Elementary Electrochemistry
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Experimental Method to Calculate Transport Number

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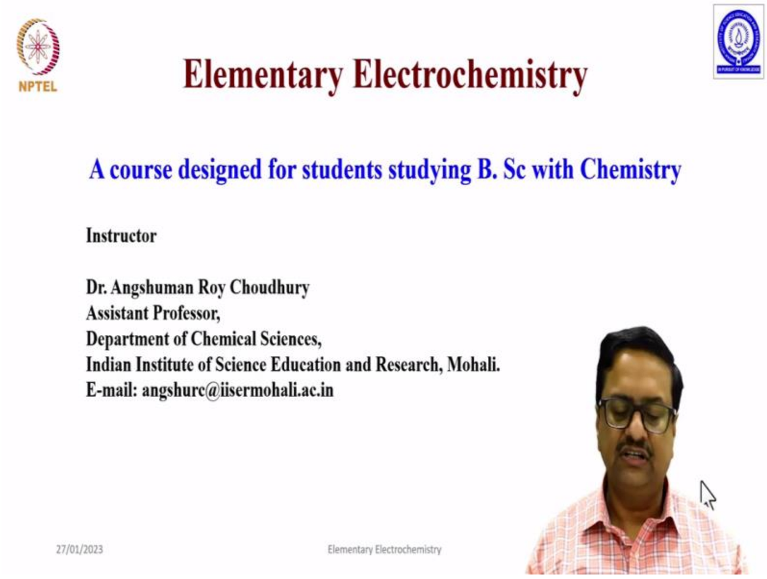

Welcome back to the course Elementary Electrochemistry. In the previous class we started discussing about Hittorf's rule and simultaneous determination of the transport number using some experimental methods. So, in the previous lecture we talked about Hittorf's tube and we learned how to calculate or how to determine the transport number of a cation using three chambers Hittorf's tube. So, today we are going to discuss about another method for the determination of transport number.

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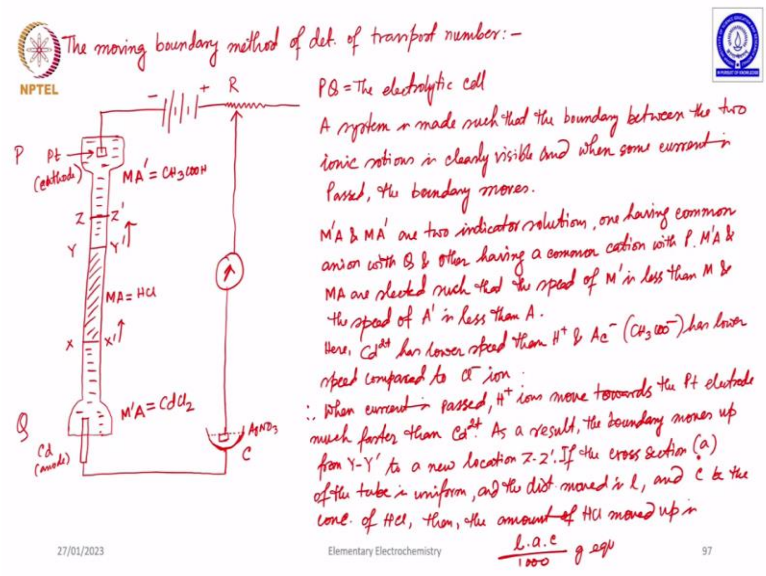

So, this is called the moving boundary method of determination of transport number. So, in this method we will be using a different type of an electrochemical setup which I am going to draw here and we will continuously explain what I am drawing. I have a glass tube which is reasonably long glass tube with two ends fact like this for the introduction of the corresponding electrodes.

So, we have a platinum cathode here connected to some set of cells and with a resistance varies like this and this is platinum and this end you can understand is minus plus and this is plus and you have another electrode on this side which is made up of cadmium. It is anode and that is cathode. This is connected through a coulometer which you know as it is used to determine how much amount of electricity is passed.

