Title of Topic: Potentiometry- I and II

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Potentiometry is the field of electro analytical chemistry in which potential is measured under the conditions of no current flow. It is a classical analytical technique with roots before the twentieth century. However, the rapid development of new selective electrodes and more sensitive and stable electronic components since 1970 has tremendously expanded the range of analytical applications of potentiometric measurements. Selective potentiometric electrodes are currently widely used in many fields, including clinical diagnostics, industrial process control, environmental monitoring, and physiology.
The measured potential may then be used to determine the analytical quantity of interest, generally the concentration of some component of the analytic solution. The potential that develops in the electrochemical cell is the result of the free energy change that would occur if the chemical phenomena were to proceed until the equilibrium condition has been satisfied.

These methods rely on the measurement of E-cell for quantification. A number of common reference and ion selective electrodes are reviewed along with general calculations and analytical approaches.

When a potentiometric titration is being performed, interest is focused upon changes in the EMF of an electrolytic cell as a titrant of known concentration is added to a solution of unknown. The method can be applied to all titrimetric reactions provided that the concentration of at least one of the substances involved can be followed by means of a suitable indicator electrode. The critical problem in a titration is to recognize the point at which the quantities of reacting species are present in equivalent amounts. The titration curve can be followed point by point, plotting as ordinate, successive values of the cell EMF (pH) vs the corresponding volume of titrant added.

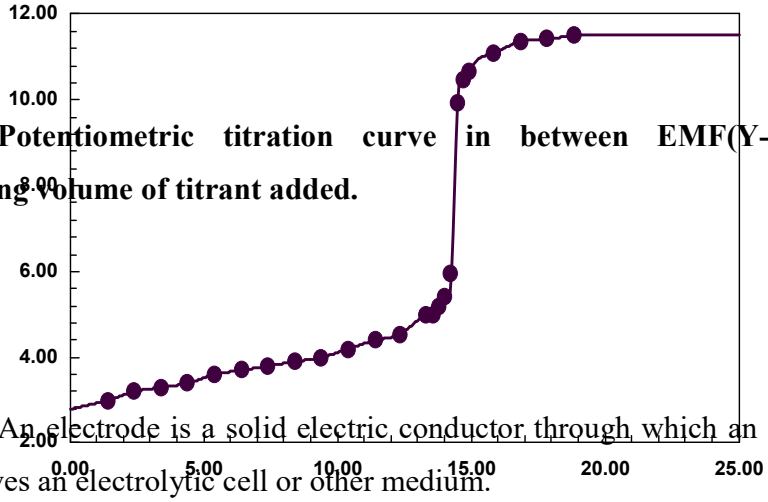

Figure 1 Potentiometric titration curve in between EMF(Y-axis) vs the corresponding volume of titrant added.

Module 1

Electrodes: An electrode is a solid electric conductor through which an electric current enters or leaves an electrolytic cell or other medium.

Ion Selective Electrodes (ISE)

Ion Selective Electrodes (ISE) are membrane electrodes that respond selectively to ions in the presence of others. These include probes that measure specific ions and gasses in solution. The most commonly used ISE is the *p*H probe. Other ions that can be measured include fluoride, bromide, cadmium and gasses in solution such as ammonia, carbon dioxide and nitrogen oxide.

An Ion Selective Electrode measures the potential of a specific ion in solution. (The *p*H electrode is an ISE for the Hydrogen ion.). This potential is measured against a stable reference electrode of constant potential. The potential difference between the two electrodes will depend upon the activity of the specific ion in solution. This activity is related to the concentration of that specific ion, therefore allowing the end-user to make an analytical measurement of that specific ion. Several ISE's have been developed for a variety of different ions.

