Electrochemical Technology in Pollution Control
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Lecture – 11
Potentiometry Types of electrode 2

Greetings to you, welcome to the next class on Potentiometry. We were discussing about the electrical double layer.

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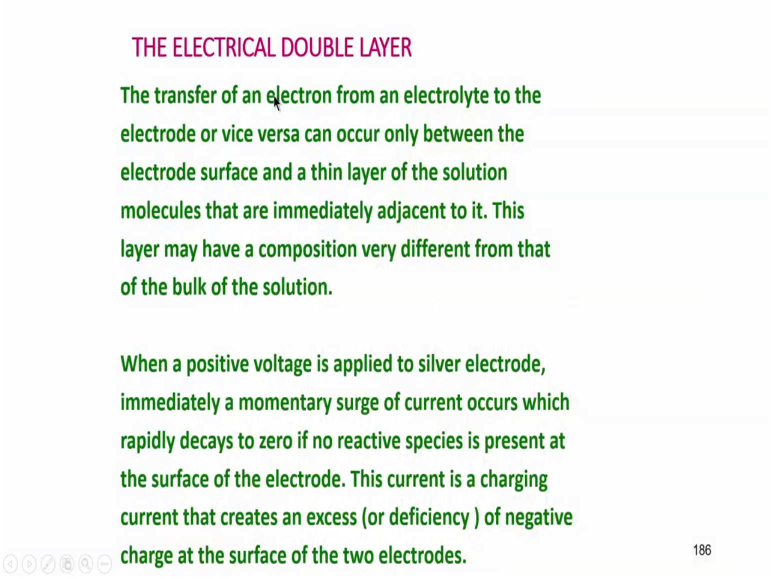

THE ELECTRICAL DOUBLE LAYER

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.

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So, what I had told you that when transfer of electrons from the electrolyte to the electrode or vice versa can occur only between the electrode surface and the liquid junctions around it, a thin layer of solution, I asked you to imagine and then I told you that around the electrode, there will be all cations will be moving towards the cathode and all anions will be moving towards the anode.

So, when a positive voltage is applied to the electrodes into the system the, there will be a momentary surge of current occurs which rapidly decays to 0, if there is no chemical reaction that is no transfer of electron. So, this current is known as charging current that creates an excess of positive ions near the cathode, if there is no reaction and negative ions around the anode, if there is no reaction.

So, there will be in the in around the cathode in that small space, containing the cations of the same shape of the same shape as the cathode surrounding it, there will be deficiency of anions and in the anode section in the same space, there will be deficiency of the cations. So, the there will be excess charge of cations and negative charge excess charge of the anions around the this thing and then I had also told you that immediately surrounding it there is a compact inner layer of the solution.

The potential will decrease linearly with distance from the electrode surface and there is another portion which where the potential will decrease exponentially. So, this entire array of charge species and oriented dipoles at the electrode solution is known as interfacial diagram. Yesterday, I had taught you all this and I had shown you this figure.

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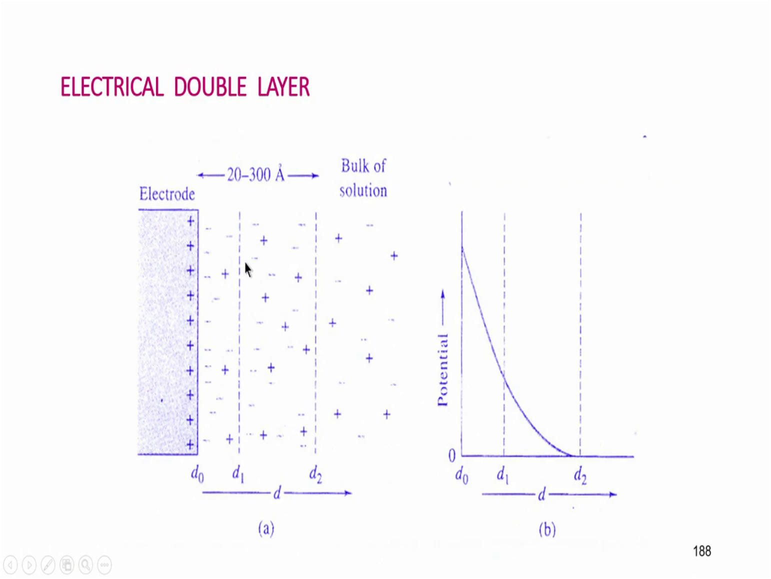

ELECTRICAL DOUBLE LAYER

So, this is the electrode surface positive ions are here, this is the immediate space around it and then slightly different space around it, that is the of the order of about 20 angstrom units. Here, it will be about 300 angstrom units and this will be the bulk of the solution. So, in this region there is almost a linear decrease in the electrode potential and in this region d 1 to d 2 there will be exponential decrease of the charged of the charge potential.

