Elementary Electrochemistry
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Lecture 28
Ionic Mobilities in terms of ion Conductivities

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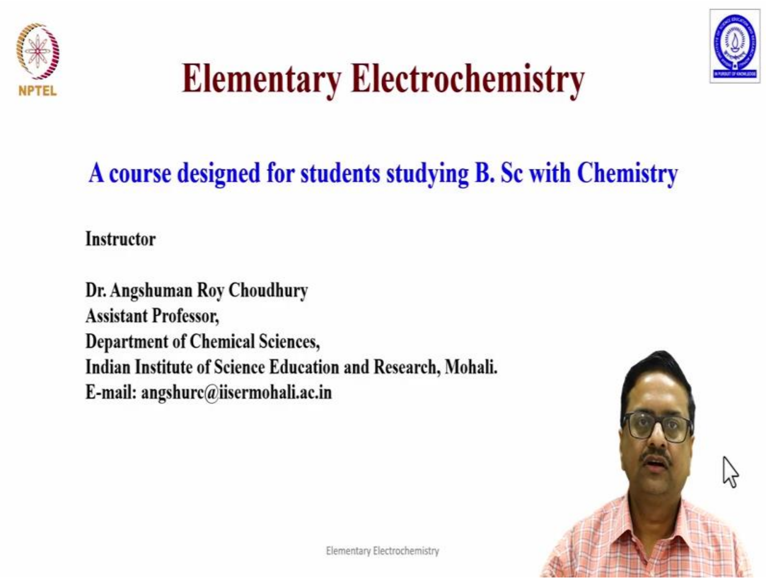

Welcome back to the course entitled Elementary Electrochemistry. In this course, in the previous lecture, we have discussed about the ionic conductivities and based on the limiting ion conductivity is for different ions and then the corresponding limiting conductivity of the electrolyte that is the equivalent limiting conductivity or equivalent conductivity at conductance at in dilution. We have discussed how one can calculate the value of equivalent conduct insert infinite dilution for some unknown electrolyte which may be strong or a weak electrolyte.

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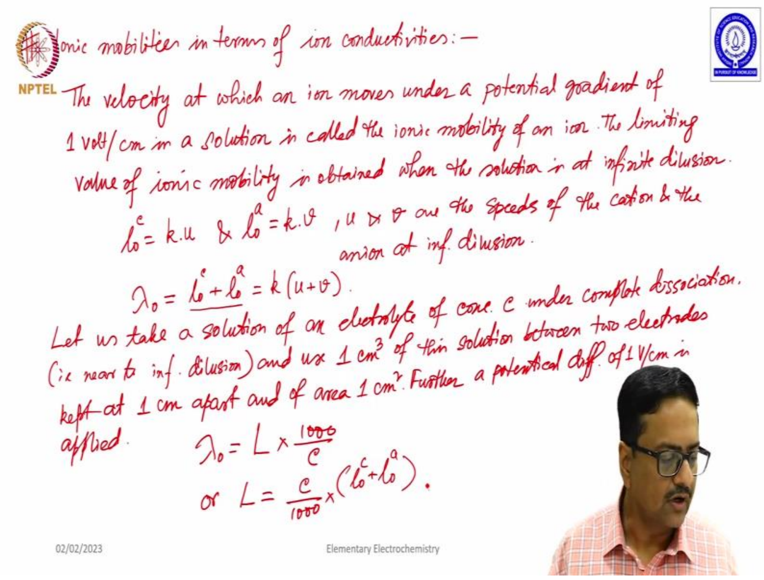

So, in today’s lecture, I am going to discuss about the ionic mobilities in terms of ion conductivities. The velocity at which an ion moves under a potential gradient of 1 volt per centimeter in a solution is called the ionic mobility of an ion. The limiting value of ionic mobility is obtained when the solution is at infinite dilution. So, one can write that 0 0 cation is equal to some constant k into u and l 0 anion is equal to the same constant k into v where u and v are the speeds of the cation and the anion infinite dilution. So, the lambda 0 is nothing but l 0 c plus l 0 a. So, it is nothing but k into u plus v this is what we have seen in the previous class.

Now, let us take a solution of an electrolyte of concentration c under complete dissociation that is near to infinite dilution and use 1 cubic centimeter of this solution between two electrodes kept at 1 centimeter apart and of area 1 centimeter square. Further a potential difference of 1 volt per centimeter is applied. So, what we know from our previous equations is that lambda 0 is equal to l into 1000 by c or simply l is equal to c by 1000 into lambda 0 is nothing but l 0 c plus l 0 a.