Ion-selective electrodes are mainly membrane-based devices, consisting of permselective ion-conducting materials, which separate the sample from the inside of the electrode. On the inside is a filling solution containing the ion of interest at a constant activity. The membrane is usually nonporous, water insoluble, and mechanically stable. The composition of the membrane is designed to yield a potential that is primarily due to the ion of interest (via selective binding processes, e.g., ion exchange, which occur at the membrane- solution interface). The trick is to find a membrane that will selectively bind the analyte ions, leaving co-ions behind. Membrane materials, possessing different ion recognition properties, have thus been developed to impart high selectivity.

The use of Ion Selective Electrodes offer several advantages over other methods of analysis.

First, the cost of initial setup to make analysis is relatively low. The basic ISE setup includes a meter (capable of reading millivolts), a probe (selective for each analyte of interest), and various consumables used for *p*H or ionic strength adjustments. The expense is considerably less than other methods, such as Atomic Adsorption Spectrophotometry or Ion Chromatography.

Ion Selective Electrodes work on the basic principal of the galvanic cell. By measuring the electric potential generated across a membrane by "selected" ions, and comparing it to a reference electrode, a net charge is determined. The strength of this charge is directly proportional to the concentration of the selected ion. The basic formula is given for the galvanic cell:

$$Ecell = Eise - Eref$$

The potential for the cell is equivalent to the potential of the ISE minus the potential of the reference electrode.

In Ion Selective Electrodes the sensing part is usually made from an ion specific membrane, coupled together with a reference electrode (either separate or as a combination). This membrane can be prepared as:

- **Solid membrane** (e.g. glass membrane or crystal membrane)
- **Liquid membrane** (based on e.g. classical ion-exchanger, neutral or charged carrier)
- **Membrane in a special electrode** (gas-sensing or enzyme electrode). Typically such a membrane contains an analyte-selective component which is responsible for the recognition process.

According to the nature of the binding sites, the membranes can be classified as: membranes containing fixed sites and membranes containing mobile ion-exchangers or ionophores (carriers). The binding sites are incorporated in the membrane matrix, which determines the internal polarity, lipophilicity, transport and other mechanical properties of the membrane.

Glass-membrane electrodes

The best known example of this type of electrodes is the glass electrode (*p*H electrode), in which the anionic fixed sites are created by defects in the SiO_2 membrane and the cationic vacancies due to the nonsilicon constituents of glass. When the glass membrane is exposed to water a thick hydrated layer is formed (5-100 nm), which exhibits improved mobility of the ions. The concentration of anionic binding is estimated between 3 and 10M, which determine the wide linear range of the ISE calibration curve (typically 2-12 *p*H). The membrane is manufactured as a bulb of typical wall thickness of 0.05-0.2 mm (the optimum thickness is the result of compromise between the mechanical properties and electrical resistance). Two processes occur during the interaction of glass hydrated membrane and the sample solutions are: ion-exchange and diffusion of all participating ions.

Solid-state-membrane electrodes

Other types of membranes with fixed sites include single crystals of sparsely soluble salt and heterogeneous membranes in which the insoluble salt is incorporated in some suitable inert binder. In order to consider these layers at equilibrium it is necessary to use saturated solutions. In practice, these electrodes are applied in non-saturated solutions, so

in this case the insoluble membrane slowly dissolves. Insoluble inorganic matererials as: Ag_2S, CuS, CdS, PbS, LaF_3, AgCl, AgBr, AgI and AgSCN have all been tested as cation exchange membranes, incorporated into an electrode body in the form of single crystal or compressed powder discs. These materials are ionic conductors, though the conductivity is extremely small and mainly takes place through the migration of point defects in the lattice. The response time of this membrane can be increased by incorporating aliovalent ions into the lattice (e.g. the fluoride-selective membrane LaF_3 can be doped with Eu^{2+} ions). Sensors for the detection of: Ag^+, Cu^{2+}, Cd^{2+}, Pb^{2+}, S^{2-}, F^-, Br^-, I^-, SCN^- and CN^- ions can be constructed from such membranes. The sensitivity to ions of these electrodes arises from the dissolvation equilibria at the membrane surface. The measurement ranges of such electrodes lies in the range of $1\text{-}10^{-6}$M, but interference effects are frequently encountered.