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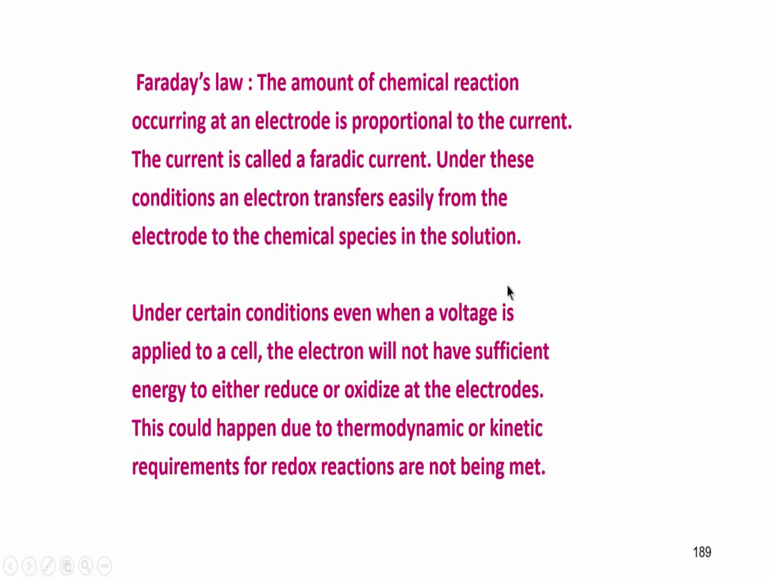

Faraday’s law : The amount of chemical reaction occurring at an electrode is proportional to the current. The current is called a faradic current. Under these conditions an electron transfers easily from the electrode to the chemical species in the solution.

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, according to Faraday’s law, these also we had covered a layer covered yesterday. So, electron transfer occurs easily from the electrode to the chemical species in the solution, because the amount of chemical reaction occurring is proportional to the electrode current.

So, that is Faraday’s law. So, under certain conditions even when a, this cell voltage is applied to a cell the electron will not have sufficient energy to get reduced or oxidized. So, what happens? This could there will not be any reduction reaction or oxidation reaction. So, the since the conditions of redox reactions are not met the electro ions will be hanging around without transferring the electron to the outer to the electrode or without any chemical reaction taking place.

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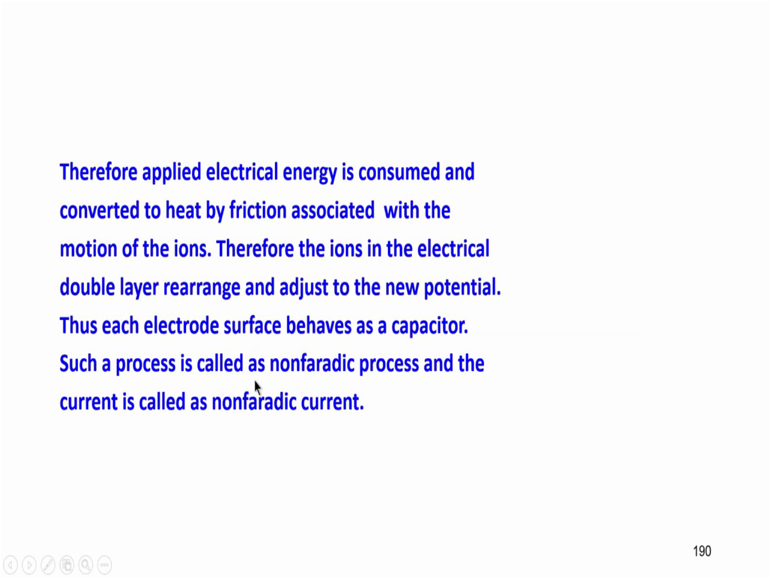

Therefore applied electrical energy is consumed and converted to heat by friction associated with the motion of the ions. Therefore the ions in the electrical double layer rearrange and adjust to the new potential. Thus each electrode surface behaves as a capacitor. Such a process is called as nonfaradic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

So, applied electrical energy is consumed, but converted to heat by a friction associated with the motion of the ions. Therefore, the ions in the electrical double layer rearrange and adjust to new potential and this new potential behaves as a capacitor, such a process is called nonfaradic process and the current is called as nonfaradic current ok.

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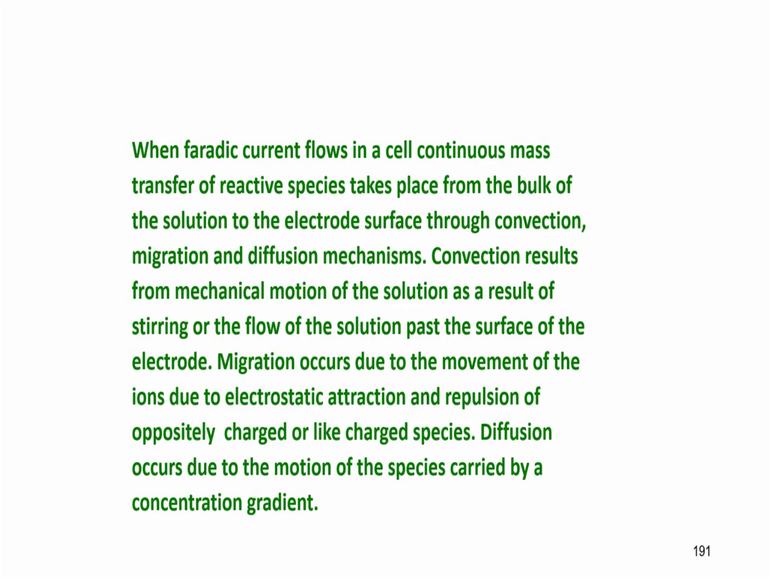

