Elementary Electrochemistry
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Lecture 27
Variation of Conductance with Concentration

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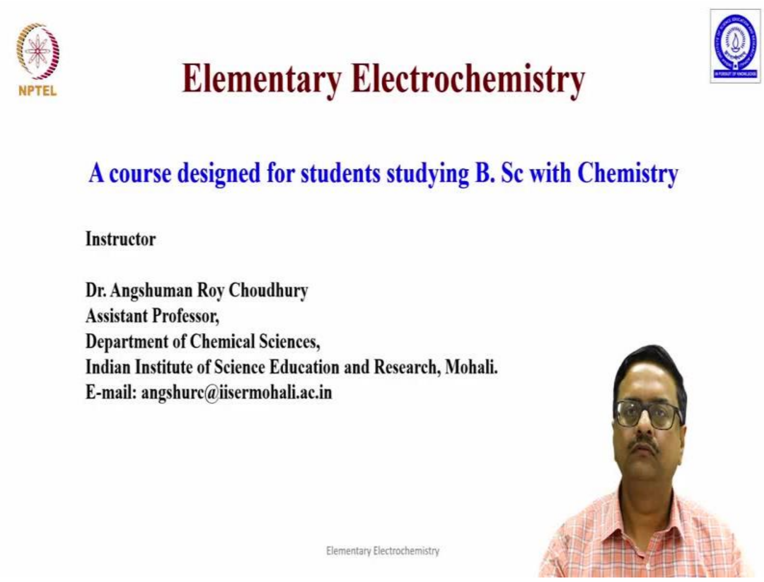

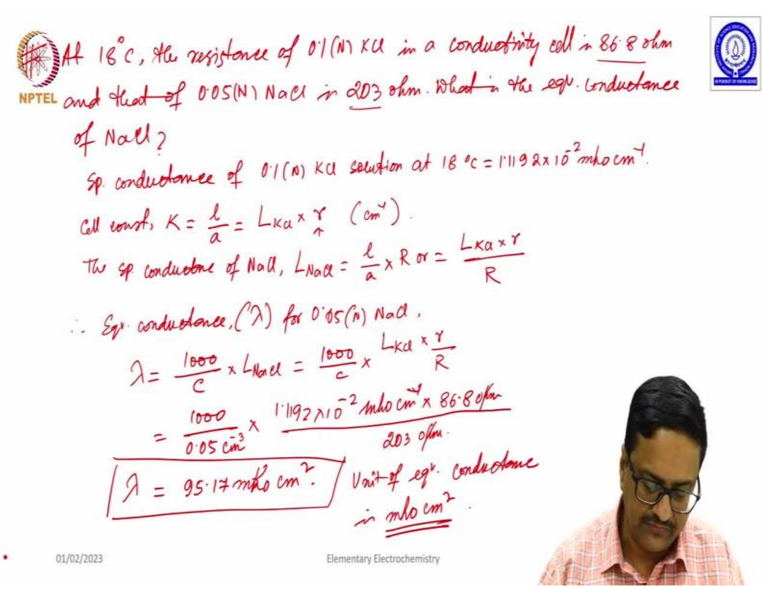

Welcome back to the course entitled Elementary Electrochemistry. In the previous lecture, we have discussed about the determination of conductance, specific conductance and equivalent conductance. And if you remember, I had given you a simple problem to work out, which is this one. So, as I said, we need the value of the specific conductance of 0.1 normal K Cl solution at 18 degrees centigrade, which we can take from the table as 1.119 into 10 to the power minus 2 mho centimeter inverse.

And what we know is that cell constant that is k is called l by a is equal to L K Cl into the corresponding resistance r and r has unit ohm, L has unit mho or ohm inverse second inverse, so this K will have unit centimeter inverse. And the specific conductance of Na Cl that is L Na Cl is equal to l by a into R or L K Cl into small r by capital R, that small r is the resistance of the solution of K Cl and capital R is the resistance of Na Cl.

