

Elementary Electrochemistry
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Conductance Measurement

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Elementary Electrochemistry



A course designed for students studying B. Sc with Chemistry

Instructor

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Elementary Electrochemistry

Welcome back to the course entitled Elementary Electrochemistry. In this course in the previous class we have started discussing about conductance and how to measure conductance and we have discussed about specific conductance and equivalent conductance.

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Determination of conductance (Λ) of a solution of an electrolyte:-

The specific conductance (κ) of a solution is determined by measuring the resistance (R) of the solution taken in a suitable apparatus, called the conductivity cell.

One has to use AC for det. of ' R ', this is req. to prevent any electrolysis.

Pt electrodes

l

a

κ

$PB = \text{wire of uniform thickness}$

$X = \frac{R_1}{R_2}$

or $X = \frac{l_1}{l_2} \times \frac{R_1}{R_2}$

$R = X$

$\Lambda = \frac{1}{R} = \frac{1}{X}$

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So, in continuation with that today I am going to discuss the method or the procedure for the determination of conductance that is Λ of a solution of an electrolyte. So, here in this

lecture we will discuss about some of the instruments that are used, some method that is used for determination of conductance. So, by doing so why we need to determine the specific conductance that is capital L of a solution which is the specific conductance of a solution is determined by measuring the resistance R of the solution taken in a suitable apparatus called the conductivity cell.

This conductivity cell is a device where you will take the solution and this device can have different shapes and the distance between the electrodes in the cell. So, one can have a conductivity cell which would look like this and you will have two conductors on two sides, two electrodes which are connected externally with liquid mercury kept in this tubes and this conductivity cell has a stopcock (S) at the bottom for draining the solution out.

And you have a length as usual and one can take a solution inside. So, what we know is the length that is the length and the surface area of that particular conductor and these electrodes are made up of platinum in general. So, now this is a similar arrangement can be made with a long tube which is like this where you have the electrodes here and there and again we know the length and the area of the electrode.

So, using a conductivity cell one has to use AC or alternating current for determination of resistance R this is required to prevent any electrolysis. If you use direct current then there will be conductance associated with electrolysis. So, the things will become complicated that is why we use alternating current to prevent electrolysis. So, what we do is we make one set up of Wheatstone bridge which I am going to draw here.

Suppose, you have a conductivity cell of the first kind and it is connected to two electrodes. This two electrodes are supplied with AC current and it is connected through the point D which has a variable resistance done like that R_3 and it is connected to a point Q and here you have a point P on which you have a uniform wire C and these two points are further connected.

And what we connect between D and the wire C is a connector which is a headphone. So, now what happens is this PQ is wire of uniform thickness that is the resistance of this wire increases as the position is changed. So, suppose the resistance of the left hand side is R_1 and the resistance of the right hand side is R_2 and R_3 is my variable resistance. So, now we have a solution of a particular electrolyte in this conductivity cell.

And we are passing AC current alternating current and we use a particular definite resistance as R_3 which can be changed, but during the experiment we do not change it, we keep it fixed at a value R_3 and with the help of this headphone we keep this variable point moving left and right such that at one point there will not be any sound heard in the headphone which will indicate the point of equivalence.

So, the resistance of this solution is x . So, we have 4 corresponding resistances in this Wheatstone bridge arrangement and by using the principle of Wheatstone bridge when we place this director this arrow mark on the uniform wire at some point such that the left hand side resistance is R and right hand resistance is R_2 which is actually determined by the lengths l_1 and l_2 because it is uniform cross section.

So, one can write that $x \times R_3 = R_1 \times R_2$ or simply $x = \frac{R_1}{R_3} \times R_2$ or $x = \frac{l_1}{l_2} \times R_3$. So, when you determine the resistance of this conductivity solution which we assumed here as R which equal to x then the corresponding conductivity λ is nothing, but $\frac{1}{R}$ which is equal to $\frac{1}{x}$. So, using this principle of Wheatstone bridge you can determine the value of conductance of a solution that is taken in this conductivity cell.