When faradic current flows in a cell continuous mass transfer of reactive species takes place from the bulk of the solution to the electrode surface through convection, migration and diffusion mechanisms. Convection results from mechanical motion of the solution as a result of stirring or the flow of 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, 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 then diffusion mechanisms. So, convection results from the mechanical motion of the solution molecules solvent molecules as a result of stirring or flow a flow through the solution, etcetera.

And migration occurs due to the movement of the ions due to electrostatic attraction that is positive attracting getting attracted to negative, negative getting attracted to positive, etcetera and diffusion occurs due to the motion of the species carried by a concentration gradient; that means, the apart from these two mechanical processes there is another species, another phenomenon that is taking place through, which ions will move that is known as diffusion.

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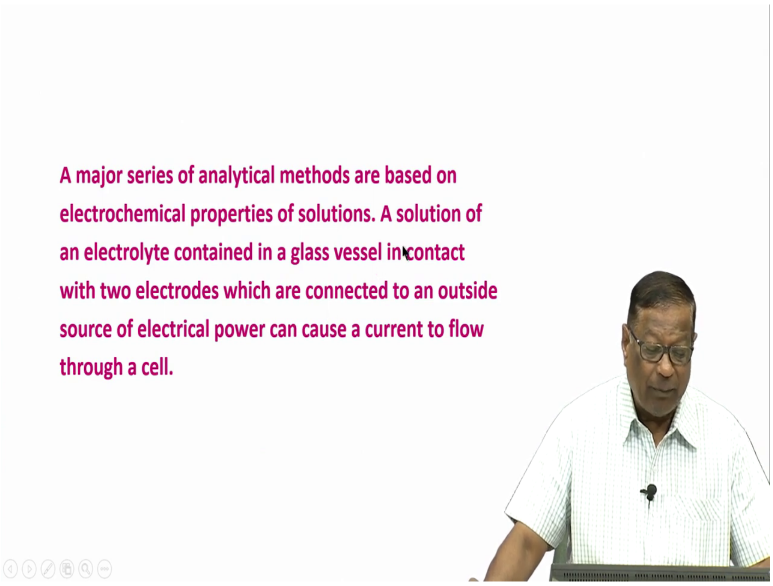

A major series of analytical methods are based on electrochemical properties of solutions. A solution of an electrolyte contained in a glass vessel in contact with two electrodes which are connected to an outside source of electrical power can cause a current to flow through a cell.

So, a major series of analytical methods are based on the electrochemical properties of the solutions. So, a solution of the 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 galvanic cell, what I had already described to you.

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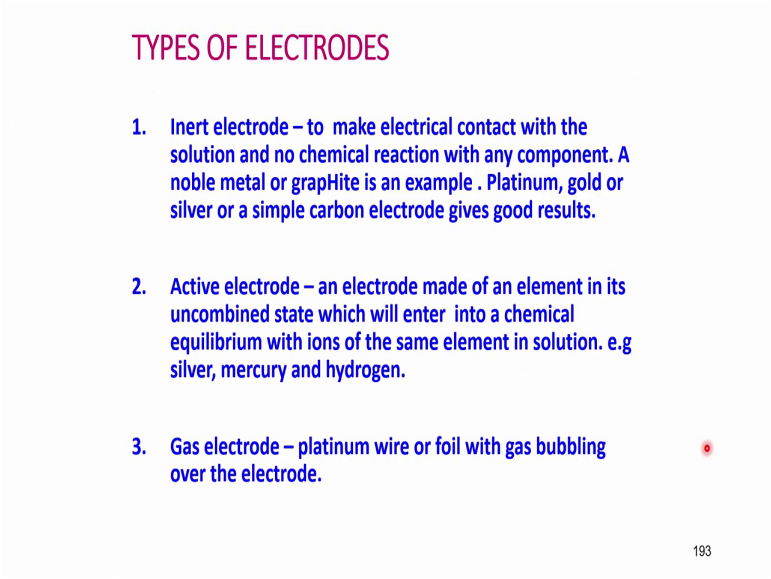

TYPES OF ELECTRODES

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.

