

PHARMACEUTICAL ANALYSIS

Method of Analysis and Assay: Potentiometry

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Keywords

Cell, Electrode, Potentiometric analysis, Instrumental analysis

Introduction

Potentiometry is the field of electro analytical chemistry in which potential is measured under the conditions of no current flow. 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.

Cell

Cell is arrangement of two electrodes and an electrolytic solution within the cell capable of producing chemical action due to passage of electricity through the cell.

Each cell is made of two electrodes

- 1) one liberates electrons and is called as oxidizing electrode
- 2) other absorbs electrons and is called as reducing electrode

e.g Voltanic cell or Daniell cell

Galvanic cell

Galvanic cell is an electrochemical cell consisting of two conductors called electrodes, each immersed in a suitable electrolyte solution (one or two) and is capable of spontaneously converting chemical energy more or less completely into electric energy and supplying this energy to an external source. In these cells, a chemical reaction involving an oxidation at one electrode and a reduction at the other electrode occurs. The electrons generated in the oxidation step are transferred at the electrode surface, pass through the external circuit and then return to the other electrode where reduction takes place. When one of the chemical components responsible for these types of reactions is depleted, the cell is no longer capable of supplying electric energy to the external source and the cell is dead.

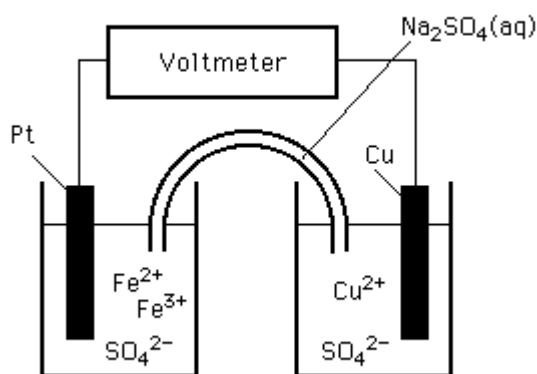


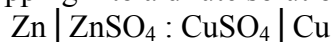
Fig 1-Galvanic cell

For current to develop in a cell, it is necessary that

- i) electrodes be connected externally by means of a metal conductor &

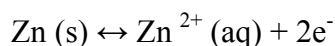
- ii) two electrolyte solution be in contact to permit movement of ions from one to another.

e.g Daniell cell. Daniell cell consists of an outer copper vessel containing a concentrated solution of copper sulphate. Inside it is a porous pot containing a zinc strip dipping into a dilute solution of zinc sulphate. The cell can be represented as

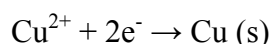


Or

At anode



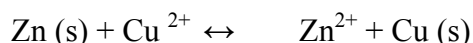
At cathode



Conductance in cell

Charge is conducted by three different processes:

- in the copper and zinc electrodes as well as in the external conductor, electrons serve as carriers
- Within the solution the flow of electricity involves migration of both cation and anion. In the half cell on the left zinc ions migrate away from the electrode, whereas sulphate and hydrogen sulphate ion move towards it. In the other compartment copper ions move towards electrode and anions away from it. Within the salt bridge, electricity is carried by migration of potassium ions to the right and chloride ions to the left. Thus all of the ions in the three solutions participate in the flow of electricity.
- A third process occurs at the two electrode surfaces. Here oxidation or a reduction reaction provides a mechanism whereby the ionic conduction of the solution is coupled with the electron conduction of the electrodes to provide complete circuit for flow of charge. The two electrode processes are described as



The potential that develops in cell is a measure of the tendency for this reaction to proceed towards equilibrium when the system reaches equilibrium the potential is 0V

Liquid junction: The interference between the two solutions containing different electrolytes or different concentration of same electrolytes is called liquid junction.

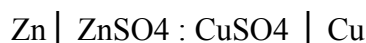
Reversible and irreversible cells

According to thermodynamics, conditions for thermodynamic reversibility are that

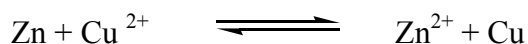
- the driving and opposing force be only infinitesimally different from each other.
- it should be possible to reverse any change occurring by applying a force infinitesimally greater than the one existing.

When these conditions are fulfilled by a cell, the cell is said to be reversible, and when these conditions are not satisfied the cell is said to be irreversible.

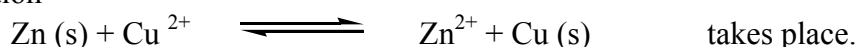
Example of reversible cell: Daniell cell



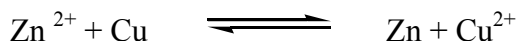
Net cell reaction



The emf of this cell is found to 1.09 V is applied to this cell, no current flows. If the external opposing emf is slightly smaller than 1.09V a current will flow and chemical reaction



But if an external emf is slightly higher than 1.09V the reaction is reversed



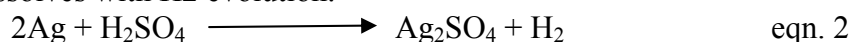
Thus cell is reversible.

Example of irreversible cell:

Zinc and silver electrode immersed in a solution of sulphuric acid. When the two electrodes are short circuited, zinc dissolves with evolution of H₂ gas to form sulphate.



When cell is connected with an external source of emf infinitesimally greater than its own, silver dissolves with H₂ evolution.



The cell may be made to satisfy the first condition of reversibility as clear from equation 1 & 2, the second does not hold. Hence the cell is irreversible.

