Indian Institute of Technology
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NP-TEL
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On
Technology Enhanced Learning

Course Title
Environmental Degradation of Materials

Module 01 Lecture 14
Broad Subject: Concentration polarization, Mixed Potential Theory

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So let us continue concentration polarization and what we have seen earlier that if this is distance from the metal surface, and this is we are considering cathodic reaction, now that case if you see the concentration profile from the metal surface to the bulk of the solution of concentration profile of M^{n+} ion, so that means this is my C_0, which is the bulk concentration.

And initially, we have started with C_0, and then with the progress of reaction, and if the rate of actual charge transfer reaction that is a anodic -- that is the activation process rate is higher than the rate at which metal ion is supplied from the bulk to the interface, if that activation polarization activation, the rate at which metal transfer occurs -- charge transfer occurs, rate at which this actual reaction happens that is higher than the rate at which metal ion is supplied from the bulk to the interface, then we experience concentration polarization or rather concentration change from the interface to the bulk of solution.

And this is C, and we have seen that this is boundary layer, and we have seen that if we follow simplistic approach that is the Fick's first law of diffusion, then i is related to -nFD, which is diffusion -- diffusivity of that metallic ion in the medium C_0 minus C by δ considering a linear concentration change.

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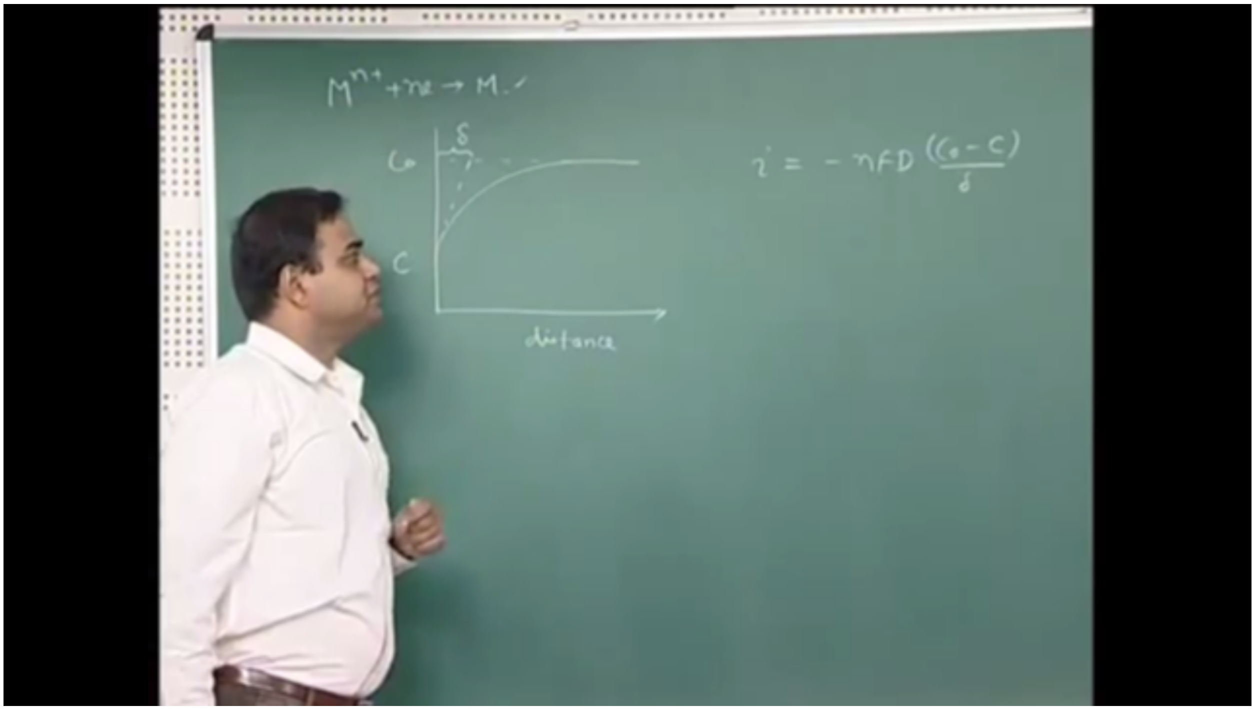

Then we have also seen that this concentration at this interface will go to zero if the current is maximum. That means when the current is maximum, that means whatever charge is coming from the bulk to the interface, those are getting reduced. So in that case, i_{max} would be equal to -nFD. Here C, since C is zero at this interface, then C would be 0, so C_0 by δ.

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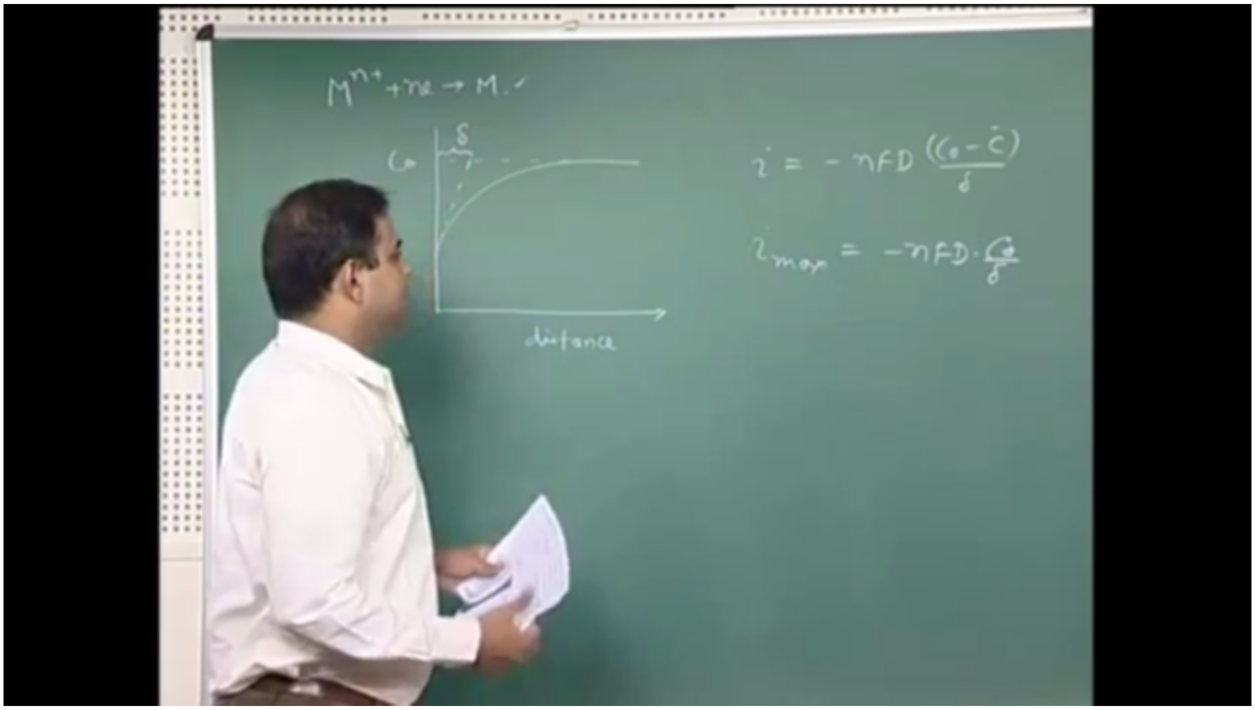

Now then we have followed the Nernst equation just to understand what is the potential at these two interfaces. So at this -- at this two position bulk, if the concentration at this interface, if the concentration is C_0 and if the concentration is C, then what would be the potential? And that would be decided by concentration potential, concentration effect. If we -- we have already seen that if the concentration of metallic species increases, then the electrode potential also will increase.

So if we write the Nernst equation works in this case $E_{M}{}^{n+}/M$ would be equal to $E^{0}{}_{M}{}^{n+}/M$ plus RT/nF into 2.303 I am putting in the form of log C. Now one case it is C, that means when the concentration goes to C at the interface, and one case it's C_0 that means when time equal to $t = 0$ when with the just start of the process of concentration difference, then there would be two potential. One is let's say this is 2 and one case it would be E^1, the initial condition, that is $E^{1}{}_{M}{}^{n+}/M$. So this term will remain because this is a constant term. Now this other terms will also remain and here you have to put C_0. C_0. Now since C_0 is greater than C_1, so $E^{2}{}_{M}{}^{n+}/M$ should be less than $E^{1}{}_{M}{}^{n+}/M$.

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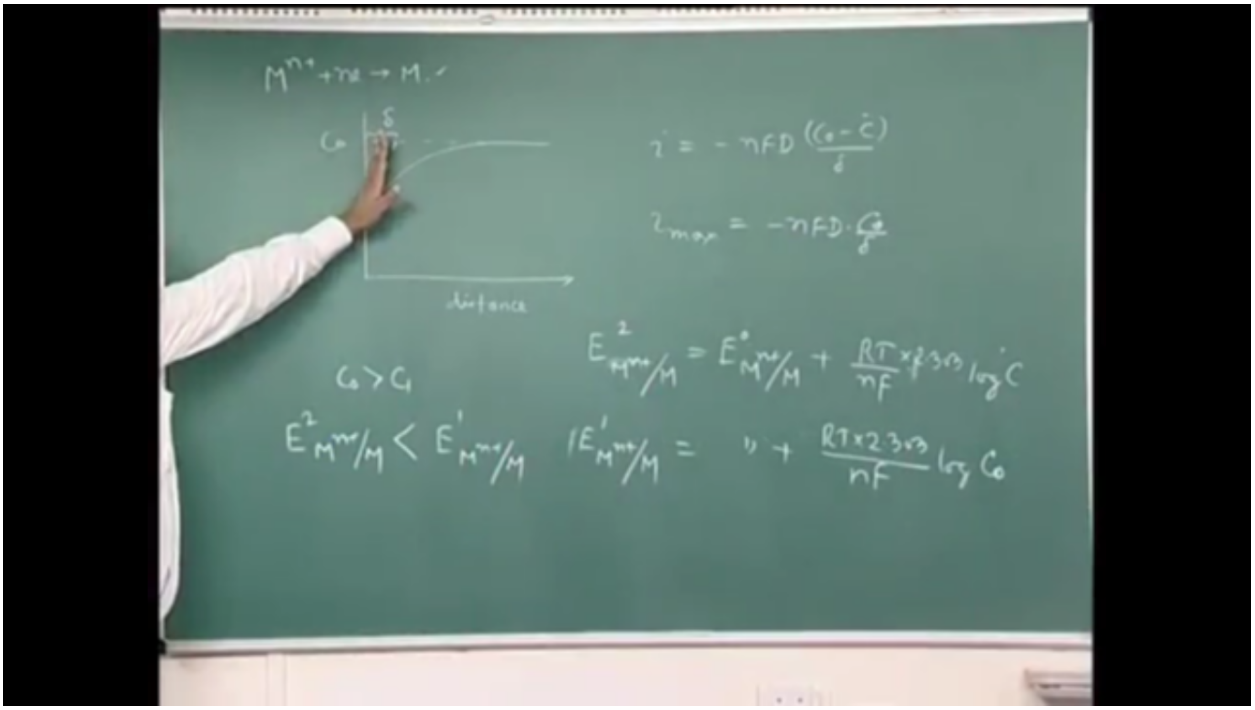

Now you see, initially, we have started with C_0. Now we have reached to C. That means we are having concentration -- lowering in concentration, and that would lead to lowering potential and also this is a cathodic reaction. We have already seen that for a cathodic reaction, if it proceeds, then we -- we get to get -- we get cathodic polarization, and the cathodic polarization here also since the cathodic polarization concept is maintained because the potential is dropped with the progress of this reaction, cathodic reaction and at the same time this effect is coming because of change in concentration. So this is a cathodic concentration polarization that would lead to lowering in potential.

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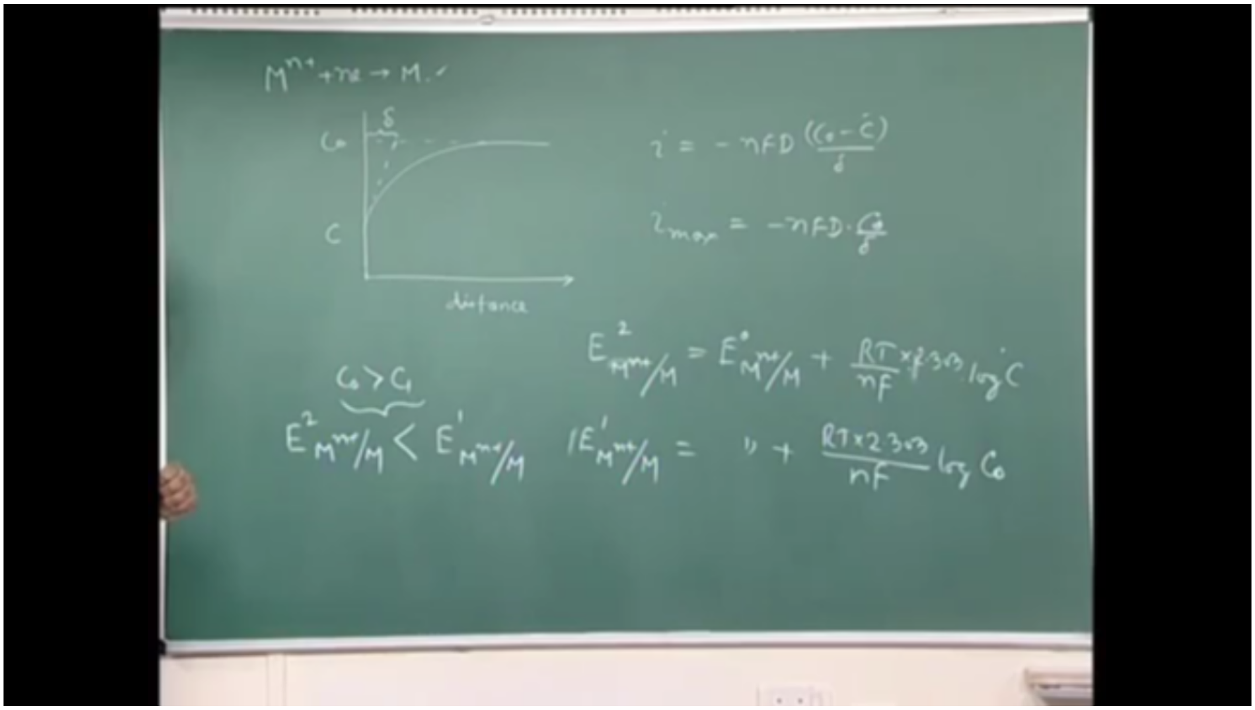

$M^{n+} + ne \rightarrow M$

$i = -nFD\frac{(C_0 - C)}{\delta}$

$i_{max} = -nFD \cdot \frac{C_0}{\delta}$

$E^2_{M^{n+}/M} = E^0_{M^{n+}/M} + \frac{RT}{nF} \times 2.303 \log C$

$\underbrace{C_0 > C_1}$

$E^2_{M^{n+}/M} < E^1_{M^{n+}/M}$

$E^1_{M^{n+}/M} = \text{''} + \frac{RT \times 2.303}{nF} \log C_0$

Now we have to quantify this polarization, cathodic concentration polarization. Then we can write that this concentration which is in the cathodic case that would be E^2 minus E^1 would be equal to now let's say we are -- this process is taking place at 25 degree Celsius temperature and 1 atmosphere pressure. Now we know what is R. I am just putting the value F -- this is Joule per mole per Kelvin. This is F is nothing but 96500 roughly, Coulomb per gram equivalent, gram equivalent.

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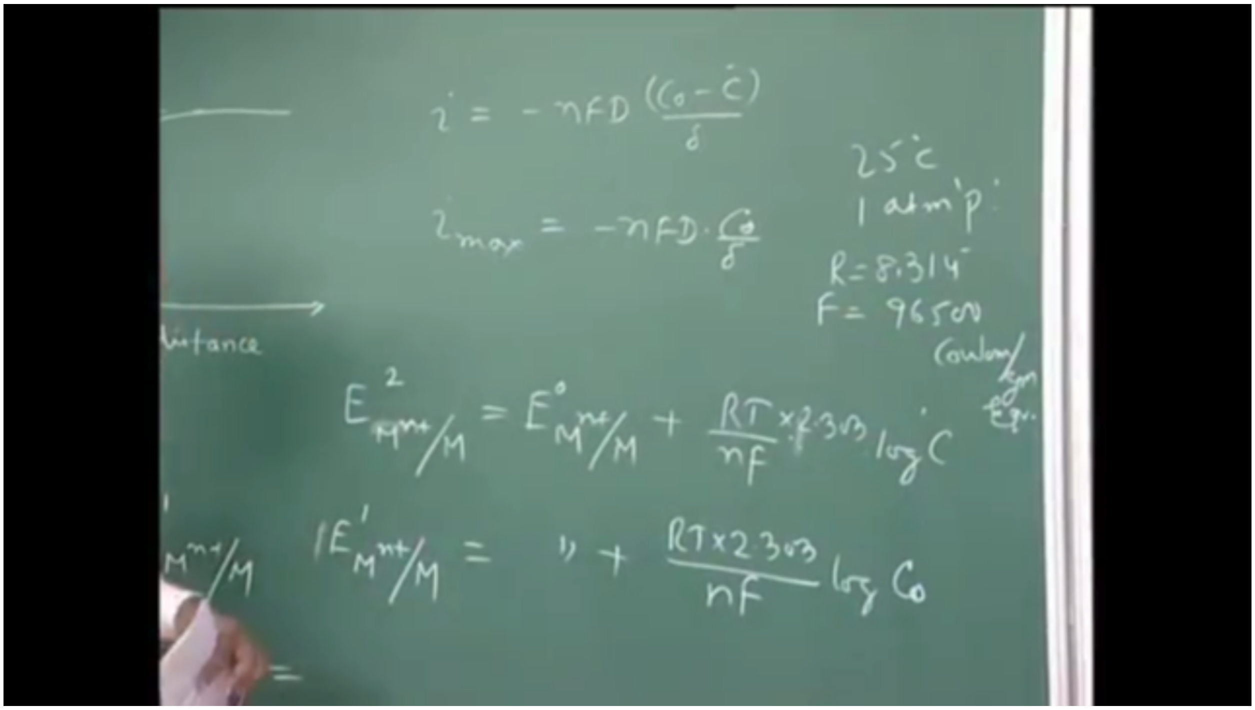

$$i = -nFD\frac{(C_0 - C)}{\delta}$$

$$i_{max} = -nFD \cdot \frac{C_0}{\delta}$$

25°C
1 atm p
R = 8.314
F = 96500 Coulomb/gm Equ.

$$E^{2}_{M^{n+}/M} = E^{0}_{M^{n+}/M} + \frac{RT}{nF} \times 2.303 \log C$$

$$E^{1}_{M^{n+}/M} = \text{''} + \frac{RT \times 2.303}{nF} \log C_0$$

Now if you put all those values, you would see that these two terms will get cancelled because we are seeing the -- what is the potential difference because of concentration change. There is a final potential, which is this minus initial potential. Then it will lead to 0.059 by n log of C by C_0. Now C/C_0 we can write it as -- we can write 1 minus 1 plus C/C_0. This would come (C_0 minus C) by C_0.

