also it will solidify and then you can put a porous plug or disc that permit the movement of the ions across them, but prevents draining of the salt bridge solution.

The salt bridge essentially 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, a salt bridge is a very convenient tool. So, at the interfaces between the electrolytes and the solid 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.

So, when the both the solutions are dipped in the same solution the liquid junction potential does not exists; that means, when both electrodes are in the same solution there is no liquid junction.

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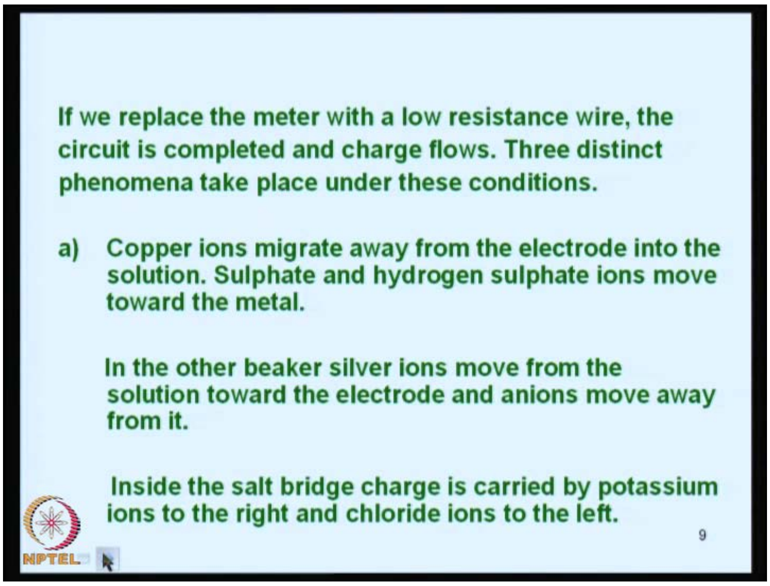

If we replace the meter with a low resistance wire, the circuit is completed and charge flows. Three distinct phenomena take place under these conditions.

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 meter in the galvanic cell; this meter was replaced with a battery here and if we do that with a low resistance wire this circuit is completed and charge flows three distinct phenomena take place under these conditions; one is copper ions, migrate from the electrode into the solution; that is copper will dissolve into the solution and sulphate and hydrogen sulphate ions move towards the metal and in the other beaker silver ions move from the solution towards the electrode and anions move away from it. So, there is cathode there is an anode and to towards the cathode, electrons will move towards the anode ions will move basically that is the phenomenon that takes place.

So, in other words silver ions move from the solutions to the electrode and anions move away from that inside the salt bridge the charge is carried by the potassium ions to the right and the chloride ions to the left. So, the whole process is complimented by the movement of the electric current either by the electrons or through the ions.

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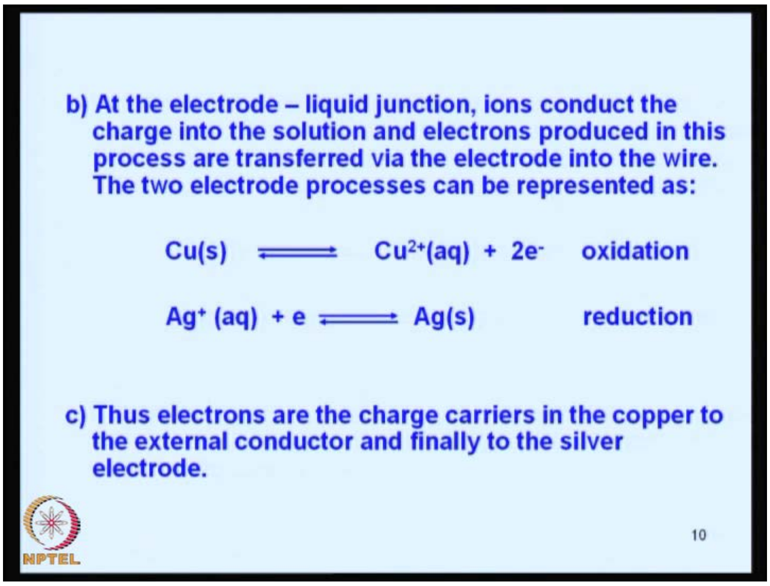

b) At the electrode – liquid junction, ions conduct the charge into the solution and electrons produced in this process are transferred via the electrode into the wire. The two electrode processes can be represented as:

$Cu(s) \rightleftharpoons Cu^{2+}(aq) + 2e^-$ 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 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 like this that coppers are solids. We have a copper solid here and it goes into Cu 2 plus an ion releasing two electrons in the process this is known as oxidation, removal of electrons is known as oxidation. And then silver ions are there they accept an electron coming from this side from the other side that is from the other beaker and form silver, supplied silver, solid silver I have put s as the solid.

Thus the electrons are the charge carriers in the copper to the external conductor and finally, to the silver electrode. So, these are the chemical reactions taking place in the electrolytic cell. So, what is the net reaction net reaction is copper will react with silver to produce the copper ions and silver solid; that means, silver would be increasing mass in mass weight and copper would be dissolving and losing the weight the voltage of this cell if you put a voltmeter somewhere in between as I had shown in that figure is a measure of the tendency for the reaction to proceed towards an equilibrium.

If you take a closer look at the previous slide here, I have put one equilibrium reaction that is one arrow goes points this side another arrow points this side; that means, the reaction can go either way.

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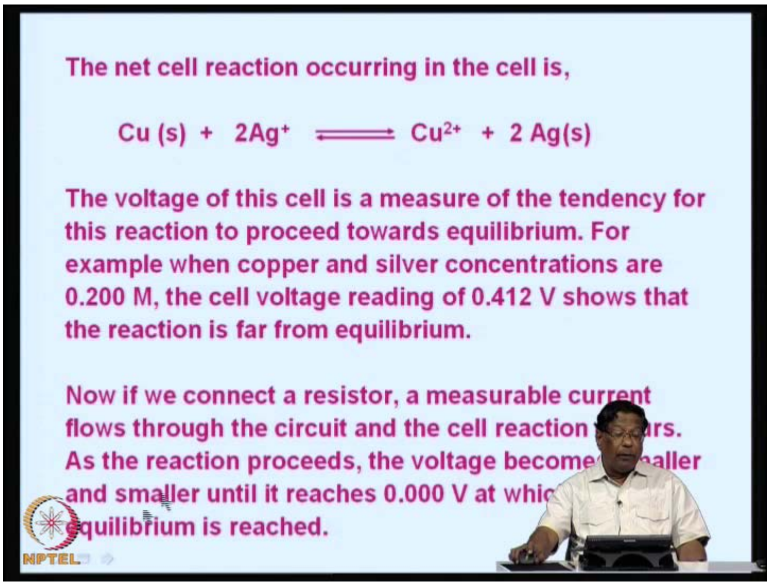

The net cell reaction occurring in the cell is,

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

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 rs. As the reaction proceeds, the voltage become aller and smaller until it reaches 0.000 V at whic quilibrium is reached.