Liquid-membrane electrode

In addition to solid membranes, immiscible liquid (organic) phases with ion-exchange properties can be used, with such phases stabilised against the external solution phase within a polymer or ceramic membrane. The main component of electroactive membrane is neutral or charged compound, which is able to complex ions reversibly and to transfer them through an organic membrane by carrier translocation. This compound is called as an ionophore or an ion carrier. There are two kinds of ionophores: charged one (usually termed liquid exchanger) and neutral carriers. They are mobile in both free and complexed forms, so the mobilities of all species are part of the selectivity coefficient together with ion-exchange equilibrium. The mobile binding sites are dissolved in a suitable solvent and usually trapped in a matrix of organic polymer (gel). Ion activity measurements are performed predominantly in aqueous media, so all membrane constituents are lipophilic. Therefore, the primary interaction between the ion in water and the lipophilic membrane containing the ionophore is the extraction process.

Typical polymeric membranes are based on plasticized poly(vinylchloride) (PVC) and contain approximately 66% of an plasticizer and 33% of PVC. Such a membrane is quite similar to liquid phase, because diffusion coefficients for dissolved low molecular weight

ionophores are in the order of 10^{-7}-$10^{-8}$$cm^2/_S$. Although other polymers like: polisiloxane, polystyrene, PMMA, polyamide or polyimide can be used as a membrane matrix, PVC is the most widely used matrix due to simplicity of membrane preparation.

Modified membrane electrode

Additional selectivity can be attained by using composite membranes, in which an enzyme present in the outer part of the membrane catalyses a specific chemical reaction to generate product ions. These ions can be detected by an internal ion-selective membrane. The well-known example is the selective detection of urea using urease as the enzyme catalyst. Similarly, enzyme reactions generating protons can be followed with glass or other proton-selective membranes. There is a multiplicity of enzyme-electrodes that can be made in this way, with substrates including aliphatic alcohols, acetylcholine, amygdalin, asparganine, glucose, glutamin, penicillin and other.

Module 2

Measurement of potential

Potentiometer is used to determine the difference between the potential of two electrodes. The one electrode is working or indicator electrode which responds to the analyte's activity, and the other electrode is the counter or reference electrode has a known, fixed potential.

Reference electrodes generally used are hydrogen electrodes, calomel electrodes, and silver chloride electrodes. The indicator electrode forms an electrochemical half cell with the interested ions in the test solution. The reference electrode forms the other half cell,

The overall electric potential is calculated as-

$$E_{cell} = E_{ind} - E_{ref} + E_{sol}$$

E_{ind} is the potential of indicator electrode. E_{sol} is the potential drop over the test solution between the two electrodes. E_{cell} is recorded at intervals as the titrant is added.

Reference electrode is a half-cell with an accurately known electrode potential. E_{ref}, is independent of the concentration of the analyte or any other ions in the solution which always treated as the left-hand electrode.

Indicator electrode is immersed in a solution of the analyte, develops a potential. E_{ind} depends on the activity of the analyte and is selective in its response

Location of end point

In potentiometric titration, the end point is determined by a number of methods. Some of them are summarize here

a) Titration Curve: Titration curve is obtained by plotting the successive values of the cell EMF on ordinate and corresponding values of volume of titrant added on the abscissa. This gives an S shaped curve. The central portion of this curve shows the steeply rising portion corresponds to the volume for the end point of the titration. When there is a small potential change at the end point like in the titration of weak acid with strong base, titration of very dilute solution etc, it is difficult to locate end point by this method.

