Rate Processes

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Module No: # 01

Lecture No: # 26

Kinetics at Electrodes

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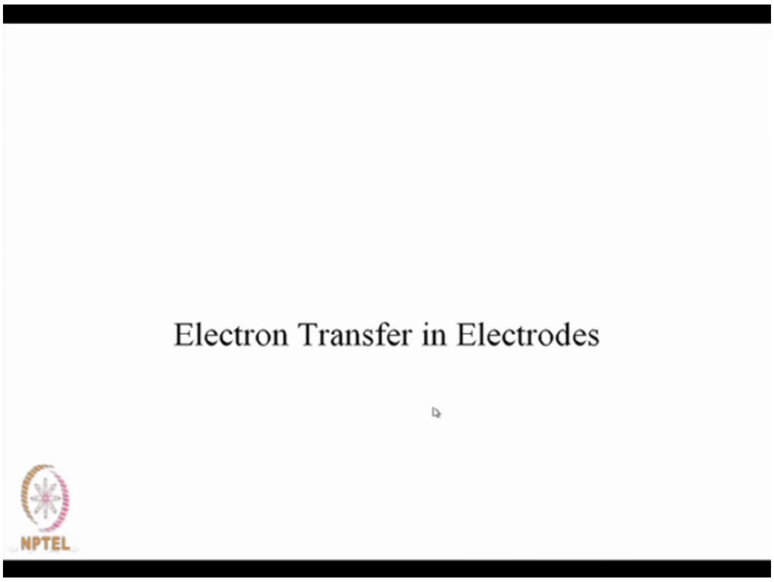

Electron Transfer in Electrodes

Hi, Good morning everybody. We are again back with rate processes. So far, we have talked on many aspects of rate processes. Last time, we talked about solution-reactions like we discussed some of the aspects of metal reactions. Typical metal reactions are solvation, also solvent exchange reaction, and also electron transfer reaction. So today, we would like to concentrate on kinetics at electrodes.

What is an electrode? Now, electrode is you know, perhaps all of you heard about this electrolysis, so suppose you have got pure water; distilled water and you have got two metal pieces like two copper rods. These two are dipped into water and in that water you add from outside some sodium chloride salt, and you pass current through the solution. What do we expect? Now, the expectation is that some reaction is expected; chemical reaction, of course is expected.

When you have not added anything, I mean just pure water and you dipped two electrodes, then if you measure the current that is passing through this circuit that will be very small, because conductivity is very less. Now, the moment you add some salt then its conductivity increases. As conductivity increases and conductivity increases means some kind of transport phenomenon, transport of charge, transport phenomena is there. As a result of this, you observe some conductivity. Now, the point is what is the role of these electrodes? Now, electrode is a medium by which electrons can flow into the solution or may be electrons can be extracted; I mean electrons can come from the solution to the electrode and complete the circuit.

So, electrode and also perhaps you heard about this electrochemical cell or may be simple you know cells like say where you get electricity from. Like in one case, the platinum, hydrogen, electrode and the other case is saturate calomel electrode. When these two electrodes are, I mean, half cells are combined you will get some electricity. So, it is a medium, by which you know you can inject electrons into the solution or you may get.

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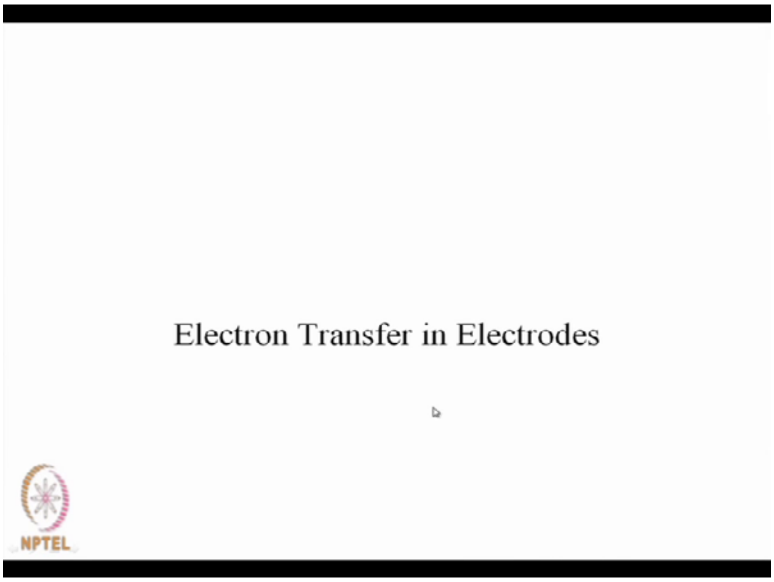

Electron Transfer in Electrodes

It is basically the electron transfers in the electrodes that will transfer of electrons that are occurring at the electrodes.

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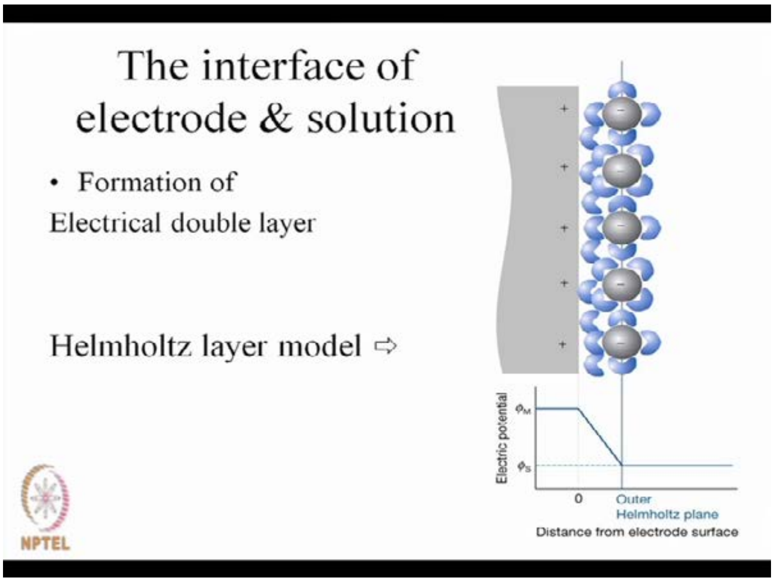

The interface of electrode & solution

- Formation of Electrical double layer

Helmholtz layer model ⇨

Now, let us look at the interface of electrode and solution. Always, you remember that interface is the region of interest in many cases, because interface means it is the region of in-homogeneity.

Suppose, if you have a solution of something, may be say surfactant, surfactant dissolved in water. Then inside, suppose the concentration is less than its critical micelle concentration. Then you may not expect any micelle in that solution and what is happening in the bulk?

It is homogeneous, but as you move on slowly towards the surface of this liquid that is surface of water then there is a region of in-homogeneity starts in and at the interface, you have got in one side aqueous phase and the other side you have got the vapour. May be these surfactant molecules are oriented in a definite fashion, depending on its charging nature and also depending on its tail.

When you dip an electrode, I mean a metal piece, say platinum in an aqueous solution of some electrolyte then, what is happening? Let us try to look at it. Interface of electrode and solution, so there is formation of electrical double layer. Electrical double layer is like this (Refer Slide Time: 06:19) that you have got this metal part, and this is your solution side, and this is the interface; interface between your metal and the solution. So, plus charge may be accumulated over here and minus charge is also here, means this plus is attracted by another minus, this plus is attracted by another minus. So, as a result of which you have got a layer of plus charge and the layer of minus charge. It is called electrical double layer, which is formed when you dip a piece of metal in a solution containing electrolyte.

As a result of which there is some electrical potential difference is created. So, it is having positive, I mean, positive potential. It is having the negative potential. So, if this is potential for the metal, say phi M and this side is a solution side then you may be expecting that something like this. So, this is your metal, then just at the interface that is where metal just stops, means there is nothing beyond this point. Then it gradually decreases, this effect of this plus charge gradually decreases, and ultimately at a certain point it minimizes and then it remains flat.

This point is called the outer Helmholtz plane (Refer Slide Time: 07:57) and this is based on the Helmholtz double layer model. This side is the distance from the electrode surface. So, electrode surface is this zero, as distance increases, it is decreasing almost linearly, so phi m is the metal potential, phi s is the solution potential, and it minimizes at outer Helmholtz plane. So, when the metal is dipped into solution then it loses electrons and that electron is gained by the solution. Therefore, this gains a positive potential and this gains a negative potential. So, this is the pictorial representation of that.