So, the the voltage of the cell is a measure of the tendency for this reaction to proceed towards equilibrium. For example, when copper and silver concentrations are approximately 0.200 molar, the cell voltage needs about 0.412 volts it means that the reaction is far from equilibrium because it shows certain potential. Now, if we connect a resistor a measurable current flow through the circuit and cell reaction will start, because we are connecting and facilitating the reaction.

So, as the reaction proceeds the voltage becomes smaller and smaller until it reaches 0.00 volts; that means, no current will be passed; that means, the dissolution process stops and equilibrium is being reached. So, this is the type of chemical reaction that occurs at the electrodes. So, the cells which produce electrical energy are called as galvanic cells; that mean, you get current out of that by connecting the electrodes they are called as galvanic cells cells which consume electricity; that means, you have to supply electricity for a chemical reaction for example, in electroplating.

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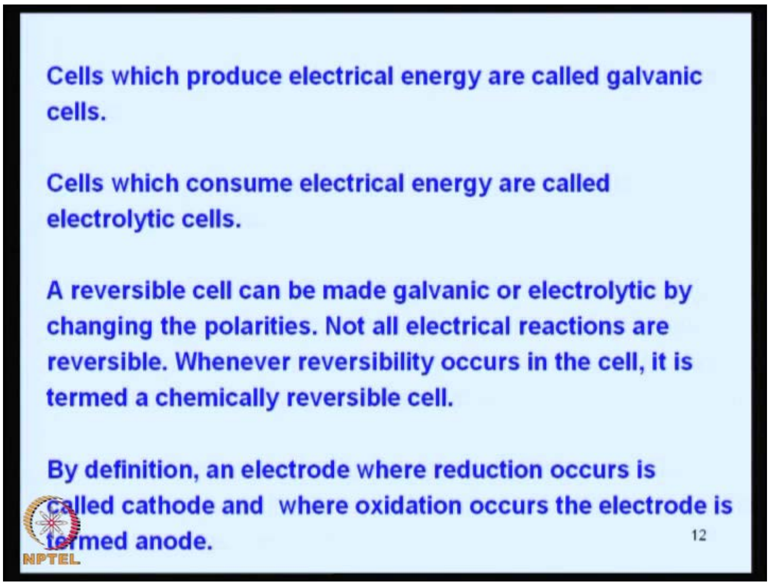

Cells which produce electrical energy are called galvanic cells.

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.

We have two solutions two plates; one object is, one object is to be plated you dip the solution make it cathode and the other one would be anode the anode would be dissolving and depositing on the cathode to make this reaction happen, you have to pass the electrical energy. So, the cells which consume electrical energy are called as electrolytic cells.

Then a reversible reaction can be made galvanic or electrolytic by changing the polarities. You just reverse the polarities change, exchange then the reaction can be made to go the other way; that means, silver can be made to dissolve and copper can be made to accept copper ions and increase in mass. So, the reversible can cell can be made galvanic or electrolytic by changing the polarities not all the electrical reactions are reversible this we have we have to remember not all reactions are reversible. So, some of them are irreversible many of the reversible reactions can be made to work either way by changing the polarities.

Whenever, reversibility occurs in a cell it is termed we call it as a chemically reversible cell by definition an electrode. Where, reduction occurs is called as cathode and where oxidation occurs is known as anode that is by convention. So, the now let us discuss about, the electro double layer this is all, what I am talking to you? Now, is a sort of introduction to the electrochemical methods of analysis, because we will be using these terms quiet commonly in our future discussions? That is why, I always wanted to want to give you some sort of a feeling towards the subject by talking rather slowly and introducing the concepts.

So, the concepts what we have learnt. So, far is that an electrochemical cell is containing electrodes one of them is termed cathode, another is anode at the cathode, electrons are released and the solid substance gets reduced at the anode the substance gets oxidized. And electrochemical cells can be reversible and if they are reversible you can make the reaction go either way by changing the polarities and we have also learnt that the electrodes that is the all not all the reactions are reversible some of them are irreversible.

Now, let us talk about the electrical double layer. So, the transfer of an electron from an electrolyte to the electrode or vice-versa can occur only between the electrodes surface and a very thin layer of the liquid surrounding the electrode it does not happen all over the bulk.

So, this layer may have a composition very very different from the bulk of the solution when a positive voltage is applied to the silver electrode that we have seen earlier. Immediately, a momentary surge of current occurs which rapidly decays to 0. If, no reactant species is present at the surface of the electrode at the electrode the moment you apply voltage the ions will start moving, but they will not reach the electrode unless certain amount of energy is reached certain amount of current is being carried.

So, if this momentary surge is not enough to carry a chemical reaction then the surge will destroy itself; that means, no reactive species present at the surface of the electrode to take away the current complete the current. So, we call this as a charging current and that creates the ions will move towards the electrode, but unable to transfer the energy to the electrode. So, along the electrode there will be a charging of the ions and this creates an access or deficiency of negative charge at the surface of the two electrodes both will happen ion captions will move towards the cathode anions will move towards the anode, but if there is no reaction all of them will be concentrating around a very small liquid layer around the electrode because no reaction is occurring.

