



Dr. Parasuram Patel's Pharmacy

Div- 6

B.Tech - 3
C.Sem - 3
CAS (W3)

Dyes And Drugs

INTRODUCTION

Drugs

The word 'drug' is derived from the French word drogue which means a dry herb. In a general way, a drug may be defined as a substance used in the prevention, diagnosis, treatment or cure of disease in man or other animals. According to WHO, a drug may be defined as any substance or product which is used or intended to be used for modifying or exploring physiological systems or pathological states for the benefit of the recipient. An ideal drug should satisfy the following requirements :

- (i) When administrated to the ailing individual or host, its action should be localised at the site where it is desired to act. In actual practice, there is no drug which behaves in this way. It generally tends to distribute itself anywhere in the tissues of the host.
- (ii) It should act on a system with efficiency and safety.
- (iii) It should not have any toxicity.
- (iv) It should have minimum side effects.
- (v) It should not injure host tissues or physiological processes. *normal functioning of body*
- (vi) The cells should not acquire tolerance or resistance of the drug after some time. In actual practice, the cells which were originally susceptible to the action of a particular drug may after sometime acquire a tolerance or resistance of that drug.

Very few drugs satisfy all the above conditions. However, the search for ideal drug continues.

⇒ Classification based on their origin:

1. Drug from natural origin: Herbal or plant or mineral or marine origin
2. Drug from chemical as well as natural origin: Derived from partial herbal and partial chemicals
3. Drug derived from chemical synthesis
4. Drug derived from animal origin
5. Drug derived from microbial origin
6. Drug derived by biotechnology, Genetic-engineering, hybridoma technique
7. Drug derived from radioactive substances.

- Pharmaceutical or drug or medicines are classified in various other groups besides their origin on the basis of pharmacological properties like mode of action and their pharmacological action or activity.
- A drug may be classified by the chemical type of the active ingredient or by the way it is used to treat a particular condition.
- Each drug can be classified into one or more drug classes.
- The World Health Organization (WHO) keeps a list of essential medicines.

⇒ Classification based on therapeutic action:

1. **Antipyretics:** reducing fever (pyrexia/pyresis). For eg. Phenacetin, Paracetamol
2. **Analgesics:** reducing pain (pain killers). For eg. Aspirin, Morphin
3. **Antimalarial drugs:** treating malaria. For eg. Chloroquine, Chemoquine
4. **Antibiotics:** inhibiting germ growth. For eg. Penicillin, Streptomycin
5. **Antiseptics:** prevention of germ growth near burns, cuts and wounds. For eg. "Surgical alcohol", Dettol, Hydrogen peroxide solution to clean and deodorize wounds and ulcers.
6. **Mood stabilizers:** It is a psychiatric medication used to treat mood disorders. For eg. Lithium
7. **Hormone replacements:** wherein the patient, in the course of medical treatment, receives hormones, either to supplement or to substitute other hormones for naturally occurring hormones, For eg. Premarin.
8. **Stimulants:** These are psychoactive drugs that induce temporary improvements in either mental or physical functions or both. Examples of these kinds of effects may include enhanced alertness, wakefulness, and locomotion, among others. Examples: Methylphenidate, Amphetamine
9. **Tranquilizers:** It induces tranquillity in an individual. For eg. Diazepam.
10. **Sulpha drugs:** act against micro-organism just like antibiotics. For eg. Sulphanilamide, Sulphadiazine.



CHAPTER

ANTIBIOTICS

Introduction

The term antibiotic has been derived from the word "antibiosis" which according to the biology concept means survival of fittest i.e., a process in which one organism may destroy another to preserve itself. The term "antibiotic" was first of all introduced by Vuillemin in 1889. The term antibiotic was first defined by Waksman (1944) and which was later on modified a little by Benedict Langlykke (1947). However, the modern definition of antibiotic is :

"It is a chemical substance produced by or derived from living cells which is capable, in small concentrations of inhibiting the life processes or even destroying the micro-organisms."

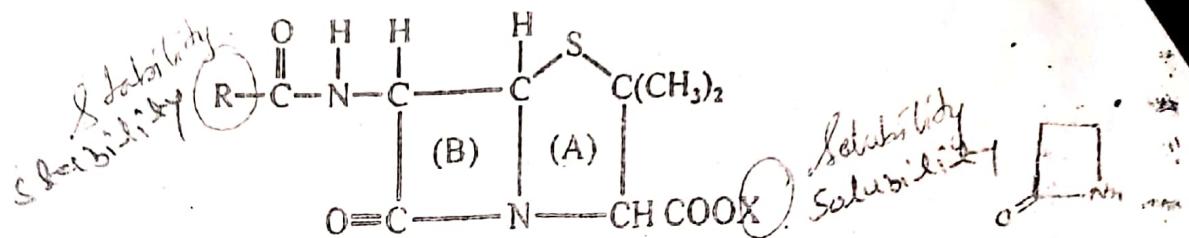
As very low concentrations of antibiotics are essential to bring about their antibiotic action they are also classified as chemotherapeutic agents. Further, the action of antibiotic is very specific, i.e., a given antibiotic has been found to be effective against certain type of micro-organisms only.

In order for a particular antibiotic to act as a therapeutic agent, it has to satisfy following conditions :

- (a) It must be effective against a bacterium or virus that cause disease.
- (b) It must not cause significant toxic side-effects.
- (c) Its stability must be appreciably high so that it can be isolated, and processed into suitable forms of dosages which are readily absorbed.
- (d) It could be stored for a long time period without appreciable loss of its activity.
- (e) The rate of detoxification and elimination from the body must be such that there exists sufficient time interval between two successive dosages and during that period a proper concentration level has to be maintained.
- (f) The antibiotic should be completely eliminated from the system soon after its administration has been stopped.

..... some important characteristic.

Introduction: Penicillin is the name given to the antibiotic of penicillins group which have molecular formula $C_9H_{11}N_2O_4SR$ and differ only in the nature of R. The general structure of penicillins is



In the above structure of penicillin, the thiazolidine ring nucleus (A) is fused to a β -lactam ring (B) which is attached to a side chain ($R-C=O$). Any chemical modification of the β -lactam or thiazolidine rings destroys the anti-bacterial activity of the molecule, e.g., Penicillinase breaks the β -lactam ring.

In the above structure of penicillin, X is sodium, potassium, aluminium, procaine, benzathine or free acid. The various salts of penicillins determine the solubility of the antibiotic. The very soluble sodium salt is available for intravenous use, the benzathine salt, very slowly soluble, is absorbed gradually from an intramuscular injection depot over a 2-to 4-week period. On the basis of various values of R, there are ~~several~~ naturally occurring penicillins.

