Instrumental Methods of Analysis

Dr. H. S. Lalithamba
Associate professor
Dept. of Chemistry
SIT, Tumkur

Introduction:

Analytical chemistry is the branch of chemistry which deals with the qualitative and quantitative determination of analyte. Where, analyte is the species of interest present in the sample which is to be determined. The two steps of chemical analysis in the characterization of matter are identification and estimation of constituents of substance.

Chemical analysis and its classification:

Chemical analysis: It is the qualitative and quantitative determination or estimation of analyte or a chemical.

Classification: Chemical analysis is classified into two types namely

1. Qualitative analysis and 2. Quantitative analysis.

Qualitative analysis: It is a type of chemical analysis which gives only the information about the presence (identification) of analyte present in the given sample.

Ex. Qualitative analysis of inorganic salts and semi-micro qualitative analysis of organic compounds

Quantitative analysis: It is a type of chemical analysis which gives information about the quantity (amount) of analyte present in given sample.

Ex: Volumetry and gravimetry

Classification of quantitative analysis: Based on the type of method used, the quantitative analysis can be classified into the following two types.

1. Chemical methods of analysis or classical methods or wet methods
2. Instrumental methods of analysis or modern methods of analysis.

Chemical methods of analysis or classical methods or wet methods

These are the old methods of quantitative chemical analysis.

Ex: Gravimetry and volumetry are considered as classical methods of quantitative chemical analysis.

Volumetry or titrimetry:

It is a classical method of chemical analysis in which the analyte species is made to react with a suitable reagent and the amount of analyte is determined by measuring the volume of reagent required to react with analyte during titration. Since the method involves the measurement of volume of reagent for the quantification of analyte it is commonly called as volumetry.

Eg. : Titration of HCl V/S NaOH:

Gravimetry:

It is a classical method of chemical analysis in which the analyte is converted into their respective precipitates by adding suitable precipitating agents and measurement of weight of the precipitate gives the concentration of analyte.

Eg: Gravimetric estimation of copper.

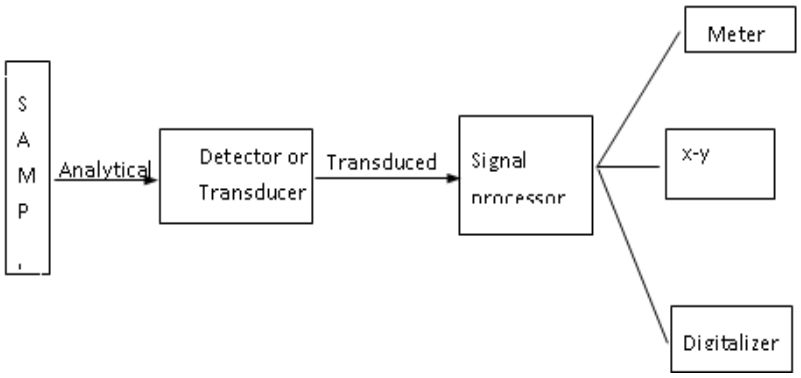
Instrumental methods of analysis or modern methods of analysis:

It is a type of quantitative chemical analysis in which the analyte is determined by using instruments. In instrumental analysis, a physical property of the substance is measured and is related to the quantitative determination of its chemical composition. The instrument used in the chemical analysis is called analytical instrument and is defined as a device which can detect and convert the physical property of the substance into easily measurable form (electrical signal). The physical property may be intensity of color in case of colorimetry, conductivity in case of conductometry, electrode potential in case of potentiometry, emission, current etc. and these properties are used to quantify the analytes.

Eg: colorimetric estimation of copper, conductometric estimation of HCl, Potentiometry estimation of FAS *etc*..

General instrumentation of analytical instrument: The block diagram of analytical instrument is diagrammatically shown in the following figure.

The schematic representation of an analytical instrument is as shown in the figure.



The impotent components of analytical instrument are summarized as follows.

Sample:

Sample is a matrix which contains analyte which is to be measured. The sample executes its characteristic physical property or analytical signal since it is its inherent property.

Detector/transducer:

It detects the analytical response or physical property obtained from the sample and converts it into an easily measurable electrical signal.

Transducers used in some instruments are listed below.

Analytical instrument	Transducer	Physical property
Colorimeter	Photocell	Detects the change in color
Potentiometer	Electrochemical cell	Detects the change in Potential
Conductometer	Conductivity cell	Detects the change in conductivity

Signal processor: This will process or transform the transduced signal into a form which can be easily recorded on a meter.

Recorder: This will records the easily measurable form of analytical signal. Recorders may be X-Y plotter or digital meters.

Advantages of instrumental methods of analysis:

i) It is faster than volumetric or gravimetric methods of analysis.

ii) It requires only small quantities (less than a milligram) of the sample.

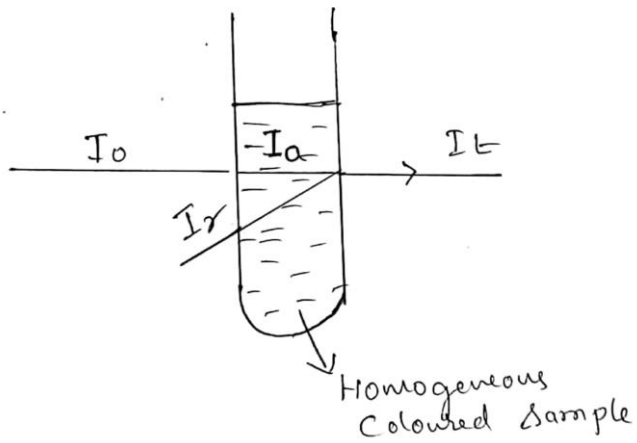
iii) Easy when a large number of samples have to be analyzed.

iv) The results are accurate.

1. Colorimetry [Colori – Colour & Metry – measurement]

The term colorimetry originates from the time where the analysis was carried by comparing the color of particular component with the standard color using naked eye. Now a day, this principle of identification and comparison of color forms the basis for modern instrumental methods also. Colorimetry is an instrumental method of quantitative chemical analysis which deals with the determination of analyte by measuring the intensity of color of analyte solution.

Principle: Colorimetry mainly works on the principle of measurement of intensity of color of analyte solution and the measured intensity is directly proportional to the concentration of analyte and the intensity of color should vary with the concentration of analyte. Therefore, the variation of concentration of analyte varies the intensity of color. Hence, the measurement of color intensity of a system provides suitable platform for the quantification of analyte. If the analyte solution is colored then the concentration of analyte is determined directly. If the analyte solution is colorless, then impart or produce or give color to the colorless analyte solution by adding a chemical species and measure the intensity of color. Therefore, the chemical species which impart color to colorless solution is called coloring agent.



