

Elementary Electrochemistry
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Electrolytic Solutions

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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 the previous lecture we have discussed about how to determine the transport number of a cation using moving boundary method and I have demonstrated the solution of a simple problem. So, in this lecture I am going to start discussing about various features related to the conductance measurement.

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The conductance of a solution: -
In case of a metallic conductor of length 'L' and uniform cross section 'a' the resistance R is given by the following eqn.
$$R = \rho \times \frac{L}{a}$$

ρ = specific resistance.
= the resistance of a conductor of unit length & unit cross section.

i.e., when $L = 1 \text{ cm}$, $a = 1 \text{ sq. cm}$, then:

$$R = \rho$$

What is the unit of R? $\rightarrow \text{ohm}$.

$$\text{ohm} = \rho \times \frac{1 \text{ cm}}{1 \text{ cm}^2}$$

$\therefore \rho = \text{ohm cm.}$



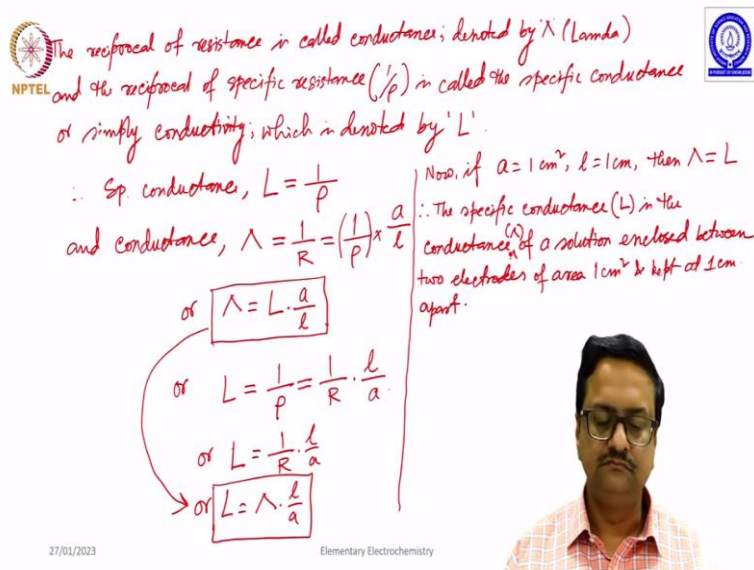
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So, when we are talking about the conductance of a solution we need to know about some of the known equations, expressions and the terms related to conduction. So, what we know about in case of a metallic conductor of length l and uniform cross section a the resistance R is given by the following equation R equal to ρ into l by a where ρ is called the specific resistance which is equal to the resistance of a conductor of unit length.

And unit cross section that is when l equal to 1 centimeter and a equal to 1 square centimeter then R is equal to ρ . What is the unit of R ? The unit of resistance ohm. So, now in this equation on the left hand side if I write unit of resistance as OHM equal to ρ into l is 1 centimeter by 1 centimeter square. Therefore, on simplification ρ will have unit as ohm centimeter. Since this is known to you from your 10 plus 2 knowledge of basic physics.

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The reciprocal of resistance is called conductance, denoted by Λ (Lambda) and the reciprocal of specific resistance ($1/\rho$) is called the specific conductance or simply conductivity, which is denoted by L .

\therefore Sp. conductance, $L = \frac{1}{\rho}$

and conductance, $\Lambda = \frac{1}{R} = \left(\frac{1}{\rho}\right) \times \frac{a}{l}$

or $\Lambda = L \cdot \frac{a}{l}$

or $L = \frac{1}{\rho} = \frac{1}{R} \cdot \frac{l}{a}$

or $L = \frac{1}{R} \cdot \frac{l}{a}$

or $L = \Lambda \cdot \frac{l}{a}$

Now, if $a = 1 \text{ cm}^2$, $l = 1 \text{ cm}$, then $\Lambda = L$

\therefore The specific conductance (L) in the conductance (Λ) of a solution enclosed between two electrodes of area 1 cm^2 & kept at 1 cm apart.

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So, now the reciprocal of resistance is called conductance denoted by the Greek letter lambda capital lambda and the reciprocal of specific resistance that is 1 by ρ is called the specific conductance or simply conductivity which is denoted by the English letter capital L . So, specific conductance which is written as L is nothing, but equal to 1 by ρ and conductance which is written by capital lambda is equal to 1 by R which is equal to 1 by ρ into a by small l that is the length of the conductor.

So, now one can further write lambda equal to one can replace this 1 by ρ by capital L that is the conductivity or specific conductance multiplied by a by l . So, this is the relationship between the conductance and specific conductance. One can further rearrange to write L

equal to $1 \text{ by } \rho$ equal to $1 \text{ by } R$ into $1 \text{ by } a$ or simply $1 \text{ equal to } 1 \text{ by } R$ into $1 \text{ by } a$ or $1 \text{ equal to } \lambda$ into $1 \text{ by } a$. So, that to hear one can directly write.

So, this is the relationship between the conductance and specific conductance. So, now if a equal to 1 centimeter square, l equal to 1 centimeter then λ is equal to L numerically which means therefore we can write that the specific conductance L is the conductance of a solution enclosed between two electrodes of area 1 centimeter square and kept at 1 centimeter apart. So, this is the definition of specific conductance.

