UNIT 3 LOW-COST INSTRUMENTS

Structure

3.1 INTRODUCTION

In this unit, we shall discuss the basic principles of colorimetry, conductometry and potentiometry. We shall explain the procedure for using low-cost instruments such as colorimeter, conductometer and mV/pH meter. You will be using these instruments for some of the experiments in this course. Three demonstration experiments will also be discussed to illustrate the use of these instruments.

Objectives

After studying this unit, you should be able to :

- state the principles of colorimetry, conductometry and potentiometry,
- explain the procedure for operating the controls in colorimeter, conductometer and mV/pH meter, and
- explain the methods of recording absorbance or conductance or e.m.f. of the given solution or system.

3.2 COLORIMETRY

Chemical analysis based on measurement of intensity of light absorbed in the visible region is termed colorimetry. Any coloured substance may be analysed by this method. If a substance is colourless, it can be made to form a coloured compound by the addition of a suitable reagent and then analysed colorimetrically. In colorimetry, generally the concentration of a substance is obtained from the intensity of light absorbed. In order to accomplish this, experiments are carried out to obtain the intensities of light absorbed by the substance in solutions of known concentrations. The simple instrument used for this measurement is termed a colorimeter. Colorimetric methods provide a simple and rapid method of estimating minute quantities of substances in solution. Hence the technique can be used to perform a wide variety of experiments such as monitoring a reaction colorimetrically in kinetics, determining equilibrium concentrations for the determination of equilibrium constants, etc. Let us now discuss Beer–Lambert law which summarises the basic principle of colorimetric estimation.

For a detailed study of Beer–Lambert law, see Unit 5 of CHE–03 (L) and Unit 8 of CHE–01 courses.

3.2.1 Beer–Lambert Law

When light of an appropriate wavelength is passed through a coloured solution contained in a cell, a fraction of the light is absorbed. The intensity of light absorbed depends on the nature or structure of the substance, its concentration in solution and the thickness of the absorbing medium. The part of light, which is not absorbed, is transmitted. Though some light is reflected back from the solution, its amount is negligibly small and is eliminated by using a control. For all practical purposes we may say,

The wavelength at which a substance exhibits maximum absorption depends on its structure.

$$I_0 = I_a + I_t$$

where,

I_0 = Intensity of incident light

I_a = Intensity of light absorbed

I_t = Intensity of transmitted light.

Beer–Lambert law relates I_a to the thickness and concentration of the medium. Let us understand Beer–Lambert law.

Beer–Lambert law is a combination of the two laws, Beer's law and Lambert's law. We are not going to discuss these two laws separately. Beer–Lambert law states that the fraction of light absorbed by a given absorbing medium is directly proportional to the thickness of the medium and the concentration of the absorbing species. The mathematical expression of this law is given below:

$$\log I_0/I = A = \varepsilon cl \qquad \ldots (3.1)$$

where,

I_0 = Intensity of incident light

I = Intensity of transmitted light

A = Absorbance

l = Thickness of the medium

c = Concentration in mol dm^{-3}

ε = Molar absorption coefficent

Eq. 3.1, $A = \varepsilon cl$, is of the type "$y=mx$", which is an equation for a straight line passing through the origin. The slope ("m") of the straight line plot of A against c is equal to the product, εl. Hence, from the values of the slope and l, ε can be found out.

$$\varepsilon = \frac{\text{slope}}{l}$$

ε, the **molar absorption coefficient,** is the absorbance of a solution having unit concentration ($c = 1$ M) placed in a cell of unit thickness, ($l = 1$ cm). Absorbance is also called **optical density (OD).**

ε can be expressed in the unit, m^2 mol^{-1} or cm^2 mol^{-1}. If l is in m unit and c is in mol m^{-3} units, then ε is in m^2 mol^{-1} units. On the other hand, if l is in cm unit and c is in molarity unit (mol/1000 cm^3 or mol/dm^3 units), then ε is in cm^2 mol^{-1} units.

According to Eq. 3.1, the absorbance or OD of a solution in a container of fixed path length is directly proportional to the concentration of a solution. A plot between absorbance and concentration is expected to be linear. Such a straight line plot (passing through the origin) shows that Beer–Lambert law is obeyed. The straight line so obtained is known as **calibration curve.** A calibration curve is useful in finding the concentration of a given solution. We shall discuss this aspect in Demonstration Experiment 1 of this unit. Dilute solutions obey Beer–Lambert law over a considerable concentration range, the upper limit varying from system to system.

Deviations from Beer–Lambert Law

Beer–Lambert law does not hold good over a wide range of concentrations, if the nature of the absorbing species changes with concentration; for example, when the species ionises, dissociates or associates in solution. Addition of large amounts of noninterfering electrolytes may shift the wavelength at which maximum asportion occurs and may also change the value of molar absorption coefficient. Also discrepancies may occur when the light used is not monochromatic.

Monochromatic light has more or less only one wavelength value.

3.2.2 Principle of Colorimeter

It is difficult to quantify colour **visually.** For this we need the help of a measuring device. A colorimeter is such a device. A colorimeter measures the intensity of light before passing through the solution and after passing through the solution. From the intensity measurements, we can estimate the concentration of a solution. You are provided with a low cost colorimeter for measurement of light intensity.

In general, the apparatus for colorimetry includes a

- light source
- slits and lenses to focus a sharp beam of light,
- filters to transmit a narrow range of wavelengths,
- a cuvette which is a small vessel in which the solution is taken,
- cuvette holders, and,
- a receiver which is helpful in determining the intensity of the transmitted beam.

The instruments of this type are known as filter colorimeters or filter photometers. A schematic diagram of a colorimeter is given in Fig.3.1. The diagram of a low–cost colorimeter is given in Fig.3.2.

A colorimeter operates on a broad range of wavelengths.

A colorimeter is useful in visible region only. But a spectrophotometer is useful in u.v. and visible regions. A spectrophotometer has special facilities for generation and selection of specific wavelength.

Fig.3.1 : Schematic diagram of a colorimeter

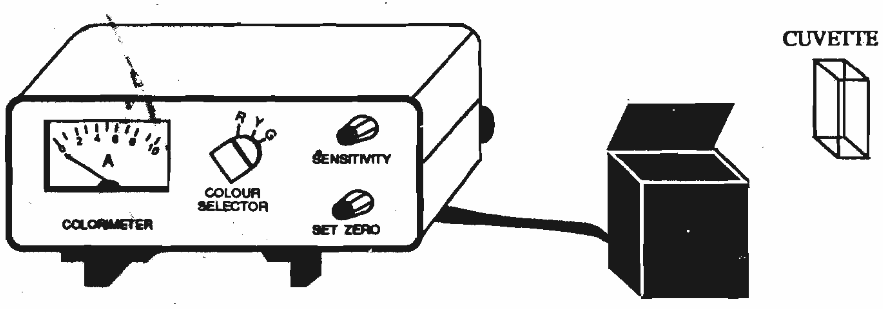

Fig. 3.2 : Low–cost colorimeter.

The diodes have the property of permitting current to flow with practically no resistance in one direction and offer nearly infinite resistance to current flow in the opposite direction. In electronic circuits, diodes have numerous applications.

A photocell converts light into electricity.

The reference sample may be pure solvent or a solution of lower concentration.

Three light emitting diodes (LEDs) are available in the low-cost colorimeter as light source. These emit light of different colours such as red, yellow or green. You would be using one of them depending on the colour of absorbing medium. The light from the source is made to pass through a slit so that we get a thin ray, which falls on the cell containing the solution. Some of the light is absorbed and the rest is transmitted. The light transmitted by the solution falls on the photocell where a current is generated. The magnitude of this current is proportional to the intensity (I) of the light transmitted by the solution. The current signal is suitably amplified and then measured with the help of an ammeter. The intensity of incident light (I_0) is measured by passing the light from the same source through distilled water taken in the cuvette. Under this condition, no light is absorbed and the whole of it falls on the photocell. In case the solution is made in a solvent other than water, the pure solvent may be taken as the reference sample. The difference between the two readings gives the amount of light absorbed. Next let us discuss the controls of the low–cost colorimeter.