When a monochromatic light of intensity I_o is incident on a transparent medium, a part of it, I_a is absorbed, a part , I_r is reflected and the remaining part, I_t is transmitted.

$$I_o = I_a + I_r + I_t$$

For a air-glass interface, I_r is negligible and hence,

$$I_o = I_a + I_t \quad \text{----- 1}$$

Lambert studied the relation between I_o and I_t while Beer extended the experiments to solutions. Hence, colorimetry is based upon Lambert's and Beer's laws.

Definitions:

i) Transmittance (T)

Transmittance is the ratio of intensity of transmitted light by the sample (I) to intensity of incident light on the sample (I_o), both being measured at the same spectral position and with the same slit width.

$$T = \frac{I_t}{I_o}$$

ii) Absorbance (A) or optical density

Absorbance is the logarithm to the base 10 of the reciprocal of the transmittance.

$$A = \log_{10} (1/T)$$

or $$A = \log_{10} (I_o/I_t)$$

Statement of Lambert's law and Beer's law

Lambert's law (Relation between absorption of radiation and thickness of the absorbing medium)

It sates that when a beam of monochromatic radiation passes through a homogeneous absorbing medium, the rate of decrease of intensity of radiation with thickness of absorbing medium is proportional to the intensity of the incident radiation.

i.e. $$-\frac{dI}{dx} \alpha I$$

$$-\frac{dI}{dx} = Ik_1$$

k_1 -- proportionality constant

$$-\frac{dI}{I} = dx\, k_1$$

Integrating this between I_o and I_t and x=0 and x=t

$$\int_{I_o}^{I_t} \frac{dI}{I} = -k \int_{x=0}^{x=t} dx$$

$$\ln \frac{I_t}{I_o} = -k_1 t$$

or $$I_t = I_o e^{-k_1 t} \quad \text{-----1}$$

The intensity of a beam of monochromatic light decreases exponentially with increase in the thickness of the absorbing substance arithmetically.

Beer's law (Relation between absorption of radiation and concentration of the absorbing) It sates that when a beam of monochromatic radiation is passed through a solution of an absorbing medium, the rate of decrease of intensity of radiation with concentration of absorbing solution is proportional to the intensity of the incident radiation.

. $-\frac{dI}{dc} \alpha I$

$-\frac{dI}{dc} = k_2 I$ k_2-- proportionality constant

c – concentration of solution

Integrating this between I_o and I_t and concentration between 0 and c

$$\int_{I_o}^{I_t} \frac{dI}{I} = -k_2 \int_0^c dc$$

$$\ln \frac{I_t}{I_o} = -k_2 c$$

or $I_t = I_o e^{-k_2 c}$ ----2 where 'c' is the concentration of the sample solution.

Beer-Lambert's law

It states that when a beam of monochromatic radiation is passed through a homogeneous absorbing medium, the rate of decrease of intensity of radiation with concentration and thickness of the absorbing medium is proportional to the intensity of the incident radiation. Combining equations for Beer's law and Lambert's law,

$I_t = I_o e^{-k_1 t}$ ……. Lambert's law

$I_t = I_o e^{-k_2 c}$ ……. Beer's law

Where I_o is intensity of incident radiation, It is intensity of transmitted radiation, c is concentration of absorbing medium, t is the thickness of absorbing medium, k and k' are constants.

Equation for Beer-Lambert's law can be written as

$I_t = I_o e^{-k1k2ct}$

Combining equations for Beer's law and Lambert's law, equation for Beer-Lambert's law can be written as

$$I_t = I_o e^{-k1k2ct}$$

$$\ln \frac{I_t}{I_o} = -k_1 k_2 ct$$

$$2.303 \log_{10} \frac{I_t}{I_o} = -k_1 k_2 ct$$

$$\log_{10} \frac{I_t}{I_o} = \frac{-k_1 k_2 ct}{2.303}$$

$$\log_{10} \frac{I_t}{I_o} = -\varepsilon ct$$

where $\varepsilon = \frac{k_1 k_2}{2.303}$

ε- molar absorptivity and is a constant for a given substance at a given wavelength. The above equation can be written as

$$\log_{10} \frac{I_t}{I_o} = -\varepsilon ct$$

This equation is referred as Beer-Lambert's law and this is the basis for optical methods of analysis.

The term $\frac{I_t}{I_o} = T$, but $A = \log \frac{1}{T}$

$$\log_{10} T = -\varepsilon ct$$

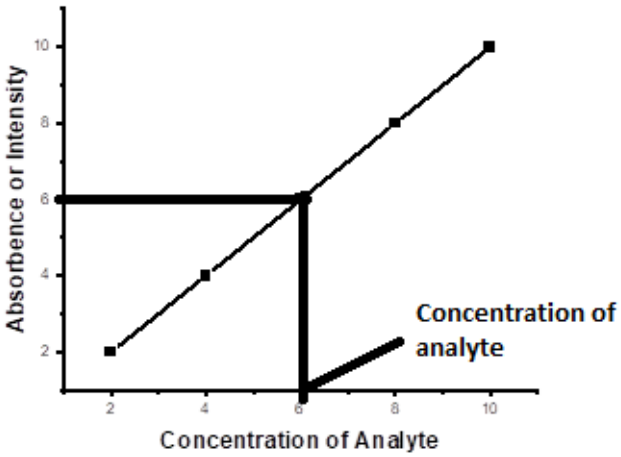
$$-\log_{10} T = \varepsilon ct$$

$$\log \frac{1}{T} = \log \frac{I_o}{I_t} = \varepsilon ct$$

$$A = \varepsilon tc$$

$$A \alpha ct$$

ε - molar extinction co-efficient, t is the path length and is constant for a given substance at a given wavelength. If t, the path length is kept constant, then, A α C. Hence a plot of absorbance against concentration gives a straight line.