Chemical Name	Other Names	R
1. Pent-2-enylpenicillin	Penicillin-I or F	$-CH_2CH=CH-CH_2CH_3$
2. Benzylpenicillin	Penicillin-II or G	$-CH_2C_6H_5$
3. p-Hydroxybenzylpenicillin	Penicillin-III or X	$-CH_2C_6H_4OH (1, 4)$
4. n-Heptylpenicillin	Penicillin-IV or K	$-(CH_2)_6CH_3$
5. n-Amylpenicillin	Dimethyl Epenicillin	$-(CH_2)_3CH_3$
6. Phenoxyethyl penicillin	Penicillin-V	$-CH_2OC_6H_5$

Modification of the prosthetic group R, attached to the 6-aminopenicillanic acid portion of the penicillin molecule, determines the relative stability of the penicillin to penicillinase. The more complex prosthetic groups impart a greater ~~ability~~ ^{stability} to hydrolysis by penicillinase.

Activity of penicillin: penicillin is active against Gram +ve bacteria.

⇒ Penicillin is a group of antibiotics derived from Penicillium fungi.

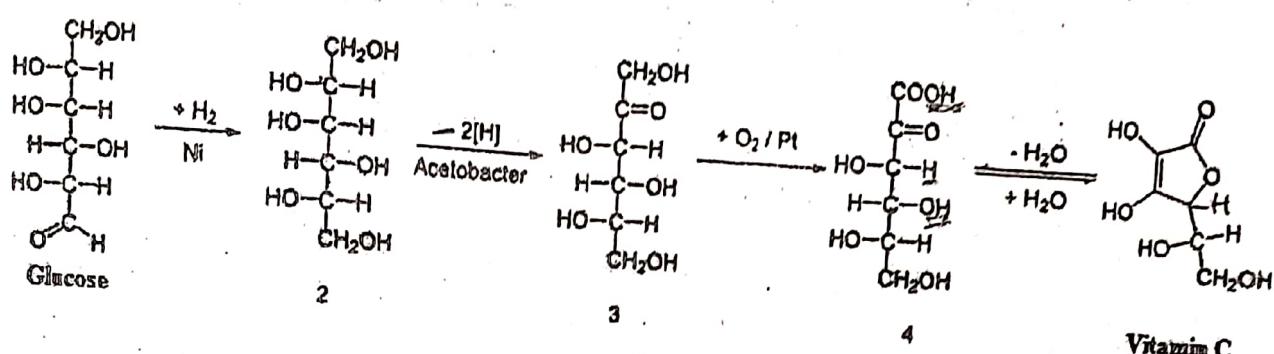
Vitamin C

(7)

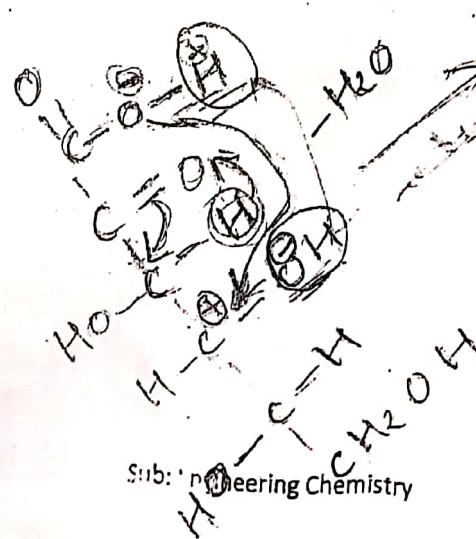
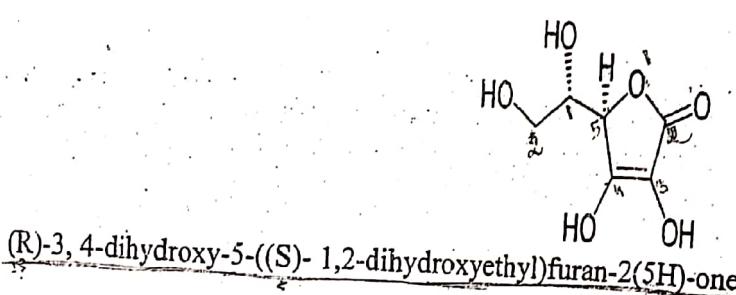
Structure of Vitamin-C or L-ascorbic acid or Ascorbate:

Vitamin C or L-ascorbic acid is a water-soluble vitamin that supports normal growth and development. Vitamin C also helps our body absorb Iron. As our body doesn't produce or store vitamin C, it's important to include vitamin C in our diet from food and other sources. Some animals can make their own vitamin C. Good sources of vitamin C are fresh fruits and vegetables, especially citrus fruits. Vitamin C can also be made in laboratory. Most experts recommend getting vitamin C from a diet high in fruits and vegetables rather than taking supplements.

Synthesis of Vitamin C from Glucose:



IUPAC name for Vitamin C:



Uses of Vitamin C:

- **Iron absorption.** Administering vitamin C along with iron can increase how much body absorbs in adults and children.
- **Age-related vision loss** (age-related macular degeneration; AMD). Taking vitamin C combination with zinc, vitamin E, and beta-carotene daily seems to help prevent vision loss slow the worsening of AMD in patients with advanced AMD. There is not enough evidence to know if this combination helps people with less advanced macular disease or if it prevents AMD. Using vitamin C with other antioxidants, but without zinc, does not seem to have any effect on AMD.
- **Decreasing protein in the urine** (albuminuria). Taking vitamin C plus vitamin E can reduce protein in the urine in people with diabetes.
- **Cancer.** Consuming vitamin C in the diet through fruits and vegetables decreases the risk of developing mouth cancers and other cancers.
- **Common cold.** Taking high doses of vitamin C might shorten the course of the cold by 1 to 1.5 days in some patients. Taking vitamin C is not effective for preventing the common cold.
- **Chronic pain condition** (complex regional pain syndrome). Taking vitamin C after a wrist fracture seems to decrease the risk of developing a chronic pain condition called complex regional pain syndrome.
- **Kidney problems** Taking vitamin C before and after an angiography seems to reduce the risk of developing kidney problems.
- **Gallbladder disease.** Vitamin C helps to prevent gallbladder disease in women.
- **High blood pressure.** Taking vitamin C does not seem to affect blood pressure.
- **Lead poisoning.** Consuming vitamin C in the diet seems to lower blood levels of lead.
- **Sunburn.** Taking vitamin C along with vitamin E seems to prevent sunburn.
- **Wrinkled skin.** Skin creams containing vitamin C seem to improve wrinkles in facial skin that is aged by sun exposure.

Deficiency of Vitamin C:

Vitamin C deficiency leads to Scurvy.

