Instrumental Analysis

Classification of Analytical Techniques

Introduction

Instrumental analysis is a field of analytical chemistry that investigates analytes using scientific instruments.

Advantages of instrumental methods:

Ability to carry out trace analysis, large numbers samples may be analyzed quickly, can be automated and less skill required to perform the analysis. It is generally more accurate, precise and more suitable for the analysis of the major constituents of a chemical sample.

Instrumental analysis is classified according to the principles by which the measurement signal is generated. The methods are listed as follows:

1-Electrochemical methods:

The electroanalytical methods measure the electric

potential in volts and/or the electric current in ampers in an electrochemical cell containing the analyte sample. These methods can be categorized according to which aspects of the cell are controlled and which are measured. The three main categories are potentiometry (the analyte is part of a galvanic cell, which generates a potential due to a drive to thermodynamic equilibrium and the difference in electrode potentials is measured) and voltammetry (the analyte is part of an electrolytic cell. Current flows on applying potential to the cell due to the participation of the analyte in a redox reaction. In the electrolytic cell the magnitude of the current is directly proportional to the concentration of analyte sample solution.).

2-Spectrochemical methods:

Spectrochemical methods of analysis measure the interaction of the molecules with electromagnetic radiation. They consist of many different applications such as atomic absorption, uv-visible and infrared absorption spectrochemical methods. Most of the methods in this category are based on the measurement of the amount of light absorb by an analyte sample.

ElectroChemical Methods

Classification

There are two main types of electrochemical methods:

1. Methods without potential imposing from the outside (potentiometry).
2. Methods with potential imposing from the outside which are based on measurement different electric parameter (all another methods)

Methods with potential imposing from the outside which are based on measurement of:

1. Electric conductivity of solutions – **conductometry**
2. Dependences of current value from the imposed potential **- voltammetry**

*1. **POTENTIOMETRY***

At the first level, interfacial electrochemical methods are divided into static methods and dynamic methods. In static methods, no current passes between the electrodes, and the concentrations of species in the electrochemical cell remain unchanged, or static. Potentiometry, in which the potential of an electrochemical cell is measured under static conditions, is one of the most important quantitative electrochemical methods. Thus, potentiometry is used to measure concentrations of specific anions and cations, sometimes in conjunction with a

titration. It measures electrical potential develops by an electrode in an electrolyte solution at zero current flow. Nernst Equation is used to relate potential to concentration of the analyte in solution.

2.***VOLTAMMETRY***

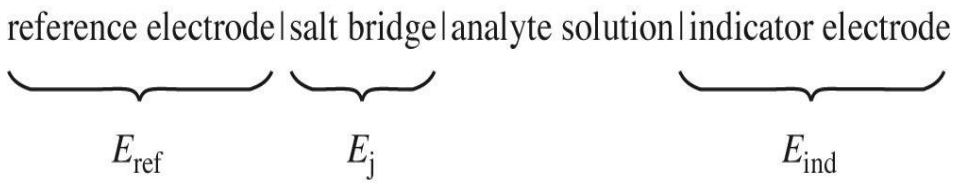
Dynamic methods use current flow and concentration change as the result of a redox reaction. They are further subdivided by whether one choose to control the current or the potential. Controlled-potential methods are subdivided further into controlled-potential coulometry and amperometry, in which a constant potential is applied during the analysis, and voltammetry, in which the potential is systematically varied. Voltammetry determine concentration of analyte in dilute solutions from current the flow as a function of voltage on variation of voltage the electrode.

3.***CONDUCTIMETRY***

Conductance is the technique measure **conductance** of a solution, using inert Electrodes, alternating current and an electrical null circuit. The concentration of analyte in solution is estimated from conductometric titration.

Potentiometry

In potentiometry, information of the sample composition is obtained from the ***potential*** develop between two electrodes. The electrolysis cell can be represented as follows:



Basic Components:

a) **Reference electrode:**

It gives reference for potential measurement.

b) **Indicator electrode:**

It is used where species of interest is measured.

c) **Potential measuring device**.

Reference Electrode

Reference electrode is a stable reversible nonpolarizable electrode which has a well-known electrode potential and shows little hysteresis with temperature. The high stability of the electrode potential is usually reached by employing a redox system with constant concentrations of each participants of the redox reaction. All standard electrode potentials, E^o, are reported relative to the Standard Hydrogen Electrode.