So, one can calculate the equivalent conductance that is lambda for 0.05 normal Na Cl using the following equation that is lambda equal to 1000 by C into L Na Cl which is then equal to 1000 by C into L K Cl into small r by capital R. So, then one can easily put the values 1000 by 0.05 centimeter to the power minus 3 cubic centimeter into 1.1192 into 10 to the power minus 2 moh centimeter inverse into 86.84 divided by 203 ohm.

So, this get canceled and from this centimeter 2 to the power minus 3 and centimeter inverse we have centimeter square. So, the value turns out to be 95.17 moh centimeter square. So, what we get is that the unit of equivalent conductance is moh centimeter square. So, this you should remember that the units of conductance specific conductance and equivalent conductance are not same, because they have different physical significance physical meaning as a result the units are also different.

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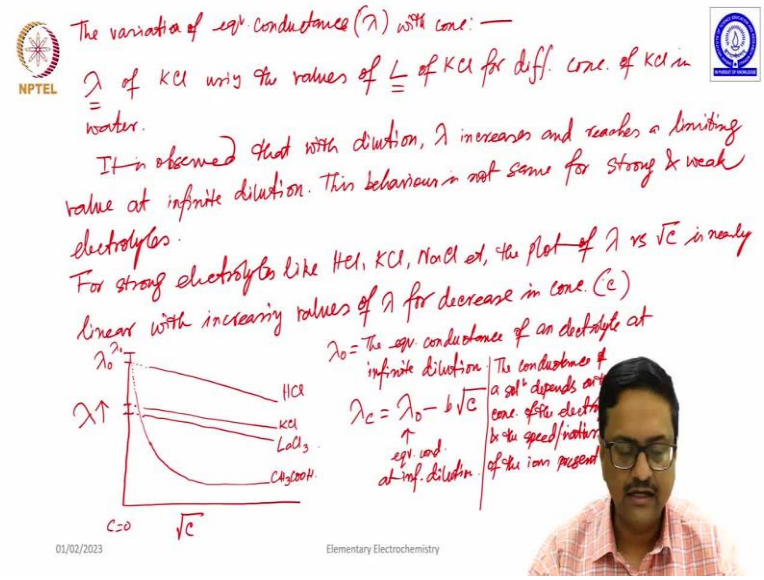

So, now in this class we will start discussing about the variation of equivalent conductance that is lambda with concentration, one can calculate the values of lambda of K Cl using the values of L of K Cl for different concentration of K Cl in water. So, if you do that if you remember that we had given you a table for 3 different concentrations and we had 3 different values of L, so from that one can calculate the value of lambda is that calculation to you see that there is a difference there is a significant change in lambda, what is observed?

It is observed that with dilution lambda increases and reaches a limiting value infinite dilution and this behavior is not the same for strong and weak electrolytes. For strong electrolytes like H Cl, K Cl, Na Cl, etc. the plot of lambda versus square root of concentration is nearly linear with increasing values of lambda for decrease in concentration that is decrease in the value of c. So, what is observe the experimental values, if you try to plot the values of lambda for different electrolytes with square root of c we see that for H Cl, the straight line is like this, for K Cl it is like that, some lanthanum chloride it is like this.

So, now, when we try to extrapolate this two a concentration c equal to 0 it reaches a value. So, the value at c equal to 0 is denoted as lambda 0. So, this lambda 0 is the extrapolated equivalent conductance of a particular salt solution at infinite density. Lambda 0 is the equivalent conductance of an electrolyte at infinite dilution. So, when you see this kind of plot it looks like it is following a straight line which is lambda c equals lambda 0 minus some concentration with some constant b square root of c, this is called the equivalent conductance at infinite dilution.

Now, what we know is the conductance of a solution depends on the concentration of the electrolytes and the speed that is the nature of the ions spirit. So, when we start thinking about it what we see is that in case of weak electrolytes like acetic acid the graph or the plot changes significantly, for weak electrolytes we see a graph like that, which tries tends to go up in this manner. So, when you try to extrapolate into the concentrations c equal to 0 it triggers again some value lambda 0.