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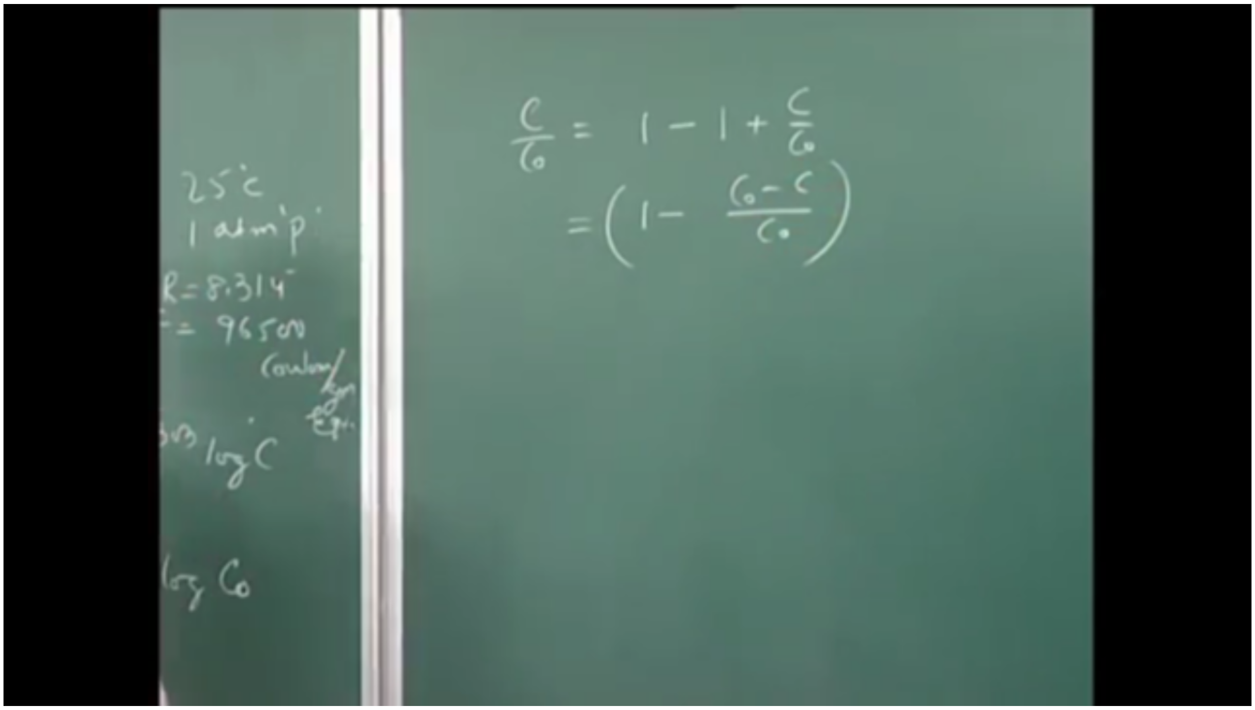

Now we know that C_0 from this equation C_0 minus C would be equal to iδ/nNF. Similarly, C_0 from this we can get C_0 equal to i_{max} δ/nFD. Let us put this values instead of C_0 minus C and C_0. Then we would get 1 minus I by i_{max}, which is the ratio between current densities.

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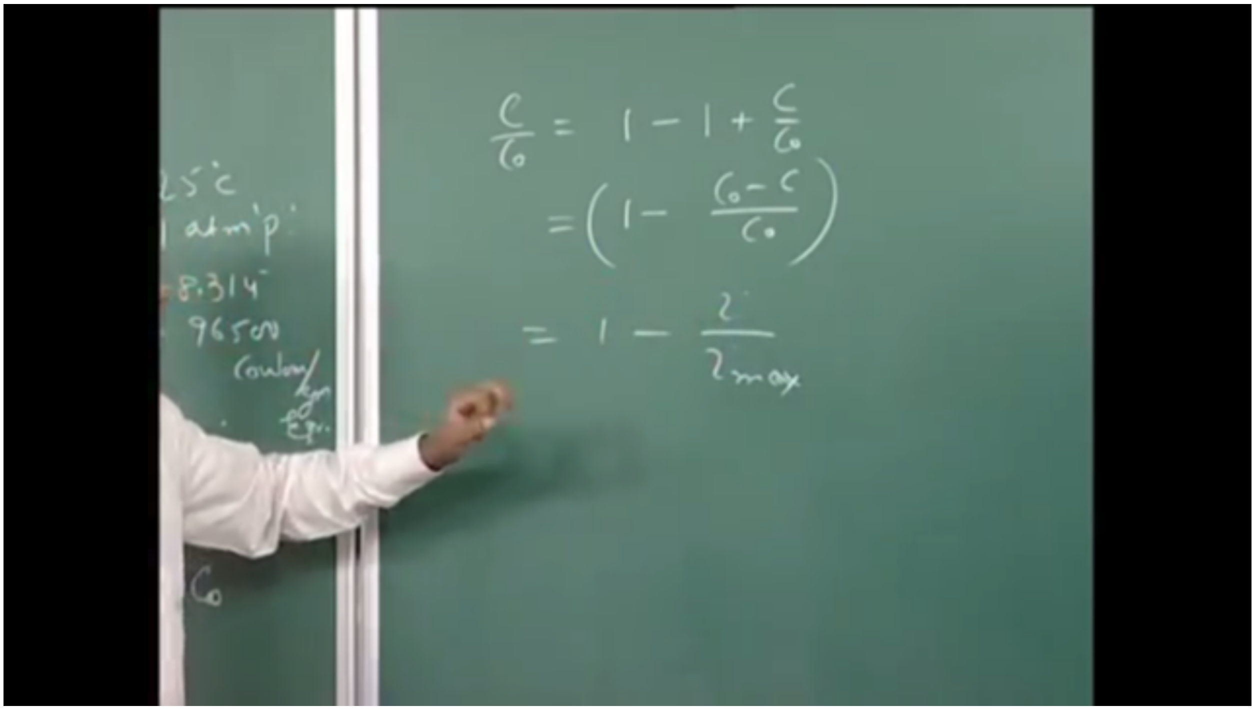

So let us put this, I will just replace this C/C_0. Instead of C/C_0, I will just write this. So it would -- 1 minus i/i_{max}. So this is an -- this is an important equation, and this quantifies the concentration polarization, and since this is in the log scale, so you will see that if you, for example, we have seen the activation polarization, activation polarization, we have seen that if this is a zero value, it varies like this. We have seen that and what are those two components? This is anodic component and this is cathodic component.

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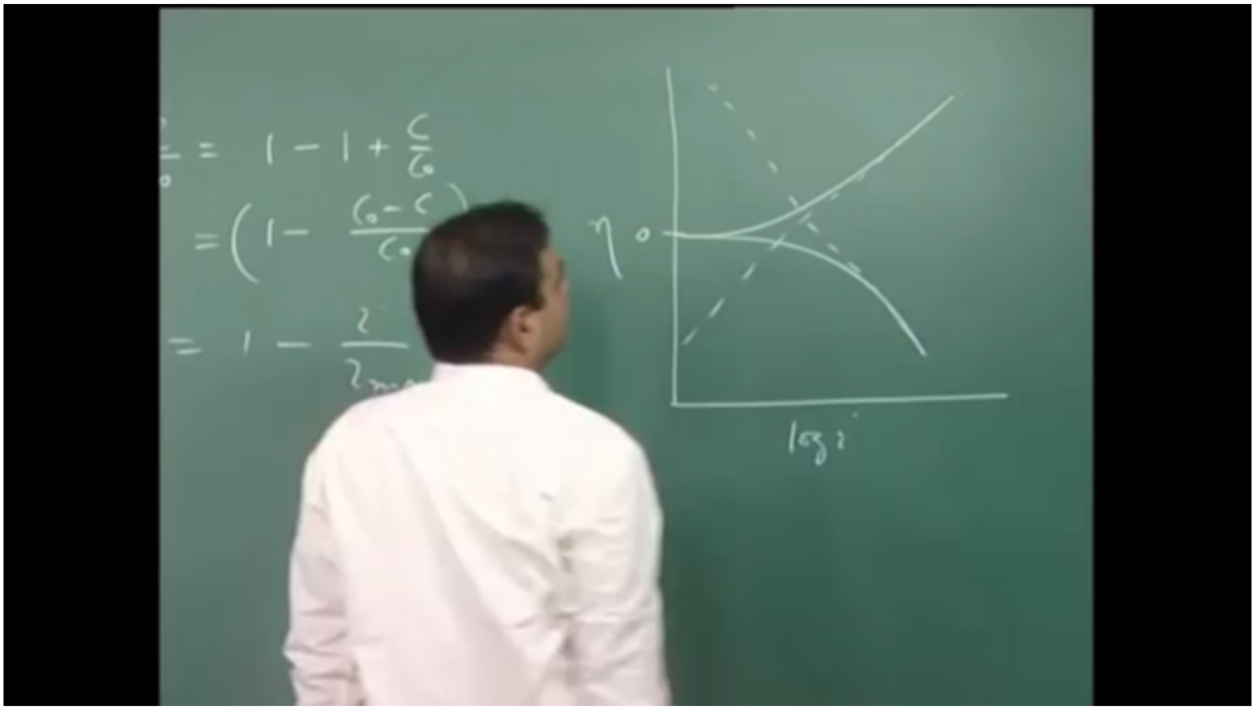

Now in this case, when i equal to 0, then definitely, this would be almost parallel. Then once i increases, this i increases and goes close to i_{max}, then this term would become infinite. So my concentration polarization case will be following this track, this nature. This is my concentration polarization.

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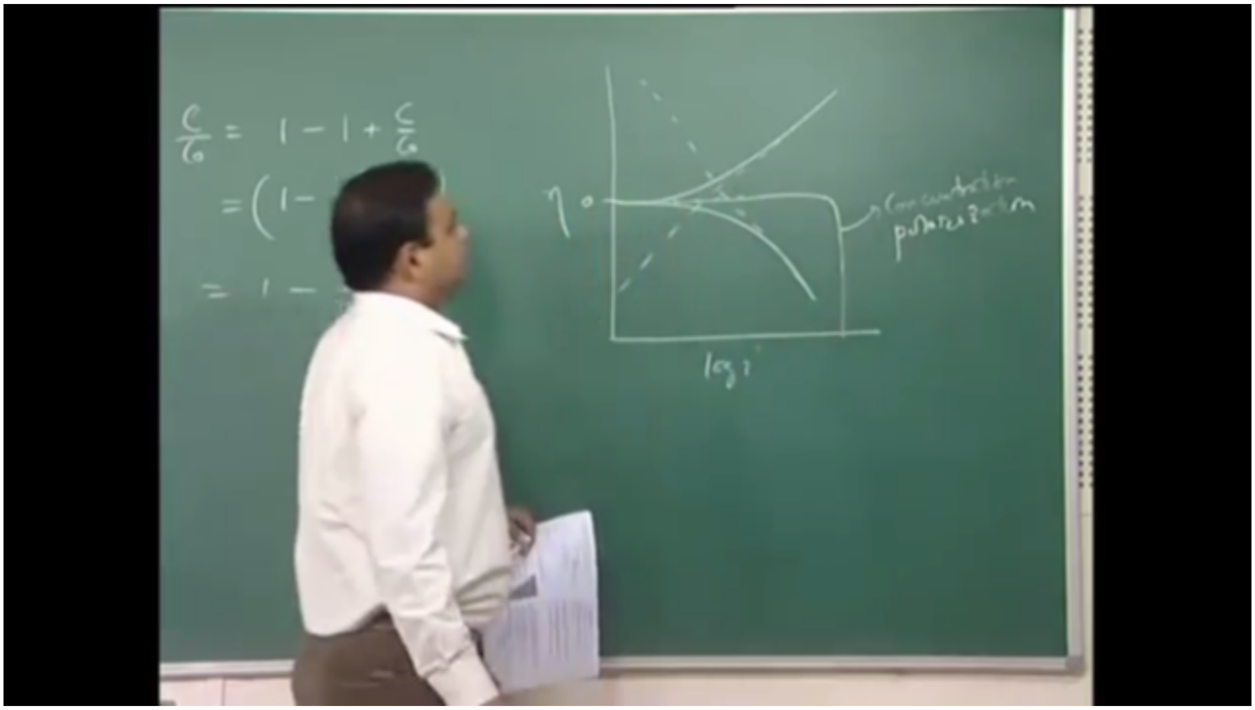

So now here at this position, at this position, i equal to i_{max} and hence this becomes infinite.

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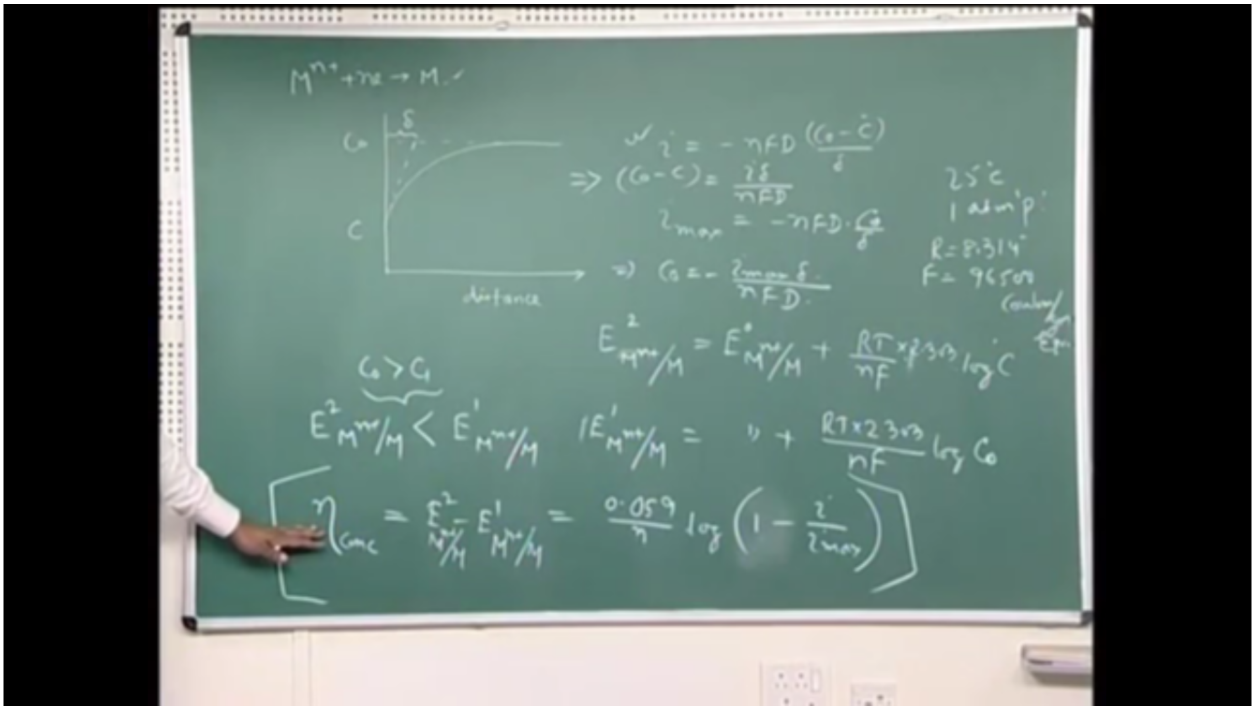

So this is my concentration polarization expression or quantification and this is my plot, but if you -- you can see that when i is less than i_{max}, then what is the effective polarization? i equal to i_{max}, then it is infinite, but when i less than i_{max}, when i less than i_{max}, let's say before it reaches close to i_{max}, then polarization, concentration polarization is almost zero, but for that times what polarization is active? Since there is no change in concentration, that means at a lower current value, there is no change in concentration at the interface, so you don't experience any concentration polarization, but still there would be active polarization, and that active polarization will take the potential to the lower side or to the negative side for a cathodic reaction.