However the layers of the solution immediately adjacent to the electrode acquire a charge of the opposite ion that is natural to understand, the charged solution solution the bulk of the solution consists of two parts; a compact inner layer in which the potential decreases, compact inner layer in which the potential decreases linearly with distance from the electrode surface

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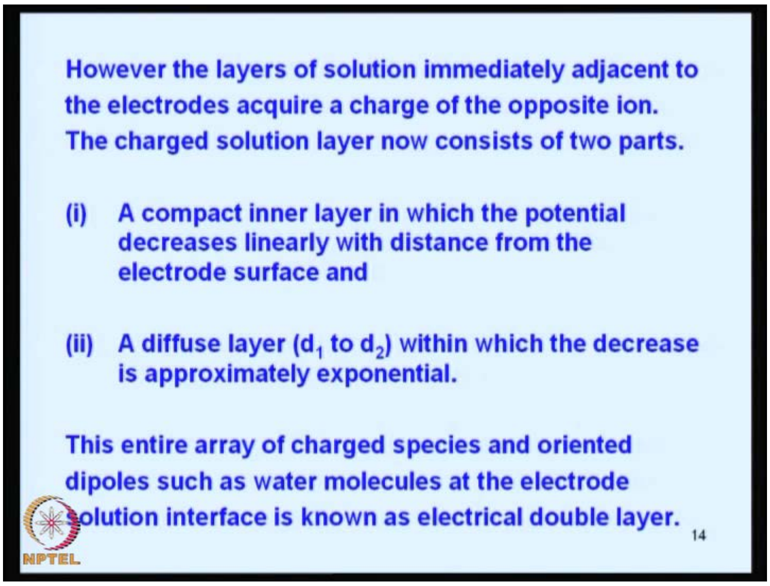

However the layers of solution immediately adjacent to the electrodes acquire a charge of the opposite ion. The charged solution layer now consists of two parts.

(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.

And there is another part that is the a diffused layer d1 to d2 within which the decrease is approximately exponential; one is linear decrease is, in one part it is linear in the other part it is exponential this entire array of the charged species and oriented dipoles such as water molecules at the electrode solution interface is known as electrical double layer.

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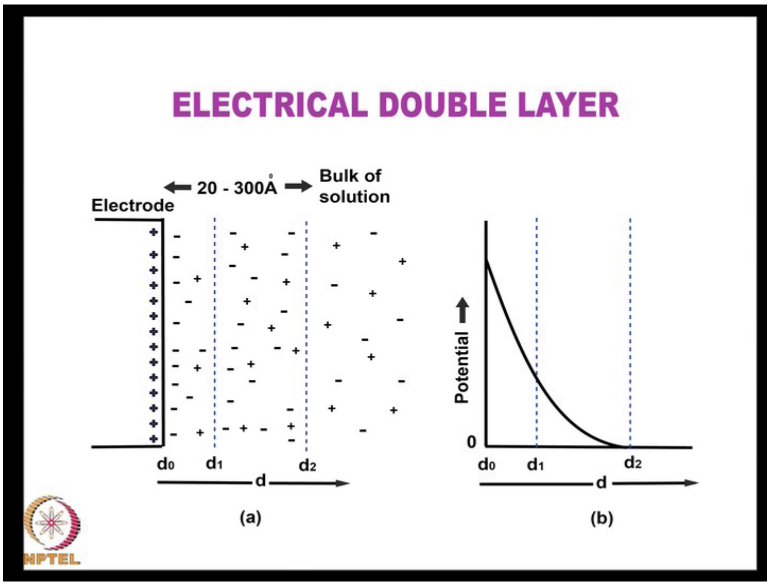

ELECTRICAL DOUBLE LAYER

Now, this situation shows you a pictorial diagram of an electrode double layer electrical double layer here. We have the electrode which is a solid species solid material carrying the positive charge and then there is an immediate bulk in this range there is diffusion current which is approximately 20 to 300 angstroms not much. And then here, the bulk of the anions are near the surface, but there is no direct contact and here the positive and negative ions are fairly well distributed that is d1 to d2; that is linear variation and here bulk of the solution they are all not much happening in the bulk of the solution. Pictorially, if you plot the potentials in this regions d0 to d1 it increases exponentially and d1 to d2 it decreases rather linearly. So, the electrical double layer is again another important concept in the electrochemical science.

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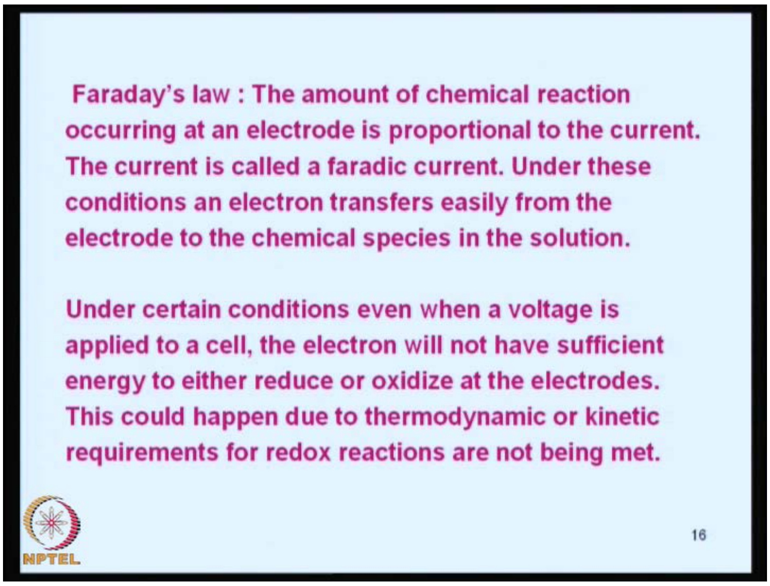

Faraday's law : The amount of chemical reaction occurring at an electrode is proportional to the current. The current is called a faradic current. Under these conditions an electron transfers easily from the electrode to the chemical species in the solution.

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.

Now, let us talk about the faraday's law, what is faraday's law? It deals with the amount of chemical reaction occurring at the electrode, what it says is? It is the amount of chemical reaction occurring at an electrode is proportional to the current; the current is called a faradic current. Because, it is faraday's law we have adopted this name faradic current under these conditions and electron transfers easily without bothering about the electrical double layer etcetera.

It 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 electrode. Under certain conditions these could happen due to thermodynamic and chemical requirements for the reduction, oxidation reactions are not being met; that means, the thermodynamic conditions are not being met. So, there would not be any reduction at the electrode surface.