Instrumentation: 6M

The essential components of colorimeter are as follows:

i) Light source: It provides the radiation continuously. For visible (Vis) region Tungsten filament and for ultraviolet region hydrogen discharge lamps are used

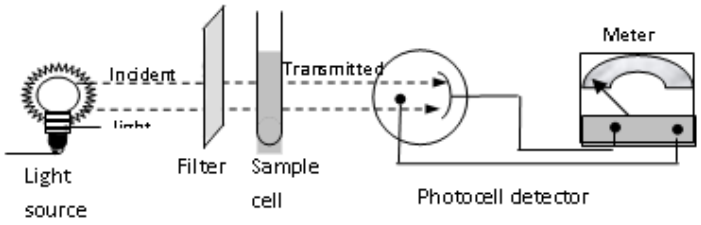
ii) **Filter:** It is used to select the radiation of desired wavelength in otherworld's monochromatic light. The light from radiation source contains all possible wavelengths but when it is passed through the filter, it allows only the radiation having the wavelength which is the characteristic for particular color by filtering all other wavelengths. Generally colored glasses and dyed gelatins are used as filters. The filter should give maximum absorbance or minimum transmittance for a given concentration of absorbing medium.

iii) **Sample holder/cell:** These are special glass tubes or cells which are used as containers for test solutions.

iv) **Detector:** It detects the intensity of transmitted light and converted it into easily measurable electrical signal. Generally Photoelectric cell (photodetector), photo multiplier is used as detectors.

v) **Measuring device:** It is used to record the output signal.

The block diagram of photoelectric colorimeter is as shown in figure.



Procedure

The systematic procedure of colorimetric measurement involves the following sequence operations.

1. Preparation of analyte solution or Stock solution: Stock solution of known concentration of analyte is prepared by dissolving known amount of analyte in known volume of water. From the stock solution a series of analyte solutions of different concentrations are prepared in a series of volumetric flasks. Then, color is developed by adding known volume of suitable coloring reagent and the volume is diluted using distilled water by making upto the mark. Blank solution is prepared as above without the analyte sample.

2. Calibration of instrument: Select the filter of required wavelength. Set the % transmittance as zero for black tube and 100 % for blank solution.

3. Measurement of color intensity (optical density) of analyte solution: Change the mode of the instrument from transmittance mode to absorbance or optical density (OD) mode and measure the OD for series of dilute solutions and also the unknown analyte solution.

4. Result analysis: Result is analyzed by using calibration curve which is constructed by plotting volume of analyte along X-axis and absorbance along Y- axis. From the calibration curve, the amount of analyte present in the given unknown solution is determined.

Advantages of colorimetry:

Colorimetric method has the following advantages when compared to the conventional methods of analysis such as, gravimetry etc.

1. It gives accurate results at very low concentration levels than the corresponding volumetry or gravimetric methods.
2. The method is simple, more rapid and less tedious hence it can be used for routine analysis.
3. Since it is possible to select the wavelength, the analysis can be done accurately.
4. It can be applied for the biological samples also.

Applications:

i) In quantitative analysis:

A large number of metal ions, anions and organic compounds can be determined by colorimetry. It is based on the application of Beer's law.

Colorimetric estimation or determination of copper:

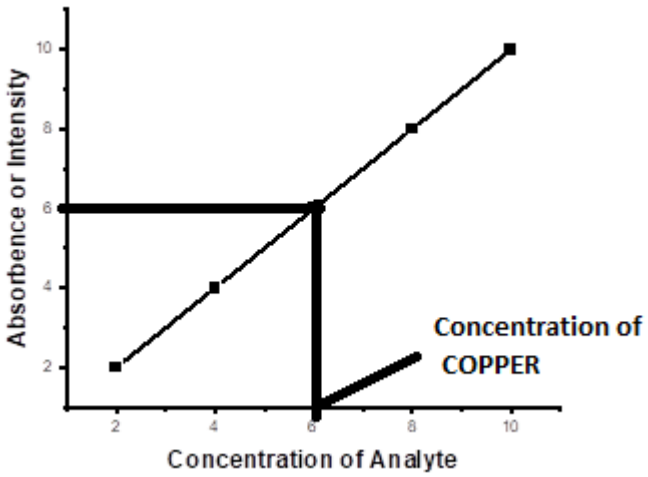
Calorimetrically copper is estimated or determined by measuring the intensity of deep blue color of cuprammonium complex formed by the reaction of copper ions with ammonia as a coloring agent.

$$Cu^{++} + 4\ NH_3 \longrightarrow [Cu(NH_3]_4]^{+2}$$

Copper ions Ammonia Cuprammonium complex (blue color)

Take a known volumes of standard copper sulphate solutions (5, 10,15, 20 ml, etc) in separate volumetric flasks. Add 5 ml of ammonia into each flasks and make up to the mark with ion exchange water. Stopper the flasks and mix the solution well. Then measure the absorbance values of the standard solutions against blank (5 ml of ammonia and water in a standard flask) at 620 nm using colorimeter. Then the calibration is obtained by plotting absorbance against concentration. The test solution in which the concentration of Cu^{+2} is to be determined is also treated with ammonia to develop colour and its absorbance is measured. From the calibration curve, the concentration Cu^{+2} in the solution can be determined.

Colorimetric estimation can be applied to estimate copper in bras, magnese in steel, glucose in fluids, etc.

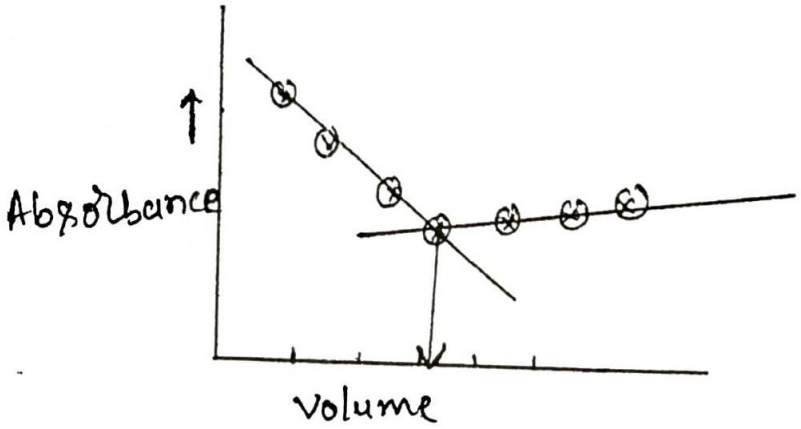


Colorimetric estimation can be applied to estimate copper in brass, manganese in steel, glucose in fluids, etc.

ii) Photometric titrations:

Colorimetric measurements are also used in locating the equivalence point in a titration, where one of the species (either the titrant or the reactant or the product) has specific absorbance (coloured) proportional to its concentration. In such a case, the plot of absorbance

versus volume of titrant added will consists of two straight lines intersecting at the equivalence point. The shape of a photometric titration curve is dependent upon the optical properties of the titrant, reactant and the product of the reaction, at the wavelength used.



2. Potentiometry [Potentio – Potential & Metry – Measurement]

Potentiometry is a type of instrumental method of quantitative chemical analysis in which the analyte is determined by measuring the electrode potential developed at the electrode – solution interface.