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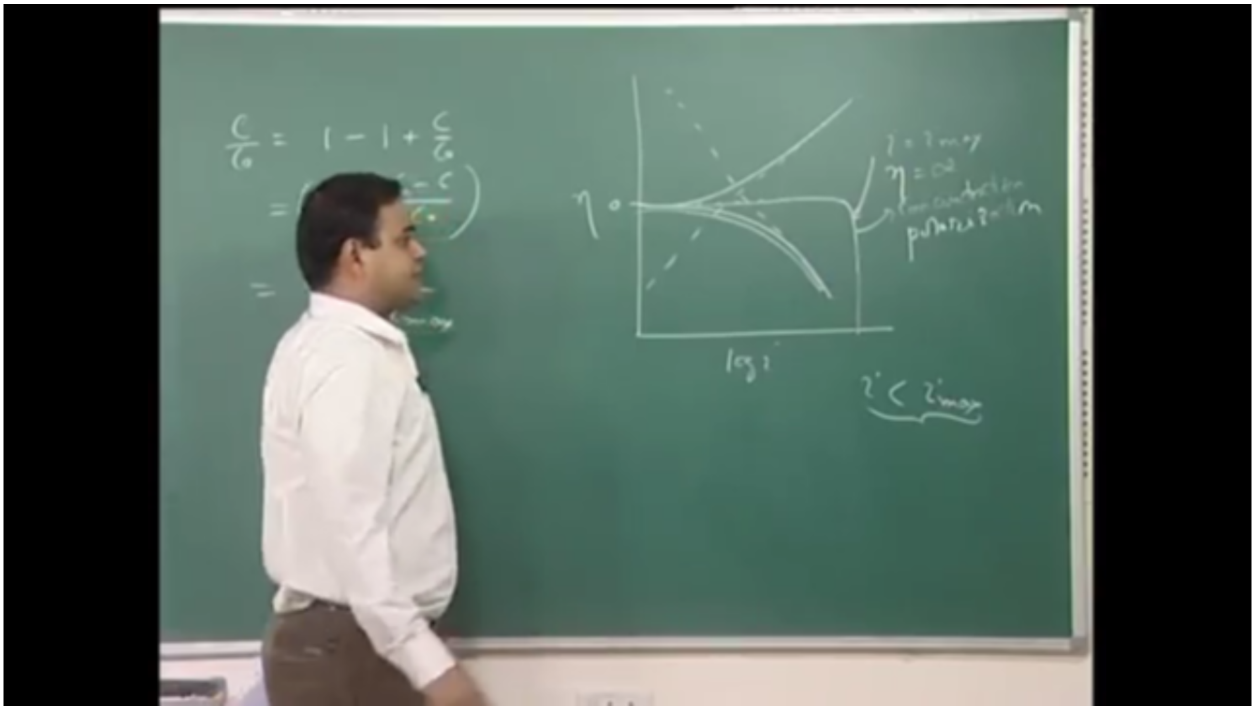

So cathodic polarization is active, this line, cathodic polarization is active. Now when it reaches to this level, so cathodic polarization will no longer be the controlling issue factor, so that time we have come across to this level, which is a very high current, which is this current and that time $i = i_{max}$, this point. So then we will -- if we extend this scale, this potential scale, then it would be like this.

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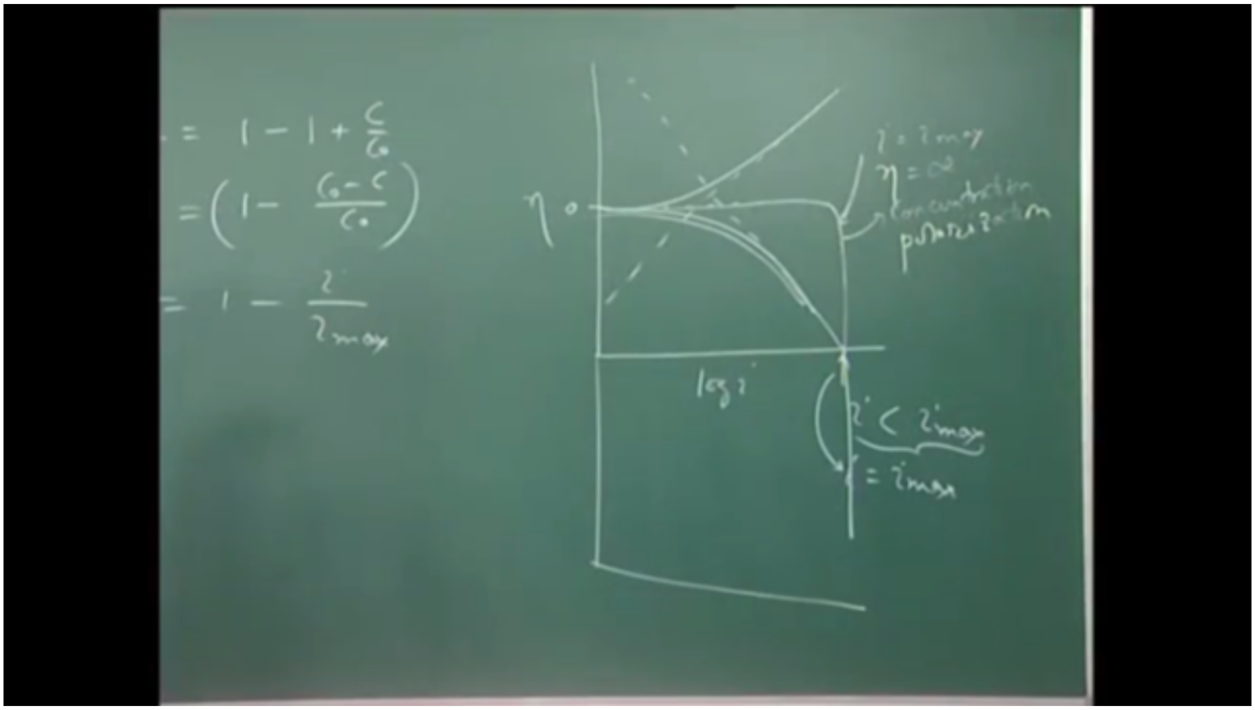

So my actual experimental polarization curve will be only -- I am just putting only this part, only this part, only this part. So rest of the part will not be there. This is my situation.

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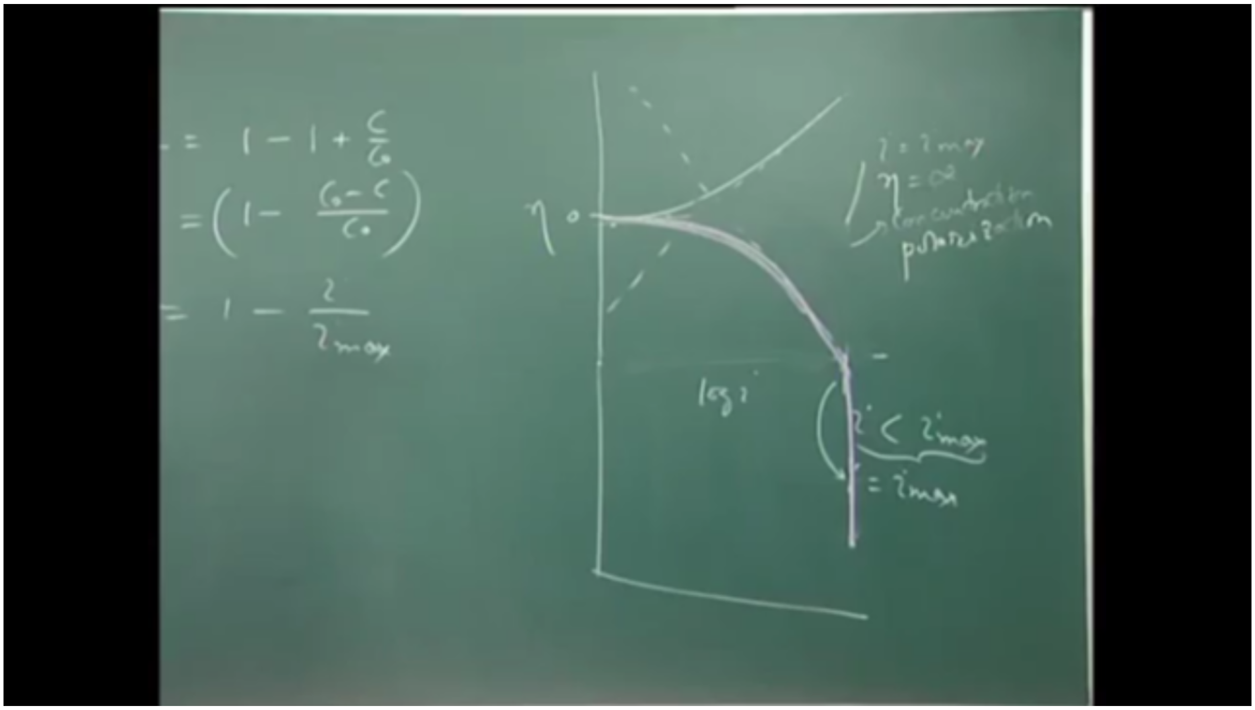

Now so I have -- we will get -- this is my polarization if we only consider the cathodic polarization.

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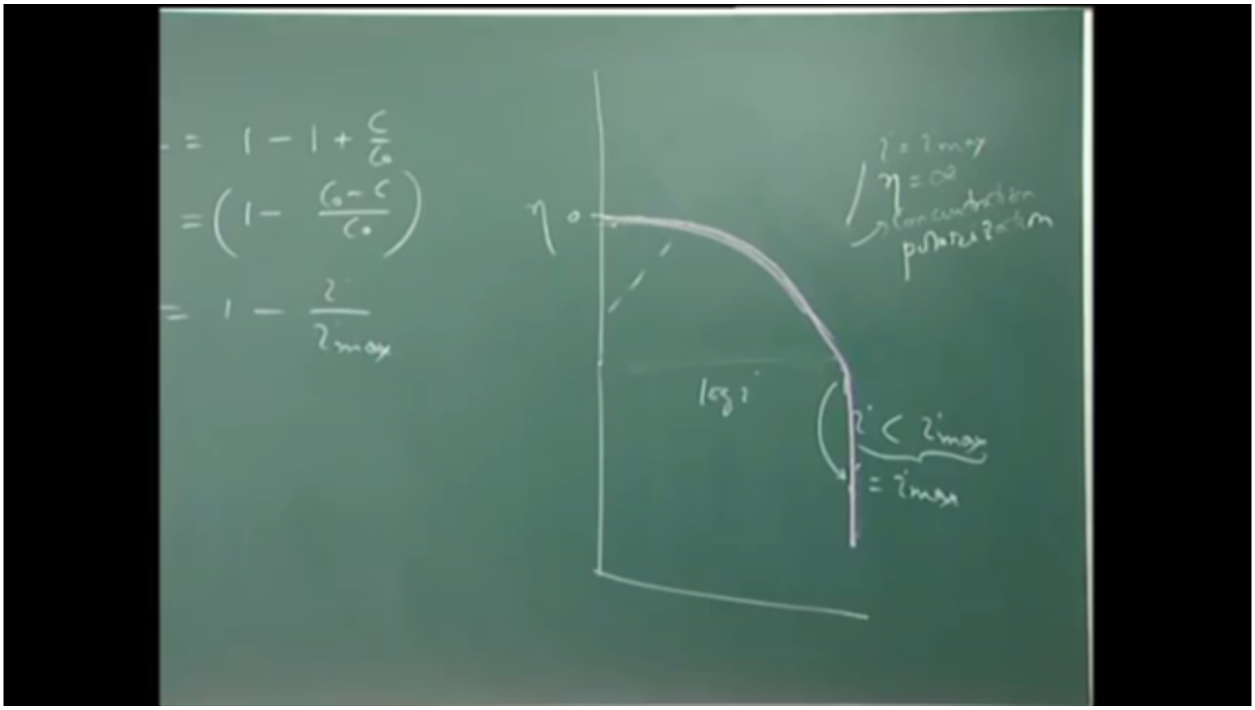

Now let us have some important information or important aspects of concentration polarization. Now if you see the expression for i_{max}, now let me write i_{max} separately. Delta. Now let's say if I increase the temperature, what would happen? If I increase the temperature, then my diffusivity would increase, the rate at which ionic species are moving in the solution that would increase. The speed would increase.

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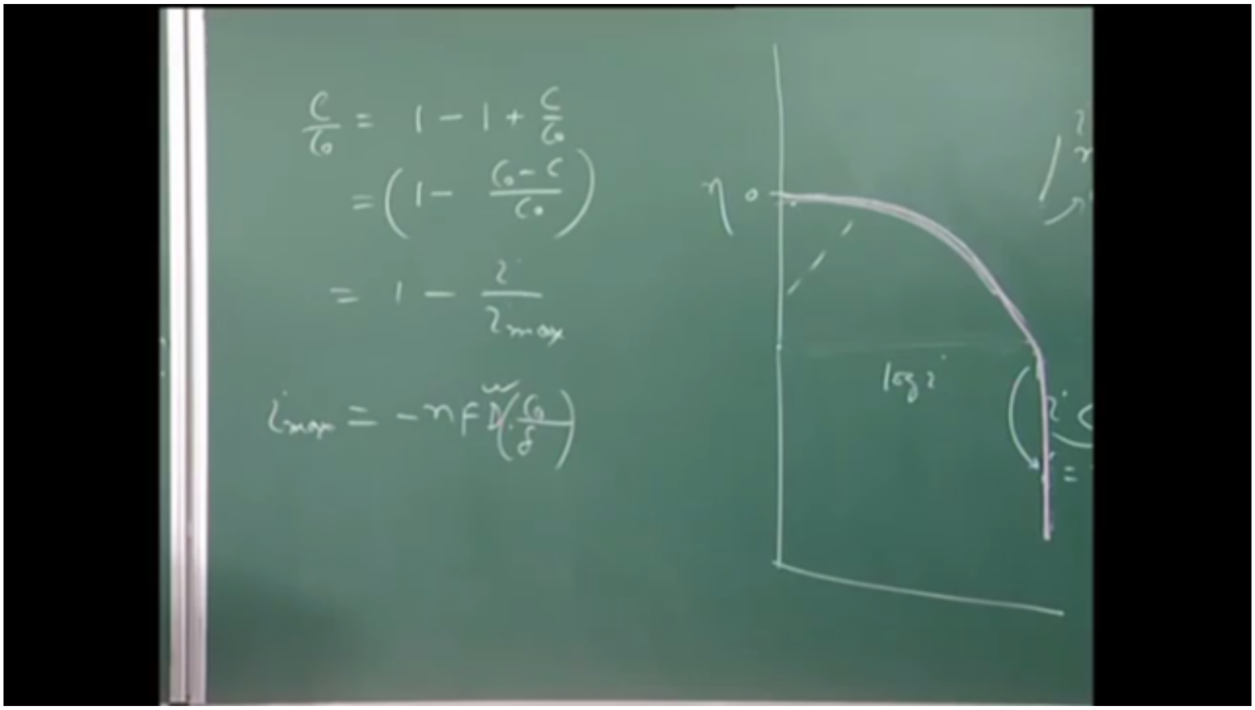

$$\frac{C}{C_0} = 1 - 1 + \frac{C}{C_0}$$
$$= \left(1 - \frac{C_0 - C}{C_0}\right)$$
$$= 1 - \frac{i}{i_{max}}$$
$$i_{max} = -nFD\left(\frac{C_0}{\delta}\right)$$

So if diffusivity increases, then what would happen to i_{max}? i_{max} would -- would increase since n F and C_0 the bulk concentration is not changing, and so this would -- i_{max} would increase.

Now let's say I consider one O_2 molecule. The diffusivity of O_2 molecule or DO_2, DO_2 in water, and D_H^+, the diffusivity -- diffusivity of O, O_2 would be less than D_H^+ since this is a very small atom -- small sized ion whereas this is a molecule which is of a big size, so it's, of course, is very easy to defuse H^+ ion compared to O2. So, this diffusivity of H^+ ion would be larger than -- would be -- would be more compared to diffusivity of oxygen, and now that case I will see that i_{max} correspondingly, i_{max} H^+ would be greater than i_{max}^{O2}. This is a size effect.

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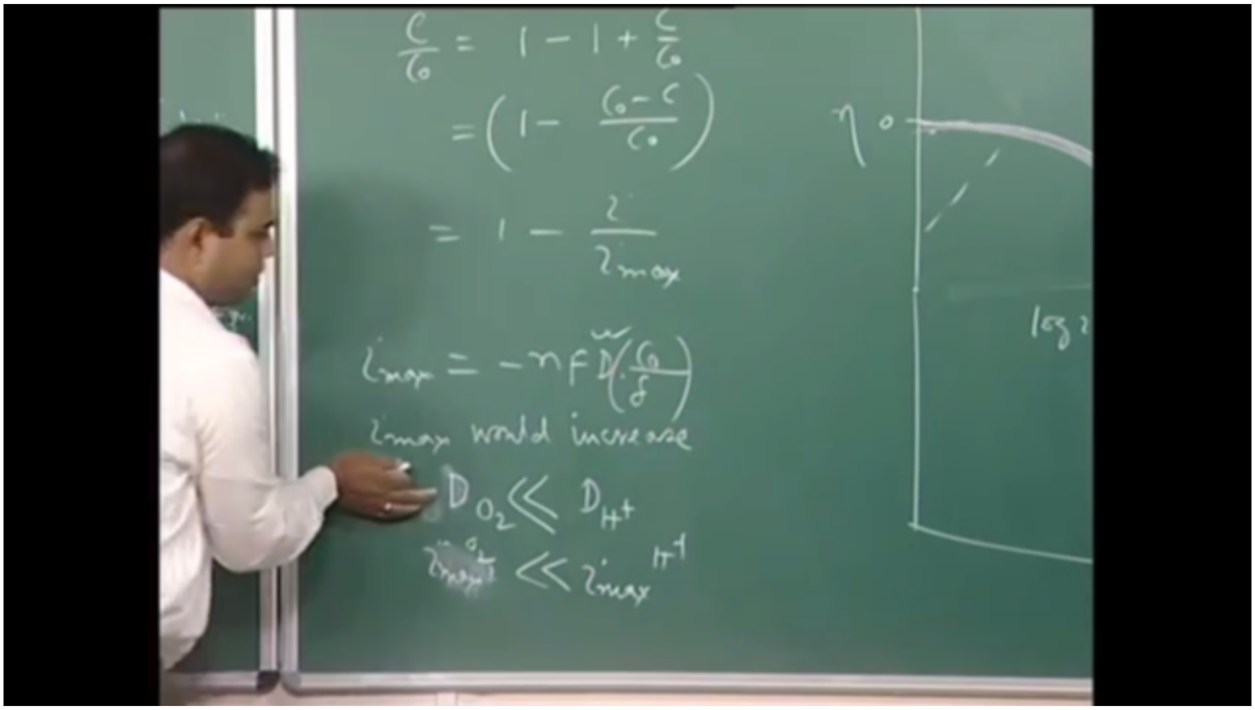

Now temperature effect, for example, in particular case, let's say H^+ ion, let's say one is at T_1, one is at T_2. Then diffusivity of H^+ at T_1 and if you say that T_1 is greater than T -- T_1 is greater than greater than T_2, so then at T_1, which is at higher temperature, diffusivity of H^+ ion would be greater than greater than D_{H+} T_2.

