

Elementary Electrochemistry
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Applications of Faraday's Laws of Electrolysis

Welcome back to the course entitled elementary electrochemistry. In the previous class, we started discussing about the Faraday's laws of electrolysis and I have just stated the 2 laws and I have shown you the first equation of electrolysis, which is the following.

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$W = Z \cdot Q = Z \cdot C \cdot t$
 $C = \text{amount of current in amp}$
 $t = \text{time in s}$

$Z = \text{Electrochemical equivalent is the quantity of substance produced at an electrode when 1 coulomb of electricity is passed. (i.e. 1 amp of current is passed for 1 Sec.)}$

Cell 1: NaCl solution
 Anode 1: $4\text{OH}^- - 4e^- \rightarrow 4\text{OH} \rightarrow 2\text{H}_2\text{O} + \text{O}_2$
 Cathode 1: $2\text{H}^+ + 2e^- \rightarrow \text{H}_2$

Cell 2: AgNO₃ sol
 Anode 2: $4\text{NO}_3^- + 2\text{H}_2\text{O} \rightarrow 4\text{HNO}_3 + \text{O}_2 \uparrow - 4e^-$
 Cathode 2: $\text{Ag}^+ + e^- \rightarrow \text{Ag (s)}$

If we pass current for such a long time that at Anode 1, 8g of O₂ is liberated then at Cathode 1, 1.008 g of H₂ will form & at Cathode 2, 107.88 g of Ag will be deposited.

We have discussed about the equation W equal to $z Q$, which is equated to z, c into t , where c is the amount of current in amperes and t is the time in seconds. So, one can calculate the value of W you should know the value of z if you determine c and t or if you determine W, c and t . If you determine W and know the c and t one can calculate the value of the electrochemical equivalent z . So, what is electrochemical equivalent or z ? This z the electrochemical equivalent is the quantity of substance produced at an electrode when 1 coulomb of electricity is passed. That is 1 ampere of current is passed for 1 second.

So, now, we will see the actual understanding of the second law of electrolysis or Faraday's second law of electrolysis. So, when we try to construct a different cell let us draw this cell first. So, I have two chambers, the first chamber contains a solution of NaCl, a second chamber contains a solution of AgNO₃. So, now, I am connecting these two solutions using an external circuit like this. What do you think what will happen? Nothing will happen because these two solutions are not connected.

So, I have the positive end dipped in one solution, the negative end is deep in another solution, but then these two solutions are not connected by any electrical connection or conductivity, therefore, nothing will happen at this point. So, now, if I put another pair of electrodes and use those electrodes to connect these two solutions, then the reaction will start then the electrolysis will happen. So, this anode, we call it as an anode 1 and of course, this will be cathode 1. Similarly, this is cathode 2 and the other one is anode 2.

So, now, we have two sets of systems one side is sodium chloride and the other side is silver nitrate. So, if we now try to write down the possible reactions that are going to happen, anode 1 is this one see this is aqueous solution of sodium chloride. So, what should happen is OH minus should release electrons get converted to OH and then eventually 4 OH should give you 2 waters plus oxygen and cathode 1 should take care of the H plus ion which will come and get the electron get neutralized to hydrogen atom and 2 such hydrogen atoms will give you hydrogen gas.

In case of anode 2, we have OH minus and nitrate but here the nitrate will get discharged 4 NO₃ minus with 2 water molecules will form 4 HNO₃ plus O₂ and release 4 electrons and cathode 2 you have silver ion in that here the silver ion will take up an electron and get deposited as silver solid. So, what will happen is this cathode will get coated with silver we will have oxygen evolution from here and also the oxygen evolution from here. But the reactions are different and from this we will have hydrogen evolution.

So, now what we have is I am passing same amount of electricity from the battery for a given amount of time in both the cells. So, as per the second law of electrolysis different amounts that are getting liberated at these 4 different electrodes should be chemically equivalent. So, if we pass current for such a long time that at anode 1, 8 grams of O₂ is liberated. Then at cathode 1, 1.008 gram of hydrogen will form and at cathode 2, 107.88 grams of Ag will be deposited. Because these amounts are chemically equivalent.

So, the quantity of electricity required to liberate 1.008 gram of hydrogen or to deposit 107.88 gram of silver one is called 1 Faraday and the amount of electricity that is corresponding to 1 Faraday is 96493 Coulombs.

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The quantity of electricity required to liberate 1.008 g of H_2 or to deposit 107.88 g of Ag (1 gm. eqn of Ag) is 96493 Coulombs.

1 Faraday
 $1 F = 96500 \text{ Coulombs (approximate)}$
 $1 F = 96493 \text{ Coulombs (actual)}$

If E_1 & E_2 are the chemical equivalents of two substances, whose electrochemical equivalents are z_1 & z_2 respectively.

