Electrochemical Impedance Spectroscopy
Prof. S. Ramanathan
Department of Chemical Engineering
Indian Institute of Technology - Madras

Lecture – 15
Assignment 03

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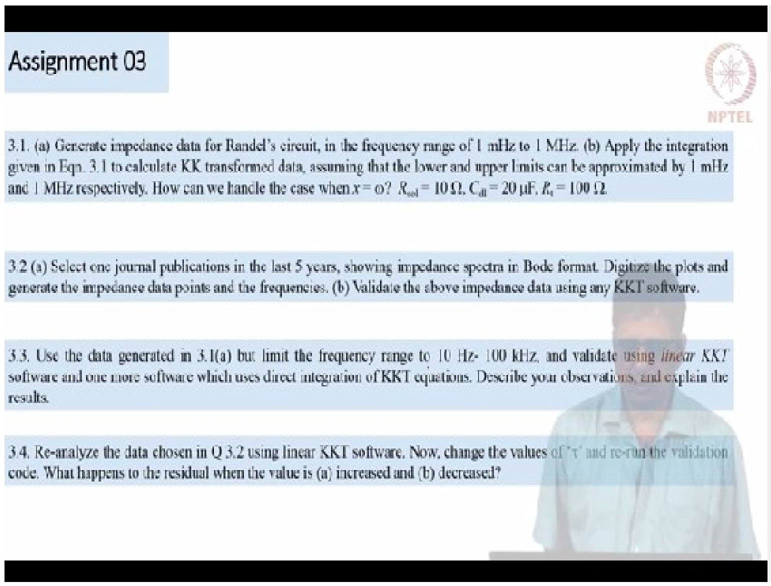

So in today's assignment, I would like you to learn about KKT by doing this homework problem. In the first part,… by now you know what the Randel's circuit is, right? So, (in the) first part, I want you to synthesize the spectrum for a Randel circuit with 10 Ω of solution resistance, 20 μF of double layer capacitance and 100 Ω for charge transfer resistance. I would like you to synthesize frequencies in the range of 1 mHz through 1 MHz.

And although I do not say it explicitly here, you have to do that in log scale and you probably want to do it in frequency spaced at 7 frequencies/decade or maybe 10 frequencies/decade. The next part, [it is a little more involved,], I would like you to write a program to do (the) KKT integration. KKT integration goes from 0 to ∞. Of course, (in practice) you go from low frequency of 1 mHz to 1 MHz, (and) that is good enough.

But you have to write the program, you have to write the equation and then write the program to (perform) that integration. You can use the simple integration (scheme) like trapezoidal integration or, [you know] Simpson rule. (Either one of them is fine). I just want you to try this. And in the KKT equations, you will have a case where x(ω) will come in the denominator. So, when you use the particular ω, I want you to think about how to handle it. It is not that difficult, but I would like you to think about it and then perform this integration.

So, (first) generate the spectrum which will have (the following) data : frequency, real and imaginary part (of impedance). And then, using your program, use the frequency (*f*) and real part ($Z_{Re\text{-}original}$) and transform, and get the transformed part for the imaginary ($Z_{Im\text{-}transformed}$). And compare ($Z_{Re\text{-}transformed}$) with that imaginary that you got from the original simulation($Z_{Im\text{-}original}$). We will call the first set as original [simulation]; (and the) transform data, we will (call it as) KK transform data. Similarly, using the frequency and imaginary data ($Z_{Im\text{-}original}$), integrate this, use these integral equations and then predict the value of real impedance ($Z_{Re\text{-}transformed}$) and then compare with this, original data ($Z_{Re\text{-}original}$).

In the next part, I would like you to just select some publication, [general publication, from good quality journals]; look at the impedance spectrum. If you [have] (can find) Bode plots, that is good. You should learn how to digitize data. There are free software available to help you do this. This will be useful not just in this course, (but) in general (for other research activities as well). So you should do this. Digitize the data, so you have magnitude *vs.* frequency and phase versus frequency. Or real *vs.* frequency and imaginary vs. frequency.

Then I would like you to subject this to KKT. You can use your own program or you can use any of the freely available program or a commercial software, it is fine. You cannot use complex plane plot data and digitize it and get this because you will need frequency data as an input to the KKT program. Now the third part, what I want to do is this. Although you have generated data from 1 mHz to 1 MHz. Let us just pretend that the data is available only from 10 Hz to 100 kHz. Now you can use different methods of applying KKT.

In one method, I want you to use integration, actual integration equations. It could be something that is written by you, it could be something that is available in a commercial program, it does not matter. But I would like you to try a method where equations are used and actual integration is performed. Second, I would like you to try the software, Linear KKT, that is available for free.

Now, when I use truncated set of data, there is going to be difference (in the results), based on whether the KKT evaluation is performed by integrating that equations or whether it is performed by using measurement model approach or Linear KKT. So, what *is* the difference? I would like you to actually try and see. (Then, I want you to repeat the same exercise with the data that is taken from publication)

If you use "Linear KKT" vs. if you use "equations and integration of those equations", do you see any difference? So, this is also helpful for you to learn what is a good way to validate the data.