So, one can take solutions of KCL, NaCl, HCl of different concentration and determine the conductance of it. So, what we are determining is just the conductance and this conductance is related to the concentration. So, one cannot directly compare the conductance so for that one has to convert the conductance into the corresponding equivalent conductance.

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To know the specific conductance, 'L', it is necessary to determine the area of cross section of the electrodes and the distance between them.

The ratio $\left(\frac{l}{a}\right)$ is called the cell constant (K), unit $\frac{\text{cm}}{\text{cm}^2} = \text{cm}^{-1}$.

$l = \text{known}$
 $a = \text{known}$ $\Rightarrow K = \frac{l}{a}$ $\Lambda = L \times \frac{a}{l} = \frac{L}{K}$, $K = \frac{L}{\Lambda} = \frac{L \times R}{1}$

Using such conductivity cell, one can det. the value of L for pure KCl solutions at diff. conc. & at diff. temp as well.

Kohlrausch & coworkers det. the value of L of pure KCl solⁿs.

Conc. (eq/L)	0°C	18°C	25°C
0.01	4.751×10^{-4}	1.2227×10^{-3}	1.4114×10^{-3}
0.10	7.154×10^{-3}	1.1192×10^{-2}	1.2886×10^{-2}
1.00	6.543×10^{-2}	9.62×10^{-2}	1.1173×10^{-1}

Unit: mho/cm

So, what we have determined is we have obtained the value of lambda, but to know the specific conductance that is capital L it is necessary to determine the area of cross section of the electrodes and the distance between them that is l and a. The ratio l by a is called the cell constant. So, what will be the cell constant which is written as capital K, what will be the unit of cell constant?

Unit of cell constant L if it is measured in centimeter area in centimeter square that means per centimeter will be the unit of cell constant. So, now for all experimental purposes we should know the value of L and we should also know the value of a which essentially means we know the value of cell constant k which is l by a. So, one can design this conductivity cells with a particular length with distance between the two electrodes.

And one can make electrodes of very accurate cross section and we know the cross section and all that. So, using such conductivity cells one can determine the value of L for pure KCl solutions at different concentrations and at different temperature as well. So, many, many years ago Kohlrausch and coworkers determine the value of L of pure KCl solutions and here are those values with different concentration and at different temperature.

So, concentration it is equivalence per liter, temperature is in degree centigrade that is 0 degree centigrade, 18 degree centigrade and 25 degree centigrade. What we are reporting are the values of L in moh per centimeter unit. So, 0.01 if this is the concentration then this specific conductance L was found to be 7.51 into 10 to the power minus 4 then at 18 degree centigrade it was 1.2227 into 10 to the power minus 3.

And at 25 degree centigrade it is 1.4114×10^{-3} , the unit is moh centimeter inverse. With 0.10 normal the value changes to 7.154×10^{-3} then it is 1.1192×10^{-2} and at 25 degree centigrade it is 1.2886×10^{-2} and then at one equivalent that is suppose 1 normal 6.543×10^{-2} 9.82 into 10 to the power minus 2.

And this is 1.1173×10^{-1} . So, what we observe with that with increase in concentration the specific conductance value L increases and also with increase in temperature the value of specific conductance increases. So, the value of specific conductance it is clear that depends on both temperature and concentration and you see the specific conductance is what?

It is the conductance of this solutions with the electrodes kept at 1 centimeter apart with 1 square centimeter area. So, that has been taken care of by knowing the values of l and a . If you remember λ equal to L into l by a . So, what they have done? They have determined the values of conductance of these solutions at different temperature with the conductivity cell for which the l and a were known.

So, using this equation the value of l has been calculated and reported. So, this value of L are now corrected for the values of l and a . So, to calculate these values of L the simple expression that λ equal to L into a by small l was used which essentially means that L by cell constant K is used which means K equal to capital L by the conductance of that solution or if you write in terms of resistance that is K into R .

So, what they have done is they have measured the value of the resistance of these solutions at different temperature and with the known values of l and a they have then calculated the value of k and determine the value of L that is the L that is the specific conductance.

