Elementary Electrochemistry
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Experimental Methods to Determine Transport Number

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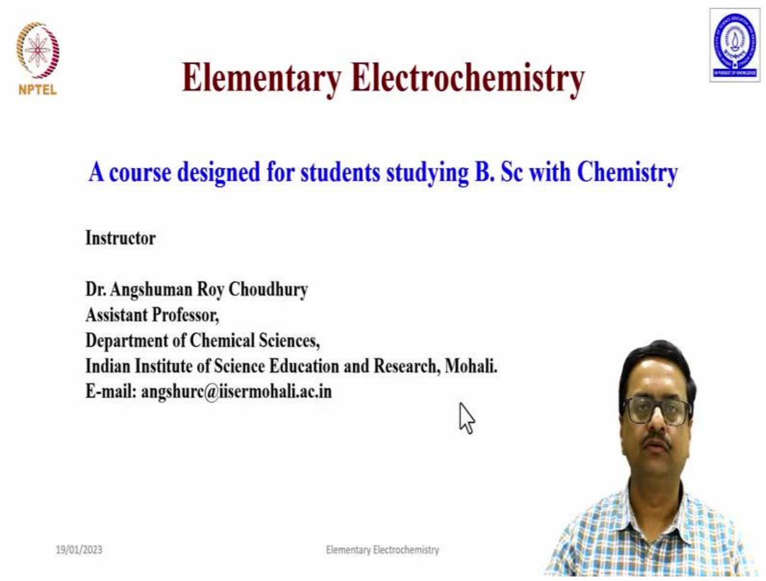

Welcome back to the course entitled elementary electrochemistry in the previous class, we have discussed about the transport number and we have derived the expression for transport number in terms of fraction of current carried by the cation by the total current pass through the solution. So, in this class today we are going to discuss about the migration of ions using a particular example, and then we will discuss a method for the determination of transport numbers.

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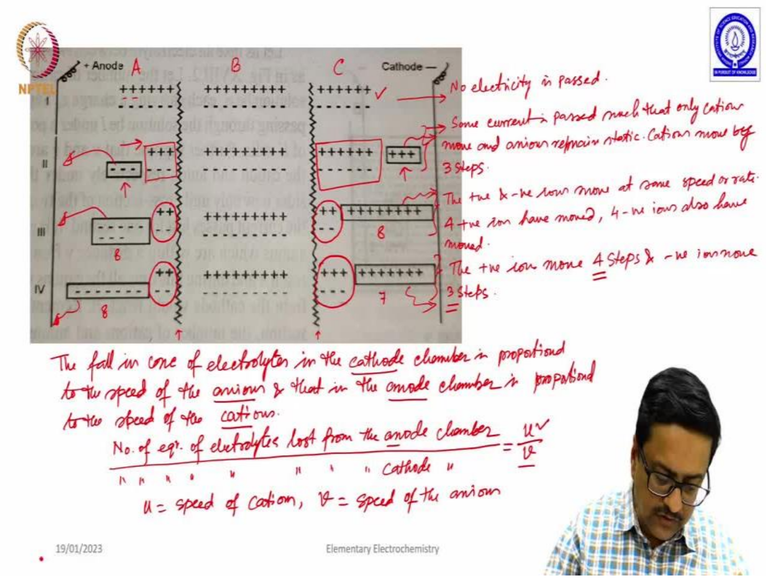

So, here I have a figure to demonstrate 4 different situations that one can think of inside an electrochemical system. So, I have taken some ions, you can see we have some cations marked as plus and some anions marked as minus, you can assume them as H plus and Cl minus for simplicity. And I have divided this electrochemical cell divided these cell into 3 imaginary components with imaginary boundary lines like this, just for our easy understanding.

Suppose, this chamber I call it as A, this is the middle chamber B, and this is the cathode chamber C. So, we have 3 chambers anode B and cathode, B is the middle chamber. And when we have not passed any electricity, this is the condition 1 no electricity is passed. So, in this condition, the concentration of ions in both chambers anode and cathode is same, there is no difference in the concentration you can see that there are 6 cations and there are 6 anions in each of these left and right side chambers that is chambers A and C.

