Elementary Electrochemistry
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Electrolytic Conduction:
Arrhenius Theory of Electrolytic Dissociation

Welcome back to the course entitled elementary electrochemistry. In the previous two lectures, we have discussed about Faraday's laws of electrolysis and we have discussed about the units that one should use while solving some mathematical problems related to electrolysis and the conduction.

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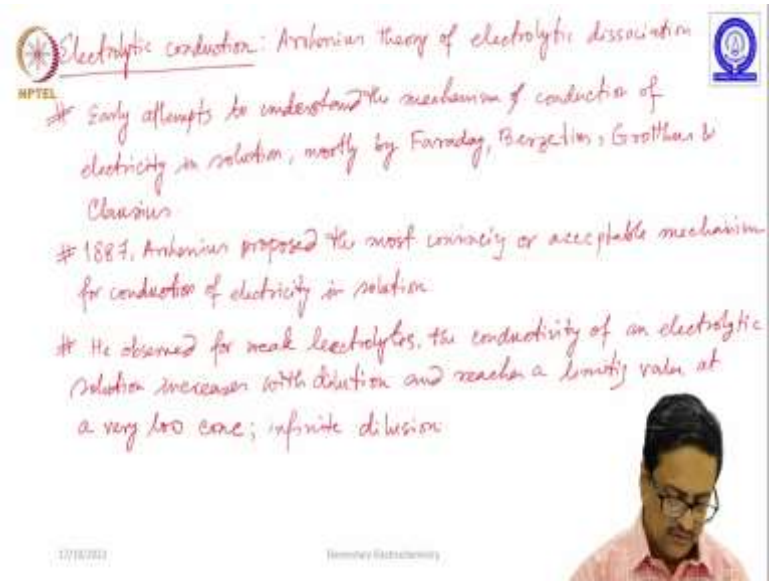

So, in today's lecture now, I am going to discuss about electrolytic conduction. And while discussing about electrolytic conduction, I will discuss about the Arrhenius theory of electrolytic dissociation. There have been a few early attempts to understand the mechanism of conduction of electricity in solution, mostly by Michel Faraday, Berzelius, Grotthus and Clausius. Among these in 1887 Arrhenius proposed the most convincing or acceptable mechanism for conduction of electricity in solution. He observed for weak electrolytes the conductivity of an electrolytic solution increases with dilution and reaches a limiting value at a very low concentration, which he termed as infinite dilution.

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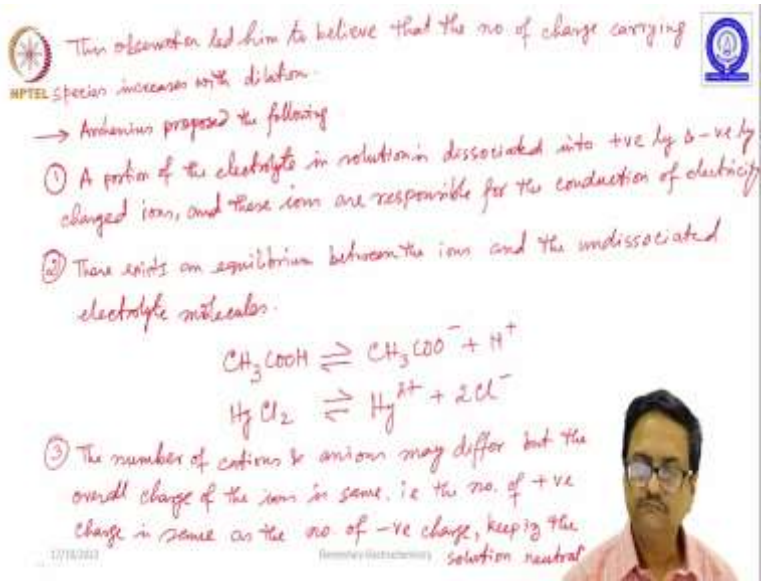

So, this observation led him to believe that the number of charge carrying species increases with dilution. So, from this observation Arrhenius proposed the following number 1, a portion of the electrolyte in solution is dissociated into positively and negatively charged particles or ions and these ions are responsible for the conduction of electricity. Secondly, he also proposed that there exists an equilibrium between the ions and the undissociated electrolyte molecules.

So, what he essentially meant is that for example, if it is acetic acid in solution it remains in equilibrium with CH3COO minus and H plus that is the 2 ions that acetic acid generates. Similarly, Mercury chloride remains in equilibrium with a Hg 2 plus plus 2 Cl minus. So, based on this proposition number 2 the third point straightaway emerges is that the number of cations and anions may differ. But the overall charge of the ions is same that is the number of positive charge is same as the number of negative charge, keeping the solution neutral always.

