

Electrolytic Conductivity

Introduction

Reference - Willard, Merritt, Dean - *Instrumental Methods of Analysis* and Atkins - *Physical Chemistry*, 7th ed. p. 832-834

Electrolytic conductivity is a measure of the ability of a solution to carry an electric current. Solutions of electrolytes conduct an electric current by the migration of ions under the influence of an electric field. Like a metallic conductor, they obey Ohm's Law so that the current varies inversely with the resistance, measured in ohms, of the solution. The reciprocal of the resistance is called the conductance (G) and has units of mhos, now called Siemens.

A related unit to conductance is the specific conductance or conductivity. The units of specific conductance are the mho/m or Siemens/m. The relationship of (κ) to the distance (d) between the electrodes and the area (A) of the electrodes is:

$$\frac{1}{R} = G = k \frac{A}{d}$$

The electrical conductance of a solution is a summation of contributions from all the ions present. It depends on the number of ions per unit volume of the solution and upon the velocities with which these ions move. In order to express the ability of individual ions to conduct, a function called the equivalent conductance or molar conductivity (Λ) is employed.

$$\Lambda = \kappa/C_s$$

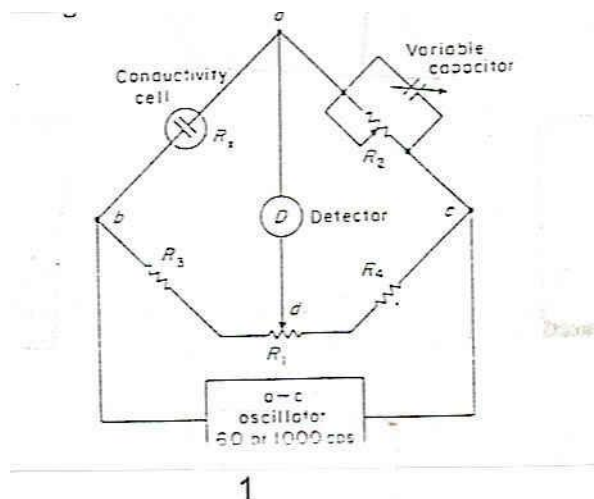
where C_s is the molar concentration of the electrolyte in mole/m³.

At infinite dilution the ions are independent of each other and each ion contributes its part to the total conductance, thus for a 1-1 electrolyte

$$\Lambda_{\infty} = \sum(\lambda_{+}) + \sum(\lambda_{-})$$

where (λ_{+}) and (λ_{-}) are the ionic conductances of cations and anions at infinite dilution. Small, highly charged ions have large values and large, low charged ions have low values.

Conductivity measurements usually involve determination of the resistance of a column of solution using a short duration pulse of current. Some variation of a Wheatstone bridge is used, using a detector such as an oscilloscope.



A condition of balance of the Wheatstone bridge is that

$$\frac{R_2}{R_x} = \frac{dc}{db}$$

and so R_x , the resistance of the solution in the conductance cell, can be measured.

In the equation relating the resistance (R), the specific conductivity (κ), the area of the electrodes (A) and the distance between them (d) for the conductance cell,

$$\frac{1}{R} = k \frac{A}{d}$$

the ratio A/d is a constant and is determined by measuring R when the cell contains a standard solution of known specific conductance (usually potassium chloride).

Thus $1/R$ is proportional to conductance and can be used to follow the course of a titration.

The titrant is introduced by means of a buret or micropipette, and the conductance readings ($1/R$) corresponding to various increments of titrant are plotted against the latter. The titrant should be at least ten times as concentrated as the solution being titrated to keep the dilution effect small. A correction term of the type below may be applied as below with " V " being the initial volume of the solution and " v " being the added volume

$$\left(\frac{1}{R}\right)_{actual} = \left(\frac{V+v}{V}\right) \left(\frac{1}{R}\right)_{observed}$$

One goal in this experiment is to follow the conductance of two titrations, (1) HCl and NaOH, and (2) acetic acid and NaOH, and to explain the shapes of the graphs. You will also compare the Molarities of the unknown acid solutions obtained from the acid/base titrations with phenolphthalein and the Molarities obtained from the conductance titrations. This will better enable you to understand about the uses of conductance and the behavior of ions in solution.

Procedure

1. Add 10.00 ml (by pipette) of approximately 0.1 M HCl and 20.0 ml of water to a small beaker. Insert the conductance cell and assemble the Wheatstone bridge circuit and oscilloscope.
2. Determine the resistance of the cell by changing the variable resistance in the bridge until a zero voltage is obtained on the oscilloscope. The variable resistance equals the resistance of the cell.
3. Add 0.500 M NaOH in .400 ml increments. Calculate an approximate value of where the equivalence point should be and make sure that you have added several increments past the end point of the titration. Apply the correction factor for dilution to the measured resistance.
4. Plot the titration curve with conductance on the dependent axis and ml of base added on the independent axis.
5. Repeat the experiment with approximately 0.1 M acetic acid titrated with 0.500 M NaOH.
6. Do regular acid/base titrations with burets and with phenolphthalein as an indicator to get comparison data for the HCl and acetic acid. You should have 3 good titrations for each acid.

Things to include in the lab report

- Include the conductance titration curves of both experiments. From those curves determine the equivalence points and use the equivalence points to calculate the concentrations of the acids.
- Determine the average concentrations of the acids using the indicator endpoints and the acid/base equivalence equation in the usual way for procedure #6. Calculate a percentage difference using your phenolphthalein titration as the standard.
- Analyze and explain the shapes of the conductance titration curves in terms of the contributions of the individual ions.
- Discuss applications as well as advantages and disadvantages of this technique. (See texts such as *Williard, Merritt and Dean* or *Skoog* for help)
- No propagated error analysis is required.