Then suppose this case of number 2, some current is passed such that only cations move and anions remained static. Suppose, cations moved by 3 steps. So, what we see is in chambers C we have excess of 3 cations and because of movement of 3 cations from left to right from A to C although the anions did not move we have 3 excess anions on the chamber A. To maintain electro neutrality of these chambers, these ions cannot stay like this, they need to get discharged to the corresponding electrodes.

And as a result what we see is that the concentration of the cations and anions that is the concentration of the electrolyte in chamber C has not changed it remained as before whereas, the concentration of cations and anions has reduced in the chamber A, which is close to the anode. This difference has come because the two ions one of them has moved and the other ion did not move at all. So, this is a second condition of assumption. Then you consider this third condition, some current is passed as before the cations positive and negative ions move at same speed or rate.

So, if we assume that 4 cations have moved positive ions have moved then 4 anions also have moved, so what is the result? Result is on the chamber C we have 8 excess cations and 8 excess anions on the chamber A. Once again as usual to maintain the electro neutrality of these imaginary chambers, these ions need to get discharged at the corresponding electrodes and once it is discharged the chambers have this and that amount of electrolyte.

So, now, you see when the cation and anion they have moved to the, their respective directions in equal amount the change in concentration in the chamber A and C is same. So, the final concentration at chamber A and chamber E becomes same. Then if we consider the fourth condition where the positive ions move 4 steps and negative ions move 3 steps, which means 4 positive ions have moved from A to B, simultaneously 4 move from B to C by that process 3 anions have moved from C to A, C to B and then B to A, as a result, we have 7 excess cations on the chamber C and A and 8 times on the chamber A.

As usual this gets deposited this gets discharged to maintain the electro neutrality of the entire solution and the corresponding chambers. As a result, what we see is now the concentration of ions in two different chambers, the chamber A and chamber C are different and this difference comes because of the difference in the speeds of those ions or the rate at which they cross the boundary is different. So, by understanding this in theory, it is evident that the fall in concentration of electrolytes in the cathode chamber is proportional to the speed of the anions and that in the anode chamber is proportional to the speed of the cations.

So, one can write the number of equivalents of electrolytes lost from the anode chamber and divided by the number of equivalents of electrolytes lost from the cathode chamber is equal to u by v, where u equal to speed of cations and v equal to the speed of the anions, because here it is anode chamber is cations, so this is u and cathode chamber is proportional to anion that is why it is v.

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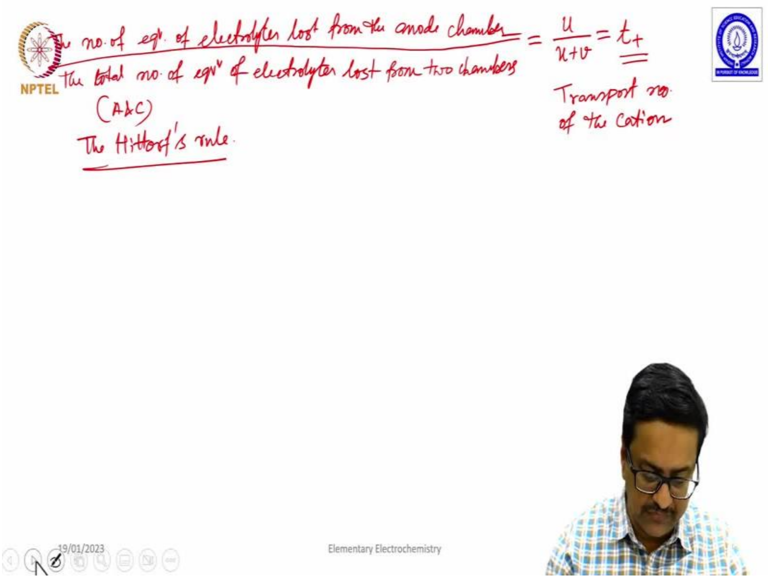

So, one can write that the number of equivalents of electrolytes lost from the anode chamber divided by the total number of equivalents of electrolytes lost from two compartments or chambers A and C together is equal to u by u plus v which is nothing but what we learned in the previous class is t plus the transport number of the cation.