In adults,

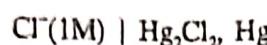
→ Initial symptoms of scurvy include:

- Feeling very tired and weak all the time (fatigue)
- Pain in ~~your~~ limbs, particularly ~~your~~ legs
- Appearance of small red-blue spots on ~~your~~ skin
- Swollen gums, with frequent bleeding

→ In infants,

- Lack of appetite
- Poor weight gain
- Diarrhea

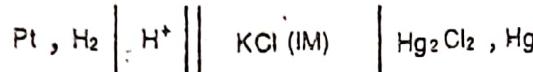
The calomel electrode is represented as



and the half-cell reaction is



The emf of the cell



at 25°C is + 0.280 V. That is, the calomel electrode emf with respect to the standard hydrogen electrode is + 0.280 V. This means that 0.280 must be added to any electrode potential measured against a calomel electrode. This would give the standard potential on the standard hydrogen scale.

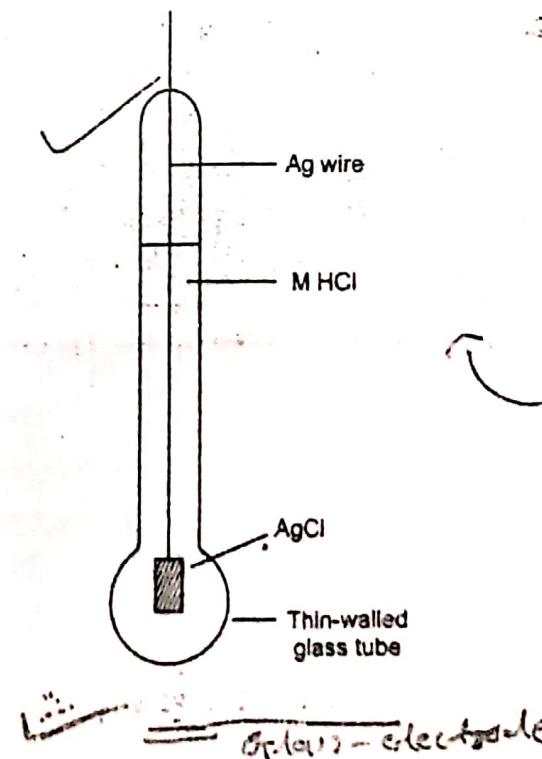
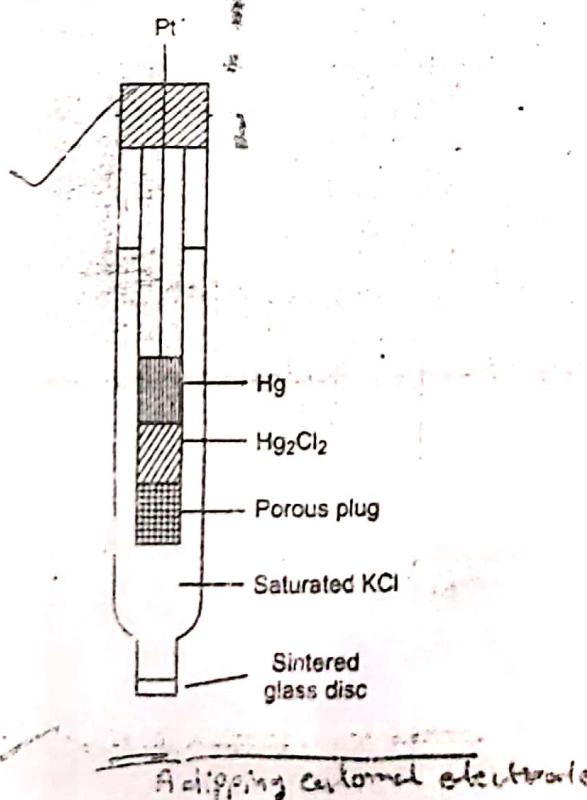
Note. The potential of the calomel electrode depends on the concentration of KCl solution taken in the half-cell. Thus for 0.1M KCl solution emf is 0.3338 Volt; for 1M solution emf is 0.2800 Volt; and for saturated KCl solution emf is 0.2415 Volt.

Determination of emf of the standard zinc half-cell using calomel electrode

The zinc half-cell is connected with the standard calomel electrode as shown in Fig. 29.14. The emf of the complete cell is then measured with the help of a voltmeter. It is found to be 1.040 V. Since zinc forms the negative electrode of the cell, its emf with respect to calomel electrode will be -1.040 V. The addition of 0.280 gives the standard electrode potential of zinc.

$$(-1.040 + 0.280) = -0.76 \text{ V}$$

~~standard calomel electrode~~ Calomel electrode For many purposes, a calomel electrode is manufactured as a self-contained unit. It is used by simply dipping the tip of the electrode in the solution of another electrode whose emf is to be determined. This type of electrode is often referred as the dipping calomel electrode (Fig. 29.15).



A dipping calomel electrode

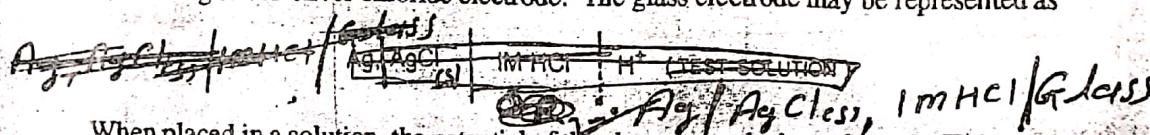
B.P.(av)-electrode

(Hg) The mercury and calomel (Hg_2Cl_2) are held in a narrow central tube by a porous cotton wool plug. A platinum wire dips into the mercury. The KCl saturated solution contained in the electrode makes contact with the other electrode solution through a sintered glass disc. This disc functions as a 'salt bridge' between the two electrode solutions. Thus a galvanic cell is set up and its emf is measured with the help of a voltmeter.

The Glass Electrode

A commonly used ~~standard~~ electrode is the so-called glass electrode. Its emf is determined by coupling with a standard calomel electrode (SCE). The glass electrode provides one of the easiest methods for measuring the pH of a given solution.

A simple type of glass electrode (Fig. 29.16) consists of a glass tube having a thin-walled bulb at the lower end. The bulb contains a 1M HCl solution. Sealed into the glass-tube is a silver wire coated with silver chloride at its lower end. The lower end of this silver wire dips into the hydrochloric acid, forming silver-silver chloride electrode. The glass electrode may be represented as

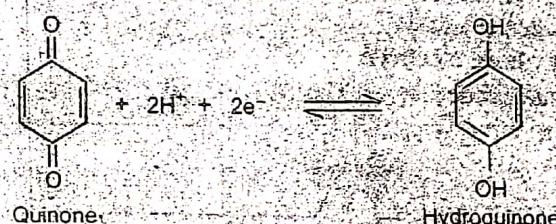


When placed in a solution, the potential of the glass electrode depends on the H^+ ion concentration of the solution. The potential develops across the glass membrane as a result of a concentration difference of H^+ ions on the two sides of the membrane. This happens much in the same way as the emf of a concentration cell develops.

The potential of a glass electrode can be determined against a standard calomel electrode (SCE).