Saturated Calomel Electrode:

Saturated **c**alomel **e**lectrode (SCE) is based on the reaction between elemental mercury and mercureous, Hg(I), chloride. The aqueous phase in contact with the mercury and the mercury(I) chloride (Hg_2Cl_2, "calomel") is a saturated aqueous solution of potassium chloride, c.f. Fig. 1. The electrode is normally linked *via* a porous frit to the solution in which the other electrode is immersed. This porous frit is a salt bridge. It is based on the reaction between mercury and mercury(I) chloride. The calomel electrode contains mercury, which poses much greater health hazards than the silver metal used in the Ag/AgCl electrode.

½ cell: Hg/Hg_2Cl_2 KCl (sat) || E° = 0.2444 V at 25 °C

The electrode is based on the following reaction:

$$Hg_2Cl_{2(s)} + 2e^- \rightleftharpoons 2Hg_{(l)} + 2Cl^-_{(aq)}$$

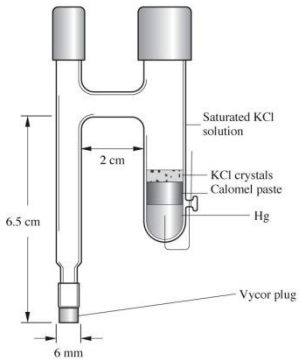


Fig.1: **S**aturated **c**alomel **e**lectrode

The Nernst equation for this reaction is:

$$E_{Calomel} = E^{o}_{Hg_2^{2+}/Hg} - \frac{RT}{2F} ln \frac{a^2_{Hg} . a^2_{Cl^-}}{a_{Hg_2Cl_2}}$$

$$E_{Calomel} = E^{o}_{Hg_2^{2+}/Hg} - \frac{RT}{2F} ln a^2_{Cl^-}$$

where E^0 is the standard electrode potential for the reaction and a_{Hg} is the activity for the mercury (the activity for a liquid mercury and mercureous chloride are 1.0). Thus, only variable in this equation is the activity (or concentration) of the chloride anion. But since the inner solution is saturated with potassium chloride, this activity is fixed by the solubility of potassium chloride. The saturated the redox potential of the calomel electrode is +0.2444 V versus. SHE at 25 °C. By replacing the activity in the Nernst equation with the value in the solubility equation, one get

$$E_{Calomel} = E^{o}_{Hg_2^{2+}/Hg} - \frac{RT}{F} \ln [Cl^-]$$

Thus, the response is to chloride ions.

Silver/Silver Chloride Electrode:

A silver chloride electrode is another type of reference electrode, commonly used in electrochemical measurements. For environmental reasons it has widely replaced the saturated calomel electrode. For example, it is usually the internal reference electrode in pH meters and it is often used as reference

in reduction potential measurements. The electrode functions as a redox electrode and the reaction is between the silver metal (Ag) and its salt silver chloride. The corresponding equations can be presented as follows:

½ cell: Ag/AgCl (sat), KCl (xM)|| E° = 0.199 V at 25 °C

½ electrode reaction:

$$AgCl_{(s)} + e^- \leftrightharpoons Ag_{(s)} + Cl^-_{(aq)}$$

This reaction is characterized by fast electrode kinetics, meaning that a sufficiently high current can be passed through the electrode with the 100% efficiency of the redox reaction. The reaction has been proven to obey these equations in solutions of pH values between 0 and 13.5. The Nernst equation below shows the dependence of the potential on the activity or effective concentration of chloride-ions:

$$E_{Silver} = E^o_{Ag^+/Ag} - \frac{RT}{F} \ln [Cl^-]$$

The standard electrode potential E^0 against standard hydrogen electrode (SHE) is 0.230V ± 10mV. The potential is however very sensitive to traces of bromide ions which make it more negative.

Advantage: One advantage over SCE is that Ag/AgCl electrode can be used at temperatures > 60°C.

Disadvantage: Ag reacts with more ions.

Indicator Electrodes:

It responds to the **Analyte**. It includes:

1- Metallic Indicator Electrodes

2- Membrane Indicator Electrodes

1-Metallic Indicator Electrode (Four Main Types)

Four types of metallic electrodes are commonly used in potentiometry, each of which is considered in the following discussion.