Types of reversible electrodes

a) Electrodes reversible with respect to cation or electrode of first kind

It consists of a metal dipping into a solution containing its own ions. e.g. copper rod dipped in copper sulphate solution. The electrode is said to be reversible to its own ions i.e. the potential of each of these electrodes is determined by the activities of its own ions in the solution in which the metal is immersed.

The electrode reaction may be denoted as



The electrode potential is given by

$$E_M = E_M^\circ - \frac{RT}{nF} \log e a^{M^{+n}}$$

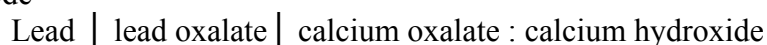
Other examples are zinc, hydrogen, halogen electrode etc.

b) Electrodes reversible with respect to anion or electrode of second kind

This type of electrodes involve metal, sparing salt of this metal and a solution of a soluble salt of same anion. E.g. silver silver electrode, lead sulphate electrode, silver bromide electrode, calomel electrode etc

c) Electrodes of third kind:

It consists of a metal, one of its insoluble salts, another insoluble salt of the same anion and a solution of soluble salt having the same cation as the later salt. e.g. Lead electrode

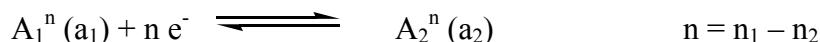


d) Oxidation reduction electrodes or electrodes of fourth kind

It consists of solution of metal having both type of ions and inert electrode. e.g. platinum wire dipped in solution containing ferrous and ferric ion, same is true for

solution of cerous ceric ion, stannous stannic ions, manganous permanganate ions. The electrode emf's from the tendency of ions in one state of oxidation to pass over into a second more stable state. The platinum metal merely acts as a conductor for making electric contact.

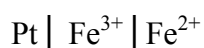
General reaction



Electrode potential is written as

$$E = E^\circ - RT/nF \log a_2/a_1$$

e.g. Ferric ferrous electrode



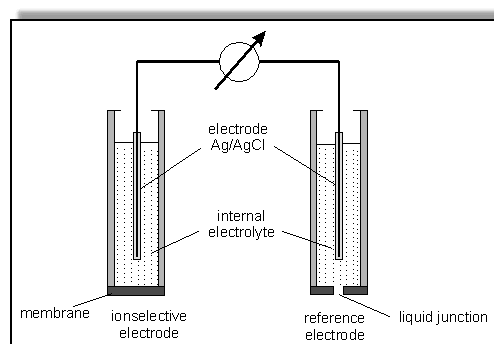
Electrode potential is $E = E^\circ - RT/nF \log a_{\text{Fe}^{2+}}/a_{\text{Fe}^{3+}}$

Electrodes

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 pH probe. Other ions that can be measured include fluoride, bromide, cadmium, and gasses in solution such as ammonia, carbon dioxide, and nitrogen oxide. 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 pH or ionic strength adjustments. The expense is considerably less than other methods, such as Atomic Adsorption Spectrophotometry or Ion Chromatography. ISE determinations are not subject to interferences such as color in the sample. A large number of indicator electrodes with good selectivity for specific ions are based on the measurement of the potential generated across a membrane. Electrodes of this type are referred to as ion-selective electrodes. The membrane is usually attached to the end of a tube that contains an internal reference electrode.

Fig 2: Diagrammatic representation of ion selective electrode



This membrane electrode and an external reference electrode are then immersed in the solution of interest. Since the potentials of the two reference electrodes are constant, any change in cell potential is due to change in potential across the membrane.

Different membrane materials have proved to give optimal responses for certain species. For example, a glass membrane is unsurpassed for measuring H^+ activity, pH. This ISE may be referred to as a glass or pH electrode. Liquid membrane electrodes have non-glass, solid-state crystals or pellets as the membrane component of the electrode. This approach has proved effective for numerous cations and anions. The most successful example is the excellent electrode for fluoride ion, which is based on a crystal of LaF_3 doped with $Eu(II)$ to create crystal defects to improve conductivity.

Gas-sensing electrodes or combination electrodes that respond to the concentration of gases dissolved in aqueous solution. The electrodes consist of an ion-selective electrode, usually pH, in contact with a thin layer of solution that is held in place with a membrane permeable to the desired gas such as NH_3 or CO_2 . When the gas passes through the membrane, the change of pH in the thin layer of solution is sensed by the glass membrane pH electrode.

Other combination electrodes consist of an enzyme immobilized on an ISE. The ISE is chosen to respond to a product of the enzyme-substrate reaction and the selectivity is provided by the enzyme.

An Ion Selective Electrode measures the potential of a specific ion in solution. (The pH 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.

Standard solutions of known concentrations must be accurately prepared. These solutions are then measured with the pH/mV meter. The mV reading of each solution is noted and a graph of concentration vs. mV reading must be plotted. Now the unknown solution can be measured. The mV value of the unknown solution is then located on the graph and the corresponding solution concentration is determined.

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:

$$E_{\text{cell}} = E_{\text{ise}} - E_{\text{ref}}$$

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

Types of Electrodes

Several types of sensing electrodes are commercially available. They are classified by the nature of the membrane material used to construct the electrode. It is this difference in membrane construction that makes an electrode selective for a particular ion.