Quinhydrone Electrode

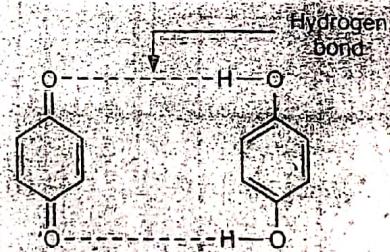
It is a widely used ~~secondary~~ standard electrode. It involves the redox reaction between quinone (Q) and hydroquinone (QH_2),



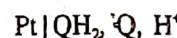
or, simply



The hydroquinone half-cell consists of a platinum strip immersed in a saturated solution of quinhydrone at a definite H^+ ion concentration (buffered solution). Quinhydrone is a molecular



compound which gives equimolar amounts of quinone and hydroquinone in solution. The electrode system may be represented as



Saturated calomel electrode (SCE)

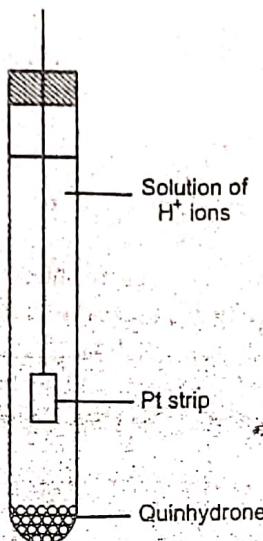


Fig. 29.17. The Quinhydrone Electrode.

The potential developed is measured against a hydrogen electrode or calomel electrode. The emf with respect to a standard hydrogen electrode is 0.2875 V at 25°C.

DETERMINATION OF pH OF A SOLUTION

A half-cell is set up with the test solution as electrolyte. The emf of the cell depends on the concentration of H^+ ions or pH of the solution. The emf of the half-cell is determined by coupling it with another standard half-cell and measuring the emf of the complete cell. The commonly used standard electrodes are :

- (a) The hydrogen electrode
- (b) The quinhydrone electrode
- (c) The glass electrode

Using Hydrogen electrode

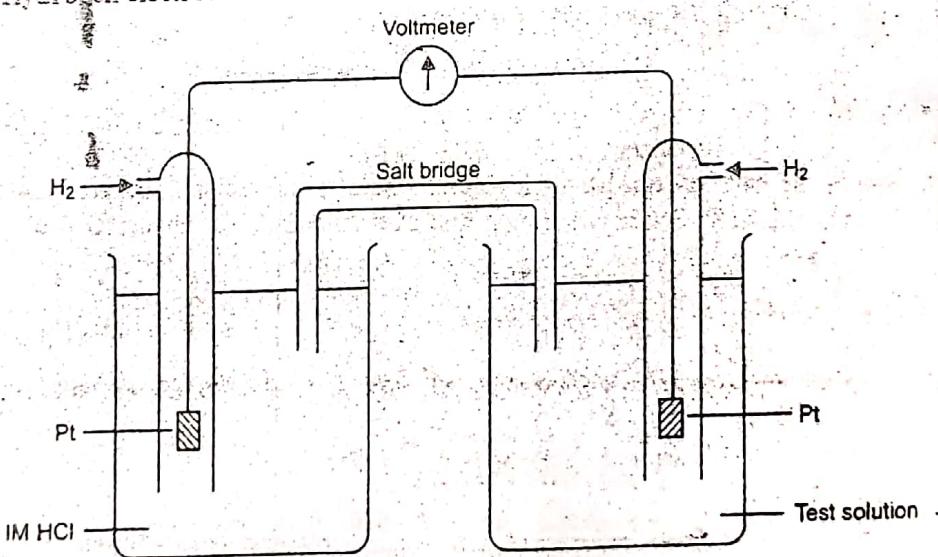


Fig. 29.18. Determination of pH with Hydrogen electrode.

Q. 2. The Glass electrode

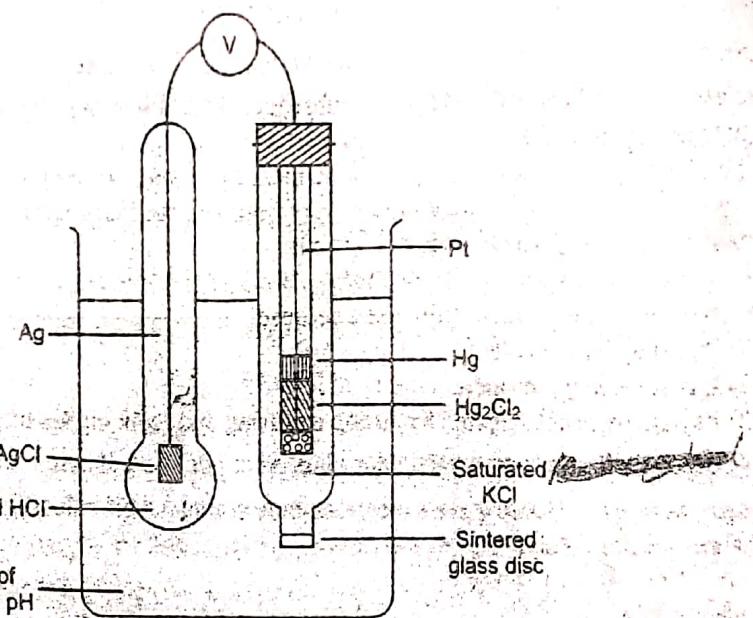
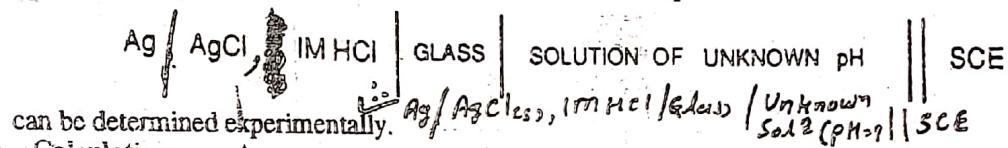


Fig. 29.20. A glass electrode coupled with standard calomel electrode.

A glass electrode is immersed in the solution of unknown pH. It is coupled with a standard calomel electrode (SCE) as shown in Fig. 29.20. The emf of the complete cell



Calculations

The potential of the glass electrode, E_G , at 25°C is given by the equation

$$E_G = E_G^\circ - \frac{2.303 RT}{nF} \log [H^+] \quad E_G = E_G^\circ + \frac{2.303 RT}{nF} \text{ pH}$$

$$E_G = E_G^\circ - \frac{2.303 RT}{nF} \log [H^+] \quad = E_G^\circ + 0.0591 \text{ pH}$$

We know that

$\log [H^+]$
i.e.,

$$R = 8.314 \text{ J mol}^{-1} \text{ K}^{-1}$$

$$T = 25^\circ \text{C} = 298 \text{ K}$$

$$F = 96,500 \text{ C}$$

$$n = 2 \text{ (e.g. 1 mol)}$$

Substituting the value of E_G from (A)

$$E_{\text{cell}} = E_{\text{SCE}} - (E_G^\circ + 0.0591 \times \text{pH})$$

or

$$\text{pH} = \frac{E_{\text{SCE}} - E_G^\circ - E_{\text{cell}}}{0.0591} \quad \dots (B)$$

Value of the potential of calomel electrode is known while E_{cell} can be found experimentally. Therefore, we can find pH of a given solution if E°_{G} is known. It can be determined by using a solution of known pH in the cell and measuring E_{cell} . This value of E°_{G} is constant for a particular glass electrode and can be used for any subsequent determinations of pH of unknown solutions with the help of equation (B).

