

BCHET-141
ANALYTICAL METHODS IN
CHEMISTRY

Block

3**THERMAL AND ELECTROANALYTICAL METHODS**

UNIT 8**Thermal Methods of Analysis****7**

UNIT 9**Potentiometry****30**

UNIT 10**Conductometry****64**

Course Design Committee

Prof. N.K. Kaushik, (Retd.)
Department of Chemistry,
University of Delhi, New Delhi

Prof. B. S. Saraswat (Retd.)
School of Sciences, IGNOU,
New Delhi

Prof. Nafisur Rehman,
Department of Chemistry,
A.M.U. Aligarh

**School of Sciences,
IGNOU, New Delhi 110068**

Prof. M.S. Nathawat
Prof. Sunita Malhotra
Prof. B.I. Fozdar
Prof. Javed A. Farooqi
Prof. Sanjiv Kumar
Prof. Lalita S. Kumar
Prof. Kamalika Banerjee

Block Preparation Team

Prof. Bharat Inder Fozdar
School of Sciences, IGNOU
New Delhi

Prof. Nafisur Rehman (Editor)
Department of Chemistry,
AMU, Aligarh

Course Coordinator:

Prof. J. A. Farooqi

Print Production

Mr. Rajiv Girdhar
Assistant Registrar (Pub),
MPDD, IGNOU, New Delhi

Mr. Hemant Kumar Parida
Section Officer (Pub),
MPDD, IGNOU, New Delhi

Acknowledgements: Sh. Sarabjeet Singh for CRC preparation

Material partially adapted from the MCH-004 Course of PGDAC Programme.

March, 2022
@ Indira Gandhi National Open University, 2022

ISBN:

All rights reserved. No part of this work may be reproduced in any form, by mimeograph or any other means, without permission in writing from Indira Gandhi National Open University.

Further information on Indira Gandhi National Open University courses may be obtained from the University's office at Maidan Garhi, New Delhi-110068 or IGNOU website www.ignou.ac.in

Printed and published on behalf of Indira Gandhi National Open University, New Delhi by the Registrar, MPDD, IGNOU.

Printed at:

BLOCK 3: THERMAL AND ELECTROANALYTICAL METHODS

In the preceding blocks of this course, you studied about the various chromatographic techniques. In this block our focus will be on thermal and electroanalytical methods. This block consists of three units. Unit 8: **Thermal Methods of Analysis**, deals with the methods which are based on the determination of changes in chemical or physical properties of material on heating. These analytical methods are known as **thermal methods**. These have been developed based on the scientific study of changes in the properties of a sample which occur on heating. In this unit our focus will be on thermogravimetric methods of analysis. Unit 9 and Unit 10 deal with three important electroanalytical methods i.e. potentiometry, pH metry and conductometry. In Unit 9, we are going to cover classification of electroanalytical method, principle of potentiometry and pH metry, and different types of reference and indicator electrodes. Procedural details of measurement of potential and pH along with potentiometric titration and pH metric titration have also been discussed in detail.

Unit 10, deals mainly with Conductometry is one of the oldest and in many ways simplest among the other electroanalytical techniques. This technique is based on the measurement of electrolytic conductance. In this unit we have covered principle and application of conductometry in acid base titrations.

Both thermal methods and electroanalytical could be employed for the determination of elemental concentration or compound in varying sample size of complex matrices of geological, biological, environmental, forensic, pharmaceuticals and other industrial products.

Expected Learning Outcomes

After studying this block, you should be able to:

- describe the basic thermal methods of analysis;
- explain the basic principles of the thermogravimetric analysis;
- describe components of the instruments used for TGA;
- illustrate applications of the thermal methods in the characterizations of inorganic and organic compounds;
- classify electroanalytical methods in different groups;
- describe the basic principles of potentiometry and pH metry;
- illustrate the applications of potentiometric and pH metric methods;
- describe the basic principle of conductometric methods of analysis;
- describe components of the instruments and their use in measurement of conductance.

UNIT 8

THERMAL METHODS OF ANALYSIS

Structure

8.1	Introduction	8.6	Factors Affecting TG Curve
	Expected Learning Outcomes	8.7	Applications of Thermogravimetric Analysis
8.2	Thermogravimetric Analysis	8.8	Summary
8.3	Instrumentation	8.9	Terminal Questions
8.4	Sources of Error in TGA	8.10	Answers
8.5	Interpretation of TG Curve		

8.1 INTRODUCTION

In the preceding blocks you have studied various chromatographic methods. These methods are commonly used to separate mixtures. We now turn our attention to other analytical methods which are based on the determination of changes in chemical or physical properties of material on heating. These analytical methods are known as **thermal methods**. These have been developed based on the scientific study of changes in the properties of a sample which occur on heating. You may be familiar with the facts like, when ice is heated, it melts at 0 °C and then boils at 100 °C, when sugar is heated; it first melts, and then forms brown Caramel. In your undergraduate Organic Chemistry lab you may have used melting points of organic solids in assessing the purity and characterization of organic compounds. Melting points are independent of experimental conditions whether we were using an oil bath or a heating block. Basically in this process we are subjecting the organic sample to a heating procedure and measuring a physical property (melting point) by observing the physical change of the material, as it is heated. In fact, every material behaves in a characteristic way when heated. The thermal methods of analysis are based on the determination of change in chemical or physical

properties of material as a function of temperature in a controlled atmosphere. These methods are good analytical tools to measure:

- thermal decomposition of solids and liquids;
- solid-solid and solid-gas chemical reactions;
- material specification, purity and identification;
- adsorption behaviour of material;
- phase transitions.

These informations help us in the characterization of organic and inorganic chemicals, polymers, metals, semiconductors and other common classes of materials. Not only this, thermal methods also help us in understanding the likely behaviour of chemicals and materials with change of temperature during reactions, transport and storage. On that basis, one can suggest to take possible precaution in handling the particular chemical or material.

Here we have summarized the variety of materials which can be usefully studied by the thermal methods.

1. Organic and Inorganic compounds
2. Pharmaceuticals
3. Polymers and Plastics
4. Textiles and Fibers
5. Minerals, Soils and Clays
6. Ceramics and Glass
7. Building materials such as cement and concrete
8. Catalysts
9. Biological Materials e.g. kidney stone
10. Explosives
11. Fats, oils, soaps and waxes
12. Flame retardants
13. Foodstuffs and additives
14. Liquid crystals
15. Metals and alloys

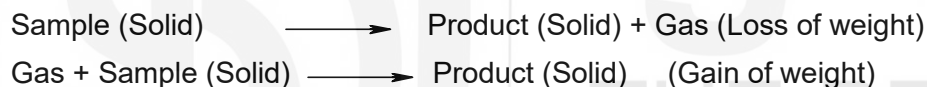
The more frequently used thermal methods of analysis are shown in Table1, with the brief names commonly used for them.

Table 8.1: Thermal methods

Technique	Abbreviation	Property	Uses
Thermogravimetry or (Thermogravimetric analysis)	TG TGA	Mass	Decompositions Oxidations
Differential thermal analysis	DTA	Temperature difference	Phase changes, reactions
Differential scanning calorimetry	DSC	Power difference or heat flow	Heat capacity, phase changes, reactions
Thermometric Titration	TT	Enthalpy	Acid-base and Non-aqueous systems

Though in this unit our focus will be on thermogravimetric analysis, but a brief description these techniques is given below.

TGA: This is a technique in which weight of a material is measured as a function of temperature in controlled conditions. This technique provides information regarding weight change of a material on heating and enables the stoichiometry of the reaction involved during process. When we heat a sample there may be two situations, sample either loses weight or gain weight, which are shown below:



DTA & DSC: In DTA techniques, the difference in the temperature (ΔT) between the material and an inert reference material is measured as function of temperature under control conditions. DSC is very similar to DTA as both shows an endotherm on melting and an endotherm (or exotherm) when decomposition of material occurs. DSC differs from DTA in that instead of allowing a temperature difference to develop between the sample and reference, DSC measures the energy that has to be applied to keep the temperature same. Beside these techniques thermometric titrations have many applications in analytical chemistry. In such titrations we plot a graph of change in temperature (ΔT) against the volume of titrant added. These titrations are used for quantitative analysis.

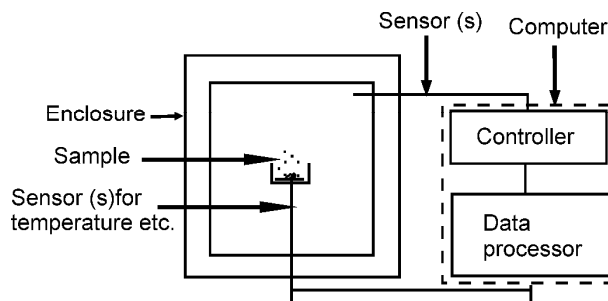
Instrumentation for thermal methods

The modern instrumentation used for any experiment in thermal methods is usually consists of five major parts:

- The sample and a container or holder,
- Sensor to detect and measure a particular property of the sample and to measure temperature,
- An enclosure within which the experimental parameters such as temperature, pressure, gas atmosphere may be controlled,

- A programmer to control the experimental parameters, such as the temperature programmer,
- Recorder to collect the data from the sensors and to process the data to produce meaningful results

Basic components of an instrument used for thermal methods are shown schematically below.



Schematic of a typical instrument used to measure thermal properties

Expected Learning Outcomes

After studying this unit you should be able to:

- ❖ describe the basic thermal methods of analysis;
- ❖ explain the principle of TGA;
- ❖ describe the experimental setup of TGA;
- ❖ interpret the analytical information from TGA curves; and
- ❖ describe the applications of TGA in qualitative and quantitative analysis of inorganic, organic and polymer materials.

8.2 THERMOGRAVIMETRIC ANALYSIS

Thermogravimetric analysis (TGA) is the most widely used thermal method. It is based on the measurement of mass loss of material as a function of temperature. In thermogravimetry a continuous graph of mass change against temperature is obtained when a substance is heated at a uniform rate or kept at constant temperature. A plot of mass change versus temperature (T) is referred to as the thermogravimetric curve (TG curve). For the TG curve, we generally plot mass (m) decreasing downwards on the y axis (ordinate), and temperature (T) increasing to the right on the x axis (abscissa) as illustrated in Fig. 8.1. Sometime we may plot time (t) in place of T . TG curve helps in revealing the extent of purity of analytical samples and in determining the mode of their transformations within specified range of temperature.

In thermogravimetry, the term 'decomposition temperature' is a complete misnomer. In a TG curve of a single stage decomposition, there are two characteristic temperatures; the initial T_i and the final temperature T_f (see Fig. 8.1). T_i is defined as the lowest temperature at which the onset of a mass change can be detected by thermo balance operating under particular

conditions and T_f as the final temperature at which the particular decomposition appears to be complete. Although T_i has no fundamental significance, it can still be a useful characteristic of a TG curve and the term **procedural decomposition temperature** has been suggested. The difference $T_f - T_i$ is termed as reaction interval. In a dynamic thermogravimetry a sample is subjected to continuous increase in temperature usually linear with time whereas in isothermal or static thermogravimetry the sample is maintained at a constant temperature for a period of time during which any change in mass is noted. Now we will take up the instrumentation commonly used to obtain TG Curve.

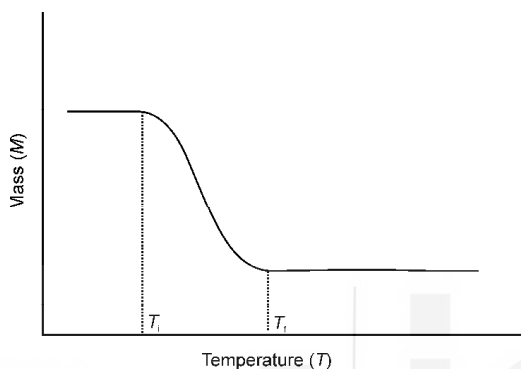


Fig. 8.1: A Typical TG Curve

8.3 INSTRUMENTATION

The instrument used in thermogravimetry (TG) is called a **thermobalance**. It consists of several basic components in order to provide the flexibility necessary for the production of useful analytical data in the form of TGA curve as shown in Fig. 8.4.

Basic components of a typical thermobalance are listed below:

- i) Balance
- ii) Furnace: heating device
- iii) Unit for temperature measurement and control (Programmer)
- iv) Recorder: automatic recording unit for the mass and temperature changes

These components may be represented by simple block diagram as in Fig. 8.2

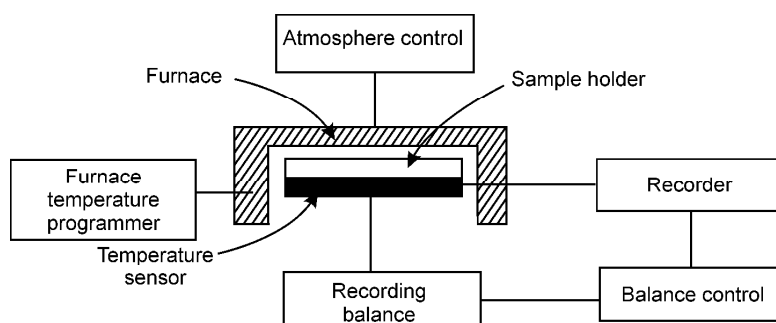


Fig. 8.2: Block diagram of a Thermobalance.

Balance

The basic requirements of an automatic recording balance are accuracy, sensitivity, reproducibility, and capacity. Recording balances are of two types, null point and deflection type. The **null type balance**, which is more widely used, incorporates a sensing element which detects a deviation of the balance beam from its null position. The sensor detects the deviation and triggers the restoring force to bring the balance beam back to the null position. The restoring force is directly proportional to the mass change. **Deflection balance** of the beam type involve the conversion of the balance beam deflection about the fulcrum into mass – change curves identified by (a) photographic recording i.e. change in path of a reflected beam of light available of photographic recording, (b) recording electrical signals generated by an appropriate displacement measurement transducer, and (c) using an electro-mechanical device. The different balances used in TG instruments are having measuring range from 0.0001 mg to 1 g depending on sample containers used.

Furnace

The furnace and control system must be designed to produce linear heating rate over the whole working temperature range of the furnace and provision must be made to maintain any fixed temperature. A wide temperature range generally from ambient temperature to 2000 °C of furnaces is used in different instruments manufacturers depending on the models. The range of furnace basically depends on the types of heating elements are used.

Temperature Measurement and Control

Temperature measurement are commonly done using thermocouples, chromel – alumel thermocouple are often used for temperature up to 180°C whereas Pt/(Pt–8% Rh) is employed for temperature up to 1750°C. Temperature may be controlled or varied using a program controller with two thermocouple arrangement, the signal from one actuates the control system whilst the second thermocouple is used to record the temperature.

Recorder

Graphic recorders are preferred to meter type recorders. X-Y recorders are commonly used as they plot weight directly against temperature. The present instrument facilitate microprocessor controlled operation and digital data acquisition and processing using personal computer with different types of recorder and plotter for better presentation of data.

In Fig. 8.3, we have shown a schematic diagram of the specific balance and furnace assembly as a whole to better understand the working of a thermobalance. In this diagram you can clearly see that the whole of the balance system is housed in a glass to protect it from dust and provide inert atmosphere. There is a control mechanism to regulate the flow of inert gas to provide inert atmosphere and water to cool the furnace. The temperature sensor of furnace is linked to the programme to control heating rates, etc. The

balance output and thermocouple signal may be fed to recorder to record the TG Curve.

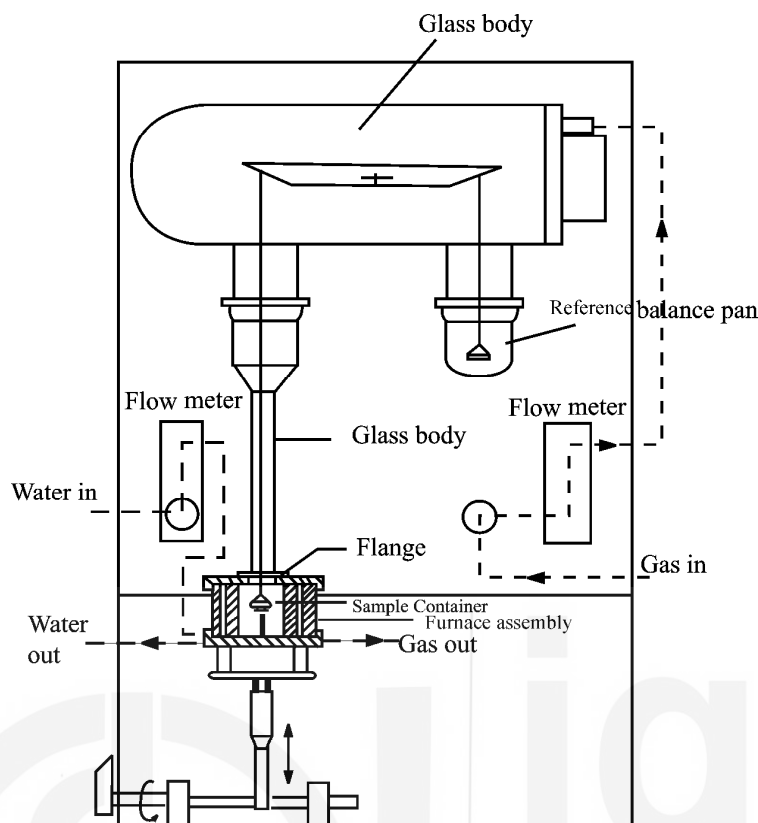


Fig. 8.3: Schematic diagram of a typical balance and furnace assembly.

Thermogravimatic Curves

So far we have discussed the instrumentation of TG now we turn our attention to quantitative aspects of TG. As discussed earlier TG curves represent the variation in the mass (m) of the sample with the temperature (T) or time (t). Normally, we plot mass loss downward on the ordinate (y) axis and mass gain upwards as shown in Fig. 8.4.

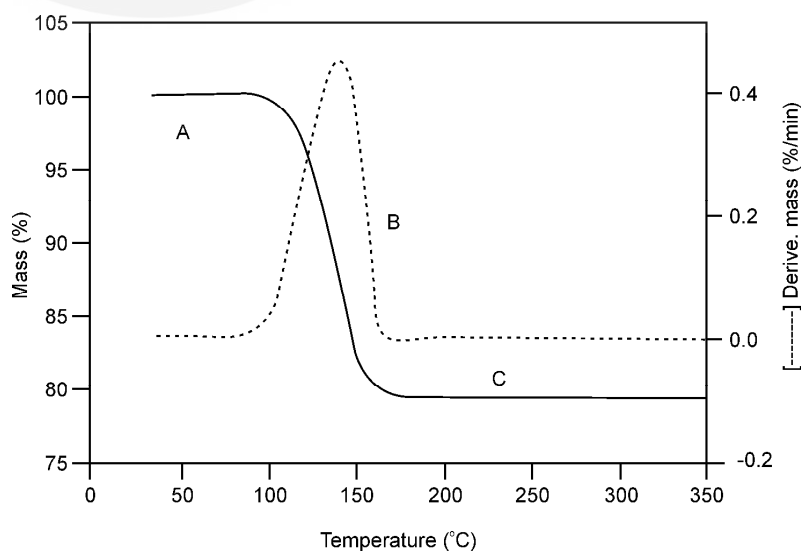


Fig. 8.4: TG Curve. Note the plateau of constant weight (region A), the mass loss portion (region B), and another plateau of constant mass (region C)

Sometime we also record derivative thermogravimetric (DTG) Curves. A DTG curve presents the rate of mass change (dm/dt) as a function of temperature, or time (t) against T on the abscissa (x axis) as shown in Fig. 8.4 when substance is heated at uniform rate. In this figure, the derivative of the Curve is shown by dotted lines.

SAQ 1

List the different components of a thermobalance.

8.4 SOURCES OF ERRORS IN TGA

There are a number of sources of error in TGA, and they can lead to inaccuracies in the recorded temperature and mass data. Some of the errors may be corrected by placing the thermobalance at proper place and handling it with great care. For understanding we are discussing some common source of errors during operation of a thermobalance.

- i) **Buoyance effect:** If a thermally inert crucible is heated when empty there is usually an apparent weight change as temperature increases. This is due to effect of change in buoyancy of the gas in the sample environment with the temperature, the increase convection and possible effect of heat from the furnace in the balance itself. Now, in most modern thermobalances, this effect is negligible. However, if necessary, a blank run with empty crucible can be performed over the appropriate temperature range. The resultant record can be used as a correction curve for subsequent experiment performed in the same condition.
- ii) **Condensation on balance suspension:** Condensation of the sample will also affect the mass of the sample and consequently the shape of TG curve. This can be avoided by maintaining a dynamic atmosphere around the sample in the furnace so that all the condensable product may be driven by the flowing gases.
- iii) Random fluctuation of balance mechanism
- iv) Reaction between sample and container
- v) Convection effect from furnace
- vi) Turbulence effect from gas flow
- vii) Induction effect from furnace

Errors of type (iii) can be avoided by proper placing of balance in the laboratory and error (v) can be avoided by sensible choice of sample container. Last three errors (v-vii) have to be considered in the design of the furnace, the balance and its suspension system. By avoiding excessive heating rate and proper gas flow rate some of above mentioned errors may be avoided.

In the light of above discussion it is necessary to calibrate thermobalance before to use.

Calibration of thermobalance for the measurement of mass: It can be done by adding known mass of the sample container and noting the reading of the chart.

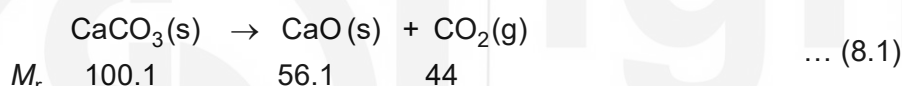
Temperature calibration: ferromagnetic standards are used for this purpose. In a magnetic field these substances show detectable mass changes. The ferromagnetic standards are quite suitable for the temperature range from 242 to 771° C.

SAQ 2

What are common source of errors in thermogravimetric analysis?

8.5 INTERPRETATION OF TG CURVES

TG curves of a pure compound are characteristic of that compound. Using TG curve we can relate the mass changes to the stoichiometry involved. This can often lead us directly to the quantitative analysis of samples whose quantitative composition is known. To further illustrate, let's consider the example of TGA curve of CaCO_3 , (Fig. 8.5.) This curve indicates that CaCO_3 decomposes in a single step between 600° C and 900° C to form stable oxide CaO and the gas carbon dioxide. This can be explained the chemistry of CaCO_3 when it is heated:



Where M_r is relative mass. Now again consider the Fig. 8.5 (c), it indicates the % mass lost by the sample is 44 (100.1–56.1) between 600 and 900° C. This exactly corresponds to the mass changes calculations based on stoichiometry of the decomposition of CaCO_3 expressed by the chemical Eq. (8.1). As in this case, percentage weight loss of CaCO_3 will be

$$\begin{aligned} m \% &= \frac{M_r(\text{CO}_2)}{M_r(\text{CaCO}_3)} \times 100 \quad \dots (8.2) \\ &= \frac{44 \times 100}{100.1} = 44 \end{aligned}$$

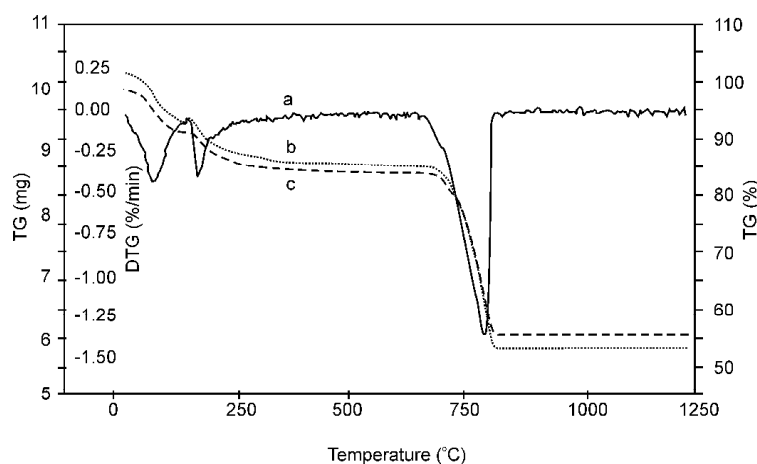


Fig. 8.5: TG and DTG Curve of CaCO_3 at various heating rates (b = 8 °C, c = 3 °C)
(DTG = Rate of Change of mass, dm/dt) curve.

We have seen above how TG Curves is related to stoichiometry (quantitative interpretation). Now we see in next example how it can be used to compare thermal stability of materials (qualitative interpretation). Such information can be used to select material for certain end-use application, predict product performance and improve product quality. Fig. 8.6 gives TG Curves of some polymers. TG Curves clearly indicate that polymer (PVC) is the least thermally stable and polymer (PS) is most thermally stable. Polymer (PS) loses no weight at all below about 500° C and then decomposes abruptly by about 600° C. The other three polymers have all decomposed by about 450° C. Polymers (PMMA) decomposes more slowly overall than the others as indicated by slopes of TG curves. TG curve of polymer (PMMA) has less slope than the others.