1. Polymer Membrane Electrodes (Organic Ion Exchangers and Chelating Agents) -- Polymer membrane electrodes consist of various ion-exchange

materials incorporated into an inert matrix such as PVC, polyethylene or silicone rubber. After the membrane is formed, it is sealed to the end of a PVC tube. The potential developed at the membrane surface is related to the concentration of the species of interest. Electrodes of this type include potassium, calcium, chloride, fluoroborate, nitrate, perchlorate, potassium, and water hardness.

2. **Solid State Electrodes (Insoluble Conductive Inorganic Salts)** -- Solid state electrodes utilize relatively insoluble inorganic salts in a membrane. Solid state electrodes exist in homogeneous or heterogeneous forms. In both types, potentials are developed at the membrane surface due to the ion-exchange process. Examples include silver/sulphide, lead, copper (II), cyanide, thocyanate, chloride and fluoride.
3. **Gas Sensing Electrodes** -- Gas sensing electrodes are available for the measurement of dissolved gas such as ammonia, carbon dioxide, nitrogen oxide, and sulfur dioxide. These electrodes have a gas permeable membrane and an internal buffer solution. Gas molecules diffuse across the membrane and react with a buffer solution, changing the pH of the buffer. The pH of the buffer solution changes as the gas reacts with it. The change is detected by a combination pH sensor within the housing. Due to the construction, gas sensing electrodes do not require an external reference electrode.
4. **Glass Membrane Electrodes** -- Glass membrane electrodes are formed by the doping of the silicon dioxide glass matrix with various chemicals. The most common of the glass membrane electrodes is the pH electrode. Glass membrane electrodes are also available for the measurement of sodium ions.

Glass electrode is a potentiometric sensor made from glass of a specific composition. Almost all commercial electrodes related to ion-selective sensors with electrode function for single charged ions, like H^+ , Na^+ , Ag^+ . Only few chalcogenide glass electrodes have electrode function for double-charged ions, like Pb^{2+} , Cd^{2+} and some other.

There are two main glass-forming systems:

- (i) Silicate matrix based on molecular network of silicon dioxide (SiO_2) with additions of other metal oxides, such as Na, K, Li, Al, B, Ca, etc.
- (ii) Chalcogenide matrix based on molecular network of AsS, AsSe, AsTe.

Corresponding general electrode function usually marked as *pH glass electrode*, *pNa glass electrode*. Usually one glass electrode has only one general electrode function, for example pH or pNa, and such electrodes called ion-selective electrodes. But parameters of any ion-selective electrodes depend on concentrations of interfering ions. Because of the ion-exchange nature of glass membrane, it is possible for some other ions concurrently interact with ion-exchange centers of glass and to distort linear dependence of measured electrode potential on pH or other general electrode function. In some cases it is possible to change electrode function from one ion to another. One of these cases is a silicate pNa electrode which can be changed to pAg function after soaking it into silver salt solutions.

Dependence of the electrode potential of pH glass electrode on composition of studied solution can be represented by following equation (also known as Nikolsky equation):

$$E = E^0 + \frac{RT}{F} \ln (a_{H^+} + K_{HNa} * a_{Na^+}),$$

where electrode has "general" pH electrode function with interfering influence of Na-ions. a_{H^+} , a_{Na^+} - activity of hydrogen and Sodium ions;

In more common case for series of single charged ions:

$$E = E^0 + \frac{RT}{F} \ln \left(a_{H^+} + \sum_j^N K_{Hj} * a_j \right)$$

K_{HNa} - selectivity coefficient shows magnitude of interference influence. For example, $K_{HNa}=10^{-12}$ means that selectivity of the glass electrode for Na-ion is 10-12 less than for H^+ .

Complete realization of general electrode function, where dependence of potential on pH has linear behavior and within which such electrode really works as ion-selective electrode for pH.

$$E = E^0 - \frac{2.303RT}{F} pH,$$

Alkali error range - at low concentration of hydrogen-ions (high values of pH) contributions of interfering alkali metals (like Li, Na, K) are comparable with one of hydrogen-ions. In this situation dependence of the potential on pH become non-linear. Acidic error range - at very high concentration of hydrogen-ions (low values of pH) it can be detected the influence of the anions of corresponding acid solution as well as destruction of the glass matrix.

There are different types of pH glass electrode; some of them have improved characteristics for working in alkaline or vice versa, acidic medium. But almost all electrodes have sufficient properties for working in the most popular pH range from pH=1 till pH=12. Special electrodes should be used only for working in aggressive conditions.

Most of text written above is also correct for any ion-exchange electrodes.

Construction

Scheme of typical pH glass electrode

1. a sensing part of electrode, a bulb made from a specific glass
2. sometimes electrode contain small amount of AgCl precipitate inside the glass electrode
3. internal solution, usually 0.1M HCl for pH electrodes or 0.1M MeCl for pMe electrodes
4. internal electrode, usually silver chloride electrode or calomel electrode
5. body of electrode, made from non-conductive glass or plastics.
6. reference electrode, usually the same type as 4
7. junction with studied solution, usually made from ceramics or capillary with asbestos or quartz fiber.

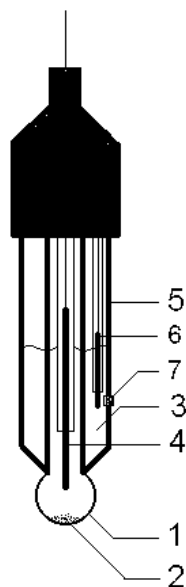


Fig 3: A glass electrode

A typical modern pH probe is a combination electrode, which combines both the glass and reference electrodes into one body. The bottom of a pH electrode balloons out into a round thin glass bulb. The pH meter is best thought of as a tube within a tube. The inside most tube (the inner tube) contains an unchanging saturated KCl and a 0.1M HCl solution. Also inside the inner tube is the cathode terminus of the reference probe. The anodic terminus wraps itself around the outside of the inner tube and ends with the same sort of reference probe as was on the inside of the inner tube. Both the inner tube and the outer tube contain a reference solution but only the outer tube has contact with the solution on the outside of the pH probe by way of a porous plug that serves as a salt bridge.