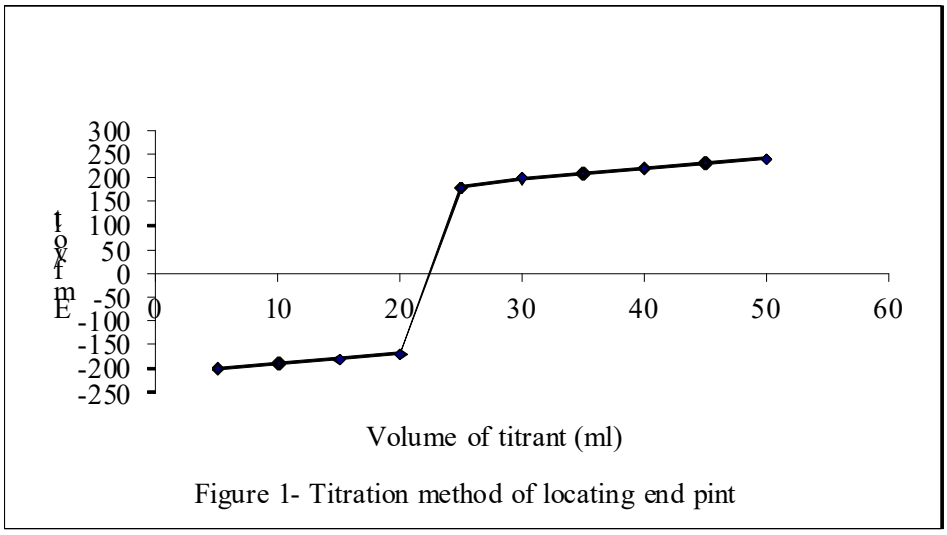

Figure 1- Titration method of locating end pint

b) Analytical or Derivative Method: In this method the end point can be more precisely located from the first or second derivative curves. The first derivative curve involves the plot of slope of the titration curve (ΔE/ΔV-ration of change in EMF and change in volume added) against the volume of the titrant added. Most frequently ΔE/ΔV is plotted against the average volume of titrant added corresponding to the values of EMF taken. Volume on the x-axis corresponding to the peak of the curve is the end point of the titration.

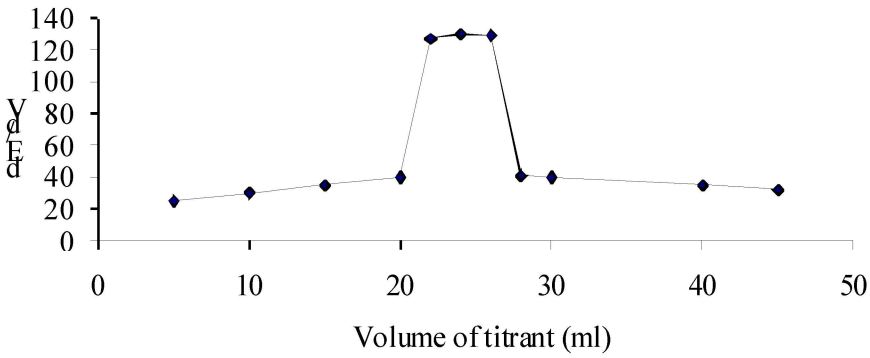

Figure 2- First derivative curve

In second derivative curve we plot the slope of first derivative curve ($\Delta^2E/\Delta V$) against volume. The point on volume axis where the curve cuts through zero on the ordinate gives the end point. This point corresponds to the largest steepest point on titration curve and maximum slope of the ΔE/ΔV curve.

Above mentioned methods need values of potential corresponding to very small change in volume of titrant added near the end point for good result. In the immediate vicinity of the end point the concentration of the original reactant becomes very small, and it usually becomes impossible for the ions to control the indicator electrode potential. The cell EMF becomes unstable and indefinite because the indicator electrode is not longer bathed with sufficient quantities of each electroactive species. Therefore the above

methods may not give satisfactory results. Again also, results obtained by above methods may be in error if the reaction is not symmetrical e.g. in titration of silver ions with chromate ions.

