

CHAPTER 4

Measurement of Conductances in Solutions

I. Introductory Words

A conductor is a substance that allows an electric current to flow through it. While in an electronic conductor, electrons are the current-carriers, the ions perform such work in an electrolytic solution. In both cases, the electric current experiences a resistance while flowing. Conductance is the reciprocal of resistance. Larger is the conductance, easier is the passage of current. Mathematically, resistance

$$R = \rho \cdot \frac{l}{a}, \quad (1)$$

l and a are length and area of the conductor respectively and ρ is the 'resistivity' or 'specific resistance' for the conductor of unit length (l) and unit area (a).

$$\text{Conductance, } C = \frac{1}{R} = \frac{1}{\rho} \cdot \frac{a}{l} = \kappa \cdot \frac{a}{l}$$

$$\text{or, } \kappa = C \cdot \frac{l}{a} \quad (2)$$

$$\text{or, } \kappa = C \cdot K_c \quad (3)$$

κ (kappa) is the specific conductance, which is the conductance of a solution kept between two electrodes of unit area of cross section each and at unit distance apart, or it may be regarded as the conductance of a solution of unit volume. K_c is the 'cell constant' of the particular conductivity cell in use.

Unit of specific conductance, κ , generally used is $\text{ohm}^{-1} \text{cm}^{-1}$ or S cm^{-1} .

The S.I. unit is $\text{ohm}^{-1} \text{m}^{-1}$ or S m^{-1} [S = siemens]

Unit of cell constant, K_c , is cm^{-1} or m^{-1} .

Equivalent conductance (Λ):

This is the most important term used in conductance measurement and is defined as the conductance of a solution in which one gram-equivalent of the experimental electrolyte is present and is placed between two large electrodes at one cm apart so as to accommodate the solution.

As construction of large electrodes and to do work with these are far from reality, the equivalent conductance, Λ , of a solution is expressed with the equation

$$\Lambda = \frac{1000\kappa}{c}, \quad (4)$$

where c is the number of gram-equivalent of the electrolyte dissolved in 1000 cm^3 of the solution, i.e. the 'normality' of the solution. Unit of Λ is $\text{S cm}^2 \text{ g-equiv}^{-1}$. The S.I. Unit is $\text{S m}^2 \text{ g-equiv}^{-1}$.

Molar Conductance (Λ_m):

The molar conductance of a solution is the conductance of that volume of the solution which contains one mole of the electrolyte and is placed between two electrodes at unit distance apart and having enough area of cross-section each to accommodate the solution.

Molar conductance is measured from specific conductance by the relation

$$\Lambda_m = \frac{1000\kappa}{M} \quad (5)$$

where M is the molarity of the solution.

Unit of molar conductance is $\text{S cm}^2 \text{ mol}^{-1}$. The S.I. unit is $\text{S m}^2 \text{ mol}^{-1}$.

Relation between Equivalent Conductance (Λ) and Molar Conductance (Λ_m)

$\Lambda_m = \Lambda \times \text{total charge of cations or anions produced from one molecule of the electrolyte}$

For example, $\Lambda_m(\text{CaCl}_2) = \Lambda \times 2$

$\Lambda_m(\text{Al}_2(\text{SO}_4)_3) = \Lambda \times 6$, etc.

Variation of κ , Λ and Λ_m with the concentration of the solution

The conductance of an electrolytic solution mainly depends upon the number of ions present in a definite volume of the solution enclosed by the two electrodes, i.e., it depends upon the concentration of the solution. Another factor also plays a role behind the conductance value—the ease with which the ions move overcoming the interionic attraction of two oppositely charged ions. However, the overall effect of concentration on different types of conductances should be considered separately for strong and weak electrolytes.

Strong electrolytes

Specific conductance (κ) decreases with lowering the concentration of the solution (c).

Both equivalent conductance (Λ) and molar conductance (Λ_m) increase smoothly with decreasing concentration, the slope having a constant value.

Weak electrolytes

κ decreases with lowering of c , but not as sharp as for strong electrolytes due to increasing degree of dissociation.

Both (Λ) and (Λ_m) increase with changing slope for lowering c . The curve of Λ_m may be to some extent different for that of Λ , depending upon the valency-type of the electrolyte. However, the nature (i.e., increasing or decreasing tendency) of curves remains same.