So, what are the different types of electrodes we use? I have been talking about electrodes, etcetera and I have also told you that electrodes can be made of any metal that can pass the current or and there has to be some sort of reaction at the electrode surface, either it is cathode or anode, but there are other kinds of electrodes. For example look at the first one that is inert electrode. What is an inert electrode? An inert electrode is a metal piece that is used to make electrical contact with the solution, but no chemical reaction should take place with any component.

Such an electrode is known as inert electrode. Usually, it is a noble metal electrode or graphite electrode. You know graphite; lot of pencils, you use graphite writing pencils, you know they use graphites say cylinder like, thing in the pencil that also can be used as a inert electrode. So, platinum, gold or silver or a simple carbon electrode gives good results as an inert electrode.

So, then we term another we know another term that is known as active electrode. So, an electrode made of an element in it is uncombined state which will enter into a chemical equilibrium with the ions of the same element in solution; that means, whatever I am studying, the electro whichever metal ion, the electrode has to be made of the same element. If I am studying silver, then my electrode should be silver, if I am doing it with mercury, but it should be mercury electrode, if it is hydrogen, it has to be hydrogen electrode like that.

So, that is known as active electrode that will enter into a chemical reaction in the in our experimental setup, then we have gas electrode. What is a gas electrode? The gas electrode is a nothing, but a small platinum wire or a foil with gas bubbling over the electrode. So, what I do is normally, I take a beaker, put a platinum electrode, bubble the gas through that is all. There is a nothing very special about gas electrode.

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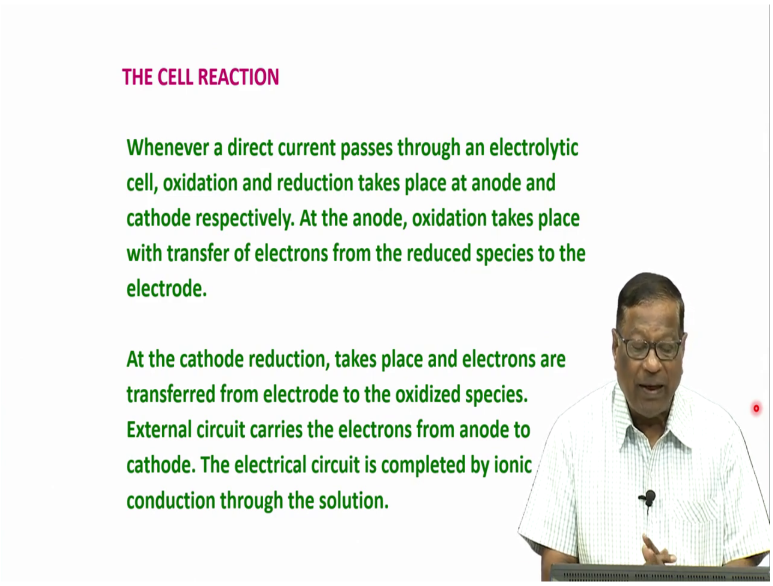

THE CELL REACTION

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.

And then we define what is known as cell reaction. So, whenever a direct current passes through an electrolytic cell, oxidation or reduction should take place at the anode and cathode respectively. This you already know. At the anode oxidation takes place with transfer of electrons from the reduced species to the electrode. At the cathode, the reduction takes place and the electrons are transferred from the electrode to the oxidized species. So, external circuit carries the electrons from anode to cathode, the electrical circuit is completed by ionic conduction through the solution. This is the typical setup of a cell reaction.

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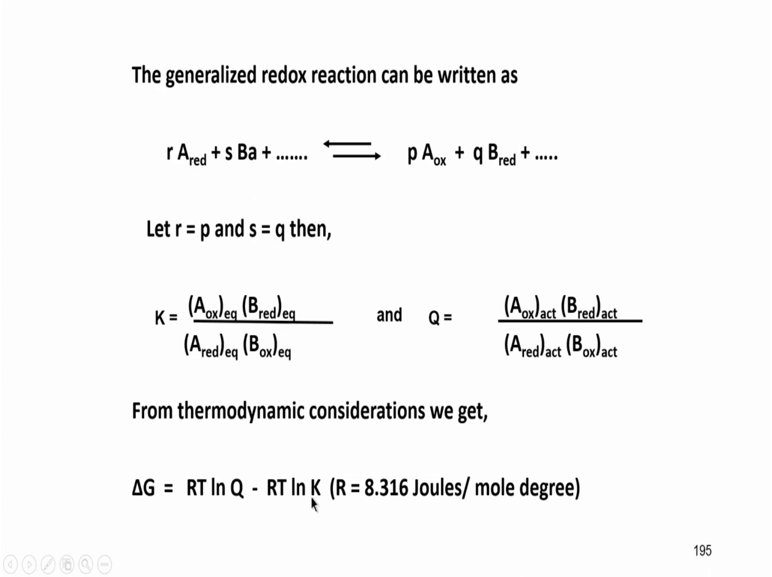

The generalized redox reaction can be written as

$$r\,A_{red} + s\,Ba + \ldots\ldots. \rightleftarrows p\,A_{ox} + q\,B_{red} + \ldots..$$

Let r = p and s = q then,

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

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 the generalized redox reaction like this r molecules of A that is a reductant can react to with s molecules of B as a oxidant and that will react with p to give you p molecules of A as the oxidant, that is a species, A is getting oxidized from reduced species and B is getting reduced to B is oxidized species is getting reduced to be reduced species.