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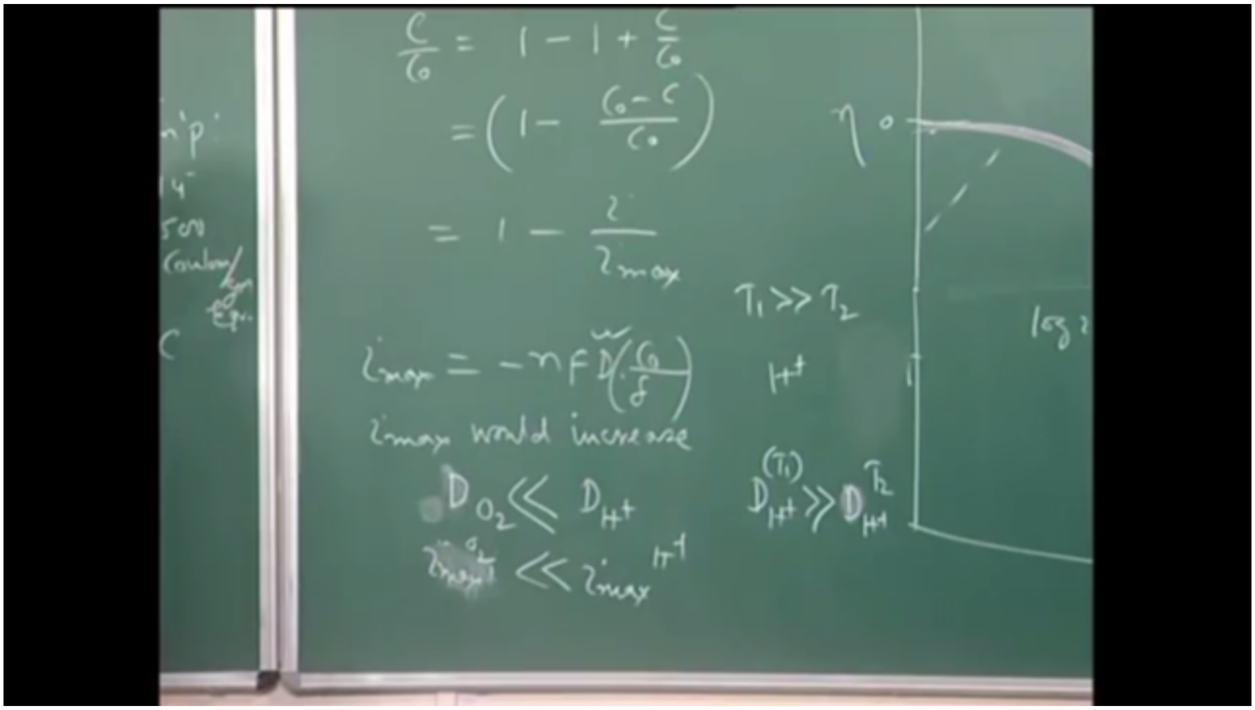

$$\frac{C}{C_0} = 1 - 1 + \frac{C}{C_0}$$

$$= \left(1 - \frac{C_0 - C}{C_0}\right)$$

$$= 1 - \frac{i}{i_{max}}$$

$$i_{max} = -nF\tilde{D}\left(\frac{C_0}{\delta}\right)$$

i_{max} would increase

$$D_{O_2} \ll D_{H^+}$$

$$i_{max}^{O_2} \ll i_{max}^{H^+}$$

$$T_1 \gg T_2$$

H^+

$$D_{H^+}^{(T_1)} \gg D_{H^+}^{T_2}$$

And correspondingly, from this equation, if diffusivity increases, there would be corresponding -- there would be increase in i_{max}, which is the maximum current where whatever ions that are coming from the bulk solution to the interface, those will get reduced. So hence the concentration at this interface would go to zero, that means C would start from zero. So that case, I will see that i_{max} H^+ at T_1 greater than greater than i_{max} of H^+ ion at T_2.

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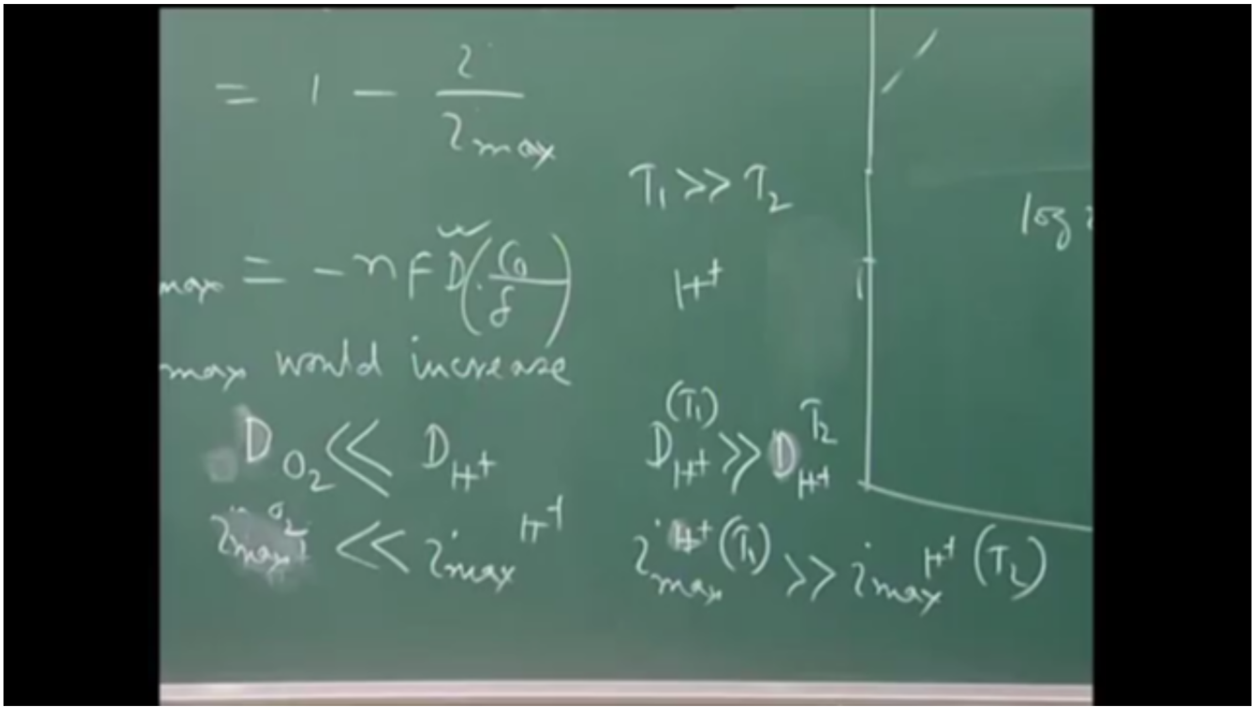

So what are the effects of this situations, size effect as well as -- size effect of these diffusing species as well as temperature? We'll see the difference here. Now i_{max}, if i_{max} increases, so I will experience the i_{max}. Let's say i_{max} increase in this case. i_{max} actually increases means I will experience this i_{max} point here. So in order to reach to that i_{max}, I will have to still have some sort of concentration -- anodic activation polarization. Then it will meet and then it will proceed further. So this part again goes off. So this is this curve is when i -- this is let's say this is i_{max}^2. This is i_{max}^1 and the relation between i_{max}^2 and i_{max}^1 is this is this.

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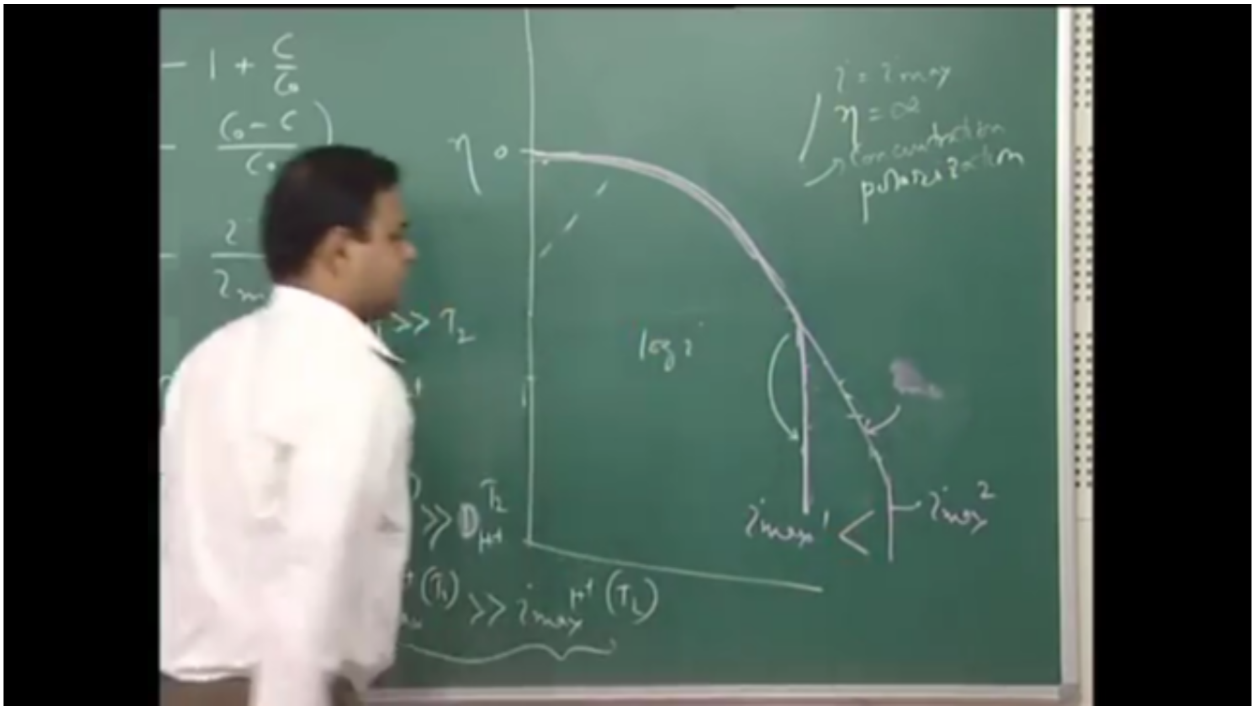

So I will see that this activation polarization still continues until it reaches the current reaches to i_{max}. Then the polarization would be governed by concentration effect and that time it would be infinite polarization. Now this effect can be due to this or due to this.

Let us have one example, what happens if we have this situation because we experience O_2 reduction or dissolve oxygen reduction and hydrogen ion reduction in water medium. Let us plot it here. So this is log i. Now let me remove this part. Let's say if it is acidic medium, so if pH of the medium is less than 7, then and if your -- if the water contains dissolve oxygen, then there could be two reactions, two cathodic reactions and there could be one more reaction. This is one reaction and this is one reaction.

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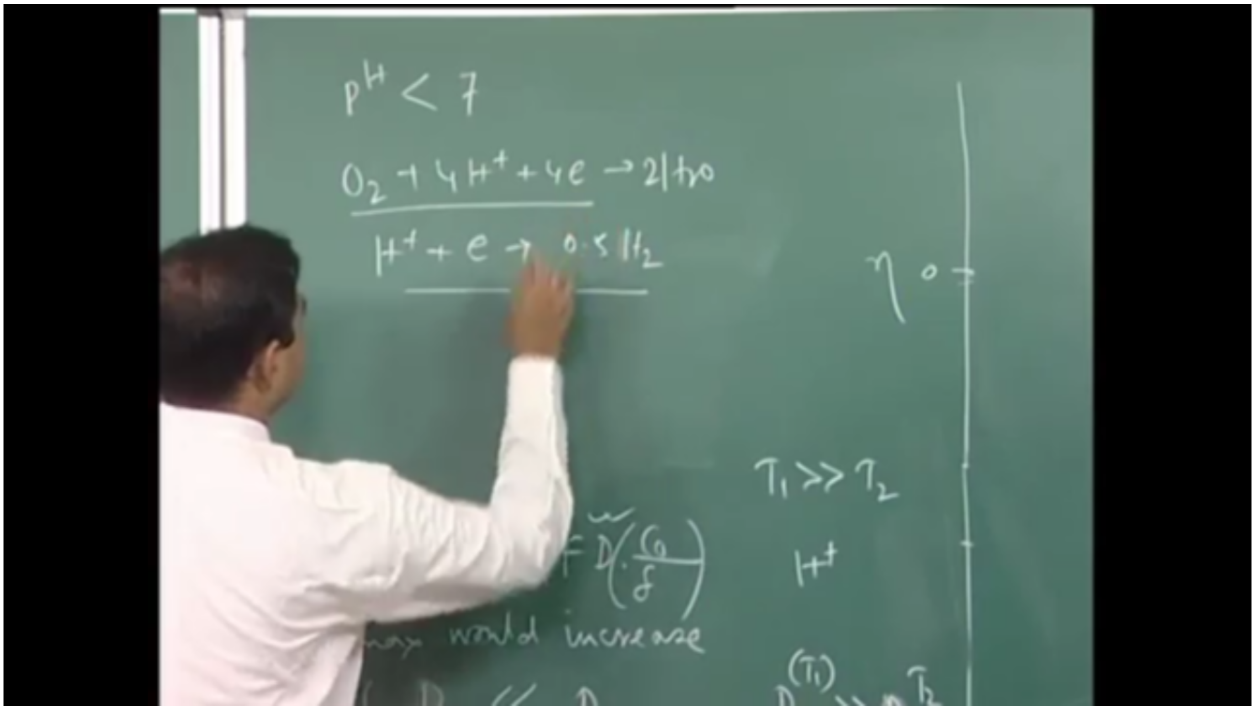

Now let me plot the polarization effect starting from I equal to zero. So that case, this is my polarization axis, which is this. Let me put this is as zero. Now when -- and this potential is about zero point -- it is about two point -- 1.23 volt. So the potential at which this will start which is 1.23 volt, and this in case this is E^0, E^0 value, and here E^0 value is 0 volt. So if you consider the absolute potential, the absolute potential for this case would be where the reaction has reached equilibrium because we have to start from the equilibrium value since the polarization says that the deviation of potential from the equilibrium value. So then this value, this point will be lying above this point corresponding to this reaction.

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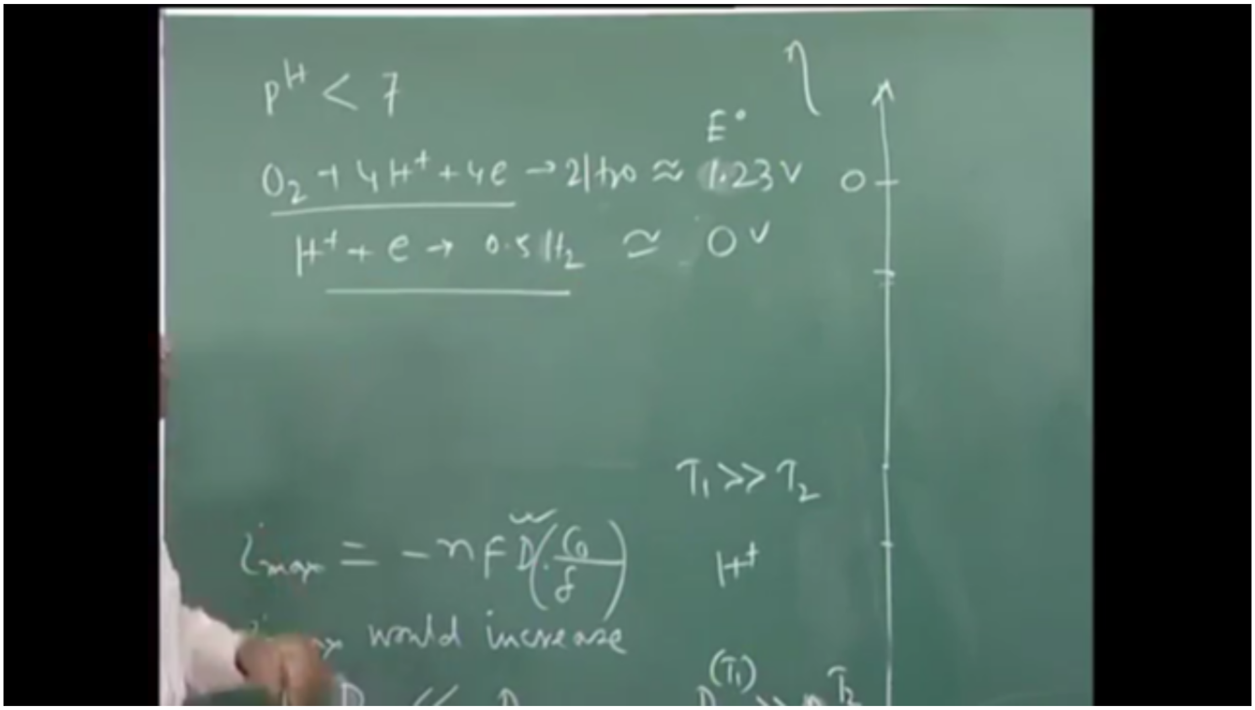

So let's say this is E. In that case, this would be 1.23 volt and 0 volt would be let's say at this point. Let's say this point 0 volt. Now if you consider polarization, now let us -- this is -- this axis is potential and this axis is -- let me plot it. This is potential axis, absolute potential on the basis of absolute potential. Let's say this one is with respect to polarization. Now this reaction if you consider the polarization will start here, and that case the value of this point would be 1.23 volt if we consider that this is all the species are maintained at unit activities or the standard reduction potential if you consider.