Consider Nernst equation, $E = E_0 + \frac{0.0591}{n} \log_{10} [Mn+]$

E- Electrode potential, E_0- standard electrode potential, n- number of electrons involved in redox process.

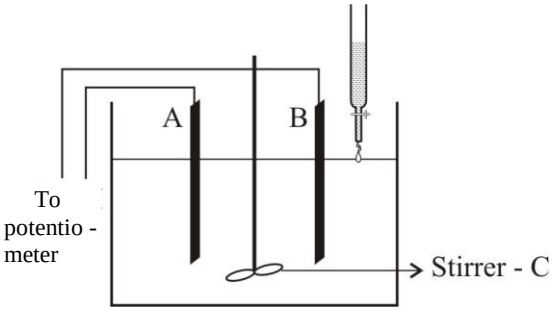
According to Nernst's equation, the electrode potential mainly depends on the concentration of ions present in the solution. Therefore, the concentration of solution (analyte) is measured by measuring the electrode potential.

Potentiometric titrations: These are the titrations in which analyte is determined by measuring the electrode potentials at the electrode - solution interface when the titration is in progress. In these titrations, the equivalence point can be detected by a sudden change in the potential plot of potential (emf) v/s volume of the titrant. In all the cases the potential is measured by using an instrument called potentiometer.

Potentiometer - Instrumentation:

The potentiometer is a device or instrument which measures the potential developed at the electrode analyte solution interface.

A schematic representation of arrangement of potentiometric titration is shown in the following figure.



It consists of two electrodes, one is indicator electrode (A) at which the analyte reacts and therefore any change in the concentration of analyte is indicated by this electrode. The other is reference electrode (B) which maintains constant potential and the potential developed at the indicator electrode is measured with reference to this electrode. These electrodes are dipped into a beaker containing analyte solution which is provided with mechanical stirrer (C) for uniform mixing of solution.

Measure the potential of the cell before and after the addition of solution from burette at regular volume intervals say 0.5 mL upto equivalence point and then continue the measurement for 3 to 4 more additions just to ensure the equivalence point. The equivalence point is determined by relatively more rapid change of the potential.

Advantages

The following are the advantages of potentiometric titrations over titrimetric methods.

i)Indicators are not needed in the determination of end points.

ii)Since the indicators are not needed the method is applicable to color solutions also.

iii) The prior knowledge of relative strengths of acids and bases to select a proper indicator is necessary in ordinary titrations, while no such knowledge is required in the case of potentiometric titrations.

iii) It is possible to determine an approximate end point in the titration of very weak acids or very weak bases when the indicator methods are quite undesirable.

Applications:

Based on the nature of chemical reactions, the potentiometric titrations are classified as

i) Neutralization (Acid-Base Titrations)

ii) Redox titrations

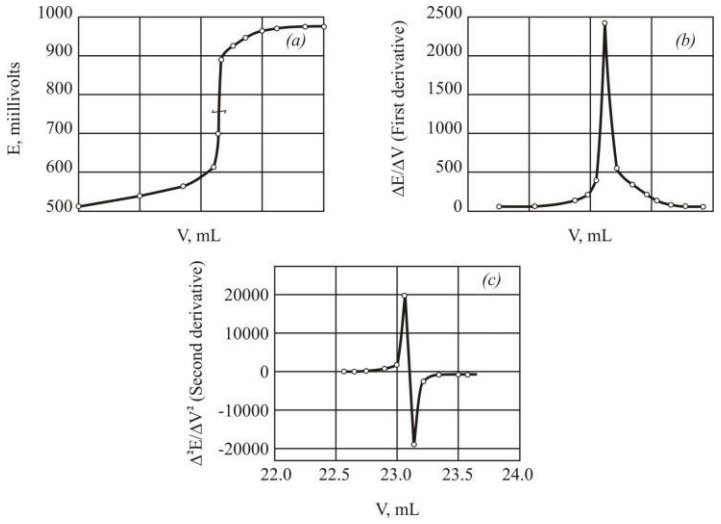
iii) Precipitation titrations

i) Neutralisation (Acid-Base) Titrations

In case of neutralization titrations the end point is determined by measuring the pH of acid solution after each addition of base. The change of pH value of solution for the addition of a given amount of base is maximum at the equivalence point and hence it can be identified. The pH of solution can be determined by using an electrochemical cell constructed by using glass electrode as an indicator electrode whose potential mainly depends on hydrogen ion concentration and calomel electrode as reference electrode.

Potentiometric titration of HCl with NaOH.

In this case, the indicator electrode (glass electrode) is placed in an HCl solution and coupled with calomel reference electrode to form a cell. The potential of the indicator electrode is given by EG = constant + 0.0591pH. The change in electrode potential of the constructed cell is proportional to the change in pH of solution during titration. As the titration proceeds the concentration of H+ ions decreases and hence pH increases therefore the electrode potential of the cell increases. In the beginning the potential changes slowly and then rapidly as it approaches the neutralization point. The equivalence point is determined graphically which is obtained by plotting pH along Y axis and volume of base along X axis which is shown below (fig.a) and the end point is the volume corresponding to the steepest position of the curve (fig.b). The equivalence point can be located by plotting $\Delta pH/\Delta V$ (Fig. b) or $\Delta^2 pH/\Delta V^2$ (Fig. c) against volume of titrant.



ii) Redox Titrations

These are the titrations in which reduction and oxidation reactions takes place simultaneously. These can be carried out potentiometrically. Consider a general redox reaction.

Oxidized form + n electrons $\rightarrow$ Reduced form

According to Nernst equation, the electrode potential (E) for this redox reaction is given by

$$E = Eo + \frac{0.0591}{n} \log_{10} \frac{[\text{oxidised}]}{[\text{Reduced}]}$$

where E – Electrode potential, E_0- standard electrode potential & n-number of electrons involved in redox reaction.

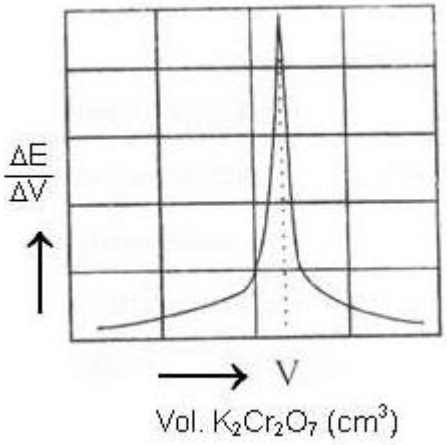
From the above equation it is clear that the determining factor for a redox reaction is the ratio of the concentrations of the oxidized and reduced forms of ionic species present in the solution. Therefore, the potential of indicator electrode is controlled by the ratio of concentrations.