So, that is the lambda 0 of say acetic acid. So, it is very clear that when we have strong electrolyte, the behavior of equivalent conductance is nearly a straight line with respect to change in concentration, whereas, when you have a strong weak electrolyte like acetic acid, then the nature of the plot changes. So, this dilution experiment we will be demonstrating during the experimental section. So, from that I just explained what experiment we will be doing during this experimental session.

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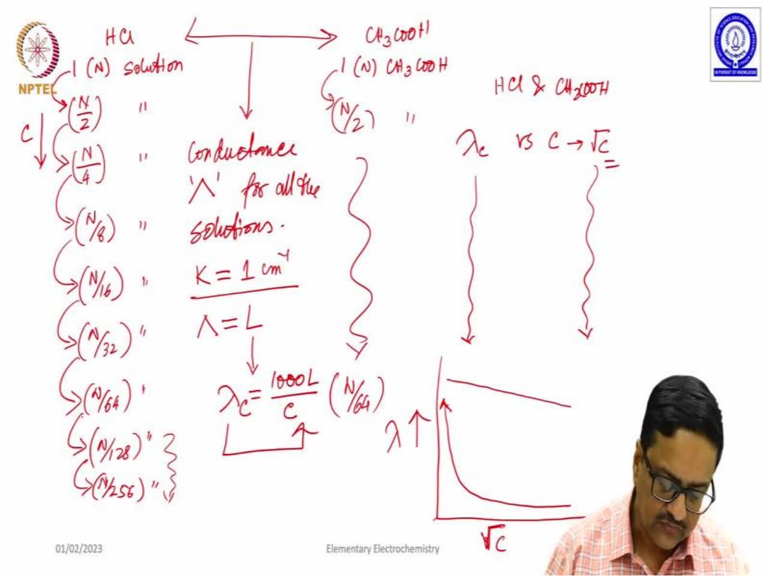

So, we will be taking 2 types of solutions H Cl and acetic acid, we will take one normal H Cl solution and one normal acetic acid solution in 2 volumetric flasks and using very standard burette 50 ML burette, we will prepare exactly half dilute that is N by 2 solution, then from that again by half dilution we will prepare N by 4 solution, from that we will prepare N by 8, from that we will prepare N by 16, from that we will have N by 32 and then again N by 64. And then if somebody wants to continue you can go down to N by 128 and then N by 256 ths depends on how many solutions you want to measure.

But what happens is for very-very dilute solutions, the resistance increases significantly and then the measurement of resistance using the standard device becomes difficult. So, we may not be able to determine the conductance of these solutions during the experiment, which I have to do and then to demonstrate, we will see what happens, I am just explaining what the experiments we are planning. So, like that you will do N my 2 acetic acid way down to N by 64 acetic acid solution.

So, what we will measure in these 2 cases 2 different sets of solutions, we will measure the conductance lambda for all these solutions and we will be using a conductivity cell of cell constant equal to 1 centimeter inverse so that whatever conductance we measure is directly converted to specific conductance L and from those L's using the value of the concentration of the solutions, we will calculate the values of lambda C, lambda C is nothing but 1000 L by C. So, using this expression what we have is a table of lambda C versus C which then can be converted to the square root of C.

So, we will have values of lambda C for one normal solution to a lowest value and we will have this for both H Cl and acetic acid and then we will try to plot those values of the equivalent conductance versus square root of C and we will verify the plot which we have drawn in the previous slide that is lambda versus square root of concentration this experiment is called the validation of Ostwald dilution law and this is one of the very important experiments in electrochemistry to determine the nature or behavior of strong and weak electrolyte. So, by doing this experiment one can identify whether one electrolyte should be considered as a strong electrolyte or it has to be considered as one of the weak electrolytes.