A-Metallic Electrodes of the First Kind:

An electrode of this type is a pure metal in contact with a solution containing its cation. The potential is a function of concentration of M^{n+} in a M^{n+}/M. The most common one:

Copper electrode for detection of Cu^{2+} in solution.

$$Cu^{2+}_{(aq)} + n^{2-} \leftrightarrow Cu_{(s)}$$

$$E_{ind} = E^{o}_{Cu^{2+}/Cu} + 0.0592log[Cu^{2+}]$$

B-Metallic Electrodes of the Second Kind:

Electrode of this kind is a metal wire that coated with one of its anions, X, sparingly soluble precipitate or stable complexes with the electrode cations. Its potential is a function of the concentration of X in an MX_n /M redox half reaction. A common example is silver electrode and AgCl as its salt

precipitate as the following example. This kind of electrode can be used to measure the activity of chloride ion in a solution.

$$AgCl_{(s)} + e^- \leftrightharpoons Ag_{(s)} + Cl^-_{(aq)}$$

$$E_{Silver} = E^o_{Ag^+/Ag} - \frac{RT}{F} \ln [Cl^-]$$

C-Metallic Electrodes of the Third Kind:

Metal electrodes respond to a different cation linked to cation by an intermediate reaction. Can be made to detect other cations that bind to EDTA.

Example: Detect calcium by complex with EDTA.

D-Metallic Redox Indicators Fourth kind:

Inert conductors that themselves do not engage in electrochemical reactions under the conditions in which a redox reaction of interest occurs.

Example: Determination of pH using Quinhydrone Electrode and detection of Ce^{3+} with Pt electrode

2- Membrane Indicator Electrodes:

Electrodes based on determination of cations or anions by the selective ***adsorption*** of these ions to a membrane surface. Often called **I**on **S**elective **E**lectrodes (ISE).

Desired properties of ISE's

Membrane will not dissolve in solution during measurement as silica, polymers, low solubility inorganic compounds (AgX) can be used. It needs some electrical conductivity and

selectively for ion of interest. Example: the glass pH electrode.

Potentiometric Determination of EMF

Measuring the potential of an electrochemical cell under conditions of zero current is accomplished using a potentiometer ***Wheatston Bridge Potentiometer***. A schematic diagram of a manual potentiometer is shown in Figure 2.

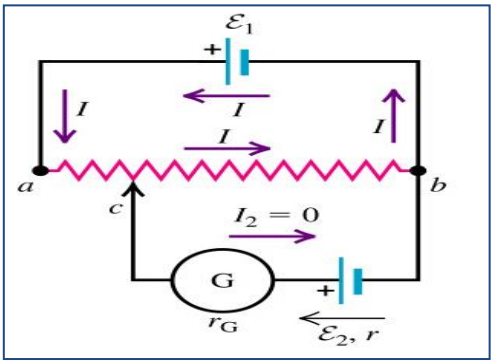


Fig. 2: *Wheatston Bridge Potentiometer*

It is used to measure the potential (or voltage) in a circuit by tapping off a fraction of a known voltage from a resistive slide wire and comparing it with the unknown voltage. To make a measurement the tap key is pressed momentarily, and the current is noted at the galvanometer. The sliding tap of the potentiometer is adjusted and the galvanometer briefly connected to both the sliding tap and the unknown potential; the

sliding tap adjusted until the galvanometer read zero deflection. This process is continued until the galvanometer registers a current of zero. At that point the galvanometer is drawing no current from the unknown source, and the magnitude of voltage can be calculated from the position of the sliding contact. As an electrical component, **potentiometer** describes a three-terminal resistor with a sliding contact that forms an adjustable voltage divider. If all three terminals are used, it can act as a variable voltage divider. If only two terminals are used (one side and the wiper), it acts as a variable resistor or rheostat. In which ε_1 is known, ***standard Cadmium Weston cell*** producing a convenient 1.018638 volt reference and had the advantage of having a lower ***temperature coefficient***, and ε_2 is unknown. Slide the point of contact "c", i.e., change the resistance R_{ab}, until the galvanometer shows no current follow. Then:

$$\varepsilon_1 = R_{ab} \, . I \qquad \varepsilon_2 = R_{cb} \, . I$$

$$I = \frac{\varepsilon_1}{R_{ab}} = \frac{\varepsilon_2}{R_{cb}}$$

$$\varepsilon_2 = \varepsilon_1 \frac{R_{cb}}{R_{ab}}$$

Potentiometric Analysis

- **1-Direct potentiometric measurement.**

- **2-Potentiometric titration.**
- **3-Standard addition.**

Direct potentiometric measurement

Direct potentiometry involves the direct measurement of a potential generates at an electrode in solution relative to a potential of a reference electrode.

