Ministry of Higher Education and Scientific Research

Al-Muthanna University

College of Science

وزارة الـتعليم الـعالـي والـبحث الـعلمي

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Electrochemistry

Lecture (4)

Stage 3

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Measurement of Electrolytic Conductance

To measure the conductivity of an electrolyte solution, it is usually determined by the equation $\left(G = k\ \frac{A}{L}\right)$

Which can be written on the following image:

$$\because G = k\ \frac{A}{L}$$

$$\because G = \frac{1}{R}$$

$$\Rightarrow \frac{1}{R} = k\ \frac{A}{L}$$

$$\Rightarrow k = \frac{L}{RA}$$

The connection can be calculated if the dimensions of the electrolytic connector are known.

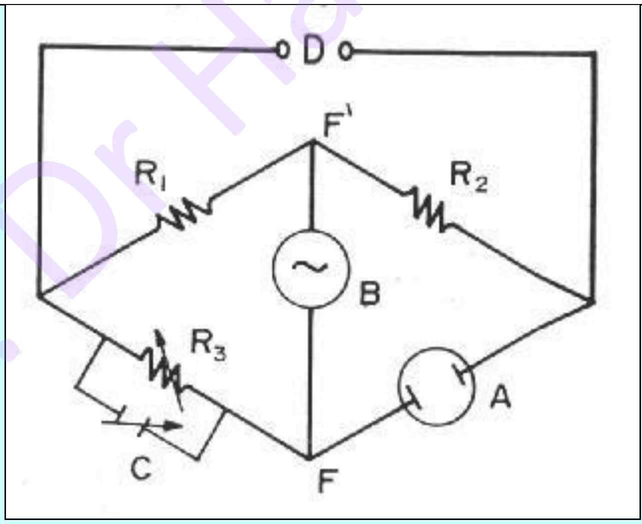

Figure (3): A whitestone bridge to determine the resistance of an electrolyte solution :
(A) : Delivery cell
(B) : AC current source
(C) : Electric condenser.
(D) : Estimated (like an oscillatory drawer.)
(R_1, R_2, R_3,) : Measuring resistors.

For this purpose, the Wheatstone arch is used, which is a circle Infrastructure has four resistors, one of which is the electrolytic conductor as it is. It is shown in Figure 3 above.

The use of direct current in the Hoytstone bridge will cause Electrolysis of the electrolyte affects the accuracy of the measurement. On this problem, it uses an alternating current (Alternating Current) with a high frequency. (1000 - 10000 Hz). The direction of the wind reflects at a high speed per second. This means that what happened from the electrolysis in the first half of the oscillation will be reflected in the second part In contrast, the phenomenon of polarization in conduction cells can be eliminated. Add to For the above, it usually resorts to coating the conductive electrodes, which are often made of Platinum metal with a layer of black platinum, which makes the actual electrode area much larger of the geometric area of the electrode, this will reduce the effect of polarization, as well as the . layer Black platinum has a catalytic effect that helps to reverse reactions every time it is reflected direction of current.

It is possible to summarize an idea in the resistance of conductor by using the shown Hoytstone bridge. Figure 3) (3) as follows:

The current from the source (B) is divided into two sections at the point (F). The first section passes through in the resistance (R2) and in the conductive cell (A), while the second section passes through the resistance (R1) and the variable resistance (R3). The value of (R3) is changed so that the current is between The points (F) and (F') are equal to zero and are used for this purpose estimated (D). The variable value capacitor (C) connected in parallel with (R3) is used to balance The electrical capacity of the conduction cell. At the equilibrium point, the **following equation becomes: correct:**

$$\frac{R_1}{R_2} = \frac{R_3}{R_C}$$

$$R_C = \frac{R_2}{R_1} R_3$$

Where R_C is the resistance of the conducting cell that contains the electrolyte solution. And because electrical conductivity (G) is the reciprocal of resistance, then

$$G = \frac{1}{R_C}$$

To measure RC, the electrolyte must be placed between the conductive electrodes in a container. A special cell known as the conductivity cell, and figure (4) shows its types. From the conduction cells that are used for different purposes.