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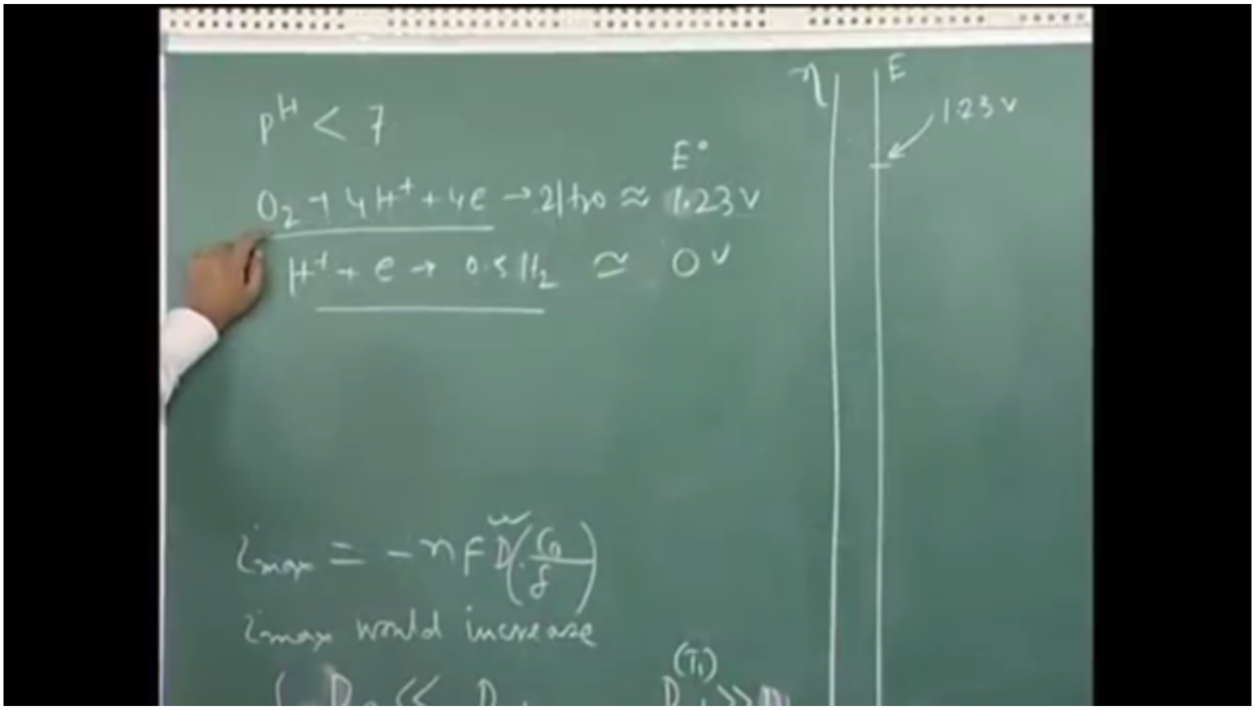

Now then, initially, activation polarization will occur. Initially, activation polarization will occur. So now let me plot the only the cathodic line. So activation polarization for cathodic line would be β_c log of i_c by i_0. Now this is my i_0. This is my i_0 point or log i_0. My line would be this. So this is i_0.

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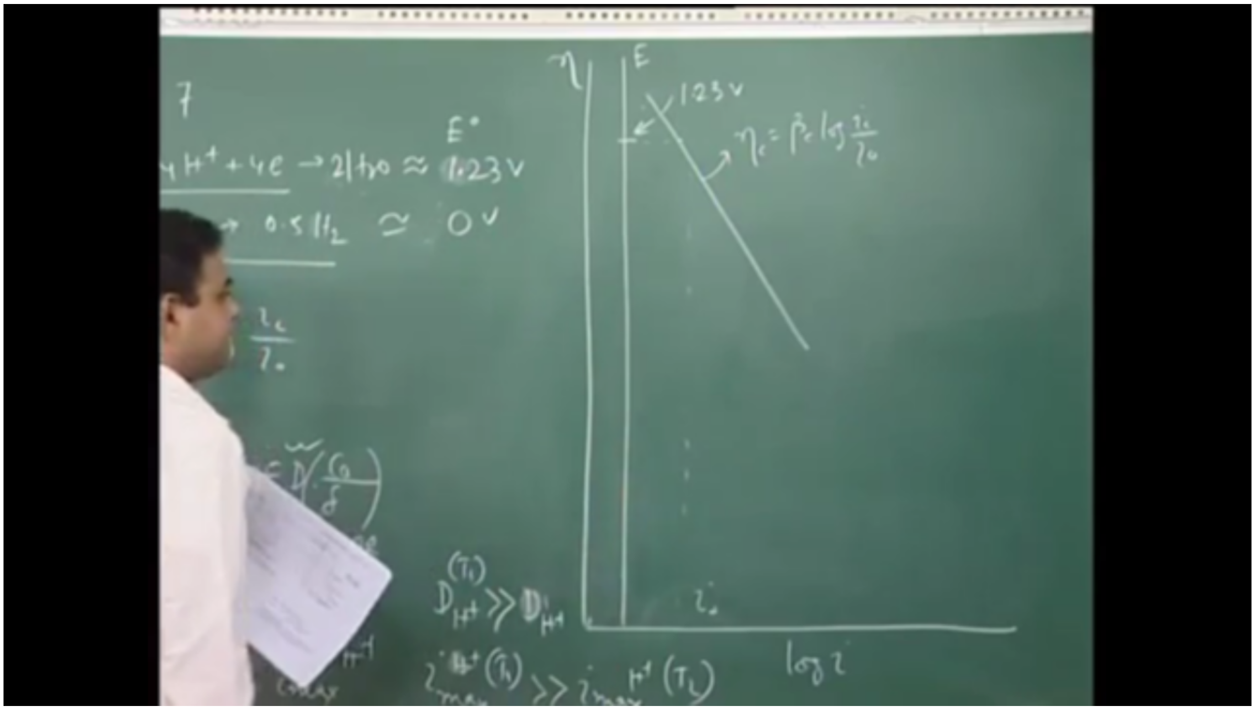

Now what would be my i_{max} for O_2. That would be decided by D value as well as C value in the water and δ, which is the which is decided by diffusion -- diffusivity of the water molecule at this O_2 molecule in water. So let's say that value is corresponding to this, which is i_{max} O_2. Now as polarization is taking place, current value is increasing, and once it reached to point -- once it reaches to i_{max} of O_2, it will start following this path and before that if you consider only the cathodic polarization, this is zero. So this is like this. This is like this, but actual situation would be following this line. This line. Polarization line would follow this.

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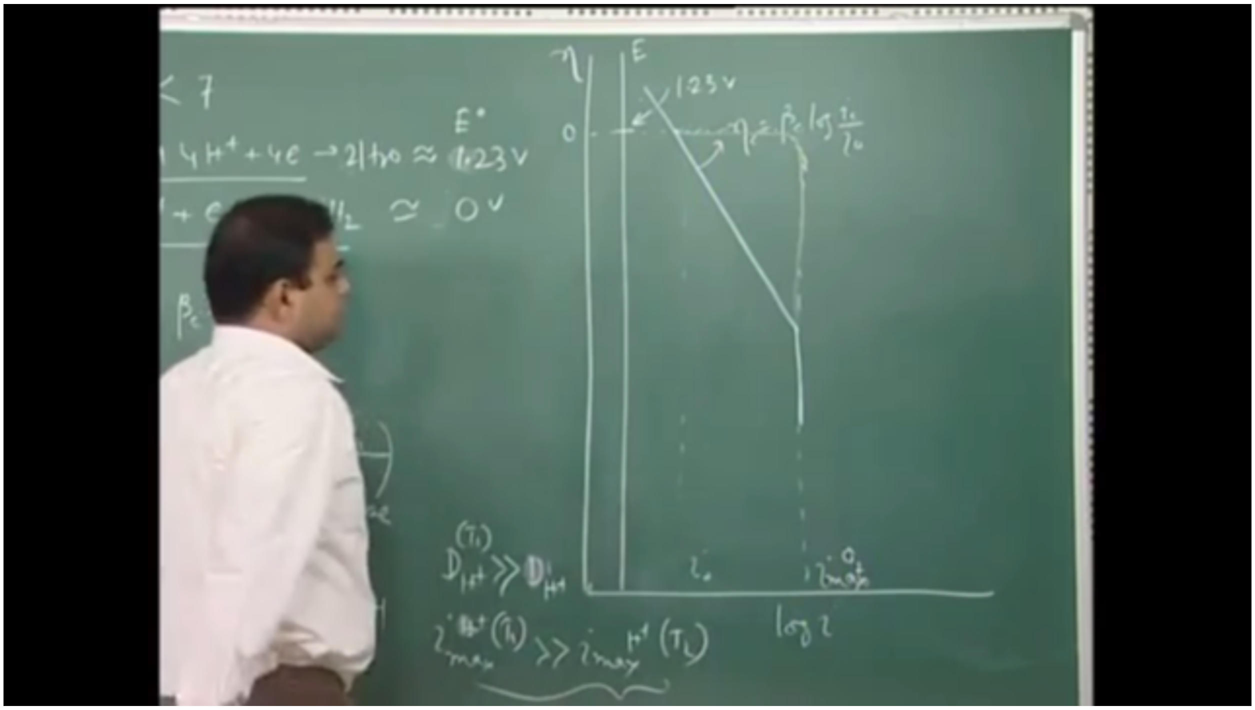

Now let's say this is my zero volt, and once we reach to zero volt, that means we are coming across hydrogen evolution reaction. So hydrogen evolution reaction, then it will start hydrogen evolution reaction once it reaches to this, as you go further down, if you go further down the polarization, if we are further having polarization or cathodic polarization, then it will come across this reaction, and it will start following the activation polarization for this.

So if you independently plot the activation polarization of this reaction, so it would be this. So then you see once we reach to this, it cannot follow this line because by the time you experience another polarization because of that current value is further increasing. Here the current value remains constant. So the line will take a bend and it will follow like this.

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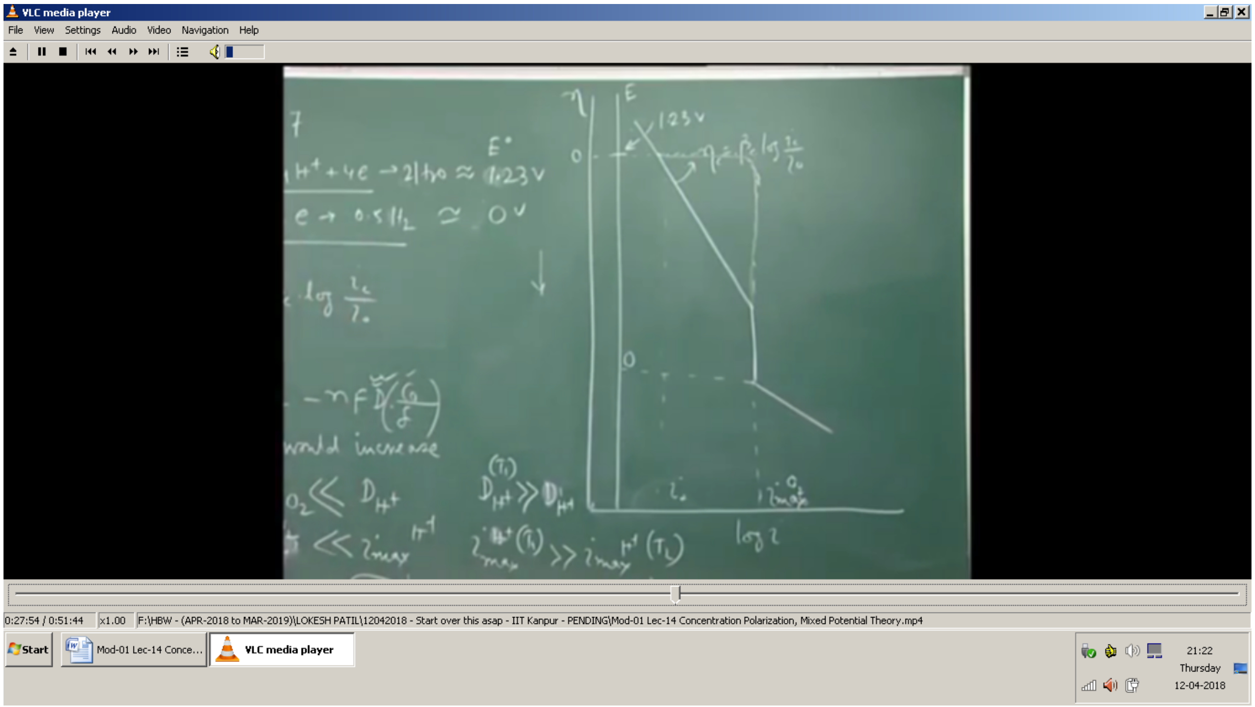

Now as we have seen that i_{max} O_2 is less than i_{max} H^+, so by the time it reaches H^+, it will keep coming along this activation polarization line for hydrogen cathodic reaction. So then you will see that there would be one more bend, which is nothing but i_{max} H^+ ion, which is the maximum current density for the hydrogen ion evolution, hydrogen gas evolution or this cathodic reaction.

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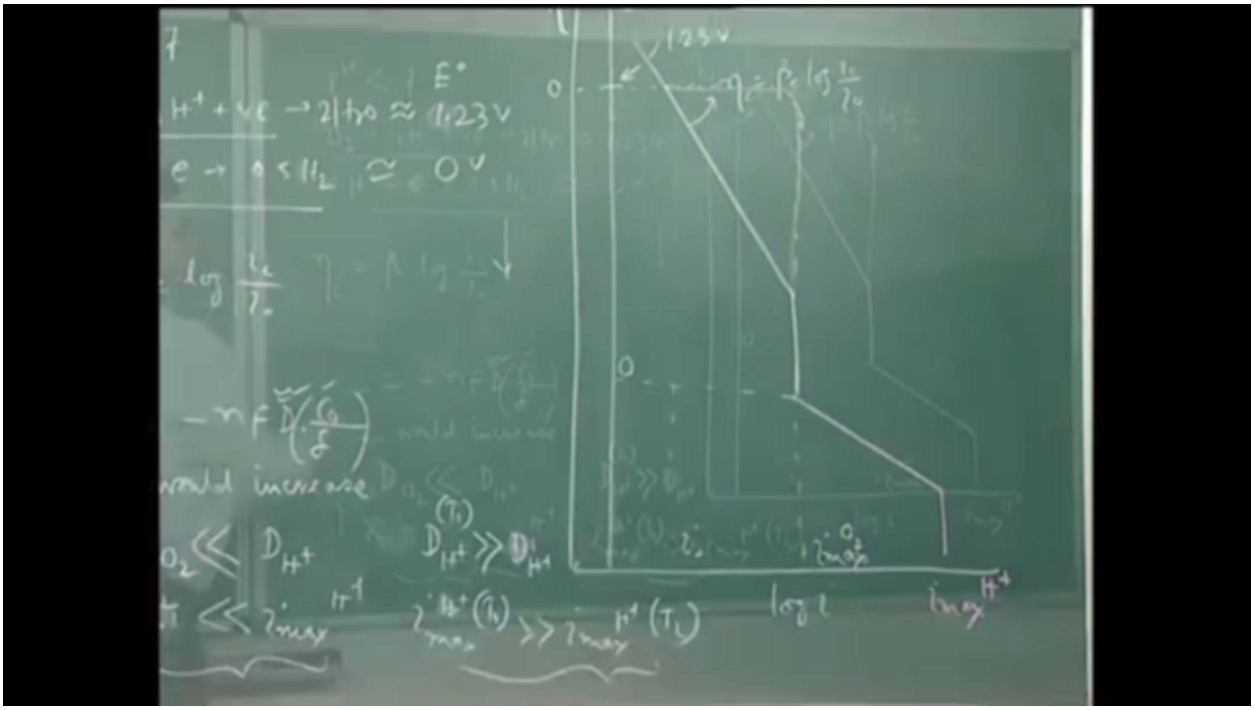

So this would be my sequence, and if you would like to see the individual situation for hydrogen concentration polarization, this is my hydrogen concentration polarization. This is my oxygen concentration polarization. This is my oxygen. This is my oxygen concentration -- oxygen cathodic polarization or activation polarization. This is my -- this is my activation polarization for hydrogen evolution hydrogen, this reaction and this is my i_{max} for hydrogen evolution reaction, H_2 gas evolution reaction or this cathodic reaction. So this would be my complete plot.

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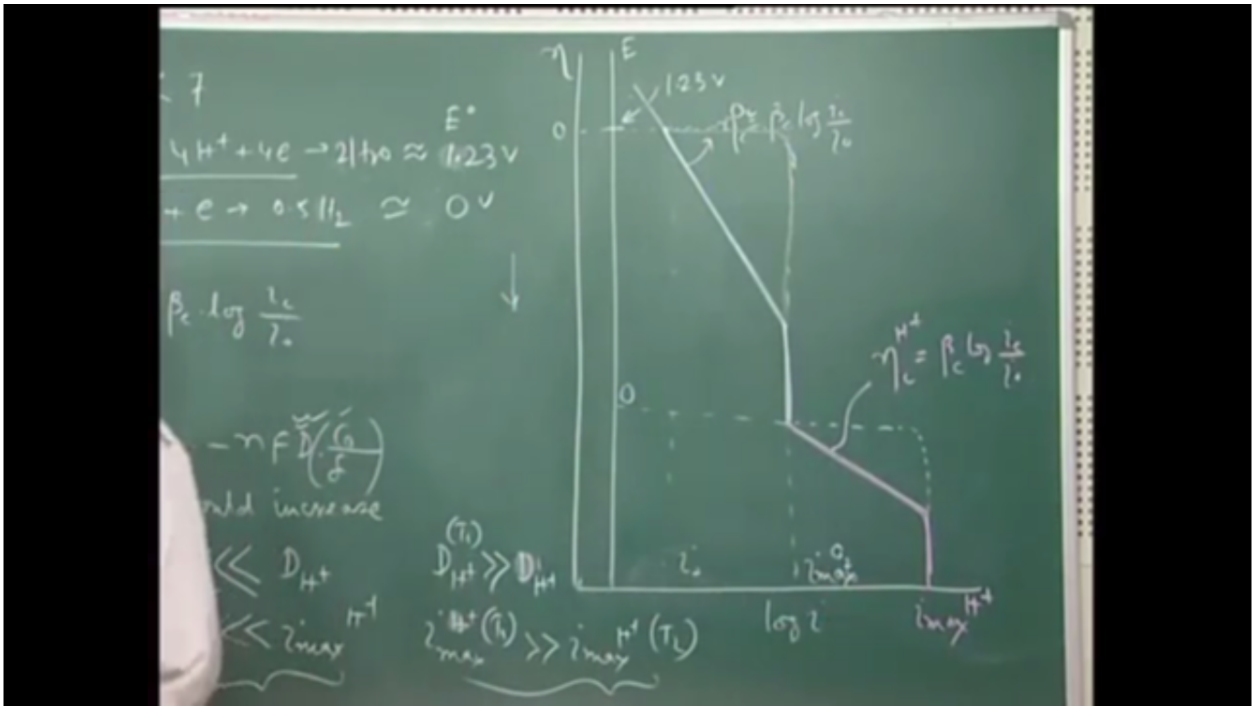

So it will start from here, it will go like this, then it will go like this and like this. So this is my overall situation as you come across different species, different activation polarization and concentration polarization.