Neutralization:

Measurement of pH

The pH is ascertained from the emf of an electrochemical cell of the following design:

Electrode reversible to hydrogen ions	Unknown (*x*) or standard (s) buffer solution	Salt bridge	Reference electrode

The potential between the two electrodes is usually measured with a pH/mV meter. In most measurements, a glass electrode is used as an indicator electrode coupled with a Ag/AgCl reference electrode probe assembly. On immersing the probe assembly in the solution of unknown pH_x, an E_x is developed. On the other hand, the emf of the probe assembly when immersed in a standard reference material with pH_s value is E_s. The pH_x is given by the following relationship:

$$(pH)_x = (pH)_s - \frac{E_s - E_x}{2.303RT/F}$$

where R is the gas constant, T is temperature, K and F is the Faraday constant.

The $(pH)_x$ of the unknown is calculated from the standard pH_s and the measured difference in the emf E_x of the electrode combination when the standard solution is removed from the cell and replaced by the unknown.

pH Electrodes

pH glass measuring electrode:

A glass electrode is a type of ion-selective electrode made of a doped glass membrane that is sensitive to a specific ion. The most common application of ion-selective glass electrodes is for the measurement of pH. Glass electrodes play an important part in the instrumentation for chemical analysis and physico-chemical studies. The voltage of the glass electrode, relative to some reference value, is sensitive to changes in the activity of certain type of ions. There are different types of pH glass electrode, some of them have improved characteristics for working in alkaline or acidic media. But almost all electrodes have sufficient properties for working in the most

popular pH range from pH = 2 to pH = 12. Special electrodes should be used only for working in aggressive conditions.

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 electrode is best thought of as a tube within a tube. The inner tube contains an unchanging 1×10^{-7} mol/L 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. It is filled with a reference solution of KCl and has contact with the solution on the outside Between measurements any glass and membrane electrodes should be kept in a solution of its own ion. It is necessary to prevent the glass membrane from drying out because the performance is dependent on the existence of a hydrated layer, which forms slowly of the pH probe by way of a porous plug that serves as a salt bridge.

The measure and reference electrodes can be joined together in a single glass body assembly known as a combined. 3.

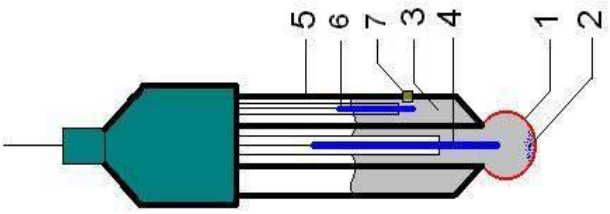


Fig. 3. 1-a sensing part, 2-AgCl ppt, 3-0.1M HCl soln,4-AgCl electrode, 5-body of electrode, 6-eference elctrode, 7-junction with study solution

$$Ag(s)|AgCl(s)|Cl^-(aq)\|H^+(aq,outside)\,\|\,H^+(aq,inside),Cl^-(aq)|AgCl(s)|Ag(s)$$

reference Electrode test solution Glass Electrode

The glass membrane permits $H^+_{(aq)}$ to exchange with Na^+ in the silicate structure:

$$H^+_{(aq)} + Na^+Cl^- \leftrightarrow N^+_{(aq)} + H^+Cl^-$$

The electrode is filled with hydrochloric acid or phosphate buffer containing Cl^- anions. Conveniently, the glass electrode has E = 0 when the external medium is at pH = 7. It is usually used in conjunction with a calomel electrode that makes a direct contact with the test solution through a salt bridge.

The electrode consists of glass tube with a thin walled glass bulb on one end containing a solution of fixed hydronium ion activity, usually 0.1 M $HCl_{(aq)}$ and an **internal reference** electrode, the silver/silver chloride cell, $Ag_{(s)|}AgCl_{(s)}$. When the bulb is immersed in a solution, an electrical potential develops across the glass membrane in response to the hydronium ion

activity in the external solution. The potential is measured against an **external** reference electrode, usually the saturated calomel electrode,

$$KCl_{(sat'd)}, Hg_2Cl_{2(s)|}/Hg_{(l)}.$$

The complete cell can be represented as:

$$Ag_{(s)} \mid AgCl_{(s)}, HCl(0.1M)\mid glass\mid H^+(xM) \parallel KCl_{(satd)}, Hg_2Cl_{2(s)} \mid Hg_{(l)}$$

The membrane itself is permeable to Na^+ and Li^+ cations but not to H^+ ions. For each face of the electrode is coated with thin layer of hydrated silica. The hydrogen ion in the test solution modify this layer to an extent that depends on their activity or/and concentration in the solution, and the charge modification of the outside layer is transmitted to the inner layer by the Na^+ and Li^+ cations in the glass. The hydronium ion activity gives rise to a membrane potential by this indirect mechanism.

