Electrochemical Impedance Spectroscopy
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Lecture – 27
Three Step Reaction with Two Adsorbed Intermediates

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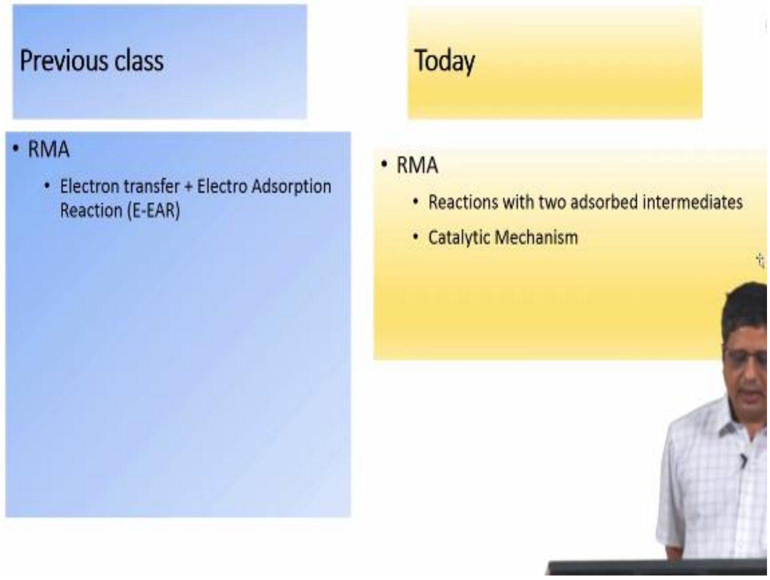

Previous class

- RMA
  - Electron transfer + Electro Adsorption Reaction (E-EAR)

Today

- RMA
  - Reactions with two adsorbed intermediates
  - Catalytic Mechanism

What we saw in the last section was to derive the expression for impedance for a mechanism, which involves one adsorbed intermediate. It involves electron transfer reaction and an adsorption reaction. Therefore, it is called E-EAR reaction.

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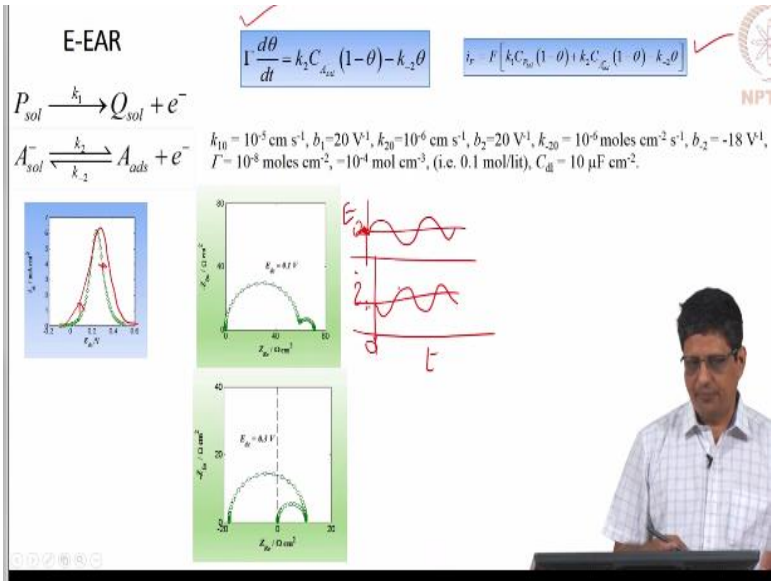

E-EAR

$$\Gamma\frac{d\theta}{dt}=k_2C_{A_{sol}}(1-\theta)-k_{-2}\theta$$

$$i_r = F\left[k_1C_{P_{sol}}(1-\theta)+k_2C_{A_{sol}}(1-\theta)-k_{-2}\theta\right]$$

$$P_{sol}\xrightarrow{k_1}Q_{sol}+e^-$$

$$A^-_{sol}\underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}}A_{ads}+e^-$$

$k_{10}=10^{-5}$ cm s^{-1}, $b_1=20$ V^{-1}, $k_{20}=10^{-6}$ cm s^{-1}, $b_2=20$ V^{-1}, $k_{-20}=10^{-6}$ moles cm^{-2} s^{-1}, $b_{-2}=-18$ V^{-1}, $\Gamma=10^{-8}$ moles cm^{-2}, $=10^{-4}$ mol cm^{-3}, (i.e. 0.1 mol/lit), $C_{dl}=10$ µF cm^{-2}.

To quickly refresh your memory, consider the reaction in which P going into Q with an electron transfer and then A in solution adsorbing and releasing in electron. We have written the mass balance equation, we have written the charge balance equation to tell the charge. Mass balance equation tells the θ, which is the surface coverage of A_{ads}. We also found how it varies with respect to time when the rate constant concentration in solution and other parameters are varied. For set of parameters, we show that the current looks like as shown in video; it increases and then decreases. At different DC potentials, if we take impedance spectrum at around 0.1, you get 2-capacitance loop, at 0.3, [somewhere here], it is a negative slope, it ends up in the negative and we discussed the meaning of negative impedance. It does not mean current goes in the opposite direction; it means current decreases when you increase the potential. Negative differential resistance means if this is the potential, current goes like this, but this is not 0, this is; has to be some large value, this is all positive and this is also all positive (refer video). The origin is somewhere here, this is time, this is current, this is potential. When you have an AC potential going like this, current also goes, but with an opposite phase.

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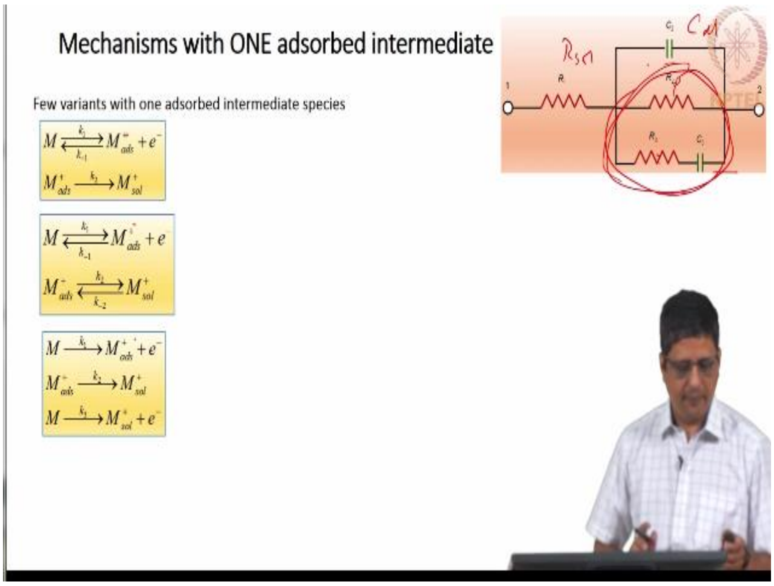

Mechanisms with ONE adsorbed intermediate

Few variants with one adsorbed intermediate species

$$M \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} M^{+}_{ads} + e^{-}$$
$$M^{+}_{ads} \xrightarrow{k_2} M^{+}_{sol}$$

$$M \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} M^{+}_{ads} + e^{-}$$
$$M^{+}_{ads} \underset{k_{-2}}{\overset{k_2}{\rightleftarrows}} M^{+}_{sol}$$

$$M \xrightarrow{k_1} M^{+}_{ads} + e^{-}$$
$$M^{+}_{ads} \xrightarrow{k_2} M^{+}_{sol}$$
$$M \xrightarrow{k_3} M^{+}_{sol} + e^{-}$$

We also saw that a circuit given here could represent this. You have solution resistance here. We have double layer capacitance here and this represents the Faradaic impedance. So one adsorbed intermediate gives us 1 Maxwell pair with the polarization resistance. We can write similar equations for other variance where you have one adsorbed intermediate here; you have one adsorbed intermediate, you have an adsorbed intermediate with a parallel reaction, you have single adsorbed intermediate, you can represent the Faraday impedance by the R polarization along with one Maxwell element. It can also be done with an equivalent ladder circuit or equivalent voigt circuit. I can replace this circuit with an equivalent set of elements.

I may have to allow for negative values here to get inductive loop, to get negative differential resistance and the number of circuit elements are sufficient. One resistance capacitance along with the resistance or one resistance inductance along with the resistance is sufficient to model this.