So, this rule is called the Hittorf's rule. Using this Hittorf's rule and the subsequent experimental method one can easily determine the transport numbers of various cations and anions by taking appropriate care. So, in the next slide I am going to demonstrate I am going to describe one of the methods of determination of transport number using Hittorf's tube.

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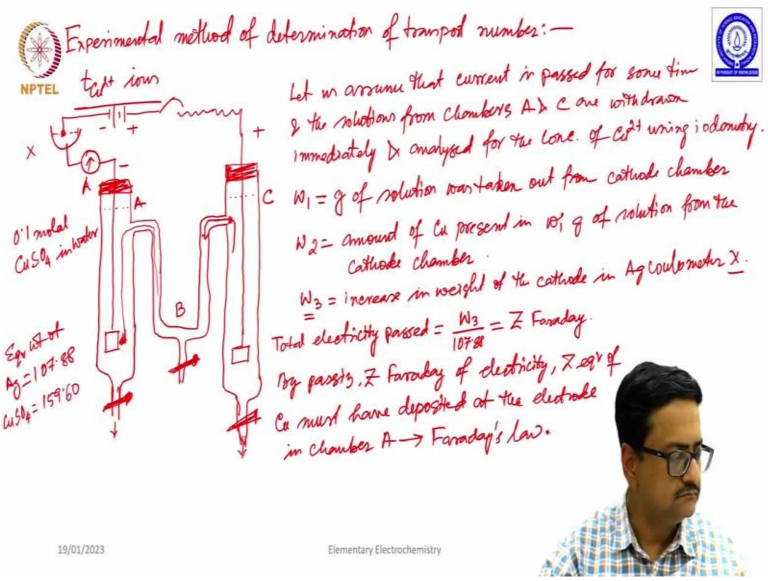

Experimental method of determination of transport number. Say we want to determine the transport number of CO 2 plus ions. So, for that what we need is a particular device which is specially made I am trying to draw it as good as possible. See what I am trying to draw is a tube two tubes are connected by a central joint like this and each tube has an opening at the bottom through which the solution can be taken out without disturbing the entire solution after the experiment is over, and the concentration of the contents can be measured. So, you have stopcock at each of these ends to drain out solution.

What we have taken here is a 0.1 modal Cu SO 4 in water and then we have inserted two electrodes on two sides and we have copper sulphate filled up to this so that the ions can move in this direction like this and come there and so on. So, then what we have here is an ammeter which measures the amount of current that is passed it is connected to a silver coulometer x and that silver coulometer is further connected to a set of electric power supply or that is battery and we have a switch and some resistance and connected here.

So, this is the positive end of the battery this is negative and so, this is plus and this is minus. So, what will happen is, copper ions will get deposited here. So, copper will move from this side to that side.

So, what we should be able to do is after finishing the experiment, we should drain this solution from bottom from both the chambers A, B and C and analyse the concentration of copper present in these 3 chambers and from that concentration we should be able to determine the transport number of copper 2 plus. In this method, we need to ensure that the copper ions do not just diffuse, copper ions only move during the passage of electricity.

So, let us assume that current is fast for some time and the solutions from chambers A and C are withdrawn immediately and analysed for the concentration of CO 2 plus using iodometry method. So, after analysis suppose we get that, w 1 gram of solution was taken out from cathode chamber and after analysis we find that w 2 is the amount of copper present in the w 1 gram of solution from the cathode chamber.

And w 3 is the increase in weight of the cathode in silver coulometer x we will use this as a standard. What we know? We know that equivalent weight of silver is 107.88 and that of Cu SO 4 is 159.60. So, from this quantity w we can calculate that total electricity passed is equal to w 3 by 107.88 that is suppose z Faraday. So, by passing z Faraday of electricity z equivalence of copper must have deposited at the electrode in chamber A this is Faraday's law.