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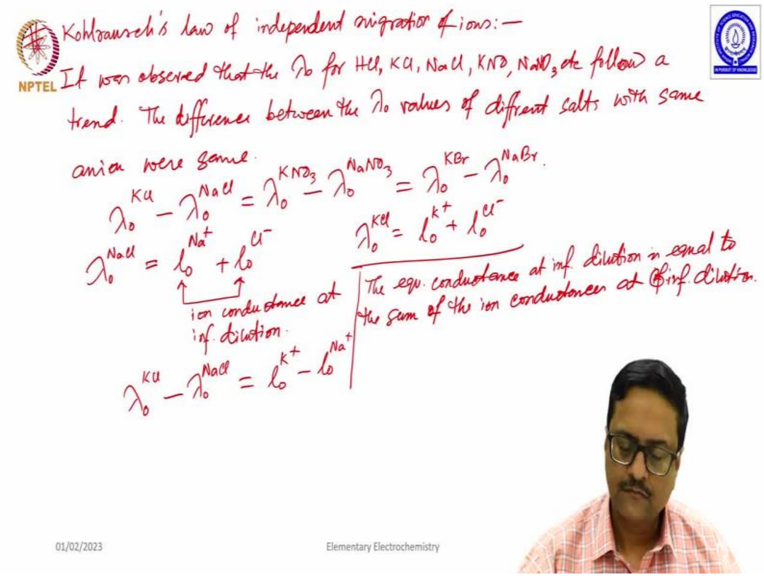

Now, I will just introduce you to the another aspect of this ion conductivities which is named after Kohlrausch's, Kohlrausch's law of independent migration of ions. It was observed that the lambda 0 for K Cl, lambda 0's for H Cl, K Cl, Na Cl, K NO 3, Na NO 3, etc. follow a trend, what is the trend? The trend is the difference between the lambdas 0 values of different salts with same anion where that is lambda 0 K Cl minus lambda 0 Na Cl is equal to lambda 0 K NO 3 minus lambda 0 Na NO 3 equal to lambda 0 K Br minus lambda 0 Na Br.

So, from this observation Kohlrausch's proposed that when we write lambda 0 Na Cl we are actually meaning that there is some l 0 Na plus and l 0 for Cl minus that is these are called the ionic conductances or simply ion conductances at infinite dilution and the values are constant. That means, lambda 0 K Cl can be written as l 0 K plus l 0 cm minus.

So, when you do the subtraction lambda 0 K Cl minus lambda 0 Na Cl it simply turns out that you are doing a subtraction of l 0 of K plus to l 0 of Na plus. So, from this what was proposed is that the equivalent conductance at infinite dilution is equal to the sum of the ion conductances at infinite dilution.

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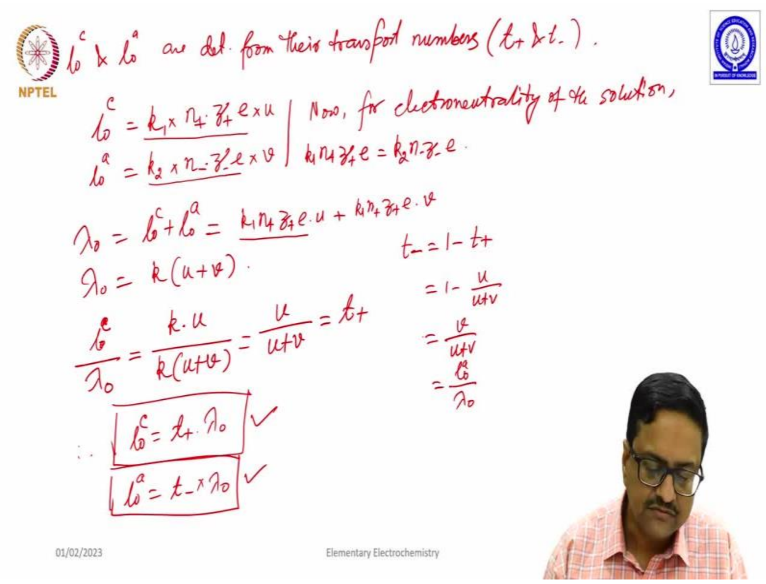

So, now the values of l 0 cation and the value of l 0 anion are determined from there transport numbers that is t plus and t minus. So, what is the value of l 0 cation it is nothing but some constant k 1 into the number of anions that is n plus into the charge of the cation that is z plus, e into u the speed of cation. Similarly, l 0 anion is another constant k 2 into n minus z minus e into v. Now, for electroneutrality of the solution the product k 1 n plus z plus e should be equal to k 2 n minus z minus e.