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The conductance of a solution, (L), depends on the number of ions present in the solution. It depends on the concentration of the electrolyte. To compare the conductivity (L) of different solutions, it is necessary to take the conc. of the solution into account. This is done using another term called the Equivalent Conductance, denoted by ' λ '.

The equivalent conductance of a solution is defined as the conductance of a solⁿ containing 1 gm. eqv. of the dissolved electrolyte such that the entire solution is placed between two electrodes which are kept at 1 cm apart.

→ The direct determination of eqv. conductance (λ) would require the electrodes to be of enormous size (area) and one has to use the eqn. $L = \frac{1}{R} \cdot \frac{l}{a}$.

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Now, we can easily understand that the conductance of a solution that is the value of λ depends on the number of ions present in the solution which essentially means it depends on the concentration of the electrolyte. So, to compare the conductivity that is capital L of different solutions it is necessary to take the concentration of the solution into account. So, this is done using another term called the equivalent conductance denoted by the letter small λ .

So, what is the definition of this equivalent conductance? The equivalent conductance of a solution is defined as the conductance of a solution containing 1 gram equivalent of the dissolved electrolyte such that the entire solution is placed between two electrodes which are kept at 1 centimeter apart. So, this essentially means that the direct determination of equivalent conductance λ would require the electrodes to be of enormous size.

That is area which essentially is very difficult to achieve because when you are trying to encapsulate 1 gram equivalent of an electrolyte in a solution and the electrodes are kept at only 1 centimeter apart which is very small length then the size of the electrode has to be extremely large. So, that is why I am saying the direct determination of equivalent conductance lambda would require the electrodes to be of enormous size or area.

And one has to use the equation L equal to 1 by R into l by a where l is the path length or the distance between the two electrodes. So, to avoid this difficulty to come across this; overcome this difficulty one can think of something else.

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 Suppose the solution of the electrolyte has a conc. 'c' g.equiv./litr, then the volume of the solution containing 1 g.equiv. of the electrolyte would be $\frac{1000}{c} \text{ cm}^3$. Now this volume of solution is imagined to be placed between two electrodes at 1 cm apart ($l = 1 \text{ cm}$) \therefore the cross section of the electrodes would be $\frac{1000}{c} \text{ cm}^2$.

\therefore Sp. conductance, $\Lambda = \frac{a}{L} \times L$


$\Lambda = \frac{1000}{c} \times L$

$\therefore \boxed{\Lambda = \frac{1000}{c} L}$


If we know 'c', conc. of the solution, L , the specific conductance of the solution \rightarrow Sp. conductance of the electrolyte.

Unit of resistance (R) = ohm.
 " " conductance (Λ) = mho
 " of specific conductance = $\frac{\text{mho}}{\text{cm}}$
 " specific conductance (Λ) = mho.cm

$\Lambda = \frac{\text{cm}^2}{\text{cm}} \times \text{mho} \text{ cm}^{-1}$
 $\Lambda = \text{mho.cm}$



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or $\boxed{L = \Lambda \cdot \frac{l}{a}}$

Now, if $a = 1 \text{ cm}^2$, $l = 1 \text{ cm}$, then $\Lambda = L$

\therefore The specific conductance (L) in the conductance (Λ) of a solution enclosed between two electrodes of area 1 cm^2 & kept at 1 cm apart.

$L = \text{mho} \cdot \frac{\text{cm}}{\text{cm}^2}$
 $= \text{mho.cm}^{-1}$



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Suppose, the solution of the electrolyte has a concentration c gram equivalent per liter then the volume of the solution containing 1 gram equivalent of the electrolyte would be $1,000$ by c cubic centimeter. Now, this volume of solution is imagined to be placed between two electrodes at 1 centimeter apart that is l equal to 1 centimeter. Therefore, the cross section of the electrodes would be $1,000$ by c centimeter square.

The cross section has to be this then only $1,000$ by c cubic centimeter of the volume can be held within 1 centimeter of the two electrodes. Therefore, one can write that the equivalent conductance that is small λ is equal to a by small l into capital L or λ equal to this area is $1,000$ by c and l is 1 centimeter into capital L . Therefore, λ is equal to $1,000$ c into L .

So, now what we have if we know c that is the concentration of the solution and capital L which is the specific conductance of the solution then one can calculate equivalent conductance of the electrolyte and then once you know the equivalent conductance of different electrolytes then you can easily compare their conductivity. So, now what we know is that the unit of resistance that is R is ohm.

So, the unit of conductance that is capital λ is equal to mho just opposite of ohm and then what will happen of unit of specific conductance. If you go back to slides this is capital L . So, now L will have unit of conductance mho into the unit that comes from l by a . So, l is in centimeter a is in centimeter square. So, the unit becomes mho per centimeter. So, one can write that mho centimeter inverse then what is the unit of specific conductance λ .

Now, we can derive the unit of λ using this equation. So, $1,000$ by c is having unit of centimeter cube and this c has the unit centimeter here into this capital L is mho centimeter inverse. So, this centimeter gets cancelled become square, this centimeter gets cancelled and become centimeter. So, λ will have unit of mho centimeter. So, this specific conductance will be mho centimeter as its unit. So, hope you can understand and follow these terms and the corresponding units. We will continue from here in the next class. Thank you.