In redox titrations, platinum electrode is used as an indicator electrode and calomel electrode is used as a reference electrode. These titrations are possible only for the reactions which contains

the species which is capable of undergoing oxidation (reducing agent) and the species capable of undergoing reduction (oxidizing agent).

Eg. Redox titration of FAS (Mohr's salt) v/s $K_2Cr_2O_7$

The graph is obtained by plotting by ploting change in e.m.f. (ordinate) versus volume of $K_2Cr_2O_7$ added.



Potassium dichromate is an oxidizing agent which is taken in a burette and ferrous ammonium sulphate is a reducing agent and is taken in a beaker. Platinum indicator electrode is dipped into a beaker containing acidified FAS and connect it to a reference calomel electrode to form a complete cell setup. Before the addition of dichromate FAS solution contains only ferrous ions (Fe^{2+}). When titration proceeds i.e. small amount of dichromate is added, redox reaction takes place and an equivalent amount of ferrous ions are oxidized to ferric ions (Fe^{3+}). At the same time as a counter reaction the chromium (Cr^{6+}) ions are get reduced to chromium (Cr^{3+}). Therefore the overall redox reaction is given as

$$3\ Fe^{2+} + Cr^{+6} \rightarrow 3\ Fe^{3+} + Cr^{3+}$$

In the beginning of the titration, before the complete conversion of Fe^{2+} to Fe^{3+}, the solution in beaker contains both Fe^{2+} and Fe^{3+} ions. This will form a redox couple ($Pt/Fe^{3+}/Fe^{2+}$) and the potential developed at this couple is due to these ions and is given by

$$E = Eo + \frac{0.0591}{n} \log 10 \frac{[Fe^{3+}]}{[Fe^{2+}]}$$

As the titration proceeds more and more ferrous iron will get oxidized to ferric form. Therefore the concentration of ferric form increases which increases the concentration gradient as well as the electrode potential also. At the equivalence point where all the ferrous form will get converted into ferric form the potential increased very sudden and sharp which can be easily identifiable.

After the equivalence point further addition of dichromate increases the concentration of Cr^{+6} ions into the beaker containing Cr^{+3} ions which were already produced during the oxidation of ferrous to ferric form. Therefore this will constitute an another redox couple ($Pt/Cr^{6+}/Cr^{3+}$) and the potential developed is due to this redox couple and is given by

$$E = E_o + \frac{0.0591}{n} \log 10 \frac{[Cr^{6+}]}{[Cr^{3+}]}$$

Further addition of Cr^{6+} increases its concentration in the beaker and the concentration of Cr^{3+} does not alter. This will increase the electrode potential after the equivalence point. The nature of graphs is similar to that of acid-base titrations.

Advantages

The following are the advantages of potentiometric titrations over the regular titrations involving the use of indicators.

i) Potentiometric titrations can be carried out in coloured solutions where indicators cannot be used.

ii) Results are more accurate.

iii) Large no of the samples can be analyzed in short period of time.

iv) The prior knowledge of relative strengths of acids and bases to select a proper indicator is necessary in ordinary titrations, while no such knowledge is required in the case of potentiometric titrations.

v) It is possible to determine an approximate end point in the titration of very weak acids or very weak bases when the indicator methods are quite undesirable.

iii) Precipitations Titrations

These are the titrations which involves the formation of precipitate.

Consider the titration of Ag^+ ion by Cl^- ion. The silver electrode is used as the indicator electrode. The potential of the half cell Ag^+, Ag is measured by connecting it with the calomel electrode. The $AgNO_3$ solution is titrated against a standard solution of KCl, the strength of which is about 10 times higher. As the reaction proceeds, the Ag^+ ions get gradually precipitated as AgCl.

$$Ag^+ + NO_3^- + (K^+ + Cl^-) \longrightarrow AgCl \downarrow + K^+ + NO_3^-$$

The concentration of Ag^+ ions decreases during the process and this decrease is relatively most rapid near the equivalence point. The potential of Ag^+, Ag electrode is given by $E = E^o + 0.0591 \log_{10}[Ag^+]$ at 25 ^oC and goes on decreasing continuously on the progressive addition of KCl solution. The electrode potential changes slowly at first but more rapidly as the end point approaches. At the end point, the concentration of Ag^+ ions is very small as this is now only on account of slight solubility of AgCl. Hence the change in electrode potential is maximum at the end point. If the addition of KCl is continued further, the concentration of Ag^+ ions remains almost unaffected except for very small decrease on account of the common ion effect. The addition of KCl beyond the end point, therefore, causes only a small change in the electrode potential. The potentiometric titration curve obtained in this case is exactly identical to the one obtained in the case of acid-base titration described earlier.

3. Conductometry:

Conductometric titration

The substances are classified into two types based on the electrical conducting capacity.

1. **Conductors:** They are the substance which conduct electric current. Eg. Graphite, all metals, aqueous solutions of salts etc.

2. Insulators: They are the substances which do not conduct electrical current. Eg. Glass, wood etc.

Based on the nature of charge carrier, the conductor is again classified into two types:

i) Electronic conductor: The charge carriers are electrons.

ii) Electrolytic conductor: The charge carriers are ions.

Electrolytes and non electrolytes:

Electrolytes: These are the substances which undergo dissociation and produce ions when dissolved in water or in molten state. Eg. All acids, all bases and salts.

Non electrolytes: these are the substances which do not undergo dissociation when dissolved in water or in molten state. Eg. Wood, glass etc.

Laws, definitions and relations:

Statement of Ohm's law: It 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.

$$i = \frac{E}{R}$$

The reciprocal of the resistance is called the conductance. The resistance of a homogeneous material of uniform cross section with an area of **a** sq. cm. and length *l* cm is given by

$$R \alpha \frac{l}{a}$$

$$R = \rho \frac{l}{a}$$

where ρ is the specific resistance. The reciprocal of the specific resistance is termed the specific conductance, κ. It is the conductance of a cube of material 1 cm. in length and $1cm^2$ in cross section.

Specific conductance:

Specific conductance of a solution is defined as the conductance of a solution present between two parallel electrodes which have $1cm^2$ area of cross section and which have kept 1 cm apart.

The specific conductance of the solution is given by

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

l/a is known as the cell constant.

The specific conductance of an electrolytic solution at any temperature depends only on the ions present and therefore varies with their concentration. On dilution of an electrolyte solution, its specific conductance decreases as the number of ions per ml also decreases.