This coulometer is having another electrode for conduction and you have silver nitrate solution in this to determine how much silver gets deposited when you pass current and you have ammeter here and this resides on a sliding resistance here. So, the PQ which is here is the electrolytic cell in which we will be taking the solutions of different ionic compounds to determine the corresponding transport number.

So, in this electrolytic cell a system is made such that the boundary between the two ionic solutions is clearly visible and when some current is passed the boundary moves. So, in this tube electrolytic cell PQ we will take two sets of compounds M prime A and M A prime these are two indicator solutions, one having common anion with Q and other having a common cation with P.

And M prime A and MA are selected such that the speed of M prime is less than M and the speed of A prime is less than A. So, we have M A prime here and M prime A there where M prime A is Cdcl2 and M A prime is acidic acid and the solution MA is HCl this is MA this middle solution is HCL and in this particular case Cd 2 plus has lower speed than H prime and acetate ion that is CH 3 Coo minus has lower speed compared to Cl minus ion.

So, when current is passed suppose this point was x x prime and this point was y y prime and this portion is your silver acetate sorry this portion is your acidic acid, this portion is calcium chloride and this portion is Hcl. So, when some current is passed H plus ions move towards the platinum electrode at a speed much faster than Cd 2 plus.

As a result the boundary moves up from y y prime to a new location Z Z prime suppose somewhere here. So, this boundary moves up simultaneously this boundary also moves up. So, if the cross section of the tube is uniform and the distance moved is l and c be the concentration of Hcl than the amount of Hcl moved up is l into a into c by 1,000 gram equivalent where the cross section a is a.

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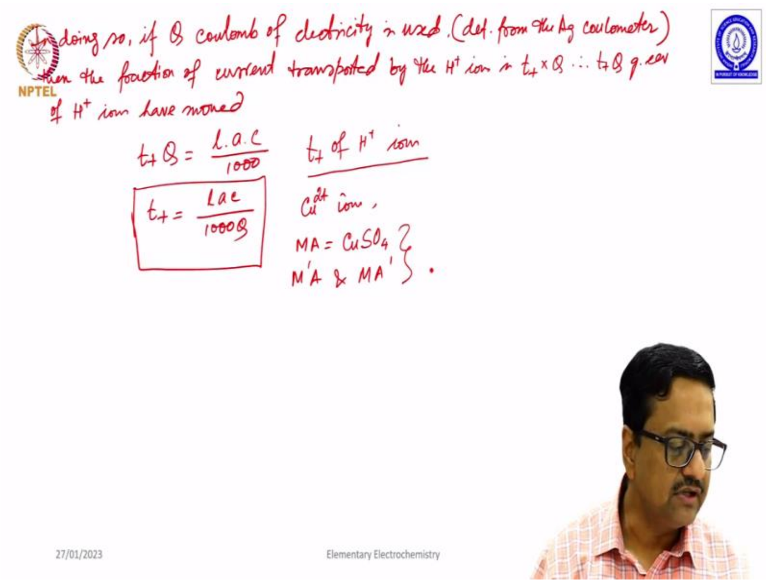