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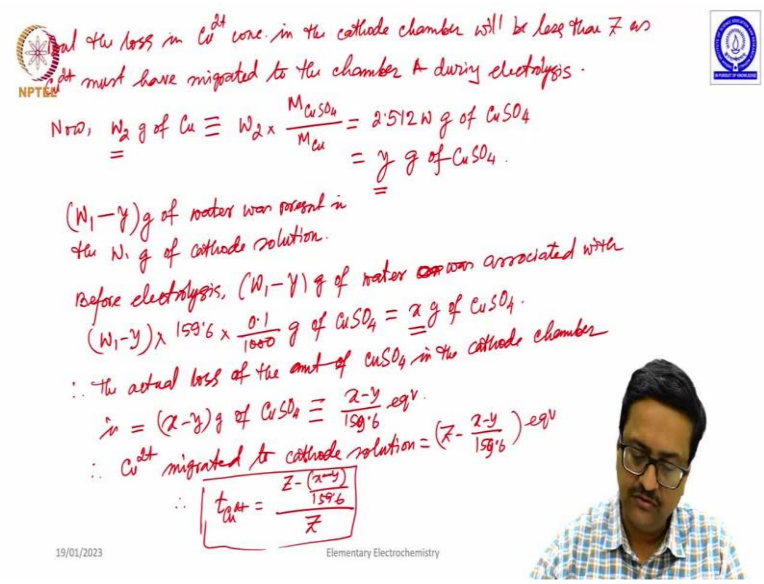

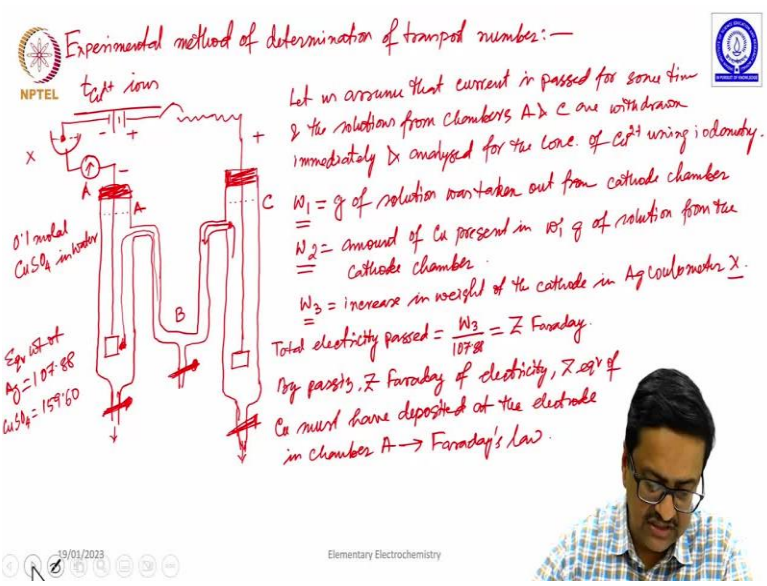

But the loss in CO 2 plus concentration in the cathode chamber will be less than z as CO 2 plus must have migrated to the chamber A during electrolysis. Now w 2 gram of copper is equivalent to w 2 into M Cu SO 4 by M Cu that is molecular weight of copper sulphide by molecular weight of copper is equal to 2.512 w gram of Cu SO 4 which we write as y gram of Cu SO 4.

So, when we analyse the cathode chamber we got w gram of copper, which corresponds to y gram of copper sulphate. And if you remember we had w 1 gram of copper cathode solution which was removed so y w 1 minus y is the amount of gram of water was present in the w 1 gram of cathode solution.

Now before electrolysis w 1 minus y gram of water was associated with w 1 minus y into 159.6 into 0.1 by 1000 gram of Cu SO 4, let us assume to be equal to x gram of Cu SO 4 afford. Therefore, the actual loss of the amount of Cu SO 4 in the cathode chamber is equal to x minus y in gram of Cu SO 4 which is equivalent to x minus y by 159.6 equivalence, correct. Therefore, CO 2 plus migrated to cathode solution during electrolysis is nothing but z minus x minus y by 159.6 equivalence. Therefore, the transport number of CO 2 plus is simply z minus x minus y divided by 159.6 divided by z.

So, once we know the values of w 1, w 2 and w 3 in this way we take out w 1 gram of the solution, we analyse the amount of copper present which is w 2 and we measure the amount of silver deposited which is w 3, once you get those 3 masses using this method, you can calculate the value of y. And similarly, after doing this you can calculate the value of x also and you can easily calculate the transport number of copper 2 plus. So, I conclude here and we will continue from here in the next class. Thank you.