3.2.3 Various Controls of the Low–Cost Colorimeter

The meter reading is called the meter response. Instead of absorbance values, meter response values are used in low–cost colorimeter experiments.

Power Switch : This is a switch on the back of the instrument and is used to switch the instrument on or off. When the instrument is connected to the mains and switched on, the LED on the front panel will glow.

Colour Selector : This control is on the front panel of the instrument with the positions marked R, Y and G signifying the three colours, red, yellow or green.

Meter Scale : The scale in the colorimeter (marked A) has markings from 1 to 10. These markings are meter response values.

Set Zero : This control is again on the front panel of the instrument. This is adjusted to set the meter response to zero when the solvent or reference solution is taken in the cuvette.

Sensitivity : This control is also on the left front panel of the instrument. This is used to give any desired scale for the range of concentrations under consideration. Suppose that in an experiment, we have solutions of concentrations varying from 0 to 8% (mass by volume). With the solvent, the set zero knob is adjusted to set the meter response to zero. Then with the 8% solution, the sensitivity knob is adjusted to set the meter response to 9.0. Let us say, in another experiment, we have solutions from 0–6% only. Instead of using the same adjustment, we could have a better scale. After setting zero with the solvent, we take the 6% solution and readjust the sensitivity knob to set the meter response to 9.0. Remember, the earlier setting gives a scale of 0–9 for concentrations 0–8%, whereas the latter setting gives a scale of 0–9 for a smaller concentration range 0–6%.

Method of Operation

1) Before connecting the instrument to the mains, check whether the needle coincides with zero in the meter. If the needle is not coinciding with zero, make it read zero using a small screw driver into the hole under the meter. Then connect the instrument to the mains and put on the power switch at the back.

2) Set the colour selector knob at the desired colour. For an unknown solution, the knob for the colour selector is set at R or Y or G depending on which LED gives the highest meter response, (i.e., the largest absorbance), when the light from LED is passed through the solution in the cuvette.

3) Take a clean cuvette and fill it with ..distilled water (or the reference sample). Wipe the outside dry with tissue paper. Make an identifying mark on one plain side of the curvette at the top and insert the curvette into the holder in such a way that the marked plain side is towards the LED. **Maintain this position everytime you insert the curvette into the holder.** Close the lid of the holder.

4) Adjust the set zero control to make the meter read zero.

5) Next rinse and fill the same cuvette with the solution of maximum concentration. Wipe the outside dry. Insert into the holder and close the lid.

6) Adjust the sensitivity control to set meter response near the end of the scale, say 9.0. Do not disturb this knob after this adjustment.

7) Rinse and fill the same cuvette again with distilled water (or the reference sample) and insert into the holder after wiping the outside dry. Check if the meter reads zero. If not, use the set zero control to get a meter reading zero. After this, do not disturb this knob. The instrument is now set for a calibration experiment or a kinetic experiment.

Precautions

1) You should not use a plastic cuvette while using organic solvents like chloroform, acetone, etc.

2) The reference sample, which is used to set the meter response to zero with the set zero control, should consist of the solvent (or a solution of lower concentration) and all reagents except the specific light-absorbing substance being studied.

3) Wash the cuvette thoroughly. Rinse it with the solvent or the solution depending on which is going to be taken in it for colorimetric measurement.

4) See to it that you do not leave any finger marks on the cuvette.

5) Keep the cuvette in the same position each time you insert it in the holder.

6) Never touch the faces of the cuvette through which light is transmitted.

7) Wipe the outside of the cuvette dry after filling and before inserting in the holder.

3.2.4 Demonstration Experiment 1 : Colorimetric Estimation of Copper Sulphate

Calibration of a colorimeter is the first step in estimating the concentration of a solution colorimetrically. In this experiment, we shall discuss the method of obtaining the calibration curve and estimating the concentration of given solution of copper sulphate.

Aim : i) To draw concentration – absorbance calibration curve for copper sulphate solution.

ii) To determine the concentration of a given copper sulphate solution.

Requirements

Apparatus

Colorimeter	–	1
Volumetric flask (100 cm^3)	–	1
Test tubes	–	10
Test tube stand	–	1
Measuring cylinder (10 cm^3)	–	1
Beaker (250 cm^3)	–	2
Burettes (50 cm^3)	–	2
Burette stand	–	2

Chemicals

Stock solution of copper sulphate (10% m/V)
copper sulphate solution of unknown concentration

Procedure

Copper sulphate solutions of various concentrations are prepared in six labelled test tubes using the stock solution. For this purpose the required volumes of water and copper sulphate solution (stock solution) are added as shown below :–

Water and copper sulphate solutions are taken in two burettes, one containing the stock solution and the other containing water.

While verifying the mass by volume percentage values entered in the table, remember that the stock solution is 10% *m/V* in strength.

Sample number	Volume of stock solution	Volume of distilled water	Mass by volume percentage of solution
1	0	10	0
2	2	8	2
3	4	6	4
4	6	4	6
5	8	2	8
6	10	0	10

It can be seen that the concentration of the six samples vary from 0 to 10% of copper sulphate (m/v).

Before estimating Cu^{2+} ions in an unknown solution, a calibration curve will have to be plotted between the concentration and the meter response in the instrument. For this we shall follow all the instructions listed under 'Method of Operation'. In keeping with instruction 2 stated there, set the selector knob on R, since copper sulphate solution has an absorption maximum in the red region. After adhering to the instructions 1 and 3 to 7, the following is done without distributing the set zero and the sensitivity knobs.

The cuvette is cleaned throughly, rinsed with sample (1) mentioned above and filled with the same. The cuvette is placed in the cuvette holder in the instrument and the meter response is recorded in observation Table 3.1. Then sample (1) is removed and the cuvette is rinsed and filled with sample (2). The cuvette with sample (2) is placed in the cuvette holder and the meter response is again noted. This procedure is repeated with the samples kept in tubes (3), (4), (5) and (6), each time noting the meter response in Table 3.1.

The cuvette is again washed, rinsed with the solution of unknown concentration (sample 7) and filled with it. The cuvette is placed in the cuvette holder and the meter response is noted in the table.

Table 3.1 : Meter Response as a Function of Concentration of Copper Sulphate

Sample number	Strength of copper sulphate in % m/v	Meter response
1	0	....
2	2	....
3	4	....
4	6	....
5	8	....
6	10	....
7	Unknown solution	

Calibration Curve

The calibration curve (Fig. 3.3) is plotted in a graph sheet using the values of strength of copper sulphate solution and meter response from Table 3.1.

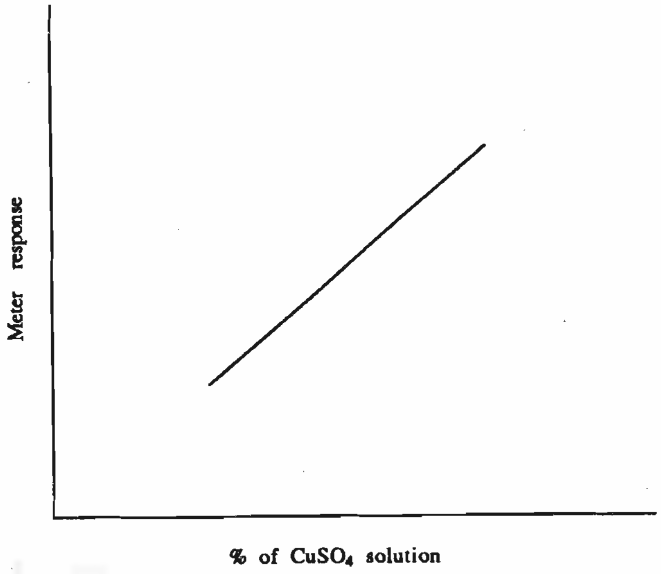

Fig.3.3 : Calibration Curve.