$E_1 = z_1 \times 96500$, $E_2 = z_2 \times 96500$

$\frac{E_1}{E_2} = \frac{z_1}{z_2}$ The electrochemical equivalents are proportional to the chemical equivalents of the substances.

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So, the quantity of electricity required to liberate 1.008 gram of hydrogen or to deposit 107.88 grams of silver that is 1 gram equivalent of silver is 96493 coulombs which is written as 1 Faraday. For practical purposes this 1 Faraday or 1 F is taken as 96500 coulombs, but actual value is 96493 coulombs. So, if you remember this conversion factor. So, if E_1 and E_2 are the chemical equivalents of two substances I am writing substances as a general term because these substances can be metal, can be a gas that is evolved, a metal that is getting deposited or a metal leaching out of the electrode and generating a cation in the solution and that is why I am writing two substances.

Whose electrochemical equivalents are z_1 and z_2 respectively hope you remember what is z that is electrical chemical equivalent then one can easily write E_1 equal to z_1 into 96500, E_2 is equal to z_2 into 96500. Therefore, E_1 by E_2 is equal to z_1 by z_2 . So, the electrochemical equivalents are proportional to the chemical equivalents of the substances.

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 A coulometer is used to determine the value of Z for a given substance.

Using a Ag coulometer.

Pt basin is first dried & weighed (W_1) accurately. A solution of $AgNO_3$ in H_2O is taken in the basin & electricity is passed for a given amount of time. Ag gets deposited on the Pt basin. The current is then stopped, the basin is washed with water & dried; then weighed (W_2).

Amount of Ag deposited $= (W_2 - W_1)g$, If C amp current passed for t sec. then the quantity of electricity $= Q = C \cdot t$.

$(W_2 - W_1) = Z_{Ag} \times Q$

$Z_{Ag} = \frac{W_2 - W_1}{Q}$

$Z_{Ag} = 0.001118 g/Coulomb$

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 The quantity of electricity required to liberate $1.008g$ of H_2 or to deposit $107.88g$ of Ag (1 gm. eqn of Ag) is 96493 Coulombs.

1 Faraday.

$1F = 96500 \text{ Coulombs (96493 Coulombs)}$

If E_1 & E_2 are the chemical equivalents of two substances, whose electrochemical equivalents are Z_1 & Z_2 respectively.

$E_1 = Z_1 \times 96500$, $E_2 = Z_2 \times 96500$

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So, to do these kinds of measurements to find out the electrochemical equivalence et cetera one has to use a small device which is called a coulometer, a coulometer is used to determine the value of z for a given substance and that is done using a silver coulometer. So, this silver coulometer looks like this the way I am drawing you have a basin which is made up of platinum, platinum basin and this platinum basin itself works as a cathode, you have an ammeter to measure the amount of current that is passed. So, one can measure the current here in amperes and you have a solution of $AgNO_3$ in this basin.

So, the current is passed in this direction. So, this is the positive electrode, this is the negative electrode. So, what will happen is when the electrolysis takes place, some amount of silver will be deposited in this platinum basin. So, the mass of this platinum basin will increase with

time when you pass the electricity. So, the platinum basin is first dried and weighed, say w_1 gram accurately using a four-digit balance. Then a solution of silver nitrate in water is taken in the basin and electricity is passed for a given amount of time.

So, in this process what happens is silver gets deposited on the platinum basin. The current is then stopped the basin is washed with water and dried, then weighed. Suppose the final weight turns out to be w_2 gram. So, amount of silver deposited is nothing but w_2 minus w_1 gram. If C ampere current is passed for t seconds then the quantity of electricity is nothing but Q that is equal to c into t .

So, now I know the difference w_2 , sorry w_2 minus w_1 is nothing but equal to the electrochemical equivalent of silver multiplied by Q . So, z silver is equal to W_2 minus W_1 by Q . Now, if we pass 1 Faraday of electricity, then what will happen? We are passing 1 Faraday of electricity to deposit silver. So, in that condition, the amount of silver that will be deposited that will correspond to z Ag equal to 0.00118 gram per coulomb. So, if we pass 96500 coulomb of electricity, then 1 gram equivalent of silver will be deposited which is equivalent to this.

So, one can determine the electrochemical equivalence of a substance using a silver coulometer and eventually when you know the electrochemical equivalence of silver, then you can determine electrochemical equivalents of any other substance using the equation that I have shown here. So, that if the value of z_1 , you get the values of E_1 and E_2 . That is their chemical equivalence that is the equivalent weight of those substances then one can determine the unknown z_2 for the second substance that is the other element or other gas that you are talking about.

So, using these simple calculations and a very simple experiment, one can utilize to determine how much of silver or how much of some other metal can be deposited or how much of some other metal like copper will be released in solution and so on. So, these types of problems you will find in your textbook, I would like to suggest that you go to the textbook and try to solve these types of problems. Of course, we will discuss a few similar problems in the coming classes. So, I will stop now at this point and we will continue from here in the next class. Thank you.