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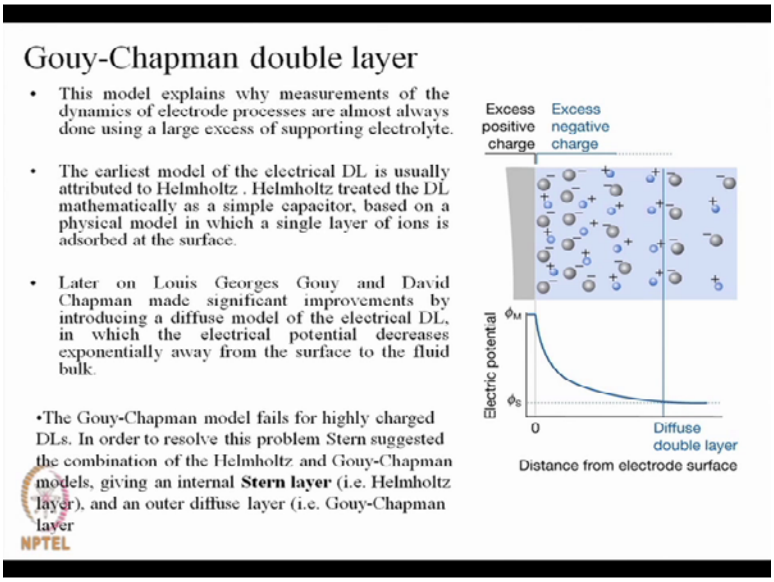

Gouy-Chapman double layer

- This model explains why measurements of the dynamics of electrode processes are almost always done using a large excess of supporting electrolyte.
- The earliest model of the electrical DL is usually attributed to Helmholtz . Helmholtz treated the DL mathematically as a simple capacitor, based on a physical model in which a single layer of ions is adsorbed at the surface.
- Later on Louis Georges Gouy and David Chapman made significant improvements by introducing a diffuse model of the electrical DL, in which the electrical potential decreases exponentially away from the surface to the fluid bulk.

•The Gouy-Chapman model fails for highly charged DLs. In order to resolve this problem Stern suggested the combination of the Helmholtz and Gouy-Chapman models, giving an internal **Stern layer** (i.e. Helmholtz layer), and an outer diffuse layer (i.e. Gouy-Chapman layer

Gouy-Chapman double layer model is another model. This model explains why measurements of the dynamics of electrode process are almost, always done using large excess of supporting electrolyte. Whenever, you measure something, I mean dynamics of electrode processes and that is done in and almost all the cases in presence of excess of supporting electrolyte.

Now, the earliest model of the electrical double layer is usually attributed to Helmholtz that is I talked about, that is the Helmholtz double layer model. Helmholtz treated the double layer mathematically, as a simple capacitor. It is a capacitor (Refer Slide Time: 09:49). You see like it is a plus, a plane of plus charges, a plane of minus charges.

So, it is simply a capacitor, based on a physical model, in which a single layer of ion is absorbed at the surface. Later on, Gouy and Chapman made significant improvement by introducing a diffuse model of electrical double layer, in which the electrical potential decreases exponentially, from the surface to the fluid bulk. So, here it decreases almost, you know, see it is shown to be linearly decreasing (Refer Slide Time: 10:39), but later on Gouy and Chapman introduced a newer idea that it introduced a diffused layer; that is there is this phi m reduces exponentially with separation.

And here this is called the diffuse double layer (Refer Slide Time: 11:06). Here, the double layer is compact, but here the double layer is diffused. It is basically, as you have reached the bulk, where it is diffused, that is plus, minus, plus, minus, but here they have not diffused, but they are some kind of tight, so as if it is you know rarefied. As you moved on away from, I mean away from a larger separation from your electrode surface, as you move to a larger separation.

Now, this Gouy-Chapman model fails for highly charged double layers. In order to resolve this problem, Stern suggested the combination of Helmholtz and Gouy-Chapman models, giving an internal Stern Layer; that is Helmholtz layer and the outer diffused layer that is you know Gouy-Chapman. So, it is a combination of this Helmholtz and Gouy-Chapman. It is a mixture; especially it is for highly charged double layers, not for the simple cases.

So, if you look at the Gouy-Chapman model, you see that here at the electrode surface, there is excess of positive charge, and as you move on in this way, away from the surface of the electrode, there is some excess of negative charge, but that is going to be diffused, going to be lowered, as you move on this way to a larger separation. So, for highly charged double layers you have to think of a different model that is a combination of Helmholtz and Gouy-Chapman and it is introduced by Stern.

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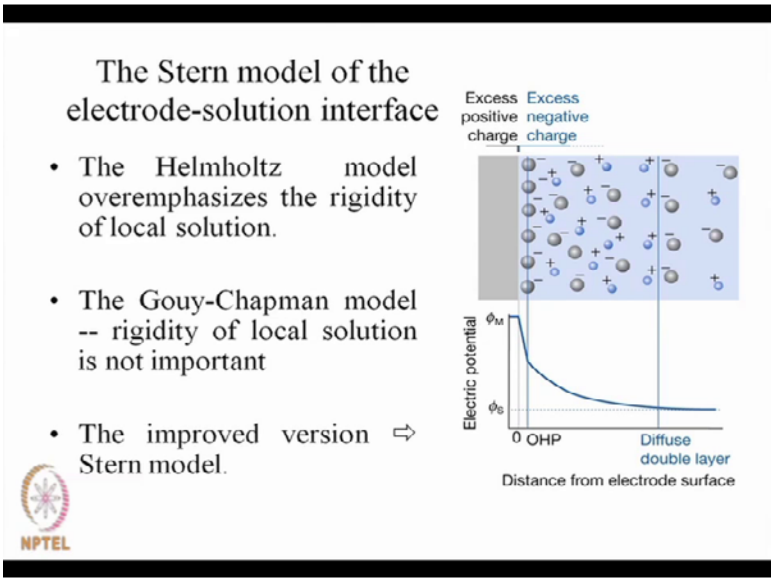

The Stern model of the electrode-solution interface

- The Helmholtz model overemphasizes the rigidity of local solution.
- The Gouy-Chapman model -- rigidity of local solution is not important
- The improved version ⇨ Stern model.

Stern model of electrode solution interface, you see here very close up to outer Helmholtz plane, it is behaving like Helmholtz double layer, and beyond that it is Gouy-Chapman. The Helmholtz model overemphasizes the rigidity of the local solution. The Gouy-Chapman model, for the Gouy Chapman model, the rigidity is not that important and improved version is your Stern model, as I talked about. So, here it is decreasing almost linearly and then exponentially up to the diffused layer.

This is what the Stern model talks about. So, again if you go back (Refer Slide Time: 14:18) this is the Helmholtz layer like this, this is Gouy-Chapman and then it is combination of these two. So, this is Helmholtz and then this is Gouy-Chapman, but the thing is that Helmholtz model overemphasizes the rigidity of local structure, local structure means here. They are thought to very rigid; they are not at all mobile, there is not much rearrangement happening, but in Gouy-Chapman model, since it is diffused kind of thing, so local solution rigidity, I mean rigidity of local solution it is not that important.

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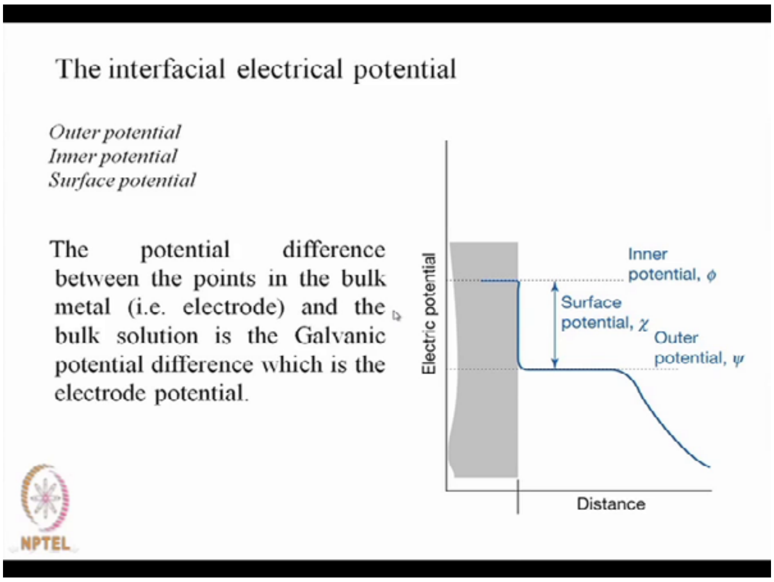

The interfacial electrical potential

Outer potential
Inner potential
Surface potential

The potential difference between the points in the bulk metal (i.e. electrode) and the bulk solution is the Galvanic potential difference which is the electrode potential.