And now you see for oxygen evolution, oxygen this reaction, so this is my 0 over voltage and for -- for hydrogen evolution or this cathodic reaction, this is my 0 over voltage, but total polarization would be this much. If you consider let's say I am at this current value, if my -- I have increased current value to i_{max} of H^+, let's say I am here, so my total polarization would be this much, and if you would like to see the what would be the polarization for hydrogen cathodic reaction, this cathodic reaction, my -- this is individual hydrogen polarization due to hydrogen rather I would write polarization due to hydrogen and this is my total polarization.

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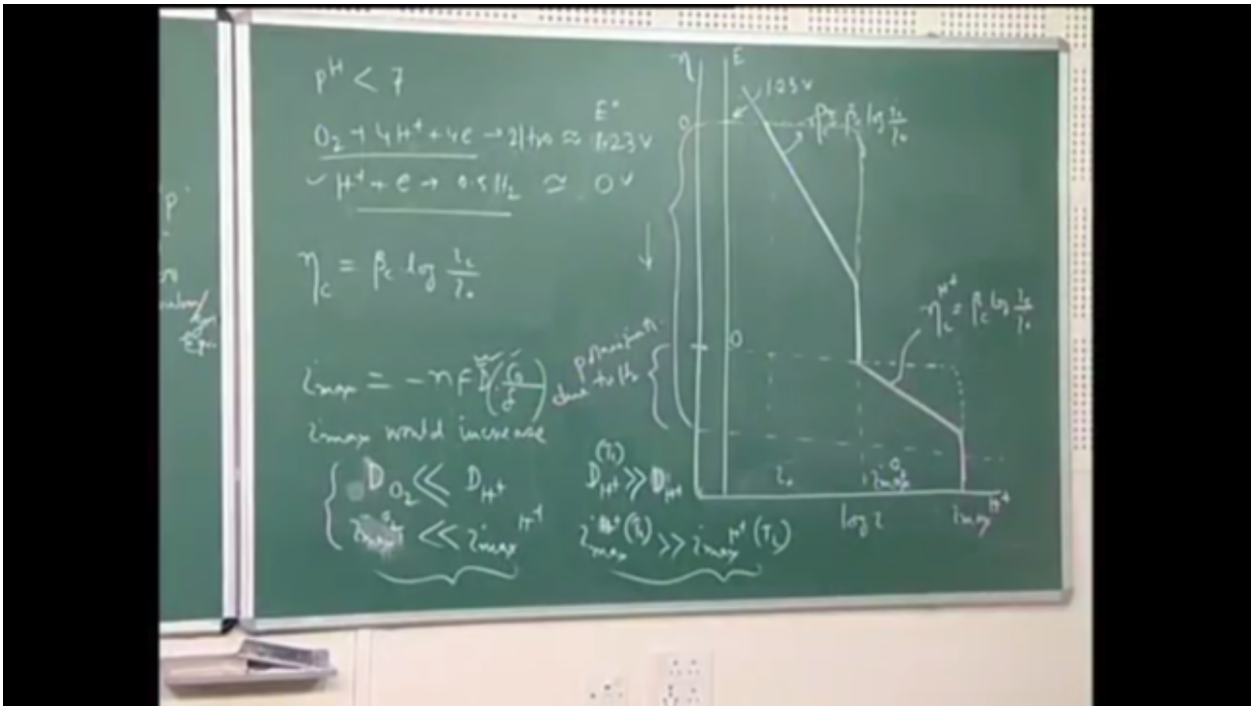

Now if you would like to measure the total polarization, now you see the total polarization is nothing but the addition of concentration polarization as well as activation polarization. Now let's say I am here. I am at this point, at this position. What would be my total polarization? Total polarization would be this much and this is total would be equal to polarization due to activation from here to this. So polarization due to activation is this much and polarization due to that means this is nothing but η_c, which is cathodic over voltage due to activation polarization, and this is my concentration for concentration polarization I would write η_{conc} that means concentration and this is for cathodic, so this is -- and here I can put activation, activation. So this would be equal to concentration. So this is my total polarization.

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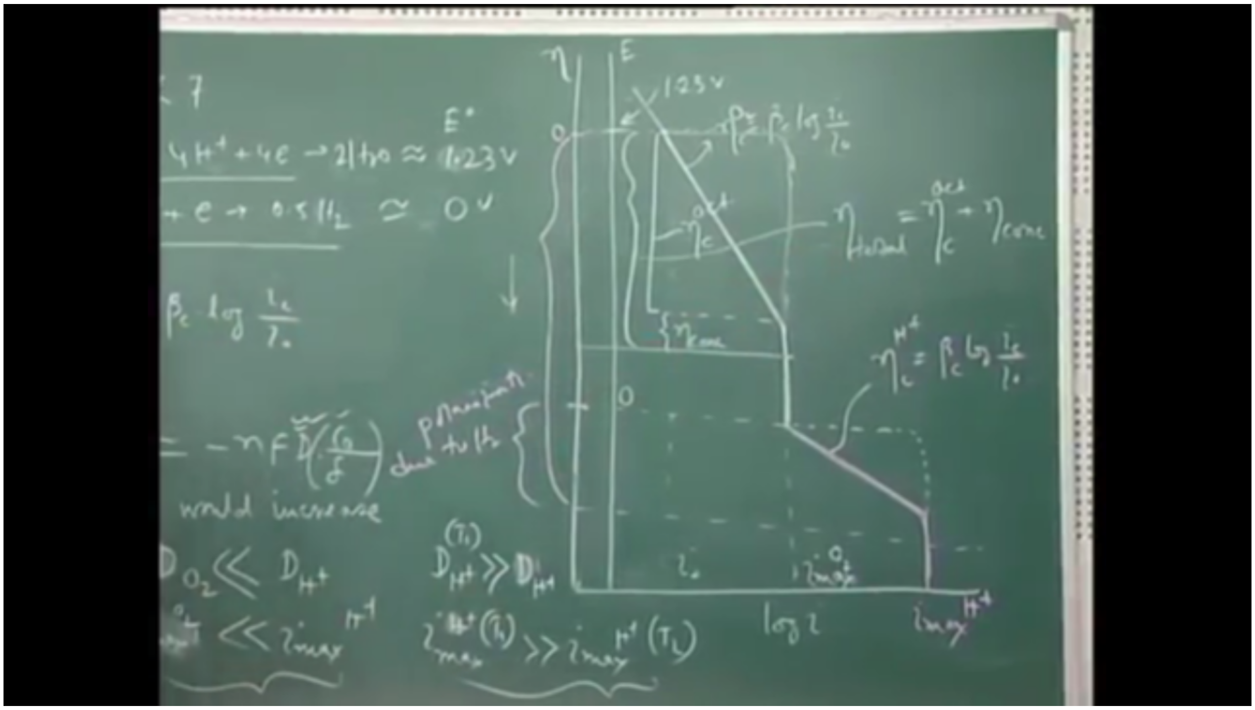

Now point is we are considering only the cathodic concentration polarization effect, but there could be also some amount of anodic polarization which is also due to concentration effect, but generally we do not come across anodic concentration polarization. The reason for this is there are two possible reasons. There are two possible reasons why do not -- we do not experience anodic polarization. One is accumulation. Whenever we see that for anodic side, you are always producing metal ion. That means this reverse reaction is taking place.

Now there would be accumulation of metal iron just at the interface. So concentration would be let's say initially you started with c_0 for the metal ion. Then concentration would increase at this interface. Just reverse would happen. What is happening in case of cathodic case, concentration is decreasing from the initial concentration, and here concentration should increase from the initial concentration.

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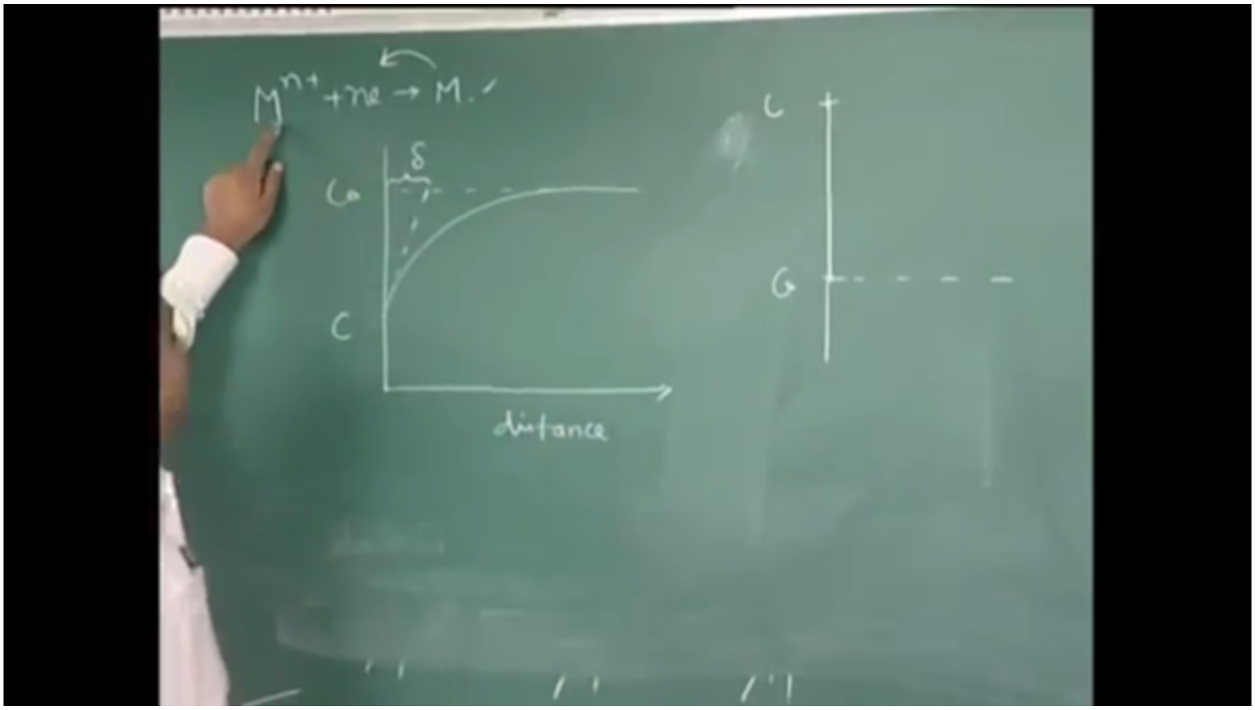

So whenever you have accumulation of this metal ion at this interface, most of the cases we form some sort of corrosion product. First reasons why anodic concentration polarization not considered, so first case is corrosion product, corrosion product formation at the interface, and once we have corrosion product formation, there would be passivation. That passivation part, it would be considered in detail later.

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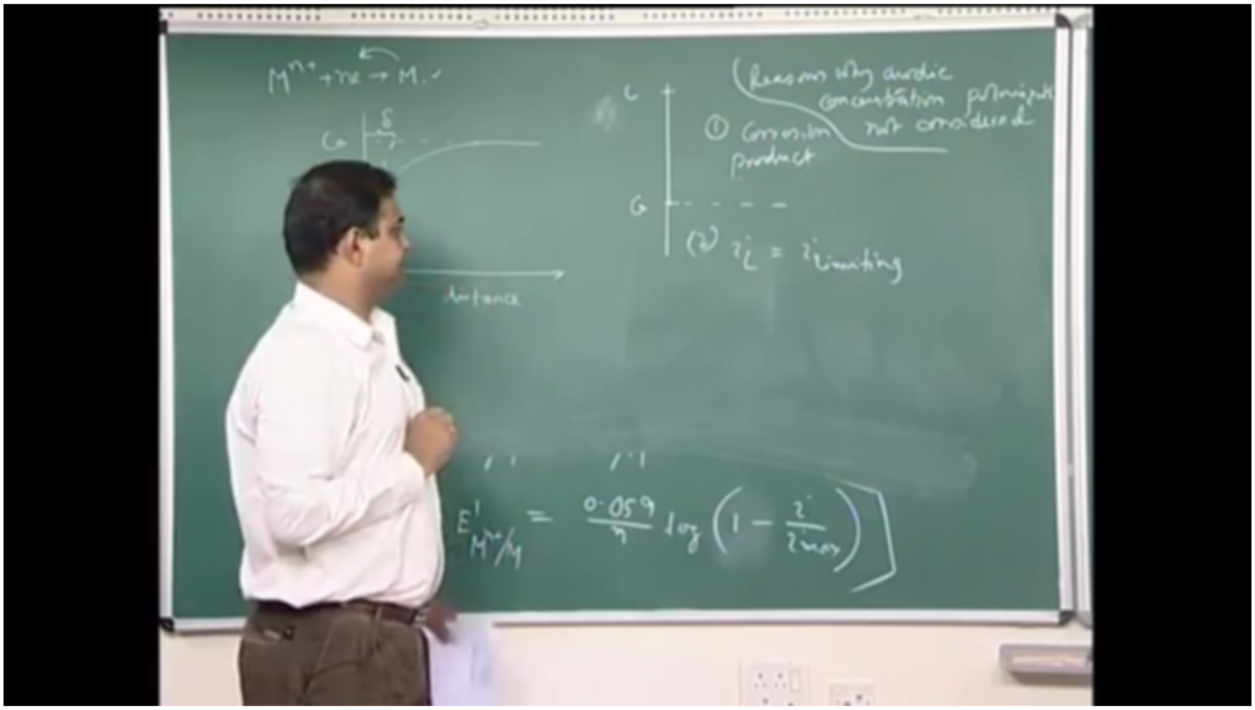

Now second reason is this limiting current or i_{max}, this is also called i_L, also called i_L. i_L means $i_{limiting}$. So that means this is the maximum current density that is possible where potential polarization would become infinite. So this i_L is significant during reduction process and in case of anodic case, you see that even if the product is not forming, there is a huge amount of metal ion supply. So you don't experience any short of metal ion depletion at this interface. So there is almost unlimited supply of metal ion because of this process. So this because of two reasons, we don't consider -- generally consider anodic concentration polarization effect.

So we see there are two polarization effect. One is activation polarization. Another one is concentration polarization. And we also see that concentration polarization is most effective in case of cathodic reaction, and we have also quantified those, the amount of polarization from the current value or the current which is going through the circuit, shorted circuit, short circuited path.

Now we have seen that there are two polarization. One is activation, activation effect would be β, which is Tafel slope. It can be for anodic a, for cathodic it is c log of i, which is in case of anodic it is a, which is c for cathodic divided by the exchange current density for that cathodic reaction. And similar way we have also seen concentration is nothing but 0.059 by n, n and this n is coming because we are considering this reaction, so log of 1 minus i/i_{max}, and instead of max we can also write i_L. So this is the concentration polarization.

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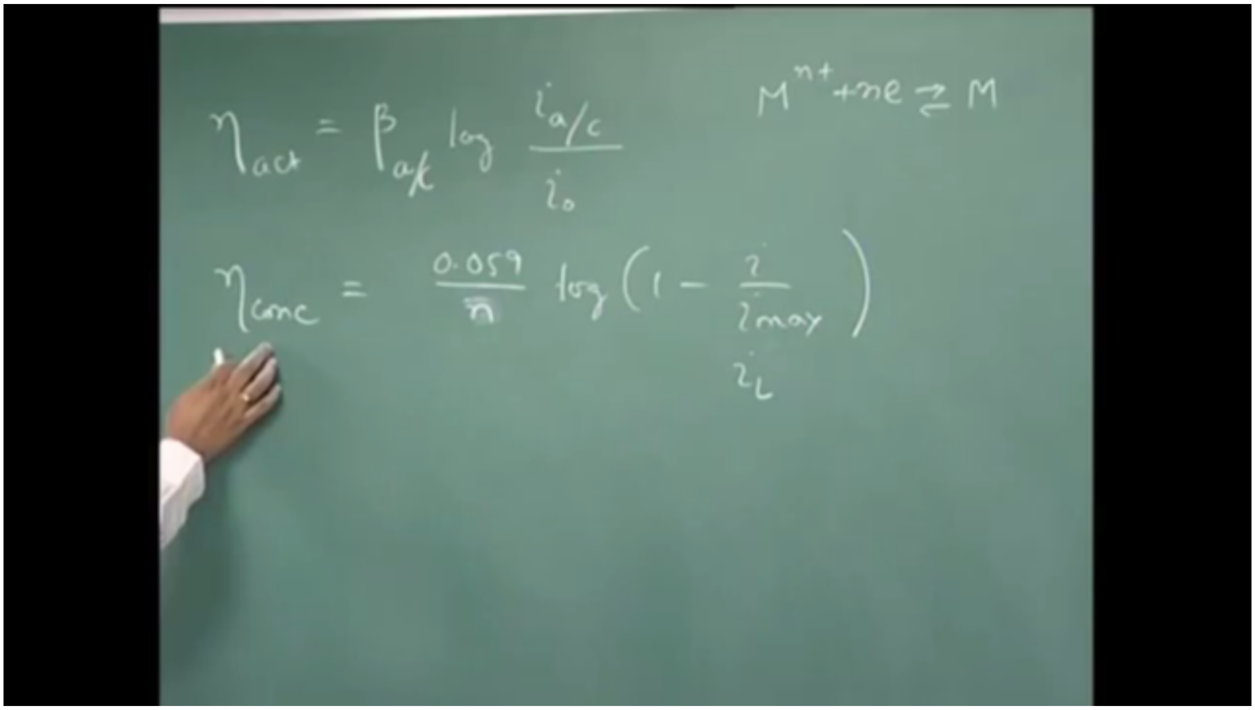

Now there is one more polarization, which is called resistance polarization. Resistance. Now whenever current is flowing into the electrolyte, there would always be some amount of resistance to the charge transfer because of inherent resistance of the water or inherent resistance of the electrolyte. Now if R is the resistance of the electrolyte, then i is the intensity or in this form case if it -- i, this i is my current, absolute current in the system, then IR is my resistance drop. This is IR is my resistance polarization. IR is nothing but the volt, so this much potential will drop.