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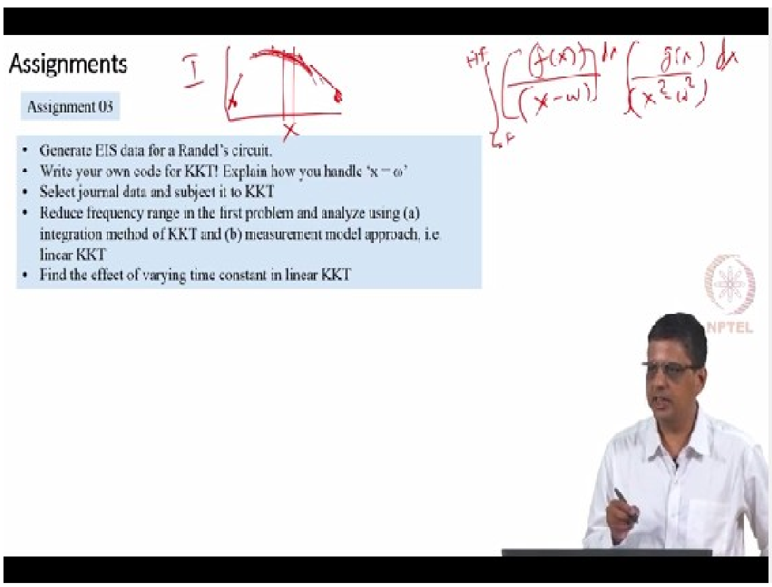

Third part, maybe I was expecting "little more than what I should" from most of you, [but it is alright], so generate a data and then I wanted you to write the KKT code; and explain how you will handle the case where x=ω because you have a case where; you have an integral with (x- ω) in the denominator. 0 to ∞, of course, (it) goes from "low frequency" to "high frequency".

So this you can call it as integrand. There are many ways of handling it. 1. if you know the function, you can use L'Hospital rule and get these results. But we do not know the function. [We just say that (we don't know the function), of course, we do know the function (in this particular example) because we are generating it here using particular circuit. But generally, you will get impedance data. That is all. If you know the function (that was used to generate the impedance, you probably do not need to bother about this (KKT validation)].

2. We do not know the function, we get impedance data but given each data, you can calculate the integrand at those values. So, if you calculate the integrand as a function of x, it will go like this: At one point, you are going to have $x=\omega$. You cannot calculate ~~it~~ (the integrand). But you can use interpolation, that is, simplest way. Next, you can fit it to a curve and then use interpolation meaning linear interpolation.

3. Fit it to a curve, then artificially say that this can be represented by a quadratic function and then I will use L'Hospital rule; fit it to a curve where numerator part is fitted to a curve, denominator is taken and then you can do this.

(Since integration) can smoothen out some of the fluctuations, even the simplest method will give you reasonable result.

4. At the end points, you will have to use extrapolation. So when you say x=low frequency or high frequency, you will have to use extrapolation. (At all other points) you will be able to use interpolation, and in all cases, it will work reasonable well. If you are not able to handle, that is (fine) but I would have liked you to try actual integration.

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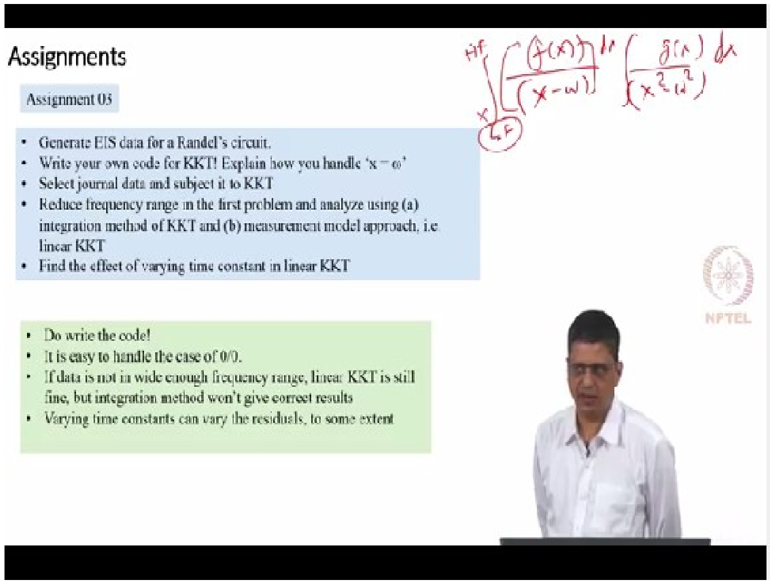

I think only 2 of you tried. Select the journal data and subject it to KKT, just for you to have an idea of how to handle (the situation) when you get your own data. If you reduce the frequency range artificially, saying that "we have not taken data at the full range" or "it is noisy at the low frequency; therefore, we had to neglect it"; then Linear KKT will give us correct information on whether the data is KKT compliant or not.

When you use actual integration, if the low frequency is not low enough, we are not really giving the correct input. Therefore, we will not get the correct result. In this case, we had taken the data which is actually KKT compliant. But we will not know it because we are not using the integration properly. We are not giving the limits properly. We are not approximating the 0 and infinity limits correctly.

Linear KKT will still handle this case; or any other equivalent approach of fitting (will hande this). And if you vary the time constant, there will be some variation in the residue. That is all, I want to (show you).