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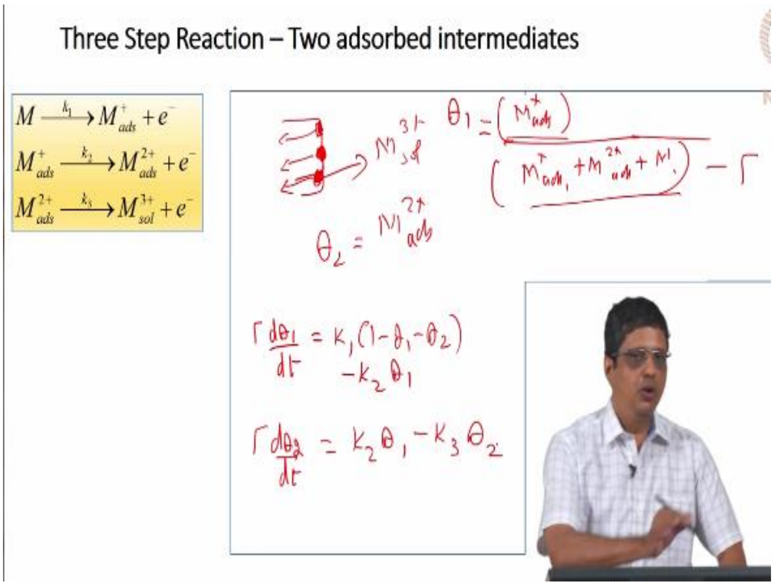

Three Step Reaction – Two adsorbed intermediates

$M \xrightarrow{k_1} M^{+}_{ads} + e^{-}$

$M^{+}_{ads} \xrightarrow{k_2} M^{2+}_{ads} + e^{-}$

$M^{2+}_{ads} \xrightarrow{k_3} M^{3+}_{sol} + e^{-}$

M^{3+}_{sol}

$\theta_1 = \frac{(M^{+}_{ads})}{(M^{+}_{ads} + M^{2+}_{ads} + M)} - \Gamma$

$\theta_2 = M^{2+}_{ads}$

$\Gamma \frac{d\theta_1}{dt} = k_1(1-\theta_1-\theta_2) - k_2\theta_1$

$\Gamma \frac{d\theta_2}{dt} = k_2\theta_1 - k_3\theta_2$

Now I want to go to the next example where you have the following reaction. Metal goes into metal 3^{+} in solution via 2 intermediates here. First it loses one electron, it becomes M_{ads}. So electron goes in, it still has not gone into solution. This site also loses an electron becomes M_{ads}. Then one of the M_{ads} loses another electron and it becomes a different species, which is called M^{2}_{ads} and that is the second step. Similarly, you can have some with M^{2}_{ads}, some with M_{ads}. Now a part of this M^{2}_{ads} can lose one more electron and go into the solution that becomes, M^{3+}_{sol}. M^{2+} and M^{+} are on the surface. Previously we said, M goes to M_{ads}, M_{ads} goes into solution. Here, we say M goes to M_{ads}, that is one species. Therefore, bare metal is one species (vacant metal), second is M_{ads}, third is M^{2+}_{ads}. So 2 intermediate species are there and the surface is there. We are going to call θ_1 as the fractional surface coverage of M^{+}_{ads}. [Denominator becomes surface coverage of M^{+}_{ads}, M^{2+}_{ads} and M. That many moles/cm^2 or atoms/cm^2, number of sites/cm^2. There is a total number of sites. We will represent denominator as Γ; this is the moles or area occupied by this per unit geometrical area. The number of sites divided by the total number of sites gives us θ_1. We call the fractional surface coverage of M^{2+}_{ads} as θ_2 and the remaining is bare metal. The fractional surface coverage of bare metal is represented as θ_v and that is going to be $1 - \theta_1 - \theta_2$.

Therefore we can say 30% of the area that is 0.3 is occupied by M_{ads}^{+}, 20% is occupied by M_{ads}^{2+} at given condition. Remaining 50% is bare metal. Bare metal can become M_{ads} as per the scheme that we have given. Once it becomes M_{ads}, it cannot become bare metal again, it is not reversible. Now whatever is M_{ads} can become M_{ads}^{2+}. When M_{ads}^{2+} goes into solution, a bare metal becomes available now, whatever is below, that gets exposed. We can write the mass balance equation for this. [We have done this before. So I would like you to try]. First species is formed by the first step and it is consumed by the second step. M_{ads} is formed by the first step, and it is consumed by the second step.

Rate of formation of the first step is k_1. What is the fractional surface coverage of metal? I am going to write θ_v it as 1 - θ_1- θ_2. The θ_1, θ_2, θ_v have a relationship that some of them have to be 1. Therefore, I can always write one of them in terms of the other. Previously for example we just write θ, we did not write θ_1, θ_v, [we could have done that, that is alright], but we just write θ for the species and 1- θ for the vacant site. We will do the same thing here. So first step forms it, second step consumes it. This is what we write for the transient equation or mass balance equation for the M_{ads} species. [For the second species can we write it?] θ_2 is formed by the second step, that is k_2 and the fractional surface coverage here is given as M_{ads} and it is consumed by the third step. [So we have written the mass balance equation, can we write the charge balance equation? Can we write the Faraday current?]. Electron is produced by the first, second and the third step with one electron each.

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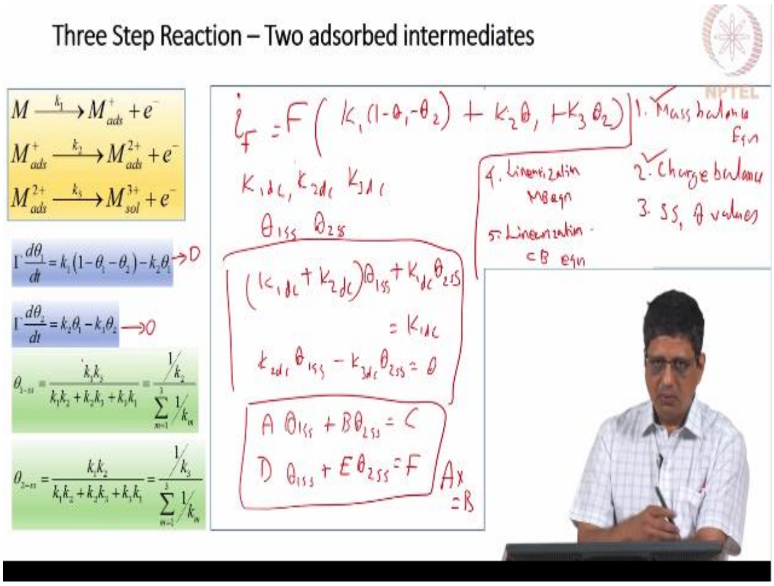

Three Step Reaction – Two adsorbed intermediates

$$M \xrightarrow{k_1} M^{+}_{ads} + e^-$$
$$M^{+}_{ads} \xrightarrow{k_2} M^{2+}_{ads} + e^-$$
$$M^{2+}_{ads} \xrightarrow{k_3} M^{3+}_{sol} + e^-$$

$$\Gamma \frac{d\theta_1}{dt} = k_1(1-\theta_1-\theta_2) - k_2\theta_1 \rightarrow 0$$

$$\Gamma \frac{d\theta_2}{dt} = k_2\theta_1 - k_3\theta_2 \rightarrow 0$$

$$\theta_{1-ss} = \frac{k_1k_3}{k_1k_2 + k_2k_3 + k_3k_1} = \frac{1/k_2}{\sum_{m=1}^{3} 1/k_m}$$

$$\theta_{2-ss} = \frac{k_1k_2}{k_1k_2 + k_2k_3 + k_3k_1} = \frac{1/k_3}{\sum_{m=1}^{3} 1/k_m}$$

$$i_F = F\left(k_1(1-\theta_1-\theta_2) + k_2\theta_1 + k_3\theta_2\right)$$

1. Mass balance Eqn
2. Charge balance
3. SS, θ values
4. Linearization MB eqn
5. Linearization CB eqn

$k_{1dc}, k_{2dc}, k_{3dc}$

$\theta_{1ss}\ \theta_{2s}$

$$(k_{1dc} + k_{2dc})\theta_{1ss} + k_{1dc}\theta_{2ss} = k_{1dc}$$
$$k_{2dc}\theta_{1ss} - k_{3dc}\theta_{2ss} = 0$$

$$A\theta_{1ss} + B\theta_{2ss} = C$$
$$D\theta_{1ss} + E\theta_{2ss} = F$$

$Ax = B$

Therefore, we would write total Faraday current as Faraday constant multiplied by first step, where the rate is given by $k_1(1- \theta_1, - \theta_2)$. It produces an electron, second step produces an electron, and third step produces an electron. Therefore, we do the following. We write the mass balance equation and charge balance equation. These are transient equations. Third, steady state theta values. Fourth, linearization of, [you can do mass balance equation first, does not matter], linearization of charge balance equation. If you linearize mass balance equation, you will get $d\theta_1/dE$, $d\theta_2/dE$ and that is lengthy. However, it is possible to do. If you do charge balance equation, you will get i_{ac} in terms of E_{ac} and $d\theta_1/dE$, $d\theta_2/dE$ where we have to substitute. [I do not expect you to write that in paper you probably are better off writing]. This is $d\theta_1/dE$, and then substitute it here and then you will get the answer, instead of writing in a very lengthy expression. We adopt this general procedure for any reaction. We had done the first part; we had done the second part. I would like you to do the steady state expression.