Now, the interfacial electrical potential let us think of that. What is an interfacial electrical potential? It has got three parts, I mean; you have to think of three things; outer potential, the inner potential and the surface potential. So, interfacial, if you think of interfacial potential, then you have to think of three things. So, this is your electrode, this is your inner potential phi, this is your outer potential, then it of course decreases. Outer potential, I mean electrode outer potential is this, it remains flat for some distance, and then it reduces. So, this gap and this difference is your surface potential. The potential difference between the points in bulk that is metal and the bulk solution is the Galvanic potential difference, which is the electrode potential, I mean, which may be regarded as the interfacial electric potential and so the outer potential, the inner potential and the surface potential.

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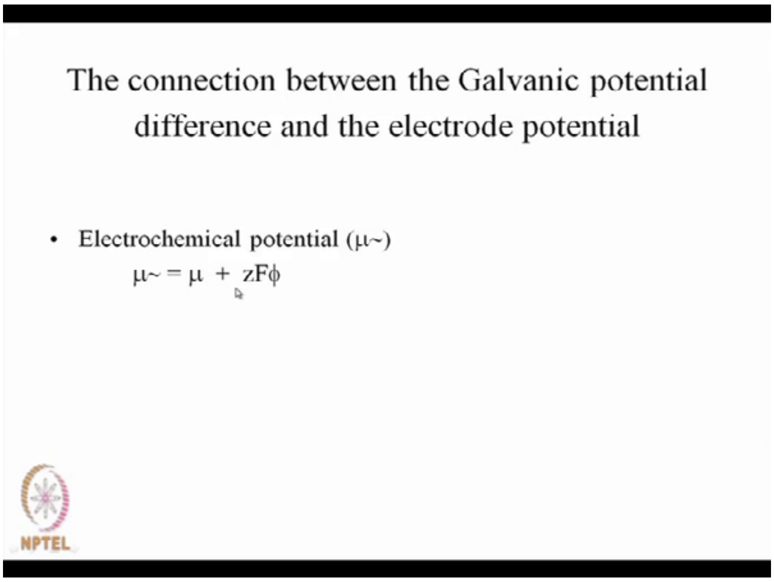
The connection between the Galvanic potential difference and the electrode potential

- Electrochemical potential (μ~)

  μ~ = μ + zFϕ

The connection between galvanic potential difference and the electrode potential; now, in a electrochemical potential, electrochemical potential is a combination of chemical potential and electrical potential. So, this is a chemical potential and this is your electrical potential that is as a result of this phi, and this is the amount of charge, I mean this is the charge in the metal, if it is for silver then it is 1, if it is other say diamond, it is 2 and so on, and corresponding potential is phi.

So, mu tilde is equal to mu plus z F phi. So, it is the electrical contribution, because of the thing I just talked about that is whenever you dip a metal, then electrons are lost from the metal to solution, and as a result of which there is a potential difference generated. So, I mean it is the electrical potential and this electrical potential combination with your chemical potential gives rise to electrochemical potential.

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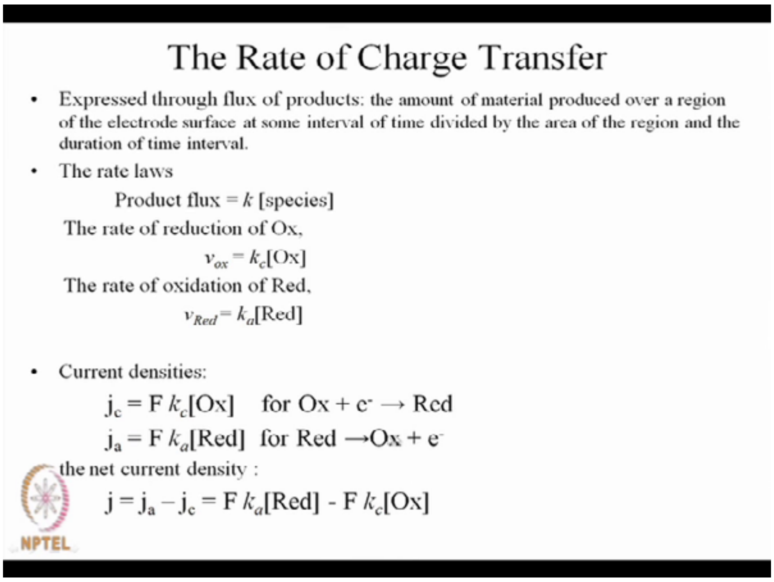

The Rate of Charge Transfer

- Expressed through flux of products: the amount of material produced over a region of the electrode surface at some interval of time divided by the area of the region and the duration of time interval.
- The rate laws

  Product flux = k [species]

  The rate of reduction of Ox,

  $v_{ox} = k_c[\text{Ox}]$

  The rate of oxidation of Red,

  $v_{Red} = k_a[\text{Red}]$

- Current densities:

  $j_c = F\, k_c[\text{Ox}]$ for $\text{Ox} + e^- \rightarrow \text{Red}$

  $j_a = F\, k_a[\text{Red}]$ for $\text{Red} \rightarrow \text{Ox} + e^-$

  the net current density :

  $j = j_a - j_c = F\, k_a[\text{Red}] - F\, k_c[\text{Ox}]$

Now, let us look the rate of charge transfer. Now, a rate of charge transfer is expressed through flux of products and the amount of material produced over a region of electrode surface, at some interval of time, divided by the area of the region, and the duration of the time interval. It is expressed in this way, the amount of material produced over a region of electrode surface, at some interval of time, divided by the area of the region and the duration of the interval.

So, rate law is product flux; product flux is equal to k into species concentration, the amount, if you think of reduction process then your rate of reduction, if you think of reduction process here, so you know for the reduction process reduction of oxidized species to reduced one. So, it is v OX, I mean rate at which this oxidized species is depleted is k c because cathodic rate constant, for the cathodic process, cathodic means reduction times OX concentration.

In the same way, the rate of oxidation of reduced substance is v Red, which is equal to k anodic into reduced species concentration. Now, how to express current density? Current density for this, (Refer Slide Time: 19:49) so cathodic density, is equal to faraday into k c this into this one, oxidation oxidized species concentration.

This is faraday, in the same way anodic is like F into k a into Red, where in this case, the process is reduction, in this case the processes is oxidation. Then what is the net current density. The net current density is difference between anodic and cathodic, anodic current and cathodic current, which is equal to F into k a Red minus F into k c OX (Refer Slide Time: 20:36). So, rate law says that the product flux this k into species concentration, and for the respective process, whether it is reduction or oxidation, we have to write the respective expression, that is v OX is this, v RED is this, then current densities is expressed in this fashion, because current density will be proportional to this rate and times your faraday will give you give you the current densities. So, net current density can be obtained in this way.