So, I have written here rspq. So, if both sides are equal r is equal to same number of molecules, rn is equal to p that is the same number of molecules getting oxidizer for the oxidizer molecules are same as reduced molecules and same thing here with respect to the other party that is B and reduced oxidized species and reduced species. I can write K is equal to A oxidant equilibrium constant, that I am writing the product divided by the reactants. A oxidant B reductant at equilibrium concentration and A reductant and B oxidant at the equilibrium at equilibrium.

So, this has to be a constant because both the forward and reverse reactions are occurring after some time there will be equilibrium. This I have already we have already discussed number of times, but I can also write a thermodynamic expression that is Q is equal to A oxidant, same equation basically, but instead of writing eq equilibrium. I am writing activated activities ok. A oxidant of activity and activity of the species B has reduced species divided by activity of A species as a reductant that is a reactant here and B activity of the B as oxidant.

So, from thermodynamic consideration we have two quantities now, K and Q and these two are related by thermodynamic equation considerations with respect to related to free energy that is delta G is equal to RT ln Q minus RT ln K that where R is room temperature this gas constant 8.316 Joules per mole per degree and then T is temperature ln Q that is activity minus equilibrium RT ln K. So, this is a very important relationship between activity and equilibrium reactions. So, this is a very standard form of expression in all equilibrium reactions.

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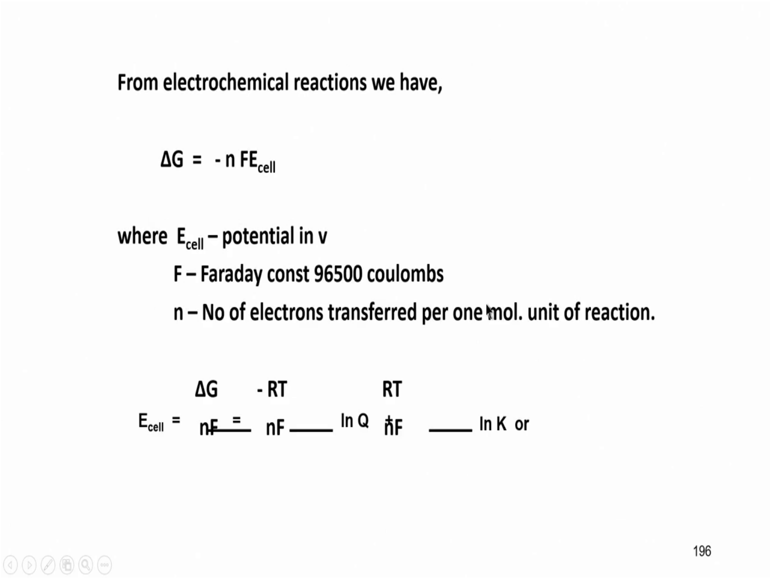

From electrochemical reactions we have,

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

where E_{cell} – potential in v

F – Faraday const 96500 coulombs

n – No of electrons transferred per one mol. unit of reaction.

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

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So, we also have another reaction that is delta G is equal to minus n into F into E cell. So, this expression also comes from thermodynamics, we are not going into details of that. But since we are going to use this equation, I am starting from here. Delta G is equal to minus n FE cell. You can look up the thermodynamics books, you have to find out how this expression is valid, how it is derived ok.

So, in this expression I have E cell is equal to potential in the volts, a F is Faraday constant that is 96500 coulombs and n is the number of electrons transferred per 1 mole of unit reaction.

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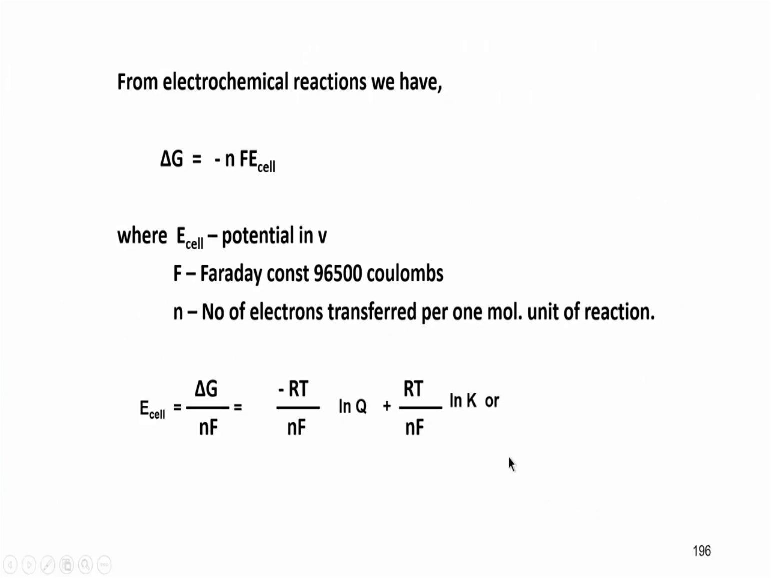