When you want to get the steady state expression, we have to set this equation to 0, set the second equation to 0 and then call k_1 as k_{1dc} because it is at a given DC potential. k_{2dc}, k_{3dc}, θ_1 as steady state, θ_2 as steady state. We should set this to 0, replace k_1 with k_{1dc}, k_2 with k_{2dc}, k_3 with k_{3dc}. k_1, k_2 and k_3 depend on potential as they are all electrochemical steps. You would get 2 equations in 2 unknowns, linear equation. Therefore, you can solve them.

[refer video 11:13]

[Do you get equation like this?]. The first equation has to be $k_{1dc} + k_{2dc}\theta_{1ss} + k_{1dc}\theta_{2ss} = k_{1dc}$, after rearranging. Second equation is lot easier, which is in the form of

$A\theta_{1ss} + B\theta_{2ss} = C$

$D\theta_{1ss} + E\theta_{2ss} = F$

I am just writing it as a dummy variable. F is not the Faraday constant. This is 2 equations, 2 unknown, you can write the expression for this. If I get 3 variables as long as it is linear, you should be able to write 3 equations, 3 unknowns, 5 equations, 5 unknowns. You should be able to write any number of intermediates in a matrix form and say theoretically you can invert the matrix and get the solution. You can write it as a matrix form Ax = B, where A is the matrix, x is the unknown vector, B is the vector and you can invert it using Gauss elimination [variety of methods are possible]. You can get an answer like this and I can rewrite it slightly differently.

Think of it as; k_1 is the rate of consumption of metal site, k_2 is the rate of consumption of M_{ads}^{+}. k_3 is the rate of consumption of M_{ads}^{2+}. [It is not the rate]. It is the rate constant corresponding to that. Inverse of k_1 is telling you how slow that is being consumed. Inverse of k_2 tells you how slowly M_{ads}^{+} is consumed. Inverse of k_3 tells you how slowly M_{ads}^{2+} is consumed. Therefore, $1/k_2$ tells you how slowly this is consumed and sum of all this $1/k_1$, $1/k_2$, $1/k_3$ can come in the denominator. This tells relatively how slowly this θ_1 or M_{ads}^{+} is consumed compared to consumption rate of other species. However, this shortcut may not work in all cases. You can look at this equation and say, $1/k_1$, $1/k_2$, $1/k_3$, fractional surface coverage of M_{ads} is going to be $1/k_1$ / $1/k_i$, sum of all these things. For this M_{ads}, it is going to be $1/k_2$, and in the denominator, you get the sum of all these things. This shortcut works in some cases, at least this has one way to check whether you have it correctly for simple cases.

“Professor - student conversation starts”

Sir should it be (()) (13:25)
This should be DC. This entire thing should have a subscript of DC for each of this case. I missed them.

“Professor - student conversation ends”

If we have 2 species here, in some reaction you will have θ_1, θ_2. Then it becomes a nonlinear equation. In all these cases, you will get a solution. In some cases, when you have nonlinear equation, you will get multiple solution, where that is a special case. [If time permits, we will see an example like that]. Generally, if you have linear equations, you will definitely get only one solution, unique solution and θ value will fall between 0 to 1 for all of these. If you have nonlinear equation, you will get 1 physically meaningful solution where all θs fall between 0 to 1. Some of them may have θ going below 0 or above 1 or come out as a complex number in which case it is not physically meaningful. You can throw away those solutions. Only the solutions where all θs have values between 0 to 1, are valid solutions.

We are going to see only simple cases in which they will definitely fall between 0 to 1. [We got this part correctly and I think (()) has not completed if you are given little more time you will be able to get this].

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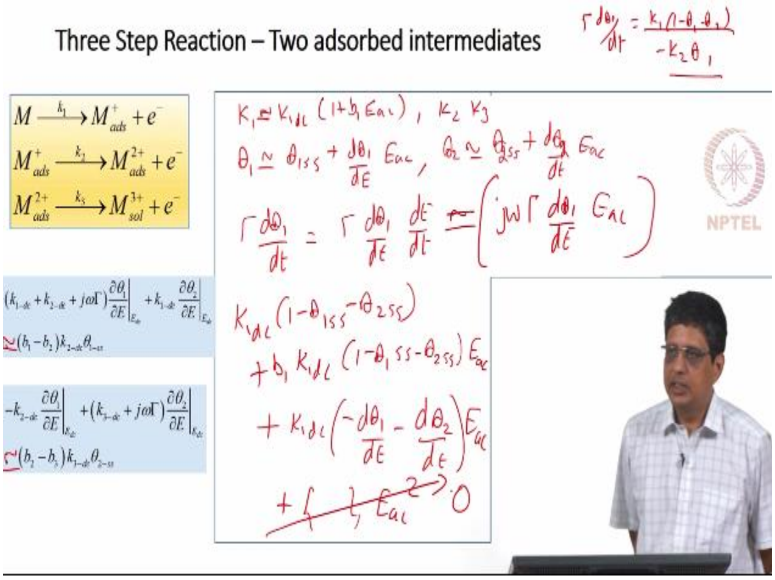

Three Step Reaction – Two adsorbed intermediates

$$\Gamma \frac{d\theta_1}{dt} = k_1(1-\theta_1-\theta_2) - k_2\theta_1$$

$$M \xrightarrow{k_1} M^{+}_{ads} + e^-$$
$$M^{+}_{ads} \xrightarrow{k_2} M^{2+}_{ads} + e^-$$
$$M^{2+}_{ads} \xrightarrow{k_3} M^{3+}_{sol} + e^-$$

$$(k_{1-dc} + k_{2-dc} + j\omega\Gamma)\left.\frac{\partial\theta_1}{\partial E}\right|_{E_{dc}} + k_{1-dc}\left.\frac{\partial\theta_2}{\partial E}\right|_{E_{dc}} \cong (b_1 - b_2)k_{2-dc}\theta_{1-ss}$$

$$-k_{2-dc}\left.\frac{\partial\theta_1}{\partial E}\right|_{E_{dc}} + (k_{3-dc} + j\omega\Gamma)\left.\frac{\partial\theta_2}{\partial E}\right|_{E_{dc}} \cong (b_2 - b_3)k_{3-dc}\theta_{2-ss}$$

$$k_1 \simeq k_{1dc}(1 + b_1 E_{ac}),\ k_2\ k_3$$

$$\theta_1 \simeq \theta_{1ss} + \frac{d\theta_1}{dE}E_{ac},\quad \theta_2 \simeq \theta_{2ss} + \frac{d\theta_2}{dt}E_{ac}$$

$$\Gamma\frac{d\theta_1}{dt} = \Gamma\frac{d\theta_1}{dE}\frac{dE}{dt} = \left(j\omega\Gamma\frac{d\theta_1}{dE}E_{ac}\right)$$

$$k_{1dc}(1-\theta_{1ss}-\theta_{2ss})$$
$$+ b_1 k_{1dc}(1-\theta_{1ss}-\theta_{2ss})E_{ac}$$
$$+ k_{1dc}\left(-\frac{d\theta_1}{dE} - \frac{d\theta_2}{dE}\right)E_{ac}$$
$$\cancel{+\{\ \}E_{ac}^2} \rightarrow 0$$

Now we will see linearization of charge balance equation and mass balance equation. Let us try the mass balance equation and see if we can linearize them. Mass balance equation look like this $\Gamma d\theta_1/dt = k_1 (1- \theta_1- \theta_2)-k_2\theta_1$ is a first mass balance equation. Here we are going to write k_1 as $k_{1dc}(1 + b_1E_{ac})$ and that is an approximation. Similarly, we will write for k_2 and k_3. Likewise, we will write θ_1 approximately equal to $\theta_{1ss} + (d\theta_1/dE) E_{ac}$. Similarly, we write θ_2 is $\theta_{2ss}+(d\theta_2/dE)E_{ac}$. We have 3 rate constants, 2 surface coverage. The third surface coverage is going to be written as $1- \theta_1- \theta_2$. Therefore we just leave it as it is. I want to take the first equation, rewrite it, take second equation, expand in Taylor series, truncate it after the first term and then get the expression. We always write the top expression $\Gamma d\theta_1/dt$ as $\Gamma d\theta_1/dE \times dE/dt$ and we know that it is exactly equal to $j\omega\Gamma d\theta_1/dE\times E_{ac}$. I want to take the first equation, write it, we will expand it, rearrange it, second equation we will write it, expand it, truncate it and rearrange it. I have written left hand side first equation here. You have 2 terms at the right hand side. First term will give me (refer video):

In first term, when I write k_1 and when I expand the θ_1 and do all the calculations, I would get 4 terms there; one is a constant, independent of E_{ac}; 2 terms will depend on E_{ac}, one term will depend on E_{ac}^2. Expansion of the first term after expanding in Taylor series, truncating it and then multiplying it, throwing away the E_{ac}^2, you should get 3 terms out of that. [It is lengthy, and it will take some time. It is not going to be difficult in terms of complexity and is not something beyond your capacity or beyond your ability to get this. All that you need to do is substitute it, carefully do the multiplication and throw away the terms, which are higher order than E_{ac}.