This device is essentially a galvanic cell. The reference end is essentially the inner tube of the pH meter, which for obvious reasons cannot lose ions to the surrounding environment (as a reference is good only so long as it stays static through the duration of the measurement). The outer tube contains the medium, which is allowed to mix with the outside environment (and as a consequence this tube must be replenished with a solution of KCl due to ion loss and evaporation).

The measuring part of the electrode, the glass bulb on the bottom, is coated both inside and out with a ~ 10 nm layer of a hydrated gel. These two layers are separated by a layer of dry glass. The silica glass structure (that is, the conformation of its atomic structure) is shaped in such a way that it allows Na^+ ions some mobility. The metal cations (Na^+) in the hydrated gel diffuse out of the glass and into solution while H^+ from solution can diffuse into the hydrated gel. It is the hydrated gel, which makes the pH electrode an ion selective electrode.

H^+ does not cross through the glass membrane of the pH electrode, it is the Na^+ which crosses and allows for a change in free energy. When an ion diffuses from a region of activity to another region of activity, there is a free energy change and this is what the pH meter actually measures. The hydrated gel membrane is connected by Na^+ transport and thus the concentration of H^+ on the outside of the membrane is 'relayed' to the inside of the membrane by Na^+ .

All glass pH electrodes have extremely high electric resistance from 50 till 500 MOhm. Therefore glass electrode could be used only with high impedance measuring device like pH meter or more universal measuring device - ionometer.

Between measurements any glass and membrane electrodes should be kept in the solution of its own ion (Ex. pH glass electrode should be kept in 0.1M HCl or 0.1M H₂SO₄). It is necessary to prevent insiccation of the glass membrane.

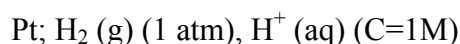
Single electrode potential

In a cell, at one electrode oxidation takes place i.e. electrons are evolved and at other reduction takes places i.e. electrons are taken up.

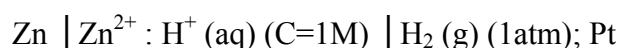
The tendency of an electrode to lose or gain electrons when it is in contact with its own ions in solution is called as electrode potential. Since the tendency to gain electrons mean tendency to get reduced, this tendency is called as reduction potential and it's vice versa known as oxidation potential. Therefore if the reduction potential of a electrode under given conditions is 1.5V, then its reduction oxidation potential is taken as -1.5V and vice versa.

It is not possible to determine experimentally the potential of a single electrode (i.e. of a half cell). It is only the difference between the potential of two electrodes that can be measured by combining them to give a complete cell. By arbitrarily fixing potential of one electrode at zero it is possible to assign numerical value to potential of the various electrodes.

Accordingly, the potential of a reversible hydrogen electrode in which the gas at one atmospheric pressure is bubbled through a solution of hydrogen ions of unit activity (or unit concentration) has been fixed as zero. The electrode is known as standard hydrogen electrode and is represented as



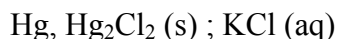
All other single electrode potential measured with respect to standard hydrogen electrode is referred to as potential on the hydrogen scale. e.g. to measure the potential of zinc electrode. The electrode dipping in a solution of zinc sulphate is combined with the standard H₂ electrode so as to have a complete cell.



The emf of the cell, determined potentiometrically, is the equal to the potential of the zinc electrode (on the H₂ scale) since potential of standard H₂ electrode is taken as zero.

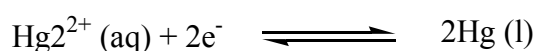
But it is not convenient to use standard H₂ electrode as reference electrode because it is difficult to maintain the activity of H⁺ ions in the solution at unity and to keep the pressure of gas uniformly at one atmosphere. Therefore calomel electrode is used as reference electrode. It can be set conveniently and can be used for long without any subsequent attention.

Calomel electrode: Calomel electrode consists of mercury, solid mercurous chloride and a solution of potassium chloride. The electrode is represented as

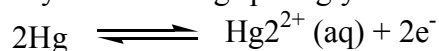


Two types of cell reactions are possible in calomel electrode:

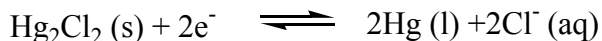
1. If the electrode reaction involves reduction the Hg_2^{2+} ion furnished by the sparingly soluble mercurous chloride would be discharged at the electrode. Hence, more and more of calomel would pass into solution. The result is increase in concentration of Cl^- ions. The reaction is



2. On the other hand, the electrode reaction involves oxidation it would liberate electrons and send Hg_2^{2+} ions into solution. The Hg_2^{2+} ions will combine with Cl^- ions/ furnished by KCl forming sparingly soluble Hg_2Cl_2 . The reaction is



Thus in case of calomel electrode the electrode reaction may be represented as



The electrode therefore is reversible with respect to chloride ions.

