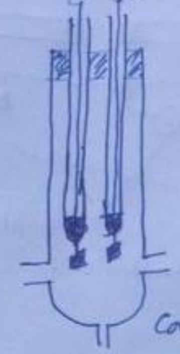
17.9.2020.

Measurement of the conductance of solution Page 1

1. Conductivity water. 4.3×10^{-5} ohm^{-1} KMnO$_4$ & KOH
2. Conductivity cells.



Conductivity cell.

3. Cell constant.

Since the electrodes are not exactly 1 unit apart and may not possess a surface area of 1 sq unit the reciprocal of resistance, R does not give the specific conductivity of the solution. Actual measurement of these dimensions being inconvenient, indirect method is employed to calculate the value of K by determining the cell constant.

From the equation

$$K = \frac{1}{R}\times\frac{l}{a}$$

$$= L\times\frac{l}{a}$$

$$\text{Cell constant} = \frac{l}{a} = \frac{K}{L}$$

$$\text{cell constant} = \frac{\text{Specific conductance, } K}{\text{observed conductance, } L} \quad (1)$$

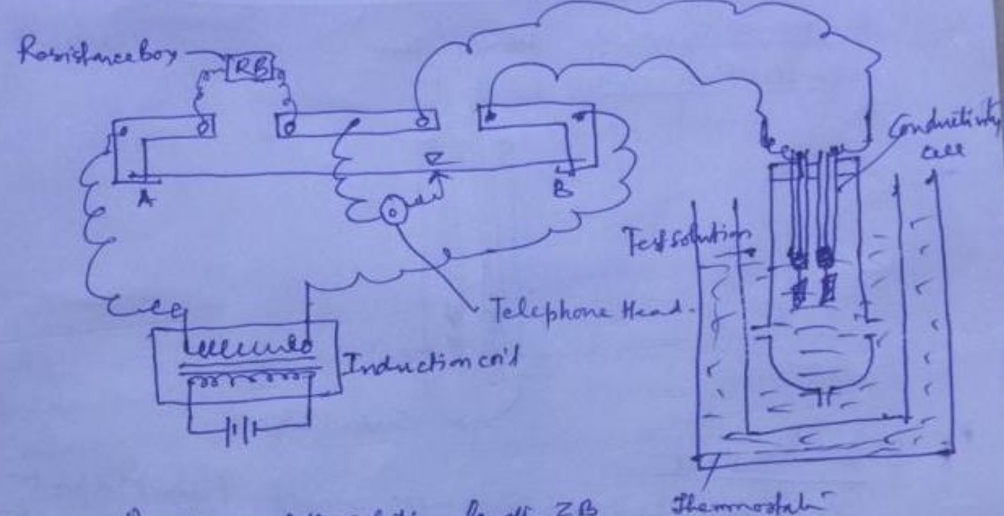
Specific conductance, K = L × cell constant.

$$\text{Unit Cell constant} = \frac{K}{L}$$

$$= \frac{Sm^{-1}}{S} = m^{-1}\ (SI)$$

The resistance of the cell is measured when filled with a standard solution say ($\frac{N}{10}$ KCl solution) in a given temperature and cell constant is calculated from the equation 1:

4. Measurement of conductance



$$\frac{\text{Resistance of the solution}}{\text{Resistance, } R} = \frac{\text{length } ZB}{\text{length } ZA}$$

Numericals 1

When a solution of conductance $1.342\ S\,m^{-1}$ was placed in a cell with parallel electrode, the resistance was found to be $170.5\ \Omega$. The area of the electrode has $1.86 \times 10^{-4}\ m^2$. Determine the distance apart of the electrode and the cell constant.

Solution:

$a = 1.86 \times 10^{-4}\ m^2$.

$l = ?$

$R = 170.5\ \Omega$.

$K = 1.342\ S\,m^{-1}$

i). $\text{cell constant} = \dfrac{\text{specific conductance, } K}{\text{observed conductance } L}$

$= \dfrac{1.342\ S\,m^{-1}}{1/170.5\ \Omega}$

ii) $= 228.8\ m^{-1}$

$\text{Cell constant} = \dfrac{l}{a}$

$l = \text{Cell constant} \times a$

$= 228.8 \times 1.86 \times 10^{-4}$

$l = 4.2515 \times 10^{-2}\ m.$

Unsolved numericals.