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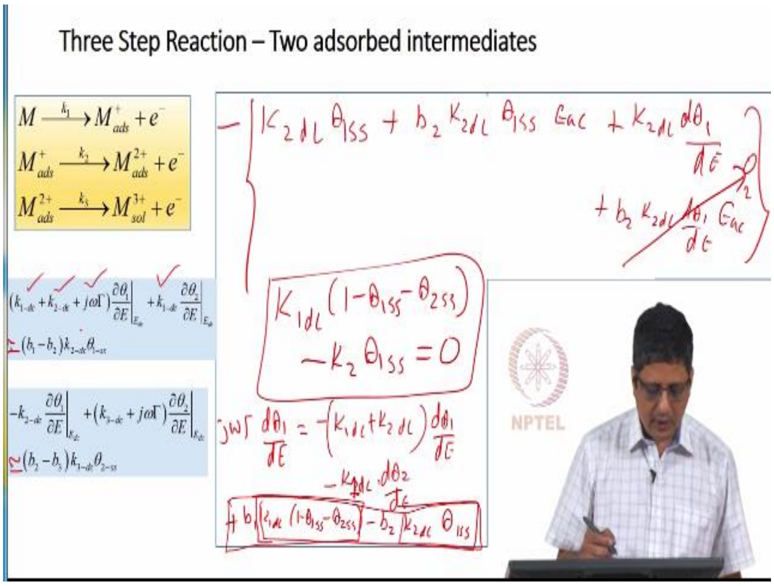

Three Step Reaction – Two adsorbed intermediates

$$M \xrightarrow{k_1} M^{+}_{ads} + e^{-}$$
$$M^{+}_{ads} \xrightarrow{k_2} M^{2+}_{ads} + e^{-}$$
$$M^{2+}_{ads} \xrightarrow{k_3} M^{3+}_{sol} + e^{-}$$

$$(k_{1-dc} + k_{2-dc} + j\omega\Gamma)\left.\frac{\partial\theta_1}{\partial E}\right|_{E_{dc}} + k_{1-dc}\left.\frac{\partial\theta_2}{\partial E}\right|_{E_{dc}}$$
$$\simeq (b_1 - b_2)k_{2-dc}\theta_{1-ss}$$

$$-k_{2-dc}\left.\frac{\partial\theta_1}{\partial E}\right|_{E_{dc}} + (k_{3-dc} + j\omega\Gamma)\left.\frac{\partial\theta_2}{\partial E}\right|_{E_{dc}}$$
$$\simeq (b_2 - b_3)k_{3-dc}\theta_{2-ss}$$

$$-\left\{K_{2dc}\theta_{1ss} + b_2K_{2dc}\theta_{1ss}E_{ac} + K_{2dc}\frac{d\theta_1}{dE} + \cancel{b_2K_{2dc}\frac{d\theta_1}{dE}E_{ac}^2}\right\}$$

$$\boxed{K_{1dc}(1-\theta_{1ss}-\theta_{2ss}) - k_2\theta_{1ss} = 0}$$

$$j\omega\Gamma\frac{d\theta_1}{dE} = -(K_{1dc}+k_{2dc})\frac{d\theta_1}{dE} - k_{1dc}\frac{d\theta_2}{dE}$$
$$\boxed{+b_1\boxed{k_{1dc}(1-\theta_{1ss}-\theta_{2ss})} - b_2\boxed{k_{2dc}\theta_{1ss}}}$$

Second term is going to come with a negative sign in front (refer video), and I am going to put that in bracket and I have to remember to put the correct subscript for $d\theta_1$, [not steady state], and I will cancel the term involving $(d\theta_1/dE)\,E_{ac}^2$. You have to expand and write it. [As I am little familiar with this, I am able to write it without going through the detailed calculation. When you practice it you would be able to do it without any problem].

“Professor - student conversation starts” (()) (19:35)

No, please check what the equation $k_2\theta_1$ is. [You have to do it with care. Then it should not be difficult]. Then when I take the first equation, I recognise the constant terms. If I combine them together, they will go to 0. First term gives you a constant term; second term gives you a constant term on the right hand side. They will go to 0 because that is the definition of θ_{1ss} and θ_{2ss}.

“Professor - student conversation ends”.

That means I can rewrite it and say JωΓ(dθ_1/dE); E_{ac} is there and I can divide by E_{ac} throughout this. After rearranging, I should get something like this. On the left hand side, I am left with this; I am dividing by E_{ac} throughout this. Then I will not have E_{ac} here. On the right hand side, I will combine all the terms that are relevant for dθ_1/dE. I will group all the terms relevant for dθ_2/dE. Whatever is remaining, I will write them and this is what is remaining here. I can bring this to the left side and I will get k_{1dc} + k_{2dc} + JωΓdθ_1/dE. I can bring this to the left side, [that becomes, I am sorry, this is k_{1dc}, because this has come from $k_1(1-\theta_1 - \theta_2)$, from that only we got dθ_2/dE]. This comes to the left side and it becomes k_{1dc}dθ_2/dE. I can keep what remains on the right side as it is or I can recognise the terms within the square here or equal to the terms in the square here and then make it in a little simpler form. [It is not necessary, it just, when you write it, it is easy. When you do the calculation, it would not matter, you can keep it as it is. If you are done with the first part, please proceed with the second equation. Now I will pause here].

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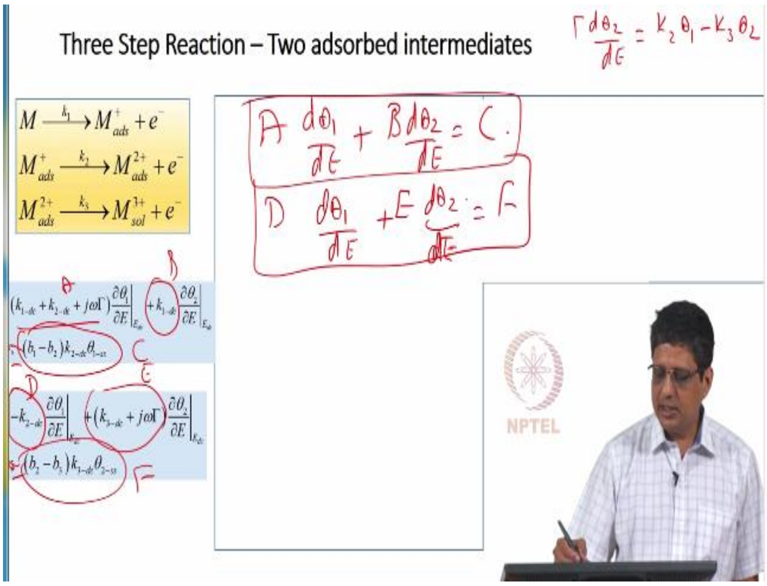

Three Step Reaction – Two adsorbed intermediates

$$\Gamma\frac{d\theta_2}{dE} = k_2\theta_1 - k_3\theta_2$$

$$M \xrightarrow{k_1} M^{+}_{ads} + e^{-}$$
$$M^{+}_{ads} \xrightarrow{k_2} M^{2+}_{ads} + e^{-}$$
$$M^{2+}_{ads} \xrightarrow{k_3} M^{3+}_{sol} + e^{-}$$

$$\boxed{A\frac{d\theta_1}{dE} + B\frac{d\theta_2}{dE} = C.}$$

$$\boxed{D\frac{d\theta_1}{dE} + E\frac{d\theta_2}{dE} = F}$$

$$\underbrace{(k_{1-dc} + k_{2-dc} + j\omega\Gamma)}_{A}\left.\frac{\partial\theta_1}{\partial E}\right|_{E_{dc}} \underbrace{+k_{1-dc}}_{B}\left.\frac{\partial\theta_2}{\partial E}\right|_{E_{dc}}$$
$$\underbrace{-(b_1 - b_2)k_{2-dc}\theta_{1-ss}}_{C}$$

$$\underbrace{-k_{2-dc}}_{D}\left.\frac{\partial\theta_1}{\partial E}\right|_{E_{dc}} \underbrace{+(k_{3-dc} + j\omega\Gamma)}_{E}\left.\frac{\partial\theta_2}{\partial E}\right|_{E_{dc}}$$
$$\underbrace{-(b_2 - b_3)k_{3-dc}\theta_{2-ss}}_{F}$$