Principle:

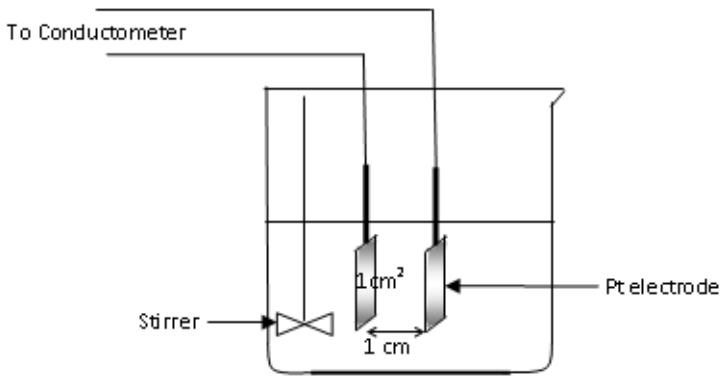
Conductometric titrations are the titrations in which the end point is determined by measuring the change in conductivity of the electrolytic solution (electrical conductivity). The conductance of an electrolytic solution mainly depends on the following two factors

1. Total number of ions present in the given electrolytic solution.
2. Ionic mobility.

These factors form the principal of conductometric titrations and the equivalence point is observed by the sudden change in conductance and is obtained by plotting conductance along Y – axis and titre value along X – axis.

Instrumentation

The instrument used to measure the conductance is called conductometer or conductivity meter and the method is called conductometry. Conductivity-meter consists of a cell consisting of a pair of platinum electrodes which are firmly fixed in position. The two electrodes have unit area of cross section and are placed unit distance apart. The assembly responds rapidly to the changes in the concentration of the analyte (the solution under the study). A simple arrangement of conductometric titration is as shown in figure. The solution to be estimated is taken in the beaker..



Procedure:

Pipette out a known volume of acid solution into a beaker. Clean the conductance cell with distilled water, dry it with filter paper strips and dip in the acid solution. Connect the conductivity cell to the condcutometer and select a suitable range for conductance. So that, maximum number of digits is displayed on the display of the conductometer. Titrate the acid with a base. After each addition, the conductance of the solution is measured. The titration is continued till the decreasing trend of conductance changes to increasing trend. The plot of conductance values along Y-axis and volume of base added along the X-axis gives two straight lines. The point of intersection between the two lines corresponds to the equivalence point.

Advantages:

i) Mixture of acids can be titrated more accurately by conductometric titration.

ii) Conductometric titrations may be applied where visual or potentiometric methods fail to give results owing to considerable solubility or hydrolysis at the equivalent point.

iii) Accurate in dilute solution as well as in more concentrated solution.

iv) It can be employed with colored solutions.

v) Very weak acids which cannot be titrated potentiometrically in aqueous solutions can be titrated condcutometrically with relative ease.

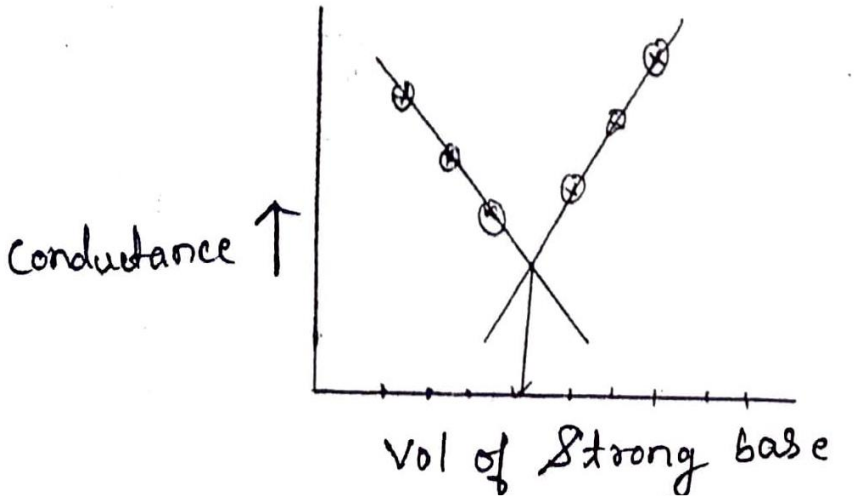
Applications:

1. Strong acid with a strong base: Eg. Titration of HCl against NaOH

Consider a reaction of the type $HCl + NaOH \rightarrow NaCl + H_2O$

In a case of strong acid and strong base, the conductance first decreases, due to the replacement of highly mobile H^+ ion (mobility 350 $ohm^{-1}m^{-1}$) by the added cation (mobility 40-80 ohm^{-1} m^{-1}). After the equivalence point, the conductance rapidly rises with further additions of strong alkali and is due to increase in the concentration of the OH^{-1} ions (mobility 198 $ohm^{-1}m^{-1}$). The plot of conductance ($ohm^{-1}m^{-1}$) versus volume of alkali added (cm^3) gives a graph as depicted in figure. The two curves are straight lines when the volume of the alkali added is negligible. The point of intersection of the curves gives the equivalence point.

This titration is of particular interest when the solutions are dark or deeply coloured or if they are very dilute (10^{-3} – 10^{-4} N).



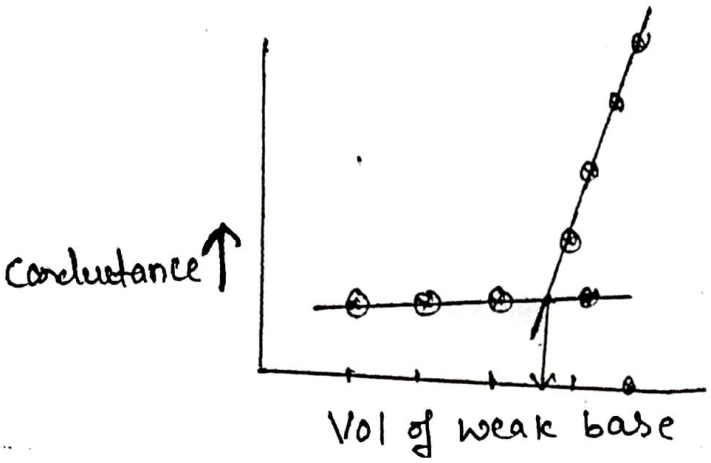
2.Weak acid with a strong base

e.g., Titration of dilute CH_3COOH with dilute NaOH solution

$$CH_3COOH + NaOH \longrightarrow CH_3COO^-Na^+ + H_2O$$

In this titration, the conductivity first decreases owing to the formation of salt which suppress the ionization of weak acid. As more NaOH is added, highly ionized salt sodium acetate is formed thereby increasing the conduction. When the acid is neutralized, further addition of