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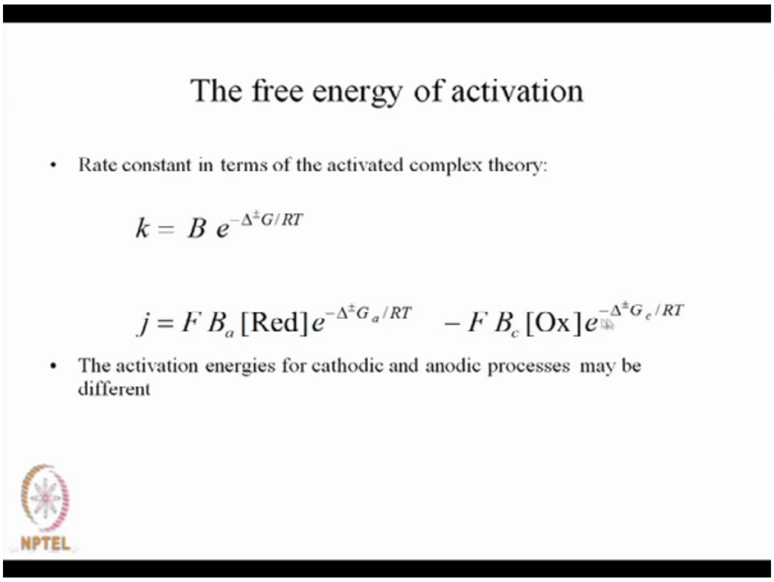

The free energy of activation

- Rate constant in terms of the activated complex theory:

$$k = B\, e^{-\Delta^{\ddagger}G/RT}$$

$$j = F\, B_a [\text{Red}] e^{-\Delta^{\ddagger}G_a/RT} \quad - F\, B_c [\text{Ox}] e^{-\Delta^{\ddagger}G_c/RT}$$

- The activation energies for cathodic and anodic processes may be different

Next is free energy of activation. From the activated complex theory, we can directly write this that k is equal to B into E to the power minus delta G activation divided by R T. And the corresponding net current density that is j is F B a into Red into E to the power minus delta G a divided by R T minus this quantity. So, it is the pre exponential factor. So, in terms of activation energy, we can write in this way. The activation energy is for the cathodic and anodic process, the anodic process is this, this is for the cathodic process, so activation energies may be different that may not be same. So, rate of charge transfer can be expressed in this way, of course, in terms of activation free energy of activation, we can write this way.

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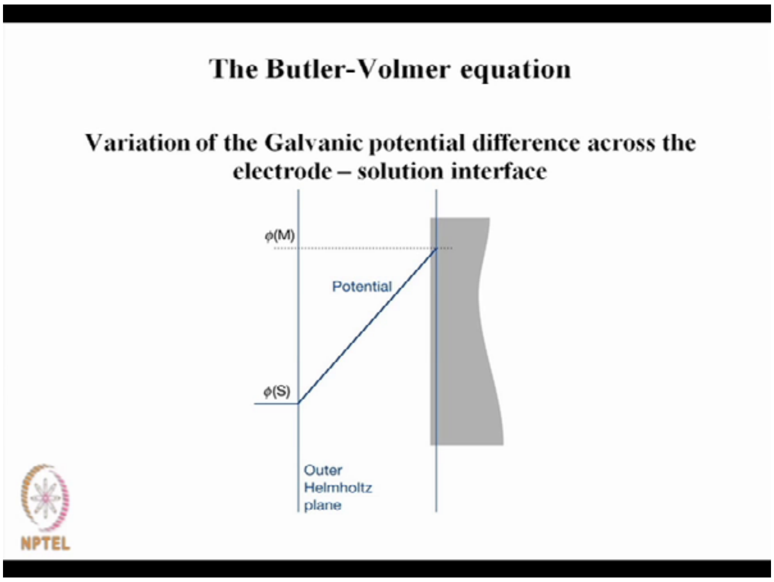

The Butler-Volmer equation

Variation of the Galvanic potential difference across the electrode – solution interface

Next, we will concentrate on Butler-Volmer equation, this is another equation. So, variation of galvanic potential difference across the electrode and solution interface. So, this is your metal, this is your solution, phi M, phi S. This is your outer Helmholtz plane. So, this is the potential function, as a function of distance. So, this is phi M, this is phi S and with distance it follows some curve.

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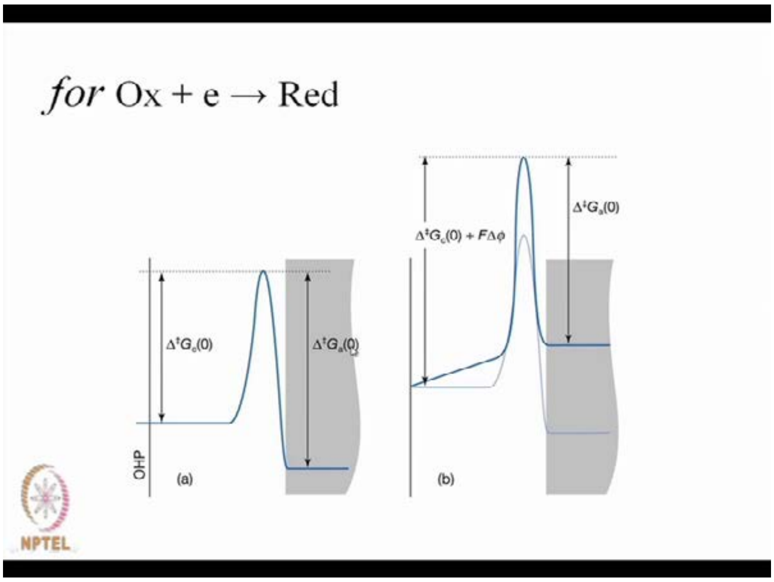

for Ox + e → Red

Now, for process we can we can think of various curves like this. This is your anodic one, maybe it is it can start from here and giving rise to this one and I mean this is your cathodic activation; this is your anodic activation. It may be different. So, cathodic is delta G c 0 is plus F delta phi, so it is the potential difference, so F delta. In this way you can write.

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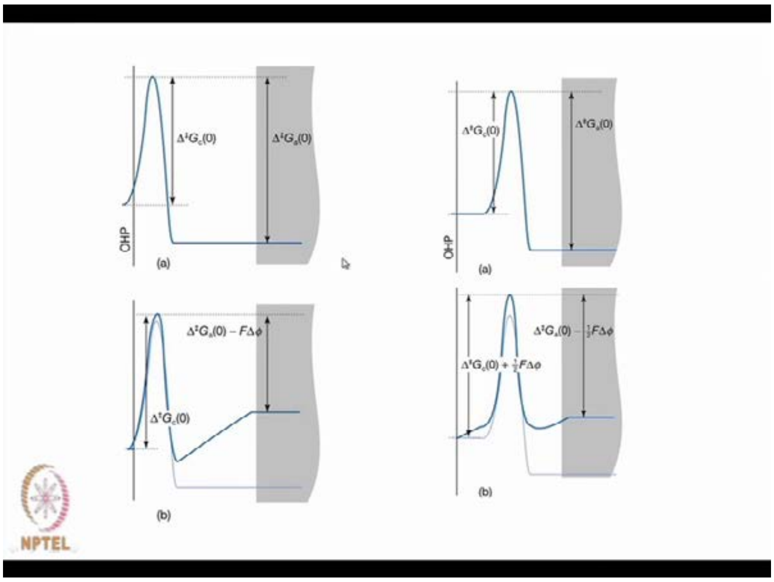

So, the point is, there may be other options.

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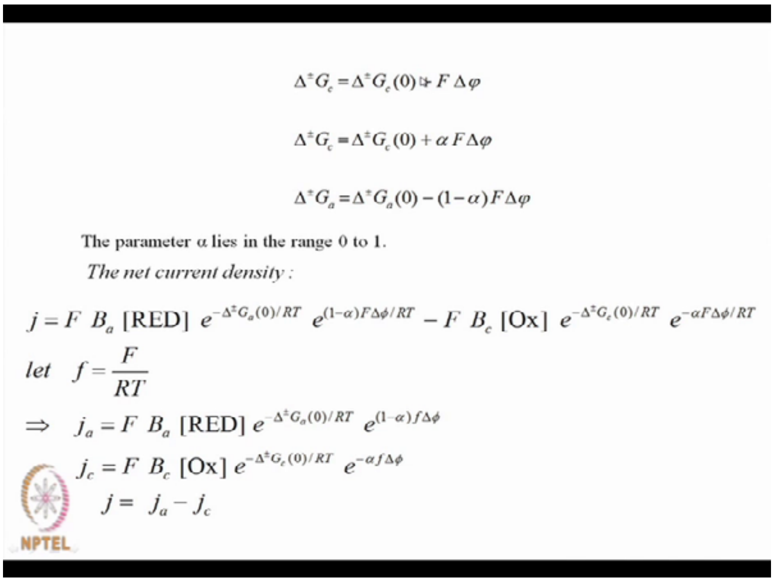

$$\Delta^{\ddagger}G_c = \Delta^{\ddagger}G_c(0) + F\,\Delta\varphi$$

$$\Delta^{\ddagger}G_c = \Delta^{\ddagger}G_c(0) + \alpha F\Delta\varphi$$

$$\Delta^{\ddagger}G_a = \Delta^{\ddagger}G_a(0) - (1-\alpha)F\Delta\varphi$$

The parameter α lies in the range 0 to 1.

