

Elementary Electrochemistry
Professor Angshuman Roy Choudhury
Department of Chemical Sciences
Indian Institute of Science Education and Research, Mohali
The Laws of Electrochemistry and Electrolysis

Welcome back to the course, entitled elementary electrochemistry. We will start discussing about Faraday's laws of electrolysis from today.

(Refer Slide Time: 00:34)

I hope you are able to see what I am writing on the screen. So, this is the class one, that is the first class that we are having on this electrochemistry course other than the introductory lecture that we had previously. So, in the first class, we will talk about the Faraday's laws of electrolysis. So, what we know about the chemicals that are reacting with what? The acids, the bases and the salts in their molten state or in solution conduct electricity.

So, whenever you have an acid, maybe HCL or nitric acid or any other weak organic acid like formic acid, acetic acid, etc or bases, sodium hydroxide, potassium hydroxide or some salts like sodium chloride, potassium chloride; some are organic salts like sodium acetate, potassium acetate, etc. in their molten state or when they are dissolved in water, they conduct electricity and when they conduct electricity, a process takes place and that process is called the electrolysis.

So, electrolysis is a process where using electricity as a source of energy, one can break and generate individual components of a given compound and sometimes you can get a different products like when you do electrolysis of a solution of sodium chloride, you will get

hydrogen and oxygen. Whereas, if you do the electrolysis of molten sodium chloride, you will end up getting sodium and chlorine gas at the electrodes. So, depending on the condition of electrolysis, your products of electrolysis may be different.

In case of metallic conductors, electrons carry electricity and conducts current through the metal. Here, in case of solutions of electrolytes, ions, namely cations, that is positively charged ions and the anions, that is the negatively charged ions, conduct electricity. So, this conduction links, the cations and the anions move from one electrode to the other in solution or in liquid state. So, as soon as it is no longer the electrons, the ions that are moving you can understand that there will be lot of aspects associated with it because the ions have different size; ions can conduct different amount of charge.

So, there can be a cation with a single positive charge, with two positive charges and three positive charges and so on. Similarly, the anion also can be singly negative, doubly negative or triply negative, just like chloride, bromide which are mono negative; then sulfate, carbonate, those are di-negative and something like phosphate is something which is 3 minus in charge. So, as a result the amount of charge and the complexity of the cation and anion is different in case of electrolytic conduction and immediately the theories need to be developed to discuss about their effects.

So, the movement of ions in solution results into the specific chemical reaction to take place. This process is called electrolysis or simply the decomposition of the electrolyte.

(Refer Slide Time: 9:44)

The entry and the exit path of electricity is called the electrode. These can be +ve and -ve, denoted as + and -.

When we study the reactions taking place at these electrodes, we observe that both oxidation & reduction reactions take place.

Reduction ← Cathode reaction
Oxidation ← Anode reaction

At Cathode: $H^+ + e^- \rightarrow H$, $2H \rightarrow H_2$

At Anode: $OH^- - e^- \rightarrow OH$, $4OH \rightarrow 2H_2O + O_2$

Overall: $H_2O + \text{a few drops of } HCl$

So, when we talk about a battery or any electrochemical device which can deliver electricity, the entry and the exit part of electricity is called the electrode. These can be positive and negative, denoted as these two signs. So, this side is plus and the other side is minus. When we study the reactions taking place at these electrodes, we observe that both oxidation and reduction reactions take place. So, when you can see these that there are oxidation and reduction happening, based on the nature of reaction happening at those electrodes, we call them as anode and cathode.

So, conventionally, the electrode at which the oxidation takes place is called the anode and the reaction where reduction takes place is called the cathode. You will see during this particular course, in some places the anode is positive and cathode is negative and in some cases the anode is the negative electrode and cathode is the positive electrode. Let us try to understand this using simple electrolysis of water.

So, if I just have water held in a container and I have dipped two electrodes which are then connected externally using a battery, which has the positive and negative terminals like this. So, what will happen is the electrons will flow in this direction in the outer circuit while the current is flowing in this direction. So, I is this direction and flow of electrons is in the opposite direction. So, this is a solution of water plus a few drops of say HCL, making it conducting. You know that 100 percent pure water does not conduct electricity, it is a covalently bonded compound, its electrical conductance is extremely low.