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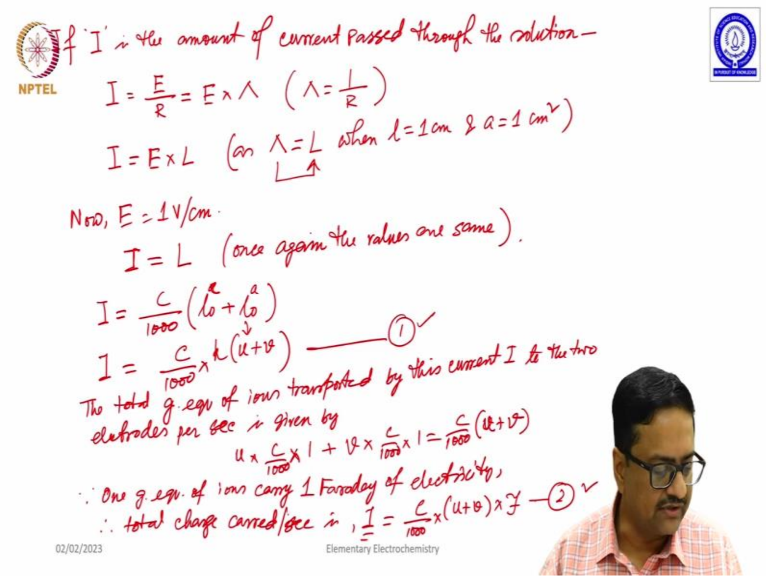

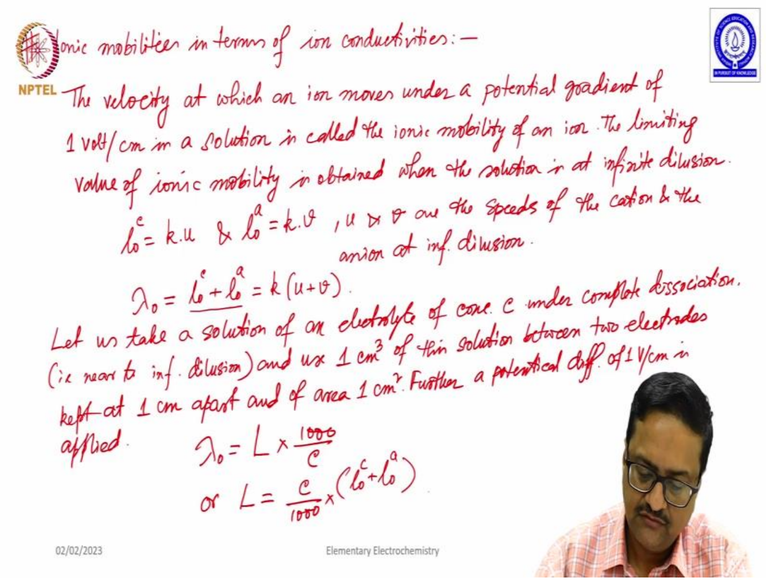

So, now if I is the amount of current passed through the solution then I equal to E by R which is equal E to into lambda where lambda is equal to 1 by R. So, now, one can further simplify I equal to E into L as capital lambda becomes equal to l when small l that is the path length is equal to 1 centimeter and the area of the cross section is 1 centimeter square. This equality is a numerical equality that is these values are same, but the units are different if you have remember.

Now, in this case E is equal to 1 volt per centimeter. So, therefore, one can write I equal to L once again the values are same do not confuse that the unit of L and I are same. So, I if it is ampere, so, Ls whatever the value of Ls it is in ampere. So, now, one can further write that I equal to L which is nothing but c by 1000 into l 0 C plus l 0 a or simply equal to C by 1000 into k into u plus v. Let us take this equation as equation number 1. We have written this from the previous page which is here.

Now, the total gram equivalent of ions transported by this current I to the two electrodes per second is given by u into C by 1000 into 1 that is the 1 volt per second and v into C by 1000 into 1. So, that is equal to C by 1000 into u plus v. Now, since 1 gram equivalent of ions carry F Faraday or rather 1 Faraday of electricity so, total charge carried is carried per second is I equal to C by 1000 into u plus v into F. This is the equation number 2. So, now, we see that equation number 1 and 2 has same quantity on the left hand side.

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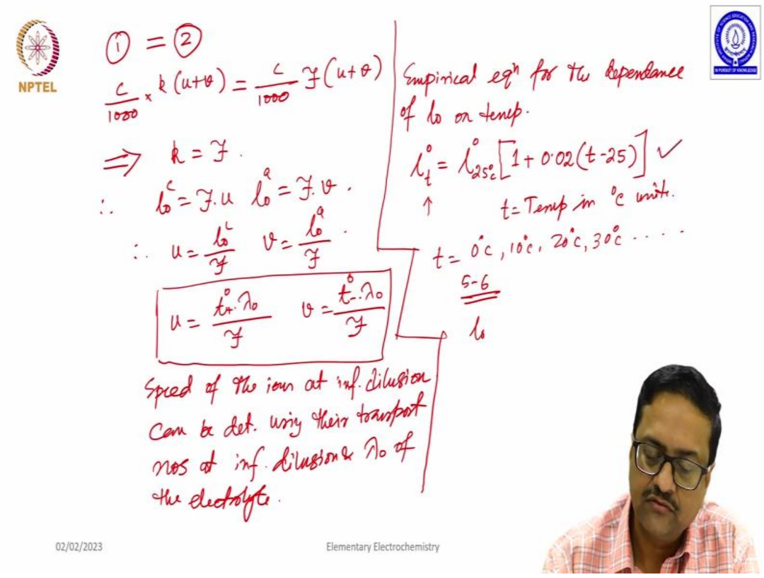