The potential of calomel electrode on the H_2 scale has been measured carefully by connecting it to a standard H_2 electrode. The potential of the electrode depends upon the concentration of KCl solution. The values for 0.1M KCl, 1.0M KCl and saturated solution of KCl are 0.3335V, 0.2810V and 0.2422V respectively at 25 °C. The calomel electrode with saturated KCl is most commonly used and is referred as saturated calomel electrode (SCE).

Standard electrode potential: The potential of an electrode at a given temperature depends on concentration of ions surrounded electrode. The potential of electrode when the concentration of ions is unity and temperature in 25 °C is termed as standard electrode potential.

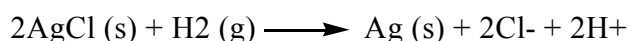
Cell Potential

Theoretically electrode and cell potential, activities are used rather than molar concentration, where the activity a_x of the species x is given by

$$a_x = f_x [x]$$

f_x is activity coefficient of solute x and bracketed term is the molar concentration of x.

Assuming the f_x approached zero so that the molar concentration and activity of a species are identical using the e.g



The equilibrium constant 'k' for this can be

$$k = \frac{a_{\text{H}^+}^2 a_{\text{Cl}^-}^2 a_{\text{Ag}}}{p_{\text{H}_2} a_{\text{AgCl(s)}}^2}$$

a - activity
p_{H2} - is partial pressure of H₂ in atmosphere

By convention activity of pure solid is unity when present in excess (i.e. activity of a_{AgCl}, a_{Ag}=1)

A second quantity is used for convenience e.g. W at any time before equilibrium.

$$k = \frac{(a_{\text{H}^+})_i^2 (a_{\text{Cl}^-})_i^2}{(p_{\text{H}_2})_i^2}$$

i = is instantaneous activity and not the equilibrium activity

W = is constant but changes continuously until equilibrium is reached where W= k and i is deleted.

Thermodynamically the change in free energy ΔG for a cell reaction (i.e. the maximum work obtainable at constant temperature and pressure) is given by

$$\Delta G = RT \ln W - RT \ln k$$

This relationship implies that the magnitude of the free energy for the system depends on how far the system is from equilibrium state. The cell potential E_{cell} is related to free energy by the relationship

$$\Delta G = -nFE_{\text{cell}}$$

F – Faraday (96,485 coulombs/mole of electron), n = no of moles of electrons associated with the oxidation/ reduction process.

Therefore we can write

$$- nFE_{\text{cell}} = RT \ln W - RT \ln K$$

$$E_{\text{cell}} = - \frac{RT}{nF} \ln W + \frac{RT}{nF} \ln k$$

Or

$$E_{\text{cell}} = - \frac{RT}{nF} \ln \frac{(a_{\text{H}^+})_i^2 (a_{\text{Cl}^-})_i^2}{(p_{\text{H}_2})_i^2} + \frac{RT}{nF} \ln k$$

The last term $\frac{RT}{nF} \ln k$ is constant and is called standard electrode potential and is represented as E°_{cell} for the cell.

Therefore the above equation can be written as

$$E_{\text{cell}} = E_{\text{cell}}^{\circ} - \frac{RT}{nF} \ln \frac{(a_{\text{H}^+})^2_{\text{i}} (a_{\text{Cl}^-})^2_{\text{i}}}{(p_{\text{H}_2})^2_{\text{i}}}$$

Potentiometric titrations

Modes of titration

Titration are performed **manually** point by point, or **automatically**, where the titrant is introduced continuously (monotonically or dynamically). In modern analytical chemistry automation is of increasing importance. Automation of a point-by-point titration is seldom trivial. Kinetic factors concerning the chemical reaction and the response of the indicating system are of paramount importance. Cell configuration, stirring, positioning of end-point detector and of input of titrant are to be considered for ensuring high accuracy.

Equilibrium throughout the titration curve can be attained only when the titrant is added at an infinitely low rate. Two factors determine the rate at which a potentiometric curve approaches the state of equilibrium: the kinetics of the chemical reaction and the kinetics of the electrode process. Both factors are slowest in the vicinity of the equivalent point, the region with utmost importance, from which the end point is determined (Fig.4-4a). At faster titration rates compared to the kinetics of the system, a delayed end point is obtained (Fig.4-4b).

The degree of the delay of the end point depends on the concentration of analyte, the composition of the solution, the concentration of titrant and the rate of the titrant adding. The larger the concentration of the analyte, the smaller the delay. The larger the amount of titrant added per unit of time, the larger the delay.

Several strategies are used to virtually eliminate the delay:

- (a) Modifying the rate of titrant adding, either by reducing it throughout the entire titration curve - *the monotonic mode*, or by reducing it only along the vicinity of the equivalence point - *the dynamic mode*. With the dynamic mode, the rate of the titration is inversely proportional to the rate of potential change, $\partial E / \partial \lambda$ (Fig.4-4c), where λ is the progress of the titration.
- (b) Performing a *repetitive-monotonic titration* (Fig.4-4d). In this mode a series of titrations is performed in a consecutive manner. The measurements are made under non-equilibrium conditions. The titrant is introduced, or electrochemically generated, at a fast and constant rate. Each titration is discontinued at some time after the end point (the actual time is of no importance). A new portion of sample is added to the cell and the titration is resumed at the previous rate. The new aliquot can be added also without suspending the flow of the titrant. The end points of the titrations are usually delayed. Each end point in a series of titrations is delayed only once, by a period of time depending on the specific type of titration. Previous delays are not accumulated. The delay of the previous titration is always nullified a short time after a new portion of an analyte is added, since the response of the system is slow only around the equivalence point, but not far away from it.