The potential of the cell, E_{cell} , cannot be measured using ordinary potentiometer or voltmeter as the resistance of the glass membrane is very high and the current small. Therefore, an electronic voltmeter is required which reads pH directly.

Merits and demerits of Glass electrode :-

A glass electrode is universally used because

- (1) It is simple to operate.
- (2) It is not easily poisoned.
- (3) Its activity is not affected by strong oxidising and reducing agents.

(4) Since E°_{G} depends on a particular glass electrode used, it is not a universal constant and also changes with time. Hence a glass electrode ~~only measures selective~~ ^{only compares} pH values while the hydrogen electrode measures pH absolutely.

Using Quinhydrone electrode

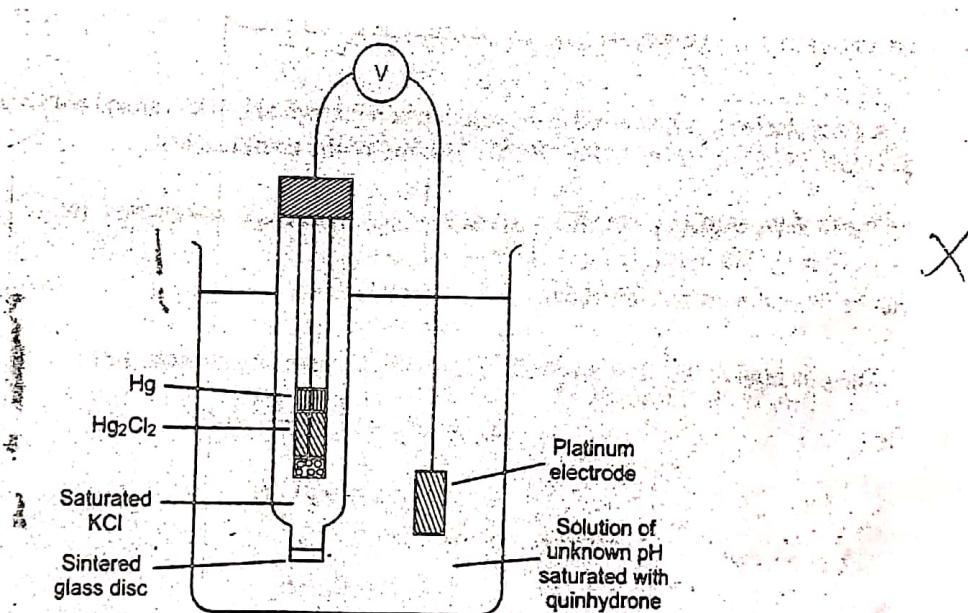
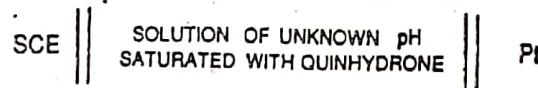


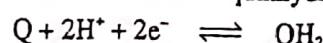
Fig. 29.21. Quinhydrone electrode coupled with standard calomel electrode.

A platinum electrode is suspended in a solution whose pH is to be determined. The solution is saturated with quinhydrone compound. This half-cell is then combined with a standard calomel electrode (SCE). The complete cell can be represented as



The emf of the complete cell (E_{cell}) is determined with the help of a voltmeter.

Calculations. The reduction half-cell reaction of quinhydrone electrode is



The exact meaning of the "p" in "pH" is disputed, but according to the Carlsberg Foundation pH stands for "power of hydrogen". Another suggestion of "p" meant potential hydrogen. It is also suggested that Sorenson used the letters "p" simply to label the power of test solution (p).

Mathematically pH can be defined as:

$$pH = -\log[H^+]$$

pH meter:

is an electronic device used for measuring the pH (acidity or alkalinity) of a liquid. A pH meter provides a value as to how acidic or alkaline a liquid is. A typical pH meter consists of a special measuring probe (a glass electrode) connected to an electronic meter that measures and displays the pH reading.

Basic principle:

measures the concentration of hydrogen ions (H^+).

Acids dissolve in water forming positively charged hydrogen ions (H^+). The greater this concentration of hydrogen ions, the stronger the acid is.

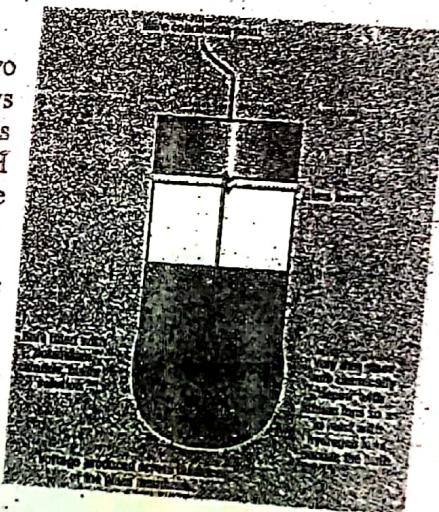
Similarly alkali or bases dissolve in water forming negatively charged hydroxyl ions (OH^-). The stronger base is the higher the concentration of negatively charged hydroxyl ions are.

A pH value of 7 indicates a neutral solution. Pure water should have a pH value of 7. Now pH values less than 7 indicate an acidic solution while a pH value greater than 7 will indicate an alkaline solution. A solution with pH value of 1 is highly acidic and a solution of pH value of 14 is highly alkaline.

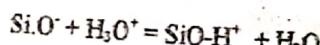
Instrumentation:

A pH meter will be made up of a probe, which itself is made up of two electrodes. This probe passes electrical signals to a meter which displays the reading in pH units. The glass probe has two electrodes because one is a glass sensor electrode and the other is a reference electrode. Some pH meters do have two separate probes: one would be the sensor electrode and the other the reference point.

Both electrodes are hollow bulbs containing a KCl solution with a $AgCl$ wire suspended into it. The glass sensing electrode has a bulb made up of a very special glass coated with Si and metal salts. This glass sensing electrode measures the pH as the concentration of H^+ surrounding the tip of the thin walled glass bulb. The reference electrode has a bulb made up of a non-conductive glass or plastic.