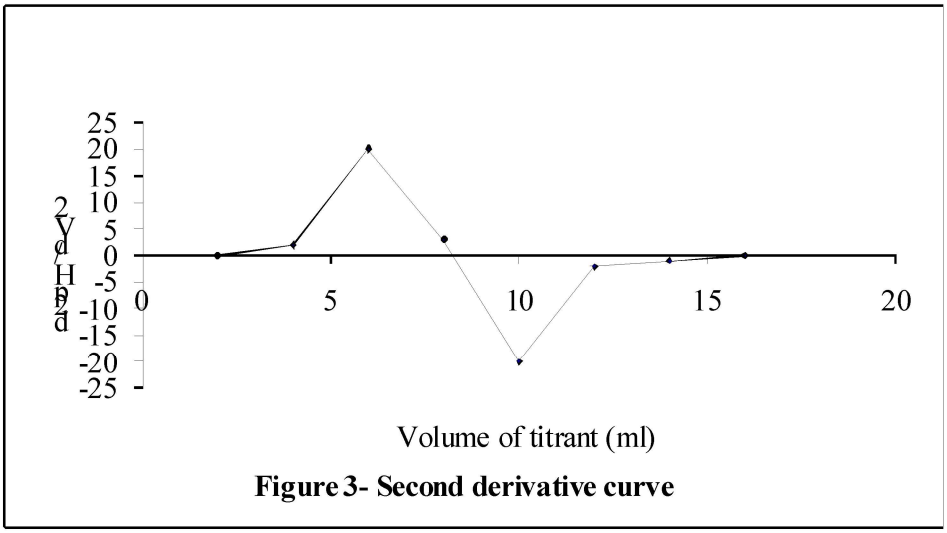

Figure 3- Second derivative curve

c) Gran Plot: This is a new method of end point location in potentiometric titration developed by *G. Gran* in 1952 and modified by others. This method does the numerical manipulation of titration curves into linear straight lines intersecting at the equivalence point. During the potentiometric titration of KI with $AgNO_3$ following reaction occurs:

$$KI(aq) + AgNO_3(aq) \rightarrow AgI(s) + KNO_3(aq).$$

The cell for the titration is SCE//KI,AgI/Ag and the EMF of the cell is given by

$$E_{cell} = E^{o}_{cell} - 2.303*(RT/F)*\log(I)$$

The EMF of the cell increases during potentiometric titration of KI with $AgNO_3$. By manipulating above equation one can derive the following equation for locating the end point by Gran's method.

$$\frac{(V_0 + V)}{(V_0)} 10^{-FECell/2.303RT} = 10^{-FEoCell/2.303RT}\, \gamma C_{Ag+} \frac{(V_e - V)}{(V_0)}$$

Where V_0 = Initial volume of KI taken, V = Volume of $AgNO_3$ solution added, V_e = Volume of $AgNO_3$ solution at end point, C_{Ag^+} = Concentration of $AgNO_3$ solution added, F = Faraday's constant, R = Gas constant, T = Temperature, γ = Activity coefficient.
In above equation the term

$$\frac{(V_0+V)}{(V_0)}10^{-FECell/2.303RT}$$

is called Gran's function. When Gran's function is plotted against volume of $AgNO_3$ added 'V', a straight line will be obtained. Such a plot is called Gran Plot.
Above equation best fits for the data points taken only before the equivalence point. The end point can also be obtained from the data points after the end point by plotting against the volume of titrant added.

$$\frac{(V_0+V)}{(V_0)}10^{-FECell/2.303RT}$$

Thus the end point from Gran Plot can be obtained either taking the points before the end point or taking the points after the end point. It is obvious that the results obtained from linear curves would be more accurate than from the nonlinear ones. The linear straight lines can be extrapolated to the volume axis to locate the end point. By the development of calculator, later on computer and using ion selective electrode, use of Gran Plot is increasing.
The advantages of using Gran's method of locating end point are: Simplicity of measurement, Simplicity of Calculation, Versatility and Precision.

Module 3

Equipment

The basic apparatus required for all potentiometric titrations are the same and is shown in Figure 4. The common parts of potentiometer includes-

• Indicator electrode – used to respond to changes in the species of interest

• Reference electrode – produces an unchanging voltage regardless of solution changes; most commonly used reference electrode is calomel electrode

• Voltmeter/pH meter – used to measures the voltage/pH of the solution

• Stirrer and follower – is used to avoid the need to manually swirl the solution between additions

• Burette – to add the titrant of course.