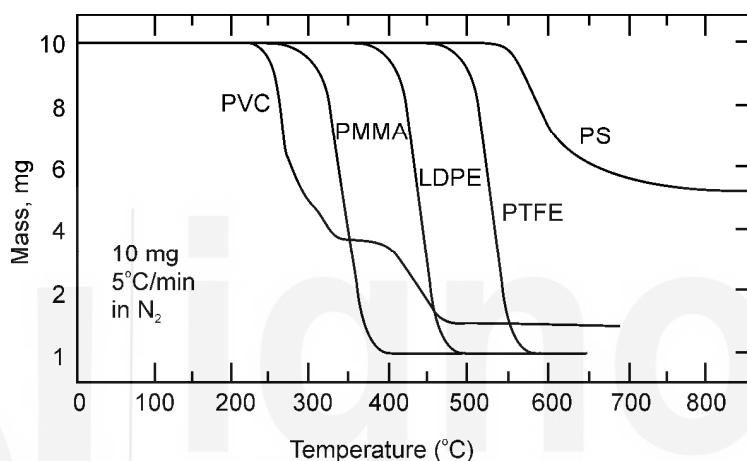


Fig. 8.6: TG Curves of some polymers: PVC = polyvinyl chloride; PMMA = polymethyl methacrylate, LDPE = low density poly ethylene; PTFE = polytetra fluoroethylene; and PS = polystyrene.

SAQ 3

Calculate the percentage mass change ($m\%$) for the following reactions.

- $\text{Ca(OH)}_2(\text{s}) \xrightarrow[\text{Heat}]{\Delta} \text{CaO}(\text{s}) + \text{H}_2\text{O}(\text{g})$
- $6\text{PbO}(\text{s}) + \text{O}_2(\text{g}) \xrightarrow{\Delta} 2\text{Pb}_3\text{O}_4(\text{s})$
- $\text{NH}_4\text{NO}_3(\text{s}) \xrightarrow{\Delta} \text{N}_2\text{O}(\text{g}) + 2\text{H}_2\text{O}(\text{g})$
- $\text{CuSO}_4 \cdot 5\text{H}_2\text{O} \xrightarrow{\Delta} \text{CuSO}_4 \cdot 4\text{H}_2\text{O} + \text{H}_2\text{O}$
- $\text{CuSO}_4 \xrightarrow{\Delta} \text{CuO} + \text{SO}_3$

SAQ 4

A thermogram of a magnesium compound shows a loss of 91.0 mg from a total of 175.0 mg used for analyte. Identify the compound either as MgO , MgCO_3 , or MgC_2O_4 .

8.6 FACTORS AFFECTING TG CURVE

In the beginning of this units we talked about the lowest temperature, T_i at which the onset of a mass change can be detected by the thermobalance operating under particular conditions and T_f is the final temperature at which the decomposition completed. We may like to call this as decomposition temperature, which is not correct. Actually in TGA experiments, both T_i and T_f do not have fundamental significance, but they can still be a useful characteristic of a TG curve and the termed **procedural decomposition temperature**. It is often used for the temperature at which mass change appears to commence. This indicates us that procedural decomposition temperature does not have a fixed value, but depends on the experimental procedure employed to get it. Similar to this there are many factors which influence a TGA curve. These factors may be due to instrumentation or nature of sample. We have listed the main factors which affects the shape, precision and accuracy of the experimental results in thermogravimetry.

1. Instrumental factors:
 - i) Furnace heating rate.
 - ii) Recording or chart speed
 - iii) Furnace atmosphere
 - iv) Geometry of Sample holder/ location of sensors
 - v) Sensitivity of recording mechanism.
 - vi) Composition of sample container.
2. Sample Characteristics:
 - a) Amount of sample
 - b) Solubility of evolved gases in sample.
 - c) Particle size
 - d) Heat of reaction
 - e) Sample packing
 - f) Nature of sample
 - g) Thermal conductivity.

Now we will take up some important factors in some detail.

a) **Furnace heating rate**

At a given temperature, the degree of decomposition is greater the slower the heating rate, and thus it follows that the shape of the TG curve can be influenced by the heating rate. For a single stage endothermic reaction it has been found that:

- i) $(T_i)_F > (T_i)_S$

$$\text{ii) } (T_f)_F > (T_f)_S$$

$$\text{iii) } (T_f - T_i)_F > (T_f - T_i)_S$$

where subscripts F and S indicate fast and slow heating rate respectively. For example, polystyrene decomposes 10 % by mass when heating rate is 1 °C per min by 357 °C and 10 % by mass when heating rate is 5 °C per min by 394 °C. More specifically, it is observed that the procedural decomposition temperature T_i , and also T_f (the procedural final temperature) will decrease with decrease in heating rate and the TG curve will be shifted to the left. This effect is illustrated in Fig. 8.5. The appearance of an inflection in a TG curve at a fast heating rate may well be resolved into a plateau at a slower heating rate. Therefore, in TGA there is neither optimum nor standard heating rate, but a heating rate of 3 °C per min. gives a TG curve with maximum meaningful resolution.

b) Recording or Chart Speed

The chart speed on the recording of the TG curve of rapid or slow reaction has pronounced effect on the shape of the TG curves. For a slow decomposition reaction low chart speed is recommended for recording the TG curve because at high chart speed the curve will be flattened and it will not show the sharp decomposition temperature. For a slow reaction followed by a rapid one at the lower chart speed the curve will show less separation in the two steps than the higher chart speed curve. For fast-fast reaction followed by slower one similar observation was observed in shorter curve plateaus.

c) Furnace Atmosphere

The effect of atmosphere on the TG curve depends on (i) the types of the reaction (ii) the nature of the decomposition products and (iii) type of the atmosphere employed. The effect of the atmosphere on TG curve may be illustrated by taking the example of thermodecomposition of a sample of monohydrates of calcium oxalate in dry O_2 and dry N_2 as shown in Fig. 8.7.

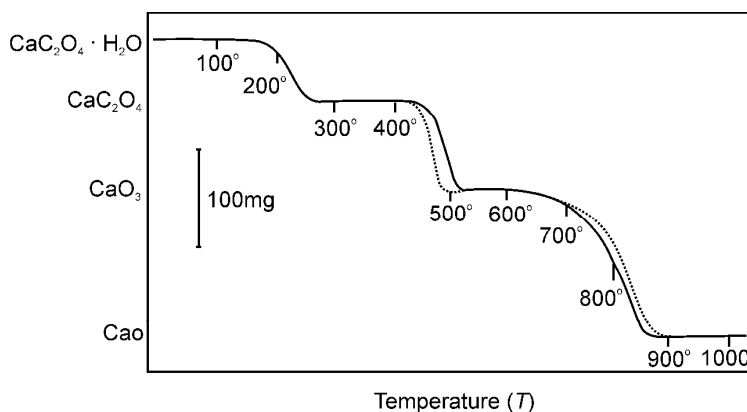
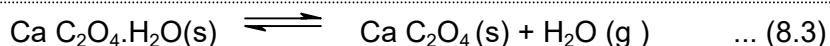
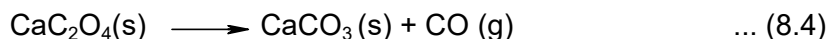


Fig. 8.7: TG Curve of Calcium Oxalate in O_2 and N_2 atmosphere: [———— N_2 , - - - - - O_2]

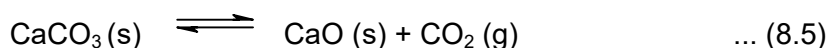
The first step, which is dehydration is reversible reaction.



This is unaffected because both gases are equally effective in sweeping the evolved water vapours away from the sample surface. For the second step,



The curve diverges in O_2 atmosphere because the oxygen reacts with evolved CO , giving a second oxidation reaction which is highly exothermic and so raises the temperature of the un-reacted sample. The temperature accelerates the decomposition of the compound more rapidly and completely at a lower temperature as shown in the above diagram in dry O_2 than in N_2 atmosphere. The third step in decomposition reaction is also reversible reaction.



This step should not be influenced by O_2 or N_2 . However there is a slight difference in curves for the two gases as shown in diagram. The small difference was due to the difference in the nature/composition of CaCO_3 formed in the two atmospheres. This is due to the particle size, surface area, lattice defects or due to the other physical characteristics of CaCO_3 formed.

d) **Sample Holder**

The sample holders range from flat plates to deep crucible of various capacities. The shape of the TG curve will vary as the sample will not be heated in identical condition. Generally, it is preconditioning that the thermocouple is placed on near the sample as possible and is not dipped into the sample because it might be spoiled due to sticking of the sample to the thermocouple on heating. So actual sample temperature is not recorded, it is the temperature at some point in the furnace near the sample. Thus it leads to source of error due to the thermal lag and partly due to the finite time taken to cause detectable mass change. If the sensitivity of recording mechanism is not enough to record the mass change of the sample then this will also cause error in recording the weight change of the sample. If the composition of the sample contains is such that it reacts either with the sample, or product formed or the evolved gases then this will cause error in recording the mass change of the sample.

e) **Effect of Sample Mass**

The sample mass affects the TG curve in the following circumstances:

- i) The endothermic and exothermic reactions of the sample will cause sample temperature to deviate from a linear temperature change.
- ii) The degree of diffusion of evolved gases through the void space around the solid particles.
- iii) The existence of large thermal gradients throughout the sample particularly, if it has a low thermal conductivity.

Thus, it is preferable to use as small a sample as possible depending on the sensitivity of the balance.

f) **Effect of Sample Particle Size**

The particle size will cause a change in the diffusion of the evolved gases which will alter the reaction rate and hence the curve shape. The smaller the particle size, greater the extent of decomposition at any given temperature. The use of large crystal may result in apparent rapid mass loss during heating. This may be due to the mechanical loss of part of the sample by forcible ejection from the sample container, when the accumulated evolved gases within the coarse grains are suddenly released.

g) **Effect of Heat of Reaction**

The heat of reaction will affect the extent to which sample temperature proceeds or succeeds the furnace temperature. This depends on whether the reaction is exothermic or endothermic and consequently the extent of decomposition will also be affected.

The other sample characteristics such as sample packing, nature of the sample and its thermal conductivity will also affect the shape of TG curves. If the sample is packed loosely then the evolved gases may diffuse more easily than if the sample packed tightly.

If the sample reacts with the sample container on heating then it will not give the mass of the product formed so the sample will change. We can avoid this effect by a sensible choice of sample container.

SAQ 5

What are the common instrumental factors affecting TG curves.

8.7 APPLICATIONS OF THERMOGRAVIMETRIC ANALYSIS

In the previous section we have seen how TGA can be used to understand the chemistry of decomposition of a particular compound. TGA also provides information about the temperature range over which a particular sample appears to be stable or unstable. We have also interpreted TG curves qualitatively. Beside these there are many other applications of thermogravimetric analysis. Some are listed below:

- i) Purity and thermal stability.
- ii) Solid state reactions.
- iii) Decomposition of inorganic and organic compounds.
- iv) Determining composition of the mixture.

- v) Corrosion of metals in various atmosphere.
- vi) Pyrolysis of coal, petroleum and wood.
- vii) Roasting and calcinations of minerals.
- viii) Reaction kinetics studies.
- ix) Evaluation of gravimetric precipitates.
- x) Oxidative and reductive stability.
- xi) Determining moisture, volatile and ash contents.
- xii) Desolvation, sublimation, vaporizations, sorption, desorption, chemisorptions.

It is not possible to discuss all these applications at this level; it is worth to describe some of the applications which are more common.

Analysis of Inorganic and Organic Mixtures

We have already seen that single and pure compound gives characteristic TG curves. Now, we will see how TG Curves can be used in predicting relative quantities of the components of a mixture.

Binary mixtures

Consider a mixture of two compounds AB and CD having characteristic TG Curves which are different from each other as shown in Fig. 8.8

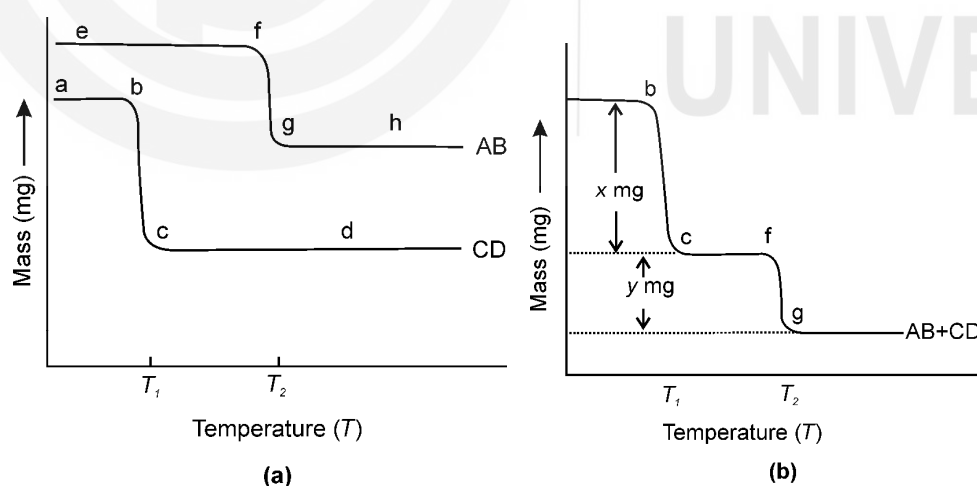


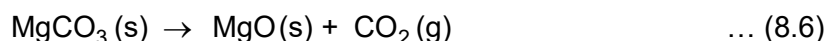
Fig. 8.8: (a) Thermogravimetric curves of two compounds AB and CD and (b) their Mixture.

The decomposition of pure compound AB and CD occur at T_1 , and labeled as bc and temperature T_2 , and labeled as fg respectively, as illustrated in Fig. 8.8 (a). The TG curve of mixture of AB and CD together is shown in Fig. 8.8 (b). You can see in this figure, the plateaus (corresponding to the regions of constant mass) commence at about the same temperature as they

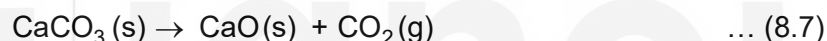
do in the TG Curves for the pure compounds AB and CD. You can also notice that the mass loss overall up to T_1 is x mg and from T_1 to T_2 it is an additional y mg. By measuring these two quantities x and y from the TG curves of Fig. 8.8 (b), we can determine the relative quantities of AB and CD in the original binary mixture. To understand further consider the mixtures of calcium and magnesium carbonates.

i) **Analysis of a mixture of calcium and magnesium carbonates**

A typical TG curve of a mixture of calcium and magnesium carbonates is shown in Fig. 8.9. You can notice that a significant mass loss occurs before 28°C . This is due to the moisture present in the mixture. Another mass loss at about 480°C is due to the following reaction:



Earlier we mentioned that CaCO_3 decomposes at about 800°C . In Fig. 8.8 mass loss between about 600°C and 900°C can be interpreted due to decomposition of CaCO_3 .



Portion of the curve ab represents a mixture of MgO and CaCO_3 and cd represents a residue of the mixture of MgO and CaO . Both these plateaus ab and cd represent weight m_1 and m_2 , respectively. In fact mass m_1 is due to $\text{CaCO}_3 + \text{MgO}$.

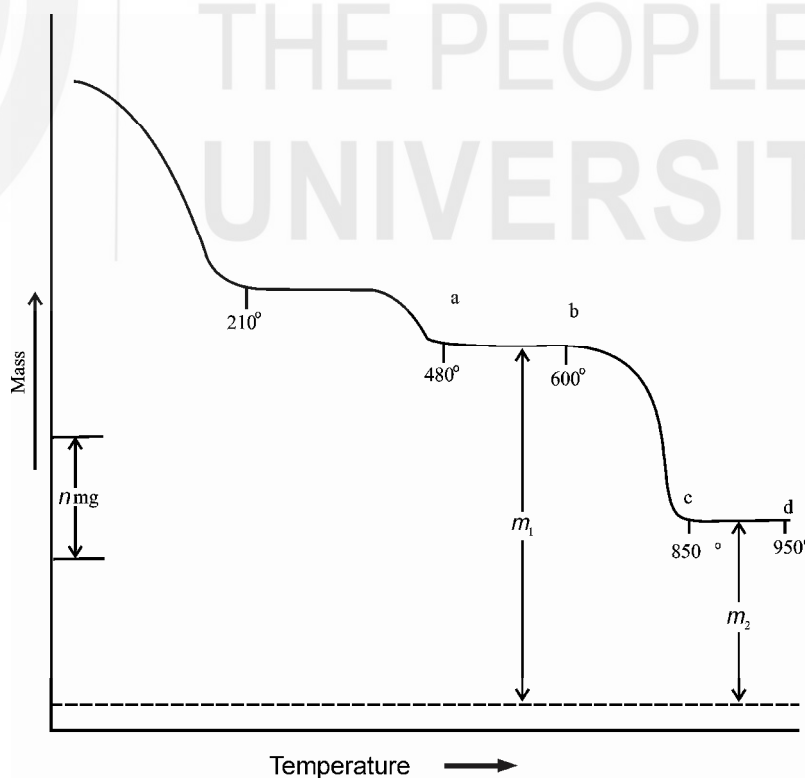


Fig. 8.9: TG curve of mixture of calcium and magnesium carbonate.

Thus, $m_1 - m_2$ is the loss of CO_2 between 600°C and 900°C due to the decomposition of CaCO_3 . Using TGA curve we can relate the mass of different components formed during TGA experiment.

The mass of CaO (m_3) formed can be calculated using following Eq. (8.8)

$$m_3 = 1.27 (m_1 - m_2) \quad \dots (8.8)$$

This equation can be obtained as follows:

The CaO is formed by the evolution of CO_2 on the decomposition of CaCO_3 ,



$$M_r \quad 100.1 \qquad 56.1 \qquad 44$$

From the above equation 1mole of CaCO_3 gives 1 mole of CO_2 and 1mole of CaO . Thus, moles of CO_2 in the given examples $= \frac{(m_1 - m_2)}{M_r(\text{CO}_2)}$

and this is equal to moles of CaO formed

$$\text{Thus the amount of CaO must be, } m_3 = \frac{(m_1 - m_2)}{44} \times M_r(\text{CaO})$$

where, $M_r(\text{CaO})$ is the relative molar mass of CaO .

$$m_3 = \frac{(m_1 - m_2)}{44} \times 56.1 \text{ g}$$

$$m_3 = 1.27(m_1 - m_2) \text{ g}$$

We know the mass of residue left, i.e., m_2 , the mass of MgO (m_4) can be calculated.

$$m_4 = m_2 - m_3$$

Here m_3 is the mass of CaO formed, which is equal to $1.27 (m_1 - m_2)$.
Thus

$$m_4 = m_2 - 1.27 (m_1 - m_2)$$

Mass of the Ca (m_{Ca}) in the original sample can also be related to m_1 and m_2 by the following formula

$$m_{\text{Ca}} = 0.91 (m_1 - m_2)$$

This can be obtained as follows:

You know amount of Ca in CaCO_3 and CaO will be equal in moles, therefore amount of Ca in

$$m_{\text{Ca}} = m_3 \times \frac{A_r(\text{Ca})}{M_r(\text{CaO})} = 1.27 (m_1 - m_2) \times \frac{A_r(\text{Ca})}{M_r(\text{CaO})}$$

where, $A_r(\text{Ca})$ and $M_r(\text{CaO})$ are the relative atomic mass and relative molar mass of Ca and CaO , respectively. Thus,

$$= 1.27 (m_1 - m_2) \times 40/56.1 = 0.91 (m_1 - m_2)$$

Similarly, mass of magnesium in the original sample can be related to m_1 and m_2 :

Thus, the mass of Mg in original sample (m_{Mg})

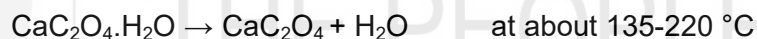
$$= (\text{mass of residue} - \text{mass of CaO}) \times \frac{A_r(\text{Mg})}{M_r(\text{MgO})}$$

$$m_{\text{Mg}} = (m_2 - m_3) \times \frac{A_r(\text{Mg})}{M_r(\text{MgO})} = (m_2 - m_3) \times \frac{24.3}{40.3}$$

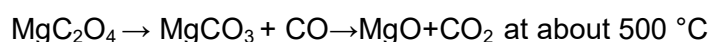
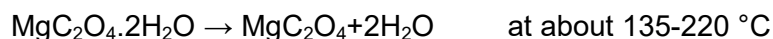
$$m_{\text{Mg}} = 0.60 (m_2 - m_3)$$

ii) Mixture of calcium and magnesium oxalates

Calcium oxalate monohydrate is unsatisfactory weighing form for determining calcium as oxalate because its tendency to retain excess moisture even at 110 °C, co-precipitated ammonium oxalate remain undecomposed. The anhydrous calcium oxalate is hygroscopic but CaCO_3 is excellent weighing form if heated to 500 ± 25 °C as can be seen in TG curve of $\text{CaC}_2\text{O}_4 \cdot \text{H}_2\text{O}$. Above 635 °C the decomposition of CaCO_3 commences to become significant under usual laboratory conditions and completely converted to CaO at 900 °C. Thus, calcium oxalate monohydrate decomposes in three steps, first dehydration, second removal of CO and formation of CaCO_3 then third step CaCO_3 decomposes to CaO (see Fig. 8.10).



But magnesium oxalate dihydrate decomposes in two steps instead of three steps. First, dehydration then removal of CO and CO_2 simultaneously and forming MgO , there is no horizontal corresponding to MgCO_3 as it is thermally unstable at this temperature.



The TG curve for the mixture of $\text{CaC}_2\text{O}_4 \cdot \text{H}_2\text{O}$ and $\text{MgC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$ shows two mass losses up to 500 °C, first at about 200 °C due to loss of water and the second mass loss occurs in the 390-500 °C range which is due to decomposition of both calcium and magnesium oxalates. Thus, at 500 °C, the composition of the mixture will be CaCO_3 and MgO . Third mass loss after 500 °C is due to only the decomposition of CaCO_3 . If m_1 and m_2 are the mass of the mixture at 500 °C and 900 °C then similar to the previous example we can calculate the amount of calcium and magnesium in the original sample.

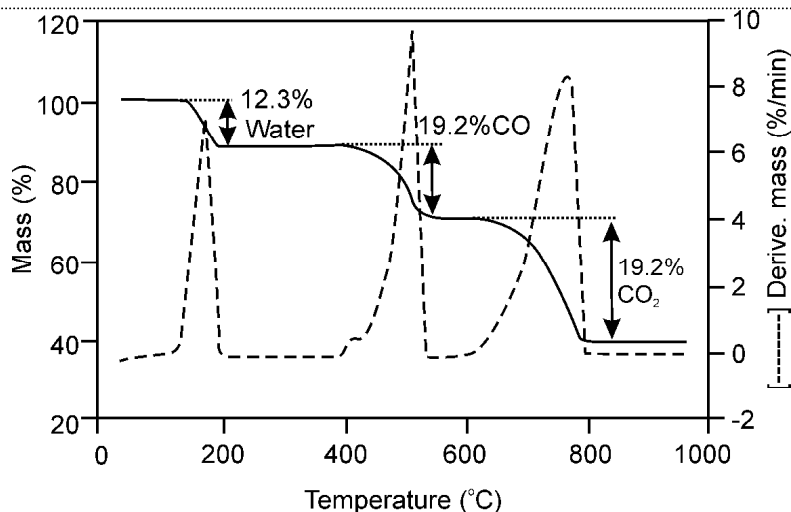


Fig.8.10: DTG/TG curve of calcium oxalate.

Organic Mixtures

TGA also provides quantitative information on organic compound decompositions and is particularly useful for studying polymers. For example TGA can be used in the determination of the amount of vinyl acetate in copolymers of vinyl acetate and polyethylene. When vinyl acetate is heated it loses acetic acid at about 340 °C. TG curves shown in Fig. 10.11 for several vinyl acetate polyethylene copolymers are clearly indicating the loss of acetic acid at about 340 °C due to the decomposition of vinyl acetate. Each mole of vinyl acetate loses one mole of acetic acid. The amount of vinyl acetate in the polymers can be calculated.

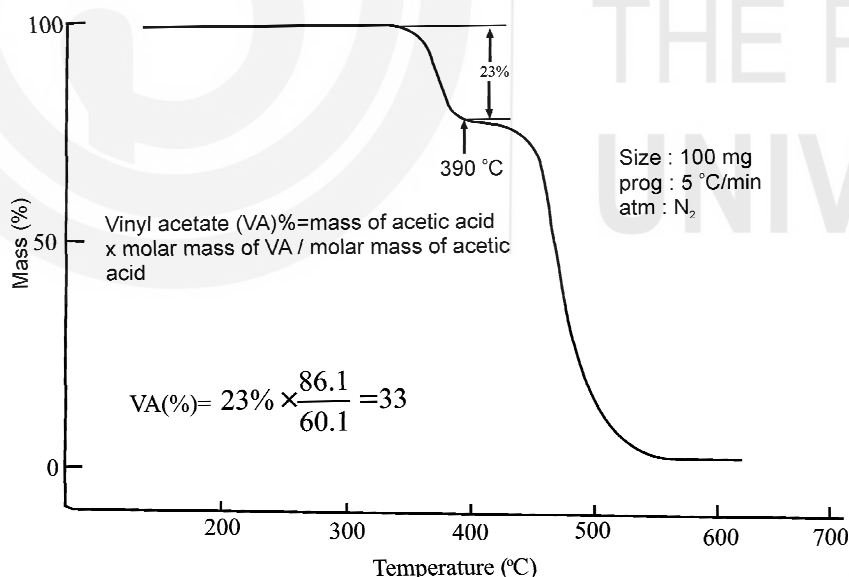


Fig. 10.11: TG curve of vinyl acetate copolymer

SAQ 6

A mixture of CaO and CaCO_3 is analysed by TGA. The result indicates that mass of the sample decreases from 250.6 mg to 190.8 mg only between 600°C and 900°C. Calculate the percentage of calcium carbonate in the mixture.