The potential difference between the inside of the glass electrode and the outside is caused by the oxides of silicon inside the glass:



pH Meter Operation:

When you place the probe or probes into a solution, the hydrogen ions in the solution will move toward the glass electrode replacing some of the metal ions on the glass coating. This will cause a tiny voltage across the glass bulb. This voltage is picked up by the silver wire and passed to the voltmeter where the voltmeter will amplify and change the voltage value into a value we can use, pH units. The greater the concentration of hydrogen ions the greater the increase in voltage will be. This greater voltage corresponds to an increase in acidity causing the reading on pH meter to decrease. Remember the more acidic the lower the pH value. Similarly a decrease in hydrogen ions or increase in hydroxyl ions indicates an increase in alkalinity, causing a decrease in voltage and therefore an increase in the pH.

reading.

Calibration: To ensure accurate measurements from your pH meter the meter will need to be calibrated both before its first use and on an ongoing basis. This is usually done by dipping the probe into a buffer solution of a known pH of 4, 7 and 10 and following the calibration steps based on our specific pH meter.

pHmetry experiment:

DETERMINATION OF AN ACID; USING A pH METER

The pH meter is an instrument that measures the pH of a solution and affords a direct method of obtaining a titration curve. A titration curve is a graph of measured pH values versus the volume (milliliters) of titrant added. The figure below is an example of a titration curve, illustrating the numerous data points and the best smooth curve drawn through the points. The equivalence point is the point at which an equal amount of acid has been added to the amount of base present or vice versa. The equivalence point occurs on the titration curve in the region where there is a relatively large change in pH with a relatively small change in volume. The steeper the curve in the region of the equivalence point the more precisely it may be established.

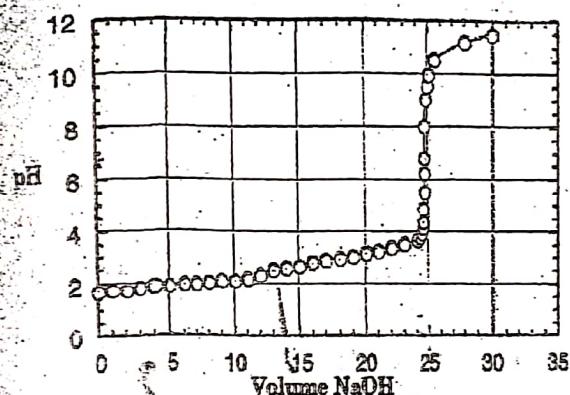
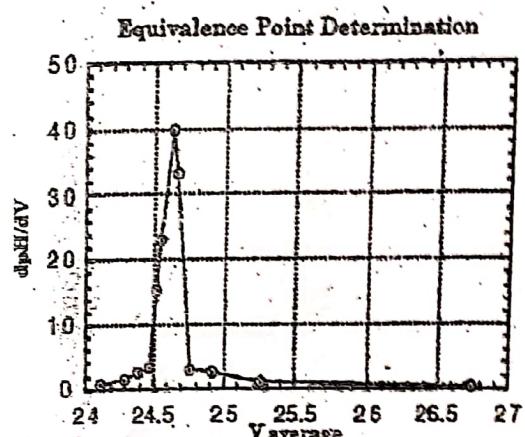


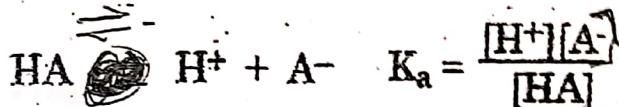
Figure 1. Titration Curve of acid HA



Selection of the equivalence point

To determine the equivalence point a graph is constructed of $d\text{pH}/dV$ vs. V_{mL} . The graph above illustrates this method. The volume at the point where the graph reaches the maxima is the equivalence point of the titration.

The ionization constant, K_a , for a generic acid HA:



taking \log both sides

now

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

OR

Therefore when $[\text{A}^-] = [\text{HA}]$

$$\text{pH} = pK_a$$

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

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



POTENTIOMETRY

ELECTROMOTIVE FORCE

POTENTIOMETRIC TITRATIONS

In a potentiometric titration, a suitable electrode immersed in the solution to be titrated acts as the 'indicator'. The indicator electrode is paired with a reference electrode and the two electrodes are connected to an electronic voltmeter. The emf of the indicator electrode changes gradually with the change of concentration of ions caused by the addition of titrant from the burette. The equivalence point is indicated by a sharp change in electrode potential.

Since the reference electrode potential has a constant value, any change in the indicator electrode potential is reflected by a similar change in the cell potential. Therefore, the equivalence point can be found by plotting a graph between the cell emf and the volume of titrant added from the burette. A sharp rise of the curve shows the equivalence point and the corresponding volume on the graph is the volume of the solution used for the titration.

The potentiometric titrations may be of three types :

- (a) Acid-base titrations
- (b) Oxidation-reduction titrations
- (c) Precipitation titrations

Acid-base Titrations

The apparatus used for potentiometric acid-base titrations is shown in Fig. 29.22. A hydrogen electrode or a glass electrode is immersed in solution of the acid whose strength is to be determined. The glass electrode is coupled with a standard calomel electrode. The cell thus formed is connected to the potentiometer or electronic voltmeter. When alkali is added, pH of the solution changes. The emf of the cell also changes with pH of the solution in accordance with the relation:

$$E = E^\circ + 0.0591 \text{ pH}$$

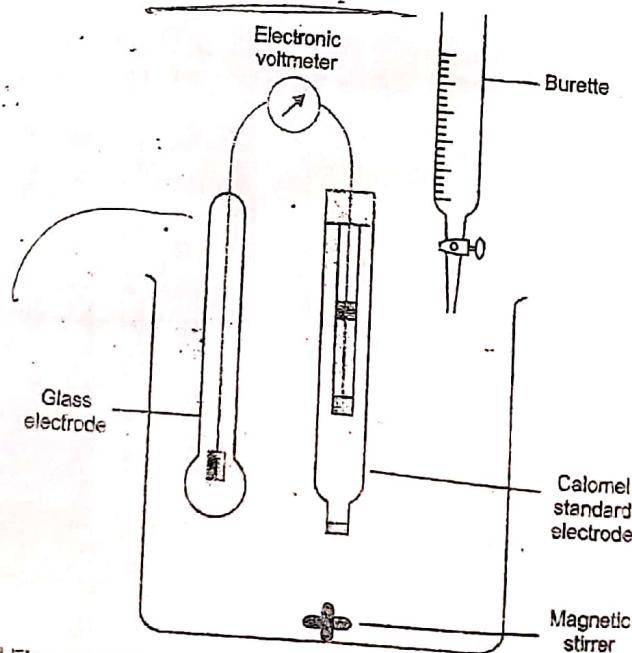


Figure 29.22

Apparatus for potentiometric acid-base titrations.

The standard alkali solution is then added from the burette in small volumes. After each addition, the emf of the cell is recorded. The emf is then plotted against the volume of alkali added. The shape of the curve for the titration of a strong acid against strong alkali (HCl versus NaOH) is shown in Fig.

