Elementary Electrochemistry
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Conductance and Conductivity of the Solution

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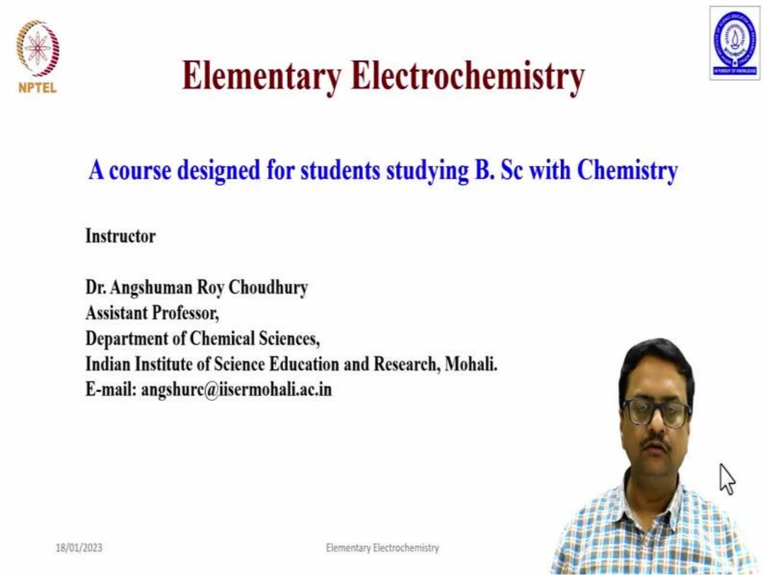

Welcome back to the course Elementary electrochemistry. In the previous four weeks, we have discussed about the potentiometric methods, we have talked about electrochemical cells and learned how the electrochemical cells can be used for practical applications. And we have also demonstrated some of the experiments based on potentiometric measurements.

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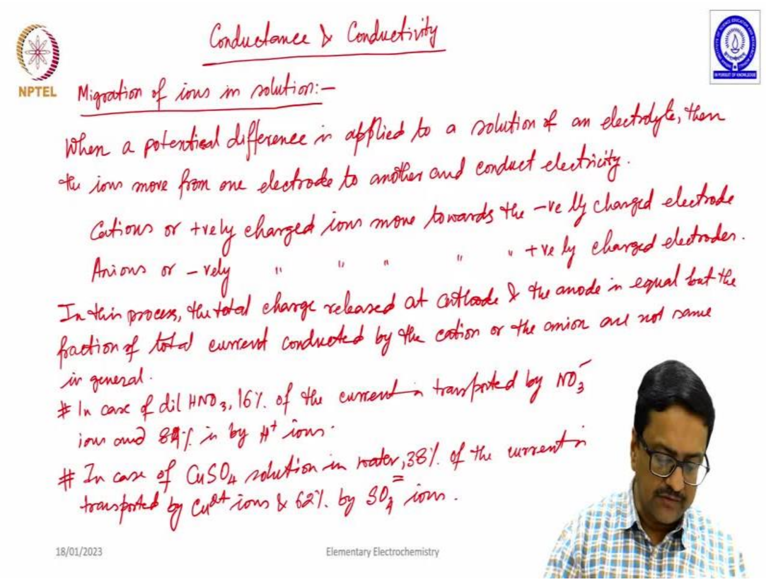

In the current week onwards, we are going to talk about the conductance and conductivity of solutions. So, when we talk about conductance or conductivity of solution of a an ionic solution, we try to understand how the ions migrate. So, we need to discuss a little bit about the migration of ions in solution.

So, when a potential difference is applied to a solution of an electrolyte then the ions move from one electrode to another and conduct electricity. So, what we know about this movement, we know that cations or positively charged ions move towards the negatively charged electrode and the anions or the negatively charged ions move towards the positively charged electrodes.

So, in this process the total charge released at cathode and the anode is equal but the fraction of total current conducted by the cation or the anion are not same in general. What is observed is in case of dilute nitric acid 16 percent of the current is transported by NO 3 minus ions and at 84 percent is by H plus ions. Similarly, in case of copper sulphate solution in water about 38 percent of the current is transported by CO 2 plus ions and 62 percent by So 4 2 minus ions.

So, from these observations it is clear that the conduction of current is dependent completely dependent on the nature and the charge of the ion that is there in the corresponding ions that are formed by the electrolytic dissociation of the electrode by the ionic compounds. So, in case of nitric acid H plus nitrate ions, they have different capability of transportation of electricity and copper sulphate copper and sulphate ions have different capability of transporting the electricity.