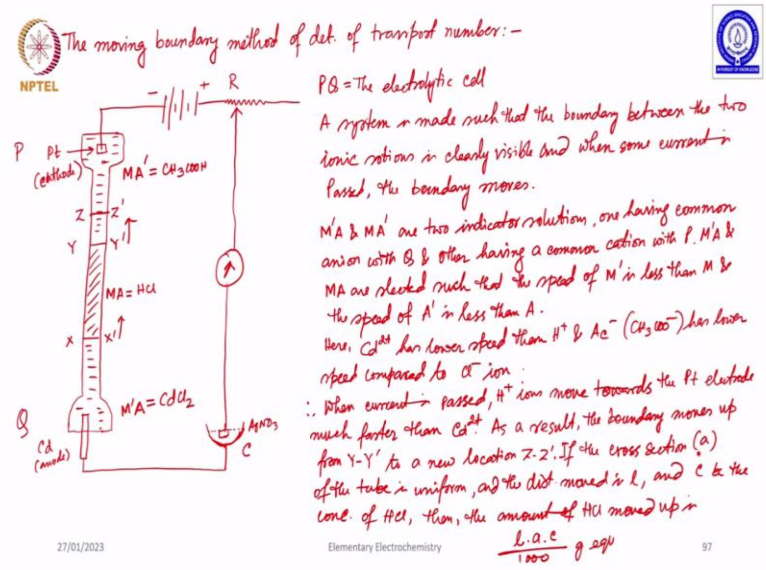

So, in doing so if Q coulomb of electricity is used this Q can be determined from the silver coulometer because you see when you pass some current through this solution the silver coulometer some silver will get deposited to the coulometer and you can way the coulometer and find out how much silver is deposited and based on that you can calculate the value of Q then the fraction of current transported by the H plus ions is nothing, but t plus into Q.

Therefore, t plus Q gram equivalence of H plus ions must have moved ions have t plus Q gram equivalent of H plus ions have moved that means t plus Q is equal to l into a into c by 1,000 which was found in the previous slide. So, one can calculate t plus as l a c by 1,000 Q. So, you can determine the transport number of H plus ions in this method. So, now you can understand that if I want to determine the transport number of Cu2 plus ions.

We should have M A as Cu SO4 and accordingly we should choose M prime A and MA prime such that one can determine the transport number of R copper sulphate ions. So, if you remember that I gave you one problem in one of the previous classes. So, we will try to work it out now using the method that we have just discussed.

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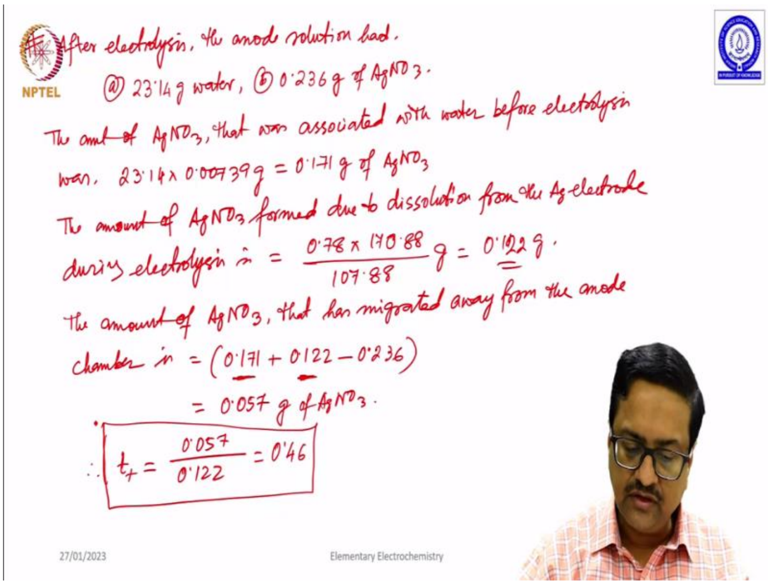

So, in the problem we said that after electrolysis the anode solution had number a 23.14 gram water and 0.236 gram of Ag NO3. Now we can calculate that the amount of Ag NO3 that was associated with water before electrolysis was 23.14 into 0.00739 gram or equal to 0.171 gram of Ag NO3. Now the amount of Ag NO3 formed due to dissolution from the Ag electrode during electrolysis is equal to 0.78 into 170.88 divided by 107.88 gram or simply equal to 0.122 gram.

So, the amount of Ag NO3 that has migrated away from the anode chamber is equal to 0.171 plus 0.122 because you see this is the amount that is there. This is the amount that is formed and the amount that has actually gone out which is 0.236. This was initially there, this was formed and this is there at the end of the solution. So, this is total equal to 0.057 gram of Ag NO3.

Therefore, transport number of Ag NO3 is nothing, but 0.057 divided by this 0.122 which is equal to 0.46. So, this is how you can calculate the transport number of silver nitrate using Hittorf's tube method. So, you should try to consult the prescribed textbooks for various problems like this and you try to solve those problems and during this course in the weekly assignments I will also give you some problems like this for you to solve and learn yourself. So, thank you very much we will start from here in the next class.