Using the Calibration Curve

In the interpolation method, the concentration of the unknown solution lies between the upper and lower limits of concentrations of standard solutions used for colorimetric measurement.

The concentration of the test solution (solution of unknown concentration of copper sulphate) is found out by interpolation method. For this, a dotted straight line is drawn from the point corresponding to the meter response of the test solution. The *x*–coordinate corresponding to the point of intersection of the calibration curve and the dotted line gives the strength of the test solution as shown in Fig. 3.4.

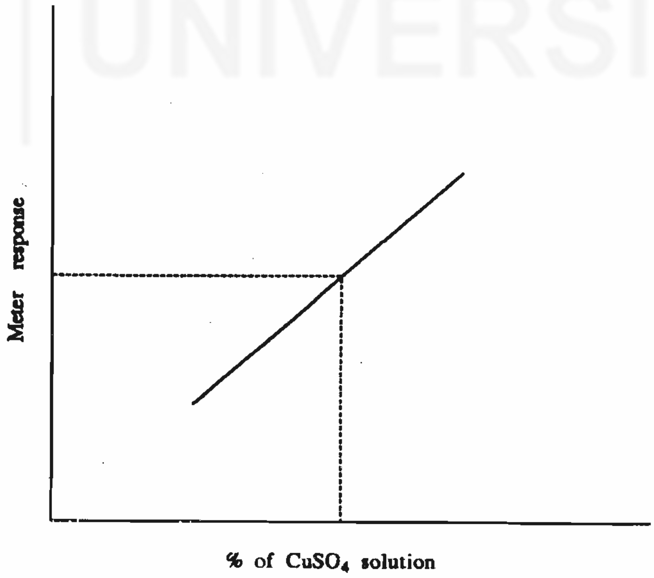

Fig. 3.4: Finding the concentration of the unknown solution using the interpolation method.

Result

From the graph, % of copper sulphate solution = ... % *m*/*V*

SAQ 1

For a substance, ε is equal to 245 $m^2 mol^{-1}$ at a wavelength of 450 nm. Calculate the concentration (in molarity units) of its solution which has an absorbance of 0.1250, when placed in a cell of thickness 1.00×10^{-2} m.

Hints : (i) Use Eq. 3.1 (ii) Note that ε is in $m^2 mol^{-1}$ units and l is in m unit. Hence c will be in mol m^{-3} units.

To get c in molarity unit, use the following relationship:

$$\begin{aligned} 1 \text{ mol m}^{-3} &= 1 \text{ mol } (10 \text{ dm})^{-3} \\ &= 1 \times 10^{-3} \text{ mol dm}^{-3} \\ &= 1 \times 10^{-3} \text{ M} \end{aligned}$$

$$\left[\text{since } 1 \text{ M} = 1 \text{ mol dm}^{-3} \right.$$

$$\left. = 1 \text{ mol per litre}\right]$$

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3.3 CONDUCTOMETRY

Conductometry deals with the measurement of electrical conductance of solutions containing ions. These solutions conduct electric current due to the movement of ions towards oppositely charged electrodes. The ability of a solution to conduct current is given by its conductivity. The conductivity of a solution is proportional to the number of ions, the charge on each ion and the speed with which the ions move. The speed with which an ion moves in turn depends on the nature of the ion, nature of the solvent, presence of other ions, temperature and the applied field.

Conductometric measurements find a wide range of applications. These are used in determining equilibrium constants, e.g. ionisation constants of weak electrolytes, solubility products of sparingly soluble salts, hydrolysis constant, etc. Reactions that proceed with the formation or disappearance of ions can be conveniently monitored conductometrically for getting their kinetic parameters. Some substances which cannot be volumetrically or potentiometrically analysed can be estimated conductometrically with ease.

3.3.1 Theory

Ionic solutions obey Ohm's law just as metallic conductors do. In accordance with Ohm's law, the current I passing through a given solution is proportional to the potential difference, E. The proportionality constant R is the resistance of the solution.

$$E = IR \qquad \ldots (3.2)$$

The conductance G is defined as the reciprocal of resistance.

$$G = 1/R \qquad \ldots (3.3)$$

Resistance is measured in ohm (Ω)and conductance in siemens (S), $1S = 1\ \Omega^{-1}$.

The resistance of a homogeneous body of uniform cross section is proportional to its length, l and inversely proportional to its cross-section, A. The proportionality constant is called the resistivity (specific resistance), ρ. The units of ρ are Ω m.

$$R = \rho\ (l/A) \qquad \ldots (3.4)$$

The conductivity κ (Kappa) is the inverse of resistivity.

i.e., $$\kappa = \frac{1}{\rho} \qquad \ldots (3.5)$$

The units of κ are $S\ m^{-1}$.

Conductivity of a solution can be defined as the conductance of a solution contained between two parallel electrodes which have cross-sectional area 1 meter square and which are kept 1 meter apart.

Taking the inverse of Eq. 3.4, $\frac{1}{R} = \frac{1}{\rho} \cdot \frac{1}{(l/A)}$

$$= \kappa/(l/A) \qquad \text{(using Eq. 3.5)}$$

using Eq. 3.3., $G = \kappa/(l/A)$

or $$\kappa = G\ (l/A) \qquad \ldots (3.6)$$

The ratio l/A is called the cell constant and it depends on the geometry of the cell — the distance between the electrodes (l) and the area of the electrodes (A). Eq. 3.6 can be written as

$$\text{Conductivity} = \text{Conductance} \times \text{cell constant} \qquad \ldots (3.7)$$

The cell constant values are usually obtained by an indirect method and not by measuring l and A directly. The indirect method involves measuring the conductance G of a standard solution of KCl of known conductivity, κ. Table 3.2 gives the κ values of KCl solutions at three different concentrations and at three different temperatures.

Table 3.2 : Conductivity of KCl solutions

[KCl]/M	κ/S m^{-1} at 20°C	κ/S m^{-1} at 30°C	κ/S m^{-1} at 40°C
0.10	1.167	1.412	1.662
0.02	0.250	0.304	0.357
0.01	0.127	0.154	0.179

Standard KCl solution is taken in the cell for which cell constant is to be determined. Conductance of this solution is then measured and its temperature is noted. The conductivity at the temperature is obtained from Table 3.2.

We can get the κ value of KCl at temperatures other than those given in Table 3.2 from a plot of conductivity against temperature using the values given inTable 3.2.

Then the cell constant can be calculated using Eq. 3.7:

$$\text{Cell constant} = \frac{\text{Conductivity of KCl solution}}{\text{Conductance of the same solution}} \qquad \ldots (3.8)$$

This cell of known cell constant is used for finding out the conductivity of any other sample. For this, we have to measure the conductance of a given sample and then use Eq.3.7.

Conductivity of a molar solution is termed molar conductivity. Molar conductivity is represented by the symbol, Λ_m.

$$\Lambda_m = \frac{\kappa}{c} \qquad \ldots (3.9)$$

where κ is the conductivity of a solution of concentration c mol m^{-3}. Λ_m is expressed in units of S m^2 mol^{-1}.

Concentration in mol m^{-3} units = Concentration in molarity × 1000

You are provided with a low-cost conductometer (Fig. 3.5) for conductance measurement. It has an operational amplifier based circuit. Operational amplifier consists of many components mounted on a single silicon chip. Operational amplifiers have a variety of uses and, are particularly useful in low-cost instruments. We shall not discuss the principle behind the functioning of operational amplifiers, since the same is not necessary to do our experiments. For a detailed discussion on operational amplifiers, you are advised to go through Unit 9 of Block 3 of Electrical circuits and Electronics (PHE–10) course.