The Debye-Hückel-Onsager equation correlating Λ or Λ_m and concentration is given by

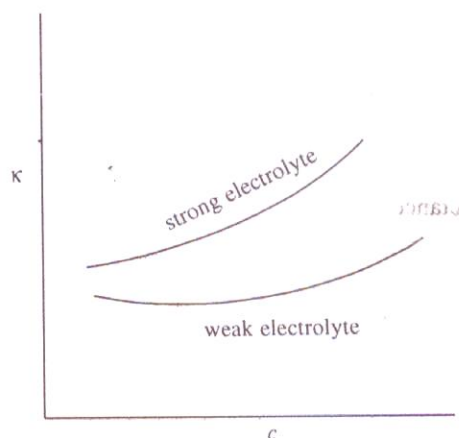
$$\Lambda = \Lambda^\circ - b\sqrt{c} \quad (6)$$

Λ° = equivalent conductance at infinite dilution

c = concentration of the solution

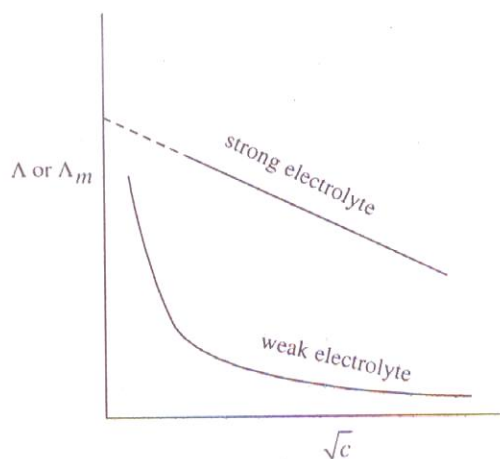
b = a constant, whose value depends upon the nature of the solvent and temperature.

The general characters of the curves are shown here.



Graph I

Specific conductance vs. concentration



Graph II

Equivalent or molar conductance vs. concentration

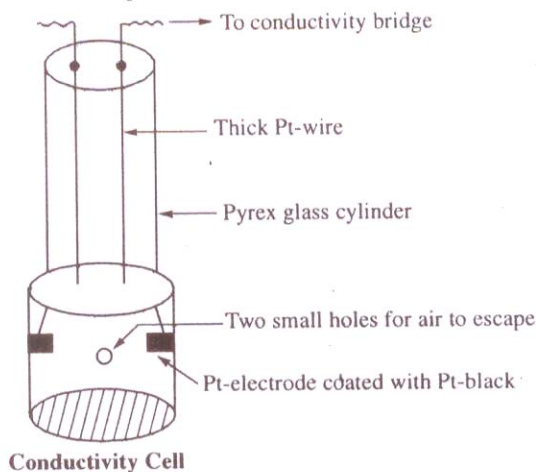
The instruments

1. **The conductivity bridge:** It provides a means to know the **resistance** of the solution, an outcome of the famous **Wheatstone Bridge principle**. In old days after its formation, an ear-phone was in use for indication of no current through the detector. For its noisy disturbances, it has completely been replaced by magic-eye electronic detector or cathode ray oscilloscope. At present **Digital conductometers** are largely in use. In either of the arrangements the indicator provides directly the conductance-readings.

An **alternating current (AC)** of high frequency (~ 1000 cycles/s) must be used to avoid electrolysis of the electrolytic solution under study and polarisation.

2. **The conductivity cell:** A different varieties of conductivity cells are used in the laboratory. These are constructed generally of Pyrex glass or other very good quality resistance glass in which two platinised platinum electrodes are welded with thick platinum wires fused in the Pyrex glass. The platinum electrodes are coated with Pt-black to minimize the polarisation. These wires are connected through mercury with the wires of the conductivity bridge. The Pt-electrodes are of at least one square cm area each and very stoutly fixed at about one cm apart.

When not in use, the cell is to be kept immersed in conductivity water.



Important: Users are advised to go through the circuit diagram and users' manual supplied by the manufacturers of the instruments before connection of the conductivity cell to the conductivity bridge.

The conductivity water: For precise work and particularly for research purposes, all experiments regarding conductance must be done with conductivity water. It is prepared as follows.

Add a pinch of KMnO_4 crystal and 2-4 beads of NaOH to about 5 lit of distilled water. Distill and reject about 100 ml from the first portion of distillate. Collect in a bottle washed with conductivity water, tight well the mouth of bottle and use for experiment.

EXPERIMENTS

Experiment 1

To determine the cell constant of a conductivity cell.