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To ascertain the value of cell const of an unknown conductivity cell, one has to use the value of L from the table and measure the resistance ' r ' of a solution of 0.1 or 0.01 (M) KCl taken in that conductivity cell.

$$K = \frac{L}{a} = L \times r \rightarrow \text{def.}$$

L or L_s = specific conductance.
 Now, as we know ' r ', K is calculated, Now, Λ can be then calculated using.

$$\Lambda = \frac{1000 L}{c} \Rightarrow \text{Equiv. conductance of a solution by measuring the resistance 'r' and hence the conductance } \Lambda$$

Pure form of water with min conductance, i.e., very high resistance

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To know the specific conductance, ' L ', it is necessary to determine the area of cross section of the electrodes and the distance between them.

Λ & a .
 The ratio $\left(\frac{L}{a}\right)$ is called the cell constant (K), unit $\frac{\text{cm}}{\text{cm}^2} = \text{cm}^{-1}$.

$$L = \text{known} \begin{cases} a = \text{known} \end{cases} \Rightarrow K = \frac{L}{a} \quad \Lambda = L \times \frac{a}{c} = \frac{L}{K}, K = \frac{L}{\Lambda} = \frac{L \times R}{\Lambda}$$

Using such conductivity cell, one can det. the value of L for pure KCl solutions at diff. conc. & at diff. temp as well.
 Kohlrausch & co-workers det. the value of L of pure KCl sol^{ns}.
 $\bar{L} \rightarrow \text{mho/cm}$

Conc. (eq/L)	0°C	18°C	25°C
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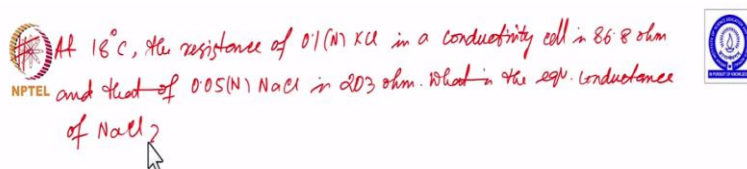
So, to ascertain the value of cell constant of an unknown conductivity cell one has to use the value of L from the table and measure the resistance say small r of a solution of 0.1 or 0.01 molar kcl taken in that conductivity cell. So, this cell constant K is nothing, but 1 by a which is equal to L into r which we have shown in the previous picture that is L into r . So, this value of L from table and r is determined using the Wheatstone bridge principle.

In some places you will see that L or it is written as L_s which means the specific conductance. So, now as we know r K is calculated and now Λ can be then calculated using the equation $\Lambda = 1000 L / c$ that means one can calculate the equivalent conductance of a solution by measuring the resistance r and hence the conductance Λ and specific conductance L as well.

So, now when we are trying to measure the conductance of a solution and we are using water as a solvent one has to use a very pure form of water with minimum conductance that is very high resistance. So, how this water is produced? First one has to distill a normal water tap water or any water, one has to distill it at least two times one time distilled collected and redistilled and collected.

And then that water is passed through ion exchange columns to remove any residual ions of carbonate, bicarbonate which maybe there because of dissolution of carbon dioxide in water so that the water that comes out of the ion exchange resins cation exchange and anion exchange resins should not have any ions H plus, OH minus or any other ions like carbonate or bicarbonate or dissolved sulfur dioxide which forms SO_3^{2-} ions. So, those ions should not be there in the water one has to use that ultra pure water for the determination of conductance of any solution.

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At 18°C , the resistance of 0.1N KCl in a conductivity cell is 86.8 ohm and that of 0.05N NaCl is 203 ohm . What is the eqv. conductance of NaCl?



So, before we end today's class I would like to give you one problem to solve. The problem is at 18°C the resistance of 0.1 normal KCl is in a conductivity cell is 86.8 ohms and that of 0.05 normal NaCl is 203 ohm . What is the equivalent conductance of NaCl? So, you will need the value of specific conductance of KCl solutions at 18°C from the table and then you try to solve this problem. We will continue from here in the next class. Thank you.