8.8 SUMMARY

Thermogravimetric Analysis (TGA) technique has been described for its basic principle, instrumentation and applications. The interpretation of results and applications are discussed by taking different examples. The elementary calculation are included to elaborate the topics. The probable cause of errors, their remedies, interpretation of result are also discussed.

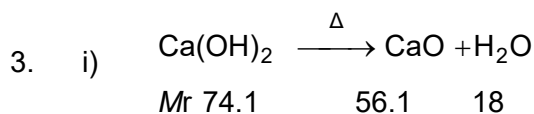
8.9 TERMINAL QUESTIONS

1. Formulate the solid state reaction of sodium bicarbonate when heated. It decomposes between 80 and 225 °C with evolution of water and carbon dioxide. The combined loss of water and carbon dioxide totaled 36.6% by mass whereas the mass loss due to carbon dioxide alone was found to be 25.4 %. Explain.
2. What types of standard are required to calibrate the mass variation obtained with a TGA equipment?
3. What type of standards is required for temperature calibration of any TGA?
4. A mixture of CaCO_3 and CaO is analysed using TGA technique. TG curve of the sample indicates that there is a mass change from 145.3 mg to 115.4 mg between 500–900 °C. Calculate the percentage of CaCO_3 in the sample.
5. A 250 mg hydrated sample of Na_2HPO_4 decreases to a mass of 145.7 mg after heating to 150 °C. What is the number of water hydration in Na_2HPO_4 .
6. Draw a labeled diagram of the TG curve obtained by heating a mixture of 80 mg of $\text{CaC}_2\text{O}_4 \cdot \text{H}_2\text{O}$ and 80 mg of $\text{BaC}_2\text{O}_4 \cdot \text{H}_2\text{O}$ to 1200 °C. Calculate the amount of all mass losses.

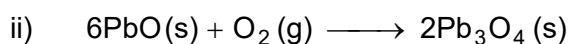
8.10 ANSWERS

Self Assessment Question

1. Balance; furnace; unit for temperature measurements and control; and recorder.
2. Common source of error in thermogravimetric are listed in Sec. 8.3.



$$\text{Percentage loss} = \frac{(74.1 - 56.1)}{74.1} = 24.3\%$$

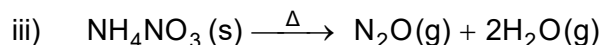


$$\text{Mr } 223.2 \times 6 \qquad 685.6 \times 2$$

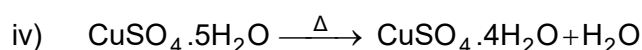
$$1339.2 \qquad 1371.2$$

$$\text{So, percent gain} = \frac{(1371.2 - 1339.2)}{1339.2} \times 100$$

$$= 2.4\%$$



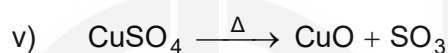
In this case, both the products are volatile when NH_4NO_3 is heated at 300°C no solid residue is left. The percentage loss in this case is 80%.



$$\text{Mr } 249.7 \qquad 231.7 \qquad 18$$

$$\text{percent loss} = \frac{(249.7 - 231.7)}{249.7} \times 100 = \frac{18}{249.7} \times 100$$

$$= 7.2\%$$

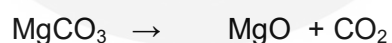
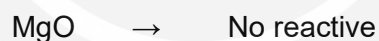


$$\text{Mr } 231.7 \qquad 151.7 \qquad 80$$

$$\% m = \frac{231.7 - 151.7}{231.7} \times 100$$

$$\% m = \frac{80}{231.7} \times 100 = 34.5\%$$

4. Decomposition reaction of the MgO , MgCO_3 and MgC_2O_4



$$\% \text{ mass loss for } \text{MgCO}_3 = \frac{44}{84.3} \times 100 = 52.2\%$$

$$\% \text{ mass loss for } \text{MgC}_2\text{O}_4 = \frac{(44 + 28)}{112.3} \times 100 = 64.3\%$$

$$\% \text{ mass loss of the sample} = \frac{91.0}{175} \times 100 = 52\%$$

Therefore, this compound is MgCO_3 .

5. Instrumental factors: Furnace heating rate, recording chart speeds, furnace atmosphere, geometry of sample, holder/location of sensors, sensitivity of recording mechanism, composition of sample container, etc.

6. The possible decomposition in the mixture may be written as



$$Mr \quad 100.1 \qquad 56.1 \qquad 44.0$$

Mass loss in the mixture is due to the formation of $\text{CO}_2 (\text{g})$. We can calculate the m moles of CO_2 , i.e. $(250.6 - 190.8) \text{ mg}/44 = 1.359 \text{ mmol}$. From the above chemical equation, 1 mole of CaCO_3 give 1 mole of CO_2 . Therefore the amount of CaCO_3 in the mixture must be 1.359 mmol. This will equal to $= 1.359 \times 100.1 \text{ mg} = 135.9 \text{ mg}$.

So percentage of CaCO_3 in the sample will be $\frac{135.9}{250.6} \times 100 = 54.2\%$ by mass.

Terminal Questions

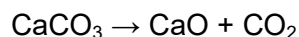
1. Reaction proceed in following steps

Above 60°C , it gradually decomposes into sodium carbonate and water and carbon dioxide.



Total calculated mass loss should be 36.9, dehydration is 8.71 and decarbonylation is 26.19. The observed mass loss is quite similar i.e. total 36.6, dehydration 11.2 and decarboxylation is 25.4%.

2. There are no standards available for TGA calibration. It is only possible to calibrate the balance using calibrated masses. However, it is possible to use some materials with known mass variations, such as copper sulphate pentahydrate or calcium oxalate, to check for good operation of the thermobalance. The latter materials are generally agreed as working standards but do not use the first mass loss, corresponding to the first hydrate.
3. Temperature calibration of the TGA requires the use of a metal that is 99.99% pure and magnetic. A magnet has to be adjusted on the TGA furnace.
4. Write the decomposition reaction of CaCO_3



$$Mr \quad 100.1 \quad 56.1 \quad 44.0$$

This equation indicates that one mole of CaCO_3 produces one mole of CaO and one mole of CO_2 . Therefore,

$$m \text{ moles of } \text{CO}_2 = m \text{ moles of } \text{CaCO}_3$$

$$m \text{ moles of } \text{CO}_2 = \text{mg lost}/Mr (\text{CO}_2)$$

$$= (145.3 - 115.4) \text{ mg}/44.0$$

$$= 29.9/44.0$$

$$= 0.682 \text{ m moles}$$

A mount of CaCO_3 in sample = m moles of $\text{CaCO}_3 \times Mr (\text{CaCO}_3)$

$$= 0.682 \times 100.1 \text{ mg}$$

$$= 68.2 \text{ mg}$$

$$\% \text{ of } \text{CaCO}_3 = \frac{68.2}{145.3} \times 100 = 46.9\%$$

5. Molar mass of hydrated Na_2HPO_3 is 215.9. We can calculate mass loss corresponding to each mole of hydrated water (n).

m % loss	8.8	16.7	25.0	33.3	41.7
n	1	2	3	4	5

$$\text{In this problem \% mass loss} = \frac{(250 - 145.7)}{250} \times 100$$

$$= 41.7\%$$

This corresponds to a mass loss of 5 moles of water of (hydration).
Therefore given sample must be of $\text{Na}_2\text{HPO}_3 \cdot 5\text{H}_2\text{O}$.

6. Table the help of Fig.8.12 to draw a labeled diagram of the TG curve for mixture of $\text{CaC}_2\text{O}_4 \cdot \text{H}_2\text{O}$ and $\text{BaC}_2\text{O}_4 \cdot \text{H}_2\text{O}$.

$$\begin{aligned} \text{Total mass loss} &= 49.3 (\text{CaC}_2\text{O}_4 \cdot \text{H}_2\text{O}) + 29.6 (\text{BaC}_2\text{O}_4 \cdot \text{H}_2\text{O}) \\ &= 78.9 \text{ mg.} \end{aligned}$$

POTENTIOMETRY |

Structure

9.1	Introduction	Measurement of Potential
	Expected Learning Outcomes	Direct Potential
9.2	Classification of Electroanalytical Methods	Electrodes
	Potentiometry	9.4 Potentiometric Titrations
	Voltammetry	Types of Potentiometric Titrations
	Polarography	9.5 pH Metric Titration
	Amperometry	9.6 Summary
	Coulometry	9.7 Terminal Questions
	Conductometry	9.8 Answers
9.3	Basic Principle of Potentiometry	

9.1 INTRODUCTION

Electroanalytical methods find applications in all branches of Chemistry, industries, engineering and a number of other technologies. The possibility of the determination of low level of pollutants has prompted the use of these methods in environmental studies.

An electroanalytical method can be defined as one, in which the electrical response of a chemical system or sample is measured. These methods can be classified into a number of types characterized by measuring the electrical response in terms of different electrical quantities such as: potential, current, quantity of current, resistance and voltage etc. and bear the corresponding names as potentiometry, amperometry, coulometry, conductometry and voltammetry etc. During the past few years, there has been sudden increase in interest in electroanalytical techniques. This is partially attributed to the development in instrumentation and partially due to the heavy demands by environmental scientists for the determination of a large number of heavy metal, organic and inorganic substances present in water and soil samples. In this unit our focus will be on potentiometry.

We hope you are already aware of the electrode potentials and how it can be calculated using Nernst equation from your earlier studies. In this unit, we are going further to discuss how the electromotive force developed in a cell can be measured using a potentiometer. This method consists of measuring the potential between any two electrodes immersed in the solution to be analysed. For measuring the potential, we require two electrodes, an indicator electrode and a reference electrode along with a device called potentiometer.

Potentiometric methods have many applications in the area of analytical chemistry. These methods can be used for direct and selective measurement of analyte concentrations, for determining end point in various types of titrations and for the determination of several types of equilibrium constants.

In this unit, first we study the classification of electro analytical methods. After that you will describe different types of reference and indicator electrodes. There will be a brief description about instrumentation and potentiometric titrations and pH titrations too.

Expected Learning Outcomes

After studying this unit, you should be able to:

- ❖ describe the classification of the electroanalytical techniques;
- ❖ explain the principle of potentiometric methods of analysis;
- ❖ describe some common types of reference and indicator electrodes;
- ❖ describe chemical reactions involved in potentiometric titrations;
- ❖ explain the principle of potentiometric titration; and
- ❖ state the experimental details of pH titrations.

9.2 CLASSIFICATION OF ELECTROANALYTICAL METHODS

Although the variety of electrochemical methods may seem to be large, all of them are based on a rather limited number of percepts, the particular combination of which determines the nature of the technique. A general classification of electroanalytical methods is based on

- i) the particular electrical property or properties measured by keeping the other quantities constant and
- ii) the mode of mass transport as: diffusion, convection and migration.

Further many of these techniques may be divided into two types on the basis of the procedures adopted for the analytical determination:

1. methods in which little or no chemical transformation occurs and the measurement of an electrical quantity gives a direct measure of

concentration, this is sometimes indicated by prefixing 'direct, before the name of the technique (such as direct potentiometry)

- the second type involves methods based on titration procedures in that the analyte undergoes a stoichiometric chemical transformation affected by an electrochemical reaction, however, the end point may or may not be determined electrochemically. These methods are named by adding titration after the original name of the technique, such as, potentiometric titration, amperometric titration, etc.

On the basis of above consideration the various electroanalytical methods are classified and discussed briefly as below.

9.2.1 Potentiometry

This technique involves the measurement of potential at zero current flow. Analytical use of this technique is made in two ways. In one, known as *direct potentiometry*, in this technique, we utilize the single measurement of potential and the *Nernst Equation* is used to relate cell potential to the concentration of analyte. The liquid-junction potentials and activity coefficients influence the value of cell potential. In the other technique, known as *potentiometric titration*, a set of measured potential is used to detect the changes in concentration that occur at the equivalence point of a titration. In these titrations the change in the potential is of importance and thus the influence of junction potentials and activity coefficients may be ignored. Let us discuss more about these techniques.

a) Direct Potentiometry

In direct potentiometry, we measure a potential difference between two electrodes immersed in a solution and connecting the cell so formed to a voltage measuring device (potentiometer, vacuum tube voltmeter). The cell formed by two electrodes (half-cells) and the solution is known as an electrochemical cell (a galvanic cell). The net cell reaction can be considered as the sum of the two half-cell reactions in which the each half-cell reaction is the representation of the actual chemical process that occurs at the individual electrode of the galvanic cell. A half-cell reaction always include the electrons transferred.

Usually, one of the electrodes (half-cell) is chosen such that its potential is invariant and is termed as *reference electrode*. The potential of the other electrode is then a function of the concentration (more correctly activity) of the species involved in the electron transfer process (a redox reaction), through the Nernst Equation. This electrode is termed the *indicator electrode*. Under these conditions the cell emf is given by

$$E_{\text{cell}} = (E_{\text{ind}} - E_{\text{ref}}) + E_j \quad \dots(9.1)$$

where

E_{cell} is emf of galvanic cell,

E_{ind} = half-cell potential of the indicator electrode,

E_{ref} = half-cell potential of the reference electrode,

E_j = liquid-junction potential developed at the interface between two electrolytes.

Concentration of the solution is determined by a single measurement of cell potential applying the Nernst Equation.

pH-metry is also based on direct potentiometry, in this case the glass electrode commonly used for pH measurement. Glass electrode is an ion selective membrane electrode. Further details of these methods will be discussed in Section 9.3, 9.4 and 9.5.

Potentiometric Titrations

By far the most common application of potentiometry is in the potentiometric titrations. In these titrations, the potential between appropriate indicator and reference electrode immersed in the sample is monitored during the titration. The titrations can be performed manually or with automatic titration equipment. The cell potential (or in pH titrations the pH) is plotted as a function of the volume of titrant.

Further details of these methods will be discussed in Section 9.3, 9.4 and 9.5.

9.2.2 Voltammetry

In voltammetry an electroactive species is consumed (oxidized or reduced) only at the surface layer of the indicator electrode in an electrolytic cell. The resulting current, due to the electron transfer process is measured as a function of applied potential. Such electrolysis is carried out under controlled conditions of diffusion (or/and convection). In diffusion layer electrolysis methods only a thin layer of solution immediately adjacent to the electrode undergoes electrolysis. In these methods, the electrical variable is related to the concentration of the bulk, and usually, the time of electrolysis is short that only a negligible fraction of the reactant is electrolysed and the reactant concentration in the bulk solution is not altered (theoretically).

In voltammetry we study the relationship between the current and electrode potential and their applications to chemical analysis. The voltammetric curves are known as current-volts curves or current-potential curve. The shape of the I - E curve depends on the polarization of the indicator electrode, when the other electrode known as the reference electrode remain unpolarized and does not influence the shape of the I - E curve.

9.2.3 Polarography

Various types of electrodes can be used in voltammetry, but one of them, the dropping mercury electrode (dme), is particularly useful and the corresponding voltammetric method is referred to as *polarography*.

The use of dme in chemical analysis was originated at the Charles University in Prague, Czechoslovakia in the early 1920s by Heyrovsky who coined the name polarography to designate this technique. The dropping mercury

electrode is essentially composed of a capillary connected to mercury reservoir. The bore of the capillary, the length of the capillary, and the head of mercury are adjusted in such a way that a drop is dislodged every 2-6 sec. A platinum wire is immersed in the mercury reservoir, and the dme is coupled with unpolarized electrode.

Polarography consists of electrolysing a solution of an electroactive substance between a dme (cathode) and some reference electrode (anode). The area of the anode is large correspondingly so that it may be regarded as unpolarized and the potential of such electrode remains fairly constant.

The current-potential characteristics can be studied with the type of an apparatus (Fig.9.1) in a simple manner in which the voltage applied to the cell **C** is adjusted by means of a potentiometer **P** and the current through the cell is read on a galvanometer **G**.

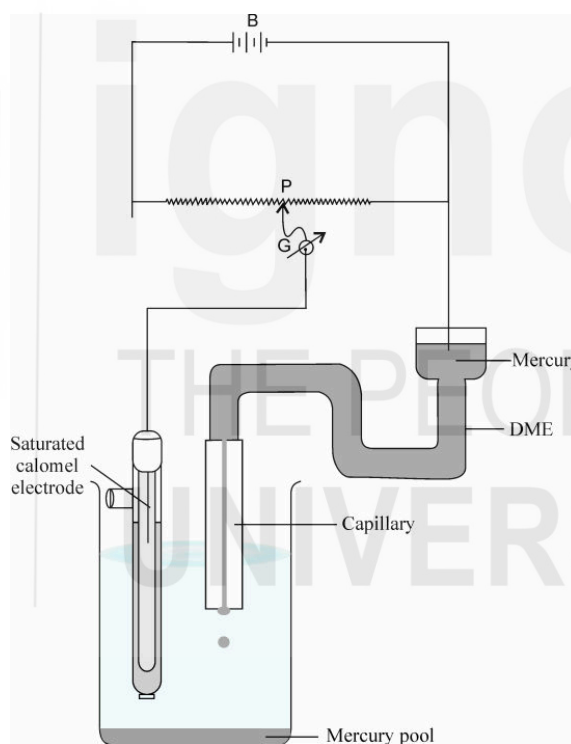
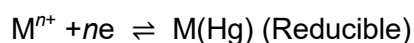


Fig. 9.1: Manual polarographic circuit

On applying the potential between two electrodes and increasing its value in a stepwise manner the following processes take place. At first only a small current flow-the so called residual current. This continues until the decomposition potential of the reducible ionic species is reached. At this point the following reaction takes place,



Afterward a steep rise in current is observed and will continue to rise with increasing potential till the current reaches a limiting value (Fig. 9.2).

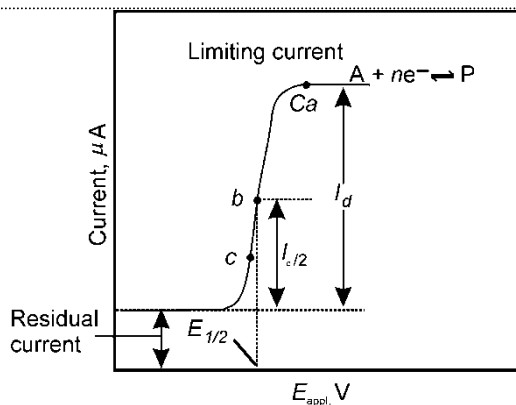


Fig. 9.2: I - E curve for M^{n+} (Polarogram)

The conditions are set such that the diffusion is the main process of mass transfer. This can be done by minimising convection and migration. The limiting current under these conditions is known as the diffusion current (I_d).

The factors affecting the diffusion current were examined by D. Ilkovic and he gave the following equation which is known as the Ilkovic equation.

$$I_d = 708 \, nm^{2/3} D^{1/2} t^{1/6} c \quad \dots (9.2)$$

where I_d is the diffusion current, n is the number of electrons consumed in the reduction of M^{n+} , D is the diffusion coefficient, m is the rate of flow of mercury, t is the time and c is the concentration of M^{n+} in the solution and 708 is the combination of constants and conversion factors involved in changing in units taken into account.

Equation 9.2 gives a direct relation between I_d and concentration, hence can be applied for quantitative measurements, we can write from equation 9.4,

$$I_d \propto c \quad \text{or} \quad I_d = Kc \quad \dots (9.3)$$

where K can be evaluated by noting the current with a standard solution of the substance of interest.

The curve shown in Fig.9.3 is called I - E or polarogram or polarographic wave. Two important features of a polarogram are (i) the half wave potential $E_{1/2}$, and (ii) the diffusion current.

SAQ 1

Distinguish between voltammetry and polarography.

9.2.4 Amperometry

In Polarography, we have seen that in a particular polarogram, the limiting current of an electroactive substance, at a suitable (fixed) potential depends on the substance concentration only. If we reduce the concentration of the electroactive substance by its interaction with another substance, the current will be reduced. This principle is made to get the equivalence point by measuring the current flowing at an indicator electrode. This technique is

known as amperometric titration. Thus, amperometry named after the unit of current, “ampere” is based on the measurement of current when the voltage across the electrodes of a cell is kept constant. In amperometric titrations the current passing through the cell (containing the analyte) at a suitable constant voltage is measured as a function of the volume of titrant (or of time if the titrant is generated by a constant current coulometric process). By far, the application of amperometry is in amperometric titrations.

Amperometric titrations are more accurate than voltammetric methods. Furthermore, this titration can be performed even when the substance being determined is not reactive, since an equally satisfactory equivalent point can be located with either a reactive titrant or when the product is reactive.

9.2.5 Electrogravimetry and Coulometry

Faraday's law of electricity gives a direct proportion between quantity of electricity and the amount of substance consumed or obtained after oxidation and reduction taking place when a current is passed for a sufficient period through an electrochemical cell. Two electroanalytical techniques are based on the above statement, they are electrogravimetry and coulometry. These are the bulk electrolysis methods.

Electrogravimetry

It is the oldest of electroanalytical techniques and was well established by the end of nineteenth century. It involves the controlled potential reduction of a solution of a metal salt which is continued till the current falls near to zero. Thus, electrolysis is used as a means of chemical transformation (reduction of the metal ion). The product of analysis (i.e., after electrolysis) is weighed as a deposit on one of the electrodes (working electrode). The increase in the weight of the previously weighed working electrode leads to the determination of the metal content of the sample solution. Since the reaction product after electrolysis is determined ordinarily by weighing, hence the name “electrogravimetry”.

The method is very simple to apply in the analysis of a single element in the absence of any other substance which might be deposited. For this analytical method the appropriate electrode potential is essential. The potential for the selective deposition of a metal can be calculated from the Nernst equation or it can be determined from data obtained by voltammetry.

Coulometry

In the bulk electrolysis method, when the amount of the constituent to be determined is not weighed but calculated by measuring the quantity of electricity and making use of Faraday's law the technique is called *coulometry*, the term derived from coulomb, the quantity of current. In these methods, the analyte is quantitatively converted to a different oxidation state by passing the current through the electrolytic cell.

In primary coulometric analysis the substance being determined may directly undergo reaction at one of the electrodes. In secondary coulometric analysis the substance being determined may react in solution with another substance

which is generated by an electrode reaction. Further, in coulometric analysis which consider the reactions proceeding with 100% current efficiency, so that the quantity of the species reacted can be calculated via Faraday's law from the quantity of electricity passed.

According to Faraday's law, a given amount of chemical change caused by electrolysis is direct proportional to the amount of electricity passed through cell. For a general reaction,



where n is the number of electrons in the involved reaction, O is the reactant to be reduced and R the reduction product. Faraday's law relate the number of moles of the analyte n_A to the charge

$$n_A = \frac{Q}{nF} \quad \dots (9.4)$$

where, n = the number of moles of electrons in the analyte half-reaction,

F = Faraday, this is the quantity of charge that corresponds to one mole or 6.022×10^{23} electrons. Since each electron has charge of 1.6022×10^{-19} C, the faraday also equals 96,485C, and

Q = Quantity of electricity consumed in coulomb.

The value of Q can be determined as:

i) for a constant current, I amperes, operate for t seconds, $Q = It$, and

ii) for a variable current, i , $Q = \int_0^t i dt$

In coulometry we can directly calculate the amount of the reactant/product by the relation (9.4) and the calibration or standardisation is not ordinarily required.

Coulometry can be classified as (a) potentiostatic coulometry, and (b) amperostatic coulometry.

a) Potentiostatic Coulometry

In potentiostatic coulometry, that is, coulometry at constant potential, the potential of the working electrode is maintained at a constant level, so that only analyte gets quantitatively oxidized or reduced there is no involvement of the less reactive species. Here the current is initially high but decreases exponentially with time and approaches zero at a time required to attain a reaction position that is quantitatively complete ($\sim 10^{-6}$ M).

Q may be evaluated by a current time integrator or graphical, $Q = \int_0^t i dt$ as

shown in Fig. 9.3.

$$\text{Area} = Q = \int_0^t i dt$$

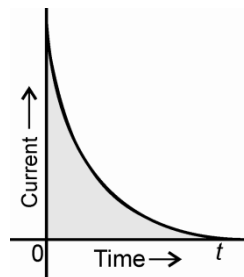


Fig. 9.3: Current and time relationship in potentiostatic coulometry

b) Amperostatic Coulometry or constant-current coulometry

The current, in a coulometric titration is carefully maintained at a constant and accurately known level by means of an amperostat, ($It=Q$) required to reach an end point. Q is proportional to the quantity of the analyte involved in the electrolysis. The essential requirement is 100% current efficiency to a single change in the analyte.