Theory: The resistance of a conductor of length l and area of cross-section a is given by

$$R = \rho \cdot \frac{l}{a}, \quad (1)$$

where ρ , the specific resistance or resistivity, is the resistance of the conductor of unit length and unit area. The conductance (C) is the reciprocal of resistance and is expressed as

$$C = \frac{1}{R} = \frac{1}{\rho} \cdot \frac{a}{l} \quad (2)$$

$$\text{or, } C = \kappa \cdot \frac{a}{l}$$

where κ , the specific conductance, is the conductance of a conductor of unit length and unit area. For electrolytic conductor, the specific conductance is the conductance of the solution of unit volume of the electrolyte, generally of 1 cm^3 of the electrolytic solution.

$$\text{From (2), } \kappa = C \cdot \frac{l}{a} \quad (3)$$

$$\text{or, } \kappa = C \cdot K_c$$

where K_c is the cell constant of the conductivity cell. The conductivity bridge gives conductance, C , of the solution. Hence knowing K_c , specific conductance (κ) and equivalent conductance (Λ) is determined. The unit of K_c is cm^{-1} .

$$\text{From (3), } K_c = \frac{\kappa}{C} \quad (4)$$

Using a 0.1 N or 0.01 N KCl solution, the κ is taken from Kohlrausch's table at a definite temperature and C is observed from conductivity bridge. Thus,

$$K_c = \frac{\text{Kohlrausch value for a definite concentration of KCl}}{\text{Observed conductance of the same solution of KCl}}$$

- Apparatus required:**
- i. Conductometer
 - ii. Conductivity cell
 - iii. Two 100 ml volumetric flasks
 - iv. Thermometer.

- Materials required:**
- i. KCl (G.R.)
 - ii. Conductivity water.

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Table 1:

Table 2:

Table 3:

different ion conductance from that of the replaceable ion. Thus when H^+ ($\Lambda_{H^+}^0 \sim 350 \text{ ohm}^{-1}\text{cm}^2 \text{ mol}^{-1}$) is replaced by Na^+ ($\Lambda_{Na^+}^0 \sim 50 \text{ ohm}^{-1}\text{cm}^2 \text{ mol}^{-1}$), there is sharp decrease of conductance. But when Cl^- ($\Lambda_{Cl^-}^0 \sim 76.3 \text{ ohm}^{-1}\text{cm}^2 \text{ mol}^{-1}$) is substituted by NO_3^- ($\Lambda_{NO_3^-}^0 \sim 71.4 \text{ ohm}^{-1}\text{cm}^2 \text{ mol}^{-1}$), there is not much appreciable change in the conductance.

With the addition of the titrant, the plot of fall or rise of conductance vs. the drop (i.e., volume) of the titrant gives two straight lines with different slopes before and after the end point. The point of intersection of the two straight lines give the end point of the titration. The corresponding drops of the titrant is converted into the required volume for completion of the titration.

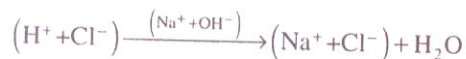
The following points are important

- i. To avoid much increase in volume, which affects the conductance value, the titrant should be 5-10 times stronger than the solution to be titrated.
- ii. It is preferable to use microburette.
- iii. For precise curve and its explanation, the hydrolysis of the titration-product, if any, is to be considered.
- iv. Much care is to be taken, not necessarily near the end point, but some readings at the beginning and a little bit away from the end point.
- v. Write the electrolyte to be titrated, in ionic form, titrant either in molecular or ionic form and the products, if strong electrolyte in ionic form; if weak, then in molecular form. Compare the ion-conductances of those which are being changed.

Experiment 7

To determine the strength of a hydrochloric acid solution by titrating against a standard caustic soda solution conductometrically (or vice versa).

Theory: When a definite volume of HCl solution is titrated with a standard caustic soda solution from the burette, H^+ ions with large ionic mobilities are gradually replaced by Na^+ ions with much lower ionic mobilities. The result is the sharp fall of conductance of the whole solution. When all the H^+ ions are exactly replaced by the equivalent number of Na^+ ions, the end point is achieved, showing the lowest conductance value of the resulting solution mixture. On further addition of alkali, a rise in conductance will be exhibited due to mainly OH^- ions from alkali. The changes in conductance can be explained by the following equations:



Thus two straight lines are obtained, one before and the other after the end point, when conductances of the solution are plotted against drops of alkali added. However, the slopes of the two straight lines are different, the latter being flatter. The intersection of the two lines indicates the neutral point and the corresponding drops of alkali, converted to volume is the required volume of the titrant.

Instruments and equipments: Conductometer, conductivity cell, one 50 ml volumetric flask, two 250 ml beakers, one 100 ml beaker for conductometric titration, one 100 ml conical flask, funnel, 10 ml pipette, microburette.

Materials: Oxalic acid, NaOH, HCl (conc.), phenolphthalein solution as indicator, conductivity water.