All modes of automatic titrations have to be tested for accuracy if no previous knowledge is available.

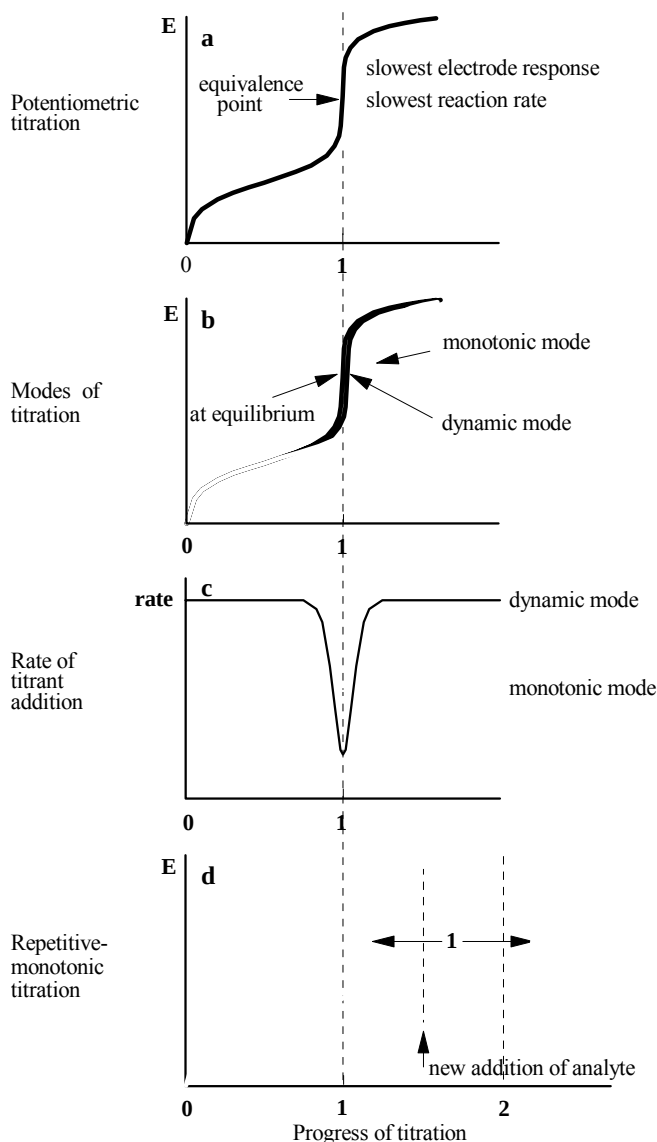


Fig.4: Continuous potentiometric titrations

Oxidation reduction titration

Oxidation reduction titration can be followed by an indicator electrode. The electrode assumes a potential proportional to the logarithm of the concentration of the two oxidation state of the reactant or the titrant, which ever is capable of properly poisoning the electrode. e.g. The iron (III/II) system in the titration with cerium (IV). At the start of the titration the minute amount of oxidized form of iron (III) leaves the system without a definite electrode potential. However, as soon as a drop or two of cerium (IV) are added the concentration ratio of iron (III/II) assumes a definite value and likewise the electrode potential of the indicator electrode. During the major portion of the titration the electrode potential changes gradually only as the equivalence point is approached does the concentration ratio changes rapidly again. Past the equivalence point the indicator electrode ceases to be affected by the iron (III/II) system and will assume potential dictated by cerium (IV/III) system.

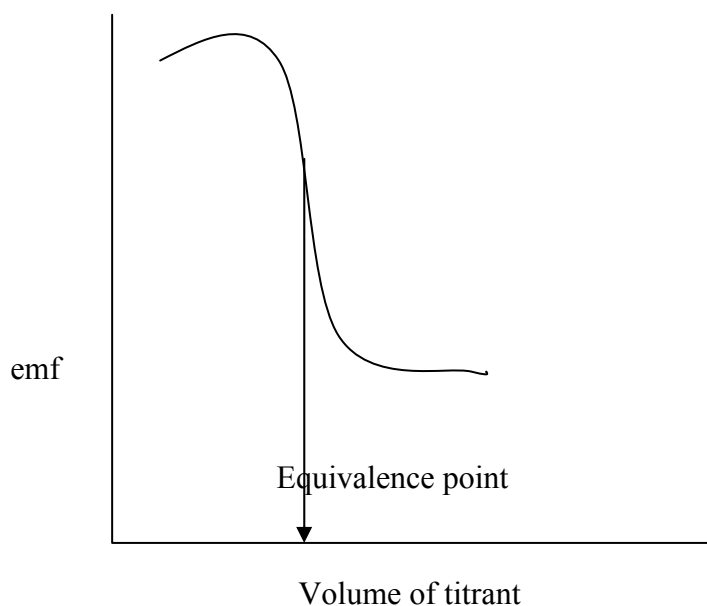
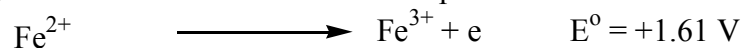


Fig 5: Titration curve for oxidation redox titration

Such type of reactions consists essentially of two half reactions whose standard potential may be used to calculate the standard potential of the reaction.