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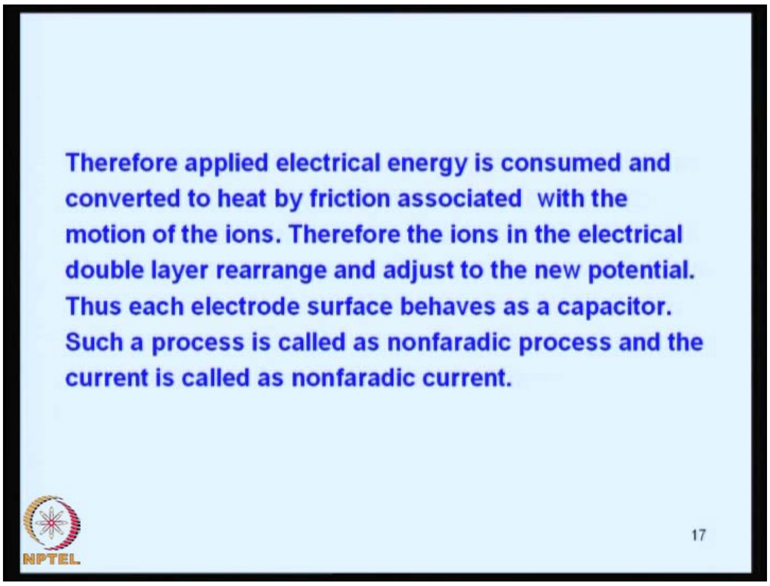

Therefore applied electrical energy is consumed and converted to heat by friction associated with the motion of the ions. Therefore the ions in the electrical double layer rearrange and adjust to the new potential. Thus each electrode surface behaves as a capacitor. Such a process is called as nonfaradic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

Therefore, applied electrical energy is consumed and the current, what happens to the current? It gets converted to heat by the friction associated with the motion of the ions ions will keep on moving left and right and it gets converted to heat. Therefore, the ions in the electrical double layer rearrange and adjust to the potential thereby each electrode surface behaves like a capacitor.

So, you apply current no reaction occurs, but the current is taken away to the electrical double layer, it assumes another potential and you again increase the current again there is no reaction due to thermodynamic and chemical conditions and again there is no reaction. So, current will increase. So, the sort of capacitor behavior is seen along the electrode such a process is called as non faradic process where there is no deposition, but applied current is taken up to assume a new value and the current is called as non faradic current because it does not do any work work means we thermodynamic work.

So, when faradic current flows in a cell continuous mass transfer of the reactive species takes place from the bulk of the solution to the electrode surface through convection it could be due to migration also it could be due to diffusion also, but during the faradic current current flow there is continuous mass transfer from the bulk of the solution to the electrode; that means, it keeps on getting deposited on the cathode convection usually results from the mechanical motion of the solutions; that is ions as a result of steering or flow of the solution passed to the surface of the electron. Around the surface of the electrode, migration occurs due to the movement of the ions due to electrostatic attraction positive ions will will attract the negative ions; negative ions will attract positive ion. So, these kinds of migration are known as electrostatic attraction and like charges repel each other unlike charges attract each other.

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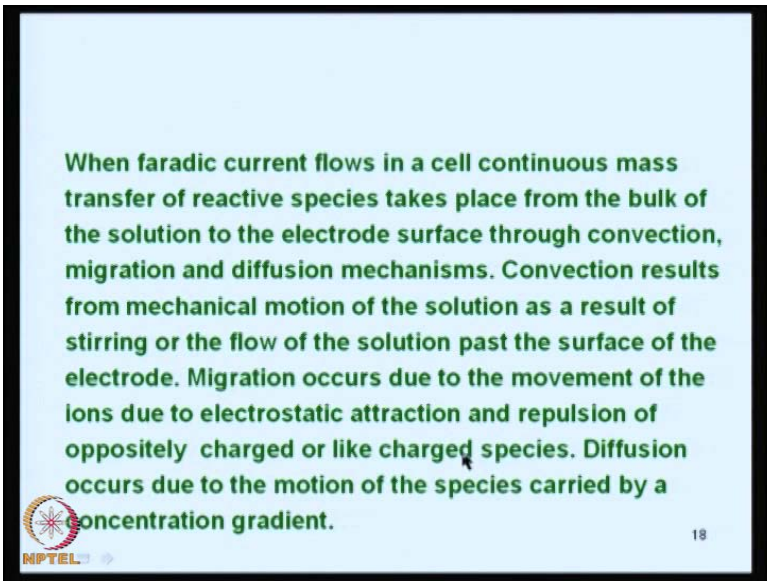

When faradic current flows in a cell continuous mass transfer of reactive species takes place from the bulk of the solution to the electrode surface through convection, migration and diffusion mechanisms. Convection results from mechanical motion of the solution as a result of stirring or the flow of 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, the repulsion of oppositely charged or like charged species is a specific phenomenon occurring around this range. So, diffusion occurs due to the motion of the species carried by a concentration gradient suppose there is a concentration gradient the diffusion will occur slowly among the two until the equation, until the concentrations become approximately equal. So, the concentration gradient itself could be a driving force.

So, major series of analytical methods are based on the electrochemical properties of the solutions; a solution of an electrode electrolyte contained in a glass vessel in contact with two electrodes which are connected to an outside source of electrical power can cause a current to flow through a cell. This is a simple concept electrolyte contained in a glass vessel in contact with two electrodes and connected to an outside source. So, this can cause a current to flow through the cell. So, we have to differentiate now what are the different kinds of electrodes we use, I have explained to you that we have used copper and silver electrodes earlier in my slides.

Now, there are different kinds of electrodes and they are basically of the three types and a known as the electrode of the first kind electrode, of the second kind electrode, of the third kind.

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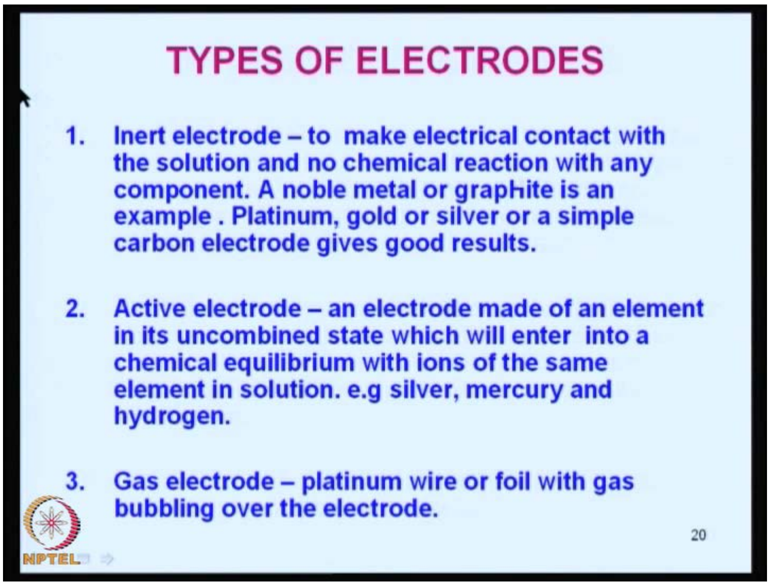

TYPES OF ELECTRODES

1. Inert electrode – to make electrical contact with the solution and no chemical reaction with any component. A noble metal or graphite is an example . Platinum, gold or silver or a simple carbon electrode gives good results.
2. Active electrode – an electrode made of an element in its uncombined state which will enter into a chemical equilibrium with ions of the same element in solution. e.g silver, mercury and hydrogen.
3. Gas electrode – platinum wire or foil with gas bubbling over the electrode.