In these titrations, the titrant is generated at one of the electrodes. The reaction may take place directly on the same electrode or on the other electrode. To remove the interferences, when may occur, the reagent is separated from the solution by the use of sinter glass.

The reagent can be generated externally also, which removes the interferences. Such a cell has mainly been used to generate H^+/OH^- ions.

SAQ 2

Differentiate between potentiostatic coulometry and amperostatic coulometry.

SAQ 3

A 9.65 ampere current is passed through a solution of $AgNO_3$ for 50 minutes. Calculate the amount of Ag deposited at the cathode.

9.2.6 Conductometry

In conductometry we examine the transport of electricity in solution and application of this phenomenon to chemical analysis. The principle advantage of this technique is its simplicity and relatively good sensitivity. It is, one of the earliest techniques to study the behaviour of electrolytic solutions. Since the conductance (which is reciprocal of resistance) of an electrolytic solution depends on the number of ions present, their charge, their mobility, and temperature; analytical applications of conductometry are thus possible. More detail discussion on the methods is given in Unit 10.

RELATIONSHIPS OF ELECTROANALYTICAL METHODS

As we have seen there are a wide variety of electroanalytical methods available for the analytical purposes. Some of these methods differ only in very few aspects but often the differences are important and require a good

understanding of the techniques. For the most of methods discussed so far, we are interested in the relationships between four variables: current, emf, analyte concentration and time. The only exceptions to this is the conductometric techniques. These methods are based on conductance of the solution. For the purpose of classification, these methods can be divided into interfacial methods and bulk methods, former are based upon phenomena that occur at the interface between electrode and solution and latter are based upon phenomena that occur in the bulk of the solution. Further interfacial methods can be divided into major sub-group, static and dynamic, based upon whether electrochemical cells are operated in the absence or presence of current flow. Potentiometry and potentiometric titrations come under the category of static (zero current) methods. In dynamic interfacial methods current play important roles. These methods are further divided in several categories like voltammetry, amperometry, coulometry and electrogravimetry as shown in Fig. 9.4. Polarography name is given to voltammetric methods when a dropping mercury electrode is used. Details of all these techniques will be discussed in subsequent units

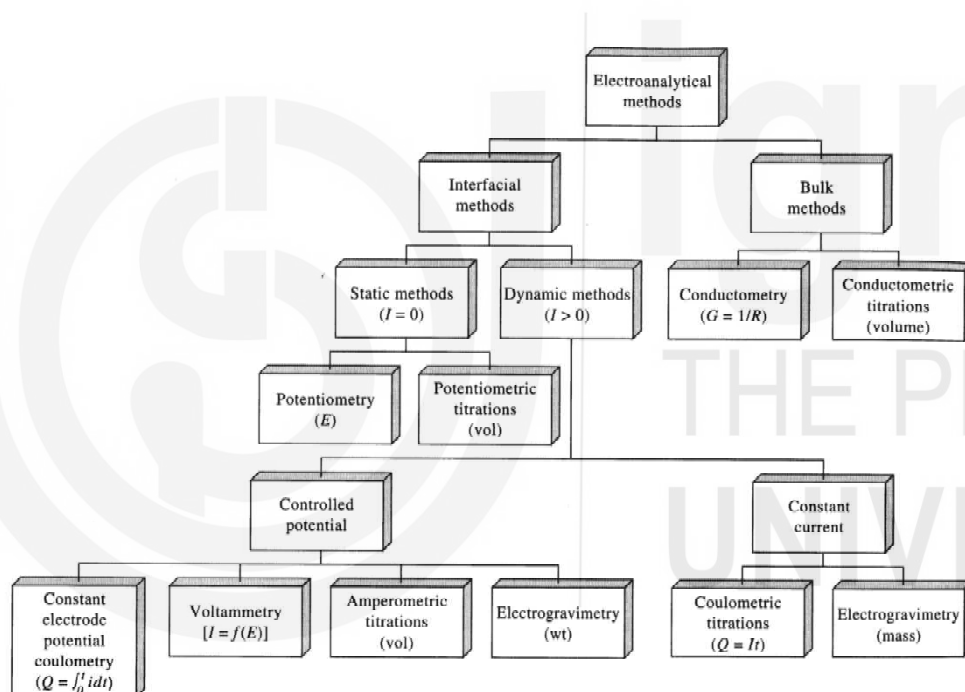


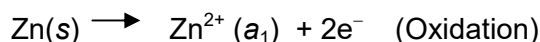
Fig. 9.4: Classification of electroanalytical methods. Quantity measured is given in parentheses. Where I = current; E = potential; R = resistance; G = conductance; Q = quantity of charge, t = time; V = volume of a standard solution, m = mass of an electrolyte

9.3 BASIC PRINCIPLE OF POTENTIOMETRY

Potentiometry deals with the measurement of difference in potential between two electrodes which have been combined to form an electrochemical cell. The difference in potential between the two electrodes in electrochemical cell is known as cell potential. The cell potential depends on the composition of the electrodes, concentration of the solution or more correctly activity of a species in solution (or pressure of gases) and the temperature. Relationship connecting the cell potential with the activity 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 earlier semester course. Based on the dependence of cell potential on the activity or concentration of the species in the electrochemical cell, we use this concept to obtain the activity or concentration, and pH of a species in solution from potential difference measurements using potentiometer or pH meter.

In order to understand the above concept, we shall study the galvanic cell in some detail. For example, consider the simple galvanic cell illustrated in Fig.9.5. In this cell there are two half cells. Where a half cell is the combination of an electrode and the solution with which it is in contact. In one half cell zinc gets oxidized to Zn^{2+} ions.



This electrode is negatively charged relative to the solution and is referred to as **anode** i.e. oxidation always occurs at the anode. On the other hand, in second half cell Copper (II) ions get reduced to copper.

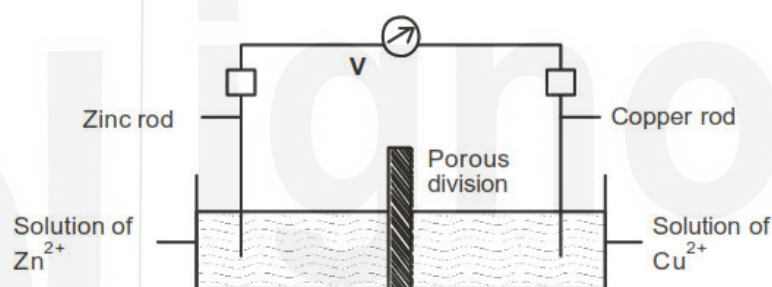


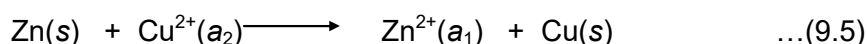
Fig. 9.5: Simple galvanic cell having Cu^{2+}/Cu and Zn^{2+}/Zn half cells.



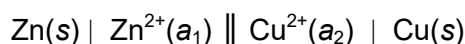
This electrode is, therefore positively charged relative to the solution and, this is referred to as **cathode**. Note that reduction always occur at the cathode.

As shown in the Fig.9.6 both electrodes of half cells are connected externally via an electric circuit and the circuit is completed by ionic conduction through the solution and KCl salt bridge. The voltmeter will then measure the difference in potential between the two electrodes.

Note that the one half cell involves an oxidation process and the other half cell a reduction process. These are then combined in the cell to give a redox reaction represented below by Equation,



Using IUPAC convention this can be represented by

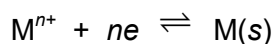


This notation starts with the left hand electrode and move to the right through the solution to the right hand electrode. The simple vertical bars signify phase

boundary, whilst the double vertical bar the salt bridge. a_1 & a_2 are the activities of two ions.

Measurement of Potential Difference

The potential difference between the electrode and solution in a half cell is referred to as the electrode potential. It is impossible to determine the potential of a single electrode and rather it is the potential difference that is measured. A number of conventions have been established in order to compare the potential of different half reactions. The half-reaction is written as a reduction process i.e. for the metal, M and its own ion M^{n+} , it is written as



If the constituents in the half-cell are present at unit activity, the potential difference is measured at 25°C with respect to a standard hydrogen electrode (SHE), which has been arbitrarily assigned the zero potential. Under these conditions the potential difference or electrode potential is known as the *standard electrode potential*, E° . We will take up standard hydrogen electrode in detail in the next section.

In general, the potential difference of a cell is given by the difference between the two electrode reduction potentials E_1 and E_2 , of the cathode and anode, respectively

$$E_{\text{cell}} = E_1 - E_2$$

The junction potential developed at the junction between the two half cells are also contributing to the cell potential, the E_{cell} calculation can be rewritten as:

$$E_{(\text{cell})} = [E_1 - E_2] + E_j$$

Where E_j is the liquid junction potential and can be a positive or negative quantity. By using salt bridge between two half cell the liquid junction potential can be minimized.

Using Nernst equation, the relationship between cell potential and activity of species involved can be developed.

The Nernst equation is:

$$E = E^\circ - \frac{RT}{nF} \ln \frac{a(\text{reduced})}{a(\text{oxidised})} \quad \dots (9.6)$$

Where R is the universal gas constant, T is the absolute temperature, n is the numbers of electron involved in the transfer, F is Faraday's constant and $a(\text{reduced})$ and $a(\text{oxidized})$ are the activities of the reduced and oxidized species of each half cell.

For the Copper half cell of the galvanic cell mentioned earlier it is written as

$$E_{\left(\text{Cu}^{2+}/\text{Cu}\right)} = E_{\left(\text{Cu}^{2+}/\text{Cu}\right)}^\circ - \frac{RT}{2F} \ln \frac{a(\text{Cu})}{a(\text{Cu}^{2+})}$$

But we can take the activity of a pure substance to be unity, so

$$E_{(\text{Cu}^{2+}/\text{Cu})} = E^0_{(\text{Cu}^{2+}/\text{Cu})} - \frac{RT}{2F} \ln \frac{1}{a(\text{Cu}^{2+})}$$

Above equation can be simplified by introducing the known values of R , F , and T , and converting natural logarithms to base 10 by multiplying by 2.3; it then becomes:

$$E_{(\text{Cu}^{2+}/\text{Cu})} = E^0_{(\text{Cu}^{2+}/\text{Cu})} + \frac{0.0591}{n} \log \frac{1}{a(\text{Cu}^{2+})}$$

For most purposes in quantitative analysis, it is sufficiently accurate to replace $a(\text{Cu}^{2+})$ with $[\text{Cu}^{2+}]$, the concentration of the copper ions in mol/dm^3 .

$$E_{(\text{Cu}^{2+}/\text{Cu})} = E^0_{(\text{Cu}^{2+}/\text{Cu})} - \frac{0.0591}{n} \log [\text{Cu}^{2+}]$$

Or
$$E_{(\text{Cu}^{2+}/\text{Cu})} = E^0_{(\text{Cu}^{2+}/\text{Cu})} + \frac{0.0591}{n} \log [\text{Cu}^{2+}]$$

A similar expression could be written for the left-hand half-cell:

$$E_{(\text{Zn}^{2+}/\text{Zn})} = E^0_{(\text{Zn}^{2+}/\text{Zn})} - \frac{0.0591}{n} \log \frac{1}{[\text{Zn}^{2+}]}$$

Or
$$E_{(\text{Zn}^{2+}/\text{Zn})} = E^0_{(\text{Zn}^{2+}/\text{Zn})} + \frac{0.0591}{n} \log [\text{Zn}^{2+}]$$

If the liquid junction potential is negligible, the potential of the cell is then given by:

$$E_{\text{cell}} = E_{(\text{Cu}^{2+}/\text{Cu})} - E_{(\text{Zn}^{2+}/\text{Zn})}$$

Clearly the potential of the cell will depend upon the concentration of both the copper(II) and zinc(II) ions. In such situation it is not possible to determine the activity or concentration of the two ions from the cell potential. In practice, we determine the activity or concentration of a single substance, rather than a combined value for two or more substances. For this reason if we keep the concentration of zinc(II) ions at a fixed value so that its potential also remain constant. Then,

$$E_{\text{cell}} = E^0_{(\text{Cu}^{2+}/\text{Cu})} + \frac{0.0591}{2} \ln a(\text{Cu}^{2+}) - E_{(\text{Zn}^{2+}/\text{Zn})}$$

As $E^0_{(\text{Cu}^{2+}/\text{Cu})}$ and $E_{(\text{Zn}^{2+}/\text{Zn})}$ are both constant, they can be combined into one value K . Then,

$$E_{\text{cell}} = K + \frac{0.0591}{2} \log [\text{Cu}^{2+}]$$

Now, the measurement of cell potential is clearly proportional to the natural logarithm of the concentration of the Copper(II) ion. This equation relates the

concentration (activity) of the oxidized form of the metal to potential. However, a general equation can be written for both oxidized and reduced forms of electrodes.

$$E_{\text{cell}} = K \pm \frac{0.0591}{n} \log [I]^{n\pm}$$

Or
$$E_{\text{cell}} = K \pm \frac{0.0591}{n} \log a_{M^{n+}} \quad \dots (9.7)$$

Where n is the charge on the ion, I , and K is a constant incorporating the potential of first half cell which is kept constant, standard potential of the second half cell containing the solution under investigation, the first half cell and junction potential if any. Note the $\pm$ sign in the equation is used to signify that it will be positive if I is a cation and negative if I is an anion. This equation can be applied to a typical cell used in potentiometric analysis and shown in Fig. 9.6. This is the common practice in potentiometric measurements.

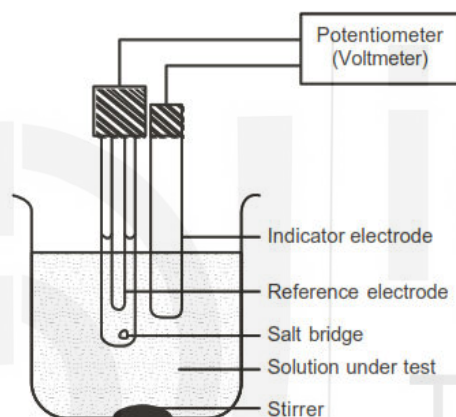


Fig. 9.6: Diagrammatic representation of a cell used for potentiometric analysis.

The first half cell which is having constant potential is referred to as a **reference electrode**. The second electrode in combination with the reference electrode is called an **indicator electrode** and its response should be dependent upon changes in activity or concentration of the species of interest.

Before considering electrodes in detail, let us now discuss the measurement of cell potential. If a current is drawn from a cell as discussed above, in the course of measurement of cell potential, the cell reaction proceeds and the concentration of the solutions will 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 less than zero or negligible current flow is called **electromotive force (e.m.f)** of the cell. The instruments which used for accurate measurement of potential are potentiometer and pH meter. These instruments draw only negligible current.

SAQ 4

Calculate the potential of a copper electrode immersed in 0.044 M CuSO_4

SAQ 5

Calculate the potential of a zinc electrode immersed in 0.060 M ZnSO₄.

SAQ 6

Calculate the cell potential for the cell made by combining the half-cell in SAQs 4 and 5 in the following way:

**9.3 1 Direct Potentiometry**

For direct potentiometric measurement, the potential of the cell can be expressed in terms of the potential developed by the indicator electrode and the reference electrode:

$$E_{\text{cell}} = (E_{\text{ind}} - E_{\text{ref}}) + E_j \quad \dots (9.8)$$

Consider the indicator electrode whose potential vary with cation activities or concentrations, we can write Nernst Equation similar to Eq. 9.7.

$$(a) \quad E_{\text{ind}} = E_{\text{ind}}^{\circ} + \frac{0.0591}{n} \log a_{\text{M}^{n+}} \quad \dots (9.9)$$

Substitution of Eq. 9.9 into Eq. 9.8 yields:

$$E_{\text{cell}} = (E_{\text{ind}}^{\circ} + \frac{0.0591}{n} \log a_{\text{M}^{n+}}) - E_{\text{ref}} + E_j$$

On rearrangement

$$\log a_{\text{M}^{n+}} = \frac{n(E_{\text{cell}} - K)}{0.0591} \quad \dots (9.10)$$

$$(b) \quad \text{or} \quad \text{pM} = -\log a_{\text{M}^{n+}} = -\frac{n(E_{\text{cell}} - K)}{0.0591} \quad \dots (9.11)$$

For anion Aⁿ⁻ Eq. 9.11 will have reversed sign

$$\text{pA} = -\log a_{\text{A}^{n-}} = \frac{n(E_{\text{cell}} - K)}{0.0591} \quad \dots (9.12)$$

where pM and pA are the negative logarithm of the metal ion activity $a_{\text{M}^{n+}}$ and an anion $a_{\text{A}^{n-}}$, respectively. These terms are more general forms of the familiar term pH. K is summation of several constants, including standard electrode potential of metal ion or anion, potential of reference electrode, junction potential, asymmetrical potential if membrane electrode is involved.

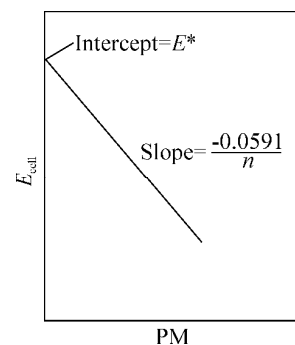
All direct potentiometric methods are based on Eqs 9.11 and 9.12. Both these equations in terms of E_{cell} may be written as

$$E_{\text{cell}} = K - \frac{0.0591}{n} \text{pM} \quad \dots (9.13)$$

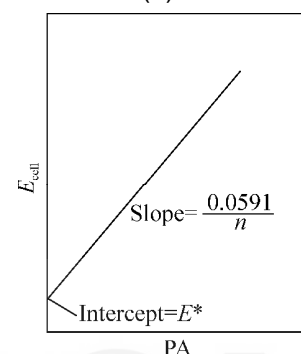
$$E_{\text{cell}} = K + \frac{0.0591}{n} \text{pA} \quad \dots (9.14)$$

Using Eqs. 9.11 and 9.12, we can determine concentration of metal ions or cations and anions in terms of pM and pA, respectively. Further, Eq. 9.13 also indicates that for a metal ion-selective electrode, an increase in pM results in decrease in E_{cell} as shown in Fig. 9.7. But before that constant K should be known to us. As you know K is made up of several constants, including the junction potential, which cannot be measured directly or calculated from theory without assumptions. This problem can be overcome by electrode calibration method using standard solution of the analyte. Though calibration methods are simple, take less time and convenient to the continuous monitoring of pM or pA, but suffer somewhat limited accuracy because of uncertainty in junction potential.

In the electrode-calibration method, K is determined by measuring E_{cell} for one or more standard solution of known pM or pA. The calibration is performed just before the determination of pM or pA for the unknown. There is an assumption that K is unchanged when standard is replaced by the unknown analyte solution. Some time instead of calculating K using emf value of standard solution, a calibration graph is plotted using measured emf of standard solutions against $\log a/(\text{concentration})$, pM or pA. The sample is then treated in the same way as the standards and the concentration (or activity) read directly from the calibration graph. For getting fast results, a graph between cell potential and $\log a$ is plotted and for this we can use graph paper called semi-log paper for drawing calibration curve and concentration of a sample can be read off directly from the graph. To further understand this let's try following SAQ.



(a)



(b)

Fig. 9.7: (a) A plot of Eq. 9.13 for a metal ion electrode; (b) A plot of Eq. 9.14 for an anion electrode

SAQ 7

Following emf readings are obtained for the standard solutions of Ca^{2+} ions in a potentiometry experiment. What is the concentration of a sample if its emf 33 mV?

Concentration of $\text{Ca}^{2+}/\text{mol dm}^{-3}$ (M)	emf/mV
1.00×10^{-4}	-2
5.00×10^{-4}	+16
1.00×10^{-3}	+25
5.00×10^{-3}	+43

9.3.2 Electrodes

In previous part we saw that an electrochemical cell is composed of two electrodes: indicator and reference electrodes. A reference electrode must be easy to construct, and must maintain a constant, reproducible potential even if small currents are passed. An indicator electrode responds to change in

activity of the species to be measured. Now we are going to consider some systems which can be used as reference electrodes.

Reference Electrode

There are three common reference electrodes used for potentiometric analysis:

- Standard Hydrogen Electrode
- Calomel Electrode
- Silver-Silver Chloride Electrode

Standard Hydrogen Electrode (SHE)

The standard hydrogen electrode (Fig. 9.8) is constructed from a platinum foil plate, which has been platinized, that is coated with platinum black (finely divided platinum) by chemical or electrochemical reduction of chloroplatinic acid. The finely divided layer of platinum black helps in achieving the largest possible surface area. Its composition can be formulated as

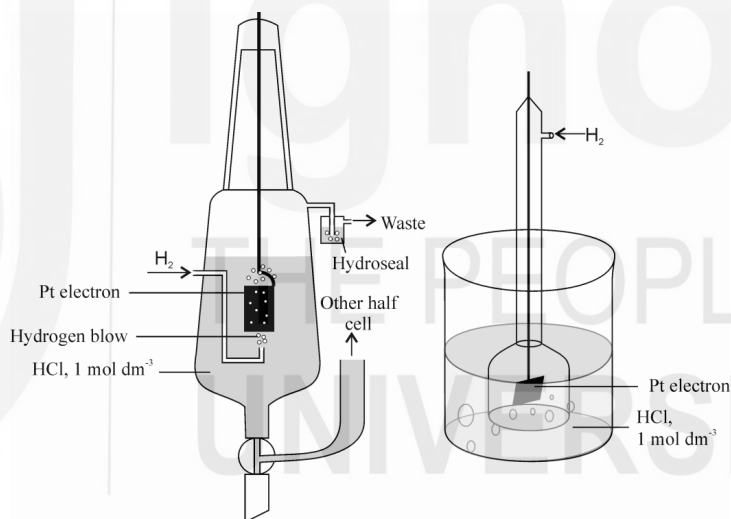
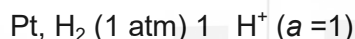
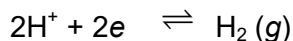


Fig.9.8: Common design of Hydrogen Electrodes

The half cell reaction, may occur in either direction depending upon the type of electrode which is coupled with it.



The potential of a hydrogen electrode is given by the Nernst equation:

$$E = E^0 + \frac{2.303 RT}{2F} \log \frac{(a_{\text{H}^+})^2}{p_{\text{H}_2}} \quad \dots (9.15)$$

where E^0 , the standard electrode potential for hydrogen electrode is zero. For the standard hydrogen electrode, having H^+ activity, a_{H^+} equal to one and pressure exerted by hydrogen gas p_{H_2} also equal to one atmosphere, the logarithmic term on the right of Eq. (9.15) becomes equal to zero and $E = E^0 =$

0. By convention, the potential of SHE is assigned the value of exactly zero volt at all temperatures.

The SHE was selected as a primary reference electrode for several reasons as given below:

- (i) It can be used for the entire pH range.
- (ii) The accuracy in measurement is high.
- (iii) The reagents used in its preparation can easily be purified.
- (iv) The potential of the electrode is not affected by mechanical stress of the electrode.

Besides these advantages, the use of SHE has certain limitations as:

- (i) It can not be used in solutions containing strong oxidizing and reducing substances.
- (ii) It is not handy and hence transfer from one place to another is not easy.
- (iii) The platinum surface is poisoned in presence of species like H_2S , CN^- and Hg.

However, for experimental measurement of the electrode potential the use of SHE requires many precautions, therefore, other electrodes of simpler design whose potentials are well known with respect to the SHE e.g. Saturated Calomel Electrode (SCE) and Ag/AgCl electrodes. Such electrodes are known as secondary reference electrodes and are generally preferred.

Saturated Calomel Electrode (SCE)

A saturated calomel electrode is the most frequently used reference electrode. Many designs of saturated calomel electrodes have been reported in literature. One of those is shown in Fig. 9.9.

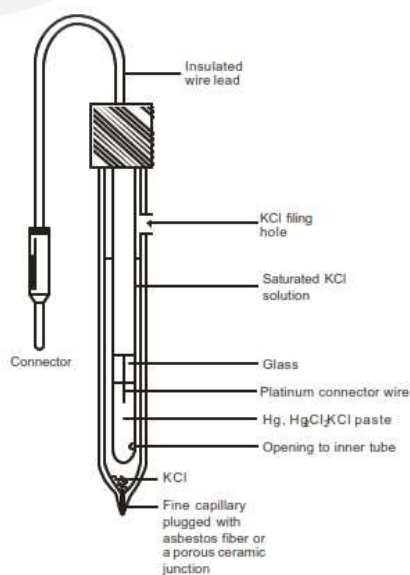
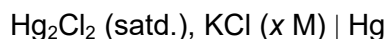


Fig.19.9: A commercial calomel electrode.