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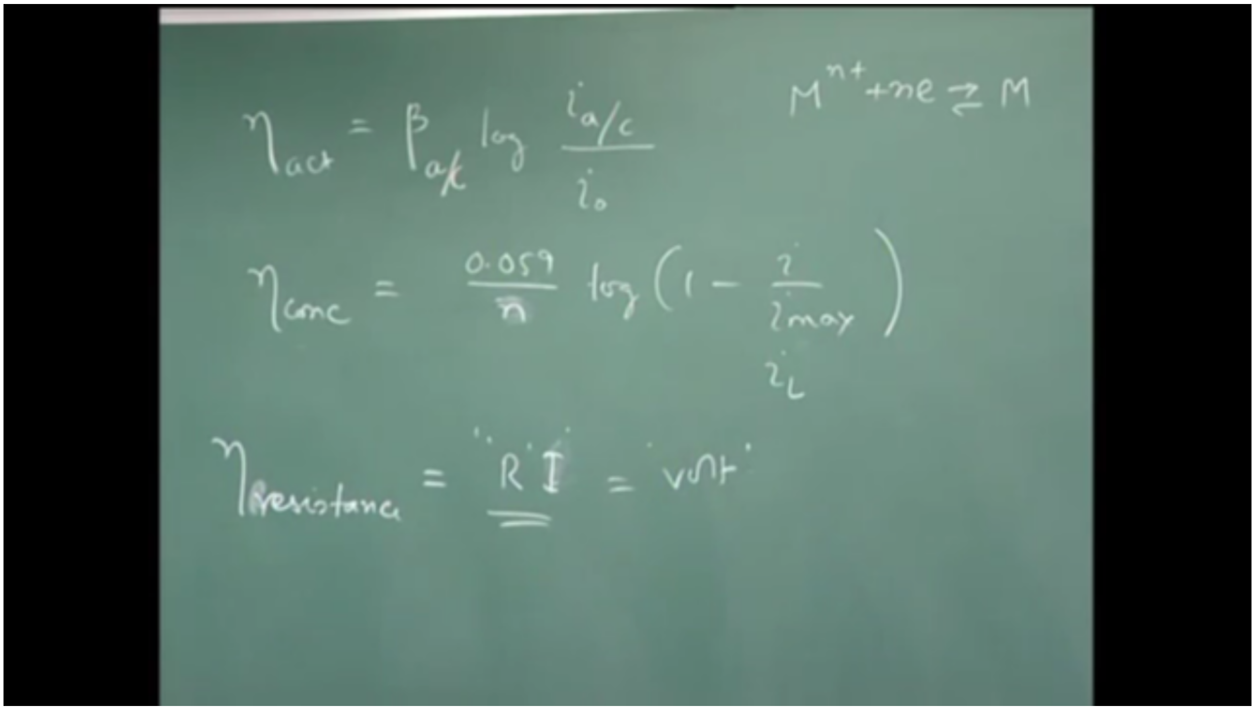

$M^{n+} + ne \rightleftarrows M$

$$\eta_{act} = \beta_{a/c} \log \frac{i_{a/c}}{i_0}$$

$$\eta_{conc} = \frac{0.059}{n} \log\left(1 - \frac{i}{\underset{i_L}{i_{max}}}\right)$$

$$\eta_{resistance} = \underline{\underline{'RI'}} = 'v\Omega t'$$

Now the implication of this resistance polarization we will see in -- when we come across mixed potential theory and then what is my total overpotential? It would be combination of -- of all these three.

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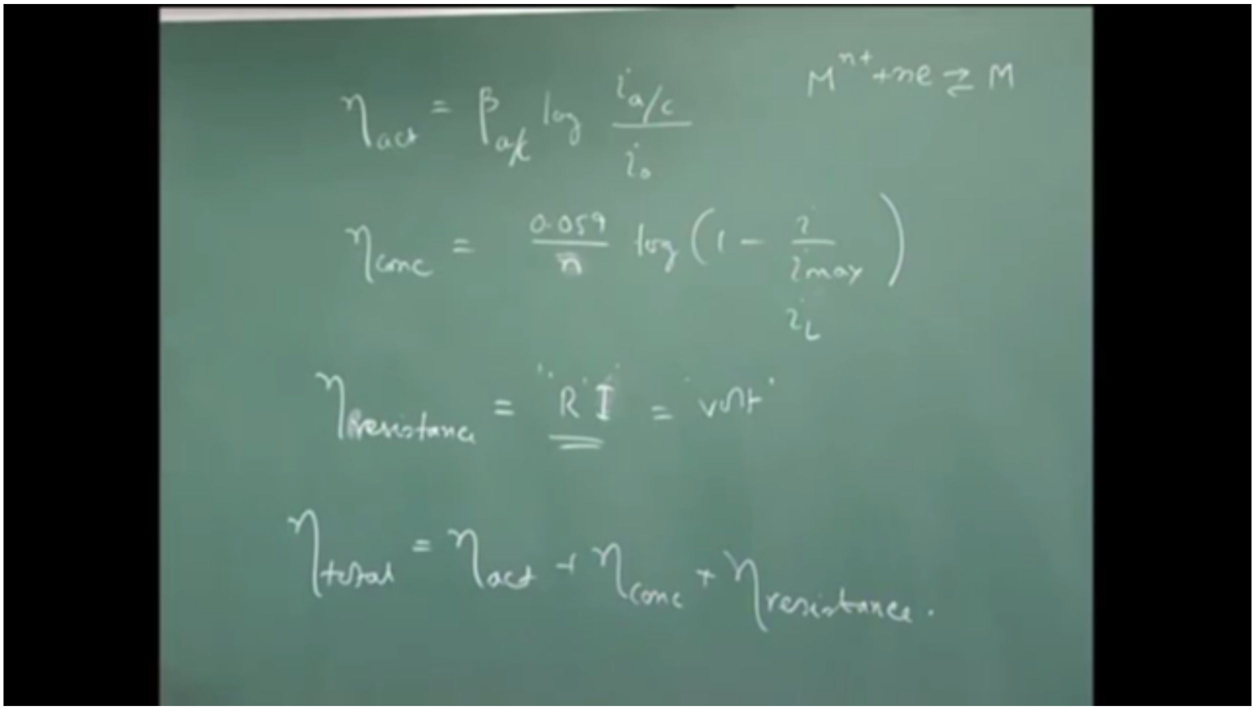

$M^{n+} + ne \rightleftarrows M$

$$\eta_{act} = \beta_{a/c} \log \frac{i_{a/c}}{i_0}$$

$$\eta_{conc} = \frac{0.059}{n} \log\left(1 - \frac{i}{\underset{i_L}{i_{max}}}\right)$$

$$\eta_{resistance} = \underline{\underline{'RI'}} = 'v\Omega t'$$

$$\eta_{total} = \eta_{act} + \eta_{conc} + \eta_{resistance}.$$

So once we know this, now we can understand how the rate reactions all -- all the corrosion reactions or the electrochemical reactions are taking place in a particular system. Now for that we need to understand along with this polarization, this is polarization, we need to also understand the Mixed Potential Theory. So let us talk about mixed potential theory. Now this -- on this -- on the basis of this theory, we can understand many of those practical corrosion problems or corrosion examples.

Now I will start mixed potential theory. This theory was introduced by Wagner and Traud in 1938, and this is a very, very important aspect of understanding corrosion effect, and it is based on -- this theory is based on two postulates or hypothesis. One hypothesis says I am just writing the whole thing, any electrochemical reaction can be divided in to two or more partial oxidation and reduction reaction.

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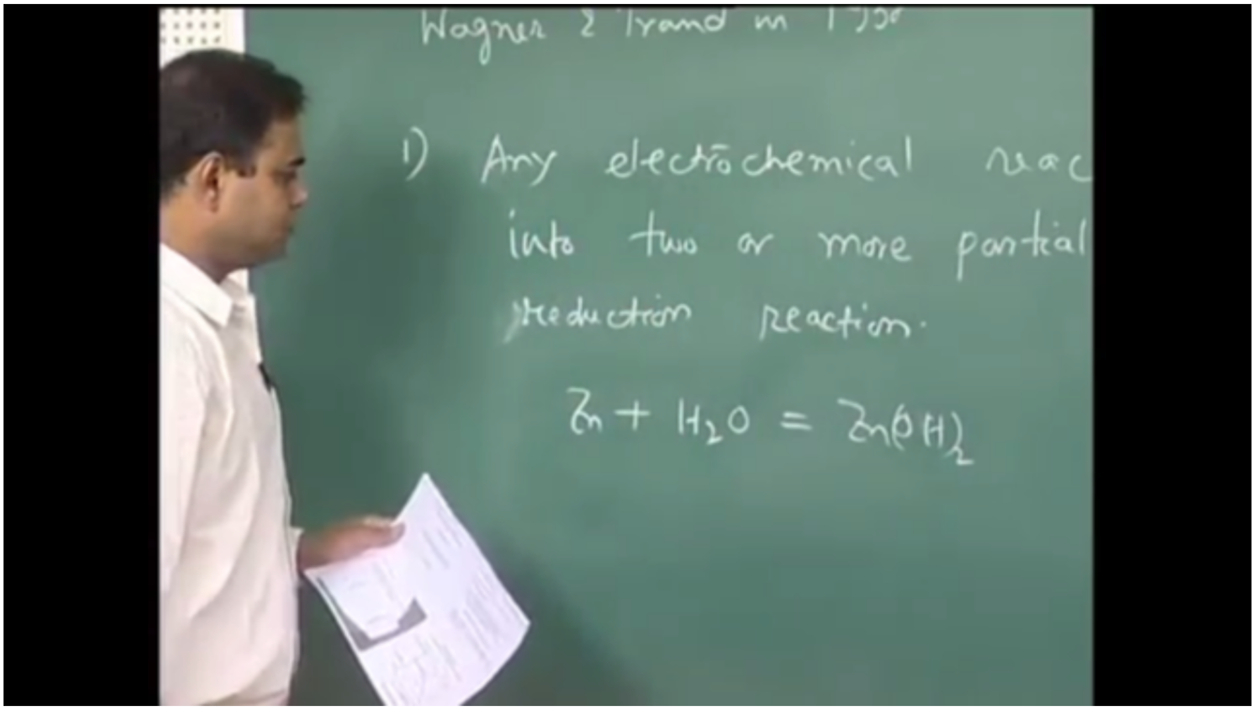

Wagner & Traud in 193

1) Any electrochemical reac
into two or more partial
reduction reaction.

$Zn + H_2O = Zn(OH)_2$

An example, for example, zinc corrosion in acidic medium which is deaerated. There is no oxygen. So zinc plus H_2O, it would form $Zn(OH)_2$, zinc corrosion in H_2 medium. Zinc will form Zn^{++} ion and on that because of this process, it will release two electron, and hydrogen will accept that two, this two electron and form H_2. So my reaction would be zinc plus H^+ is going to $Zinc^{++}$ plus H_2. So this is $2H^+$.

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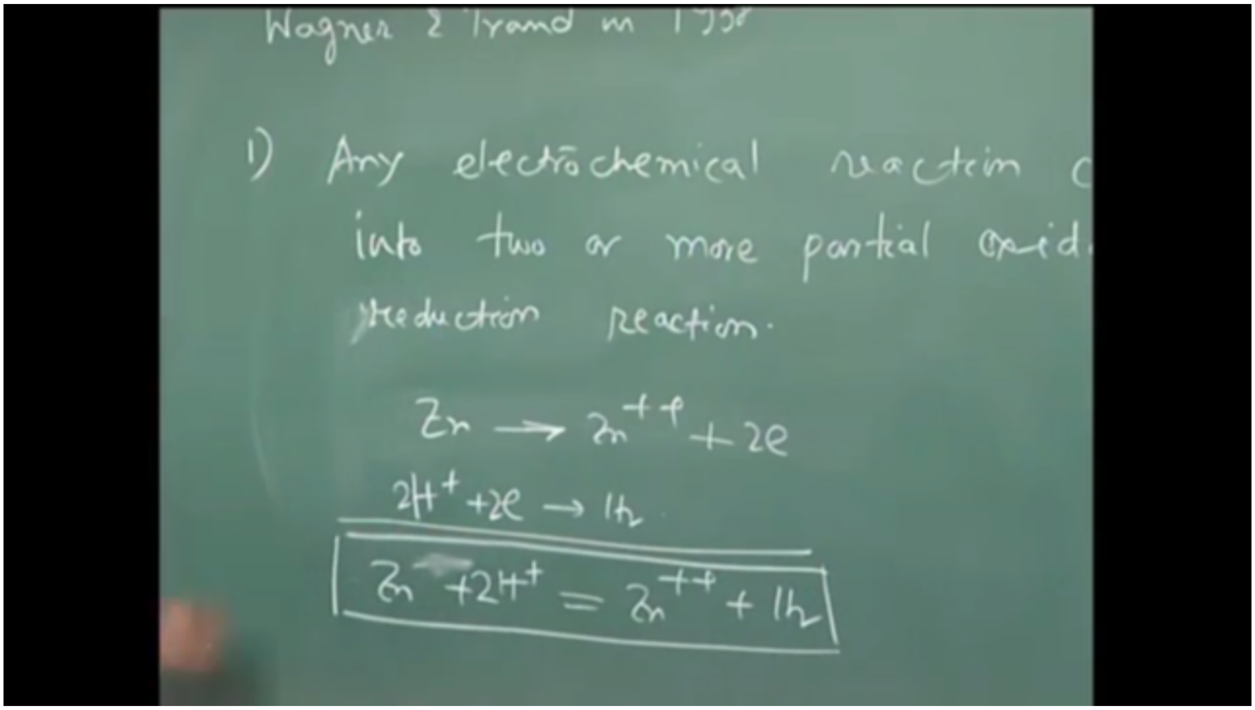

Wagner & Traud in 1938

1) Any electrochemical reaction c
into two or more partial oxid
/reduction reaction.

$$Zn \rightarrow Zn^{++} + 2e$$

$$2H^{+} + 2e \rightarrow 1H_2$$

$$\boxed{Zn + 2H^{+} = Zn^{++} + 1H_2}$$

So this is my actual reaction. What is happening in acidic media which is deaerated, deaerated HCl let's say, deaerated HCl if you put one zinc rod, natural reaction is like this. Now these reaction we can divide it into -- you can divide into two parts. One is oxidation and another one is reduction.

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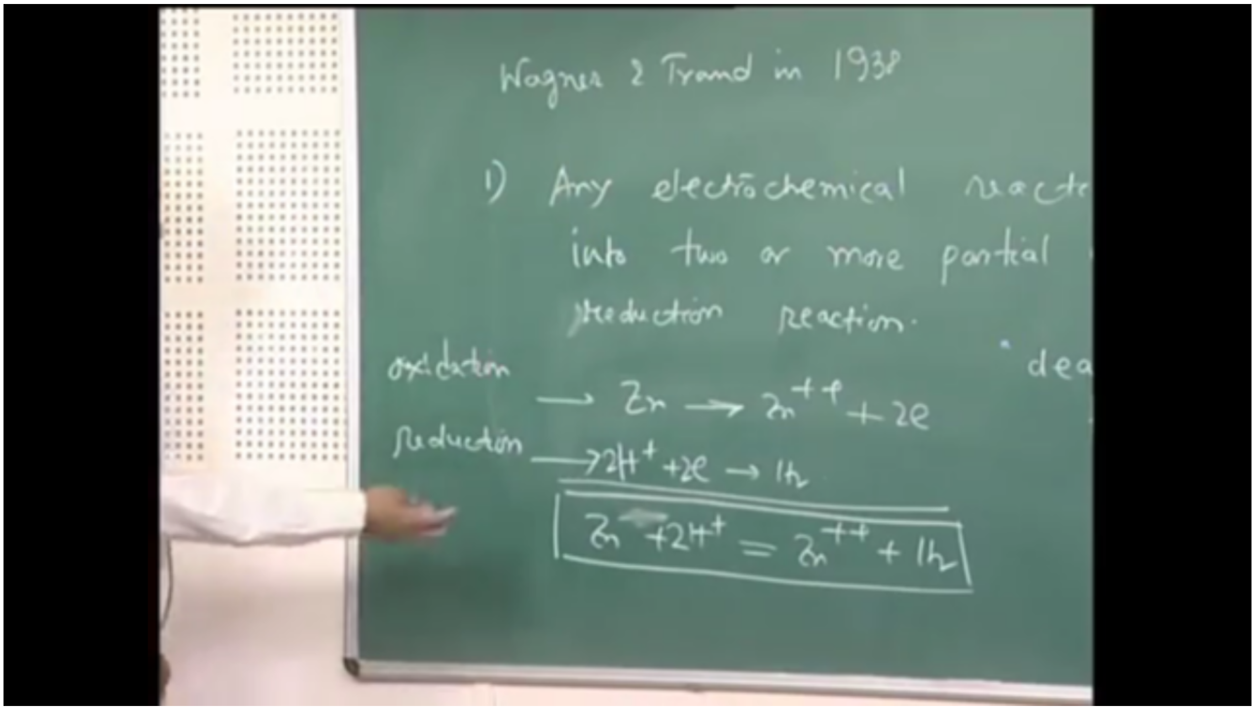

Wagner & Traud in 1938

1) Any electrochemical react
into two or more partial
reduction reaction.

dea

oxidation $\longrightarrow Zn \rightarrow Zn^{++} + 2e$

reduction $\longrightarrow 2H^{+} + 2e \rightarrow 1H_2$

$$\boxed{Zn + 2H^{+} = Zn^{++} + 1H_2}$$

So now the one electrochemical reaction is divided into oxidation, one oxidation and one reduction process. Now if it is not deaerated, then there would be one more cathodic species, cathodic reaction that can be possible in this medium which is O_2 plus $4H^+$ plus 4e going to $2H_2O$. So this can also happen and which will enhance the zinc to zinc^{++} so that case one more reaction you just have one more reaction, this cathodic reaction, this cathodic reaction plus one more cathodic reaction. These two reaction would happen and one anodic reaction or oxidation reaction.