If an acidic ferrous solution is titrated with a standard solution of cerium at 25°C, the potential (relative to NHE) of a platinum electrode in contact with the solution will be given by either of the following equations.

$$E = E^{\circ}_{\text{Ce}^{3+}/\text{Ce}^{4+}} - \frac{0.0591}{n} \log_{10} \frac{[\text{Ce}^{3+}]}{[\text{Ce}^{4+}]} \quad \text{eqn 1}$$

$$E = E^{\circ}_{\text{Fe}^{2+}/\text{Fe}^{3+}} - \frac{0.0591}{n} \log_{10} \frac{[\text{Fe}^{2+}]}{[\text{Fe}^{3+}]}$$

$$E = E^{\circ}_{\text{Fe}^{2+}/\text{Fe}^{3+}} + \frac{0.0591}{n} \log_{10} \frac{[\text{Fe}^{3+}]}{[\text{Fe}^{2+}]} \quad \text{eqn 2}$$

Equation 2 can be used before the equivalence point as the right hand term of this equation could be found easily from the known extent of the titration. If equation 1 is used ($\text{Ce}^{3+}/\text{Ce}^{4+}$) ratio has to be calculated by means of the equivalence constant. From

equation it is evident that at the start of titration the potential should be $-\infty$ because ferrous ions are only present and there are no ferric ion. At the mid point of titration $\text{Fe}^{2+} = \text{Fe}^{3+}$

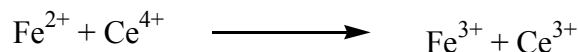
Therefore,

$$E = E_{\text{Fe}^{2+}/\text{Fe}^{3+}}^0$$

At equivalence point

$$a_{(\text{ox1})} + b_{(\text{red2})} = a_{(\text{red1})} + b_{(\text{ox2})}$$

i.e. the concentration of unchanged ferrous ions will be equal to the concentration of unchanged cerium ions, similarly concentration of ceric ions will be equal to concentration of ferric ions



$$K = \frac{[\text{Fe}^{3+}][\text{Ce}^{3+}]}{[\text{Fe}^{2+}][\text{Ce}^{4+}]} = \frac{[\text{Fe}^{3+}]^2}{[\text{Fe}^{2+}]^2}$$

$$\frac{[\text{Fe}^{3+}]}{[\text{Fe}^{2+}]} = \frac{[\text{Ce}^{3+}]}{[\text{Ce}^{4+}]} = \sqrt{K} \quad \text{eqn 3}$$

on combining equation 1 and 2 with equation 3

$$E = E_{\text{Ce}^{3+}/\text{Ce}^{4+}}^0 - \frac{0.0591}{n} \log_{10} K \quad \text{eqn 4}$$

$$E = E_{\text{Fe}^{2+}/\text{Fe}^{3+}}^0 + \frac{0.0591}{n} \log_{10} K \quad \text{eqn 5}$$

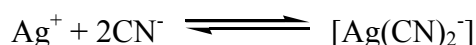
On adding equation 4 and 5

$$E = \frac{E_{\text{Ce}^{3+}/\text{Ce}^{4+}}^0 + E_{\text{Fe}^{2+}/\text{Fe}^{3+}}^0}{2}$$

when $a=b$ the titration curve is symmetrical around the equivalence point but when $a \neq b$ the titration curve will be markedly asymmetrical and the point of inflection will not coincide with equivalence point. The difference will depend upon the ratio of a/b . If $a > b$ the inflection point will occur before equivalence point when excess oxidant is present in solution and reverse is true when $a < b$.

Complexometric titration

Complexometric titration can be followed with an electrode of the metal whose ions is involved in complex formation e.g. a silver electrode may be used to follow the titration of cyanide ions with a standard solution of silver. The silver ion concentration will be governed by the equilibrium constant for the complex formation reaction.



The solid $\text{Ag}(\text{CN})_2$ begins to precipitate soon after the equivalence point. The further addition of silver neither changes the concentration of complex nor changes the concentration of silver ion of any extent so that the titration curve has an almost horizontal portion shortly after the equivalence point.

This is not so easy in case of many complexometric reactions because more than one complex is formed. Thus, the reaction in case of mercuric ion with cyanide are:

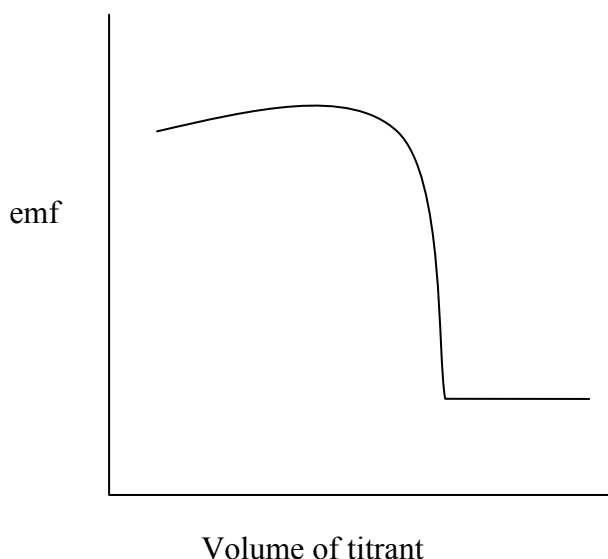
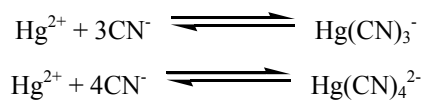


Fig 6: Titration curve for complexometric titration

These situations can be easily handled by the use of metal chelating agent such as EDTA. e.g complexometric titration of a solution containing two metal ion, both of which form complex with a reagent L. If only M1 were present in the sample curve A would be obtained. If M2 is also present, curve B results.