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$$E_{cell} = \frac{\Delta G}{nF} = \frac{-RT}{nF} \ln Q + \frac{RT}{nF} \ln K \text{ or}$$

So, I can write E cell is equal to delta G. I can write E cell is equal to delta G. I transfer all these parameters on this side. E cell is equal to delta G by n F. There should be 1 minus sign here, that is equal to minus RT by n F ln Q and RT by n F ln K.

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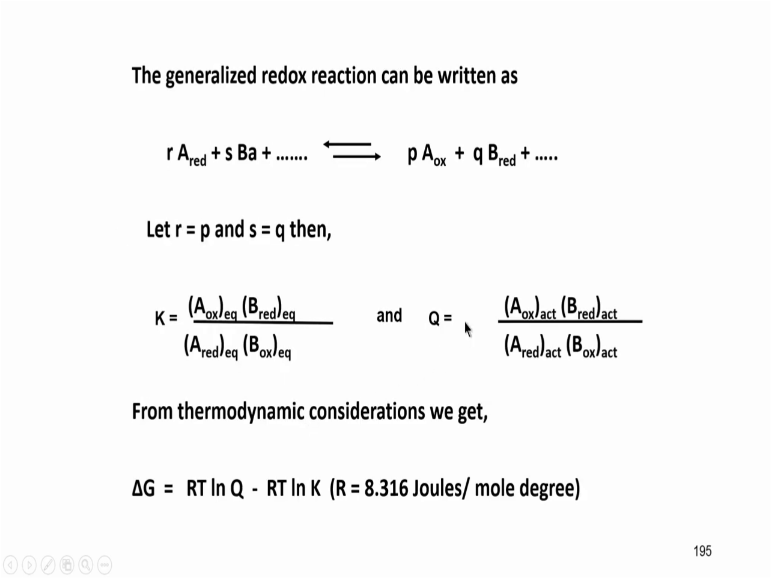

The generalized redox reaction can be written as

$$r\,A_{red} + s\,Ba + \ldots\ldots. \rightleftharpoons p\,A_{ox} + q\,B_{red} + \ldots..$$

Let r = p and s = q then,

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

From thermodynamic considerations we get,

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

This expression is obtained by equating the previous equation that is RT ln Q minus RT ln K. I am replacing delta G with that expression delta E cell is equal to, so look at it.

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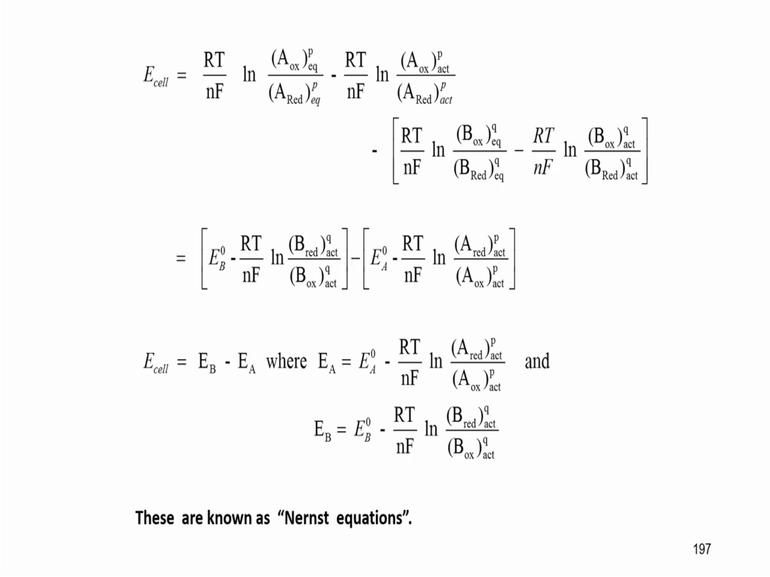

$$E_{cell} = \frac{RT}{nF} \ln \frac{(A_{ox})^{p}_{eq}}{(A_{Red})^{p}_{eq}} - \frac{RT}{nF} \ln \frac{(A_{ox})^{p}_{act}}{(A_{Red})^{p}_{act}}$$

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

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

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

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

These are known as "Nernst equations".

Now, I can write E cell. I can reorganize this Q. I am going to put the value of Q and value of K in terms of activity coefficients. So, I can write E cell is equal to my RT by n F ln A oxidant divided by A reductant minus RT by n F ln A oxidant activity, A reductant activity, p is the stoichiometry that comes in the exponential form pq etcetera. So, this quantity minus RT by n F with respect to B that is reactant B oxidant A at equilibrium raise to q divided by B reductant equally at equilibrium raise to q minus RT by n F ln same thing. Same thing as this except eq replaced by activity.