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But, before we proceed to that I want to make certain observations you can look at this slide. I have written inert electrolyte; this is an electrode, insert electrode it is used to make electrical contact with the solution; that means, it is just dipped in the solution and no chemical reaction occurs at the inert electrode surface for example, we can use a noble metal or a graphite, ion graphite as an example platinum gold or silver or a simple carbon electrode also gives good results.

Active electrode we call it another type that is an electrode made of an element in its uncombined state which will enter into a chemical equilibrium with ions of these same element in solution. For example, I can have a silver electrode dipped in silver solution, silver nitrite solution, mercury electrode dipped in mercury solution and I can have hydrogen ions with platinum electrode. So, this is these are all active electrode; that means, it makes an element its in the uncombined state, but it will enter into a chemical reaction unlike an inert electrolyte.

So, there is a gas electrode; it is nothing but, a platinum wire dipped in a soil dipped dipped in a water containing gas bubbling over the electrode. So, you can take a look at this like this, that if I have a platinum wire dipped in a solution and I have hydrogen gas bubbling this is a platinum wire. So, if this is known as a standard a platinum wire, but electrode and this is known as gas electrode it has it is nothing, but a platinum wire or soil gas bubbling over the electrode.

Now, the cell reaction, what is a cell reaction? When a direct current passes through an electrolytic cell either oxidation must take place or reduction must take place oxidation takes place at the anode and reduction takes place at the cathode. At the anode the various transfers of electrons from reduce to species to the electrode and at the cathode reduction take place and the electrons are transferred from the electrode to the solution.

You must try to understand the difference between the electrode; cathode, anode, catholic reaction, anodic reaction and what happens actually? Whether electrons get transferred from the electrode to the solution or from the solution to the electrode. You have to please try to understand exactly, what happens with this? I have explain to you just now and please spend a little more time in understanding these phenomenon.

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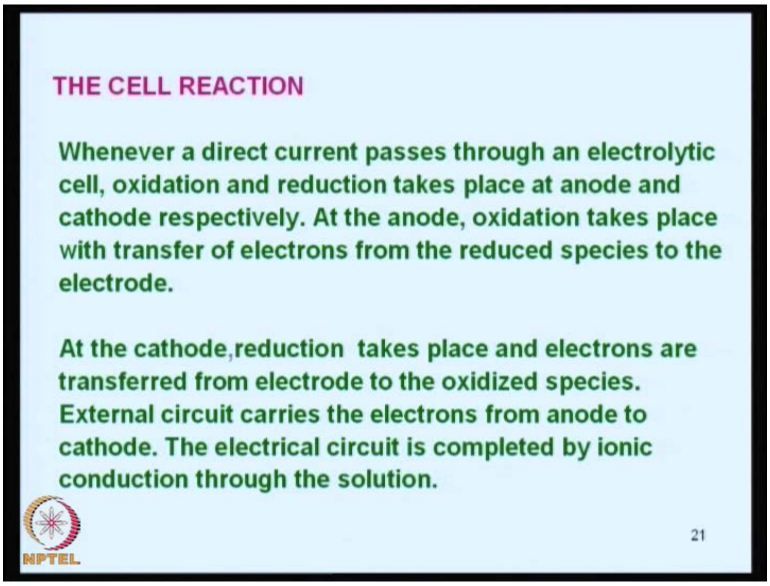

THE CELL REACTION

Whenever a direct current passes through an electrolytic cell, oxidation and reduction takes place at anode and cathode respectively. At the anode, oxidation takes place with transfer of electrons from the reduced species to the electrode.

At the cathode,reduction takes place and electrons are transferred from electrode to the oxidized species. External circuit carries the electrons from anode to cathode. The electrical circuit is completed by ionic conduction through the solution.

So, at the cathode cathode reduction takes place and electrons are transferred from electrode to the oxidized species. So, external circuit carries the electrons from the anode to the cathode, the electrical circuit is completed by ionic conduction through the…

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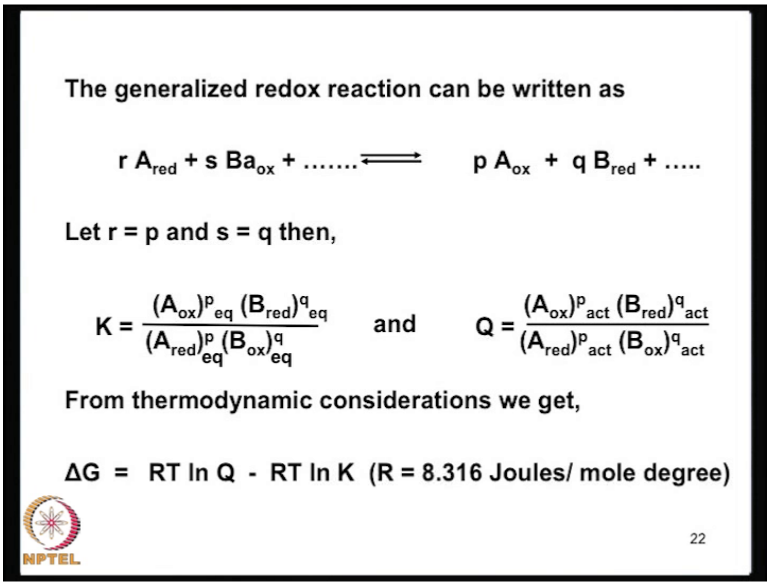

The generalized redox reaction can be written as

$$r\ A_{red} + s\ Ba_{ox} + \ldots\ldots \rightleftharpoons p\ A_{ox} + q\ B_{red} + \ldots\ldots$$

Let r = p and s = q then,

$$K = \frac{(A_{ox})^{p}_{eq}\ (B_{red})^{q}_{eq}}{(A_{red})^{p}_{eq}(B_{ox})^{q}_{eq}} \quad \text{and} \quad Q = \frac{(A_{ox})^{p}_{act}\ (B_{red})^{q}_{act}}{(A_{red})^{p}_{act}\ (B_{ox})^{q}_{act}}$$

From thermodynamic considerations we get,

$$\Delta G = RT \ln Q - RT \ln K \quad (R = 8.316 \text{ Joules/ mole degree})$$

So, I can write typical reaction like this r molecules of species A; which is A reductant will react with s molecules of species B which is an oxidant will react to give p molecules of species A. With the A reductant is converted to oxidant and q moles of B reductant is produced when r is equal to p and s is equal to q; that means, if it is any molecules reaction or bimolecular reaction in each case.