So, one can equate this equation 1 and 2 and write the following C by 1000 into k u plus v which is equal to C by 1000 F u plus v which essentially means that the value of k is nothing but F that is the quantity of electricity passed in columns. Therefore, one can write l 0 c equal to F into u l 0 a is equal to f into v. So, therefore, you can write u equal to l 0 c by F, v equal to l 0 a by F and then one can further replace this l zeroes by transport numbers u equal to t plus at infinite dilution into lambda 0 by F and v equal to T minus at infinite dilution into lambda 0 by F.

So, the speed of the ions at infinite dilution can be determined using their transport numbers at infinite dilution and the corresponding lambdas 0 of the electrolytes. So, the value of ion conductivity depends on certainly on the transport number of the ions and the transport number further depends on the concentration sorry, transport number depends on the temperature as well. So, what happens is the ionic conductivity is that is l 0 c or l 0 a depends on temperature.

So, based on several experimental determinations of ion conductivities of various ions we have there is we have arrived that in an empirical equation for the dependence of l 0 on different temperatures on temperature. What is the relationship? l 0 or rather l t 0 is equal to l 25 degrees c 0 multiplied by 1 plus 0.02 multiplied by t minus 25 where t is the temperature in degree centigrade unit. This is an empirical relationship which has been arrived that based on various experimental data for the ion conductances of a particular iron at different temperature.

So, you do the experiment at various temperatures t maybe this t can be 0 degrees centigrade, 10 degrees centigrade, 20 degrees centigrade like that 30 degree centigrade and you measure some 5 to 6 experiments at 5 to 6 different temperatures and based on the trends of those values of l 0 at all these temperatures this equation can be arrived at.

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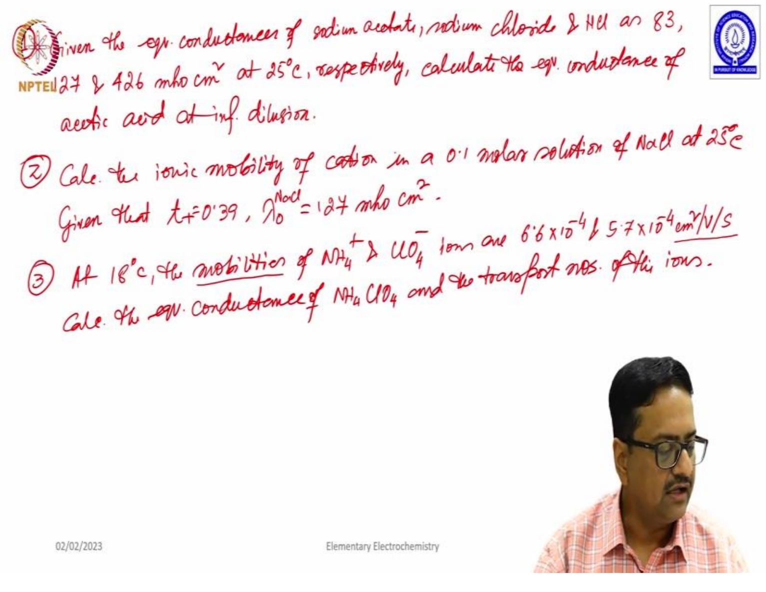

So, with this I will be giving you a few problems to solve based on the topics which we have learned in last couple of classes. So, the first problem is the following. Given the equivalent conductances of sodium acetate, sodium chloride and HCl as 83, 1.27 and 426 in mole centimeters squared unit at 25 degrees centigrade respectively. Calculate the equivalent conductance of acetic acid at infinite dilution. This is a straightforward question from the lecture that we have delivered already in the previous class.

Calculate the ionic mobility of cation in a 0.1 molar solution of NaCl at 25 degree centigrade given that t plus is equal to 0.39 and lambda 0 for NaCl is 127 mole centimeters squared. And the third problem is the following at 18 degrees centigrade the mobilities of ammonium and ClO 4 minus ions are 6.6 into 10 to the power minus 4 and 5.7 into 10 to the power minus 4 centimeter squared per volt per second. Calculate the equivalent conductance of ammonium perchlorate and the transport numbers of the ions.

You see here the unit of the mobility is given here. So, you had to take care of the unit while doing any calculation related to electrochemistry rather you should keep in mind about the unit calculation for all the physical chemistry related problems because the physical quantities come with the correct appropriate unit. Any calculation without indicating their unit is meaningless. Therefore, I would emphasize that you should get yourself associated with the units of various physical quantities that we are discussing in this course. Because when you write your final examination, marks will not be awarded if the units are not correct.

So, we will stop here at this point and we will continue in the next lecture discussing about some of the applications of conductance measurements. Thank you.