This expression, I am going to write E naught there is some difference R T this is known as E naught at equilibrium minus RT by n F ln B reductant divided by B oxidant raise to q activity divided then B oxidant raise to q of the activity. We are not using concentration terms.

Similarly, minus of E naught A and RT by n F ln A reductant raised to p divided of activity again, A oxidant raised to p activity.

So, this whole thing E naught minus RT by n F ln B reductant divided by B oxidant raise to q and activity term, I put it as EB that is a potential corresponding to B, because here everything is B, this whole term and then this whole term refers to redox reaction of the species A in terms of thermodynamics and equilibrium concentration. What I have done actually is, I have taken the terms corresponding to A and corresponding to B separately and reorganize the equation here.

So, put them together and then equilibrium concentration, I am going to put it as E A, E B and E A corresponding to each species. And so, the cell potential, what I am going to get out of this reaction, which reaction? The top one ok, A reductant B reductant oxidant reductant. So, the cell potential of the reduction reaction redox reaction of A B will be given by the actual potential difference between EB and EA, where EA is nothing, but E naught A, then this part E naught A minus RT by n F ln A reductant raised to p activity n F ln A oxidant p activity and EB also similarly.

So, these equations EA is equal to E naught A. These equations are known as Nernst equations. So, Nernst equations are the, they tell us about the actual potential of a given system for each element ok. If it is A element EA, I can write A is equal to E naught A minus RT by n F ln A reductant divided by A oxidant raise to p and all in terms of activity. Similarly, EB so, this is the Nernst equation for A and this is the Nernst equation for B.

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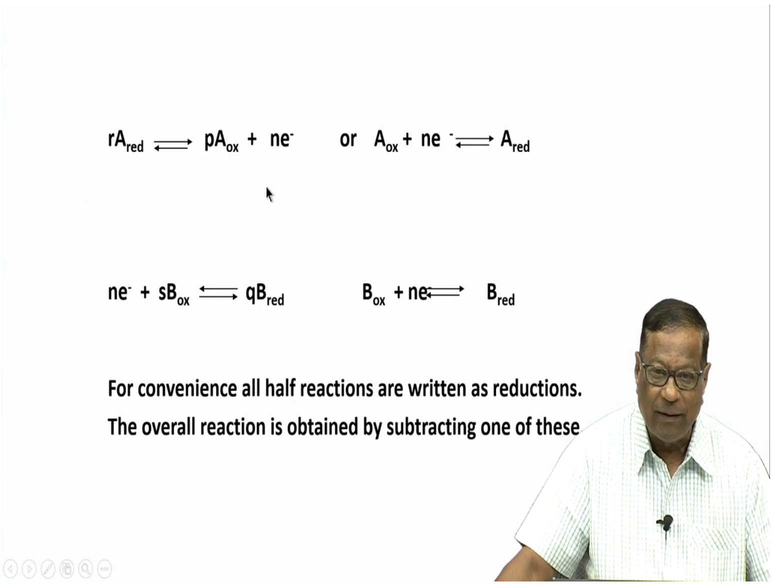

$rA_{red} \rightleftharpoons pA_{ox} + ne^-$ or $A_{ox} + ne^- \rightleftharpoons A_{red}$

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

For convenience all half reactions are written as reductions.

The overall reaction is obtained by subtracting one of these

I can write the previous equation, that is the Nernst equation EA is equal to E naught A etcetera in terms of a reduced species and oxidized species r molecules of A reductant goes to p molecules of A oxidant and plus ne minus it has to be controlled. It has to be associated with the release of electrons. And then r I can simply write A oxidant plus ne goes to A reductant if n is equal to 1 A oxidant ne number of electrons that goes to A reductant. Similarly, I can write n number of electrons can combine with s molecules of oxidant and q molecules to give you, q molecules of B reductant.

So, here s and q should be same, equal number. So, here I can simply write B oxidant plus ne goes to B reductant ok. So, for convenience, all half reactions are written as reductions. This is a convention, we should learn. So, whenever I, whatever is the positive value we write it, but you write it simply as negative. Even if the value is negative, you still write as the negative as a reduction convenience, it is only our we can write either way.