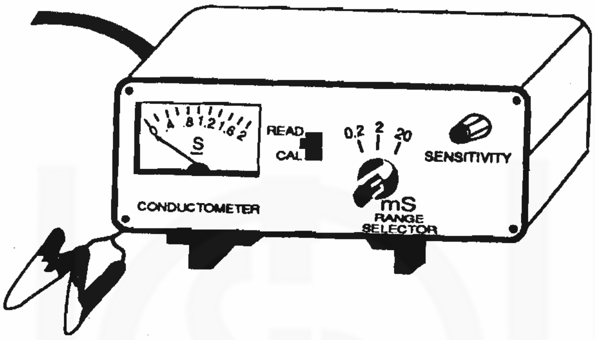

Fig. 3.5 : Low cost conductometer

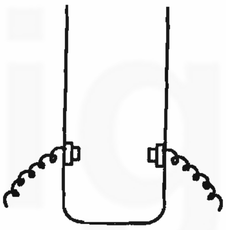

Fig. 3.6 : Low cost conductivity cell

The low cost conductometer is easy to assemble and maintain. The low cost conductometer is more convenient to use, especially for studying reactions conductometrically in kinetics experiments; we shall be using this instrument in Experiment 21 of this course.

The commercial conductometers are based on wheatstone bridge principle which is explained in Unit 16 of Block 4 of Physical Chemistry (CHE–04) course.

The commercial conductivity cells are expensive due to the usage of platinum electrodes. On the other hand low-cost conductivity cell (Fig. 3.6) is made of zero-cost carbon rods. These carbon rods are obtained from exhausted dry batteries. Using these carbon rods, conductivity cells of various designs can be easily made.

The conductance of solutions increases with increase in temperature. This is due to the increase in the velocity of ions, decrease in the viscosity of the medium, and decrease in the interactions between ions. In the case of weak electrolytes, the increase in the degree of ionisation with increase in temperature also contributes to the increase in conductance. Generally the conductivity of aqueous solutions increases by about 2% per degree celsius rise in temperature. Hence it is advisable to keep solutions in a thermostat till they acquire constancy in temperature. Conductance, conductivity and molar conductivity values are to be given along with the temperature values.

As ordinary distilled water contains impurities like CO_2, metal silicates, etc., it cannot be used for preparing solutions for very accurate conductance measurements. When conductance values of high accuracy are required, conductivity water is to be used.

For the conductance experiments of this course, distilled water or deionised water is adequate, as long as the conductivity of water is not more than 10^{-5} S cm^{-1} or 10^{-3} S m^{-1}

3.3.2 Various Controls of the Low-Cost Conductometer

Power Switch

This switch is on the back of the instrument. This is used to turn the instrument on or off. When the instrument is connected to the mains (220 V, AC supply) and switched on, the indicator LED on the front panel glows.

Range Selector

This control is on the front panel of the instrument. It has positions marked 0.2, 2, 20. These numbers stand for the full scale meter values in millisiemens (mS). This means, for example, when the selector is at 20, the meter reads between 0 and 20 mS.

Mode Selector

This control is also on the front panel of the instrument. It has positions marked CAL and READ. This is used to set the instrument in either the calibration (CAL) or read (READ) mode. The instrument is kept on CAL mode when the meter is being calibrated to read 0.1, 1, or 10 mS (mid point of the scale in the range 0.2, 2, or 20 mS, respectively) using the sensitivity control. When the instrument is on CAL mode, a standard resistor inside the instrument replaces the conductivity cell in the circuit. The cell is in circuit only when the control is on READ mode.

Sensitivity

This control, which is also on the front panel, is used while calibrating the meter.

3.3.3 Method of Operation

The following instructions will help you in using the conductometer.

1) Check the mechanical zero of the meter before connecting the instrument to the mains. If the needle is not showing zero, then adjust this using a small screw driver inserted into the hole under the meter. Then connect the instrument to the mains and switch on the instrument using the power switch.

2) Take the minimum volume of the solution (for which conductance is to be measured) in the conductivity cell and, connect the cell to the instrument.

3) Keep the mode selector at READ.

4) Set the range selector at one of the positions, 0.2. or 2 or 20, such that the position which gives a meter reading is around the middle of the scale.

5) Shift the mode selector at CAL. Then adjust the sensitivity control to set the meter reading to mid–scale. After this adjustment, do not disturb the sensitivity control. The steps 1 to 5 are collectively known as **calibration** of the conductometer.

A minimum volume of solution is required to be taken in the cell for measuring the conductance of the solution. This varies from cell to cell and has to be experimentally obtained. This minimum volume is little more than the volume of solution required to just immerse the electrodes. This volume can be determined by taking a strong electrolyte, for example, a solution of KCl. Measure out a volume, say 5 cm^3, into the cell, calibrate the meter and determine the conductance. Then add KCl solution in 1 cm^3 lots and measure the conductance after each addition. The volume of solution beyond which conductance remains constant is the minimum volume. This volume can also be obtained graphically by plotting conductance vs volume of solution (Fig. 3.7).

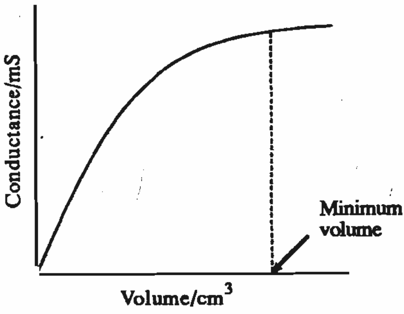

Fig. 3.7 : Conductance vs. volume of solution plot for determining the minimum volume.

For any conductance measurement using this cell, the volume of solution to be taken has to be equal to or more than the minimum volume.

6) Set the Mode selector to READ and read the meter to get the actual conductance value of the solution.

Precautions

1) Measurement of conductance in the course of a titration or a kinetic experiment may require shifting the Range Selector control. Every time you change the range, you have to check if the meter calibration is alright.

2) Conductivity cells should never be left with any solution or without proper cleaning after an experiment. After cleaning and rinsing well with distilled water or deionised water, leave the cell with electrodes well immersed in distilled/deionised water.

3) Rinse the conductivity cell well with the test solution a couple of times before filling the cell for measuring conductance.

4) You must keep the mode selector at CAL (and not at READ) under the following conditions:
   - at the time of disconnecting the conductivity cell
   - changing the solution in the cell
   - at the time of connecting the cell but before pouring the solution into it.

5) If for any experiment you have to stir the solution in the conductivity cell, then keep the stirring rod above the solution while reading the meter.

The method of measuring the conductance of a solution can be understood from Demonstration Experiment 2.

3.3.4 Demonstration Experiment 2: Determination of Conductance of Given Sodium Hydroxide Solution

We shall use the low-cost conductometer to find out the conductance of 0.01275 M NaOH solution. This experiment will help you in doing Experiment 21 of this course which deals with the kinetics of saponification of ester.

Aim : To find the conductance of 0.01275 M NaOH solution.

Requirements

Apparatus

Conductometer	–	1
Conductivity cell	–	1
Wash bottle	–	1

Chemicals

0.01275 M sodium hydroxide solution

Deionized water

Procedure

Before filling the conductivity cell with 0.01275 M NaOH solution, it is washed with water and rinsed with the given NaOH solution. The instructions 1 to 4 given under "method of operation" are followed. We find out that it is preferable to place the range selector at 20, since it leads to a meter reading around the middle of the scale. The sensitivity control is adjusted to set the meter reading to midscale. After this adjustment, the sensitivity control is not disturbed. The mode selector is shifted to "READ" position. The conductance of the given NaOH solution is found out and the value is entered as shown below:

The conductance of 0.01275 M NaOH solution = ... mS

SAQ 2

The conductivity of 0.1000 M potassium chloride solution is 1.167 S m^{-1} at 293 K. Calculate its molar conductance. (**Hint :** Use Eq. 3.9).

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3.4 POTENTIOMETRY

Potentiometry deals with the measurement of difference in potential between two electrodes which have been combined to form an electrochemical cell. The electrochemical cells are of two types, galvanic cells and electrolytic cells. In galvanic or voltaic cells, chemical energy is transferred into electrical energy. As a result of this, galvanic cells act as a source of electrical energy. Daniell cell which we are going to study in detail, is a familiar example of a galvanic cell. In electrolytic cells, electrical energy is transformed into chemical energy. In electrolytic cells, application of voltage higher than that of the cell results in a chemical reaction. For example, passage of electricity through acidified water causes electrolysis of water. It results in the production of hydrogen and oxygen at the cathode, and anode respectively.