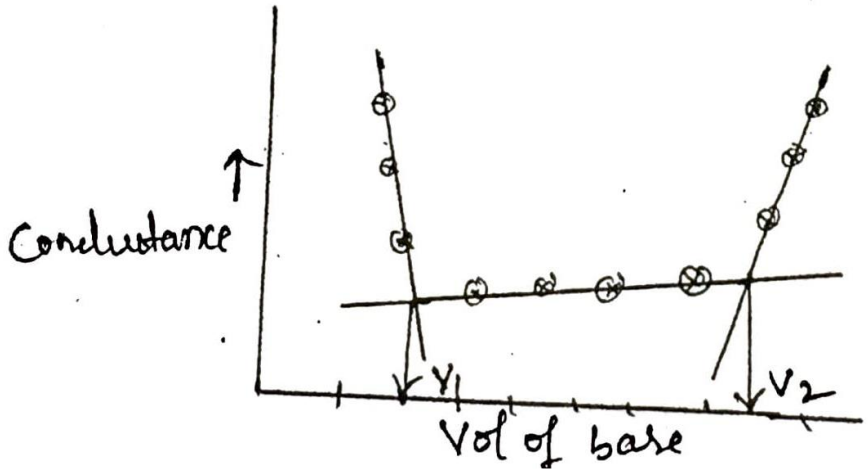
NaOH causes to rise in conductance due to addition of highly mobile OH^- ions. The intersection of the two lines represents the equivalence point.



3. Mixture of a strong acid and a weak acid with a strong base:

$$HCl + CH_3COOH + 2NaOH \longrightarrow CH_3COO^-Na^+ + NaCl + H_2O$$

On adding a strong base (NaOH) to a mixture of strong acid and a weak acid (e.g., HCl + CH_3COOH), the conductance falls until the strong acid is neutralized completely, due to the removal of H^+ ions. The weak acid remains undissociated in the presence of a strong acid. Once the strong acid is completely neutralized, the weak acid begins to dissociate and gets neutralized. This results in the increase in conductance of the solution as the weak acid is consumed and converted into its salt. When the neutralization of the second acid is complete, there is steep increase in conductance due to the ions furnished by the strong base.

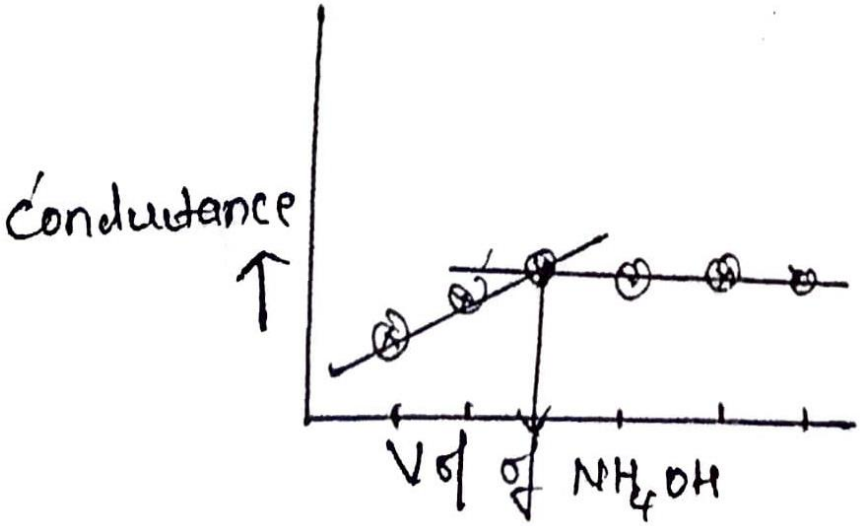


4. Weak acid against weak base:

e.g., Titration of dilute CH_3COOH with dilute NH_4OH solution.

$$CH_3COOH + NH_4OH \longrightarrow CH_3COO^-NH_4^+ + H_2O$$

In this titration, the conductivity first increases owing to the formation of ammonium acetates salt which are strong electrolytes. After the equivalence point, an excess NH_4OH solution has little effect on the conductance, as its dissociation is suppressed by the presence of ammonium salt in the solution.



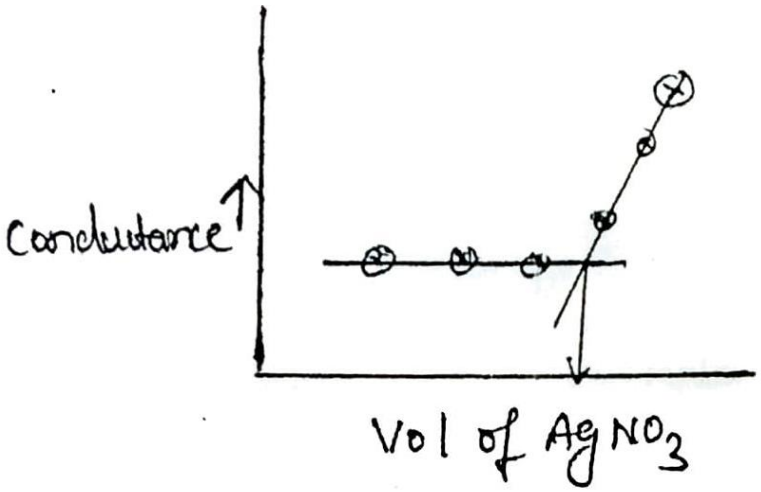
5. Precipitation titration:

The Conductometric titrations can be used for precipitation titrations also.

Consider the reaction of KCl and AgNO3.

$$KCl + AgNO_3 \rightarrow AgCl + KNO_3$$

In the titration of KCl and $AgNO_3$, the addition of $AgNO_3$ does not increase the conductance in the beginning. This is because the replaced Cl^- ions by nitrate ions have almost same ionic conductance. After the end point, the excess $AgNO_3$ added cause a sharp increase in conductance.



Problems:

1) 7.25×10^{-5} M solution of potassium permanganate has a transmittance of 44.1% when measured in a 2.10 cm cell at wavelength of 525 nm. Calculate (a) the absorbance of the solution (b) the molar absorptivity of $KMnO_4$.