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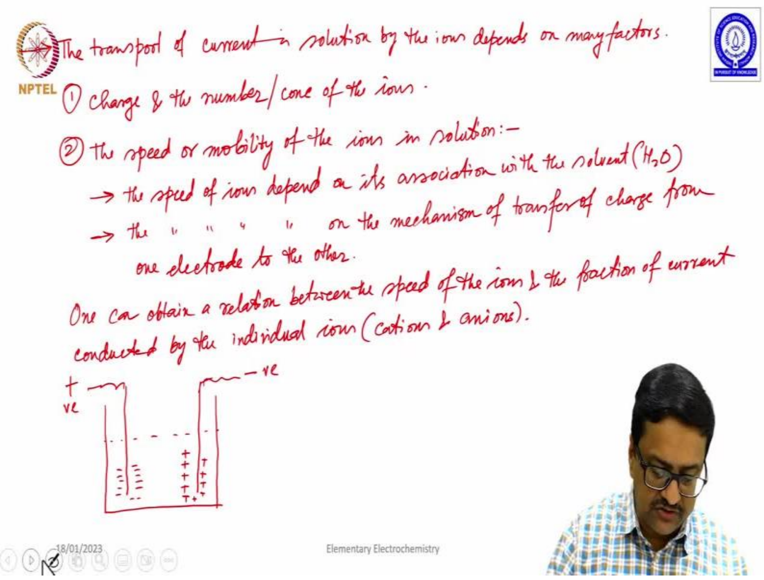

So, the transport of current in solution by the ions depends on many factors which are the factors that one can think of? The first factor is the charge and the number or I should mention say that the concentration of the ions. And number two the speed or mobility of the ions in solution. Now, this speed or mobility of ions in solution further depends on that is the speed of ions depend on its association with the solvent in this case water. And also the speed of ion depend on the mechanism of transfer of charge from one electrode to the other. We will discuss these two points in a short while.

So, what one can do is, one can obtain a relation between the speed of the ions and the fraction of current conducted by the individual ions that is cations and anions. So, if you assume that an electrolyte is taken in a cell with two electrodes dipped in that, one positive and one negative electrode, and you have some electrolyte, while you have both anions which are attracted towards the positive electrode and the cations, which are more attracted towards the negative electrode.

So, in this condition when we electricity is passed, we can try to determine the relationship or we can try to obtain a relationship between the speed of ions and the fraction of current conducted by the individual ions.

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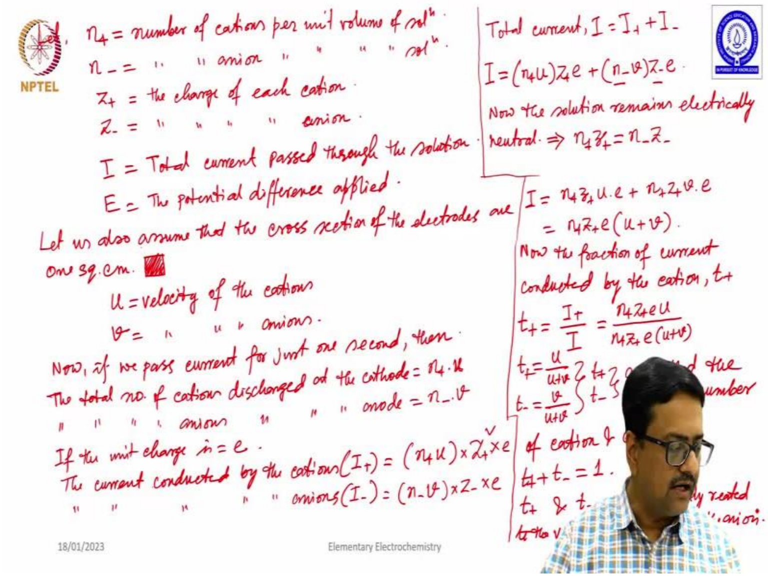

To do that, we need to consider a few quantities, let n plus be the number of cations per unit volume of solution n minus be the number of anions per unit volume of the solutions. Similarly, z plus is the charge of each cation and z minus is the charge of each anion. Let also be I be the total current passed through the solution, and E be the potential difference applied. Let us also assume that the cross section of the electrodes are one square centimeter that is 1 centimeter by 1 centimeter is the size of the electrode.

And we also take that u is the velocity of the cations and v is the velocity of the anions. So, now if we pass current for just 1 second then the total number of cations discharged at the cathode will be what? n plus into u, why? Because there are n plus number of cations present in 1 cubic centimeter volume of solution and when you pass it for 1 second the velocity of cations is u centimeter per second.

So, whatever solution cations are present within a distance of u centimeter from the electrode will be able to come and the concentration being n plus per cubic centimeter total number is n plus u n into u. So, total number of anions discharged at the anode will be simultaneously n minus into v.