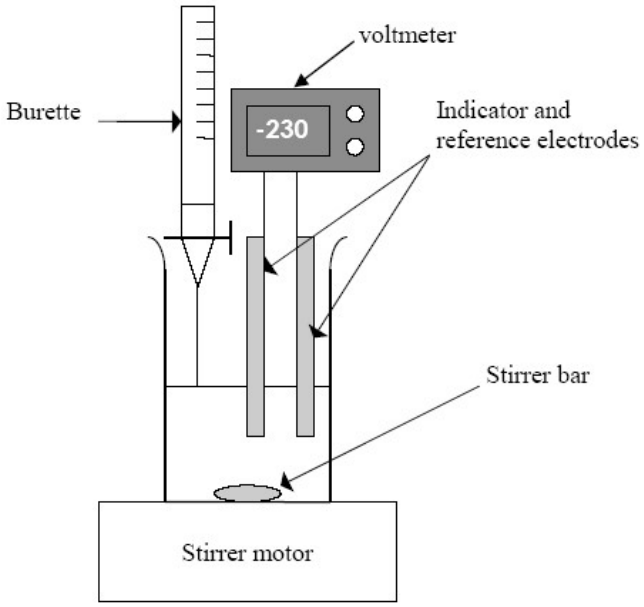

Figure 4 Schematic diagram of Potentiometric Equipment

Analytical Applications of Potentiometric Titration

Potentiometer is a versatile tool for drug analysis. It is an alternative to UV–VIS spectrophotometry because of its ease of operation and easy to handle and no special dilution required. Potentiometer can couple with an NMR spectrometer results in a powerful hyphenated technique called NMR controlled titration. Currently Potentiometric titration is a used for its number of applications, some of them are summarize here-

1. It is used to determine the solubility products of sparingly soluble salts.
2. It is used to calculate the pH of a solution.

3. Potentiometric titration is also used for assay of raw materials.
4. Potentiometric titration is used to determine thermodynamic functions.
5. It can also estimate the activities of electrolytes.
6. Determination of the end points in titrations.
7. Determination of pKa and pKb

Module 4

Before moving to our next module ie about Direct measurements of metal concentration , I would like to suggest you to visit our web site www.cec.nic.in for further reading and learning of more topic associated with your B. Pharm syllabus. Here you will find many lectures, e-content, FAQs, LORs and many more.

Hope this site will be a catalyst of learning for you ..

Direct measurements of metal concentration

In many situations, accurate determination of a metal ion concentration by measurement of a cell potential is impossible due to the presence of other ions and a lack of information about activity coefficients. In such cases it is often possible to determine the metal ion concentration directly by potentiometric titration with some other ion. For example, the initial concentration of an ion such as Fe^{2+} can be found by titrating with a strong oxidizing agent such as Ce^{4+}. The titration is carried out in one side of a cell whose other half is a reference electrode:

$$Pt(s) || Fe^{2+}; Fe^{3+} || \text{reference electrode}$$

Initially the left cell contains only Fe^{2+}. As the titrant Ce^{4+} is added, the ferrous ion is oxidized to Fe^{3+} in a reaction that is virtually completes:

$$Fe^{2+} + Ce^{4+} \rightarrow Fe^{3+} + Ce^{3+}$$

The cell potential is followed as the Fe^{2+} is added in small increments. Once the first drop of Ce^{3+} has been added, the potential of the left cell is controlled by the ratio of oxidized and reduced iron according to the Nernst equation –

$$E = 0.68 - 0.059 \log [Fe^{2+}]/ [Fe^{3+}]$$

When the equivalence point is reached, the Fe^{2+} will have been totally consumed (the large equilibrium constant ensures that this will be so), and the potential will then be controlled by the concentration ratio of $Ce^{3+} = Ce^{4+}$. The idea is that *both* species of a redox couple must be present in reasonable concentrations for a concentration to control the potential of an electrode of this kind. If one works out the actual cell potentials for various concentrations of all these species, the resulting titration curve looks much like the familiar acid-base titration curve. The end point is found not by measuring a particular cell voltage, but by finding what volume of titrant gives the steepest part of the curve.