Go to the second equation. This equation when you write it, it looks like (refer video). The second equation is also going to look like that, with different terms, which you can solve. It is again 2 unknowns, 2 linear equations, which you can solve these and get the answer. Second equation is (refer video): We have written this part and A is this term here, B is this term here, C is this term here. We want to write similarly for this. My claim is it is going to be D here, E here and F here. We will just write it and confirm that this is correct and once you get in this form, you realize you can solve for dθ_1/dE, dθ_2/dE. There are 2 simultaneous equations, you have to solve them and get the answer. It is not like what you have done in the one adsorbed species. You can rearrange and get the answer because it is 1 equation, 1 unknown and rearrangement would give you the result. Even if you had 10 equations, 10 unknowns, you can solve them. As long as you recognise that, you have to solve them simultaneously. You cannot get $d\theta_1/dE$ equal to 'some result' in the first simplification.

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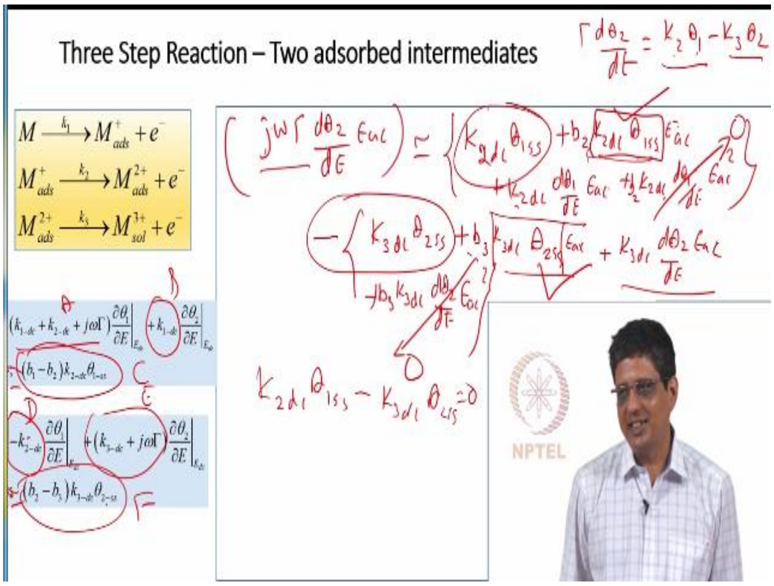

Three Step Reaction – Two adsorbed intermediates

$$M \xrightarrow{k_1} M^{+}_{ads} + e^{-}$$

$$M^{+}_{ads} \xrightarrow{k_2} M^{2+}_{ads} + e^{-}$$

$$M^{2+}_{ads} \xrightarrow{k_3} M^{3+}_{sol} + e^{-}$$

$$\Gamma \frac{d\theta_2}{dt} = k_2\theta_1 - k_3\theta_2$$

$$k_{2dc}\theta_{1ss} - k_{3dc}\theta_{2ss} = 0$$

On the left side, you are going to get $j\omega\Gamma(d\theta_2/dE)E_{ac}$ on the left hand side. Right hand side first term is going to be $(k_{2dc}\theta_{1ss} + b_2k_{2dc}\theta_{1ss}\, E_{ac} + k_{2dc}(d\theta_1/dE)E_{ac})$. It is going to give us 4 terms out of which you will retain 3. Similarly, we are going to do $k_{3dc}\theta_{2ss} + b_3k_{3dc}(d\theta_2/dE)$ $E_{ac} + k_{3dc}$. [I am sorry this is going to be θ_{2ss}, this is going to be $d\theta_2/dE\ E_{ac} + b_3k_{3dc}d\theta_2/dE$ E_{ac}^2, out of which 4 term will go to 0. The first term $k_2\theta_1$ gives you 4 different terms and the second term $-k_3\theta_2$ gives you 4 different terms. We throw away E_{ac}^2 term in each of this. The constant term – constant term will go to 0. That is because $k_{2dc}\theta_{1ss} - k_{3dc}\theta_{2ss} = 0$. That is how we get the θ_{ss} values. When the transient is 0, you get steady state values. So $k_{2dc}\theta_{1ss} - k_{3dc}\theta_{2ss}$ is automatically 0. Now you have E_{ac} here, E_{ac} here, E_{ac} here, E_{ac} here, divide by E_{ac} and rearrange. This k_2 will become $-k_2$, this is gone, this term here remains on the right side. This is not brought to the left. This term here remains on the right side. This term is brought to the left, it becomes k_{3dc}, this $j\omega\Gamma$ is for $d\theta_2/dE$, and you get 1 expression here, another expression here and on the right side we have this term, and this term where I can recognize again $k_{2dc}\theta_{1ss}$ is equal to $k_{3dc}\ \theta_{2ss}$. Therefore, you can simplify it a little bit. Even if we do not simplify and leave it as it is, it is fine. [Please try and derive the expression rather than relying on me to do it correctly and show you the result. My intention is to show you the correct results, but I could make mistakes].

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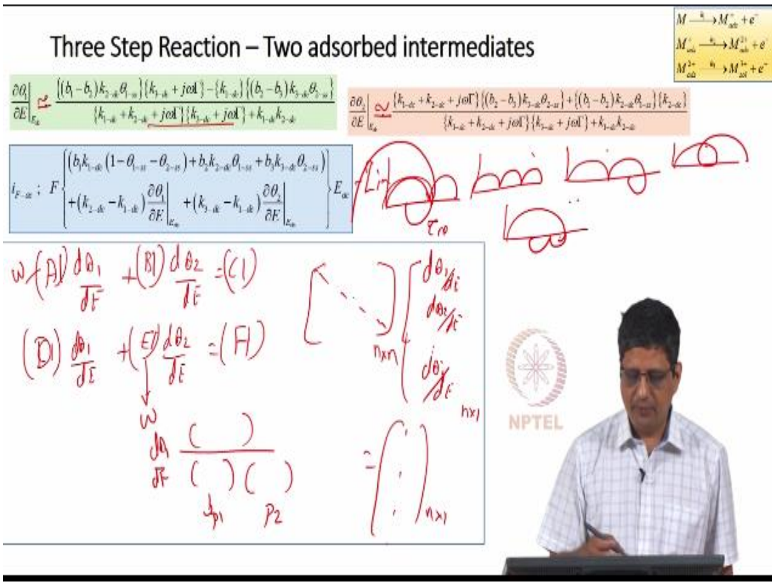

Three Step Reaction – Two adsorbed intermediates

$M \xrightarrow{k_1} M^{+}_{ads} + e^-$

$M^{+}_{ads} \xrightarrow{k_2} M^{2+}_{ads} + e^-$

$M^{2+}_{ads} \xrightarrow{k_3} M^{3+}_{sol} + e^-$

$$\left.\frac{\partial\theta_1}{\partial E}\right|_{E_{dc}} \cong \frac{\{(b_1-b_2)k_{2-dc}\theta_{1-ss}\}\{k_{3-dc}+j\omega\Gamma\}-\{k_{3-dc}\}\{(b_2-b_3)k_{3-dc}\theta_{2-ss}\}}{\{k_{1-dc}+k_{2-dc}+j\omega\Gamma\}\{k_{3-dc}+j\omega\Gamma\}+k_{1-dc}k_{2-dc}}$$

$$\left.\frac{\partial\theta_2}{\partial E}\right|_{E_{dc}} \cong \frac{\{k_{1-dc}+k_{2-dc}+j\omega\Gamma\}\{(b_2-b_3)k_{3-dc}\theta_{2-ss}\}+\{(b_1-b_2)k_{2-dc}\theta_{1-ss}\}\{k_{2-dc}\}}{\{k_{1-dc}+k_{2-dc}+j\omega\Gamma\}\{k_{3-dc}+j\omega\Gamma\}+k_{1-dc}k_{2-dc}}$$

$$i_{F-ac} \,;\, F\left\{\begin{aligned}&\left(b_1k_{1-dc}(1-\theta_{1-ss}-\theta_{2-ss})+b_2k_{2-dc}\theta_{1-ss}+b_3k_{3-dc}\theta_{2-ss}\right)\\&+(k_{2-dc}-k_{1-dc})\left.\frac{\partial\theta_1}{\partial E}\right|_{E_{dc}}+(k_{3-dc}-k_{1-dc})\left.\frac{\partial\theta_2}{\partial E}\right|_{E_{dc}}\end{aligned}\right\}E_{ac}$$

[To avoid the confusion], This E is not potential and can be written as 2 equations 2 unknowns, this is a function of ω, here this is a function of ω. The second equation jωΓ will come there. If I have many intermediate species, I will get expressions like this. Instead of this, I will get $d\theta_1/dE$, $d\theta_2/dE$, $d\theta_3/dE$ and so on. I will have n number of equations. For each species, I have a mass balance equation and the diagonal will contain ω's term there. It will come like a matrix, it is going to be $d\theta_1/dE$, $d\theta_2/dE$,..…..,dθi/dE. On the right hand side, you will have the same length of vector. Here, you will get n/n, this is going to be n/1, and it is going to be n/1 vector here. If I have n species and the diagonal elements will always have θ.