The pH measurement is comprised of two half-cell, or electrode, potentials. One half-cell is the pH sensitive glass measuring electrode and the other is the reference electrode. Just as the two half-cell potentials of a battery are required to complete a circuit so does a pH sensor. The mathematical expression for this is:

$$E = E_m - E_r$$

where E_m = the electrode potential of the measuring electrode and E_r = the electrode potential of the reference electrode.

Quinhydrone Electrode:

On addition of hydroquinone and *p*-quinone (1:1 molar ratio mixture) to a sample solution, a pH dependent oxidation-reduction couple is formed between quinone and quinol, hydroquinone. This redox potential is measured with a platinum electrode. The indicator electrode and the corresponding electrode reaction can represented as follows:

Pt, Quinhydrone, electrolyte |

$$Q_{(aq)} + 2e^- + 2H^+_{(aq)} \rightleftharpoons QH_{2(aq)} + E$$

The Nernst equation below shows the dependence of the potential on the activities of reaction constituents, hydrogen ions, quinone and hydroquinone:

$$E_Q = E^o_{Q/H_2Q} - \frac{RT}{2F} ln \frac{a_{H_2Q}}{a_Q . a^2_{H+}}$$

The activities of quinone and hydroquinone are unity. Thus, the potential depends only on the activity of hydrogen ions:

$$E_Q = E^o_{Q/H_2Q} - \frac{RT}{2F} ln \frac{a_{H_2Q}}{a_Q .} - \frac{RT}{2F} ln \frac{1}{a^2_{H+}}$$

Finally the potential depends on the effective concentration of hydrogen ions:

$$E_Q = 0.699 + \frac{RT}{F} \ln [H^+]$$

The quinhydrone electrode works best between pH 1 and pH 8. When measured against a saturated KCl-AgCl reference electrode, the quinhydrone electrode produces 59 mV/pH with the zero potential at pH 8.5. The quinhydrone electrode is often used to calibrate other reference electrodes. Quinhydrone forms a reversible oxidation-reduction couple when dissolved in water. Hydrogen ions participate in the reaction between the quinone and hydroquinone creating a pH dependent equilibrium. The redox-potential of the resulting equilibrium is proportional to the pH of the solution. The redox-potential calibrating solutions are made by adding quinhydrone to pH 4 and pH 7 buffers, creating 265 mV and 90 mV solutions respectively.

pH Measurement:

The measurement of the pH of a solution is simple in principle, so it is based on the measurement of the potential of hydrogen electrode immersed in the solution. The left-hand, i.e., the reference electrode of the cell is typically a saturated

calomel electrode (SCE) with potential $E_{(cal)}$. The pH of the cell is therefore

$$pH = (E- E_{(cal))}/ -(RT/F) \ln 10$$

or at temperature of 25^0C

$$pH = (E- E_{(cal))}/ -59.16 \text{ mV}$$

The practical definition of the pH of a solution X is

$$pH_{(X)} = pH_{(S)} - E/ -59.16 \text{ mV}$$

at 25^0C, where E is the potential of the cell

$$Pt\ |H_{2(g)}\ |\ S_{(aq)}\ ||\ 3.5MKCl_{(aq)}\ ||\ X_{(aq)}H_{2(g)}\ |\ Pt$$

and S is a solution of standard pH while $||\ 3.5MKCl_{(aq)}\ ||$denotes the salt bridge. In practice, indirect methods are much more convenient, and the hydrogen electrode is replaced by the glass electrode.

Standard Addition Method:

In many cases the intensity of the signal of the analyte is affected by the composition of the matrix, by the temperature and other factors. One of the methods to overcome these problems is the method of standard additions. Two conditions have to be fulfilled for successful application of the method:

(a) the calibration graph must be linear,

(b) the calibration curve of the analyte passes through the origin.