Module 5

Differential curves in potentiometric titration

In potentiometric titration we are interested in relating a single voltage measurement to the solution concentration: we are only interested in identifying the endpoint volume of the titration by the change in voltage from one volume addition to the next. Figure 5 shows the typical shape of a potentiometric titration curve.

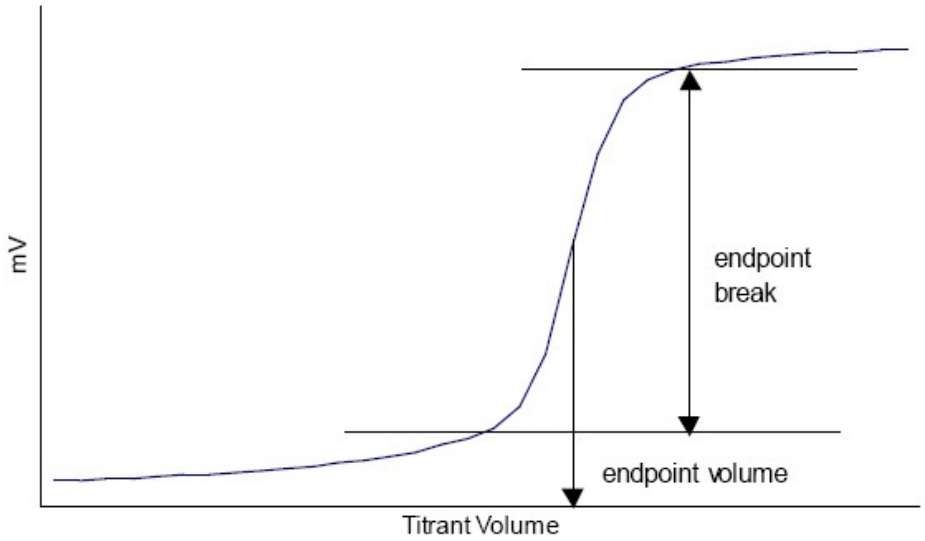

Figure 5 Typical potentiometric titration curve.

The common features of the titration curve includes-

• the wave-like shape occurs because of the rapid change in voltage around the endpoint of the reaction.

• the endpoint break is the large change in voltage around the endpoint.

• the endpoint break should be as large as possible to improve accuracy of detection: this is done by choosing the titrant carefully (discussed in later sections of this chapter).

• the endpoint volume is defined as the volume half-way up the endpoint break.

• the voltage values before the endpoint are due to the analyte.

• the voltage values after the endpoint are due to the titrant.

The other differential curves including first derivative curve, second derivative curve and Gran Plot have been discussed previously in this lecture.

Determination of KSP

Solubility product constant is simplified equilibrium constant (Ksp) defined for equilibrium between a solid and its respective ions in a solution. Its value indicates the degree to which a compound dissociates in water. The higher the solubility product constant, the more soluble the compound.

The solubility product (constant or K_{sp}) of silver chloride is given by the expression-

$$K_{sp} = [Ag^{+}][Cl^{-}]$$

Potentiometric titration curve data is utilized for the determination of solubility product.

The concentrations of ions in equilibrium with a sparingly soluble salt are sufficiently low that the Nernst equation can be used with little error. Rather than measuring the concentration of the relevant ions directly, the more common procedure is to set up a cell in which one of the electrodes involves the insoluble salt, and whose net cell reaction is just the dissolution of the salt. For example, to determine the Ksp for silver chloride, we could use the electrode in the cell

Ag(s) ı Ag+ ?M ıı Ag+; Cl¡ ı AgCl(s) ı Ag(s)

Other useful solid-state electrodes are based on silver compounds (particularly silver sulfide). Silver sulfide is an ionic conductor, in which silver ions are the mobile ions. Mixed pellets containing Ag_2S-AgX (where X = Cl, Br, I, SCN) have been successfully used for the determination of one of these particular anions. The behavior of these electrodes is basically determined by the solubility products involved.