It consists of an outer glass tube with a crack in the end of the tube. A crack is made by an asbestos filament or fitted porcelain plug or quartz fiber. A mercury and mercurous chloride paste is filled in the inner tube, which is connected to the saturated potassium chloride solution in the outer tube through a small opening. The saturated potassium chloride solution in the outer tube can be easily renewed through a lateral hole. Calomel, i.e., mercurous chloride is a sparingly soluble salt. Its solubility product (K_{sp}) is given as:

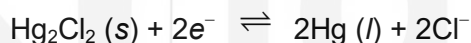
$$K_{sp} = a_{\text{Hg}_2^{2+}} \times (a_{\text{Cl}^-})^2 = 1.1 \times 10^{-18} \quad \dots (9.16)$$

A calomel electrode may be symbolised as:



Where x represents the concentration of potassium chloride and must be specified in describing the electrode. Commonly, 0.1 M, 1 M, and saturated solutions of potassium chloride have been employed and the calomel electrodes are named as decimolar, molar and saturated calomel electrodes, respectively.

The half cell reaction is



and the potential at 25° C is given by the equation:

$$E = E_{\text{Hg}}^0 + \frac{0.0591}{2} \log a_{\text{Hg}_2^{2+}}$$

Substituting for $a_{\text{Hg}_2^{2+}}$ from Eq.9.16. gives:

$$\text{or } E = E_{\text{Hg}}^0 + \frac{0.0591}{2} \log \frac{K_{sp}}{a_{\text{Cl}^-}} \quad \dots (9.17)$$

The activity of chloride ions (by excess of chloride ions obtained from potassium chloride) remains constant for a particular electrode. The experimental value of the potential of the saturated calomel electrode is 0.244 V at 25° C.

Silver-Silver Chloride Electrode

The silver-silver chloride electrode is another frequently used reference electrode. It is prepared by plating a layer of silver chloride onto a metallic silver wire and immersing in a solution containing chloride ions (usually KCl) of known concentration which is also saturated with silver chloride (see Fig. 9.10).

Silver chloride is a sparingly soluble salt. Its, solubility product, K_{sp} , is:

$$K_{sp} = a_{\text{Ag}^+} a_{\text{Cl}^-} = 1.77 \times 10^{-10} \text{ at } 25^\circ \text{C} \quad \dots (9.18)$$

The silver-silver chloride electrode may be symbolised as:

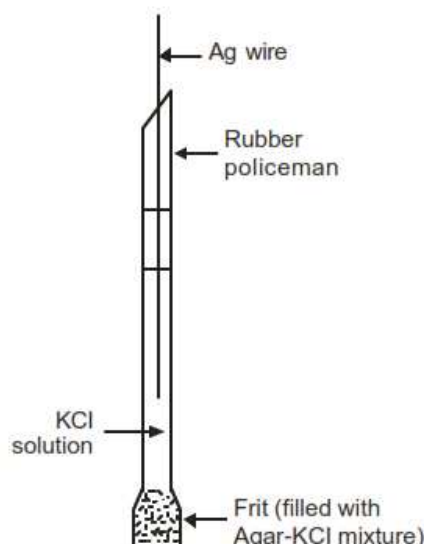
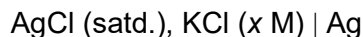


Fig. 9.10: Silver-silver chloride electrode.

Where x represents the molarity of potassium chloride solution. Normally, a saturated potassium chloride solution is taken.

The half cell reaction is:



and the potential at 25°C is given by the equation

$$E = E^0_{\text{Ag}} + 0.0591 \log a_{\text{Ag}^+}$$

Substituting for a_{Ag^+} from Eq.9.18 gives:

$$E = E^0_{\text{Ag}} + 0.0591 \log \frac{K_{\text{sp}}}{a_{\text{Cl}^-}} \quad \dots(9.19)$$

When a large excess of chloride ion (potassium chloride) is present, the contribution of chloride ions obtained from dissolution of silver chloride can be (in the half cell) controlled by the concentration of potassium chloride (which remains constant). The experimental value of potential for an electrode prepared by saturated solution of potassium chloride is 0.199 V.

Indicator Electrodes

As described earlier, electrodes that respond to a specific ion are referred to as indicator electrodes and the selection and use of such electrodes is the key to modern potentiometry. Several metals like silver, copper, mercury, lead and cadmium can be served as indicator electrodes. Usually these metal electrodes are constructed from coils of wire, flat metal, metal plates or button set in plastic or glass (see Fig. 9.11). Large surface area is preferable because of rapid attainment of equilibrium. Metal surface is to be thoroughly cleaned. Usually it is achieved by dipping in concentrated nitric acid followed by repeated rinsing with distilled water.

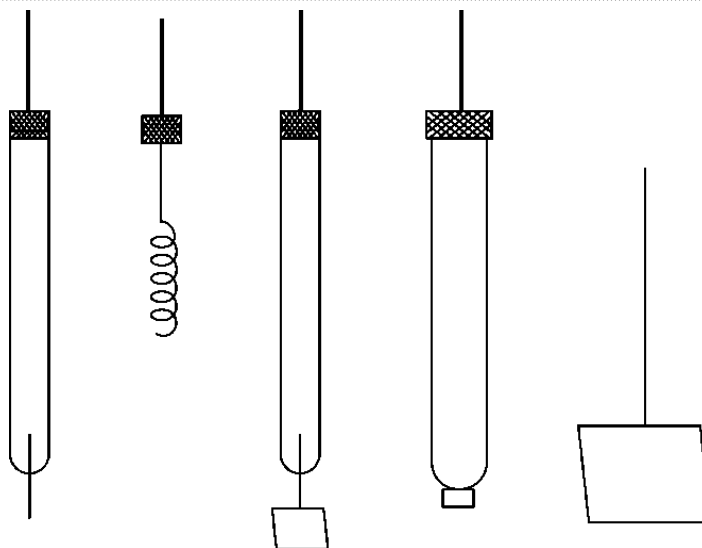


Fig. 9.11: Typical indicator electrode designs

Metal indicator electrodes are not selective as these electrodes can respond to its own ions and can also respond to a number of other metal ions. There are several other indicator electrodes which are selective to particular ions. Many of them are very valuable in potentiometric analysis and are collectively referred to as ion selective electrodes (ICE). The most common of these is the glass electrode, which is selective to H^+ ions and, consequently, pH.

Glass Electrode

The most convenient way for determining pH has been by the use of the glass electrode. It is an ion-selective electrode. Glass electrode is a membrane type electrode whose membrane is made by a special type of glass. A potential develops across a thin glass membrane separating two solutions of different acidities. The measurement of potential difference can thus be related to hydrogen ion concentration. This phenomenon was first recognized by Cremer in 1906 and systematically explored by Haber in 1909 with the construction of a glass bulb electrodes. After the work of Sorenson (1909) to determine hydrogen ion concentration in terms of pH and the use of vacuum tube voltmeter by A. Beckmann (1930) made the use of glass pH electrodes more practical. Development of transistor based pH meters and the special purpose glass for the measurement of high pH values has further improved the technology.

The glass electrodes of various sizes, shapes and for different pH ranges are commercially available. Fig. 9.12 illustrates the construction of a common type of glass electrode. It consists of a thin, H^+ sensitive glass membrane bulb at the end of a heavy-walled glass tubing. A buffer solution (or 0.1M HCl) is filled in the glass membrane bulb. A reference electrode (usually silver-silver chloride electrode) is placed in contact with the inner solution. It is connected to one terminal of the pH meter. The bottom portion (bulb) of the glass electrode is immersed in the external solution whose pH is to be measured. An external reference electrode (usually an SCE) is immersed in the external solution and is connected to the other terminal of the pH meter.

Schematic diagram of cell containing a pH glass electrode can be represented as below:

Internal	Internal	H ⁺ sensitive	External	External
Reference	buffer	glass	solution reference	
Electrode	(a _{H⁺}) ₁	membrane	(a _{H⁺}) ₂	electrode

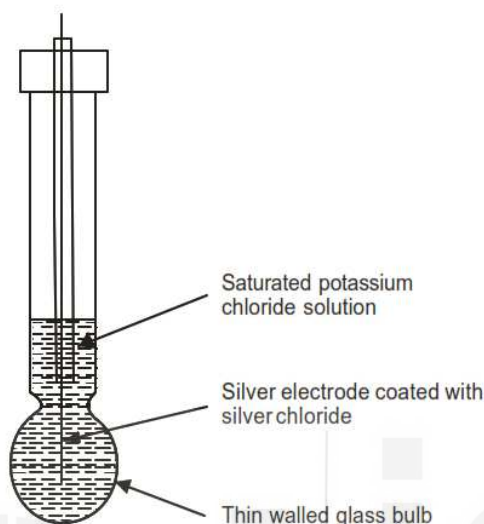


Fig.9.12: A typical glass electrode for pH measurements.

Potential of this cell:

$$E_{\text{cell}} = E_1 - E_2 + E_{\text{membrane}} + E_j$$

The potential for this cell response is related to the logarithm of hydrogen ion activities on the two sides of the glass membrane and is given by Nernst equation:

$$E_{\text{cell}} = E_{\text{asym}} - 0.0591 \log \frac{(a_{\text{H}^+})_1}{(a_{\text{H}^+})_2}$$

Where E_{asym} is asymmetry potential. This is due to the potential difference between internal and external surface of glass membrane. Now E_{cell} can be written as

$$E_{\text{cell}} = k - 0.0591 \log \frac{(a_{\text{H}^+})_1}{(a_{\text{H}^+})_2} \quad \dots(9.20)$$

Where k is a constant. The constant includes the difference in junction potential between the reference electrode and solution and the asymmetry potential for the glass membrane. The asymmetry potential is due to the difference in surface of the inner and outer layers of the glass membrane.

Since the pH on the internal side of the glass membrane is held constant using a buffer, the potential of the glass membrane electrode will depend upon the pH of the external solution $(a_{\text{H}^+})_2$. Now Eq. 9.20 can be written as:

$$E_{\text{cell}} = k_1 + 0.0591 \log (a_{\text{H}^+})_2$$

Since $\text{pH} = -\log a_{\text{H}^+}$

$$E_{\text{cell}} = k_1 + 0.0591 \text{ pH} \quad \dots (9.21)$$

Where k_1 now includes the constant factor related to a_{H^+} . Thus, the emf produced in the glass electrode system varies linearly with pH. From the Eq.18.18 the constant k_1 can be eliminated by measuring potential, first with standard buffer solution whose pH is precisely known and then with known solution. Thus for the standard buffer

$$(E_{\text{cell}})_s = k_1 + 0.0591 (\text{pH})_s$$

For unknown sample solution

$$(E_{\text{cell}})_u = k_1 + 0.0591 (\text{pH})_u$$

Then the difference in both the cell potentials

$$(E_{\text{cell}})_u - (E_{\text{cell}})_s = 0.0591 (\text{pH})_u - 0.0591 (\text{pH})_s$$

or

$$(\text{pH})_u = (\text{pH})_s + \frac{(E_{\text{cell}})_u - (E_{\text{cell}})_s}{0.0591} \quad \dots(9.22)$$

This is the operational definition of the pH.

As said above, the constant k_1 includes the asymmetry potential which exists across the glass membrane even if the two sides of the cell are of identical composition. For this reason, a pH meter is to be calibrated from time to time (preferably every time when pH measurements are done) with standard buffers.

In pH meter voltmeter is used to measure the potential of the cell. The voltage scale is calibrated in pH units so that 0.0591V correspond to 1pH Unit at 25°C. This value will change with temperature and modern pH meters have a temperature compensation device. This may be set before taking pH readings.

Combination Electrodes

For the purpose of convenient both an indicator and a reference electrodes (with salt bridge) can be combined into a single probe to make a complete cell or combination electrodes. For such electrodes only small volume is needed for potentiometric measurements. A typical assembly of combination electrodes is shown in Fig.9.13. It consists of a tube within a tube, the inner one having the pH indicator electrode and the outer one having the reference electrode and its salt bridge.

pH determination using glass electrode is most accurate and widely used method despite a few disadvantages viz. the glass membrane being very fragile, it requires great care while using. The ordinary potentiometer cannot be used for measuring the potential of the glass electrode. Thus, the electronic potentiometers are required to be used, needs frequent standardization and, cannot be employed in pure ethyl alcohol, acetic acid and gelatin. The following features of glass electrode have made it more versatile to be used as indicator electrode for pH measurement.

- It may be used in the presence of strong oxidizing and reducing solutions in viscous media and in presence of proteins which interfere with operation of other electrodes.

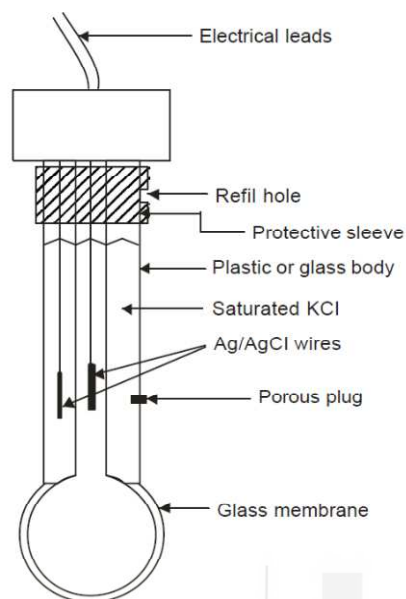


Fig.9.13: Combination pH reference electrode.

- It can be used for solutions having pH values 2 to 10 with some special glass, measurements can be extended to pH values greater than 10.
- It is simple to operate and immune to poisoning.
- The equilibrium is reached quickly

While measuring pH you should be little care full as there are few factors which limit the accuracy of pH measurements. We are listing few of them below:

- The alkaline error:** It is noticed that the ordinary glass electrode becomes sensitive to alkali ions and gives low reading in high pH range – above 9 or 10 pH units. The reason for the error is that whilst the glass membrane is selective to hydrogen ion, it also responds to other ions. This becomes more significant when the activity of the other ions is higher to activity of the hydrogen ion.
- The acid error:** At low pH range – less than 0.5, the values determined by the glass electrode tend to be somewhat higher. This error is due to the activity of water which we have ignored while writing Nernst equation for the indicator electrode. We have assumed that activity of water may be taken to be unity as it is in large excess in the solution and it behaves as a pure substance. However, in highly acidic solution, the activity of the water becomes less than unity because a good amount is used in hydrating the protons.
- Variation in junction-potential:** In most of the cases the composition of the standard buffer solution and test solution are different. In such situation, the liquid junction potential will be different.

4. **Error in the pH of the standard buffer:** There may be possibility that buffer solution is not prepared with full care or its composition may change during storage. All these factors will cause an error in subsequent pH measurements.
5. **Temperature:** A change in temperature may affect on pH measurements, because change in temperature affects the activities of the ions as well as the liquid-junction potentials. Therefore, it is advised to calibrate the electrode at the temperature of the test solution.
6. **Calibration procedures:** Buffer solution cannot be prepared more accurately than ± 0.01 pH units. Therefore, we cannot calibrate the electrode better than this.
7. **Equipment related:** These errors may be due to the power fluctuations, parallax errors in reading analogue scales, etc.

With this theoretical background now we will see how the pH is measured using pH meter, but before that try following SAQs.

SAQ 8

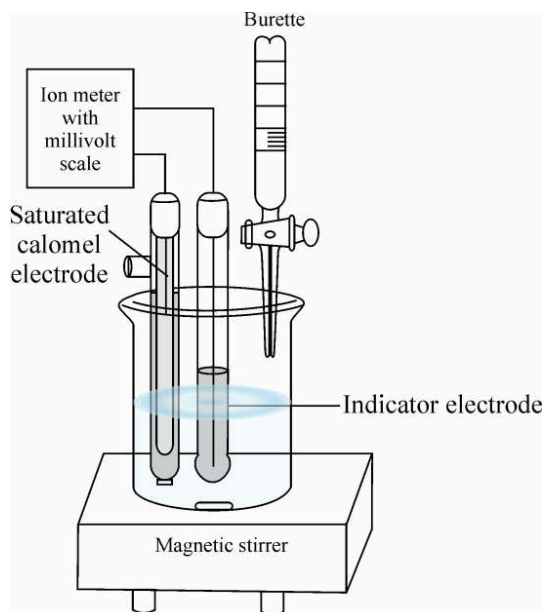
Why is it necessary to calibrate the glass electrode before use?

SAQ 9

List some factors which may cause errors in pH measurements.

9.4 POTENTIOMETRIC TITRATIONS

In a potentiometric titration, the equivalence point is detected by measuring the potential change during the titration. Fig. 9.14 shows the usual apparatus for a potentiometric titration.



Electric potential (E) is measured in volts (V). The smaller unit of potential is millivolt (mV).

$$1 \text{ mV} = 10^{-3} \text{ V}$$

Fig. 9.14: Typical apparatus for potentiometric titration

The potential between the reference electrode half cell (whose potential is known) and the indicator electrode half cell (whose potential varies with concentration of the solution) is measured at the start and after the addition of small amounts of titrant, say each 1 cm^3 , and more closely near the equivalence point, when readings start to change by larger values. After each addition the solution is stirred well and the reading is allowed to become steady.

For detecting the equivalence point in a potentiometric titration, a graph is plotted between the potential and the volume of the titrant to give a titration curve such as shown in Fig. 9.15(a)

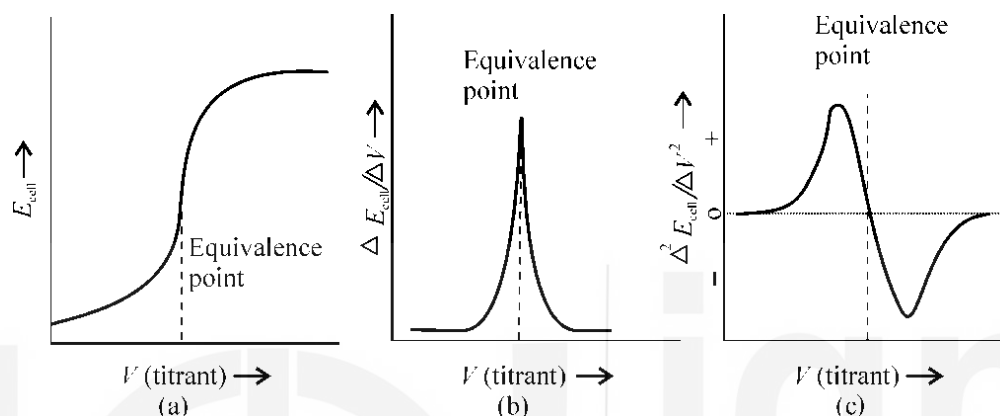


Fig. 9.15 : Methods of equivalence point determination (a) normal plot (b) first derivative (c) second derivative

Once the titration curve is at hand, we must determine where the curve is steepest, normally by some sort of inspection. We may draw a vertical line through the steep portion of the curve and find the intersection of this line with the volume axis. To overcome the uncertainty in this procedure, we plot another graph as shown in Fig. 9.15(b). This is a plot of the slope of a titration curve, that is, the change in potential with change in volume ($\Delta E / \Delta V$) against volume of the titrant. The resulting curve rises to a maximum height at the equivalence point. The volume at the equivalence point (V) is determined by drawing a vertical line from the peak to the volume axis. Fig. 9.15(c) shows a plot of the change in the slope of a titration curve ($\Delta^2 E / \Delta V^2$) against the volume of titrant. At the point where the slope $\Delta^2 E / \Delta V^2$ is a maximum, the derivative of the slope is zero. The end-point is located by drawing a vertical line from the point at which $\Delta^2 E / \Delta V^2$ is zero to the volume axis.

In contrast to direct potentiometric measurements, potentiometric titrations generally offer increased accuracy and precision. Accuracy is increased because; measured potentials are used to detect rapid changes in activity that occurs at equivalence point of the titration. Furthermore, it is a change in emf versus titre volume rather than absolute value of emf. Thus, the influence of liquid-junction potentials and activity coefficients is minimised.

Potentiometric titrations may be applied to a variety of systems including those involving oxidation-reduction, precipitation, acid-base, and complexation equilibria reactions. We will discuss all these systems in detail in subsequent sections. Further, potentiometric end-point detection also provides more accurate result than the corresponding method employing indicators. It is

particularly useful for titration of coloured or opaque solutions and for detecting the presence of unsuspected species in a solution. Titrations of more dilute solutions are possible using potentiometry. Unfortunately, it is more time consuming than a titration performed with an indicator.

9.4.1 TYPES OF POTENTIOMETRIC TITRATIONS

The majority of potentiometric titrations involve chemical reactions such as neutralisation, oxidation-reduction, precipitation and complexation. Here we will discuss neutralization and oxidation-reduction titration methods as these are most common titration methods.

1. **Neutralisation Titrations:** Potentiometric neutralisation titrations are particularly useful for the analysis of mixture of acids or polyprotic acids or bases because discrimination between the end-points can often be made. An approximate numerical value for dissociation constant of the reactant species can also be estimated from potentiometric titration curves in theory. This quantity can be obtained from any point along the curve as a practical matter. It is most easily calculated from the pH at the point of half-neutralisation e.g. in the titration of weak acid HA, we may ordinarily assume that at the mid-point $[HA] \cong [A^-] + [H^+]$ and therefore :

$$K_a = \frac{[H^+][A^-]}{[HA]} \quad \dots (9.23)$$

$$\log K_a = \log H^+ + \log \frac{[A^-]}{[HA]}$$

$$-\log K_a = -\log H^+ - \log \frac{[A^-]}{[HA]}$$

$$pK_a = pH - \log \frac{[A^-]}{[HA]}$$

At half neutralization of the acid

$$[A^-] (\text{salt}) = [HA] (\text{acid})$$

Therefore, $pK_a = pH - \log 1$ ($\log 1 = 0$)

$$\text{or } pK_a = pH \quad \dots (9.24)$$

This is the midway point to the equivalence point. Therefore, pK_a values can also be directly read from the titration curves.

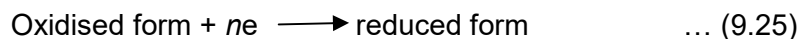
It is important to note that a dissociation constant determined from a potentiometric titration curve may differ from that shown in the table of dissociation constant in the literature by a factor of 2 or more because the latter is based upon the activities while the former is not.

2. **Oxidation-Reduction Titrations:** Indicator electrodes for oxidation-reduction are generally fabricated from platinum, gold mercury or silver. The metal chosen must be un-reactive with respect to the components of

the reaction. It is merely a site for electron transfer. Platinum electrode is most widely used for oxidation-reduction titrations.

The determining factor in the values of potential is the ratio of the activity or concentration of the oxidised and reduced forms of certain ion species.

Take a general equation



the potential acquired by the indicator electrode at 25 °C is given by

$$E = E^\circ + \frac{0.0591}{n} \log \frac{a_{\text{oxidised form}}}{a_{\text{reduced form}}} \quad \dots (9.26)$$

where E° is the standard potential of the system. The potential of the immersed electrodes are controlled by the ratio of these activities or concentration. In redox reactions, reducing agent is oxidised or oxidising agent is reduced and the ratio and the potential therefore changes more rapidly at the end point of the reaction. Thus titrations involving such reactions like Fe (II) with potassium permanganate or potassium dichromate or ceric sulphate may be followed potentiometrically and equivalence points can be obtained.

Automatic Titrations

Now-a-days large number of automatic titrators based on the principle of potentiometry have come into the market. These are highly useful in those places, where a large number of routine analysis are required. These may not be more accurate than the manual techniques, but are quite rapid and decrease the time needed to perform the experiment and thus offer some economic advantages. Two different automatic titrators are available:

1. The first type gives titration curves of V vs E or $\Delta E / \Delta V$ vs V . The end point is obtained from the curve by inspection.
2. In the second type of titrators, the titration is stopped automatically when the potential of the electrode system reaches a predetermined value and the volume of reagent delivered is read at the operators convenience or printed on a tape. These titrators usually employ a burette system with a solenoid-operated valve to control the flow or alternately it makes use of a syringe, the plunger of which is activated by a motor driven micrometer screw.

9.5 pH TITRATION

Similar to potentiometric titrations, in contrast to direct pH measurements, pH titrations generally offer increased accuracy and precision. Accuracy is increased because, measured pH are used to detect rapid changes in activity that occur at equivalence point of the titration. Furthermore, it is the change in pH versus titre volume rather than absolute value of pH that is of interest. Thus, the errors due to liquid-junction potentials and activity coefficients are minimized. pH titrations may be applied to a variety of systems including those

involving weak acids and weak bases. In such titration, it is difficult to get end point using indicator method. A typical acid-base titration using pH metry is briefed as follows.

It is known that the neutralization of acids and bases is always accompanied by the changes in the concentration of H^+ and OH^- ions. It is evident that hydrogen electrode may be employed in these titrations. The reference electrode used in these titrations is 1 M calomel electrode. The apparatus used for acid-base titrations is as shown in Fig. 9.16.

The critical problem in titration is the recognition of point at which the quantities of reacting species are presented in equivalent amounts, i.e. the equivalence point. The titration curve can be followed point by point plotting as the ordinate successive values of the pH versus the corresponding volume of titrant added as the abscissa. Addition of the titrant should be the smallest accurately measurable increments that provide an adequate density of points, particularly in the vicinity of equivalence point.

- Over most of the titration range the pH varies gradually, but near the end point the pH changes very abruptly. The resulting titration curve resembles Fig. 9.17(a).