1. If the specific conductance of 0.1N KCl solution at 298 K is 1.2886 S m^{-1} and the resistance of a cell containing this solution is 100 Ω. Calculate the constant. [Ans. 128.86 m^{-1}]

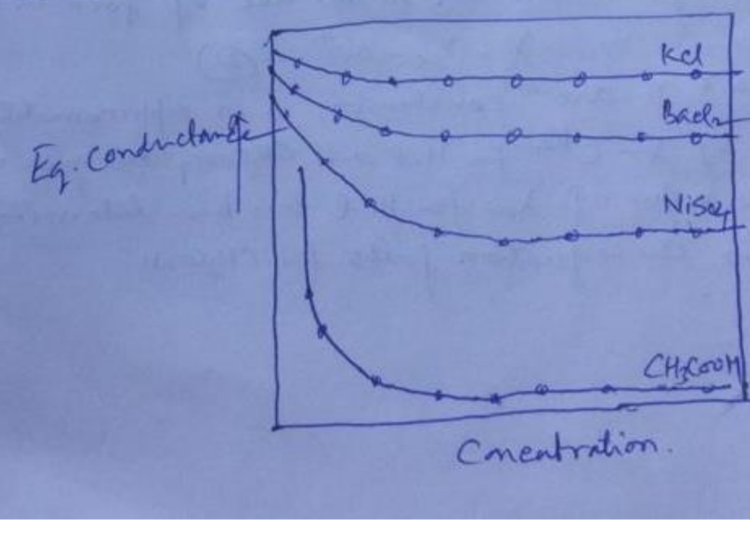
2. Conductance of 0.2N KCl solution at 298K is 0.2768 S and it had a resistance of 520 Ω. An 0.4N solution of the salt kept in the same cell was found to have a resistance of 300 Ω at 298K. Calculate i) the cell constant and ii) the equivalent conductance of the salt solution. [Ans. cell constant = 143.93 m^{-1}]

specific conductance = 143.93/300

Equivalent conductance $\lambda = \frac{1000\lambda}{C}$

$C = 0.4\ eq/l$ or $C = 0.4\ eq\,m^{-3} \times 10^{-3}$ $119.94 \times 10^{-4}\ S m^2 eq^{-1}$

Effect of dilution on Equivalent conductance.



The value at zero concentration is called equivalent conductivity a infinite dilution.

In case weak electrolyte, however, there is no indication that a limiting value can be attained. The plot of equivalent conductivity with concentration becomes parallel to equivalent conductance axis at extreme dilution for weak electrolytes.

The ratio of the equivalent conductivity λ at any concentration to that at infinite dilution λ_∞ is called conductance ratio and is given by the symbol α thus.

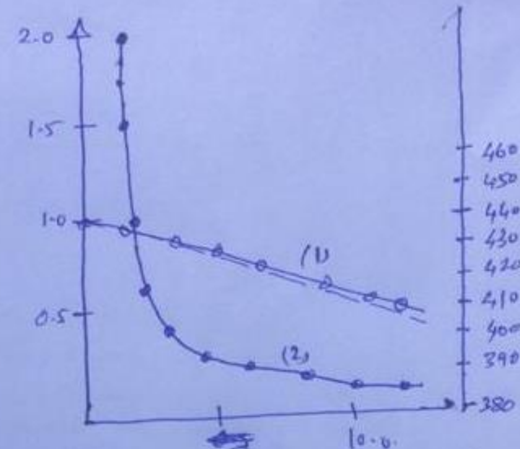
$$\alpha = \frac{\lambda}{\lambda_\infty} \quad -(1)$$

Arrhenius assumed the conductance ratio to be equal to the degree of dissociation of the electrolyte. This is approximately true for weak electrolyte but not for strong electrolyte.

A number of methods have been proposed at various times for the extrapolation of experimental λ to give λ_∞. Most of the procedure described for strong electrolyte are based on the use of formula of the type

$$\lambda = \lambda_\infty - ac^n \quad -(2)$$

where a & n are constant, n is approximately 0.5. The plot of $\lambda - C^{1/2}$ for HCl and CH_3COOH are given in fig. The value of λ_∞ for HCl has been determined where as the equation fails for CH_3COOH.



Equivalent conductance of HCl in H_2O (curve 1, scale on the right and in anhydrous CH_3COOH (curve 2. Scale on the left)

Others factors affecting equivalent conductivity

1. It increases with increase in temperature of solution.
2. Increases in ionic interaction decreases the equivalent conductance.
3. It is more or less inversely proportional to viscosity of the solvent

According to walden rule,

$$\eta\lambda = \text{constant}$$

4). Assoziatiation of ion leads to decrease in equivalent conductance.

5) Strong ion-solvent interaction can increase the size of the ions leading to decrease in equivalent conductance.