Q8

29.23 (a). The steepest portion of the curve indicates the equivalence point. However, when the solutions are very dilute, or weak acids or bases, are involved, the steepness of the curve is less marked and it is difficult to judge the end-point. In such a case, we plot the slope of the curve, $\Delta E/\Delta V$ against the volume of alkali used. The maximum of the curve indicates the end-point.

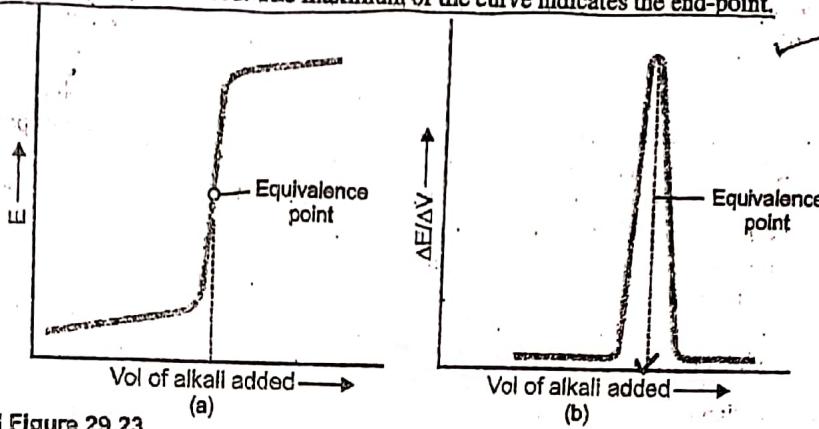


Figure 29.23
Potentiometric titration curve of an acid and a base.

Oxidation-reduction Titrations

The titration of ferrous ions (Fe^{2+}) with ceric ions (Ce^{4+}) is an example of oxidation-reduction (or redox) titration. Fe^{2+} ion is oxidised to Fe^{3+} ion, while Ce^{4+} is reduced to Ce^{3+} ion.



This titration can be carried in the apparatus shown in Fig. 29.24. The indicator electrode is a shiny platinum strip dipping in the solution of Fe^{2+} ions, and it is connected to a standard calomel electrode. The Ce^{4+} solution is added from the burette and the cell potential, E , recorded after each addition.

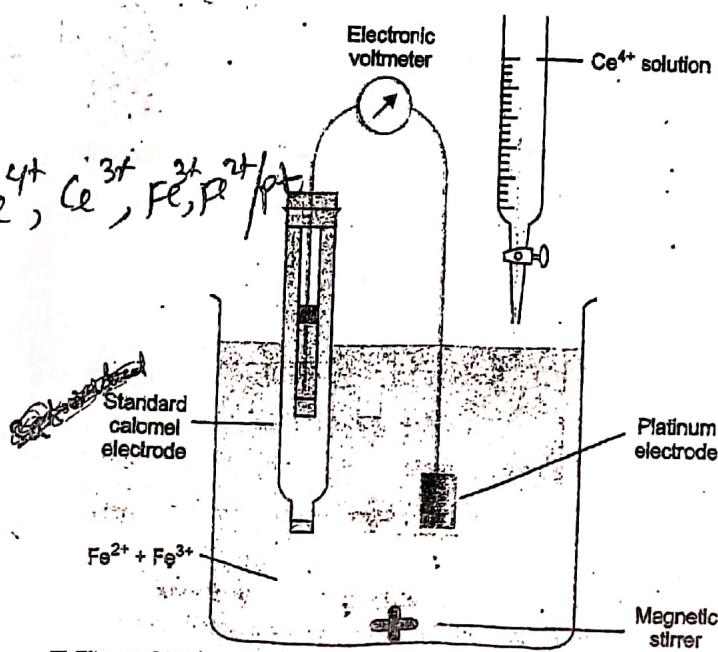


Figure 29.24
Apparatus for potentiometric titration of Fe^{2+} with Ce^{4+} .

The potential of the platinum electrode depends on the ratio $[Fe^{3+}]/[Fe^{2+}]$. The potential of the cell, E, also changes with the change of the ratio $[Fe^{3+}]/[Fe^{2+}]$. Therefore, the cell potential changes with the addition of Ce^{4+} ions from the burette. Fig. 29.25 shows how the potential of the cell changes during the titration. At the equivalence point there is a sharp rise of potential which indicates the end-point.

Potentiometric titrations of this type are particularly useful for coloured solutions in which an indicator cannot be employed.

Precipitation Titration

A typical precipitation titration is that of sodium chloride solution against silver nitrate solution. The apparatus set up for the purpose is shown in Fig. 29.26. A silver electrode dipping in the unknown sodium chloride solution is coupled with a calomel electrode through a salt bridge. However calomel electrode were in direct contact with a solution containing excess silver ions, chloride seep through the sintered base and react to form an insoluble layer of silver chloride.

Any change in the cell potential is due to changes in concentration of Ag^+ ions around the electrode.

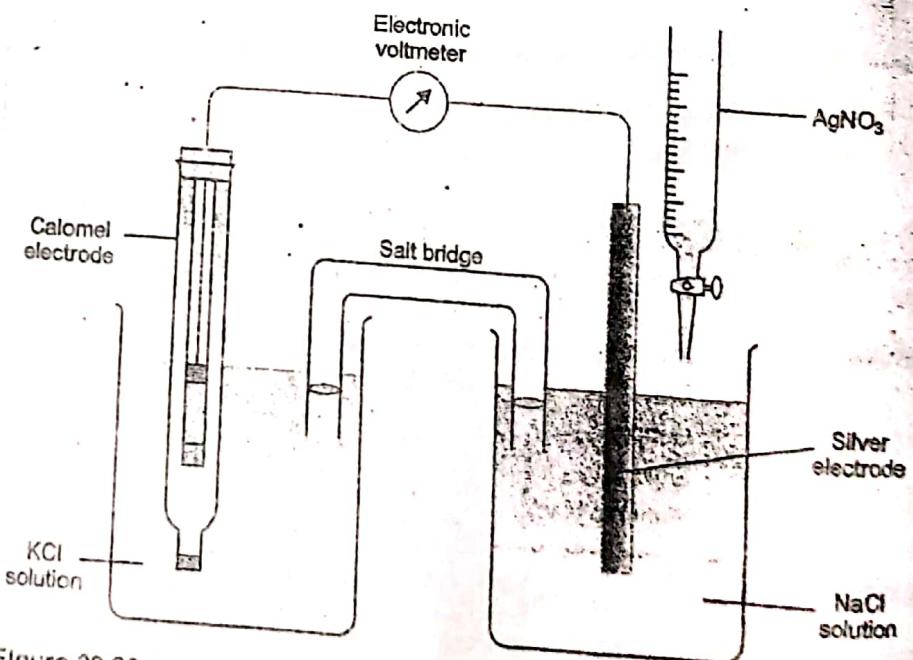
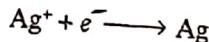


Figure 29.25

Potentiometric titration curve of Fe^{3+} ions and Ce^{4+} ions.