The difference in potential between the two electrodes of a galvanic cell is known as cell potential. The cell potential depends on the composition of the electrodes, concentrations of the solutions (or pressures of gases) and the temperature. Relationship connecting the cell potential with the concentration of the species involved in the concerned chemical reaction, known as Nernst equation, can be derived using thermodynamic principles. A detailed discussion is given regarding this in Sec. 17.6 of Unit 17 of Physical chemistry (CHE–04) course. Based on the dependence of cell potential on the concentration of the species in the cell, we have used mV/pH meter in CHE–03(L) course as an analytical tool in acid-base titration. In this course, we shall use mV/pH meter for the determination of pH of buffer solutions and the solubility product of silver chloride. In order to understand the above two experiments, we shall study the galvanic cells in a detailed way.

The mV/pH meter owes its name to the fact that it is useful in measuring the potential difference of cells (in mV units) and in determining pH of the solutions.

3.4.1 Galvanic Cells and Cell Reaction

There are many types of galvanic cells. We are interested in such galvanic cells in which the electrodes are dipped in different electrolytes. We shall illustrate the functioning of galvanic cells using Daniell cell (Fig. 3.8).

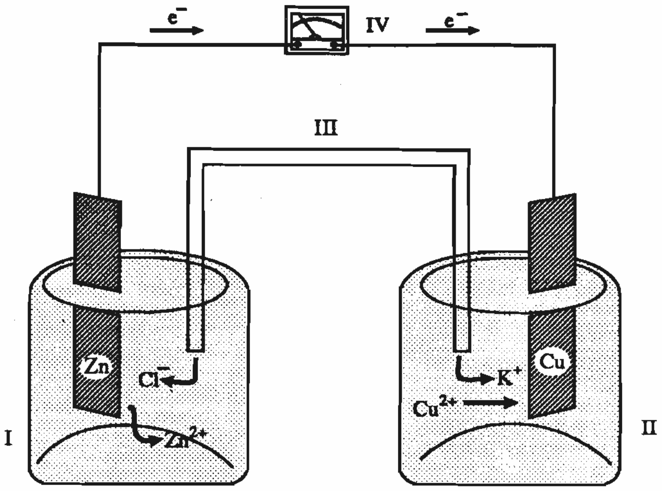

Fig. 3.8 : Daniell cell

I) anodic compartment, II) cathodic compartment, III) salt bridge, IV) voltmeter.

In Daniell cell, zinc gets oxidised to Zn^{2+} ions. Two electrons are released per each zinc ion formed. These electrons travel towards the copper electrode and are used in the reduction of Cu^{2+} ions to Cu. These two reactions can be written as follows:

$$Zn\,(s) \longrightarrow Zn^{2+}(c_1) + 2e^- \qquad \text{Oxidation} \qquad \ldots (3.10)$$

$$Cu^{2+}\,(c_2) + 2e^- \longrightarrow Cu(s) \qquad \text{Reduction} \qquad \ldots (3.11)$$

An electrode dipping in an electrolyte constitutes a half-cell. For instance, zinc rod dipping in zinc sulphate solution of concentration c_1 constitutes a half-cell and copper rod dipping in copper sulphate solution of concentration c_2 constitutes another half-cell. Daniell cell is made by the combination of two half-cells. The cell reaction in Daniell cell is the combination of two half-cell reactions (given by Eqs. 3.10 and 3.11) and is represented below by Eq. 3.12.

$$Zn\,(s) + Cu^{2+}\,(c_2) \longrightarrow Zn^{2+}(c_1) + Cu(s) \qquad \ldots (3.12)$$

Knowing the type of reaction taking place in a cell, we can represent the cell on paper. For this, the following rules will be helpful.

1) The oxidation part must appear on the left side of the cell. The reduction part must appear on the right side of the cell. The stoichiometric numbers, the electrons and water molecules appearing in the half cell reaction (or cell reaction) must not find a place in the cell representation.

2) The electrodes are shown at the extreme left and right positions. These are shown distinctly separated from the corresponding electrolytes by means of single vertical lines.

3) In case of gas electrodes, and many oxidation-reduction systems like quinone-hydroquinone, inert electrodes such as carbon rod or platinum wire are used for electrical contact.

4) The various materials present in the same half-cell in the same phase are written together separated by commas.

5) Double vertical lines are used to join the two half-cells; this means a salt bridge is used between the two half-cells. We shall shortly understand the use of salt bridge in galvanic cells.

6) Concentrations of ions, pressures of gases etc. are indicated in brackets and mentioned along with the substance.

In the light of these rules, you can understand the representation of Daniell cell which is given below:

$$\mathrm{Zn}(s) \mid \mathrm{Zn}^{2+}(c_1) \mid \mid \mathrm{Cu}^{2+}(c_2) \mid \mathrm{Cu}(s) \qquad \ldots (3.13)$$

3.4.2 Measurement of E.M.F.

The potential difference across an electrode-electrolyte interface is called electrode potential.

The cell potential of a galvanic cell (E_{cell}) is given by the difference between the two electrode potentials, E_1 and E_2, of the cathode and anode, respectively.

$$E_{\text{cell}} = E_1 - E_2 \qquad \ldots (3.14)$$

The junction potential developed at the liquid junction between the two half-cells also contributes to the cell potential. But this liquid junction potential can be minimised by having a salt bridge between the two electrodes.

A salt bridge serves to

- maintain electrical neutrality within the solutions in the two half-cells
- minimise the liquid junction potential
- complete the circuit.

Let us now study the construction of salt bridge.

Preparation of Salt Bridge

Agar-agar forms a dispersion of liquid in solid (i.e., a gel) which becomes a thick mass. It prevents the free flow of KCl/KNO_3 into the two half-cells.

Bend a glass tube in U-shape on a burner. Prepare the agar-agar solution as follows: 0.3–0.5 g of powdered agar-agar is dissolved in 10 cm^3 of saturated solution of KCl/KNO_3 at 100°C on a steam bath (add agar-agar powder in small quantities so that solution does not froth). Keep the solution at 100°C until all the agar-agar has passed into the solution. Then add 1–1.5 g of KCl/KNO_3 to produce excess of the solid. Now connect the side arm of the bent U–tube to a rubber tubing and suck the hot solution from the other end of the ruber tubing. On cooling, the agar-agar solidifies and this acts as a salt bridge.

Instead of a salt bridge, a filter paper strip soaked in a saturated solution of KCl or KNO_3 can also be used across the two half-cells.

Let us now discuss the measurement of cell potential. If a current is drawn from a cell in the course of the measurement of cell potential, the cell reactio proceeds and the concentrations of the solutions change in the two half-cells. Hence, it is important to measure the cell potential without allowing current to flow. The cell potential measured nearly under zero or negligible current flow is called electromotive force (e.m.f.) of the cell. We shall be using low-cost mV/pH meter for measurement of e.m.f. and pH.

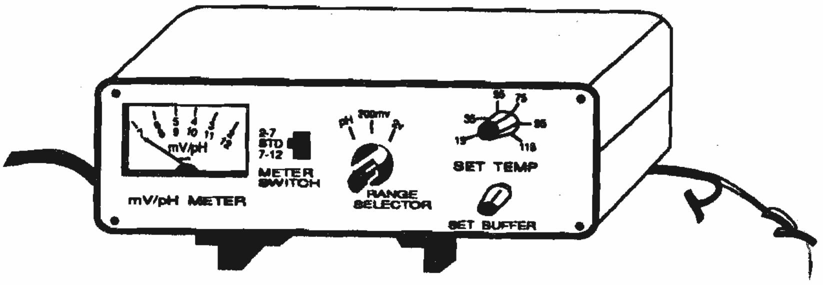

Fig. 3.9 : Low-cost mV/pH meter

The low-cost mV/pH meter (Fig. 3.9) has a circuit based on operational amplifier. This instrument draws only negligible current and hence is quite useful in the measurement of cell e.m.f. Another advantage is that it uses carbon electrodes for pH measurement. A carbon rod extracted from used dry batteries works as the electrode. This electrode is available almost at zero cost. Two carbon electrodes are provided with each low-cost mV/pH meter.