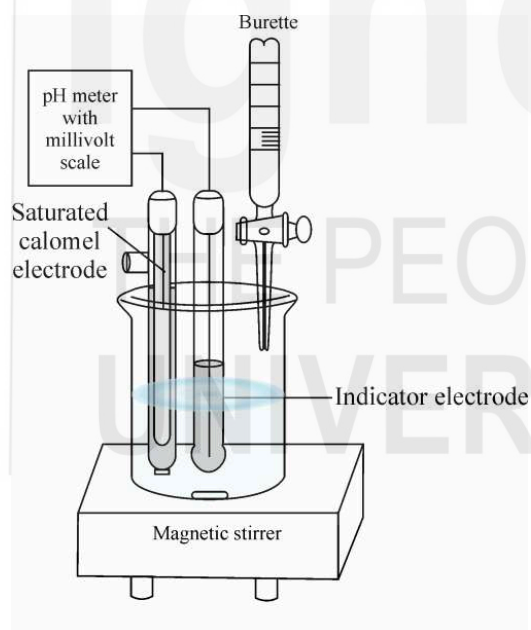


Fig. 9.16: Typical Instrumental set up for pH titration

- By inspection, the end point can be located from the inflection point of the titration curve.
- This is the end point that corresponds to maximum rate of change of pH per unit volume of titrant added (0.05 cm^3 or 0.1 cm^3).
- The distinction of the end point increases as the reaction involved becomes more nearly quantitative.
- Once the pH has been established for a given titration, it can be used to indicate subsequent end points for the same chemical reaction.

- The equivalence point can be more precisely located from the 1st and 2nd derivative curves as illustrated in Fig. 9.17(b) and 9.17(c). Solutions more dilute than 10^{-3} M generally do not give satisfactory end points. This is limitation of pH metry and potentiometric titrations.

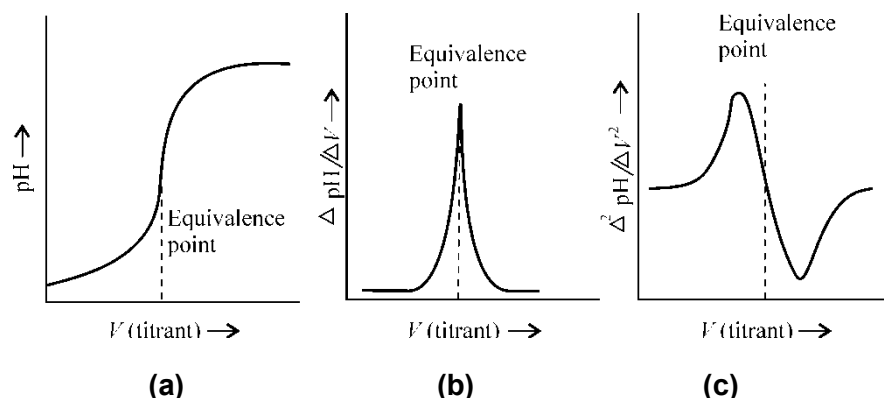


Fig. 9.17: pH titration curves; (a) Normal curve; (b) First derivative curve; and (c) second derivative curve

9.6 SUMMARY

In this unit, you have learnt that about electrode potentials, principles of potentiometer and measurement of potential, different types of reference electrodes : such as Hydrogen Electrode, Calomel Electrode, Silver-Silver Chloride Electrode and different types of indicator electrodes. You have also learnt about the measurement of potential and location of end points from the graphs obtained from the experimental values of emf and volume of titrant. Different types of titration such as acid-base titrations and redox titrations were also explained in detail. You have also learnt that pH tells the acidic or basic nature of an aqueous solution and is defined as negative logarithm of hydrogen ion concentration. pH can be readily measured in an accurate manner with the help of a pH meter. There is also detail discussion on pH titration.

9.7 TERMINAL QUESTIONS

- What is an electrode potential?
- Why the absolute value of electrode potential cannot be determined?
- What is a indicator electrode? Give some examples.
- Explain liquid-junction potential. How can it be eliminated?
- Calculate the EMF of the following electrochemical cell at 25°C :
 $\text{Cu, Cu}^{2+} (a = 0.1 \text{ M}) \parallel \text{H}^+ (a = 0.01 \text{ M}) \text{ H}_2 (0.95 \text{ atm.}), \text{Pt}$
- What is the source of the asymmetry potential in a glass membrane electrode?
- What are the advantages of a pH metric titration over a direct pH metry?

8. Drive an expression for the 'operational definition of pH'.

9.8 ANSWERS

Self Assessment Questions

1. Voltammetry is an analytical technique that is based on measuring the current that develops at a small electrode as the applied potential is varied. Polarography is a particular type of voltammetry in which a dropping mercury electrode is used.
2. In potentiostatic coulometry (coulometry at constant potential), the potential of the working electrode is maintained at a constant level, so that only analyte gets quantitatively oxidized or reduced there is no involvement of the less reactive species. In amperostatic coulometry or constant-current coulometry, the cell is operated so that the current is maintained at a constant value.

3. According to Faraday's law

$$n_A = Q/nF \quad \text{where } Q = It$$

Half-reaction for silver deposition



Thus, 1 mole of silver is equivalent to 1 mol of electrons

$$Q = 9.65 \times 50 \times 60 \text{ C} = 28950 \text{ C}$$

Further $n=1$ and $F = 96490 \text{ C}$

We can find the number of moles of Ag from Faraday's law

$$n_{\text{Ag}} = \frac{28950 \text{ C}}{1 \text{ e} / \text{mol Ag} \times 96485 \text{ C / mole e}} = 0.300 \text{ mol Ag}$$

$$\text{Mass of Ag} = 0.300 \text{ mol} \times 108 \text{ g /mol} = 32.40 \text{ g}$$

4. Half-cell reaction : $\text{Cu}^{2+} + 2e^- \longrightarrow \text{Cu(s)}$

$$\text{Nernst equation : } E = E^\circ - \frac{0.0591}{2} \log \frac{1}{[\text{Cu}^{2+}]}$$

No term of elemental Cu is included in the logarithmic term because it is a pure solid.

$$\text{or } E = E^\circ + \frac{0.0591}{2} \log [\text{Cu}^{2+}]$$

E° for Cu electrode is + 0.337 (from Table 1 Appendix 1), therefore,

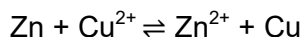
$$E = 0.337 + \frac{0.0591}{2} \log 0.044$$

$$E = 0.297 \text{ V}$$

5. You have to follow the same steps as shown for SAQ 4.

$$E = -0.799 \text{ V}$$

6. For this cell chemical reaction is:



$$E_{\text{cell}} = E_{\text{Cu}^{2+}/\text{Cu}} - E_{\text{Zn}^{2+}/\text{Zn}}$$

$$= 0.297 - (-0.799) = 1.096 \text{ V}$$

7. Draw a calibration graph using the data given in SAQ 7 on special type of graph paper called semi-log (or log/mm) paper. The calibration graph is shown in Fig. 9.18. You can find the concentration of sample from this graph is $2.1 \times 10^{-3} \text{ M}$.

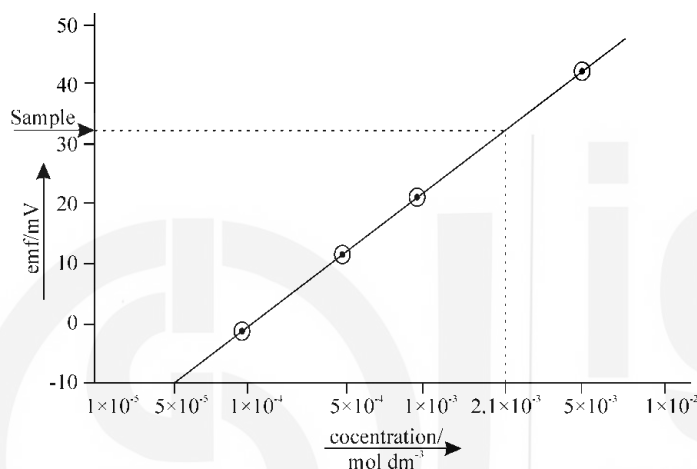


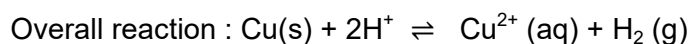
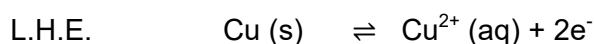
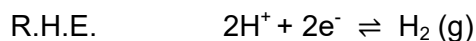
Fig. 9.18 : Calibration curve for calcium ion selective electrode

8. It is not possible to determine the values of asymmetry potential as well as liquid- junction potential in glass/calomel electrode, therefore, it is necessary to calibrate glass membrane electrode with suitable buffer solutions before use.
9. i) Alkaline error
 ii) Acid error
 iii) Variation in junction potential
 iv) Error in the pH of the standard buffer
 v) Temperature
 vi) Calibration procedures
 vii) Equipment related

Terminal Questions

- This is the tendency of an electrode to get oxidised or reduced. But as per the IUPAC conventions, it is the reduction potential of the electrode.
- Because oxidation or reduction cannot take place independently.

3. A standard electrode with reference to which the potential of an indicator electrode is determined is called "reference electrode." Some examples are Standard Hydrogen Electrode (S.H.E.); Saturated Calomel Electrode (S.C.E.).
4. This is the potential which is set up at the junction of two solutions because of difference in the speeds of ions moving across the boundary. It can be eliminated by using a salt bridge containing KCl, since K^+ and Cl^- move with almost equal speeds.
5. The half-cell reactions are :



$$E^\circ_{\text{cell}} = E^\circ = E^\circ_R - E^\circ_L = -0.34 \text{ V}$$

The EMF of the cell is given by,

$$E = E^\circ - \frac{0.0591}{2} \log \frac{a_{Cu^{2+}} \times a_{H_2}}{(a_{H^+})^2} \text{ at } 25^\circ \text{C}$$

$$= -0.337 - \frac{0.0591}{2} \log \frac{(0.1)(0.95)}{(0.01)^2}$$

$$= -0.337 - 0.088 = -0.425 \text{ V}$$

6. The asymmetry potential in a membrane arises from difference in the structure of the inner and outer surfaces. These difference may be due to the manufacture reason or due to its use.
7. pH titrations generally offer increased accuracy and precision. Accuracy is increased because measured pH are used to detect rapid changes in activity that occur at equivalence point of the titration. Furthermore, it is the change in pH versus titre volume rather than absolute value of pH that is of interest. Thus, the errors due to liquid-junction potentials and activity coefficients are minimized.
8. Cell potential for the standard buffer can be expressed as

$$(E_{\text{cell}})_s = E^* - 0.0592 (\text{pH})_s \quad \dots (i)$$

Cell potential for unknown solution will be expressed as

$$(E_{\text{cell}})_u = E^* - 0.0592 (\text{pH})_u \quad \dots (ii)$$

To eliminate E^* subtract Eq. (i) from Eq. (ii), we find

$$(\text{pH})_u = (\text{pH})_s - \frac{(E_{\text{cell}})_u - (E_{\text{cell}})_s}{0.0591} \quad \dots (iii)$$

Eq. (iii) is the operational definition of pH.

Appendix I

Standard Electrode Potentials*	
Reaction	E^0 at 25° C, V
$\text{MnO}_4^- + 8 \text{H}^+ + 2\text{e} \rightleftharpoons \text{Mn}^{2+} + 4\text{H}_2\text{O}$	+ 1.51
$\text{Cl}_2(\text{g}) + 2\text{e} \rightleftharpoons 2\text{Cl}^-$	+ 1.359
$\text{Cr}_2\text{O}_7^{2-} + 14 \text{H}^+ + 6\text{e} \rightleftharpoons 2\text{Cr}^{3+} + 7 \text{H}_2\text{O}$	+ 1.33
$\text{O}_2(\text{g}) + 4\text{H}^+ + 4\text{e} \rightleftharpoons 2\text{H}_2\text{O}$	+ 1.229
$\text{Br}_2(\text{aq}) + 2\text{e} \rightleftharpoons 2\text{Br}^-$	+ 1.087
$\text{Br}_2(\text{l}) + 2\text{e} \rightleftharpoons 2\text{Br}^-$	+ 1.065
$\text{Ag}^+ + \text{e} \rightleftharpoons \text{Ag}(\text{s})$	+ 0.799
$\text{Fe}^{3+} + \text{e} \rightleftharpoons \text{Fe}^{2+}$	+ 0.771
$\text{I}_3 + 2\text{e} \rightleftharpoons 3\text{I}^-$	+ 0.536
$\text{Cu}^{2+} + 2\text{e} \rightleftharpoons \text{Cu}(\text{s})$	+ 0.337
$\text{UO}_2^{2+} + 4\text{H}^+ + 2\text{e} \rightleftharpoons \text{U}^{4+} + 2\text{H}_2\text{O}$	+ 0.334
$\text{Hg}_2\text{Cl}_2(\text{s}) + 2\text{e} \rightleftharpoons 2\text{Hg}(\text{l}) + 2\text{Cl}^-$	+ 0.268
$\text{AgCl}(\text{s}) + \text{e} \rightleftharpoons \text{Ag}(\text{s}) + \text{Cl}^-$	+ 0.222
$\text{Ag}(\text{S}_2\text{O}_3)^{3-}_2 + \text{e} \rightleftharpoons \text{Ag}(\text{s}) + 2\text{S}_2\text{O}_3^{2-}$	+ 0.017
$2\text{H}^+ + 2\text{e} \rightleftharpoons \text{H}_2(\text{g})$	0.000
$\text{AgI}(\text{s}) + \text{e} \rightleftharpoons \text{Ag}(\text{s}) + \text{I}^-$	- 0.151
$\text{PbSO}_4 + 2\text{e} \rightleftharpoons \text{Pb}(\text{s}) + \text{SO}_4^{2-}$	- 0.350
$\text{Cd}^{2+} + 2\text{e} \rightleftharpoons \text{Cd}(\text{s})$	- 0.403
$\text{Zn}^{2+} + 2\text{e} \rightleftharpoons \text{Zn}(\text{s})$	- 0.763
$\text{Ce}^{4+} + \text{e} \rightleftharpoons \text{Ce}^{3+}$	- 1.70 V
$\text{Mg}^{2+} + 2\text{e} \rightleftharpoons \text{Mg}(\text{s})$	- 2.363

CONDUCTOMETRY

Structure

10.1	Introduction	The Wheatstone Bridge Principle
	Expected Learning Outcomes	Measurement of Conductance of a Solution
10.2	Electrolytic Conductance	
	Molar Conductivity	10.4 Application of Conductometry
	Variation of Conductance with Concentration	10.5 Summary
	Limiting Molar Conductivity	10.6 Terminal Questions
	Effect of other Factors on Conductance	10.7 Answers
10.3	Measurement of Electrolytic Conductance	10.8 Further Reading

10.1 INTRODUCTION

So far we have discussed potentiometric methods. In these methods we measure the emf of a galvanic cell which is operating near zero current. Because this emf is a function of the ionic activities within the cell, it can be used to measure ionic concentrations in titration, water samples, biological samples and other industrial and environmental samples. We have also seen that both potentiometry and pH metry are most widely used electroanalytical technique. In this unit you will study another electroanalytical technique called the conductometry, which is one of the oldest and in many ways simplest among the other electroanalytical techniques. This technique is based on the measurement of electrolytic conductance.

An application of electrical potential across the solution of an electrolyte involves the transfer of mass and charge from one part of the solution to the other. Such transport processes, enable an insight into the structure of such solution. A transport property of great significance, which can be easily measured, is the conductance. Since, an electrolytic solution consists of ions and the nature of interaction existing in the medium could be better understood in terms of the conducting power of these ions, it is more convenient to speak of conductance rather than resistance. The conducting ability of electrolytic solutions provides a direct prove of the existence of ions

in solutions. The experimental determinations of the conducting properties of electrolytic solutions are very important as they can be used to study

quantitatively the behaviour of ions in solutions. They can also be used to determine the values of many physical quantities such as solubilities and solubility product of sparingly soluble salts, ionic product of self ionizing solvents, hydrolysis constant of salts, dissociation constants of weak acids and bases and to form the basis for conductometric titration methods.

Expected Learning Outcomes

After studying this unit you should be able to:

- ❖ define electrolytic conduction;
- ❖ distinguish between the electrolytes and non-electrolytes solutions; and strong and weak electrolytes,;
- ❖ explain conductance of solutions, molar and equivalent conductivities;
- ❖ describe different factors effecting conductance; and
- ❖ explain various application of conductometry.

10.2 ELECTROLYTIC CONDUCTANCE

An electrolytic solution contains free ions in addition to other kinetically identifiable species. When electrical potential is applied across the solution the macroscopic observations are, the flow of current through the solution and the chemical changes generally resulting in the liberation or dissolution of the electrode material at the points where the current enters or leaves the solution. This phenomenon of decomposition of the solutions by electrical current is termed as electrolysis.

Electrolytic conduction, in which charges carried by ions, will not occur unless the ions of the electrolyte are free to move. Hence, electrolytic conduction is exhibited principally by molten salts and by aqueous solutions of electrolytes. The principle of electrolytic conduction is best illustrated by reference to an electrolytic cell such as that shown in Fig. 10.1 for the electrolysis of molten NaCl between inert electrodes. The entire assembly except that of the external battery of Fig. 10.1 is known as the cell.

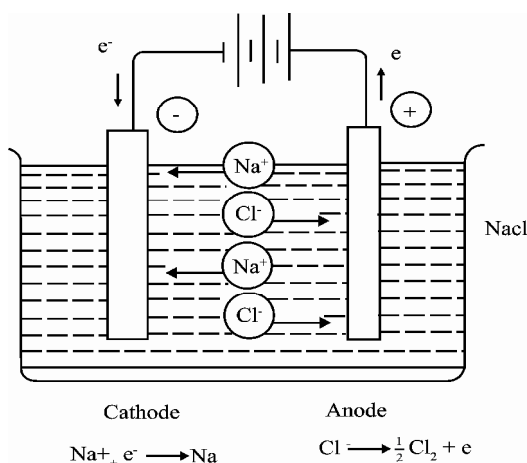


Fig. 10.1: Electrolysis of molten sodium chloride.

The electrons are received from the negative end of the external battery by the negative electrode of the cell. These are used up in the reduction reaction at this electrode. The numbers of electrons received at the negative electrode are given back to the positive end of the external battery from the positive electrode of the cell where electrons are released as the result of oxidation reaction. Within the cell, current is carried by the movement of ions; cations moves towards negative electrode called the cathode and anions towards the positive electrode called anode. This movement of ions give rise to what is known as the electrolytic conduction. The latter, thus, depends on the mobility of ions and anything that inhibits the motion of ions causes resistance to current flow. Factors that influence the electrical conductivity of solutions of electrolytes include interionic attraction, solvation of ions, and viscosity of solvents. These factors depend on the attraction i.e. solute-solute, solute-solvent and solvent-solvent respectively. The average kinetic energy of the solute ions increases as the temperature is raised and, therefore, the resistance of electrolytic conductors generally decreases, that is, conduction increases as the temperature is raised.

Electrolytes and non-electrolytes

The ionic compounds, which furnish ions in solution and conduct electric current, are electrolytes e.g. NaCl, KCl etc. There are covalent compounds, which also conduct electric current in solutions. These include HCl, CH₃COOH etc. All other substances which do not produce ions in solutions are called non-electrolytes, e.g. cane sugar, benzene, carbon tetrachloride etc.

Sometimes electrolytes are also called as true electrolytes and potential electrolytes. In true electrolytes the cations and anions do exist even in the molten states, e.g. NaCl, KCl. They are true electrolytes because they exist as Na⁺ Cl⁻ and K⁺ Cl⁻ in their normal states and in the molten states. Also when they are dissolved in water they ionize and conduct current.



The potential electrolytes do not conduct electricity in the pure normal state rather they conduct electricity when dissolved in water, e.g. HCl, CH₃COOH and NH₃.

Strong and weak electrolytes

Electrolytes can be classified as strong or weak. This has nothing to do with their concentration but related to their extent of ionisation.

Strong electrolytes: The substances, which are completely ionized in aqueous solutions, are called strong electrolytes, e.g. NaCl, NH₄Cl, KNO₃, HCl, HBr etc.

Weak electrolytes: The substances which ionize only to a certain extent are called weak electrolytes, e.g. CH₃COOH, HCN etc.

The terms strong and weak are relative. The behaviour of electrolytes also depend on the nature of solvents, e.g. NaCl behaves as strong electrolyte where as acetic acid as a weak electrolyte in water. On the other hand, when dissolved in ammonia both NaCl and acetic acid show comparable behaviour towards electricity.

Conductance of solutions

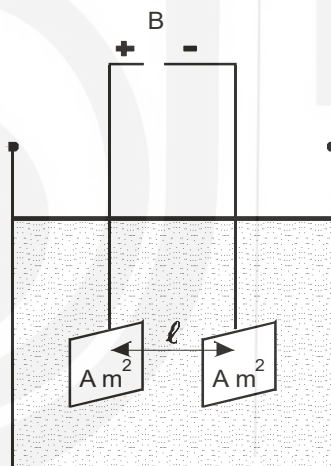
The ease of flow of electric current through a body is called its conductance. In metallic conductors it is caused by the movement of electrons, while in electrolytic solutions it is caused by applied electrical field. The electrolytic **conductance**, G , of a medium is equal to the reciprocal of its electrical resistance R in ohms:

$$G = \frac{1}{R} \quad \dots (10.1)$$

Ohm's Law states that the current I (amperes) flowing in a conductor is directly proportional to the applied electromotive force E (volts) and inversely proportional to the resistance, R (ohms) of the conductor:

$$I = \frac{E}{R} \quad \text{or} \quad I = EG \quad \dots (10.2)$$

Since a solution is a three dimensional conductor, the exact resistance will depend on the spacing (l) and area (A) of the electrodes. The resistance of a solution in such situation is directly proportional to the distance between the electrodes and inversely proportional to the electrode surface area.



Consider the electrolytic cell shown above, its two electrodes are having a cross-sectional area of $A \text{ m}^2$ and separated by $l \text{ m}$. The resistance (R) of the electrolyte solution present between the two electrodes is:

$$R \propto l$$

$$R \propto \frac{1}{A}$$

$$R \propto \frac{l}{A}$$

$$R = \rho \frac{l}{A} \quad \dots (10.3)$$

Where ρ (rho) is proportionality constant is called resistivity (formerly called specific resistance). It is a characteristic property of the material and it is the resistance offered by a conductor of unit length and unit area of cross section.

$$\rho = R \frac{A}{l} \quad \dots (10.4)$$

In SI units, l and A are measured in meters and square meters respectively, and the resistance is expressed in ohm, Ω (omega). Therefore, the unit of ρ is ohm meters ($\Omega \text{ m}$). Formerly, resistivity measurements were made in terms of a centimetre cube of a substance, giving ρ the units $\Omega \text{ cm}$.

Substitute the value R in Eq. 10.1 The expression for the conductance, G is

$$G = \frac{1}{R} = \frac{1}{\rho(A/l)} = \kappa \frac{A}{l} \quad \dots (10.5)$$

where κ (kappa) is reciprocal of specific resistance called as **specific conductance** or **conductivity**. It is measured in $\Omega^{-1} \text{ m}^{-1}$. This quantity may be considered to be the conductance of a cubic material of edge length unity. However, in SI system, the unit for conductance is 'Siemens' and, given the symbol 'S'. Hence, the unit for conductivity will be S m^{-1} ($1\text{S} = 1\Omega^{-1}$) or S cm^{-1} . It may be remembered that $\text{S m}^{-1} = 1/100 \text{ S cm}^{-1}$. However specific conductance is customarily reported in smaller units as milli Siemens per meter (mS m^{-1}) and micro Siemens per cm ($\mu\text{S cm}^{-1}$).

Cell constant: For a given cell, l and A are constant, and the quantity (l/A) is called the cell constant (K_{cell}).

$$K_{\text{cell}} = \frac{l}{A}$$

Substitute this value in Eq. (10.5)

$$\kappa = G K_{\text{cell}} \quad \dots (10.6)$$

Conductivity = observed conductance $\times$ cell constant

To obtain the value of the cell constant, it is not necessary to determine l and A directly. Instead, it is measured by a solution of known conductivity. Potassium chloride solutions are invariably used for this purpose, since their conductances have been measured with sufficient accuracy in cells of known dimensions. A given solution of potassium chloride of conductivity κ' is placed in the cell and its resistance R' is measured. The cell constant is then equal to $\kappa'R'$. Therefore,

$$\text{Cell constant} = \text{conductivity of KCl solution} \times \text{measured resistance}$$

Conductance is an additive property, e.g. in an aqueous solution containing several electrolytes, the total conductance is

$$G(\text{total}) = \sum G_i + G(\text{water}) \dots \quad (10.7)$$

Where the summation is to be carried over all the electrolytes present in the solution and $G(\text{water})$ is the conductance of water, which is utilized for making the solution. $G(\text{water})$ is often negligible in comparison to $\sum G_i$ as repeatedly distilled water (known as conductivity water) of very low conductance is employed for making the solutions.

SAQ 1

The resistance of a conductivity cell containing 0.01 mol dm^{-3} KCl is 150Ω .
 The same conductivity cell gives the resistance of 0.01 mol dm^{-3} HCl 51.4Ω .
 The conductivity of the KCl solution is $1.41 \times 10^{-3} \Omega^{-1} \text{ cm}^{-1}$. Calculate the following values:

- cell constant, and
- conductivity of the HCl solution.