This matrix will always be linear as long as we assume that truncation and linearization is applicable. You may get nonlinear terms in the steady state equation. Here you will not get nonlinear terms; you will get only linear equation. You can invert it and solve it; you can solve it in whichever way. [Now I am going to assume that if you have given some more time you will be able to get this].

It is not necessary to write $d\theta_1/dE$, $d\theta_2/dE$ in analytical expression here if you have complicated mechanism and many intermediate species. You can just say I will solve it together and give it to a program and solve it. As long as the program can handle complex numbers, you will get the answer correctly. Here I have written it just to show that it is possible to do and to note that this has come with a product here. It is constant jωΓ, another constant jωΓ plus a constant. In the denominator, you have a square term for ω. Here also, in the denominator we have a square in terms of ω. If I write it in zeros and poles, I should be able to write $d\theta_1/dE$ as something here. I will have P_1, P_2 for the poles. Sometime this is referred to as second order dynamics. That means this equation can have 2 poles, this equation can have 2 poles. They may be identical or different. It depends on the kinetic parameter value. I have given DC potential and it is possible for you to get a second order term here. It will give you 2 time constant. It means, previously we said, if it is a simple straightforward reaction with no intermediate species, you will get a semicircle in the nyquist plot, Z_{im} and Z_{real}. If there is one adsorbed intermediate, we know that we can give something like this, we know we can give something like this, we know it can even go back depending on the mechanism (As shown in the graph in the video). Therefore, it means one more loop is possible, one more time constant is possible; (()) is the time constant. If 2 time constants are possible, it means this is possible. This is possible. This is possible (Refer video). Not with this mechanism; this mechanism will not go back here; but in general 2 time constant means this is possible. This particular mechanism definitely can give rise to:

First capacitance will come, because of double layer capacitance and two inductive loops, one inductive one capacitance where inductive loops comes at the end and capacitance comes before or inductive loops first and then capacitance comes later or 2 capacitance. All this combinations are possible. 1, 2, 3, 4 are definitely possible and we will show examples where it is possible. So we can get expression for $d\theta_1/dE$, $d\theta_2/dE$.

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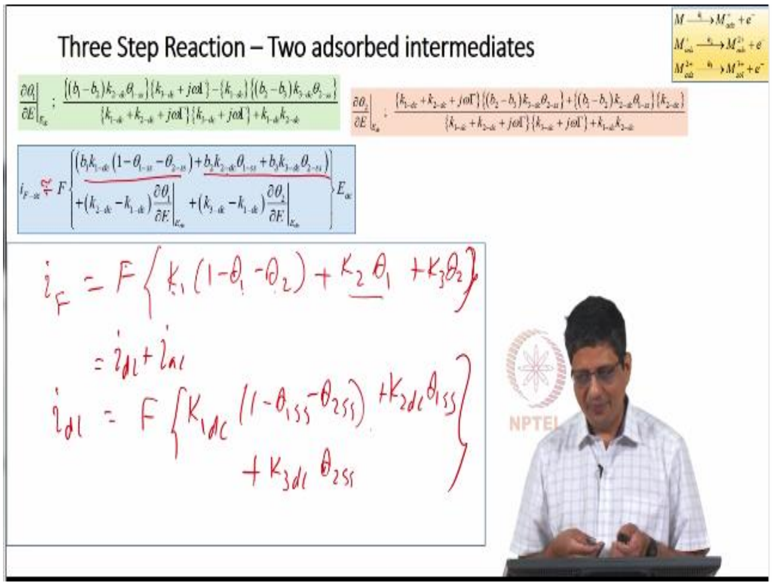

Three Step Reaction – Two adsorbed intermediates

$M \xrightarrow{k_1} M^{+}_{ads} + e^-$

$M^{+}_{ads} \xrightarrow{k_2} M^{2+}_{ads} + e^-$

$M^{2+}_{ads} \xrightarrow{k_3} M^{3+}_{ads} + e^-$

$$\left.\frac{\partial\theta_1}{\partial E}\right|_{E_{ac}} : \frac{\left[\{(b_1-b_2)k_{2\text{-}dc}\theta_{1\text{-}ss}\}\{k_{3\text{-}dc}+j\omega\Gamma\}-\{k_{1\text{-}dc}\}\{(b_3-b_1)k_{3\text{-}dc}\theta_{2\text{-}ss}\}\right]}{\{k_{1\text{-}dc}+k_{2\text{-}dc}+j\omega\Gamma\}\{k_{3\text{-}dc}+j\omega\Gamma\}+k_{1\text{-}dc}k_{2\text{-}dc}}$$

$$\left.\frac{\partial\theta_2}{\partial E}\right|_{E_{ac}} : \frac{\{k_{1\text{-}dc}+k_{2\text{-}dc}+j\omega\Gamma\}\{(b_2-b_3)k_{3\text{-}dc}\theta_{2\text{-}ss}\}+\{(b_1-b_2)k_{2\text{-}dc}\theta_{1\text{-}ss}\}\{k_{2\text{-}dc}\}}{\{k_{1\text{-}dc}+k_{2\text{-}dc}+j\omega\Gamma\}\{k_{3\text{-}dc}+j\omega\Gamma\}+k_{1\text{-}dc}k_{2\text{-}dc}}$$

$$i_{F\text{-}ac} \overset{?}{=} F\left\{\begin{aligned}&\left(\underline{b_1k_{1\text{-}dc}(1-\theta_{1\text{-}ss}-\theta_{2\text{-}ss})}+\underline{b_2k_{2\text{-}dc}\theta_{1\text{-}ss}+b_3k_{3\text{-}dc}\theta_{2\text{-}ss}}\right)\\&+(k_{2\text{-}dc}-k_{1\text{-}dc})\left.\frac{\partial\theta_1}{\partial E}\right|_{E_{ac}}+(k_{3\text{-}dc}-k_{1\text{-}dc})\left.\frac{\partial\theta_2}{\partial E}\right|_{E_{ac}}\end{aligned}\right\}E_{ac}$$

$$i_F = F\{k_1(1-\theta_1-\theta_2)+\underline{k_2}\theta_1+k_3\theta_2\}$$

$$= i_{dc} + i_{ac}$$

$$i_{dc} = F\{K_{1dc}(1-\theta_{1ss}-\theta_{2ss})+K_{2dc}\theta_{1ss}+K_{3dc}\theta_{2ss}\}$$

We can expand the Faradaic current (refer slide or video).

This is the general expression for Faraday current here. I can expand k_1 in $k_{1dc} + b_1E_{ac}$, k_2, k_3, θ_1 and θ_2, expand it, get in Taylor series, truncate it, multiply, throw away all the E_{ac}^2 terms, group all the constant terms and I will get it as $i_{dc} + i_{ac}$, where i_{dc} is going to be same expression but with the DC. This expression will not have any E_{ac}. All the expressions, which have E_{ac}, can be grouped together and I am going to claim that it is going to come like this. This will give you $b_1k_1(1- \theta_1 - \theta_{2ss})$, second will give you $b_2k_2\theta_{1ss}$, third will give you b_3, $k_{3dc}\theta_{2ss}$ and all the θ terms here. When you take the derivative, they will give you variety of terms, but you can group them and then say $d\theta_1/dE$, $d\theta_2/dE$. If you group them and then say here, I am going to substitute for this $d\theta_1/dE$ and $d\theta_2/dE$ from the answers I got from the previous expressions. Then the mass balance equation gives us the expression for $d\theta_1/dE$ and $d\theta_2/dE$.