The two half-cells constituting a galvanic cell are known as the indicator half-cell and the reference half-cell. The reference half-cell potential is maintained constant and the indicator half-cell potential is allowed to vary in an experiment.

When we use mV/pH meter for the measurement of concentration of a species (such as in the measurement of pH of buffers or determination of solubility product of a salt), the concerned species must be made the electrolyte in the indicator half-cell. Before studying the various controls of the mV/pH meter, we should familiarise ourselves with Nernst equation.

3.4.3 Nernst Equation

The relationship between e.m.f. of a cell (or half-cell potential) and the concentration of species involved in cell reaction (or half-cell reaction) is given by Nernst equation. Let us consider the following cell reaction.

$$aA + bB \rightleftharpoons cC + dD \qquad \ldots (3.15)$$

Nernst equation applicable to this reaction is given below:

$$E_{\text{cell}} = E^0_{\text{cell}} + \frac{2.303RT}{nF} \log \frac{[A]^a [B]^b}{[C]^c [D]^d} \qquad \ldots (3.16)$$

where

- A and B are reactants and C and D are products in the cell reaction
- *a, b, c* and *d* are stoichiometric coefficients.
- $E^0_{\text{cell}} = E^0_{\text{RHE}} - E^0_{\text{LHE}}$; E^0_{RHE} and E^0_{LHE} are the standard electrode potentials of the electrodes at the right hand and left hand sides. The standard electrode potentials of some electrodes are given in Table 3.3. The standard electrode potential is the potential at the electrode when the species at the electrode are in

As per IUPAC convention, the standard electrode potential is mentioned for the reduction of a specified species at the electrode.

their standard states at 1 bar (= 10^5 Pa = 1 atm) pressure at any specified temperature and at unit concentration. The temperature usually chosen is 298 K.

- n is the number of electrons involved in the cell reaction
- F is equal to 96500 coulombs
- T is temperature
- [A], [B], [C] and [D] are the concentrations of the concerned reactants and products.

Table 3.3: Standard Electrode Potentials

Half-cell reactions	E^o/V
$Li^+ + e^- \longrightarrow Li$	–3.05
$K^+ + e^- \longrightarrow K$	–2.93
$Ca^{2+} + 2e^- \longrightarrow Ca$	–2.87
$Mg^{2+} + 2e^- \longrightarrow Mg$	–2.36
$Al^{3+} + 3e^- \longrightarrow Al$	–1.66
$Zn^{2+} + 2e^- \longrightarrow Zn$	–0.76
$Fe^{2+} + 2e^- \longrightarrow Fe$	–0.44
$Sn^{2+} + 2e^- \longrightarrow Sn$	–0.14
$Pb^{2+} + 2e^- \longrightarrow Pb$	–0.13
$Fe^{3+} + 3e^- \longrightarrow Fe$	–0.04
$2H^+ + 2e^- \longrightarrow H_2$	0.00
$Cu^{2+} + 2e^- \longrightarrow Cu$	+0.34
$Cu^+ + e^- \longrightarrow Cu$	+0.52
$I_2 + 2e^- \longrightarrow 2I^-$	+0.54
$MnO_4^- + 2H_2O + 3e^- \longrightarrow MnO_2 + 4OH^-$	+0.59
$Fe^{3+} + e^- \longrightarrow Fe^{2+}$	+0.77
$Ag^+ + e^- \longrightarrow Ag$	+0.80
$Br_2 + 2e^- \longrightarrow 2Br^-$	+1.09
$Cr_2O_7^{2-} + 14H^+ + 6e^- \longrightarrow 2Cr^{3+} + 7H_2O$	+1.33
$Cl_2 + 2e^- \longrightarrow 2Cl^-$	+1.36
$MnO_4^- + 8H^+ + 5e^- \longrightarrow Mn^{2+} + 4H_2O$	+1.49
$F_2 + 2H^+ + 2e^- \longrightarrow 2HF$	+2.87

For the calculation of electrode potentials when the concentration of the species at the electrode is not equal to unity, we have to use the following modified forms of Eqs. 3.15 and 3.16.

$$\text{Half-cell reaction: } A^{n+}(c) + ne^- \longrightarrow A(s, l \text{ or } g) \qquad \ldots (3.17)$$

$$\text{Nernst equation: } E = E^0 + \frac{2.303\,RT}{nF}\log c \qquad \ldots (3.18)$$

Where E and E^0 are the electrode potential and standard electrode potential respectively and c is the concentration of the solution in contact with the electrode.

We shall next discuss the types of electrode systems.

3.4.4 Types of Electrodes

A large number of electrodes are known. For convenience, the electrode systems are divided into various types. We shall discuss the following three types:

i) Metal-metal ion type

A metal is in equilibrium with its ions in solution. We shall study the following three examples under this type.

1) zinc-zinc sulphate solution
2) copper-copper sulphate solution
3) silver-silver nitrate solution

ii) Metal-insoluble salt type

A metal is in contact with a saturated solution of its sparingly soluble salt and another soluble salt having common anion.
We shall study the following example:

Silver-silver chloride-potassium chloride solution

iii) Redox electrodes

These electrode systems have species in solution in two different oxidation states. We shall discuss the following example:

Carbon–quinone–hydroquinone

The carbon rod is an inert electrode and is used for electrical contact: Some other familiar examples of redox electrodes are given below; we will not be discussing them in detail.

Platinum–ferric ion–ferrous ion
Platinum–permanganate ion–manganous ion

These two are used in acid medium.

Let us discuss in detail some of the half-cells coming under the above types of electrodes.

1) Zinc-zinc sulphate half-cell

The half-cell representation for zinc elctrode is,

$$Zn(s) \mid ZnSO_4(c)$$

Where c is the concentration of zinc sulphate solution,
The half-cell reaction is,

$$Zn^{2+}(c) + 2e^- \longrightarrow Zn(s) \qquad \ldots (3.19)$$

This electrode is reversible with respect to Zn^{2+} ion.

The electrode is said to be reversible with respect to such ion or ions which take(s) part in the half-cell reaction.

The standard reduction potential for zinc ($E^0_{Zn^{2+}/Zn}$) is –0.76 V. The relationship useful in calculating the electrode potential of zinc electrode ($E^0_{Zn^{2+}/Zn}$) dipped in a solution of zinc sulphate of concentration c can be written using Eq. 3.18 as follows:

$$E_{Zn^{2+}/Zn} = E^o_{Zn^{2+}/Zn} + \frac{2.303RT}{2F} \log [Z\,n^{2+}] \qquad \ldots (3.20)$$

$$= E^0_{Zn^{2+}/Zn} + \frac{2.303RT}{2F} \log c$$

Construction of Zinc Electrode

A can is a container vessel.

Take a zinc rod and dip it in zinc sulphate solution of known concentration. If the zinc rod is not available, then use the can of a used dry battery. The can should be cleaned with a sand paper and the connecting wire is to be soldered.

2) Copper-copper sulphate half-cell

The half-cell representation for copper electrode is

$Cu(s) \mid CuSO_4(c)$

Where c is the concentration of copper sulphate solution.