The net current density :

$$j = F\ B_a\ [\mathrm{RED}]\ e^{-\Delta^{\ddagger}G_a(0)/RT}\ e^{(1-\alpha)F\Delta\phi/RT} - F\ B_c\ [\mathrm{Ox}]\ e^{-\Delta^{\ddagger}G_c(0)/RT}\ e^{-\alpha F\Delta\phi/RT}$$

$$let\quad f = \frac{F}{RT}$$

$$\Rightarrow\quad j_a = F\ B_a\ [\mathrm{RED}]\ e^{-\Delta^{\ddagger}G_a(0)/RT}\ e^{(1-\alpha)f\Delta\phi}$$

$$j_c = F\ B_c\ [\mathrm{Ox}]\ e^{-\Delta^{\ddagger}G_c(0)/RT}\ e^{-\alpha f\Delta\phi}$$

$$j = j_a - j_c$$

NPTEL

Basically, net we can write the free energy of activation for the cathodic process, in this way, and for the cathodic process with proper you know it is alpha is another factor which lies between 0 and 1, and for the anodic process you can write in this way.

This is your activation and this is your when this delta phi is zero, when potential difference is zero. So, net current density, we can express in this way that j is equal to F into anodic pre exponential factor into reductant concentration times these factors times these two, because we have to write, I mean, we have to write this in this way, because we can write in this way delta G c is delta G c 0, I mean, of course, double dagger plus F delta phi.

In the same way G a, you can write, delta G a, you can write in this way. So you just plug in this two over this expression over this expression (Refer Slide Time: 25:20). Just plug in the information of over these two expressions, because you have to express this activated one, activation delta G activation for the cathodic and anodic, in terms of, in terms of this figure. So, this is your cathodic delta G activation of course 0, I am sorry, and this is your anodic and this is your cathodic delta G double dagger.

So we have got this expression (Refer Slide Time: 25:53) and now, let f is equal to F by R T. Let us write another quantity F by R T, this F by R T. F is a constant quantity, R T as long as T is constant is a constant quantity, so f is equal to F by R T. You just write in place of F by R T by this.

So, j a anodic flux and this is your j c is the cathodic flux, we already have explained what is flux; it is current density. So, current density j a is this for your anodic, and for your cathodic is this, so difference net current density is j a minus j c, so you just take the difference between these two. You will be getting the net current.

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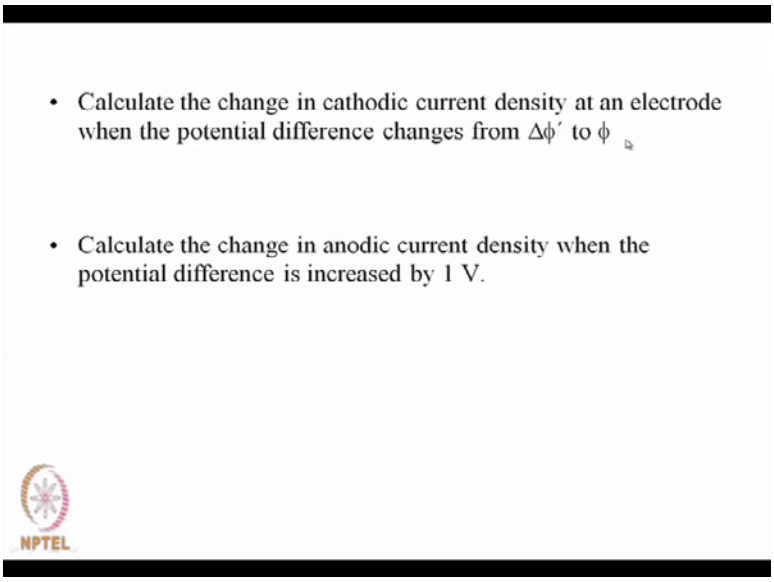

- Calculate the change in cathodic current density at an electrode when the potential difference changes from $\Delta\phi'$ to ϕ
- Calculate the change in anodic current density when the potential difference is increased by 1 V.

You can try calculating the change in cathodic current density at an electrode when the potential difference changes from phi prime to phi. Now, delta it is a typo, so phi prime to phi. What is the cathodic current density? You know cathodic current density, so this is your cathodic current density, so just delta phi, I mean if the value of your, I mean potential difference changes from say delta phi to phi, I mean prime to un primed. So, you just try to find out the value corresponding to delta phi and another corresponding to only, I mean, primed and only phi, and you should be able to have some idea of what is going on in the cathodic current, when it is changing from some prime value to another value.

Next is to calculate the change in anodic current density when the potential difference is increased by 1 volt. In that way, you can also find. So, this will give you the idea of how (Refer Slide Time: 28:21) this is changing, I mean if you change delta phi to some value or may be some value or may be exactly some value like 1 volt. How this is going to affect your cathodic current and anodic current density?

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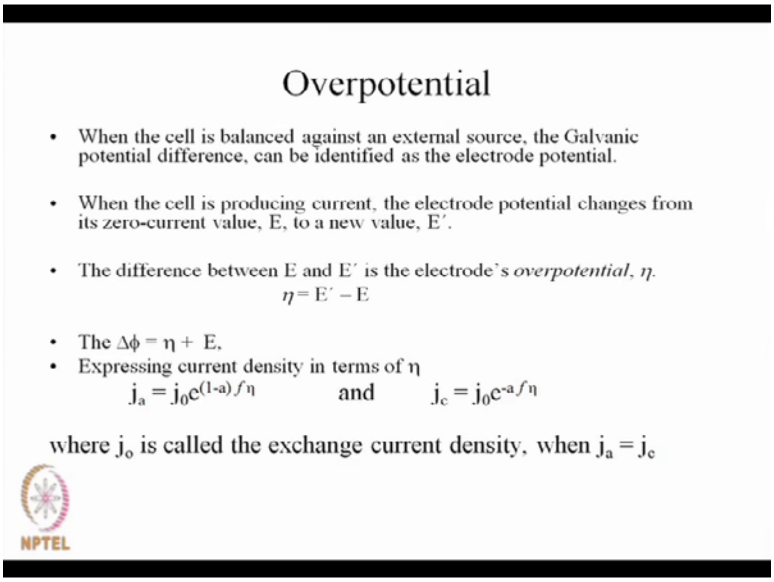

Overpotential

- When the cell is balanced against an external source, the Galvanic potential difference, can be identified as the electrode potential.
- When the cell is producing current, the electrode potential changes from its zero-current value, E, to a new value, E′.
- The difference between E and E′ is the electrode's *overpotential*, η.

$$\eta = E' - E$$

- The $\Delta\phi = \eta + E$.
- Expressing current density in terms of η

$$j_a = j_0 e^{(1-a)f\eta} \quad \text{and} \quad j_c = j_0 e^{-af\eta}$$

where j_o is called the exchange current density, when $j_a = j_c$

Next is over potential, there is another aspect which is a very important that is over potential. First of all, we have to know what is over potential. Now, when a cell is balanced against an external source, the galvanic potential difference can be identified as electrode potential. So, think of the pogenda compensation method, by which we can measure the electrode potential. So, in that case you have to have the cell balanced exactly. So, internal potential and the external potential, I mean the current flow flowing is zero. Under that condition perfect reversibility is reached and the corresponding galvanic potential difference can be retained as the electrode potential. So, specific condition that you have to think of, whenever, you try to find out the electrode potential.

Next is when the cell is producing current, so, producing current means, some reaction is going on. The electrode potential changes from its zero value to E, zero value, zero current value E to a new value E prime. So, when the cell is exactly balanced against external source, your zero current value is say E, that is the equilibrium electrode potential. Now, when you draw some electricity then what is going on? Then your value of E changes, because it is no longer balanced. So, potential is changing. Now, then the difference between this E and E prime is the electrode's over potential, and it is denoted by eta. So, eta is nothing but eta is equal to E primed minus E. So, it is the potential when it is producing current, and it is the potential when it is exactly under reversal situation that is exactly balanced from balanced against an external source. So, delta phi is n plus eta plus E.