I can write an equilibrium reaction here K is equal to an oxidant that is reactant products divided by the reactants. So, oxidant B reductant at under equilibrium condition. I have put them outside the brackets here divided by the reactant that is a reductant multiplies by B oxidant. So, the terms in the brackets represents concentrations. So, that the concentration of the oxidant multiplied by the concentration of the reductant; that is reaction product divided by the reactants gives you the ratio gives you a an equilibrium constant. If, it is if the concentration are expressly equilibrium.

Now, I can also write a thermodynamic quantity q; that is the same thing oxidant and their product divided by the reactants. So, I am writing a oxidant instead of equilibrium I am writing activate, activity of the of species A multiplied by activity of species B which are the products and divided by activity of the reluctant multiplied by the activity of the oxidant.

So, from thermodynamic considerations we get, free energy delta G is nothing but RT ln Q minus RT ln K. where, q is the activity and K is the equilibrium constant; this is activity constant, this equilibrium constant and R is 8.316 joules per one mole degree.

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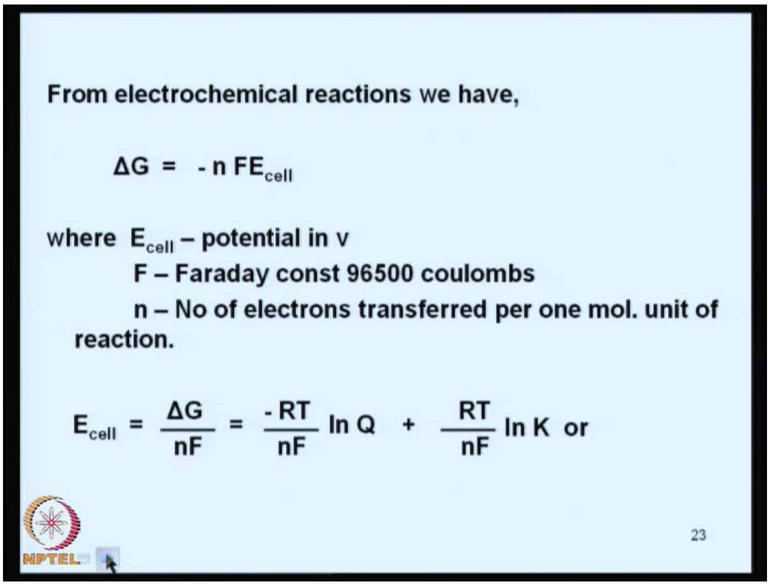

From electrochemical reactions we have,

$$\Delta G = -n\,FE_{cell}$$

where E_{cell} – potential in v
F – Faraday const 96500 coulombs
n – No of electrons transferred per one mol. unit of reaction.

$$E_{cell} = \frac{\Delta G}{nF} = \frac{-RT}{nF}\ln Q + \frac{RT}{nF}\ln K \text{ or}$$

So, this is a very standard thermodynamic equation available in all the text. Now, from electrochemical reactions we also have another equation that is free energy delta G is nothing but, the number of electrons multiplied by the faraday multiplied by the potential E cell.

So, here I am writing E cell is equal to potential on volts F is faraday’s constant that corresponds to 96500 coulombs and n is the number of the electrons transfer per one mole, unit of the reactions.

So, if I write E cell, in this E cell is nothing, why I transfer this part? n and F including the minus sign this side that is delta G by nF; that is also equal to minus RT by nF ln Q plus RT by nF ln K that is, I am transferred instead of writing delta G, I am putting that value instead of delta G, I am going to RT ln Q and minus sign takes care of the change in the signs.

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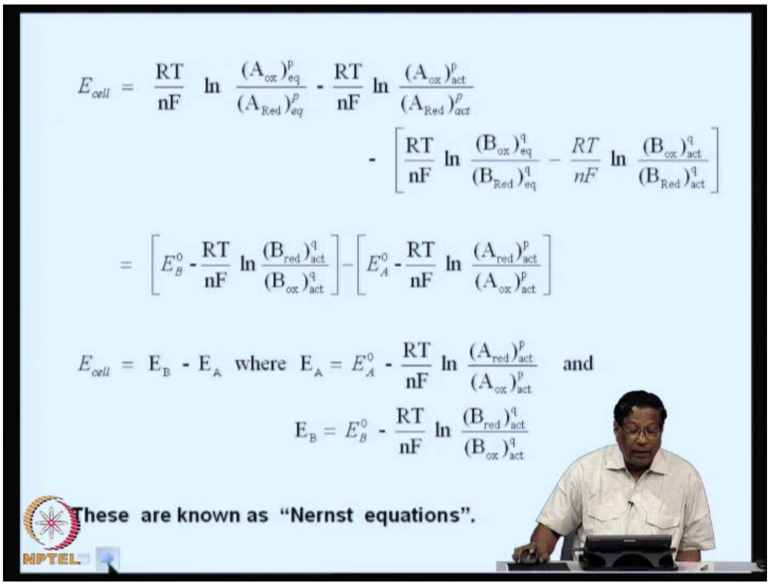

$$E_{cell} = \frac{RT}{nF} \ln \frac{(A_{ox})^p_{eq}}{(A_{Red})^p_{eq}} - \frac{RT}{nF} \ln \frac{(A_{ox})^p_{act}}{(A_{Red})^p_{act}}$$

$$- \left[\frac{RT}{nF} \ln \frac{(B_{ox})^q_{eq}}{(B_{Red})^q_{eq}} - \frac{RT}{nF} \ln \frac{(B_{ox})^q_{act}}{(B_{Red})^q_{act}} \right]$$

$$= \left[E^0_B - \frac{RT}{nF} \ln \frac{(B_{red})^q_{act}}{(B_{ox})^q_{act}} \right] - \left[E^0_A - \frac{RT}{nF} \ln \frac{(A_{red})^p_{act}}{(A_{ox})^p_{act}} \right]$$

$$E_{cell} = E_B - E_A \text{ where } E_A = E^0_A - \frac{RT}{nF} \ln \frac{(A_{red})^p_{act}}{(A_{ox})^p_{act}} \text{ and}$$

$$E_B = E^0_B - \frac{RT}{nF} \ln \frac{(B_{red})^q_{act}}{(B_{ox})^q_{act}}$$

These are known as "Nernst equations".