10.2.1 Molar Conductivity

In order to compare quantitatively the conductivities of electrolytes, a quantity called **molar conductivity** is frequently used. The molar conductivity, Λ_m (capital lambda) is the conductivity per unit molar concentration of a dissolved electrolyte. It is related to conductivity, κ by the relation:

$$\Lambda_m = \frac{\kappa}{c} \quad \dots (10.8)$$

where c is the concentration mol m^{-3} . The molar conductivity is usually expressed in $\text{S m}^2 \text{ mol}^{-1}$ or $\text{S cm}^2 \text{ mol}^{-1}$. It may be remembered that $\text{S m}^2 \text{ mol}^{-1} = 10,000 \text{ S cm}^2 \text{ mol}^{-1}$.

It is to be remembered that c in Eq. 10.8 is to be expressed in mol m^{-3} unit. If the concentration is given in terms of Molarity (mol dm^{-3}), then the following conversion is to be carried out

$$c (\text{mol m}^{-3}) = \text{Molarity} \times 1000 \quad \dots (10.9)$$

Earlier equivalent conductivity (Λ_{eq}), which is given by the following expression, was in use

$$\Lambda_{\text{eq}} = \frac{1000 \times \kappa}{c} \quad \dots (10.10)$$

Where c is the concentration expressed in terms of normality of the solution. Unit of Λ_{eq} is $\Omega^{-1} \text{ cm}^2 \text{ eq}^{-1}$. However, IUPAC recommends the use of molar conductivity only.

SAQ 2

Write the units of the following:

- Specific conductance
- Equivalent conductivity
- Cell constant
- Molar conductivity

SAQ 3

From the following data, calculate the molar conductivity of KCl in aqueous solution:

Conductivity of $5.0 \times 10^{-4} \text{ mol dm}^{-3}$ KCl = $7.44 \times 10^{-3} \text{ S m}^{-1}$

Conductivity of the water = $0.06 \times 10^{-3} \text{ S m}^{-1}$

10.2.2 Variation of Conductance with Concentration

The conductivity of an ionic solution increases with increasing concentration. For strong electrolytes, the increase in conductivity with increase of concentration is sharp. However, for weak electrolytes, the increase in conductivity is more gradual. In both cases the increase in the conductivity with concentration is due to an increase in the number of ions per unit volume of the solution. For strong electrolytes, which are completely ionized, the increase in conductivity is almost proportional to the concentration. In weak electrolytes, however, the increase in specific conductance is not large due to the low ionization of the electrolytes, and consequently the conductivity does not go up so rapidly as in the case of strong electrolytes. Table 10.1 shows the variation of molar conductivity of a number of electrolytes at various concentrations at 298 K.

Table 10.1: Molar conductivity ($10^4 \times \text{S m}^2 \text{ mol}^{-1}$) of electrolytes in aqueous solutions at 298 K

$c/\text{mol dm}^{-3}$	KCl	NaCl	HCl	AgNO ₃	CH ₃ COOH	CH ₃ COONa
1.0	111.9	89.9	332.8	-	-	49.1
0.1	129.0	106.7	391.3	109.1	5.2	72.8
0.05	133.4	111.1	399.1	115.7	7.4	76.9
0.01	141.3	118.5	412.0	124.8	16.3	83.8
0.005	143.5	120.6	415.8	127.2	22.9	85.7
0.001	146.9	123.7	421.4	130.5	49.2	88.5
0.0005	147.8	124.5	422.7	131.4	67.7	89.2

It is observed that in contrast to the conductivity, the molar conductivity, Λ_m invariably increases with decreasing concentration for both weak and strong electrolytes. If we plot the molar conductivities of a large number of electrolytes against the square root of the concentrations we find that these fall into two distinct categories. In the case of strong electrolytes (for example KCl, NaCl or acids such as HCl, H₂SO₄ etc), there is a small increase in molar conductivities with the decrease in concentration. Since these electrolytes dissociate almost completely even in concentrated solution, the number of ions do not change much with concentration. The conductivity should not vary much since it is directly related to the number of ions present in solution. The

minor changes observed are due to interionic interactions. In the case of weak electrolytes (for example CH_3COOH , ammonia, organic fatty acids etc), the ionization will increase with dilution, and hence, the molar conductivity increases with dilution. Thus the conductivity is directly proportional to the degree of dissociation of a weak electrolyte. These above results are depicted in Fig. 10.2 in which the molar conductivity, Λ_m , of two electrolytes (KCl and acetic acid) at a constant temperature is plotted against $\sqrt{c}$. It may be seen from the figure that two different types of behaviours are exhibited by these electrolytes. The strong electrolyte, KCl shows a linear plot (almost straight lines). On the other hand, the weak electrolyte, CH_3COOH seems to approach the dilute solution limit almost tangentially. It is, however, impossible to draw a sharp line of demarcation between the two categories as many substances are known to exhibit intermediate behaviour, e.g., nickel sulphate. Such electrolytes are sometimes called moderately strong electrolytes.

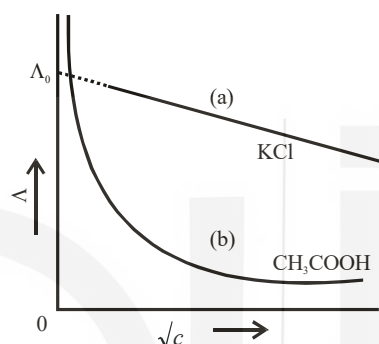


Fig. 10.2: Variation of molar conductivity on dilution (a) for aqueous solution of potassium chloride (strong electrolyte) (b) acetic acid (weak electrolyte).

The conductance of a solution depends on the number of ions and the speed with which the ions move in solution. In case of strong electrolytes, the number of ions is the same at all dilutions (since strong electrolytes are completely ionized) and the variation of equivalent conductance with dilution is therefore due to the change in the speed of the ions with dilution. In a concentrated solution of such electrolytes, the interionic attractions among the oppositely charged ions would be quite appreciable. The ions may also form some ion-pairs of the type A^+B^- that would not contribute to the conductance. These interionic forces considerably lower the speed of the ions and hence the conductivity of the solution. As the dilution is increased the interionic attractions decrease with the result that the ions will move more freely and independently of their co-ions and thus increasing the molar conductivity with dilution. At infinite dilution, the ions are quite far apart, the interionic attractions are almost absent and each ion moves completely independent of its co-ions. The molar conductivity then approaches a limiting value at infinite dilution and represents the conducting power of 1 mole of the electrolyte when it is completely split up into ions. It is denoted by Λ^∞ .

It can be concluded that in case of weak electrolytes, the increase in molar conductivity with dilution is mainly due to (a) an increase in the number of ions in the solution (degree of ionization increases with dilution), and (b) smaller interionic attractions at higher dilutions.

10.2.3 Limiting Molar Conductivity

An important relation can be obtained by extrapolating the curve for strong electrolytes (Fig. 10.2) to $c \rightarrow 0$ where all interionic effects are absent. The limiting value obtained by this extrapolation is called the molar conductivity at infinite dilution.

Observing the linearity of Λ_m versus $\sqrt{c}$ for strong electrolytes in dilute solutions, Kohlrausch suggested the following empirical relation for the variation of molar conductance of strong electrolytes with dilution.

$$\Lambda_m = \Lambda^\infty - b\sqrt{c} \quad \dots (10.11)$$

where b is a constant for the given electrolyte and Λ^∞ is the molar conductivity of the electrolyte at infinite dilution. The validity of this equation may be seen from the plot for electrolytes like HCl, KCl etc. To obtain Λ^∞ of such electrolytes the curve is extrapolated to $c \rightarrow 0$ and the intercept so obtained gives the value of Λ^∞ . The same method cannot be used for obtaining Λ^∞ for weak electrolytes because of the steep increase in Λ at high dilutions. Λ^∞ may also be computed from the molar conductivities at infinite dilution of the respective ions, since at infinite dilution, the ions are independent of each other according to the law of independent migration of ions and each contribute its part to the total conductivity, therefore,

$$\Lambda^\infty = \Lambda_+^\infty + \Lambda_-^\infty \quad \dots (10.12)$$

where Λ_+^∞ and Λ_-^∞ are the ionic conductivities at infinite dilution of the cation and anion, respectively.

The molar conductivity of the ionic species is a measure of the amount of current carried by ions in question. Comparison of the molar conductivities of ions is, therefore, more meaningful when related to per unit charge, for example when $\Lambda^\infty(\text{Na}^+)$ is compared with $\frac{1}{2}\Lambda_-^\infty(\text{Mg}^{2+})$ rather than $\Lambda_-^\infty(\text{Mg}^{2+})$ or in terms of equivalent conductivities. The value of the limiting ionic molar and equivalent conductivities for some ions in water at 25°C are given in Table 10.2.

Table 10.2: Limiting ionic molar conductivities and limiting ionic equivalent conductivities of selected ions in water at 25° C

Cation	$\Lambda^\infty / (\text{S cm}^2 \text{ mol}^{-1})$	$\Lambda^\infty / (\text{S cm}^2 \text{ eq}^{-1})$	Anion	$\Lambda^\infty / (\text{S cm}^2 \text{ mol}^{-1})$	$\Lambda^\infty / (\text{S cm}^2 \text{ eq}^{-1})$
H ⁺	349.8	349.8	OH ⁻	198.3	198.3
Li ⁺	38.7	38.7	F ⁻	55.4	55.4
Na ⁺	50.1	50.1	Cl ⁻	76.3	76.3
K ⁺	73.5	73.5	Br ⁻	78.1	78.1
Be ⁺²	90.0	45.0	I ⁻	76.8	76.8
Mg ²⁺	106.2	53.1	NO ₃ ⁻	71.5	71.5

Ca ²⁺	119.0	59.5	SO ₄ ²⁻	160.0	80.0
Ba ²⁺	127.2	63.6	CH ₃ COO ⁻	40.9	40.9
Al ³⁺	183.0	61.0	C ₆ H ₅ CO ⁻	32.4	32.4
Cu ²⁺	107.2	53.6	HCO ₃ ⁻	44.5	44.5
Ag ⁺	61.9	61.9	CO ₃ ²⁻	138.6	69.3
Zn ²⁺	105.6	52.8	Fe(CN) ₆ ³⁻	302.7	100.9
Ce ³⁺	209.4	69.8	Fe(CN) ₆ ⁴⁻	442.0	110.5

Ionic Mobilities and Transport Number

The next question which arises in connection to the values of conductivity given in Table 10.2, is why should there be a difference between the values of limiting molar conductivities of similarly charged ions, if these ions are just acting as carriers of electric charges only?

The answer lies in the fact that different ions have different mobilities in solution. The mobility of an ion in solution is mainly dependent upon the size of the hydrated ion. The ionic mobility is defined as the velocity with which an ion would move under a potential gradient of 1 V m⁻¹ in a solution. It provides a link between theoretical and measurable quantities. For instance, ionic mobility, (u) is related to limiting molar ionic conductivity (Λ^∞) by the following equations:

$$\Lambda_+^\infty = z_+ u_+ F \text{ and } \Lambda_-^\infty = z_- u_- F \quad \dots (10.13)$$

where z_+ and z_- are the valency of the ions, u_+ and u_- represent the ionic mobilities and F is the Faraday constant. In the above equation, if one of the two quantities, Λ^∞ or u , is known, the other can be calculated.

To find the values of Λ_+^∞ or Λ_-^∞ , we define yet another quantity, called *transport or transference number* of an ion indicated by the symbol t_+ or t_- . It is defined as the fraction of the total current carried by an ionic species and can be expressed mathematically as,

$$t_+ = \Lambda_+^\infty / \Lambda_m \text{ and } t_- = \Lambda_-^\infty / \Lambda_m \quad \dots (10.14)$$

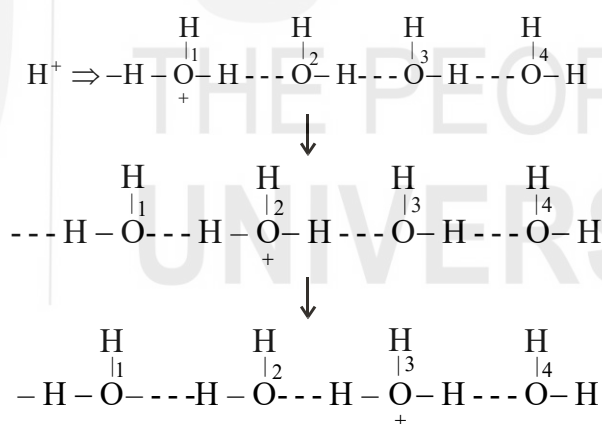
The transport number and the limiting molar conductivity are measurable quantities. Hence, the molar ionic conductivity value can be calculated from Eq. 10.14. The limiting molar conductivities of some common ions are given in Table 10.2. These values are important in predicting the molar conductivity of electrolytes and course of conductometric titrations. Finally, once the molar ionic conductivity value is obtained, we can then make use of Eq. 10.13 to calculate the ionic mobility. Some typical values of ionic mobility (in infinite dilute solutions) are listed in Table 10.3.

Table 10.3: Limiting ionic mobilities in water at 298 K

Cation	$10^8 u_+ / \text{m}^2 \text{v}^{-1} \text{s}^{-1}$
H^+	36.24
Li^+	4.01
Na^+	5.19
K^+	7.62
Ag^+	6.42

Anions	$10^8 u_- / \text{m}^2 \text{v}^{-1} \text{s}^{-1}$
OH^-	20.58
Cl^-	5.74
Br^-	7.92
I^-	8.09
NO_3^-	7.41

It is interesting to look at Table 10.3 in more detail. You will see the Li^+ ion, because of its larger hydration shell, has a lower mobility than the potassium ion. Similar argument can be applied to the F^- & Br^- ions. Exceptional mobilities are observed for the H^+ and OH^- ions. This is because, in these case charge is transported through proton jump mechanism along with general migrations mechanism, consider the case of H^+ ion.



You can see how hydrogen ion jumps from O_1 to O_2 , O_2 to O_3 , ..., this result is equivalent to as the migration of charge from left to right. This conduction mechanism is more like a charge than ion movement. Such conduction is possible because of the peculiar structure of water and therefore only found in hydrogen-bonded solvents.

10.2.4 Effect of other Factors on Conductivity

Beside concentration, there are some more factors which affect the conductivity of the electrolyte solution.

- (a) *Effect of temperature and pressure:* The conductivity of all electrolytes increases with increasing temperature. The variation of molar conductivity at infinite dilution with temperature is given by an empirical equation.

$$\Lambda^{\infty}(t) = \Lambda^{\infty}(25)[1 + x(t - 25)] \quad \dots (10.15)$$

where $\Lambda^{\infty}(t)$ and $\Lambda^{\infty}(25)$ are the value of molar conductivities at t and 25°C respectively, and x is a constant for each electrolyte. For salts x is about 0.022 to 0.025 and for acids and bases it is usually 0.016 to 0.019. It means that molar conductivity increases approximately by 2% for every one degree rise in temperature. For strong electrolytes, even at appreciable concentration, Eq. (10.15) holds well, whereas in case of weak electrolytes, the variation of Λ with temperature is not so regular. The rise in conductance with temperature is due to the decrease in the viscosity of the solution, increase in the speed of the ions and an increase in the degree of ionization in cases of weak electrolytes.

The conductivity increases slightly with increase in pressure. The effect is mainly through changes in the viscosity of the medium, which decrease by an increase in pressure. Consequently, the molar conductance of the solution will increase with rise in pressure.

- (b) *Effect of solvent:* In solvents of low dielectric constants, having small ionizing effect on the electrolytes, the electrostatic forces between oppositely charged ions would be appreciable and molar conductance will have small value. However, solvents with high dielectric constants yield more conducting solutions.
- (c) *Viscosity of the medium:* The dependence of conductance on viscosity of the medium is given by Walden's rule, according to which the molar conductance of an electrolyte is inversely proportional to the viscosity of the medium, i.e.

$$\Lambda^{\infty} \eta_0 = \text{constant} \quad \dots (10.16)$$

where Λ_0 is the molar conductance at infinite dilution and η_0 is coefficient of viscosity of the solvent. If ions are not solvated, i.e., they have the same size in all the solvents, then it follows from Walden rule that $\Lambda^{\infty} \eta_0$ should be constant and independent of the nature of the solvent. This is true only for ions like tetra-alkyl ammonium cations, which are not solvated. Ions where extensive solvation occurs, effective radii of the ions will not be constant and Walden rule will not be obeyed.

SAQ 4

List the factors which are affecting the conductivity of the solution.

10.3 MEASUREMENT OF ELECTROLYTIC CONDUCTANCE

The conductance of a solution can be determined by measuring the resistance offered by solution contained within the two electrodes of a conductivity cell.

For measuring resistance, the Wheatstone bridge principle is employed. Therefore, before taking up the measurement of conductance of solution, let us study the principle of Wheatstone Bridge.

10.3.1 The Wheatstone Bridge Principle

A Wheatstone bridge (Fig. 10.3) be employed to measure the resistance of an electronic conductor. It works on the principle of obtaining balance between two arms with the help of a balance indicator (e.g. a galvanometer) at the condition of potential being equal.

Let R_x be an unknown resistor, R_1 and R_2 two standard resistors, R_3 an adjustable resistor and G a galvanometer. The bridge is connected to a source of power S, a battery, and a tapping key K is placed in the path to control the connections.

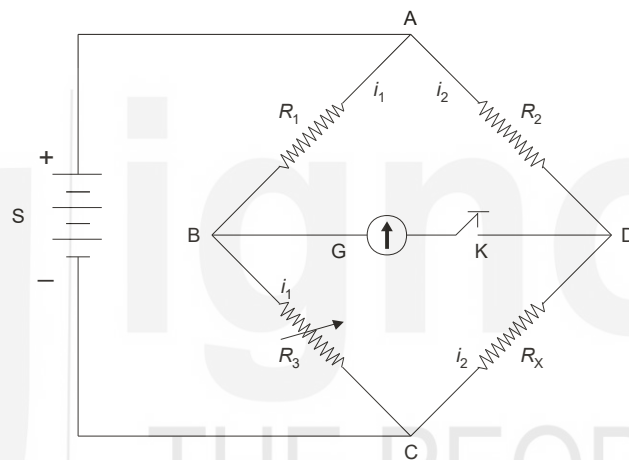


Fig. 10.3: A DC Wheatstone bridge circuit.

To measure the resistance R_x , the tapping key K is held down momentarily and the bridge is balanced by adjusting R_3 to get no deflection in galvanometer under these conditions.

In the bridge the total current is divided into two paths: i_1 through R_1 and R_3 , and i_2 through R_2 and R_x . Under the balancing conditions, the potential at points B and D must be the same, i.e. the ohmic voltage drop through the resistors R_1 and R_2 must be the same. Hence, the potential at B (E_B) must be equal to potential at D (E_D).

$$E_B = E_D \quad \dots (10.17)$$

$$\text{Or} \quad i_1 R_1 = i_2 R_2 \quad \dots (10.18)$$

$$\text{Similarly, } i_1 R_3 = i_2 R_x \quad \dots (10.19)$$

Dividing (10.18) by (10.19) we get,

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

$$\text{and} \quad R_x = \frac{R_2 R_3}{R_1} \quad \dots (10.20)$$

Thus, we can calculate R_x as R_1 , R_2 and R_3 are all known. Conductance G , being the reciprocal of resistance will be,

$$G = \frac{R_1}{R_2 R_3} \quad \dots (10.21)$$

Alternatively, the conductometric cell can be incorporated into operational amplifier control circuit, as shown in Fig. 10.4. The amplifier balances the potential of two inputs. The current from the input potential, E_i , is balanced by the current from amplifier output which passes through a feedback resistor (R_f). The output potential, E_o is in terms of resistance:

$$E_o = E_i (R_f/R_x + 1)$$

Where R_x is the resistance of conductometric cell.

With respect to the solution conductance, G , above equation becomes

$$E_o = E_i (R_f G + 1)$$

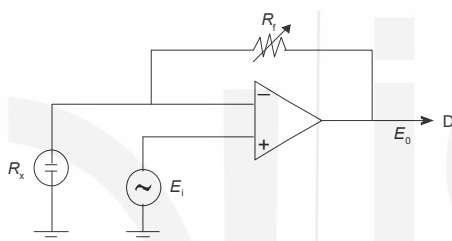


Fig. 10.4: An operational amplifier control circuit for conductometric measurement. R_x is the solution resistance and R_f is the feedback resistance

10.3.2 Measurement of Conductance of a Solution

The Principle of the Wheatstone bridge discussed above can be used to measure the conductance of solutions. However, the following considerations must also be kept in mind:

- (i) Since a direct current would polarize the electrodes in the conductivity cell by electrolyzing the solution; to avoid polarization an alternating current (ac) source of power must be used in place of a dc source (battery) usually ac voltages of 3-6 volts with frequency of 50 Hz or 1000 Hz used across points A and C of Fig. 10.5.
- (ii) A suitable conductivity cell (with electrodes dipped in the solution) is located between points C and D. Thus R_x represents the resistance of the conductivity cell.
- (iii) Since, the cell also acts like a small capacitor (C_x), and to balance its capacitive resistance a variable capacitor, C_B , must be inserted into the bridge.
- (iv) The balance indicator (BI) may be an ac galvanometer, but some other devices may also be used:
 - An earphone can act as a balance indicator if the frequency of the ac source is in audio-range.

- A magic eye, which gives a green fluorescence as a result of electrons striking a phosphor coating inside the glass tube, is used in several commercial instruments.
- For much precise conductance measurements a cathode ray oscilloscope is used as the balance indicator.

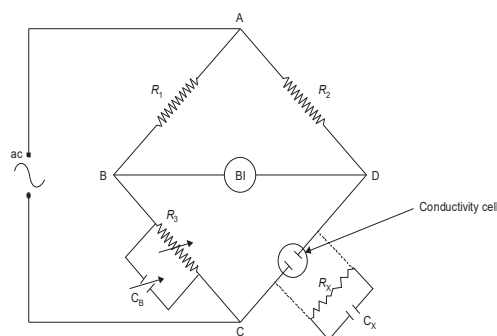


Fig. 10.5: A conductivity bridge circuit.

- (v) Conductance ($G=1/R_x$) can be read directly on commercially available instruments as a panel mounted meter. Now several digital instruments are also available, such instruments give the conductance directly as the numerical value.

Conductometer

From above discussion we can conclude that conductance is reciprocal of resistance and the resistance of a cell can be measured by placing it in an arm of a Wheatstone bridge. The inverse of the resistance gives the conductance and can be directly read on a conductivity measuring instrument, known as "Conductometer".

A typical conductometer, consists of an ac source, a Wheatstone bridge circuit, a null detector or direct reading display and a conductivity cell.

To avoid the effects of polarization, i.e. the change in composition of the measuring cell, alternating current (ac) is used. The instrument has an arrangement to convert the supply of 50 Hz to higher frequency, say 1000 Hz. For measuring low conductance solutions, the lower frequency is preferable and for high conductive solutions higher frequencies are preferably used.

Several inexpensive conductometers are commercially available. The instruments come as a line-operated unit with and without digital readout. Fig. 10.6 gives the view of a typical conductometer, which can be operated as with given instructions.

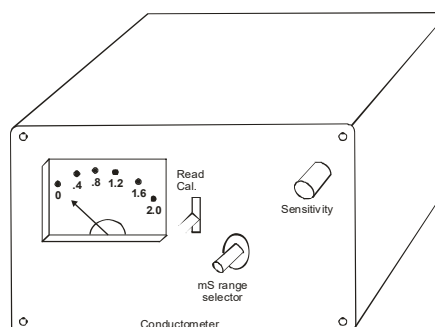


Fig. 10.6: Conductometer.

Cells

Various types of cells have been designed and are in use for the measurement of conductance of a solution. These are made of Pyrex glass fitted with electrodes of platinum or gold. To overcome the imperfections in the current and the other effects at the electrodes, these are coated with a layer of finely divided platinum black. This is achieved by electrolyzing a 3% solution of chloroplatinic acid containing a little of lead acetate. The distance between the electrodes is determined by the conductance of the solution to be measured. For highly conducting solution, the electrodes are widely spaced whereas for low conducting solutions the electrodes are mounted near each other. A cell suitable for conductometric titration is depicted in Fig. 10.7 (a, b and c); the electrodes are firmly fixed in the Perspex lid which is provided with opening for the stirrer and the jet of the burette. A magnetic stirrer can be used in place of mechanical stirrer.

For most purposes a special cell is not required and good results are obtained by clamping a commercially available dip cell [shown diagrammatically in Fig. 10.7 (b)] inside a beaker which is placed on a magnetic stirrer. With this arrangement, the dipping cell should be lifted clear of the solution after each addition from the burette to ensure that the liquid between the electrodes becomes thoroughly mixed. Since absolute conductivity values are not required it is not necessary to know the cell constant.

For spot checking on a process stream or tank, a dip-type of conductivity cell is used. In some titrations an open beaker with fixed electrodes is sufficient. However, for fairly dilute solutions an open beaker would not be satisfactory because atmospheric CO_2 may alter the conductance.