Now, if we express current density in terms of eta, then anodic current density, can be written as like this (Refer Slide Time: 31:42) and the cathodic current density can be written like this. Well j 0, I mean, is a quantity, which is called the called the exchange current density. When j a, is equal to j c, then you can have exchange current density. What is the value of the exchange current density? When cathodic current and anodic current; these two match then you can get the exchange current density.

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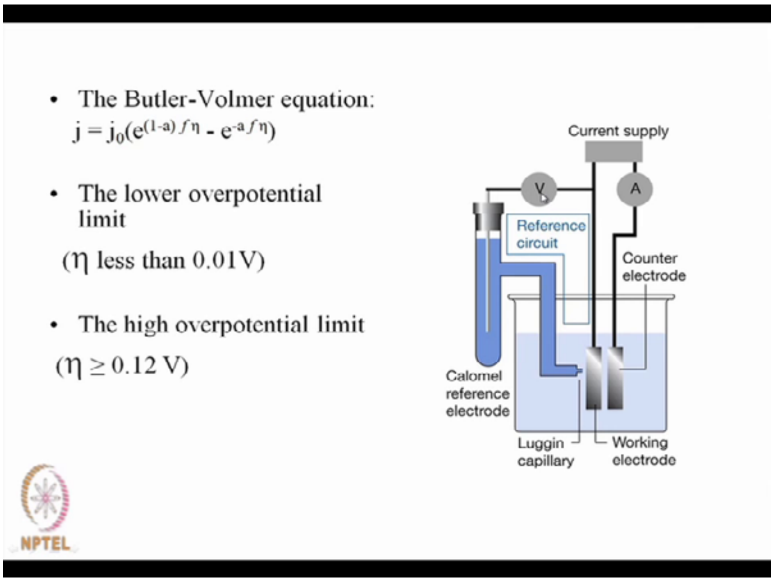

- The Butler-Volmer equation:
  $j = j_0(e^{(1-a) f \eta} - e^{-a f \eta})$
- The lower overpotential limit

  (η less than 0.01V)
- The high overpotential limit

  ($\eta \geq 0.12$ V)

Now, upon plugging in this information, these two, that is net current density, I mean to find out the net current density that is this. This is your net current density j is equal to j a minus j c. So, you just subtract this from this, so j a minus j c is this, is this one, and this is called the Butler-Volmer equation, where j is equal to j 0, j 0 is the exchange current density, that is when j equal to 0, j equal to 0, means j a equal to j c, then you can get the exchange current density. Now, two situations may arise.

One is low overpotential limit, where eta is less than 0.01 volt and the high over potential limit when eta is equal to or greater than 0.012 volt. These two situations may be there. Now, before that the experimental diagram is this. It is basically a three electrode situation. This is your reference, I mean reference electrode, Calomel electrode. This is your working electrode and this is your counter electrode. So, there are three electrodes.

So this is your current supply, this is connected to a source, which is supplying current. You have got your ammeter ampere meter, this is your voltmeter and this is your reference circuit, this constitutes the reference circuit, this part (Refer Slide Time: 34:12). So, basically you are drawing a current potential diagram. So, that is the experimental arrangement for doing these studies, which is electrode, kinetics.

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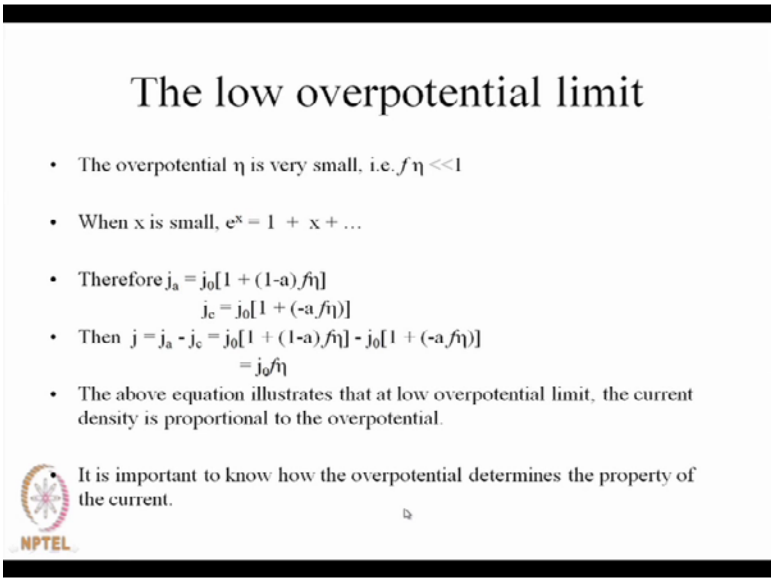

The low overpotential limit

- The overpotential η is very small, i.e. $f\eta << 1$
- When x is small, $e^x = 1 + x + \ldots$
- Therefore $j_a = j_0[1 + (1-a)f\eta]$
  $j_c = j_0[1 + (-a f\eta)]$
- Then $j = j_a - j_c = j_0[1 + (1-a)f\eta] - j_0[1 + (-a f\eta)]$
  $= j_0 f\eta$
- The above equation illustrates that at low overpotential limit, the current density is proportional to the overpotential.
- It is important to know how the overpotential determines the property of the current.

Now, lower over potential limit, let us think of lower over potential limit. What is that? Eta is less than 0.01 volt. That is eta is very small. So, f into eta is very less than 1, so you can express your E x in this way, that is E x is equal to 1 plus x. Therefore, you just put this over here. So, j a will become like this, and j c will become like this. So, then upon expressing total current, this total current density, which is equal to j a minus j c, which is equal to exchange current density times this one, so that is equal to j 0 f into eta.

So, basically you see that net current density, which is nothing but equal to j 0 into f into eta. So, the above given equation, as you see, it is a linear relationship. Therefore, j is proportional to eta. So, this equation illustrates that at low over potential limit, when over potential is very small then the current density is proportional to the over potential. So, this is very important that under low over potential limit, we get this expression. Of course, with such approximation, means this approximation is valid only, when it is very small. It is also important to know how over potential determines the property of the current.

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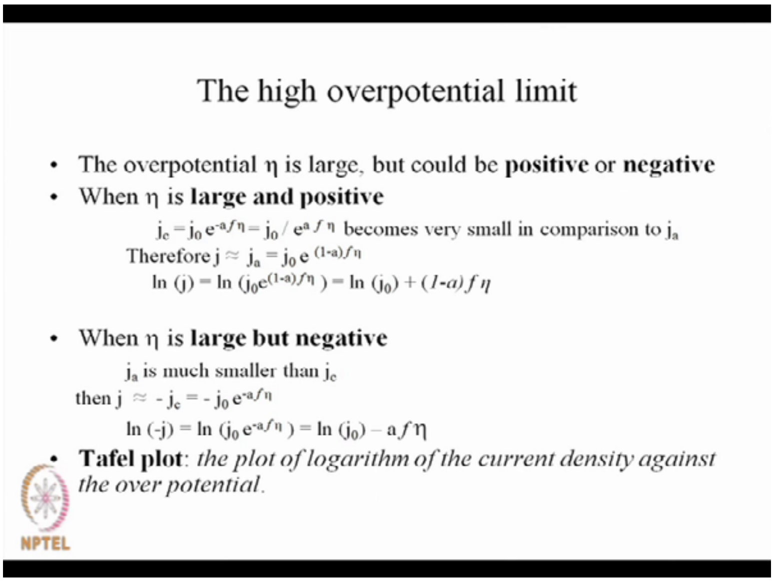

The high overpotential limit

- The overpotential η is large, but could be **positive** or **negative**
- When η is **large and positive**

  $j_c = j_0 e^{-af\eta} = j_0 / e^{af\eta}$ becomes very small in comparison to j_a

  Therefore $j \approx j_a = j_0 e^{(1-a)f\eta}$

  $\ln(j) = \ln(j_0 e^{(1-a)f\eta}) = \ln(j_0) + (1-a)f\eta$

- When η is **large but negative**

  j_a is much smaller than j_c

  then $j \approx -j_c = -j_0 e^{-af\eta}$

  $\ln(-j) = \ln(j_0 e^{-af\eta}) = \ln(j_0) - af\eta$

- **Tafel plot**: *the plot of logarithm of the current density against the over potential.*

Next is higher over potential limit. We previously talked about lower over potential limit.