So, if I write E cell; that is total voltage is given by RT by nF ln A oxidant at equilibrium condition raise to p moles divided by A reductant at equilibrium concentration raise to p minus RT by nF ln A oxidant raise to p of the under activity, minus A reductant raise to p activity of this species. And now, what I have done is? I have separated the species A oxidant and reductant and species B oxidant and reductant.

This is a very standard mathematical operation any high school student would be able to rearrange this equation, as I have written here. So, similar equation can be written in terms of B that is minus RT by nF ln B oxidant equilibrium constant.

Under equilibrium conditions raised to p, B reluctant raise to q under equilibrium and same thing subtracted by a activity terms collected all the A terms and B terms in two sets; this I can rewrite as E naught B minus RT by nF ln B reductant and the activity as activity raise to p divided by B oxidant raise to q. E naught B, minus E naught a this I am writing this as E naught; this is E naught B minus and then this is E naught a first term.

So, if I separate them like this I can write Ecell is equal to actually E B minus E A. Where, E A is nothing but, E naught A this term E naught A minus RT by nF ln A reductant and their activity condition raise to p divided by A oxidant activity term and raise to p. Similarly, I can write E B is equal to E naught B minus RT by nF ln B reductant raise to q divided by B oxidant raise to q and activity condition these equation E A and E B these are known as Nernst equations.

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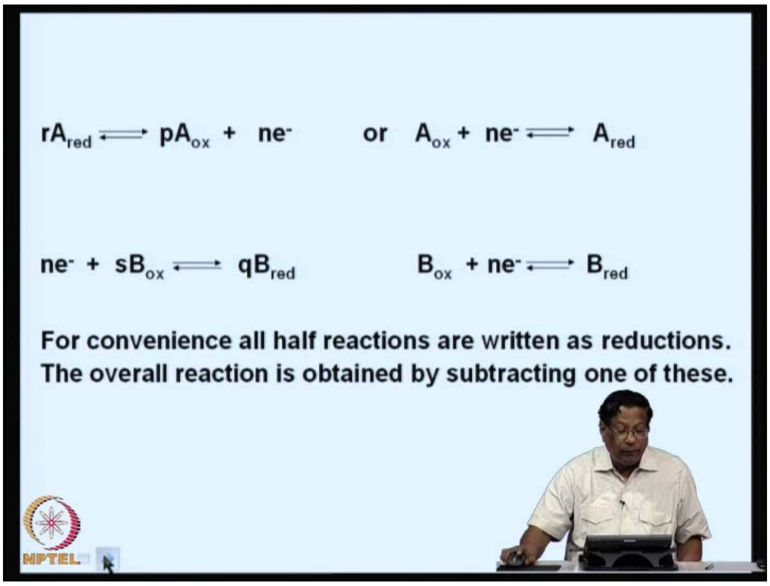

$rA_{red} \rightleftharpoons pA_{ox} + ne^-$ or $A_{ox} + ne^- \rightleftharpoons A_{red}$

$ne^- + sB_{ox} \rightleftharpoons qB_{red}$ $B_{ox} + ne^- \rightleftharpoons B_{red}$

For convenience all half reactions are written as reductions.
The overall reaction is obtained by subtracting one of these.

So, what is happing is r moles of A reductant and p moles of A oxidant go to ne or I can write oxidant, reductant going to oxidant. I can write oxidant reacting with electrons to produce A reductant. Similarly, I can write n molecule, n electron, number of electrons reacting reacting s moles of B oxidant will give you q. B reductant q moles of B reductant and this I can write as B oxidant plus ne goes to B reductant here, what I have done on the right side is? I have written is the same convention.

Whatever is the chemical reaction happening on this side, on the right side it is always oxidant plus number of electrons going to reductant and same thing I have written here. So far, convenience all the half cell reactions are written as reductions the overall reactions is to obtained by subtracting one of this.

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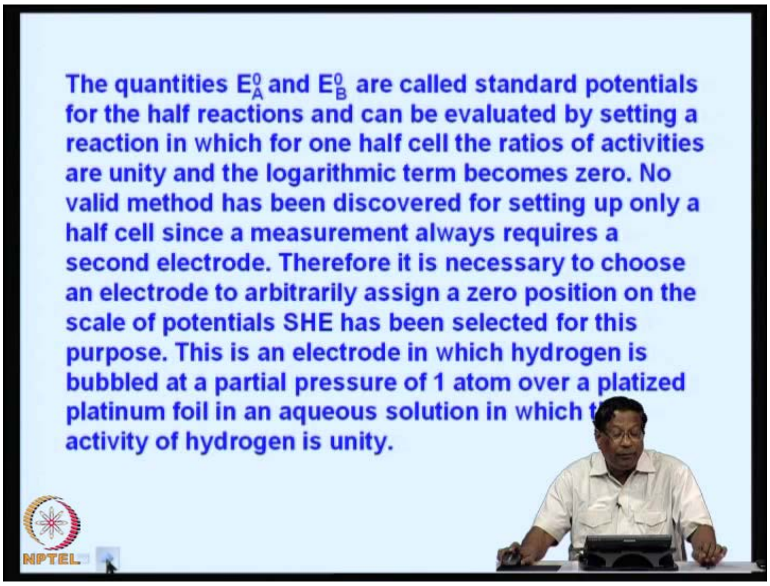

The quantities E_A^0 and E_B^0 are called standard potentials for the half reactions and can be evaluated by setting a reaction in which for one half cell the ratios of activities are unity and the logarithmic term becomes zero. No valid method has been discovered for setting up only a half cell since a measurement always requires a second electrode. Therefore it is necessary to choose an electrode to arbitrarily assign a zero position on the scale of potentials SHE has been selected for this purpose. This is an electrode in which hydrogen is bubbled at a partial pressure of 1 atom over a platized platinum foil in an aqueous solution in which t activity of hydrogen is unity.

So, the quantities E naught A, and E naught B are called standard potentials for the half reaction. Because, E naught A because we are writing everything as oxidant plus electron going to reductant whether it is the anode or anodic reaction or cathodic reaction.

So, the quantities E naught A and E naught B. if, we write according to Nernst equation we write they have called a standard potentials or half reactions for the half reactions and they can be evaluated by setting a reaction in which one half the cell is the ratio of the activities and the logarithmic terms becomes zero. So, no valid method has been discovered for setting up only a half cell you have to measure it against a standard reference material. So, the if you say you measured you have measured the half cell reaction of a chemical in isolation we will not get anything worthwhile.