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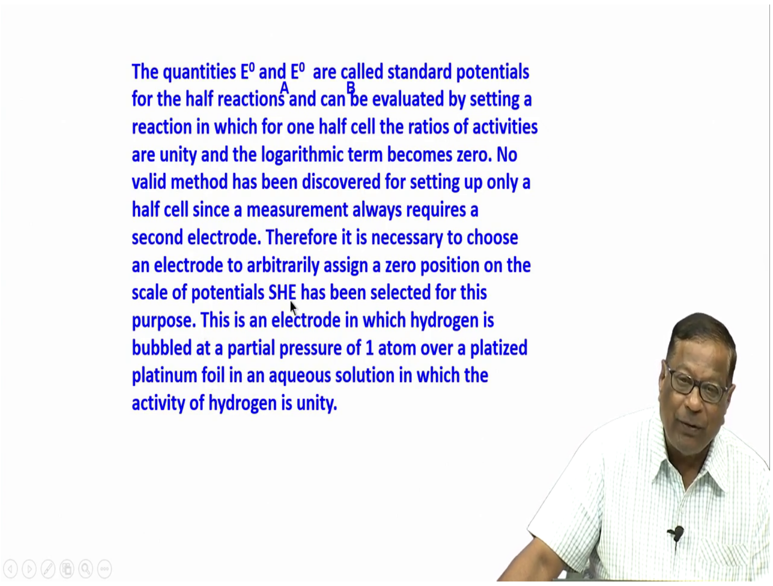

The quantities E^0_A and E^0_B are called standard potentials for the half reactions and can be evaluated by setting a reaction in which for one half cell the ratios of activities are unity and the logarithmic term becomes zero. No valid method has been discovered for setting up only a half cell since 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 the activity of hydrogen is unity.

So, the overall reaction is obtained by subtracting one of these that is the quantities E naught A and E naught B and this has a, this should come here, E naught A and E naught B, this B should be here are called as 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.

So, no valid method has been discovered for setting up only a half cell I cannot carry out a half cell reaction in any of the only half cell without I that is either oxidation or reduction to take place to for oxidation to take place there has to be a another species to take the electrons otherwise, I cannot just deduct the electrons, etcetera.

So, I cannot write either oxidation or reduction as a single entity. So, no valid method has been discovered for setting up only half cell. Since, a measurement always requires a second electrode to complete the circuit; I need a second electrode. Therefore, it is necessary to choose an electrode to arbitrarily assign a zero position either on the scale of potentials.

So, standard hydrogen electrode SHE means Standard Hydrogen Electrode has been selected for this purpose. So, this is an electrode in which hydrogen is bubbled at partial pressure of one atmosphere, over a platized foil in an aqueous solution, in which the activity of hydrogen is unity.

So, if I want to compare different kinds of redox reactions undergoing by any species, I must write reactions like this A oxidant plus ne goes to reductant B oxidant or plus ne goes to B reductant for convenience, I write all the half reactions as electrodes and the value of reduction potential will be different for different elements ok.

And because the values are different for different elements, I need to know which one is having higher value, which one is having lower value; that means, now I am going to create a scale in which I can compare this is a better reductant, this is a better oxidant, the one which is having higher value is a better reductant.

The one which is having lower value is a not so better reductant or it could be an oxidant also the either way. So, to compare every redox reaction, I need a comparison standard, but I cannot have a comparison standard with only half cell. I have to measure with another half cell and that half cell, other half cell is nothing, but a hydrogen electrode, that hydrogen electrode by convention we are giving it a value of 0 that is standard hydrogen electrode.

So, the standard hydrogen electrode has been selected for that purpose. So, the potential of standard hydrogen electrode is 0.000 according to our convention used only for our convenience, but if I set I can set up a redox reaction, using hydrogen with the another metal. So, I can compare all the metals with respect to hydrogen, because by convention hydrogen is

0. So, this is the whole idea of having a comparison of redox potential, which is a better reduction reagent, which is a better oxidation reagent.

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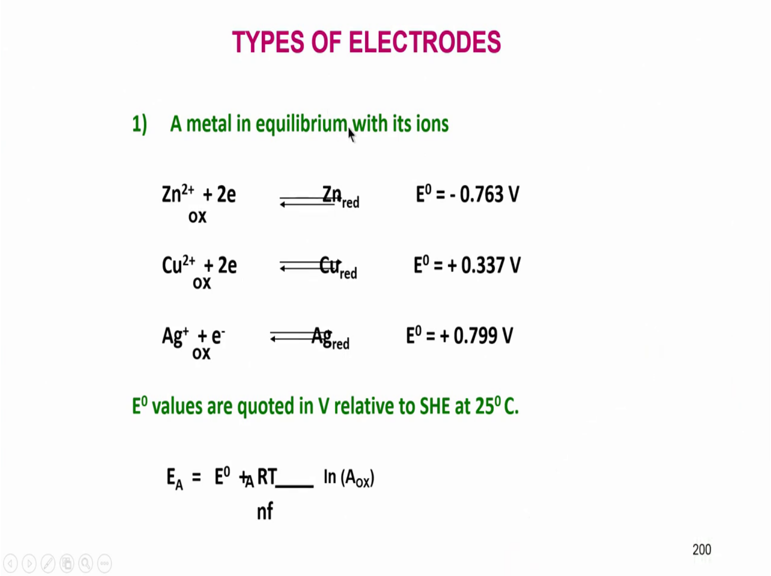

TYPES OF ELECTRODES

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 25^0 C.

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

So, we continue our discussion on the different types of electrodes. We will continue our class in the next session.

Thank you very much have a nice day.