The half-cell reaction is,

$$Cu^{2+}(c) + 2e^- \longrightarrow Cu(s) \qquad \ldots (3.21)$$

This electrode is reversible with respect to Cu^{2+} ion. The standard reduction potential for copper ($E^0_{Cu^{2+}/Cu}$) is +0.34 V. The electrode potential of copper electrode is related to the concentration of Cu^{2+} ions as per Eq. 3.22 which is written similar to Eq. 3.18.

$$E_{Cu^{2+}/Cu} = E^0_{Cu^{2}+/Cu} + \frac{2.303RT}{2F} \log [Cu^{2+}] \qquad \ldots (3.22)$$

$$= E_{Cu^{+}/Cu} + \frac{2.303RT}{2F} \log c$$

Construction of Copper Electrode

Take a copper rod and dip it in a solution of copper sulphate of known concentration kept in a beaker. If the rod is not available, then use a connecting copper wire.

3) Silver-silver nitrate half-cell

Silver wire can be used in the construction of

i) silver-silver nitrate half-cell which is reversible with respect to Ag^+ ions or

ii) silver-silver chloride half-cell which is reversible with respect to chloride ions. We shall discuss the former type now.

For silver-silver nitrate half-cell, the representation is

$Ag(s) \mid AgNO_3(c)$

where c is the concentration of silver nitrate solution.

The half-cell reaction is,

$$Ag^+(c) + e^- \longrightarrow Ag(s) \qquad \ldots (3.23)$$

Hence this electrode is reversible with respect to Ag^+ ion.

The standard reduction potential for Ag^+–Ag system is $(E^0_{Ag^+/Ag})$ is +0.80 V. The electrode potential of silver-silver ion electrode is related to the concentration of Ag^+ ions as per the equation,

$$\begin{aligned} E_{Ag^+/Ag} &= E^0_{Ag^+/Ag} + \frac{2.303RT}{F}\log[Ag^+] \\ &= E^0_{Ag^+/Ag} + \frac{2.303RT}{F}\log c \qquad \ldots (3.24) \end{aligned}$$

Construction of Silver-Silver Nitrate Half-Cell

Solder a connecting wire to a small piece of silver wire and insert it from the top of a glass tube. Use araldite at the tip of the tube and keep it overnight for drying. Dip the silver wire in a solution of silver nitrate of known concentration.

We shall be using this half-cell in the determination of the solubility product of silver chloride in Experiment 9 of Block 3 of this course.

4) Silver–Silver Chloride Half–Cell

The representation for silver-silver chloride half-cell is,

$Ag(s)\mid AgCl(s)\mid KCl(c)$

where c is the concentration of potassium chloride solution.

The half-cell reaction is,

$$AgCl(s) + e^- \longrightarrow Ag(s) + Cl^-(c) \qquad \ldots (3.25)$$

Hence this electrode is reversible with respect to Cl^- ion.

The standard reduction potential for this half-cell (E^0_{AgCl/Cl^-}) is 0.2223 V.

Nernst equation for this half-cell is given below:

$$E_{AgCl/Cl^-} = E^0_{AgCl/Cl^-} + \frac{2.303RT}{F}\log\frac{1}{[Cl^-]}$$

$$E_{AgCl/Cl^-} = E^0_{AgCl/Cl^-} + \frac{2.303RT}{F}\log\frac{1}{c} \qquad \ldots (3.26)$$

Construction of Silver-Silver Chloride Half-Cell

Solder a connecting wire to a small piece of silver wire and insert it from the top of a jet type glass tube. Use araldite at the tip of the tube and keep it overnight for drying. Keep the silver wire in contact with 0.1 M hydrochloric acid overnight. A fine coating of AgCl is obtained over silver wire. This can be used as Ag/AgCl electrode.

5) Quinhydrone Half-Cell

Quinhydrone is a 1:1 mixture of quinone $[C_6H_4O_2]$ represented by the symbol Q and, hydroquinone $[C_6H_4(OH)_2]$ represented by the symbol H_2Q. Quinhydrone electrode is an example of oxidation–reduction electrode. It consists of an inert electrode (carbon rod or platinum wire) dipped in a solution containing a mixture of oxidised (Q) and reduced (H_2Q) forms of a substance. The half-cell representation for quinhydrone electrode is

$C(s)\mid Q\text{–}H_2Q\,(s)\mid H^+\,(c)$

where c is the concentration of H^+ ions in solution.

The half–cell reaction is,

$$\underset{(Q)}{C_6H_4O_2(s)} + 2H^+(c) + 2e^- \longrightarrow \underset{(H_2Q)}{C_6H_4(OH)_2(s)} \qquad \ldots (3.27)$$

The standard reduction potential for quinhydrone electrode is 0.699 V. The relationship useful in calculating the electrode potential (E_{Q/H_2Q}) of quinhydrone electrode in a solution of H^+ concentration c can be written using Eq. 3.18 as follows:

$$E_{Q/H_2Q} = E^0_{Q/H_2Q} + \frac{2.303RT}{2F} \log [H^+]^2$$

$$= E^0_{Q/H_2Q} + \frac{2.303RT \times 2}{2F} \log [H^+]$$

$$= E^0_{Q/H_2Q} + \frac{2.303RT}{F} \log [H^+] \qquad \ldots (3.28)$$

$$= E^0_{Q/H_2Q} + \frac{2.303RT}{F} \log c \qquad \ldots (3.29)$$

$$= E^0_{Q/H_2Q} - \frac{2.303RT}{F} \text{ pH} \qquad \ldots (3.30)$$

[since – log $[H^+]$ = pH]

As per Eq. 3.27, you can understand that quinhydrone electrode is reversible with respect to H^+ ions. As per Eqs. 3.28 and 3.30, the quinhydrone electrode can be employed for the calculation of $[H^+]$ and pH. In Experiment 8 of Block 3 of this course, we shall see the use of quinhydrone electrode in the determination of pH of buffer solutions. In CHE–03(L) course, quinhydrone electrode has been used in the potentiometric titration of vinegar under Experiment 2 of Block 1.

Construction of Quinhydrone Electrode

You are provided with two carbon rods to be used as electrodes. Use one of these carbon rods and dip it in a solution containing H^+ ions. Add a pinch of quinhydrone. This is quinhydrone electrode.

With this brief introduction to the elementary concepts of potentiometry, let us now take up the functions of the various controls of a mV/pH meter and the method of operation.

3.4.5 Various Controls of the Low-Cost mV/pH Meter

Power Switch : This is located on the back panel of the instrument. This is used to turn the instrument OFF/ON. After connecting the instrument to the mains, if this switch is turned on, the LED on the front panel will glow.

Range selector : This switch on the front panel of the instrument may be put on three positions marked pH, 200 mV and 2V. This brings into the circuit the pH scale, the 200 mV scale or 2 V scale. When the switch indicates pH, the meter reads between pH 2 and 7 or between 7 and 12; at 200 mV, the meter reads between 0 and 200 mV; and at 2 V, the meter reads between 0 and 2 V.

Meter switch : This is a sliding switch with three positions on the front panel. The middle position serves as a standby position (i.e., "off" position) when the meter is not in circuit. This switch is used to reverse the polarity of connections to the meter for measurements in the pH range 2–7 or 7–12.

Set temperature : This knob on the front panel has a scale marked in degree celsius. You must adjust it to read the temperature of the test solution.

Set Zero : This knob on the front panel is used for calibrating the instrument. While calibrating for e.m.f. measurement, this knob is used to bring the meter reading to zero. When the meter is being calibrated for reading pH, this knob is used to set the meter at the pH of the indicator cell solution.

Set slope : There are two knobs located on the back panel; the lower knob is used during e.m.f. calibration and the upper one is used for the pH calibration.

Cell Connection There are two arrangements for connecting the cells to the instrument. For cells using carbon electrodes, two lead wires with black and red crocodile clips are provided. The black goes to the reference half-cell and the red to the indicator half-cell.

The other arrangement has a socket on the back panel for plugging a commercial glass electrode; a terminal is provided nearby for a reference electrode, e.g., calomel electrode.

3.4.6 Method of Operation

Before using the pH meter, it is necessary to calibrate it. Check the mechanical zero of the meter before turning it on. If the needle is not showing zero, then adjust it inserting a small screw driver into the hole under the meter. The calibration for e.m.f. measurement is given below. The calibration for pH measurement will be done in Experiment 8 of Block 3 of this course.