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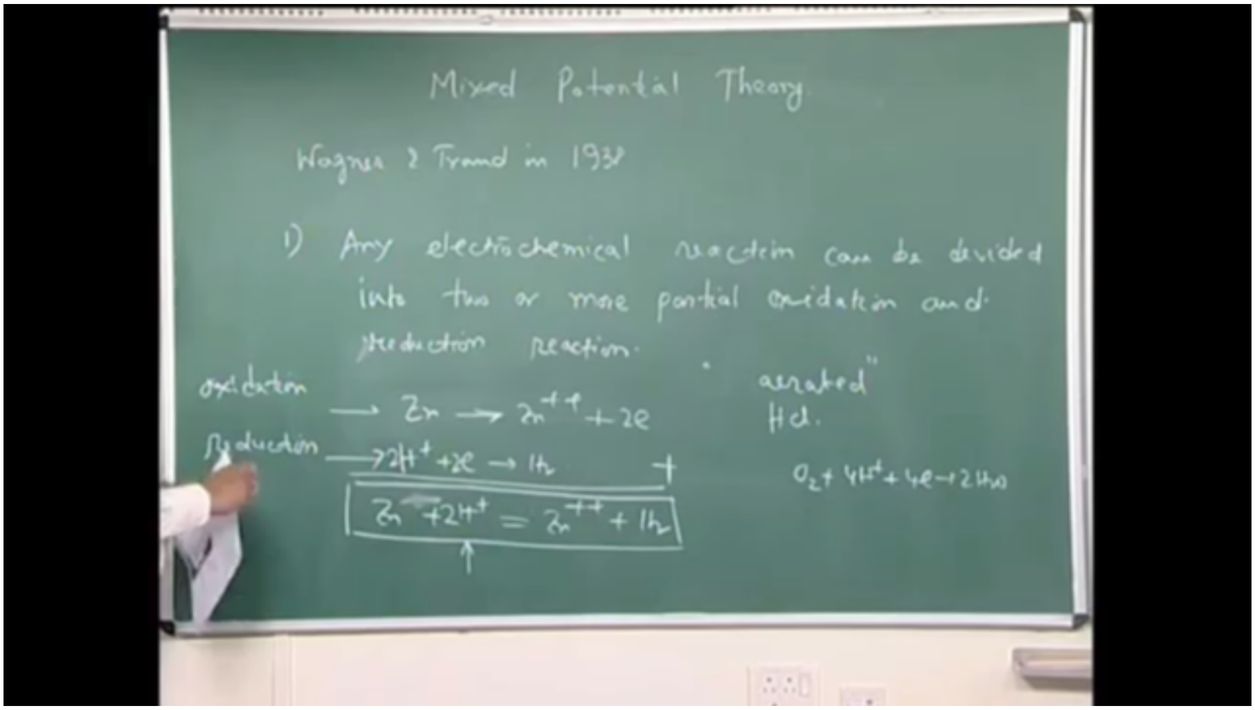

Mixed Potential Theory

Wagner & Traud in 1938

1) Any electrochemical reaction can be divided into two or more partial oxidation and reduction reaction.

oxidation → $Zn \rightarrow Zn^{++} + 2e$

Reduction → $2H^+ + 2e \rightarrow 1H_2$ +

$$\boxed{Zn + 2H^+ = Zn^{++} + 1H_2}$$

aerated" HCl.

$O_2 + 4H^+ + 4e \rightarrow 2H_2O$

So if it is aerated -- if it is deaerated, then there will be one oxidation, one -- one reduction, and if it is aerated, then there would be one oxidation reaction and two cathodic reaction, this one as well as this one. So you see the statement, any electrochemical reaction. So the, finally, the zinc reduction process, which can be divided into two or more partial oxidation and reduction reaction, and here one oxidation and two reduction reaction in if it is aerated and if it is not -- if it is not aerated, only H^+ ion. So then there would be two partial reactions. So the statement says that.

The second statement says -- says that there can be -- there can be no -- no net accumulation of electric charge -- electric charge during an electrochemical reaction -- during electrochemical reactions.

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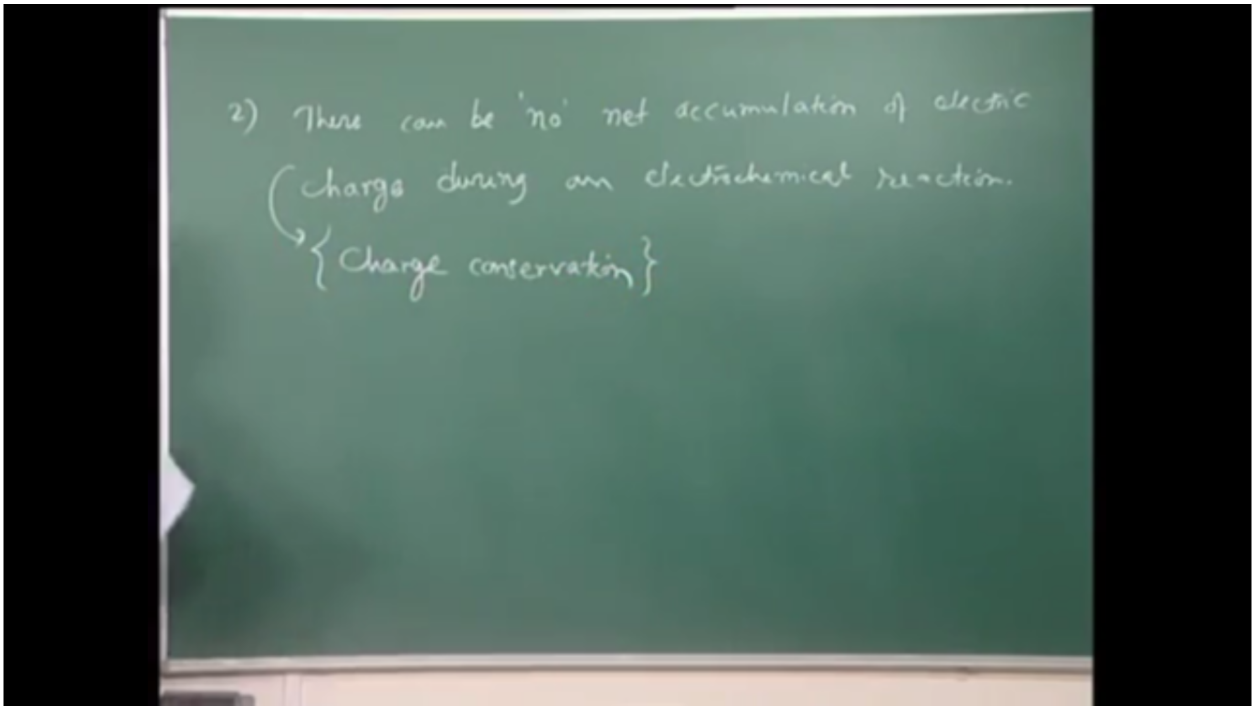

2) There can be 'no' net accumulation of electric charge during an electrochemical reaction.

{Charge conservation}

Now you see what it says? This says charge conservation. This is nothing but charge conservation. This is nothing but charge conservation. Now we get back to this. Let's say if it is deaerated, now you consider this set of reaction. If it is deaerated, zinc is going Zinc^{++}, two electrons are released. Now these two electrons will not remain as free electrons. These two electrons will be consumed by hydrogen ion and then hydrogen gas will generate because of this reduction reaction. So now you see this, whatever charge is generated because of anodic process or oxidation process, that charge will be consumed by some cathodic process or reduction process. That means the total charge should be zero after whole reaction. So that says the charge conservation.

Now let's say if it is aerated, then you have two electrons for this reaction which is generated due to zinc to zinc^{++} ion formation. That two electrons are consumed by 2H^{+} ion. Now you have the possibility of having one more cathodic reaction. So where from it would get four electron? So four electron -- electrons have to be supplied from these reactions, so the equal amount of electron should -- electrons should be generated from this reaction in order to have these two cathode reactions. So the overall electron generation per unit time would be equal to overall electron consumption per unit time.

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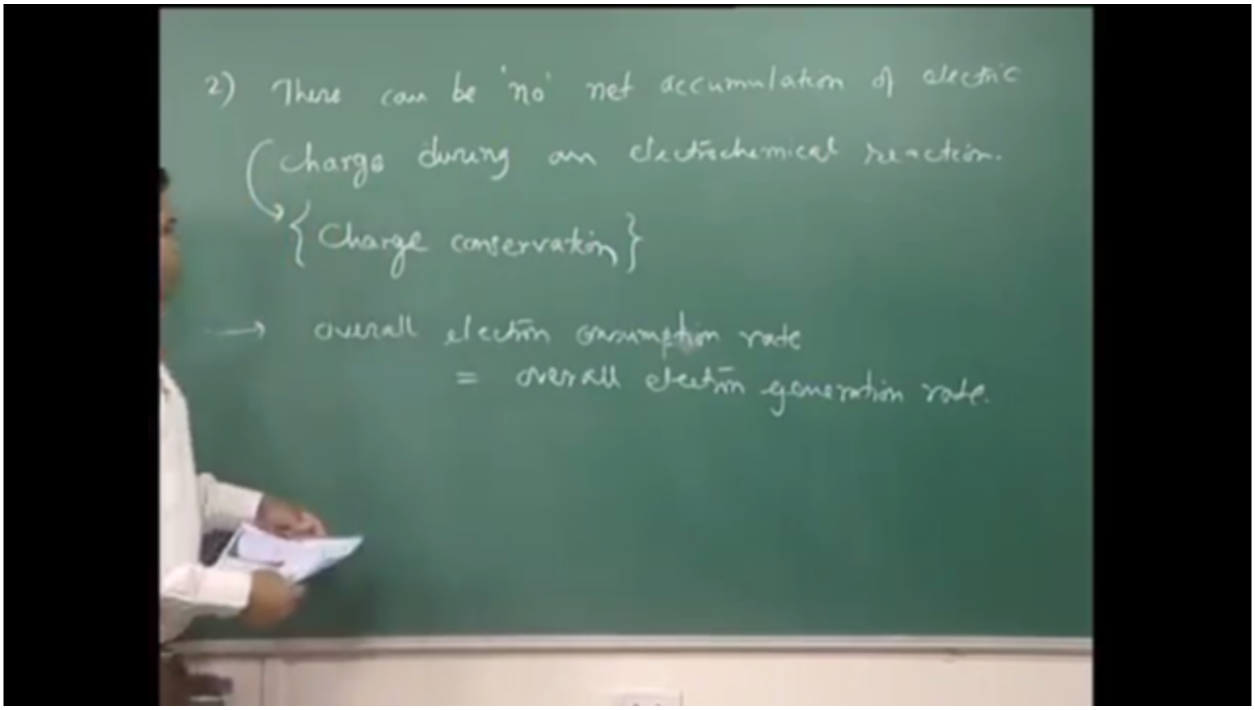

2) There can be 'no' net accumulation of electric
charge during an electrochemical reaction.
{Charge conservation}
→ overall electron consumption rate
= overall electron generation rate.

So it says that overall electron consumption rate would be equal to overall electron generation rate. So once these two are equal, that means -- that means the overall electron consumption because of cathodic reactions should be equal to overall electron generation due to anodic reaction.

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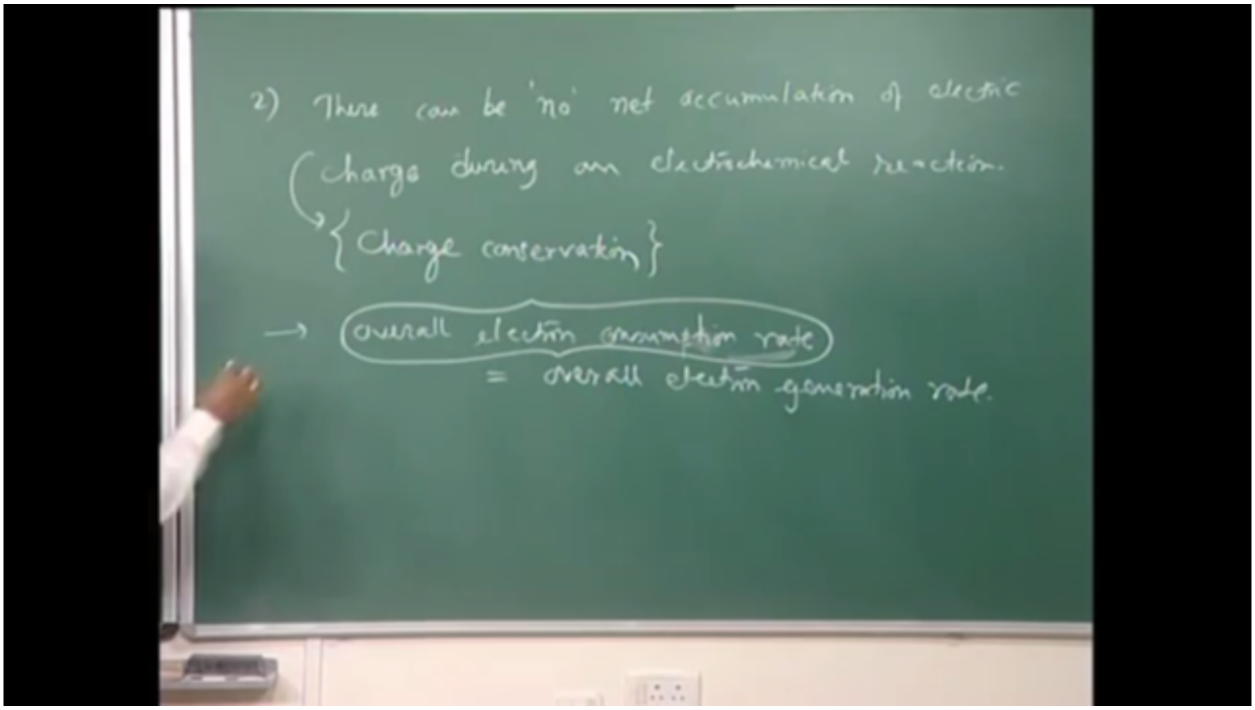

2) There can be 'no' net accumulation of electric
charge during an electrochemical reaction.
{Charge conservation}

→ overall electron consumption rate
= overall electron generation rate.

And now, again, what is this? This is what? This is what? This is nothing but the cathodic current. So that means this is nothing but i_c cathodic current, and this is nothing but i_a, and we see that these two are equal, but these two things are happening in opposite directions in order to understand that the directional nature of these two currents we put a negative sign in front of a cathodic current density.

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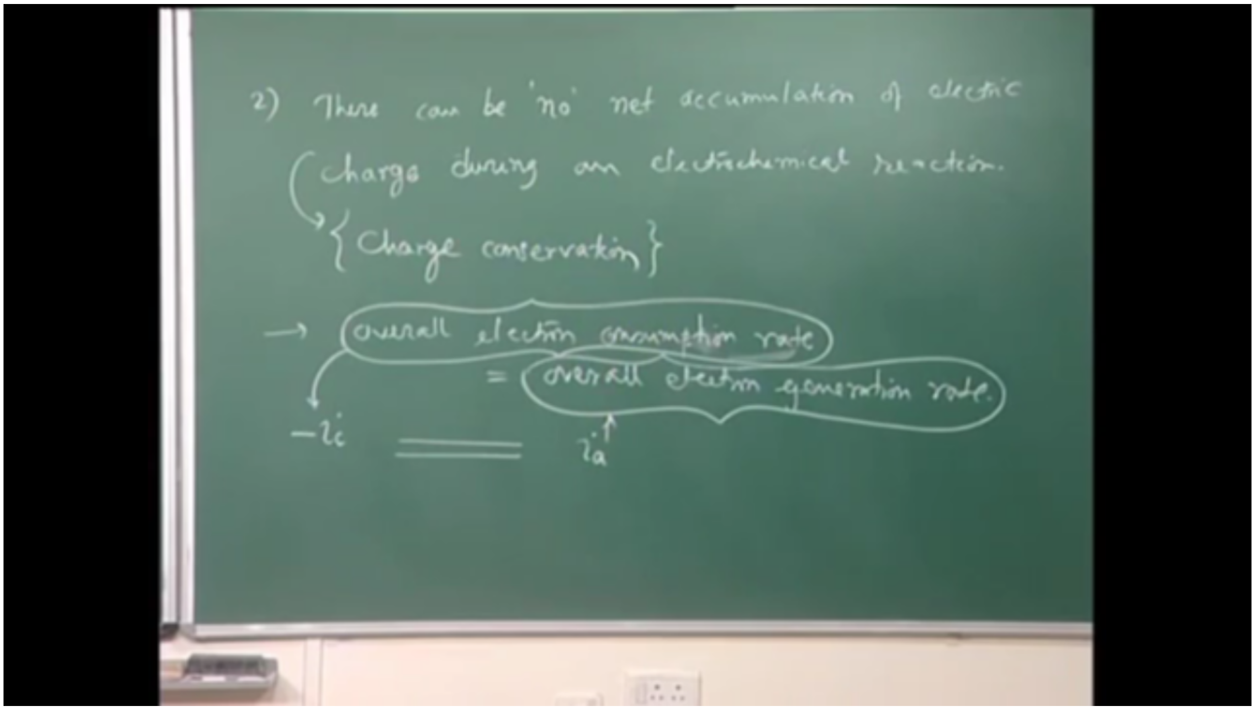

2) There can be 'no' net accumulation of electric charge during an electrochemical reaction.

{Charge conservation}

→ overall electron consumption rate = overall electron generation rate.

$-i_c = i_a$

So we see that cathodic current density is equal to anodic current density. And now what is corrosion? Corrosion is nothing but the overall electron generation rate or i_a or the dissolution rate. So this is equal to i_{corr} or corrosion current.

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