Initially the concentration of Ag^+ ions will be zero. But as silver nitrate is added from the burette silver chloride is precipitated. Now the solution will contain a small concentration of Ag^+ ions formed by the slight dissociation of silver chloride. This concentration will increase slightly as Cl^- ions

(11)

(12)

1025

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removed in order to maintain the solubility product $K_{sp} = [Ag^+][Cl^-]$. After the equivalence point the concentration of Ag^+ ions and, therefore the silver electrode potential will rise very sharply owing to the presence of excess of Ag^+ ions. The volume of $AgNO_3$ solution used to reach the equivalence point as shown in Fig. 29.27.

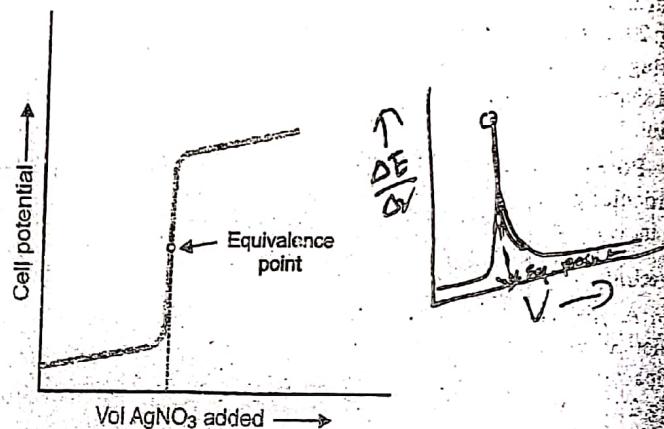


Figure 29.27
Potentiometric titration curve.

OVERVOLTAGE OR OVERPOTENTIAL

In an electrolysis cell the discharge of an ion on the cathode would occur at the standard half-reaction potential indicated in Table 29.1. Thus the H^+ ions will discharge at the cathode at $E^\circ = 0.00$ V. It has been experimentally found to be nearly true using platinum black (i.e., finely divided platinum) as the cathode. However with other metal electrodes, for example, mercury and zinc, the voltage needed for the discharge of H^+ ions (evolution of H_2) is considerably higher than 0.00 V. The difference between the observed voltage (E) and the standard half-reaction voltage (E°) is called the hydrogen overpotential. The values for hydrogen overpotentials on some metals are listed in Table 29.2.

TABLE 29.2 HYDROGEN OVERPOTENTIALS ON SOME METAL CATHODES IN DILUTE H_2SO_4

Cathode	Overpotentials
Mercury	0.78 V
Zinc	0.70 V
Copper	0.23 V
Silver	0.15 V
Platinum black	0.00 V

The hydrogen potentials are particularly well known. But an overpotential exists for any gas on any electrode and is defined as : the additional potential, over and above the standard electrode potential, which is needed to secure the evolution of the gas.

$$\text{Overpotential} = E - E^\circ$$

How Overvoltage Occurs ?

The overpotentials arise on account of the energy required for the adsorption of gas to occur on the metal surface. The mechanism of, for example, of liberation of hydrogen gas by the discharge of H^+ ions is

CONDUCTOMETRIC TITRATIONS

Reactions follow the

Id be

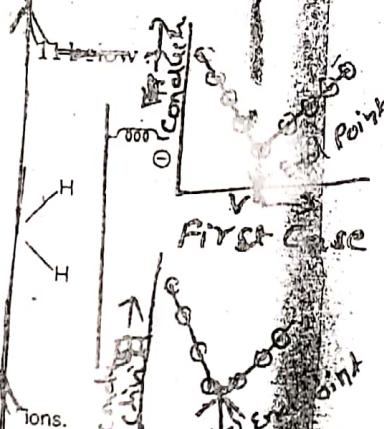
viscosity of water
(η) increases.

case of pressure due

proportional to the

tric constant of the
their conductance.

times greater than
and hydroxyl ions
high, proton jumps
ion transfer, a more
on to another takes
sway through the



example, liquor ammonia
(namely, $\text{NH}_3 + \text{H}_2\text{O} \rightleftharpoons \text{NH}_4^+ + \text{OH}^-$)

ions and anions.

CHARGE & EQUIVALENCE POINTS

17. CONDUCTOMETRIC TITRATION

(2)

During the course of titration of an analyte with a titrant, the number of ions in the solution changes and identity of ions also changes because of this conductance of the electrolytic solution also changes. If the change in conductance at the equivalence point is rapid it can be utilized for the detection of end point.

17.1 Conductometric Titration

It is a method of volumetric analysis based on the change in conductance of the solution, at the end point.

17.2 Advantages of Conductometric Titrations

(i) Prior knowledge of strength of acids and bases is not required here, which is a must for ordinary volumetric titrations for the proper selection of indicators.

(ii) Indicators are not successful for the detection of end points for the titrations involving colored solutions, but conductometric titrations can be used in such cases.

(iii) End point determination is easy in conductometric titrations as it is determined graphically. Thus no keen observation is required for end point detection.

(iv) Conductometric titrations are very useful in

(a) dilute solutions

(b) mixtures of acids or bases

(c) titrating weak acids/base which otherwise do not give sharp end point.

17.3 Procedure of Conductometric Titrations

In a conductometric titration the titrant is added from the burette and the conductivities are measured during the course of the titration. The values of the conductivities are then plotted against the volume of the titrant. There are two possibilities viz. reaction is quantitative and is not quantitative. In the first case, measured conductivity is a linear function of the concentration of ions present. Two lines will be obtained in this case which intersect each other at equivalence point.

In the second case, when the reaction is not quantitative (due to hydrolysis, dissociation of the product or appreciable solubility in case of precipitations), there may be some curvature in the curve or in line near the end point. In these cases the equivalence point is determined by extrapolating these portions of lines or curves.

In order to get straight line graphs, it is essential that the total volume of the solutions remains constant during the titration. The concentration of the titrant must be 10 times as the solution being titrated. This is done to keep the volume change small.

Since the conductivity of electrolytic solutions increases with rise in temperature, it is therefore, desirable to carry out conductometric titrations in a constant temperature bath hence thermostat should be used.

17.4 Types of Conductometric Titrations

(A) Acid-base titrations : Because of the high conductance of hydroxide and hydronium ions compared with the conductance of other ions, end point of acid-base titrations can be easily determined conductometrically.

Titration in which conductance measurements are used to determine the end-point of acidic reaction, some displacement reactions, or precipitation reactions are called Conductometric Titrations. In these titrations a very large increase is taken in fact that the conductance of a solution at a constant temperature depends upon the number of ions present in it and the mobility.