Solution:

$$A = \log \frac{1}{T}$$

$$A = \log \frac{1}{0.441}$$

$$\underline{A = 0.355}$$

$$A = \varepsilon c t$$

$$\varepsilon = \frac{A}{ct}$$

$$\varepsilon = \frac{0.355}{7.25\times10^{-5} \times 2.10}$$

$$\underline{\varepsilon = 2.33 \times 10^{3}\ L\ mol^{-1}\ cm^{-1}}$$

2) A solution of 8.75 M $KMnO_4$ has a transmittance of 0.743 in a 1.00 cm cell at 520 nm. Calculate the molar absorptivity of $KMnO_4$.

Solution:

$$A = \log \frac{1}{T}$$

$$A = \log \frac{1}{0.743}$$

$$\underline{A = 0.127}$$

$$A = \varepsilon c t$$

$$\varepsilon = \frac{A}{cl}$$

$$\varepsilon = \frac{0.127}{1.00\times8.75}$$

$$\varepsilon = 0.0145\ L\ mol^{-1}\ cm^{-1}$$

3) The molar absorptivity of a particular solute is 2.1×10^{4}. Calculate the transmittance through a cuvette with a 5.00 cm light path for 2.00×10^{-6} M solution.

Solution: $A = \varepsilon c t$

$$A = 2.1 \times10^{4} \times 2.00\times10^{-6} \times 5$$

$$A = 0.21$$

But $A = \log \frac{1}{T}$

$$\log \frac{1}{T} = A$$

$$\log_{10} T = -A$$

$$T = 10^{-A}$$

$$T = 10^{-0.21}$$

$$T = 0.616$$

4) An α-β unsaturated ketone of relative molecular mass 110 has an absorption band with λ_{max} at 215nm and ϵ = 10,000. A solution of this ketone showed absorbance A= 2.0 with a 1cm cell. Calculate the concentration of the ketone in this solution, expressed in grams per litre.

Solution: $A = \varepsilon c t$

$$c = \frac{A}{\varepsilon t}$$

$$c = \frac{2.0}{10000 \times 1}$$

$$c = 2 \times 10^{-4} \text{ mol litre}^{-1}$$

Concentration in grams per litre is

c = conc. in mol litre^{-1} × relative molecular mass

$c = 2 \times 10^{-4} \times 110$

$c = 2.2 \times 10^{-2}$ g l^{-1}

5) A compound has a molar absorptivity of 6.74×10^3 Lmol^{-1}cm^{-1}. What concentration of the compound would be required to produce a solution having a transmittance of 7.77% in a 2.5 cm cell?

Solution: $A = \varepsilon c t$

$$A = \log \frac{1}{T} = \varepsilon c t$$

$$A = -\log T = \varepsilon c t$$

$$\log T = -\varepsilon c t$$

$$c = -\frac{\log T}{\varepsilon t}$$

$$c = -\frac{\log (0.0777)}{6.74 \times 10^3 \times 2.5}$$

$$c = \frac{1.1095}{16850}$$

$$c = 6.5 \times 10^{-3} \text{ mol litre}^{-1}$$

6) If the molar absorptivity for iron(II)-1,10-phenanthroline complex is 12,000 litre mol^{-1}cm^{-1} and the minimum detectable absorbance is 0.001, then for a 1.00 cm path length, Calculate the molar concentration.

Solution: $A = \varepsilon c t$

$$c = \frac{A}{\varepsilon t}$$

$$c = \frac{0.001}{12000 \times 1}$$

$$c = 8.30 \times 10^{-8} \text{ mol litre}^{-1}$$

7) A solution of a compound with a concentration of 0.14 mol litre $^{-1}$ is measured to have an absorbance of 0.43. Another solution of the same compound is measured under the same conditions and has an absorbance of 0.37. What is its concentration?

Solution: According to Beer-Lamrert's law, absorbance (A) is directly proportional to concentration (c) of the solution i.e., $A \alpha c$.

$$\frac{c_1}{c_2} = \frac{A_1}{A_2} = \frac{0.14}{c_2} = \frac{0.43}{0.37}$$

$$(0.14)\,(0.37) = c_2\,(0.43)$$

$$c1 = 0.1204 \text{ mol litre}^{-1}$$

8) 0.5N solution of salt placed between two platinum electrodes, which are 5 cm apart, and having area of cross section 3 cm^2 has a conductance of 2 mho.

Calculate the i) Resistance ii) Specific conductance.

Solution: (i) As the resistance is the reciprocal of conductance, R = 1/C = 1/2 = 0.5 mho

(ii) Specific conductance, $\kappa = \frac{1}{R} \times \frac{l}{a}$

$$\kappa = C \times \frac{l}{a}$$

$$= (0.5)\,\frac{5}{3}$$

$$3.33$$

$$\kappa = 3.3 \text{ ohm}^{-1}\text{cm}^{-1}$$

9) Solutions of two electrolytes A and B each having a concentration of 0.1 M have specific conductance values 1×10^{-2} and 2×10^{-4} (ohm m)$^{-1}$ respectively. Which solution offers greater resistance to the flow of current and why?

Solution:

Solution A: Specific resistance = 1/ Specific conductance = $1/\,1 \times 10^{-2} = 100\ \Omega$ cm

Solution B: Specific resistance = 1/ Specific conductance = $1/\,2 \times 10^{-4} = 500\ \Omega$ cm

As the Specific resistance is directly proportional to the Resistance, the solution having more Specific resistance than the other will offer the greater resistance to the flow of current. Hence, in the above case, the solution B will offer the greater resistance to the flow of current.

Model questions

1. Distinguish between qualitative and quantitative methods of analysis.
2. What is instrumental methods of analysis? Give the schematic representation of an analytical instrument. Mentions its advantages.
3. Explain the principle and instrumentation of colorimeter.
4. State and derive Beer- Lambert's law.
5. Draw a neat sketch of a colorimeter & mention its applications (any two) in chemical analysis.
6. Discuss the advantages of colorimeter.
7. What is potentiometry? Discuss the principle and instrumentation of potentiometry.
8. Discuss the applications potentiometry in the acid base titration and precipitation titration.
9. Explain the application potentiometry in the redox titration.
10. In potentiometric titration of potassium dichromate against ferrous ammonium sulphate, justify why there is a steep jump in the potential at the equivalence point?
11. Draw a neat sketch of a potentiometer & mention its applications (any two) in chemical analysis.
12. How does the conductivity vary with volume of base added in the case of titration of mixture of strong acid and weak acid against a strong base?
13. Discuss the principle and instrumentation of conductivity meter.
14. Mention the advantages of conductmetric titrations.
15. Explain the variation of conductance in the following cases. i) Strong acid against strong base. ii) Weak acid against weak base iii) Weak acid against a strong base iv) Precipitation titrations
16. Numerical problems