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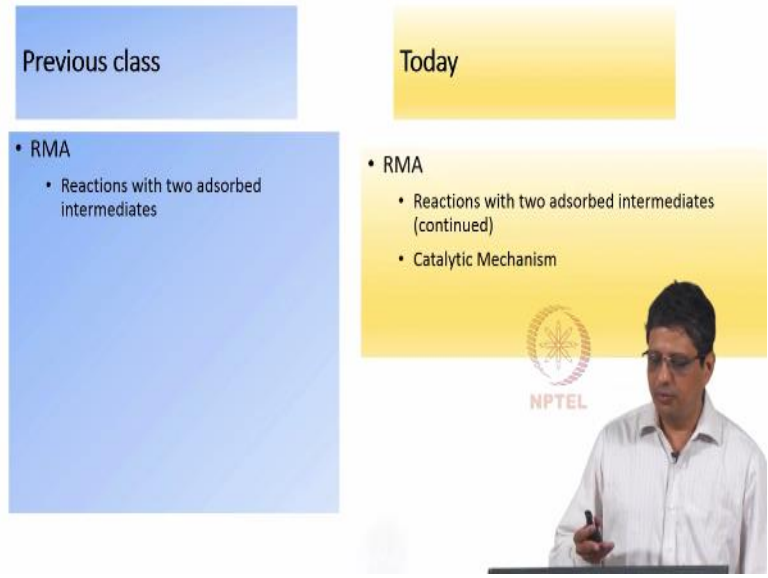

Previous class

- RMA
  - Reactions with two adsorbed intermediates

Today

- RMA
  - Reactions with two adsorbed intermediates (continued)
  - Catalytic Mechanism

Previously, we saw the derivation of equations for reaction with 2 adsorbed intermediates. We will say few more words about certain equations there, what the implications are and then move on to another type of mechanism called catalytic mechanism.

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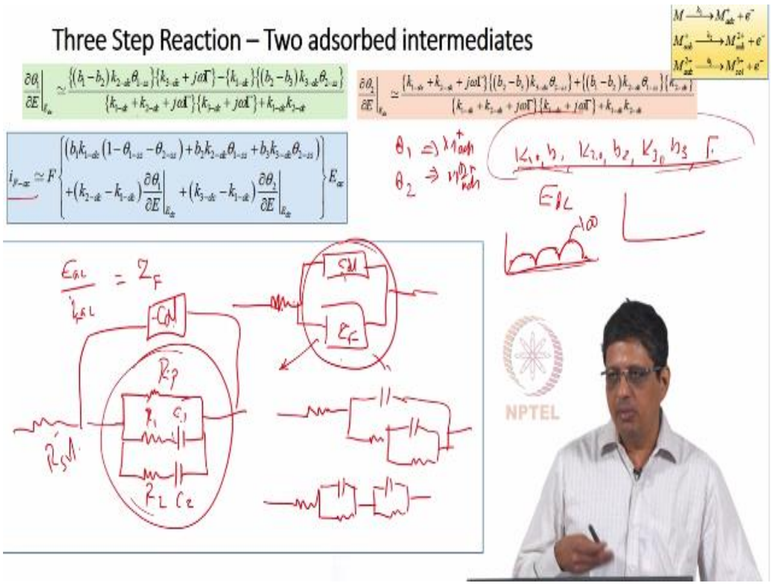

Three Step Reaction – Two adsorbed intermediates

$M \xrightarrow{k_1} M^{+}_{ads} + e^-$

$M^{+}_{ads} \xrightarrow{k_2} M^{2+}_{ads} + e^-$

$M^{2+}_{ads} \xrightarrow{k_3} M^{2+}_{sol} + e^-$

$$\left.\frac{\partial\theta_1}{\partial E}\right|_{E_{ac}} \simeq \frac{\{(b_1-b_2)k_{2-dc}\theta_{1-ss}\}\{k_{3-dc}+j\omega\Gamma\}-\{k_{1-dc}\}\{(b_2-b_3)k_{3-dc}\theta_{2-ss}\}}{\{k_{1-dc}+k_{2-dc}+j\omega\Gamma\}\{k_{3-dc}+j\omega\Gamma\}+k_{1-dc}k_{3-dc}}$$

$$\left.\frac{\partial\theta_2}{\partial E}\right|_{E_{ac}} \simeq \frac{\{k_{1-dc}+k_{2-dc}+j\omega\Gamma\}\{(b_2-b_3)k_{3-dc}\theta_{2-ss}\}+\{(b_1-b_2)k_{2-dc}\theta_{1-ss}\}\{k_{2-dc}\}}{\{k_{1-dc}+k_{2-dc}+j\omega\Gamma\}\{k_{3-dc}+j\omega\Gamma\}+k_{1-dc}k_{3-dc}}$$

$$i_{F-ac} \simeq F\left\{\begin{matrix}\left(b_1k_{1-dc}(1-\theta_{1-ss}-\theta_{2-ss})+b_2k_{2-dc}\theta_{1-ss}+b_3k_{3-dc}\theta_{2-ss}\right)\\ +(k_{2-dc}-k_{1-dc})\left.\frac{\partial\theta_1}{\partial E}\right|_{E_{ac}}+(k_{3-dc}-k_{1-dc})\left.\frac{\partial\theta_2}{\partial E}\right|_{E_{ac}}\end{matrix}\right\}E_{ac}$$

We have seen this before that you can get an expression for this particular reaction, metal going to M_{ads}, metal adsorbed going to M^{2+}_{ads} and that going into solution in the third step. You can get an expression for $d\theta_1/dE$, $d\theta_2/dE$ where θ_1, θ_2 correspond to fractional surface coverage of M^{2+}_{ads}, M_{ads}, and they come in the second order in the denominator. You can write the equations for Faradaic current, expand it and you can get a expression for $i_{F\text{-}ac}$, $i_{F\text{-}dc}$ and you can write this as the ratio of E_{ac}/i_{ac}. Here, $i_{F\text{-}ac}$ is going to be Faradaic impedance and then you would say if you have a small solution resistance, [this is derived assuming solution resistance is not significant], we have a double layer capacitance. You have the Faradaic impedance, substitute for Z_F here, whatever the double layer capacitance is, you substitute for that, you can get the total impedance. As it comes with ω terms in the denominator, product of ω, which you get as ω^2, this can be modeled using a circuit like this. I am going to say this is 2 Maxwell element with capacitor based circuit. This is going to be R_p, this you can denote as R_1 C_1, R_2 C_2. Likewise, you can replace this C with L. As long as we recognize that, it can be positive or negative it does not matter, replace the C with L. Similarly, you can write this in terms of a ladder circuit. Then you will again have the same number of elements; 2 capacitors, 3 resistance arranged in a different manner. The values of capacitance will change when you move from one to another.

All these things represent only the Faraday impedance. The double layer capacitance is in parallel to the Faraday impedance and the solution resistance, is in series to this pair of elements here. What is the value of R_1, what is the value of C_1, R_2, C_2; they are related to the kinetic parameters. They are related to the k_{10}, b_1, k_{20}, b_2, k_{30}, $b_3\Gamma$ and the DC potential at which this is (()) (39.05).

Because k_{1dc}, k_{2dc} etc. will vary with DC. Then you can write R_1, C_1, R_2, C_2, R_P, these 5 elements here in terms of 7 kinetic parameters and 1 DC potential. Now if you take impedance at 1 potential, DC potential only, let us say you get a spectrum, comes like this, you recognize that this can be modeled using a circuit with solution resistance, double layer capacitance and Z_F model like this. Then you can use the circuit with 2 Maxwell elements, one polarization resistance, one solution resistance and double layer capacitance. How many points do you need to get the value of all the parameters here?. You need 7 points, 2 points corresponding to 2 parameters of C_{dl} and $R_{solution}$, 5 points corresponding to the 5 parameters here. If you have 2 unknowns, you need minimum of 2 points to solve.