Summary

Potentiometric titration is a volumetric method in which the potential between two electrodes is measured (referent and indicator electrode) as a function of the added reagent volume. Types of potentiometric titrations for the determination of analytes in photoprocessing solutions include acid-base, redox, precipitation, and complexometric. In potentiometric titration, two electrodes are used, an indicator electrode (the glass electrode and metal ion indicator electrode) and a reference electrode. Reference electrodes generally used are hydrogen electrodes, calomel electrodes, and silver chloride electrodes. The indicator electrode forms an electrochemical half cell with the interested

ions in the test solution. The overall electric potential is calculated as $E_{cell} = E_{ind} - E_{ref} + E_{sol}$. In potentiometry, a graph of potential against volume added can be drawn and the end point of the reaction is half way between the jump in voltage. The first derivative, $\Delta E/\Delta V$, is the slope of the curve, and the endpoint occurs at the volume, V', where $\Delta E/\Delta V$ has the maximum value. E_{cell} depends on the concentration of the interested ions with which the indicator electrode is in contact. Potentiometric titrations have several applications especially determination of salts and ions concentrations.

FAQ's with answers

1. What is electrode?

An electrode is a solid electric conductor through which an electric current enters or leaves an electrolytic cell or other medium.

2. What is ISE?

Ion Selective Electrodes (ISE) are membrane electrodes that respond selectively to ions in the presence of others. These include probes that measure specific ions and gasses in solution. The most commonly used ISE is the *p*H probe.

3. What is titration curve?

Titration curve is obtained by plotting the successive values of the cell EMF on ordinate and corresponding values of volume of titrant added on the abscissa. This gives an S shaped curve.

4. What is Gran Plot?

This is a new method of end point location in potentiometric titration developed by *G. Gran* in 1952 and modified by others. This method does the numerical manipulation of titration curves into linear straight lines intersecting at the equivalence point.

5. In potentiometric titration how many types of graphs obtained?

The common graphs includes titration curve, first derivative curve, second derivative curve and Gran Plot.

6. What is KSP? Explain it.

Solubility product constant (Ksp) is defined for equilibrium between a solid and its respective ions in a solution. Its value indicates the degree to which a compound dissociates in water. The higher the solubility product constant, the more soluble the compound.

Quiz with answers

1. In Potentiometric titration the potential is measured under the conditions of (b):-
    a. Current flow
    b. No current flow
    c. Both a and b
    d. None of these
2. The basic ISE setup includes (d):-
    a. A meter (capable of reading millivolts)
    b. A probe (selective for each analyte of interest)
    c. Various consumables used for *p*H or ionic strength adjustments
    d. All of above
3. Glass membrane is the example of (a)-
    a. Solid membrane
    b. Liquid membrane
    c. Membrane in a special electrode
    d. All of above
4. In Liquid-membrane electrode the most widely used matrix is made of (d)-
    a. Polisiloxane
    b. Polystyrene
    c. PMMA

d. PVC

5. In Liquid-membrane electrode polymeric membranes are based on plasticizer and poly(vinylchloride) (PVC) having composition- approximately (c)-

a. 50% plasticizer and 50% of PVC

b. 75% plasticizer and 25% of PVC

c. 66% plasticizer and 33% of PVC

d. All of the above

6. In Potentiometric titration end point is located by the following methods (d)-

a. Titration Curve

b. Analytical or Derivative Method

c. Gran Plot

d. All of the above

7. The full form of K_{sp} is (a)-

a. Solubility product

b. Substituted product

c. Dissociation product

d. All of the above

8. The higher the solubility product constant represent (a)-

a. More soluble

b. Less soluble

c. Both a and b

d. None of above