You have to measure it against a standard. So, no valid method has been discovered for setting up only one half cell you have two have two half cell they should be connected and then through a external electrode or this thing. So, that you can either pass the current or generate the chemical reaction if it is proceeding on its own.

So, it is necessary to choose an electrode and assign an arbitrary zero position. So, if I have an electrode which shows which I assume to be zero against that zero. I can set up another half cell for an element which can be oxidize or reduced then I can compare the positions of the electrodes. So…

The potential we can compare, if I have a an electrode which shows zero, but you must understand that there is nothing like a half cell which shows zero by convention. We have to choose some material and that is standard hydrogen potential standard hydrogen electrode has been selected for this purpose. So, this is an electrode in which hydrogen is bubbled at a partial pressure of one atmosphere over a Platonized, platinum foil in an aqueous solution in which the activity of hydrogen is unity. I had shown you this figure is the hydrogen ah bubbling at one atmosphere.

And I have a platinum wire there is a solution in this is 0.1 molar hydrogen chloride. So, the activity of hydrogen is zeroing here, sorry it is one and this is known as standard hydrogen electrode. So, if we can measure the electrodes again such a platinum electrode then we can have a number of reactions number of values for each element.

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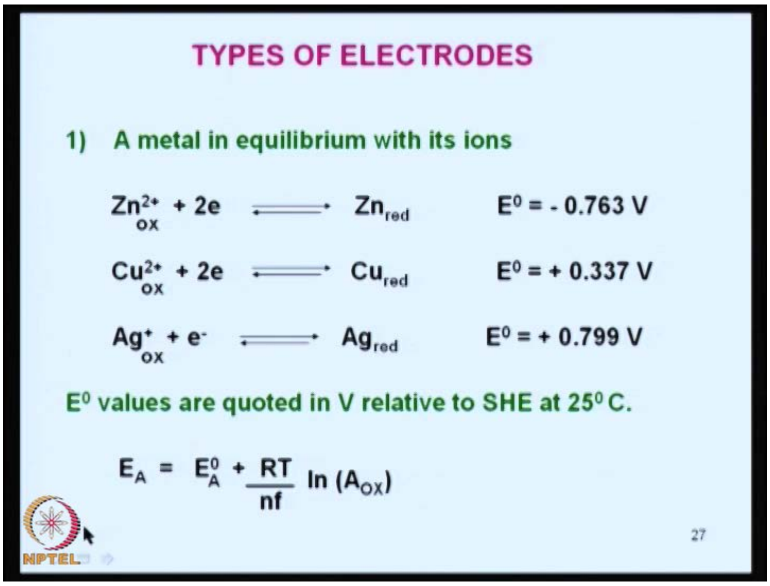

TYPES OF ELECTRODES

1) A metal in equilibrium with its ions

$Zn^{2+}_{ox} + 2e \rightleftharpoons Zn_{red}$ $E^0 = -0.763$ V

$Cu^{2+}_{ox} + 2e \rightleftharpoons Cu_{red}$ $E^0 = +0.337$ V

$Ag^{+}_{ox} + e^- \rightleftharpoons Ag_{red}$ $E^0 = +0.799$ V

E^0 values are quoted in V relative to SHE at 25° C.

$$E_A = E^0_A + \frac{RT}{nf} \ln (A_{OX})$$

For example, you can say that, if I measure the fluorine F 2, plus 2 electron goes to 2 F. if, I measure the half cell reaction of this with again standard hydrogen electrode; standard hydrogen electrode I will get 0.265 volts.

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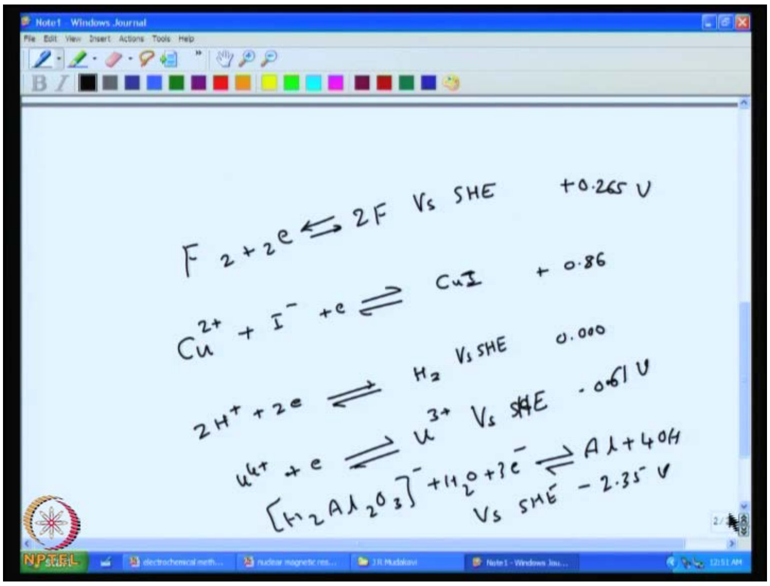

$F_2 + 2e \rightleftharpoons 2F$ Vs SHE $+0.265$ V

$Cu^{2+} + I^- + e \rightleftharpoons CuI$ $+0.86$

$2H^+ + 2e \rightleftharpoons H_2$ Vs SHE 0.000

$U^{4+} + e \rightleftharpoons U^{3+}$ Vs SHE -0.61 V

$[H_2Al_2O_3]^- + H_2O + 3e^- \rightleftharpoons Al + 4OH$ Vs SHE -2.35 V

Similarly, if I have copper 2 plus, plus I minus, plus electron this can go to copper iodide and this half cell is is measured against the SHE. I get a value of 0.86, now if I measure the same thing against hydrogen electrode the value what I should get it should be 0.000 verses standard hydrogen electrode. So, if I can measure uranium 4 plus, plus electron going to uranium 3 plus and verses SHE .I get a value of minus minus 0.61 volts; that means, it is showing a negative value of 061 and H A L 2, 3 for example, if you will take H 2, A l 2, O 3.

This is a negatively charged species plus H 2 O, plus 3 e electrons going to aluminum plus 4 OH I will get verses SHE (standard hydrogen electrode) I will get minus 2.35 volts; that means, again space standard hydrogen electrode, I get different kinds values if I measure verses a standard hydrogen electrode taken as zero, sometimes I get positive values, sometimes I get a negative value. I can grade them from maximum positive to maximum negative with hydrogen 0.00 somewhere in between.

This is known as an electro chemical series. So, we will continue our discussion on the electro chemical series. And how, we can go about, utilizing this information for chemical reactions in the next class.