So, when we try to calculate the value of lambda 0, which is nothing l 0 cation plus 1 0 anion then we can do this by doing k 1 n plus z plus e into u plus again, instead of k 2 n minus z minus e, we write k 1 n plus z plus e into v which is equal to a constant. Suppose this quantity is a constant k into u plus v. So, lambda 0 is k into u plus v. So, now, if I try to do a simple math, that is the ratio of l 0 cation by lambda 0, I think we should write lambda 0 as subscript 0 equal to lambda 0 cation is this quantity which is k into u divided by k into u plus v, which is equal to u by u plus v.

And from our earlier knowledge of transport number u by u plus v is nothing but the transport number of cation. Therefore, l 0 c is nothing but transport number of cation multiplied by lambda 0 of that particular electrolyte. Similarly, l 0 anion is equal to the transport number multiplied by lambda 0 p minus, because you will see p minus is equal to 1 minus p plus that is 1 minus u by u plus v that is equal to v by u plus v, which is then simply equal to l 0 anion by lambda 0. So, we can use these equations for determinants of all conductances for different electrolytic solutions.

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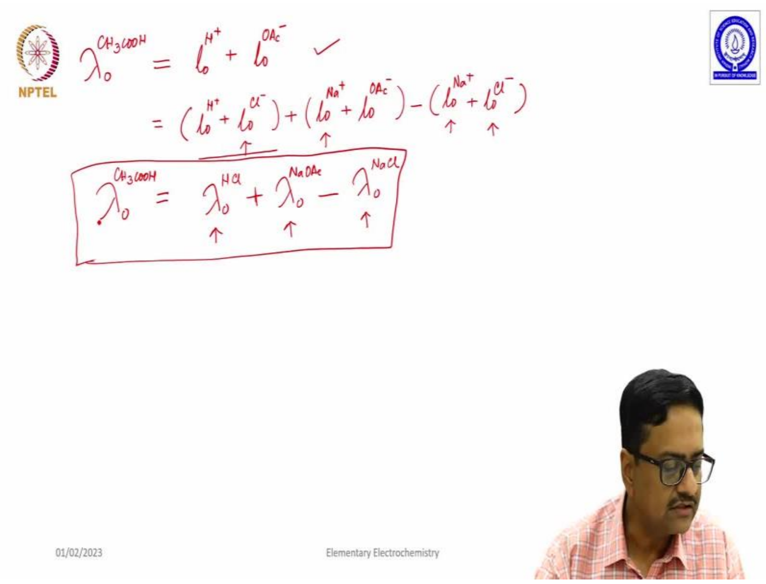

So, using this concept, one can easily determine the value of equivalent conductance infinite dilution for any other electrolyte, which are not known or new or maybe one of the weak electrolytes. So for example, if you want to determine the equivalent conductance infinite dilution for acetic acid, which is CH 3 COOH, in terms of ion conductances, one can write it as l 0 of H plus plus l 0 of acetate and ion. So, now, the values from of l 0 for H plus and OH minus can be rearranged like this, l 0 of H plus plus l 0 of Cl minus plus l 0 of Na plus plus l 0 of O Ac minus minus l 0 of Na plus and l 0 the of Cl minus. So you see, we have added l 0 for Cl minus subtracted that we have added l 0 the for Na plus and subtracted that and this equation remains the same.

So, this first term is nothing but lambda 0 for H Cl plus the second term is lambda 0 for sodium acetate and the third term is lambda 0 from of Na Cl. So, if one determines the equivalent conductance at infinite dilution for these 3 strong electrolytes H Cl, sodium acetate and sodium chloride, then by doing a simple mathematics, some addition and subtraction of these 3 quantities, one can easily calculate the value of lambda 0 for acetic acid.

So, using this law of ion conductivities or the Kohlrausch's law of ion conductances one can easily determine or calculate the equivalent conductance at infinite dilution for any electrolyte for example, acetic acid, formic acid or any other weak electrolytes. So, we will end this lecture here and we will start from here in the next class. Thank you.