So, when you do that, as I indicated in the previous introductory class, the H plus ions move towards the cathode and get converted to hydrogen gas and it is released. Similarly, the OH minus ions move toward the anode and get converted to oxygen in this process which I have also shown in the previous introductory lecture. It initially forms the OH radical and then 4 such OH radicals then combine to give you 2 water molecules plus one O₂. So, this first reaction is called the cathode reaction and the second reaction is called the anode reaction.

So, now, if you look at these two reactions carefully, you will see that in the cathode, a reduction has taken place and in case of anode, an oxidation has taken place. Overall, the oxidation is to oxygen, O minus to O zero. So, you should remember that the reduction happens at cathode and oxidation happens at anode in any electrochemical process. And this electrochemical process should always maintain the electro neutrality of the solution. That means, if 2 units of H plus is reduced and you are getting 1 hydrogen, you should end up getting only half amount of oxygen because to make 4 OH, you need 4 electrons.

So, this reaction will be only half of it. That is half a 2 OH will give you H₂O plus half O₂, that is in terms of quantity of oxygen that is released and it should maintain the 2 is to 1 ratio of hydrogen to oxygen in the evolved gas.

(Refer Slide Time: 17:48)

First law of electrolysis:-
The amount of chemical change which occurs at any electrode is strictly proportional to the quantity of electricity passed through the solution of the electrolyte.

Second law of electrolysis:-
If the same quantity of electricity is passed through different solutions of electrolytes then the different amounts of chemical changes produced at the electrodes are chemically equivalent.

If 'W' g of a substance is deposited at an electrode, when Q Coulombs of electricity is passed then from the first law,
 $W \propto Q \Rightarrow W = ZQ$
 $Q = It$
 $W = ZIt$
 $Z = \text{electrochemical equivalent of a substance}$

Q = amount of current in amp
t = time for which the electricity is passed

So, after understanding these simple chemical reactions which are happening under the influence of passage of electricity we arrive at a point where we can talk about the laws of electrolysis, that is the Faraday's laws of electrolysis. The first law, first law of electrolysis. The first law states that the amount of chemical change which occurs at any electrode is strictly proportional to the quantity of electricity passed through the solution of the electrolyte, which essentially means that if you pass more amount of electricity, more amount of chemical change will take place and more amount of the corresponding electrolyzed product will be formed; with less amount of electricity passed, the final product, amount of final product will be less.

The second law of electrolysis talks about the relative quantity of the substances generated. So, it says that if the same quantity of electricity is passed through different solutions of electrolytes, then the different amounts of chemical changes produced at the electrodes are chemically equivalent. So, it talks about the exact quantity of chemical changes, that is in some cases evolution of a gas or it may be deposition of a metal or it may be dissociation of metal from the electrode.

So, the amount of metal deposited or amount of metal dissociated out from the electrode or the amount of gas that is produced in a given electrode, these amounts are relative amounts,

are directly related to the quantity of electricity passed and if you pass the same quantity of electricity through different solutions of different electrolytes, then the chemically equivalent amount of substance generated will be same if the quantity of electricity that is passed is same.

So, it essentially indicates that if W gram of a substance is deposited at an electrode, here deposited means either it is really deposited or evolved, at an electrode when Q coulomb of electricity is passed, then, from the first law, one can write this W is proportional to Q because that is the mass of the substance or weight of the substance that is deposited or liberated or released is directly proportional to the amount of electricity that is passed. You see the unit of electricity is coulomb.

So, this essentially indicates that W can be equated to Z into Q and simultaneously, this Z into Q can be written as c into t , where c is the amount of current in ampere unit and t is the time for which the electricity is passed and here this constant Z is called the electrochemical equivalent of a substance. So, the unit of current is ampere and unit of time is in seconds. So, when you do ampere into second, that is current into time, you get coulomb.

So, this you need to remember that ampere second is equal to coulomb. That is simply like P equal to MF . So, unit of force is mass into acceleration. So, you have the unit of mass multiplied the unit of acceleration, you get the unit of force. Similarly, here the quantity of electricity is measured in coulomb and that coulomb if the mass amount of electricity is calculated based on the amount of electricity passed, that is in terms of ampere and the unit is second.

So, you can easily calculate, if you are given what amount of electricity is passed for how much of time through a solution, then you know what is the amount of electricity that is passed. So, in that way one can determine the value of electrochemical equivalent for a given substance. If I know by passing suppose 10 ampere of current for 10 seconds, one generates 5 gram or milligram of a substance, so one can determine what is the value of Z . Z is the electrochemical equivalent of a substance. So, I will stop at this point in this lecture and I will continue from here in the next class. Thank you.