If you have 5 unknowns in the Faradaic impedance, you need 5 points; one additional point for solution resistance and 1 additional point for double layer capacitance. That is absolute minimum number of points you need. You also recognise using the kinetic expression even if it gives you the DC value E_{dc}, you have 7 kinetic parameters mapped to 5 electrical elements. I will not get a unique solution for kinetic parameters if I take only one spectrum and then try fitting all the parameters. I can get multiple solution, I will get in theory, and I will get infinite number of solutions. If it is a linear equation, linear set of equations, you can solve 3 equations, 3 unknowns. For 2 equations, 3 unknowns, software will tell you that the rank of the matrix is less than 3 and you cannot solve it. When you get nonlinear equation, mostly you have to give an initial value and it will solve, it will come to some local minimum and then say this is the solution. You will not know that there is a problem. This is something that you will have to think before you actually work and get the solution. When I give you kinetic parameters and ask you to calculate the impedance, which is what you have been doing so far, it is like giving you an equation. I can give you a quadratic equation, I can give you one x value and ask you to give me the one y value as long as I give you a b c you can get it. If I give you one pair of x and y and ask you to get a b c, you will tell me that, no this is not sufficient, you need to give me 3 pairs. Likewise, here we have 7 kinetic parameters mapped to 5 electrical elements. If I want to get 7 kinetic parameters, I need at least 2 DC potentials at which I have to get the impedance values. What would happen at 1 DC potential is I will get 5 elements here. There are couple of aspects to this. I need minimum 5 points. I can give 100 points here. As long as you fit it to this circuit; C_{dl} and $R_{solution}$, I need absolute minimum or 7 points. I can give many points. I will still get only 5 elements out of this, 5 elements for Z_F and 2 elements for the $R_{solution}$ and C_{dl}. By giving more number of points at one E_{dc}, I will not be able to get unique value for k_1, b_1, k_2, b_2 etc. You cannot look at the total number of parameters and then say, I have 7 parameters for kinetics, one parameter for C_{dl}, one parameter for solution resistance, and therefore I have 9 parameters in total. If I give 100 points, I can do the regression and get the solution and that is not correct. [May be I will give more concrete example later].

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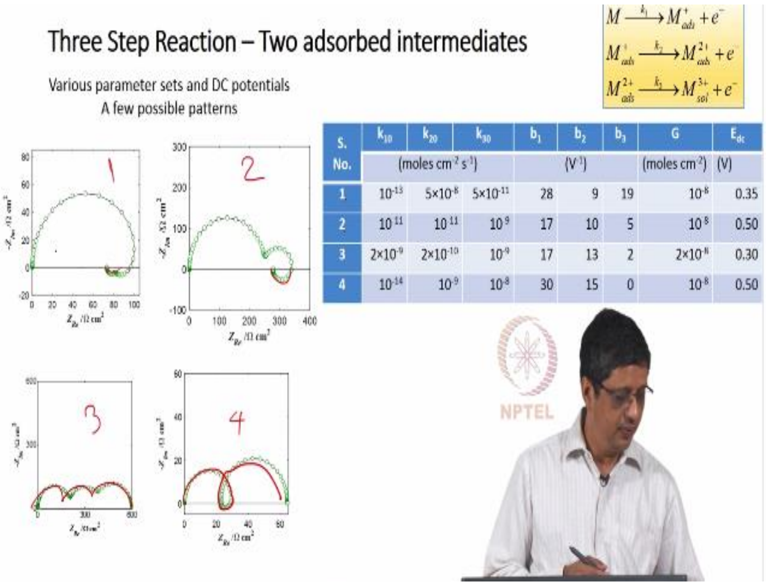

Three Step Reaction – Two adsorbed intermediates

Various parameter sets and DC potentials
A few possible patterns

$$M \xrightarrow{k_1} M^{+}_{ads} + e^-$$
$$M^{+}_{ads} \xrightarrow{k_2} M^{2+}_{ads} + e^-$$
$$M^{2+}_{ads} \xrightarrow{k_3} M^{3+}_{sol} + e^-$$

S. No.	k_{10}	k_{20}	k_{30}	b_1	b_2	b_3	G	E_{dc}
	(moles cm^{-2} s^{-1})			(V^{-1})			(moles cm^{-2})	(V)
1	10^{-13}	5×10^{-8}	5×10^{-11}	28	9	19	10^{-8}	0.35
2	10^{-11}	10^{-11}	10^{-9}	17	10	5	10^{-8}	0.50
3	2×10^{-9}	2×10^{-10}	10^{-9}	17	13	2	2×10^{-8}	0.30
4	10^{-14}	10^{-9}	10^{-8}	30	15	0	10^{-8}	0.50

What I have done is, I have taken that equation, given different set of kinetic parameter values and chosen certain DC values and created the spectrum. You can say 1 capacitive loop and 2 inductive loops here. One capacitive loop, another capacitive loop with inductive loop. This is the first one, second one. Third one I got 1, 2, 3 capacitive loops. For fourth one I got capacitive, inductive and capacitive. [This is just to say that all these things are possible]. If I change the DC potential here, spectrum could be in the same shape or it may be different. [I have not really spent lot of time, I do not know if it possible for one set of kinetic parameters with different DC potential to give all 4 spectrum at different potential. It may not be necessary for this particular mechanism. If we make some variations to this mechanism and add some kinetic parameter, it may be easier to do. I have not tried that. However, the idea is, if you have 2 adsorbed intermediates, it is possible for you to generate 2 capacitance or 1 capacitance and 1 inductance or 2 inductance in whichever order higher frequency, lower frequency range where it manifest itself. This is apart from the first capacitive loop you get at high frequency for double layer capacitance and charge transfer resistance.

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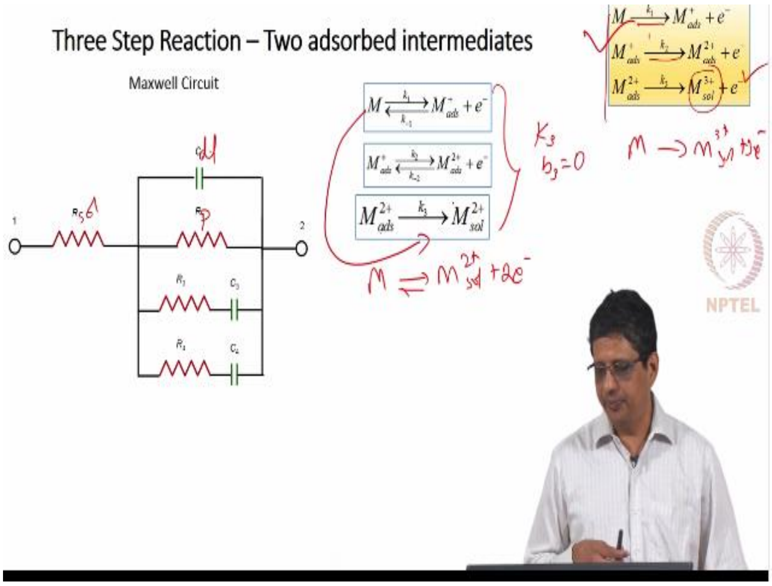

Three Step Reaction – Two adsorbed intermediates

Maxwell Circuit

$$M \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} M^{+}_{ads} + e^{-}$$

$$M^{+}_{ads} \underset{k_{-2}}{\overset{k_2}{\rightleftarrows}} M^{2+}_{ads} + e^{-}$$

$$M^{2+}_{ads} \xrightarrow{k_3} M^{2+}_{sol}$$

$$M \rightleftarrows M^{2+}_{sol} + 2e^{-}$$

K_3
$b_3 = 0$

$$M \xrightarrow{k_1} M^{+}_{ads} + e^{-}$$

$$M^{+}_{ads} \xrightarrow{k_2} M^{2+}_{ads} + e^{-}$$

$$M^{2+}_{ads} \xrightarrow{k_3} M^{3+}_{sol} + e^{-}$$

$M \rightarrow M^{3+}_{sol} + 3e^{-}$

We saw that we can use this circuit; it is going to be $R_{solution}$, C_{dl}, this is R_p in this representation. You can come up with other variance. This is just one example and this is what we have seen before. This is the next variant where I can say first step is reversible, second step is reversible. In all these cases, if you really take it near the equilibrium potential, these have to be reversible. What you assumed is [this irreversible meaning probably it is little away from the equilibrium], the reverse reaction can be neglected.

Third one, look at this; In the original equation; we have said M^{2+}_{ads} goes into M^{3+} and solution. So in solution it is charged with 3+ whereas here only M^{2+}_{ads} goes into solution. This is not just taking this mechanism and making it reversible. First and second step looks similar. However, the third step is actually different. Third step is a chemical step; it does not involve electron transfer therefore k_3 is independent of potential.

Another way to say that is b_3 is 0. What would happen is, current equation will be different, and even the mass balance equation will be different because the reverse reactions are not taken into account. This is only one variant. You can come up with multiple variants of this mechanism to tell that - maybe this reversible I have to take into account. You need to have some idea about the actual chemical reaction or overall reaction.

If you think it is Fe going to Fe^{3+}, you have to come up with this or some variation, where, in solution, it is 3+. If you think it is reaction of Cu going to solution as $CuSO_4$, then you cannot use the 3+ because, we know that Cu does not exist in 3^{+} oxidation state. It has to be based on some idea about what is supposed to be present in the solution phase. What you know here is, for example M going to $M^{3+}_{solution}$ + 3 electron. If this is the overall reaction, you can come up with this mechanism, if the reaction is reversible or irreversible, then you can come up with this mechanism or another variant where you can say this goes via intermediate, in addition, it can directly go in parallel all those things are possible.