Procedure

1. Prepare 50 ml ~ 0.1N standard oxalic acid solution.
Required weight = 0.315 g.
2. Prepare about 100 ml ~0.5 N NaOH solution in beaker
Required weight = 2.0 g (take slightly more).
3. Prepare about 100 ml ~ 0.1 N HCl solution in a beaker or volumetric flask by properly diluting the concentrated HCl in the laboratory.
4. Standardise the NaOH solution taking it in burette against 10 ml standard oxalic acid solution using phenolphthalein.
5. Wash the conductivity cell with conductivity water.
6. Pipette out 10 ml HCl solution in a 100 ml beaker and insert the cell in it. Conductivity water is to be added, if required, to immerse the electrodes completely in the solution [The dilution will not affect the end point for a conductometric titration].
7. Connect the cell with the conductometer and take reading of the conductance of the HCl solution.
8. Fill up the previous burette with the same standardised NaOH solution.
9. Add 2 drops of NaOH solution on HCl solution in the cell, shake slowly and measure the conductance. Carry on the process of addition of definite number of drops of NaOH solution, shaking and conductance reading until a minimum value of conductance reaches and thereafter 5-6 readings of increasing conductances are taken. Stop titration. [If addition of 2 drops of NaOH solution does not change the conductance value appreciably, 4 drops or even more may be added, but the counting of drops must be accurate.]
10. Count the number of drops of 1 ml NaOH solution falling from the same burette. Repeat once more. Take average number of drops for 1 ml solution. Calculate the volume of one drop of the solution.
11. Plot conductance against the number of drops of alkali (the titrant), find the required number of drops for end point, convert it into volume.
12. Use $v_1s_1 = v_2s_2$ to calculate the strength of the HCl solution.
13. Perform a mechanical titration using phenolphthalein indicator, calculate the strength of HCl and compare it to that obtained conductometrically.

Results and Calculations**Table 1:** Recording of temperature.**Table 2:** Preparation of 50 ml 0.1 N oxalic acid solution. See table 3 of experiment 3.
Required weight = 0.315 g.**Table 3: Standardisation of NaOH solution by standard oxalic acid solution**
See table 4 of experiment 3. Put NaOH in place of KOH.**Table 4: Standardisation of 10 ml of HCl solution by standard NaOH solution conductometrically**
Strength of NaOH solution = ... (N)

No. of readings	No. of drops of NaOH solution	Conductance (ohm ⁻¹)
1	0	...
2	2	...
3
...
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Table 5:

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Table 5: Estimation of the volume of one drop of alkali solution

Volume of NaOH solution (ml)	No. of drops	Volume of one drop of NaOH solution (ml)	Mean vol. of one drop of NaOH soln. (ml)
1.0
1.0

Calculation

From the graph, it is seen the number of drops of NaOH solution required for complete neutralisation of HCl solution = ... drops.

Hence the volume of NaOH = No. of drops \times vol. of one drop = ... ml

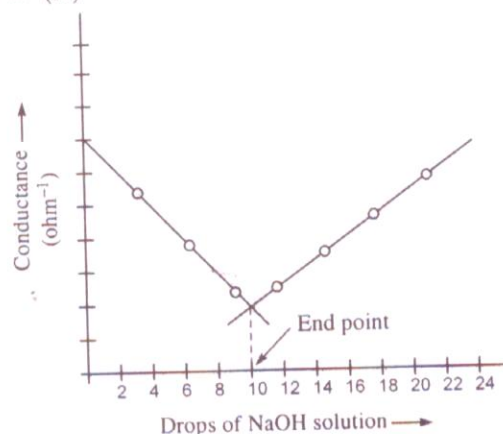
$$\therefore \text{strength of HCl solution} = \frac{V_{\text{NaOH}} \times S_{\text{NaOH}}}{10} (N) = \dots (N)$$

Conclusion: Hence the strength of the given HCl solution estimated conductometrically is ... (N).

The strength estimated through mechanical titration is ... (N)

Nature of the curve

N.B. Note the slope of the two straight lines. The first line is steeper due to the replacement of H^+ ion by much less mobile Na^+ ion. The second line is flatter due to OH^- ion which is not too less mobile than H^+ ion, comparable to Na^+ ion.

**Some similar experiments****Experiment 7A**

Standardisation of CH_3COOH solution by standard NaOH solution.

Theory: Acetic acid, being a very weak acid shows, much low conductance compare to strong acids like HCl. On addition of 1 or 2 drops of NaOH solution in a definite volume of acetic acid solution, the conductance falls due to further suppression of dissociation of CH_3COOH in presence of common CH_3COO^- ion resulting from CH_3COONa formed thereon [This fall of conductance may not be observed, if initially 6-8 drops of alkali is added instead of 1-2 drops]. On further addition of drops of alkali, the conductance increases slowly due to the dissociation of CH_3COONa , a strong electrolyte, overcoming the decrease in dissociation of CH_3COOH . After the equivalence point, the conductance rises more sharp due to OH^- ions coming from excess alkali. From the end point, the strength of the acetic acid solution is calculated. The relevant equation is