Calibration of the instrument for e.m.f. measurement

1) Connect the instrument to the mains and switch it on. The LED on the front panel should glow.

2) Short the two input leads. Shift the meter switch to 2–7 or 7–12 position. If the meter does not read zero, adjust the set zero knob until it does. Do not disturb this knob.

3) Use a calibrated voltage source, such as the AVO source to obtain 200 mV. Keep the meter switch at STANDBY position. Connect the voltage source to the mV/pH meter at the cell connection terminals — positive lead of the voltage source to the red terminals. Shift the meter switch to 2–7 position and the selector switch to the 200 mV range.

4) Adjust the lower knob of the set slope until the meter reads full scale. With this adjustment, the meter is calibrated to read between 0 and 200 mV.

After this, the lower set slope knob is not to be disturbed for the rest of the experiment.

5) This calibrates the 2 V range also. You can check that by shifting the selector switch to the 2 V range and, by including a 2 V calibrated input at the cell connection terminals. Once the instrument is calibrated, you can connect any cell for which e.m.f. is to be measured at the cell connection terminals and, read the e.m.f. Each division is equal to 4 mV in the 200 mV range and 40 mV in the 2 V range.

To explain the construction of a galvanic cell and the use of mV/pH meter in e.m.f. measurement, the following demonstration experiment is given.

3.4.7 Demonstration Experiment 3: Construction of Daniell Cell and Measurement of E.M.F.

We shall illustrate the way of construction of a galvanic cell and measuring the e.m.f. For this, we shall construct Daniell cell. This experiment will help you in performing experiments 8 and 9 of Block 3 of this course.

We shall construct Daniell cell using 0.01 M $ZnSO_4$ and 0.1 M $CuSO_4$. The cell can be represented as follows:

$$\mathrm{Zn}(s) \mid \mathrm{Zn}^{2+}(0.01\,\mathrm{M}) \mid\mid \mathrm{Cu}^{2+}(0.1\,\mathrm{M}) \mid \mathrm{Cu}(s)$$

The cell reaction for Daniell cell can be written as follows:

$$\mathrm{Zn}(s) + \mathrm{Cu}^{2+}\,(0.01\,\mathrm{M}) \longrightarrow \mathrm{Zn}^{2+}(0.01\,\mathrm{M}) + \mathrm{Cu}(s) \qquad \ldots (3.31)$$

You can see that this equation is obtained by subtracting Eq. 3.19 from Eq. 3.21 since, Zn gets oxidised to Zn^{2+} and Cu^{2+} gets reduced to Cu. You know that Eqs. 3.19 and 3.21 are written for the reduction of the concerned species only. Again Nernst equation applicable to Eq. 3.31 is obtained as follows by subtracting Eq. 3.20 from Eq. 3.22.

$$E = E^0_{\mathrm{Cu}^{2+}/\,\mathrm{Cu}} + \frac{2.303RT}{2F}\log\,[\mathrm{Cu}^{2+}] - \left(E^0_{\mathrm{Zn}^{2+}/\,\mathrm{Zn}} + \frac{2.303RT}{2F}\log\,[\mathrm{Zn}^{2+}]\right)$$

$$= \left(E^0_{\mathrm{Cu}^{2+}/\,\mathrm{Cu}} - E^0_{\mathrm{Zn}^{2+}/\,\mathrm{Zn}}\right) + \frac{2.303RT}{2F}\log\frac{[\mathrm{Cu}^{2+}]}{[\mathrm{Zn}^{2+}]} \qquad \ldots (3.32)$$

$$E = \left(1.1 + \frac{2.303RT}{2F}\log\frac{[\mathrm{Cu}^{2+}]}{[\mathrm{Zn}^{2+}]}\right)\,\mathrm{V} \qquad \ldots (3.33)$$

Aim

i) To construct Daniell cell

ii) To find the e.m.f. of Daniell cell

Requirements

Apparatus

Copper rod
Zinc rod
Salt bridge or filter paper strip
Beaker (100 cm^3)
mV/pH meter
Connecting wires

Chemicals

0.1 M copper sulphate solution

0.01 M zinc sulphate solution

Saturated potassium nitrate solution.

rocedure

First mV/pH meter has to be calibrated as per the instruction given under "calibration of the instrument for e.m.f. measurement".

Next the zinc rod is dipped in a solution of 0.01 M zinc sulphate. The copper rod is dipped in 0.1 M copper sulphate solution. The zinc half-cell is connected to the indicator terminal of the mV/pH meter. The copper half-cell is connected to the reference terminal of the instrument. The two half-cells are connected by means of a potassium nitrate salt bridge or by means of a filter paper soaked in saturated potassium nitrate solution.

The diagram of Daniell cell is given in Fig. 3.8.

The e.m.f. of the cell is measured. The measurement is made at least two more times and the average e.m.f. value is taken. The result is entered as follows:

Temperature = ... K

The e.m.f. of Daniell cell containing 0.1 M $CuSO_4$ solution and 0.01 M $ZnSO_4$ solution measured using mV/pH meter:

i) first measurement = ... V

ii) second measurement = ... V

iii) third measurement = ... V

Average e.m.f = ... /3 V

= V

The calculated value of e.m.f. of the above Daniell cell using Eq. 3.33 = 1.295 V

SAQ 3

Calculate the e.m.f. of the following cell at 298 K:

$$Zn(s) \mid ZnSO_4\,(5.0\times10^{-3}M) \parallel CuSO_4\,(5.0\times10^{-1}\,M) \mid Cu(s)$$

Hints: (i) Use Eq. 3.33 (ii) Since $E^0_{Cu^{2+}/Cu}$ and $E^0_{Zn^{2+}/Zn}$ are quantities defined by standard state, $E^0_{Cu^{2+}/Cu}$, $E^0_{Zn^{2+}/Zn}$ and $E^0_{Cu^{2+}/Cu} - E^0_{Zn^{2+}/Zn}$ (which is equal to 1.1 V) are considered to be exact quantities. Hence '1.1' is supported to have infinite significant figures. (iii) $\frac{2.303RT}{F} = 0.059$ V

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3.5 SUMMARY

In this unit, we have discussed the principles of colorimetery, conductometry and potentiometry. We have explained the use of low-cost instruments in measuring absorbance, conductance and e.m.f. We have described three demonstration experiments to illustrate the use of the low-cost instruments.

3.6 ANSWERS

1) According to Eq. 3.1, $c = \frac{A}{\varepsilon l}$

$$= \frac{0.1250}{245 \times 1.00 \times 10^{-2}} \text{ mol m}^{-3}$$

$$= \frac{0.1250 \times 10^{-3}}{245 \times 1.00 \times 10^{-2}} \text{ mol dm}^{-3}$$

$$= 5.10 \times 10^{-5} \text{ M.}$$

2) Using Eq. 3.9, $\Lambda_m = \frac{\kappa}{c} = 11.67 \text{ S m}^2 \text{ mol}^{-1}$

3) $[Cu^{2+}] = 5.0 \times 10^{-1}$ M

$[Zn^{2+}] = 5.0 \times 10^{-3}$ M

Using these values in Eq. 3.33,

$$E = \left(1.1 + \frac{0.059}{2} \log \frac{5.0 \times 10^{-1}}{5.0 \times 10^{-3}}\right) \text{V}$$

$$= \left(1.1 + \frac{0.059}{2} \times 2.00\right) \text{V}$$

$$= (1.1 + 0.0590) \text{ V}$$

$$= 1.1590 \text{ V}$$

FURTHER READING

1. Senior Practical Physical Chemistry, B.D. Khosla, A. Gulati and V.C. Garg, R. Chand & Co., New Delhi, 4th ed., 1985.

2. Practical Chemistry, S. Giri, D.N. Bajpai and O.P. Pandey, S. Chand & Company Ltd., New Delhi, 7th ed., 1993.