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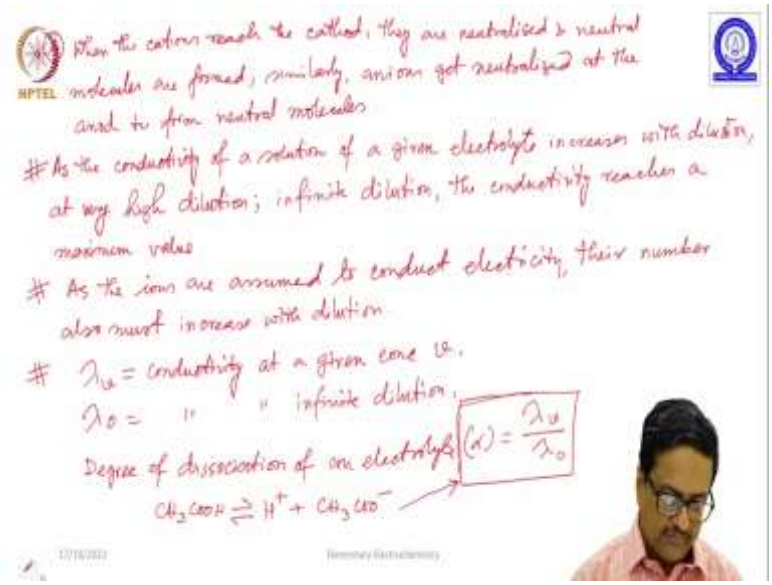

The fourth point that was also proposed is that when the cations reach the cathode they are neutralized and neutral molecules are formed, and similarly anions get neutralized at the anode to form neutral molecules. As the conductivity of a solution of a given electrolyte increases with the dilution, at a very high dilution which is also denoted as infinite dilution the conductivity reaches a maximum value. Simultaneously as the ions are assumed to conduct electricity their number also must increase with dilution. This is what was proposed by Arrhenius.

So, if lambda v is the conductivity at a given concentration v and if lambda 0 is the conductivity at infinite dilution. Then he proposed that the degree of dissociation of an electrolyte that is alpha should be denoted by lambda v by lambda 0. So, this is how he tried to define the degree of dissociation that is, when you are considering the dissociation of acetic acid into H plus and CH 3 COO minus. The degree of dissociation alpha for this equilibrium can be determined by the corresponding conductivity of the solution at a given concentration v and at infinite dilution.

When we demonstrate our experiments, when we discuss about the experimental verifications of these proposals, we will demonstrate one experiment where we will show how this is practically or technically achieved.

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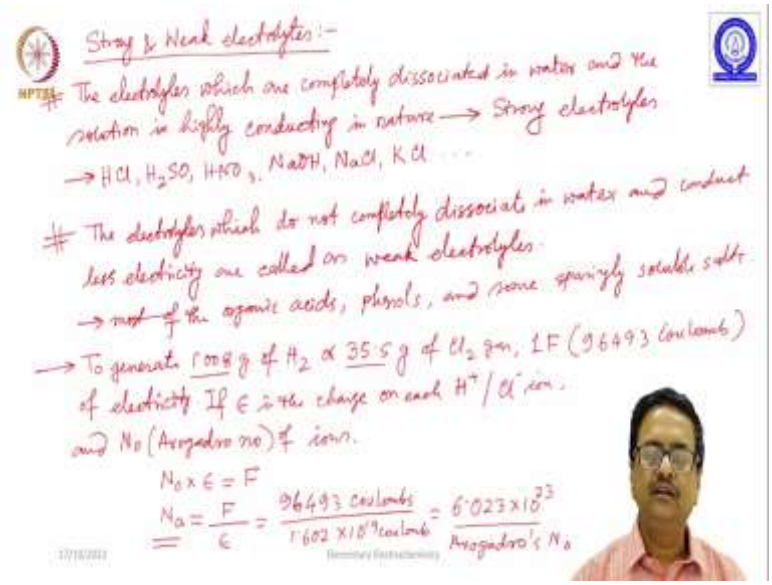

So, while doing the measurements of conductivity of different solutions Arrhenius was able to identify the electrolytes as two different types. So, he identified some electrolytes as strong and some as weak electrolytes. The electrolytes which are completely dissociated in water and the solution is highly conducting in nature they are termed as strong electrolytes, examples of such strong electrolytes are the mineral acids HCL, H2SO4, nitric acid, sodium hydroxide, sodium chloride, potassium chloride et cetera all the inorganic salts which are soluble in water are classified as strong electrolytes.

The electrolytes which do not completely dissociate in water and conduct less electricity are called as weak electrolytes. The examples are most of the organic acids, phenols and some sparingly soluble salts. So, it was observed that to generate 1.008 gram of hydrogen or 35.5 gram of chlorine gas, 1 Faraday that is 96493 coulomb of electricity. So, if E is the charge on each H plus or Cl minus ion and this is the 1 gram equivalent of hydrogen, 1 gram equivalent of chlorine, which essentially means that it contains N 0 that is Avogadro's number of ions.

So, then, N 0 into charge of each ion is nothing but the total amount of electricity that is 1 Faraday. So, now, one can easily calculate what is the value of N 0 by dividing F by charge of electron, F is 96493 columns and charge of 1 electron is 1.602 into 10 to the minus 19 coulomb. So, when you do this division, you arrive at a number 6.023 into 10 to the power 23, which is nothing but the Avogadro's number.

So, using again, the concept of electrochemistry, the number of ions discharged, and the corresponding charge on each ion and the amount of electricity required to pass through to

generate 1 gram equivalent of hydrogen gas or 1 gram equivalent of chlorine gas, one can calculate the Avogadro number fairly accurately. So, with this concept, you will be able to work out a few problems. We will continue from here in the next class. Thank you.