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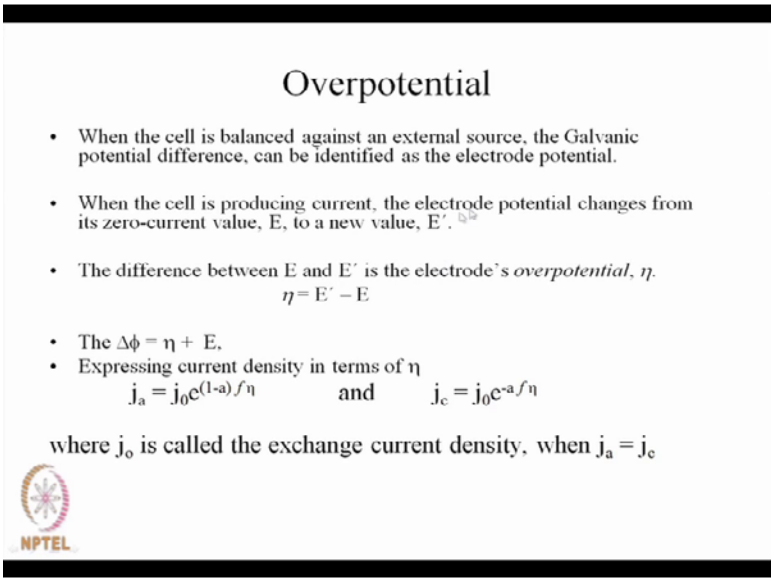

Overpotential

- When the cell is balanced against an external source, the Galvanic potential difference, can be identified as the electrode potential.
- When the cell is producing current, the electrode potential changes from its zero-current value, E, to a new value, E′.
- The difference between E and E′ is the electrode's *overpotential*, *η*.

  $\eta = E' - E$

- The $\Delta\phi = \eta + E$.
- Expressing current density in terms of η

  $j_a = j_0 e^{(1-a)f\eta}$ and $j_c = j_0 e^{-af\eta}$

where j_o is called the exchange current density, when $j_a = j_c$

And over potential is nothing but the difference in... This electrode potential changes from zero current value to some new value when there is some current flowing. So you see that this is when this difference is very small. I mean to say that low over potential limit means when this difference between E prime and E is very small, they are very close to each other. Then and only then, your current density is proportional to over potential. This is very important. It is a very important conclusion.

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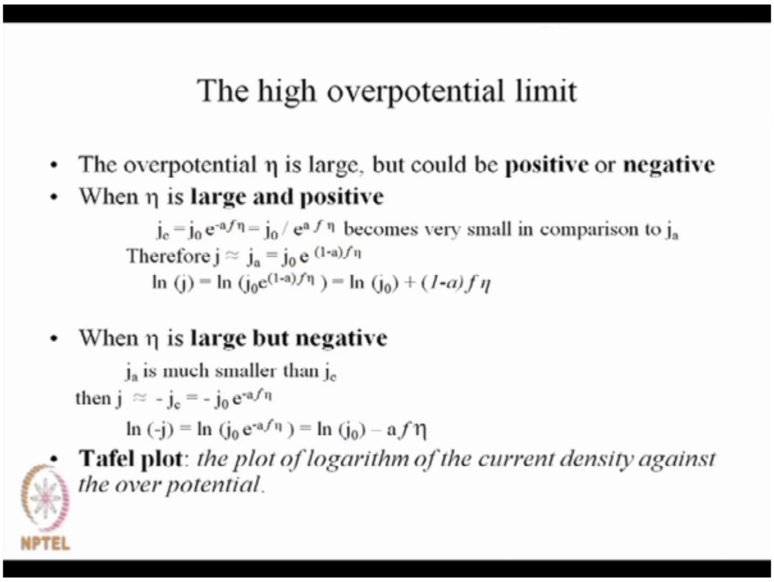

The high overpotential limit

- The overpotential η is large, but could be **positive** or **negative**
- When η is **large and positive**

  $j_c = j_0\, e^{-a f \eta} = j_0 / e^{a f \eta}$ becomes very small in comparison to j_a

  Therefore $j \approx j_a = j_0\, e^{(1-a) f \eta}$

  $\ln(j) = \ln(j_0 e^{(1-a) f \eta}) = \ln(j_0) + (1-a) f \eta$

- When η is **large but negative**

  j_a is much smaller than j_c

  then $j \approx -j_c = -j_0\, e^{-a f \eta}$

  $\ln(-j) = \ln(j_0\, e^{-a f \eta}) = \ln(j_0) - a f \eta$

- **Tafel plot**: *the plot of logarithm of the current density against the over potential.*

NPTEL

Next is, what is going to happen when we are in the high over potential limit that is eta is large, greater than or equal to 0.12. Then, it could be, I mean over potential large, means it could be large in positive sense or large in negative sense also. If it is large positive what is going to happen? Then that cathodic current density j c is equal to j 0 into exponential minus a f eta and which becomes very small in comparison to j a.

Therefore, j is approximately equal to j a, which is equal to j 0 into e to the power 1 minus a into f into eta. So, if you take l n on both the sides, you will be getting l n j is equal to l n j 0 plus 1 minus a f eta. So, under that condition, initially when over potential is low, then there is direct correlation, I mean, linear correlation between j, I mean linear relationship between j and eta, but now it is a logarithmic dependence. It is a logarithmic dependence. Now, when eta is large, but it is negative that is large and negative. Under that condition, the reverse is happening, that j a is much smaller than j c, cathodic term much smaller than j c. Therefore, under that condition when large but negative, eta is large but negative, then j is approximately equal to minus j c, because j is equal to j a minus j c, and j a is much smaller, therefore you can neglect j a.

Therefore, j is equal to minus j 0 e to the power minus a f eta. If you again take l n, so you will be getting l n minus j, minus j means you know you are taking a negative sign, means it is not a logarithm of negative quantity, but it is basically l n j. So, l n j is equal to l n j 0 minus a f eta. So, here you have seen that when it is large and positive is 1 minus a f eta, but here it is minus a f eta.

Now, this is basically the Tafel plot, which is a plot of logarithm of current density against over potential; is the Tafel plot. So, again let us go back to Butler-Volmer equation (Refer Slide Time: 40:47). So, Butler-Volmer, you have you have got this from here, like here. From Butler-Volmer you have reached using the higher over potential limit you have reached this graph, I mean this plot that is logarithm l n plot of your over potential, and this is called your Tafel plot, so when it is high over potential. When it is low over potential then you get a linear co-relationship between j and eta, but when it is high over potential, it is no longer a linear situation.

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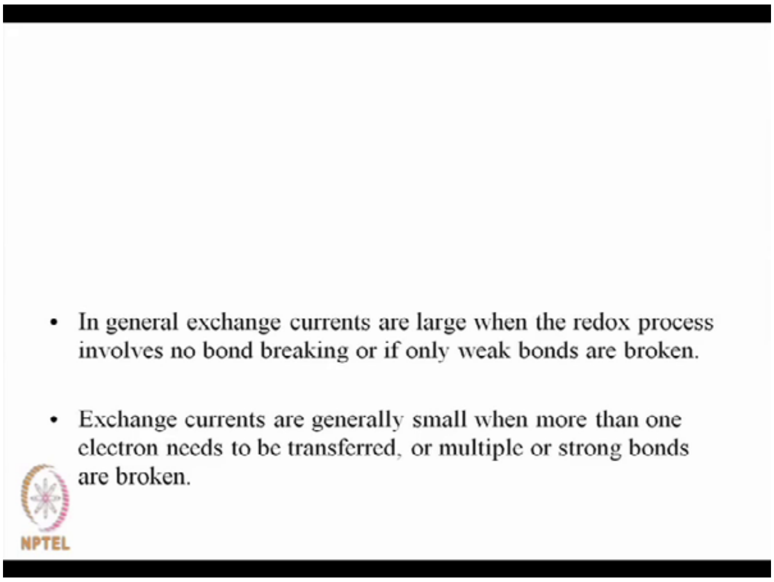

- In general exchange currents are large when the redox process involves no bond breaking or if only weak bonds are broken.
- Exchange currents are generally small when more than one electron needs to be transferred, or multiple or strong bonds are broken.

Now, in general, exchange currents are large when redox processes involves no bond breaking or if only weak bonds are broken, when exchange currents are high, and when exchange currents are small, generally small, when more than one electron needs to be transferred or multiple or strong bonds are broken.