Now, if the unit charge is equal to e that is each cation is carrying a charge e then the current conducted by the cations that is I plus is equal to n plus u into z plus into the charge of electron. Similarly, the current conducted by the anions which is equal to I minus is nothing but n minus v into z minus into e. Now, I will try to complete this derivation here so, that the entire derivation is there in one slide.

So, total current I is equal to I plus plus I minus, current conducted by the cation plus current conducted by anion is the total current that was conducted. So, if you try to do I plus and I minus we write I equal to n plus u into z plus e plus n minus v z minus e, z minus into e.

Now, the solution remains electrically neutral, what does it mean? The electrically neutrality means, the charge carried by n plus amount of cations is n plus z plus is equal to n minus z minus. So, we replace n minus z minus by n plus z plus and write I equal to n plus z plus u into e plus n plus z plus v into e. So, one can take out n plus z plus e, I have inside then u plus v that is the total current.

So, now, the fraction of current conducted by the cation which is represented as t plus that is the fraction of current, we write t plus is equal to I plus by I, because total current conducted by cation divided by the total current. So, I plus is nothing but this one, n plus z plus e u and total current is n plus z plus e into u plus v. So, one can easily see that t plus is equal to u by u plus v.

Similarly, t minus is equal to v by u plus u by u v. So, what are these two quantities t plus and t minus? These quantities t plus and t minus are called the transport number of cation and anion, and what we see t plus plus t minus if you do that you end up getting 1. So, it is easy to calculate transport number of one if you can calculate the transport number of the other because the sum of those two is 1 and these transport numbers t plus and t minus are directly related to the velocity of the cation and the anion.

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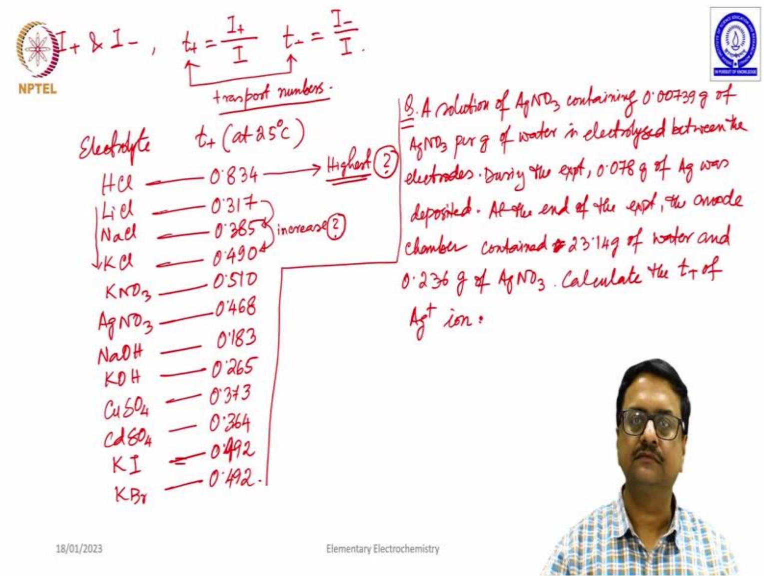

So, we have learned that the current that is conducted by the cation and the current conducted by the anion which are I plus and I minus the fraction of current conducted by the cation is t plus which is nothing but I plus by I and t plus t minus is nothing but I minus by I and these are called the corresponding transport numbers. So, now I am going to give a list of transport numbers for the cations for a series of electrolytes this numbers are taken from a textbook but we will require these numbers in future so I am listing them that is why I am listing them out.

Electrolyte and the corresponding transport number of the cation at 25 degrees C, for HCL it is 0.834, for Li Cl it is 0.317, for Na Cl this is 0.385, for K Cl it is 0.490, for K NO 3 it is 0.510, Ag NO 3 it is 0.468, Na OH it is 0.183, K OH it is 0.265, Cu SO 4 it is 0.373, Cd SO 4 it is 364, potassium iodide it is 0.492 and K Br it is 0.492 once again.

So, now what we see is that among all that this is highest, the question is why? And then you see from H plus to lithium to sodium to potassium there is a steady increase, the question is why? These two questions are leaving for you to try to sort out till we come back in the next lecture, where we will discuss the reason behind these observations. When you go down the period from H plus to lithium to sodium to potassium, you see there is a difference and we want you to find out the reason for that difference.

In addition to this, I want to give you a mathematical problem to solve because you already know a little bit about the electrochemistry and Faraday's laws of electrolysis. So, here from that those concepts you have to solve this problem.

A solution of Ag NO 3 containing 0.00739 gram of Ag NO 3 per gram of water is electrolyzed between the electrodes. During the experiment 0.078 gram of Ag was deposited. At the end of the experiment the anode chamber contained 23.14 gram of water, 0.236 gram of Ag NO 3. Calculate the transport number that is t plus of Ag plus ion. So, I would like to conclude this lecture here and we will continue from here in the next class, thank you.