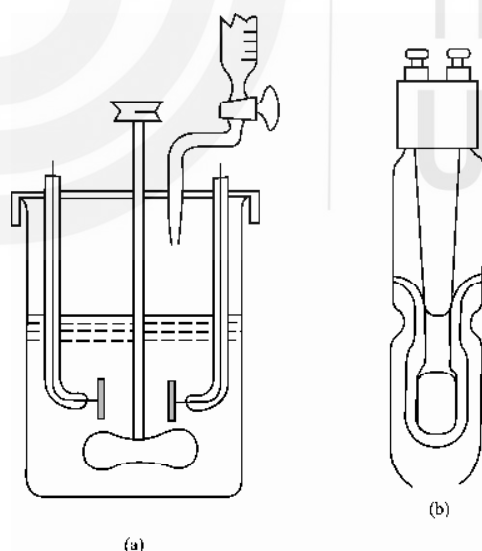


Fig. 10.7: Typical designs of conductivity cells.

Procedure for Direct Measurement of Conductivity

1. Plug the instrument to an ac supply.
2. Put the frequency selector switch to required frequency (say 1000 Hz).
3. Set the mode selector on CAL and set the range selector on the desired setting e.g., 2, 20 or 200. These figures refer to the full scale meter value

in milli Siemens (mS). With the help of sensitivity knob keep the pointer roughly midway between the lowest and highest sensitivity say at 1 position.

4. Connect the conductivity cell electrodes to the appropriate terminals of the instrument. Clean the conductivity cell with distilled water (Conductivity water).
5. Take the standard KCl solution (say 0.1M) in a clean beaker. Introduce a stirring rod (to be used for magnetic stirring) in the solution and put the solution beaker on a magnetic stirrer plate.
6. Insert the conductivity cell in the solution. Ensure that the platinum plate electrodes are completely immersed in the solution and they do not touch the stirring rod or the sides or the bottom of the beaker.
7. Switch on the instrument and allow it to warm up for 2-5 minutes.
8. Measure the conductance, G_s , of the standard KCl solution by putting meter switch to READ position.
9. Remove the KCl solution from the beaker, wash the conductivity cell properly with distilled water. Take the unknown solution in the beaker and measure its conductance, G_u , in the manner as for standard KCl solution.
10. Calculate the cell constant, from the conductance and conductivity values of the standard,

$$K_{cell} = \frac{\text{Conductivity (specific conductance)}}{\text{Observed conductance of the standard}}$$

$$K_{cell} \text{ cm}^{-1} = \frac{\kappa_s}{G_s} \text{ cm}^{-1}$$

11. Calculate the conductivity (specific conductance) of the unknown solution
= cell constant $\times$ observed conductance

$$\kappa_u = K_{cell} G_u$$

12. For titration work, the value of cell constant, K_{cell} is not required to be calculated, since the cell constant will remain unchanged during the course of any given titration.

Notes:

- (i) When the range selector is switched to a new position, it is essential to check the calibration again. Set the meter again to read one with the sensitivity control, if any deviation is observed.
- (ii) The conductivity cell, when not in use, should be kept in distilled water to prevent drying the platinum electrodes.
- (iii) In case of fouling the conductivity cell electrode plates, clean them by keeping in dilute $K_2Cr_2O_7$ containing H_2SO_4 solution (i.e. dilute chromic acid) for 24 hours and then washing with running water followed by rinsing with distilled water.

SAQ 5

At 298 K, the resistance of 2.00×10^{-2} M KCl is 195.96Ω and that of 2.50×10^{-3} M K_2SO_4 is 775.19Ω . The conductivity (κ) of 2.00×10^{-2} M KCl at 298 K is 0.2768 S m^{-1} . Calculate molar conductivity of K_2SO_4 solution.

10.4 APPLICATIONS OF CONDUCTOMETRY

The high sensitivity of the conductometric measurements makes it an important analytical tool for environmental analysis and certain other applications. A continuous or spot check measurement of conductance is employed, usually, with a dip electrode cell and meter. In certain cases continuous recording of conductance is also employed. Since conductance depends on ionic concentrations, the purity of steam distillate, demineralized water, and the ionic contents of raw water can be checked with measuring conductance directly. Metal industries, electroplating baths and rinse baths are monitored by conductance methods.

Perhaps the most common application of direct conductometry has been for estimating the purity of distilled water. Kohlrausch with a painstaking work after 42 successive distillations of water in vacuo obtained a conductivity water with specific conductance, $\kappa = 4.3 \times 10^{-8} \text{ S cm}^{-1}$ at 18°C . Traces of an ionic impurity will increase the conductance appreciably. Ordinary distilled water in equilibrium with the carbon dioxide of the air has a conductivity of about $7.0 \times 10^{-7} \text{ S cm}^{-1}$. The sea water has much higher value of conductivity and the conductometric measurements are widely used to check the salinity of water in oceanography.

Measuring conductance of soil helps in finding the moisture content of soils at various places with portable instruments. All soils contain varying amount of water soluble salts upto 0.1% or even more. These salts are usually present as sulphate, chloride, carbonate or bicarbonate of sodium, potassium, calcium and magnesium and contribute to the conductance of the soil. The soil may be classed as saline and non-saline depending on the nature and quantity of the salts present. Conductivity of a saturated extract with water of saline soil at 25°C has a conductivity greater than 4 mS cm^{-1} .

Based upon the relative change in the conductance/resistance of a solution with the addition of another electrolyte, methods have been developed for the titration of a strong acid with a strong base, weak acid versus strong base or a weak base and a mixture of a strong acid and weak acid versus a strong base. Other types of titrations which can be performed conductometrically include displacement titrations: a salt of a weak acid (sodium acetate) versus a strong acid like HCl or a salt of weak base (ammonium chloride) versus sodium hydroxide; precipitation titrations: silver nitrate versus KCl; complexometric titrations: mercuric nitrate versus KCN or EDTA versus metallic ions and oxidation – reduction (redox) titrations like the titration of Fe(II) versus $KMnO_4$.

Conductometric methods based upon precipitation or complex formation reactions are not as useful as those involving neutralization processes.

Conductance changes during these titrations are seldom as large as those observed with acid-base reactions because no other reagent approaches the great ionic conductance of either hydronium or hydroxide ion. The main advantage to the conductometric end point is its applicability to very dilute solutions and to systems that involve relatively incomplete reactions. For example, while neither a potentiometric nor indicator method can be used for the neutralization titration of phenol ($K_a = 10^{-10}$) a conductometric end point can be successfully applied.

Direct measurement of conductivity is potentially a very sensitive procedure for the determination of various parameters like the degree of dissociation of a weak electrolyte and its dissociation constant, ionic product of water, solubility and solubility product and hydrolysis constant of a salt. We have already discussed these parameters in the earlier semester course. Now we will take up the principle of conductometric titrations.

Conductometric Titrations

The principle of conductometric titration is based on the fact that during the titration, one of the ions is replaced by the other and invariably these two ions differ in the ionic conductivity with the result that conductivity of the solution varies during the course of titration. The equivalence point may be located graphically by plotting the change in conductance as a function of the volume of titrant added.

The main advantages to the conductometric titration are its applicability to very dilute, and coloured solutions and to system that involve relative incomplete reactions. For example, which neither a potentiometric, nor indicator method can be used for the neutralization titration of phenol ($K_a = 10^{-10}$) a conductometric endpoint can be successfully applied.

Some Typical Conductometric Titration Curves:

1. **Strong Acid with a Strong Base, e.g. HCl with NaOH:** Before NaOH is added, the conductance is high due to the presence of highly mobile hydrogen ions. When the base is added, the conductance falls due to the replacement of hydrogen ions by the added cation as H^+ ions react with OH^- ions to form undissociated water. This decrease in the conductance continues till the equivalence point. At the equivalence point, the solution contains only NaCl. After the equivalence point, the conductance increases due to the large conductivity of OH^- ions (Fig. 10.8).

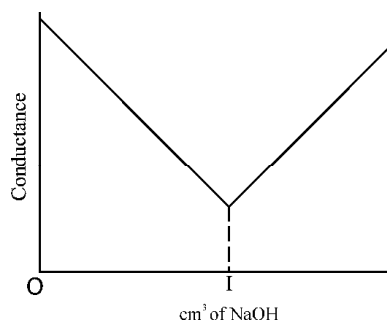


Fig. 10.8: Conductometric titration of a strong acid (HCl) vs. a strong base (NaOH)

2. **Weak Acid with a Strong Base, e.g. acetic acid with NaOH:** Initially the conductance is low due to the feeble ionization of acetic acid. On the addition of base, there is decrease in conductance not only due to the replacement of H^+ by Na^+ but also suppresses the dissociation of acetic acid due to common ion acetate. But very soon, the conductance increases on adding NaOH as NaOH neutralizes the un-dissociated CH_3COOH to CH_3COONa which is the strong electrolyte. This increase in conductance continues raise up to the equivalence point. The graph near the equivalence point is curved due the hydrolysis of salt CH_3COONa . Beyond the equivalence point, conductance increases more rapidly with the addition of NaOH due to the highly conducting OH^- ions (Fig. 10.9).

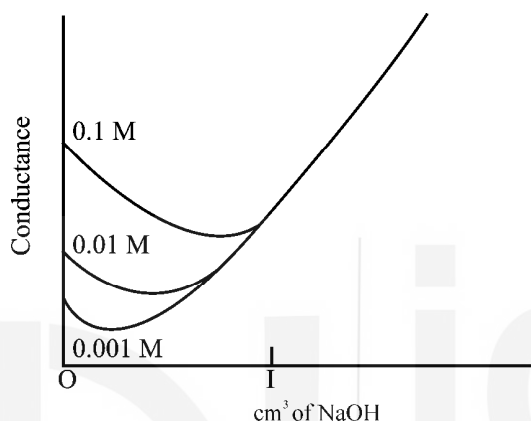


Fig. 10.9: Conductometric titration of a weak acid (acetic acid) vs. a strong base (NaOH)

3. **Strong Acid with a Weak Base, e.g. sulphuric acid with dilute ammonia:** Initially the conductance is high and then it decreases due to the replacement of H^+ . But after the endpoint has been reached the graph becomes almost horizontal, since the excess aqueous ammonia is not appreciably ionised in the presence of ammonium sulphate (Fig. 10.10).

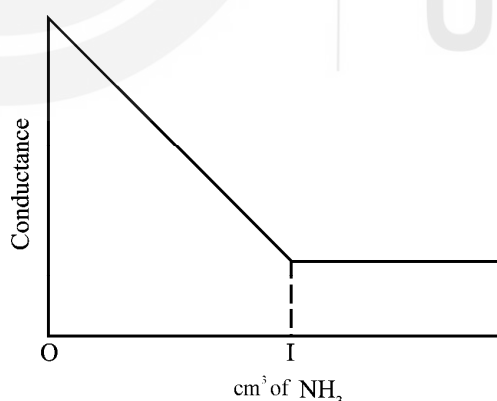


Fig. 1010.: Conductometric titration of a strong acid (H_2SO_4) vs. a weak base (NH_4OH)

4. **Weak Acid with a Weak Base:** The nature of curve before the equivalence point is similar to the curve obtained by titrating weak acid against strong base. After the equivalence point, conductance virtually remains same as the weak base which is being added is feebly ionized and, therefore, is not much conducting (Fig. 10.11).

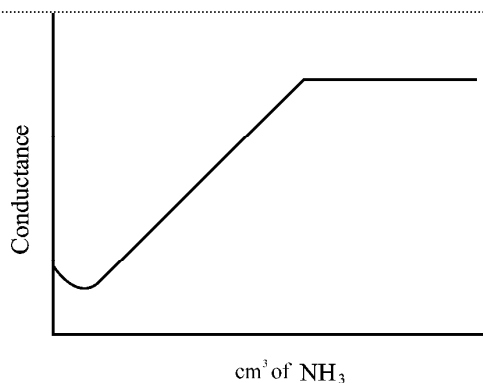


Fig. 10.11: Conductometric titration of a weak acid (acetic acid) vs. a weak base (NH_4OH)

5. **Precipitation Titration:** A reaction may be made the basis of a conductometric precipitation titration provided the reaction product is sparingly soluble. The solubility of the precipitate should be less than 5%. The addition of ethanol is sometimes recommended to reduce the solubility in the precipitations. An experimental curve is given in Fig. 6.8 (ammonium sulphate in aqueous-ethanol solution with barium acetate). If the solubility of the precipitate were negligibly small, the conductance at the equivalence point should be given by AB and not the observed AC . The addition of excess of the reagent depresses the solubility of the precipitate and, if the solubility is not too large, the position of the point B can be determined by continuing the straight portion of the two arms of the curve until they intersect (Fig. 10.12).

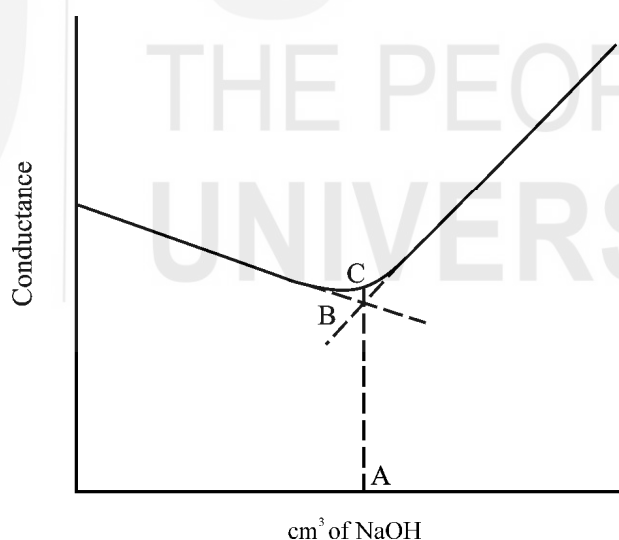


Fig. 10.12: Precipitation titration. Conductometric titration of $(\text{NH}_4)_2\text{SO}_4$ vs. barium acetate

A slow rate of precipitation, particularly with micro-crystalline precipitate, prolongs the time of titration. Seeding or the addition of ethanol (concentration up to 30-40 %) may have favourable effect.

If the precipitate has pronounced adsorptive properties, the composition of the precipitate will not be constant, and appreciable errors may result. Occlusion may take place with micro crystalline precipitates.

In spite of the obvious limitations of the method, still a large number of precipitation titrations have been carried out; thus silver nitrate, lead nitrate, barium acetate or barium chloride, uranyl acetate, lithium sulphate and lithium oxalate have been utilized in precipitation reactions.

10.5 SUMMARY

In this unit, various parameters like resistance (R), conductance (G), resistivity (ρ), conductivity (κ), equivalent conductivity (Λ_{eq}), molar conductivity (Λ_m), molar conductivity at infinite solution (Λ_o) and cell constant have been defined in detail along with their units for measurements. The relationships among these parameters have also been worked out. Various factors affecting the conductance of solution are also given. At the end detail procedure for the measurement of conductance is given.

10.6 TERMINAL QUESTIONS

1. What are electrolytes? How are they classified?
2. Define molar conductivity and equivalent conductivity of an electrolyte. How are they related to each other?
3. Write expression for a cell constant and conductivity of an electrolyte.
4. What are the various factors affecting the conductance of solution?
5. Explain the necessity of maintaining a constant temperature in conductometric measurements.
6. The conductivity of 0.1 M HCl is $0.0394 \Omega^{-1} \text{ cm}^{-1}$. What is the molar conductivity of the solution?
7. The resistance of 0.1 M solution of a salt occupying a volume between two platinum electrodes 1.80 cm apart and 5.4 cm^2 in area was found to be 32 ohms. Calculate the molar conductivity of the solution.
8. A certain conductance cell was filled with 0.0100 M solution of KCl, whose conductivity is $0.001409 \Omega^{-1} \text{ cm}^{-1}$ (S cm^{-1}) at 25°C , it had a resistance of 161.8Ω , and when filled with 0.0050 M NaOH, it had a resistance of 190Ω . Calculate the cell constant, conductivity and molar conductivity of NaOH solution.
9. A conductivity cell shows a resistance of 3950Ω at 25°C when filled with the experimental solution and 4864Ω at the same temperature when filled with 0.02 M KCl solution. If the conductivity of the solution is $2.767 \times 10^{-3} \text{ S cm}^{-1}$, calculate the conductivity of the experimental solution.
10. The resistance of a conductivity cell was 702 ohms when filled with 0.1 M KCl when filled with 0.1 M KCl solution ($\kappa = 0.14807 \text{ ohm}^{-1} \text{ m}^{-1}$) and 6920 ohm when filled with 0.01M acetic acid solution. Calculate the cell constant and molar conductance for the acid solution.

10.7 ANSWERS

Self-Assessment Questions

1. (i) $K = \kappa_{\text{KCl}} / G_{\text{obs.}}$ or $= \kappa_{\text{KCl}} \times R_{\text{obs.}}$

$$= 1.41 \times 10^{-3} \Omega^{-1} \text{ cm}^{-1} \times 150 \Omega = 0.2115 \text{ cm}^{-1}$$

 (ii) $\kappa = KG_{\text{obs.}} = K/R_{\text{obs.}} = 0.2115 \text{ cm}^{-1} / 51.5 \Omega = 4.11 \times 10^{-3} \Omega^{-1} \text{ cm}^{-1}$
 (S cm⁻¹)
2. (a) conductivity: S m⁻¹ or $\Omega^{-1} \text{ m}^{-1}$
 (b) Equivalent conductivity: $\Omega^{-1} \text{ cm}^{-1} \text{ eq}^{-1}$
 (c) Cell constant : m⁻¹ or cm⁻¹
 (d) Molar conductivity: S m² mol⁻¹ or S cm² mol⁻¹
3. $\kappa_{\text{KCl}} = \kappa_{\text{sol.}} - \kappa_{\text{water}}$

$$(7.44 - 0.06) \times 10^{-3} = 7.38 \times 10^{-3} \text{ S m}^{-1}$$

$$\Lambda_m = \kappa / c = \frac{7.38 \times 10^{-3} \text{ S m}^{-1}}{5.0 \times 10^{-4} \times 10^3 \text{ mol m}^{-3}} = 1.476 \times 10^{-2} \text{ S m}^2 \text{ mol}^{-1}$$
4. Concentration ionic Mobility, temperature and pressure, nature of solvent, viscosity of medium.
5. Consider following equation:

$$K_{\text{cell}} = \kappa \times R$$

$$= 0.2768 \text{ S m}^{-1} \times 195.96 \Omega$$

$$= 54.24 \text{ m}^{-1}.$$

Conductivity of K₂SO₄ solution can be given by,

$$\kappa = \frac{K_{\text{cell}}}{R} = \frac{54.24 \text{ m}^{-1}}{775.19 \Omega} = 0.06997 \text{ S m}^{-1}.$$

Concentration of K₂SO₄ in mol m⁻³ unit:

$$c = 1000 \times 2.50 \times 10^{-3} \text{ mol m}^{-3}$$

$$= 2.50 \text{ mol m}^{-3}$$

Molar conductivity of K₂SO₄ can be expressed as

$$\Lambda_m = \frac{\kappa}{c} = \frac{0.06997}{2.50} \text{ S m}^2 \text{ mol}^{-1}$$

$$= 0.028 \text{ S m}^2 \text{ mol}^{-1}$$

Terminal Questions

1. The ionic compounds which forming ions in solution and conduct electric current are called electrolyte e.g. NaCl , KCl etc. They can be classified strong and weak electrolyte on the basis of their degree of ionisation.
2. Molar conductivity: It is the conductivity for Unit molar concentration of a dissolved electrolyte.

$$\Lambda_m = \frac{\kappa}{c} = \frac{\kappa}{M \times 1000} \text{ S m}^2 \text{ mol}^{-1} = \frac{1000 \kappa}{M} \text{ S cm}^2 \text{ mol}^{-1}$$

Equivalent Conductivity: It is the conductivity of 1 g equivalent of an electrolyte when present in $V \text{ cm}^3$ of solution

$$\Lambda_{eq} = \kappa V$$

If c is the concentration of the solution in g equivalent per dm^3 , then

$$\Lambda_{eq} = \frac{1000 \kappa}{c}$$

Its unit is $\text{S cm}^2 \text{ eq}^{-1}$

Relationship

$$\Lambda_{eq} = \frac{\text{Molar Conductance (S cm}^2 \text{ mol}^{-1})}{\eta}$$

where η = molecular mass/equivalent mass

3. Cell constant: The quantity (l/A) is called the cell constant.

Conductivity = observed conductance $\times$ cell.

4. To overcome the imperfection in the current and the other effects at the electrode.
5. Detail procedure is given in sub section 10.2.4.
6. Because conductivity of all electrolytes increases with increasing temperature.
7. $\Lambda_m = \kappa/c$, therefore,

$$\begin{aligned} \Lambda_m &= 0.0394 (\Omega^{-1} \text{ cm}^{-1}) / 0.1 \text{ M} = 0.0394 (\Omega^{-1} \text{ cm}^{-1}) / 0.1 \times 10^{-3} \text{ mol cm}^{-3} \\ &= 394 \Omega^{-1} \text{ cm}^2 \text{ mol}^{-1} \end{aligned}$$

8. Cell constant = l/A , $1.8/5.4 = 1/3 \text{ cm}^{-1}$

$$\text{Observed conductance} = 1/32 \Omega^{-1}$$

$$\kappa = \text{Cell constant} \times \text{conductance} = 1/3 \times 1/32 = 1/96 \Omega^{-1} \text{ cm}^{-1}$$

$$\Lambda_m = \kappa/c = 1/96 (\Omega^{-1} \text{ cm}^{-1}) \times 1/0.1 \text{ M}$$

$$= 1/96 (\Omega^{-1} \text{ cm}^{-1}) \times 1/0.1 \times 10^{-3} (\text{mole cm}^{-3}) = 104.16 \Omega^{-1} \text{ cm}^2 \text{ mol}^{-1}$$

9. Cell constant = $\kappa R = 0.001409 \Omega^{-1} \text{ cm}^{-1} \times 161.8 \Omega = 0.228 \text{ cm}^{-1}$
 $\kappa_{\text{NaOH}} = \text{Cell constant}/R = 0.228 \text{ cm}^{-1}/190 \Omega = 1.2 \times 10^{-3} \Omega^{-1} \text{ cm}^{-1}$
 $\Lambda_m = \kappa/c = 1.2 \times 10^{-3} \Omega^{-1} \text{ cm}^{-1}/0.0050 \times 10^{-3} \text{ mol cm}^{-3} = 240 \Omega^{-1} \text{ cm}^2 \text{ mol}^{-1}$
10. Cell constant = $\kappa R = 2.767 \times 10^{-3} (\text{S cm}^{-1}) \times 4864 (\Omega)$
 Conductivity of the experimental solution = $\kappa = \text{Cell constant}/R$
 $= 2.767 \times 10^{-3} \times 4864 (\text{cm}^{-1})/3950(\Omega) = 3.407 \times 10^{-3} \text{ S cm}^{-1}$
11. Cell constant = $\kappa R = (0.14807 \times 702) (\text{ohm}^{-1} \text{ m}^{-1}) (\text{ohm}) = 103.94 \text{ m}^{-1}$
 $= 1.039 \text{ cm}^{-1}$
 Conductivity of acetic acid $\kappa = (1/R) (l/A)$
 $= (1 / 6920 \Omega) (1.039) \text{ cm}^{-1}$
 $= 1.501 \times 10^{-4} \Omega^{-1} \text{ cm}^{-1}$
 $= 1.501 \times 10^{-2} \Omega^{-1} \text{ m}^{-1}$
 Concentration = $0.01 \text{ M} = 0.01 \text{ mol dm}^3 = 0.01 \times 10^3 \text{ mol m}^{-3}$
 $\Lambda_m = \kappa/c = 1.501 \times 10^{-2} \Omega^{-1} \text{ m}^{-1}/0.01 \times 10^3 \text{ mol m}^{-3}$
 $= 1.501 \times 10^{-3} \text{ mol}^{-1} \Omega^{-1} \text{ m}^2$

8.11 FURTHER READING

1. H.H. Willard, L.L. Meritt Jr., J.A. Dean, F.A. Settle Jr., *Instrumental Method of Analysis*, Wadsworth Publishing Company, USA, 1988.
2. M.E. Brown, *Introduction to Thermal Analysis*, Kluwer Academic Publisher, London, 2001.
3. W.W. Wandlandt, *Thermal Analysis*, Wiley, New York, 1986.
4. H. Gunzzler and A. Williams, *Hand Book of Analytical Techniques*, Wiley-VCH, Weinheim, Vol -2, 2001.
5. G.W. Ewing, *Analytical Instrumentation Handbook*, Marcel Dekker Inc, New York, 2005.
6. R.A. Meyer, *Encyclopedia of Analytical Chemistry*, John Wiley & Sons Ltd, Vol 15, 2000.
7. Skoog, Douglas A., F. James Holler and Timothy Nieman. *Principles of Instrumental Analysis*. Seventh Edition, 2018.
8. Dean, John A, *The Analytical Chemistry Handbook*. New York. McGraw Hill, Inc. 204.