So, in high exchange current and low exchange current, the situations are different, so no bond breaking or formation is there, when large exchange current, but when small exchange current is there, then there may be one or more electrons are needed to be transferred that is bonds are really to be broken.

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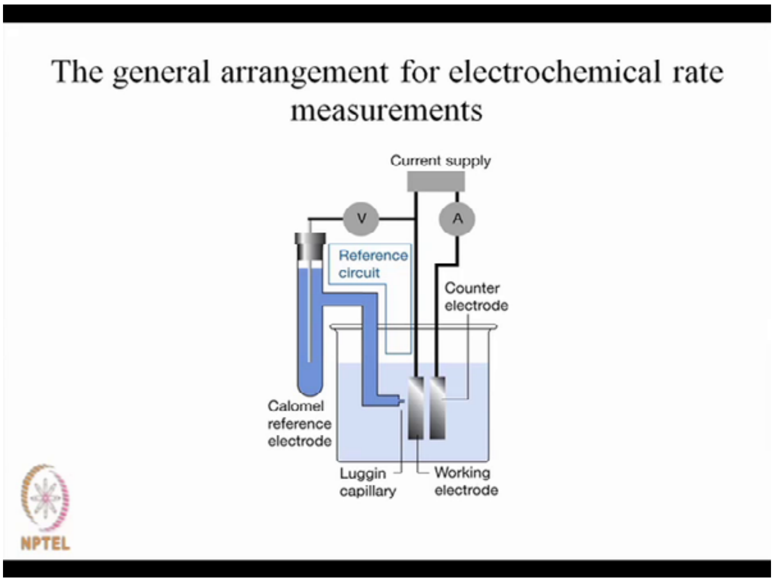

The general arrangement for electrochemical rate measurements

This is the general arrangement for measurement of electrochemical rates, as I told you earlier, that it is basically do a current potential diagram. It is a arrangement for doing a current potential diagram, so basically, if you think of your Tafel plot or may be the Butler-Volmer plot, everywhere you see that it is you are plotting your current density. Current density means it is basically difference of your anodic and cathodic.

So you are measuring the current density. In all cases, whenever you do some measurement on this electrochemical rate process, rates that is occurring at the electrodes then you supply current from here (Refer Slide Time: 44:16). It is a source of electricity, I mean there is a counter electrode, there is a working electrode and you have got your reference electrode.

You measure with respect to your you know, voltage is measured with respect to reference electrode that is how much of voltage is created, potential difference is created, as a result of supply of current between these two. You are supplying current between these two and that is an ammeter.

This is your working electrode. This is your counter electrode, so it completes the circuit, and you want to measure. So, this is the working electrode means where the reaction is taking place and you need a counter electrode to complete the circuit. You have got your solution over here, so actually the process is occurring; I mean in this these two electrodes, between these two. So, actual reaction is taking place over here, and because of the supply, various electronic transfers and other redox processes are occurring. Therefore, may be your concentration, I mean concentration of certain substance is or may be electrode is getting altered. So, electrode potential accordingly changes.

So you have to measure that electrode potential, as how much and how it is changing. In one case, whether as a function of time, that is how much time is required or as a function of your current supply.

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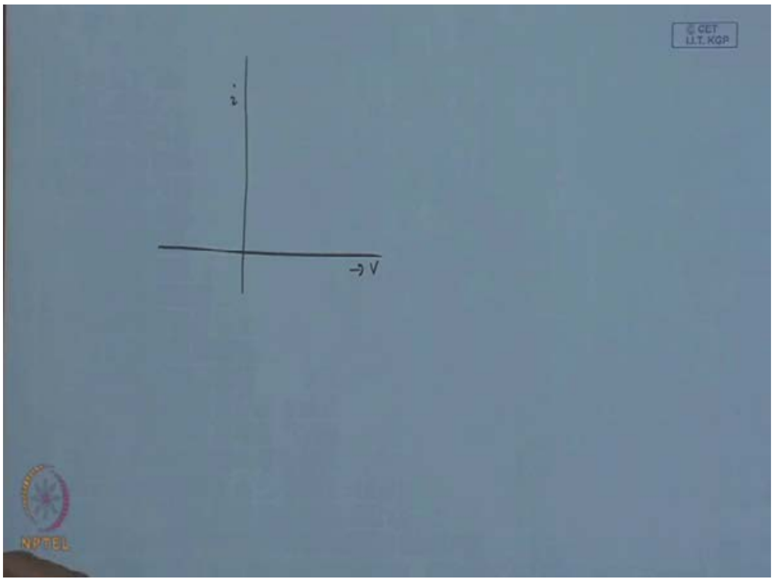

So, you draw a current potential diagram, so this may be v, this is i, current potential diagram you do, and from this current potential diagram, you find out how this is changing, that is the functional dependence, that is the functional dependence of your potential; potential changes means your electrode, I mean, various electrode reaction is occurring. Therefore, may be because of the electron transfer, because of electron transfer, this electron electrode is getting either you know, its potential is getting effected.

So, this way you can you can measure. That is a rough sketch. In the next class, we will talk more on this. There are various techniques. Techniques, you know to measure electrochemical rates, because it is the reaction that is occurring at the interface at the electrode.

So, let us have look at what we have learnt so far. So, we have started with electron transfer in electrodes. Now, when it is the case of electrode, then the electrode has to be dipped into a solution of electrolyte. When an electrode is dipped into a solution of electrolyte then what is going to happen that, the moment it is dipped, this electrode is losing some electron to the solution. Therefore, it becomes positively charged and the solution becomes negatively charged.

So, one positively charged thing, another negatively charged thing, there is a possibility of formation of a double layer. Formation of double layer is similar to a capacitor. Helmholtz actually introduced this idea, and his main idea was based on the model of a capacitor, and here is the plot of electric potential we have already talked about that it is linearly changing with separation.

Next, we talked about Gouy-Chapman model. It is they have introduced a diffused earlier where the potential is reducing, changing, exponentially with distance. And for highly charged double layers, may be this model or may be the earlier model is not sufficient to explain the behaviour. So, in that case, Stern introduced a combination of these two, that this is outer Helmholtz sphere, which is nearby portion, is guided by your Helmholtz type of model, and the outer portion is guided by your Gouy-Chapman model.

Then we talked about interfacial electrical potential that this is a electrode. This is your inner potential. This is your outer potential and this is the surface potential, which is nothing but the difference between these two. The relation between we talked about, I mean what is the relation between chemical potential and electrochemical potential. So, this is the chemical potential and this is your electrochemical potential, where this z F phi is the contribution from the electrical portion.

Then we talked about rate of charge transfer and which is nothing but, the product flux, which is nothing but the rate at which the electron is transferred times the species concentration, and we talked both in terms of oxidant and reductant, I mean, oxidized species and reduced species. Current densities are expressed in this way, and net current density as well expressed in this way. Then we talked about this current density in terms of free energy of activation, and we have used activated complex theory and tried to explain this, I mean tried to improvise that and introduced that here.

Then we got this Butler-Volmer equation, which is based on this calculation and this Butler-Volmer equation is this, which relates your current density, net current density with over potential where f is a constant. So, over potential, so this we expressed, I mean in terms of over potential, let us go back to the original expression that, net is this, alpha or a, means alpha or a, here you see that this part is cathodic contains alpha, anodic part contains 1 minus alpha. This is your 1 minus a means this is actually alpha.

We have then talked about over potential, I mean we have discussed in terms of two case situations; lower over potential, higher over potential. Lower over potential, you know current density is linearly dependant on eta, I mean, the over potential but for higher over potential limit we get Tafel equation and also we talked about this general electrochemical measurements.

You know whenever it is the case of equilibrium situation that we do not want to get in electricity, then it is E, and when you know it is we are getting some current, then it is E prime. So, difference is basically your over potential. So, when there is flow of current, I mean, we are getting something, some energy, then cell is working, then reactions are proceeding. So, your current density, because of this various electrode processes, like cathodic processes, anodic processes, your current density will change, and how this current density will change, that the current density will change with over potential that we tried to explain in terms of you Butler-Volmer equation.

So, that is a very important equation. In the next piece of lecture, we will explore electrochemical measurements like voltammetry. So, that will be taken up in the next lecture. For this particular piece, you may consult any standard electrochemistry textbook, under the heading electrodex and may be bokerstic this text will be useful and may be some internet resources will also be helpful. So, till then thank you.