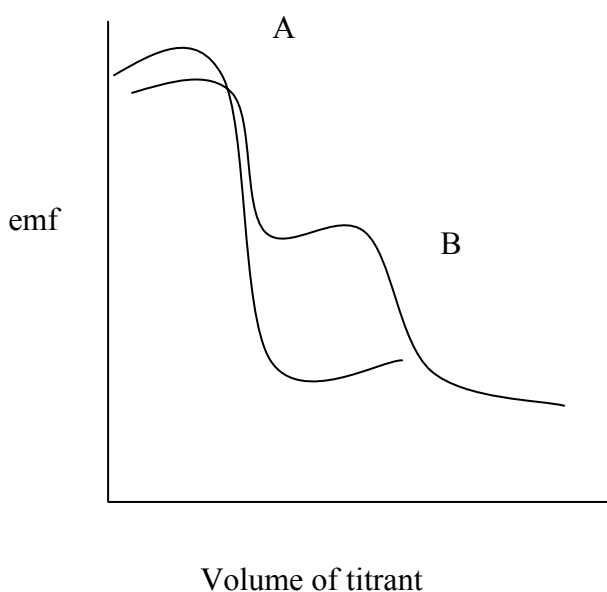


Fig 7: Titration curve for complexometric titration

In this case after all the M1 has been complexed by L at the first end point, the concentration of L increases up to a point where the second complex involving M2 begin to form. This type of titration is very useful as it allow an electrode sensitive to M1 to be used to titrate any metal M2 that forms a less sable complex with a given reagent than does M1.

Acid Base titration

Neutralization of acids and bases is always accompanied by the change in the concentration of H^+ and OH^- . Therefore hydrogen electrode may be employed in this titration. The reference electrode used is N-Calomel electrode (NCE).

A known volume of the acid to be titrated is kept in a beaker having an automatic stirrer. It also contain standard hydrogen electrode connected to NCE through a salt bridge. The hydrogen and calomel electrode are connected to a potentiometer which records the EMF of the solution. After the each addition of base the EMF is measured and the values are plotted against volume of titrant. The point where the EMF rapidly increases is the end point.

The potential of any hydrogen electrode is given by

$$E = E^\circ - 0.0591 \log a_{H^+} \text{ at } 25^\circ C$$

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

Therefore, the change in EMF is proportional to change in pH during titration.

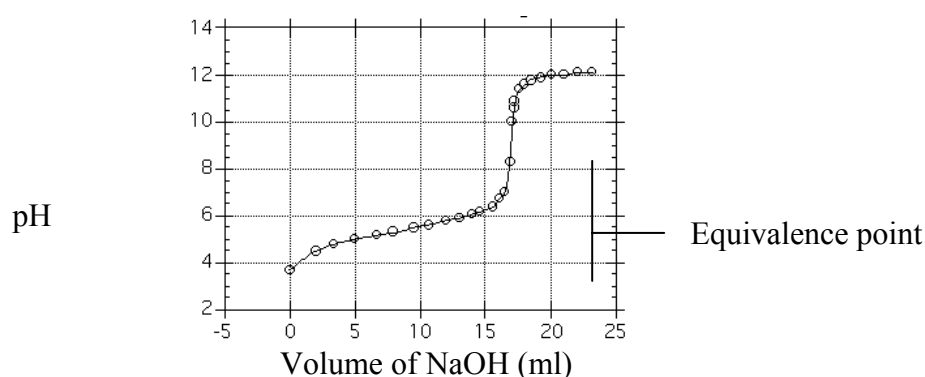


Fig 8: Titration curve for acid base titration

A more sensitive method of finding end point is to plot slope of the curve i.e. $\Delta E / \Delta V$ against V.

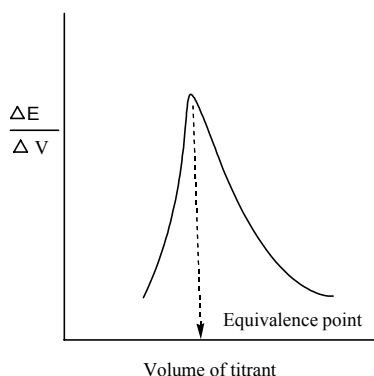


Fig 9: Titration curve for acid base titration

Precipitation titration

The indicator electrode used may be made of metal involved in the reaction or may be electrode whose potential is governed by the concentration of the anion being precipitated. The magnitude of the end point depends on the solubility of the substance being precipitated as well as the concentration involved e.g. the titration of silver ion with chloride ion using silver metal as indicator electrode. The other electrode to complete the cell is unimportant provided that it is a true reference electrode i.e. it maintains a constant potential. In case of silver chloride, normal hydrogen electrode is used.

The potential of silver electrode will be governed by

$$E = E^{\circ}_{\text{Ag}^+/\text{Ag}} + \frac{0.0591}{n} \log_{10} [\text{Ag}^+]$$

Suggested Readings:

1. Bassett J, Denney RC, Jeffery GH, Mendham J. Vogel's textbook of Quantitative Inorganic Analysis. The ELBS and Longman, London.
2. Beckett AH and Stenlake JB. Practical Pharmaceutical Chemistry, Vol. I and II. The Athlone Press of the University of London.
3. Connors KA. Textbook of Pharmaceutical Analysis. Wiley Intersciences, Newyork
4. Willard and Merrit. Instrumental methods of Analysis. Van Nostrand Reinhold Newyork.