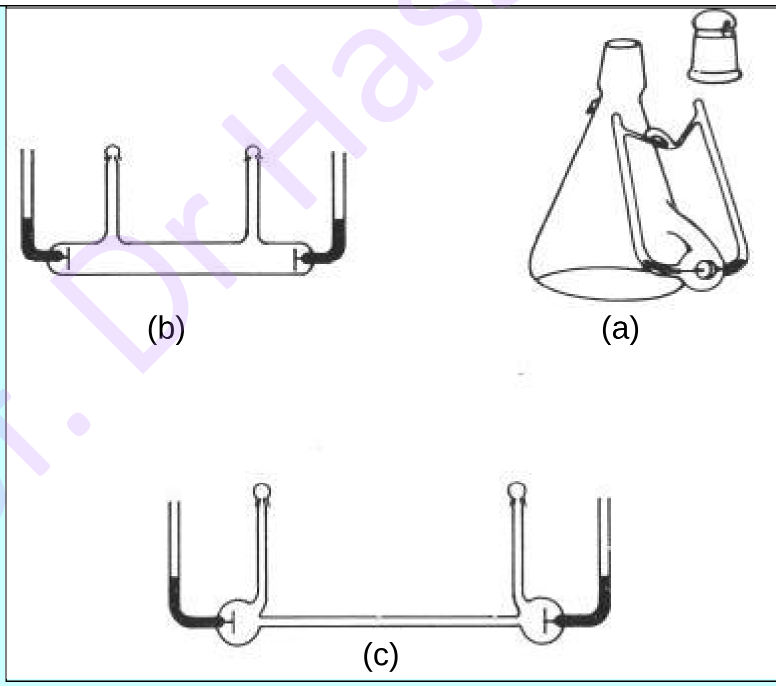

Figure (4): Some types of conduction cells, which are used in the case of concentrations:
a) low b) medium c) high

It is difficult to measure the dimensions of the electrolyte, which is expressed by What is the area of the poles (A) and the distance between them (L) so that each cell Connectivity The values of (L) and (A) must be constant and well known and the ratio between them i.e.) L/A is called the cell constant and is symbolized by the (K) symbol.

The value of the cell constant depends on the accuracy of the conductivity of the electrolyte solution, and therefore For high conductivity measurements, a highly stable conduction cell is used. The poles are small and separated by large distances, and on the contrary, they measure the connections The electrolyte is low, the cell constant must be small, that is, with large electrodes. And the distance between them is small.

Usually, the cell constant is not measured by geometrical dimensions (L and A), but A goes to Conduction calibration using an electrolyte solution that has a known resistance with high accuracy. usually Potassium chloride (KCl) solution is used to calibrate the conduction cells, as it has been designated Its resistance under different conditions of concentration and temperature. Al-Waj Al-Dowal (4) explains the value of Conductivity at different concentrations and temperatures of potassium chloride.

Table (4): Conductivity values at different concentrations and temperatures of potassium chloride

Molarity	**k (Ω^{-1} cm^{-1})**		
	0 ºC	**18 ºC**	**25 ºC**
1.0	0.065144	0.097790	0.11187
0.1	0.0071344	0.0111612	0.012896
0.01	0.00077326	0.00121992	0.001427

To determine a cell constant, measure the resistance of a solution (KCl) at a concentration and temperature. Information from previous laws:

$$R = \rho\left(\frac{L}{A}\right)$$

$$G = \frac{1}{R}$$

$$G = \frac{1}{\rho\left(\frac{L}{A}\right)} \Rightarrow G = \frac{1}{\rho}\left(\frac{A}{L}\right)$$

$$G = k\left(\frac{A}{L}\right)$$

$$\frac{1}{R} = k\left(\frac{A}{L}\right)$$

$$\Rightarrow k = \frac{1}{R}\left(\frac{L}{A}\right)$$

$$k = \frac{1}{R}\,K$$

$$\Rightarrow K = k\,R$$

or

$$K = \frac{L}{A}$$

If the conductivity of a solution (KCl) is (k_1) and its resistance is (R1), then the cell constant K can write on the picture

$$K = \frac{L}{A} = k_1 \,.\, R_1$$

When the resistance of another solution (R2) is measured in the same cell, its conductivity (k2) is given. With the following relationship:

$$K = \frac{L}{A} = k_2 \,.\, R_2$$

And the value of the constant K in both cases is equal, so:

$$K = k_1R_1$$

$$K = k_2R_2$$

$$k_1R_1 = k_2\,R_2$$

$$\Rightarrow k_2 = \frac{k_1 R_1}{R_2}$$

Example

A sample conduction cell was used with a fixed concentration of (KCl) 0.1 mol L-1 and a resistance of it about d (25 ºC equal to R_{KCl} = 110,533 Ω) and the following was measured at this temperature (k = 0.012896 Ω^{-1} cm^{-1}). Conducting a solution of (HCl) with a concentration of (0.1 mol L^{-1}), so the resistance of it in the same cell is equal to (R_{HCl}) = 36.791 Ω, so calculate its conductivity?

Solution

From the relationship:

$$k_1 R_1 = k_2 R_2$$

$$k_{KCl} R_{KCl} = k_{HCl} R_{HCl}$$

$$k_{HCl} = \frac{k_{KCl} R_{KCl}}{R_{HCl}}$$

$$k_{HCl} = \frac{0.012896\ \Omega^{-1} cm^{-1} \times 110.533\ \Omega}{36.791\ \Omega}$$

$$k_{HCl} = 0.0387\ \Omega^{-1} cm^{-1}$$