The observed electrode potential of the sample solution is measured, E_1, The potential is as follows:

$$E_1 = \text{const} + 2.303RT/F \log C_u$$

On addition of a known volume of the standard solution, C_s (which should be about 10 times the estimated sample concentration) the potential is varied to E_2. After correction for dilution of the original sample by the addition, and the corresponding correction of the added standard, the potential becomes as follows:

$$E_2 = \text{const} + 2.303RT/F \log (C_u + C_s)$$

Combining equations, one gets

$$\Delta E = E_2 - E_1 = S\ log\left(\frac{C_u - C_s}{C_u}\right)$$

Volume corrections are

$$C_u = C_u \frac{V_u}{V_u + V_s} \text{ and } C_s = C_s \frac{V_s}{V_u + V_s}$$

The concentration of the unknown can be explicitly determined by solving the equation

$$C_u = C_s + C_u x 10^{\Delta E/s}$$

$$C_u = \frac{C_s}{\left(1 - 10^{\Delta E/s}\right)}$$

Sample addition is the inverse of the standard addition method. It is useful for samples that are small, highly concentrated, or dirty. It cannot be used when the unknown species is complexed. With this technique the sample is added to a known volume or a standard solution. The unknown concentration is determined by solving this equation:

$$C_u = \frac{C_s}{\left(1 - 10^{\Delta E/S}\right)}$$

Known addition and subtraction methods are particularly suitable for samples with a high unknown total ionic strength. If the species being measured is especially unstable, known subtraction is preferred over known addition.

Potentiometric Titration

In potentiometric titration, the end point is determined by measuring the potential of an indicator electrode as a function of the volume of titrant added. This technique can be applied to all types of analyses which involve titrimetric methods. The electrical potential is produced by a galvanic cell, and the magnitude of the potential depends on the activities (concentrations) of the solutes in the cell solutions. The relationship between potential and activity is the basis for potentiometry as an analytical tool. In a potentiometric titration,

the cell is composed of an ***indicator electrode*** (which is responsive to the analyte activity) and an external ***reference electrode*** (an electrode which produces a constant potential). The electrical potential between the two electrodes is a measure of the analyte activity. A titration curve is plotted between potential difference versus the volume of added reagent The equivalence point comes at the inflection point of the curve, i.e., the value of the *x* axis (volume of titrant added) at which the slope reaches its maximum value. Advantages of potentiometric titrations over 'classical' visual indicator methods are:

1. Can be used for coloured, turbid or fluorescent analyte solution.
2. Can be used for titration of polyprotic acids, mixtures of acids, mixtures of bases or mixtures of halides.

The location of the end point of the titration is at the inflection point on the titration curve. The simplest graphical method is to locate by inspection the maximum slope on this curve. This, of course, is subject to errors of judgment and can be improved upon with a simple mathematical trick. If one differentiate this titration curve once: Volume of titrant, V dE/dV, one can see that the equivalence point is not an inflection point, but a maximum, c.f., figure 4. On considering the second derivative of the titration curve, volume of titrant, V, d^2E/dV^2 one can see that the equivalence point is at the volume

for the rapid passes through zero. The **equivalence point** of the titration is the point at which exactly enough titrant is added to react with all of the substance being titrated. In other words, at the equivalence point, the number of moles of titrant added corresponds exactly to the number of moles of substance being titrated according to the reaction stoichiometry.

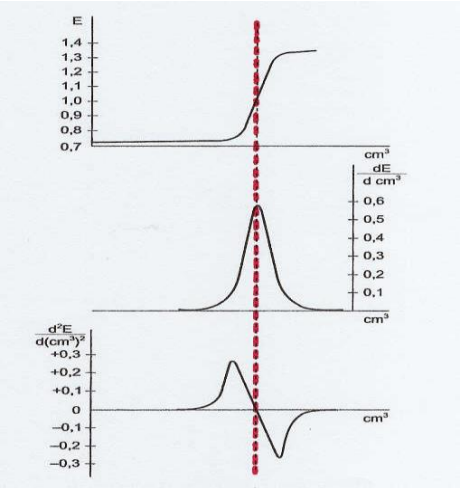


Figure 4: location of the end point of the titration

The equipment required for direct potentiometric measurements includes an indicator electrode, a reference electrode, and potential-measuring device.

Types of Potentiometric Titration

Depending on the type of the reactions involved to which potential measurement is applied for end point detection, potentiometric titrations is classified into followings.

(a) Acid-Base Titration:

An electrode, responsible to hydrogen ion (e.g. glass, quinhydron) is employed in order to follow the progress of acid-base reactions. The potential of such electrode at 25^{o} C is given by an equation following equation:

$$E = E^{o} + 0.0591pH.,$$

where E^{o} is a constant potential.

(b) Complexometric Titration:

Complexometric titration can be followed with an electrode of the metal whose ion is involved in complex formation. For instance a number of ion selective electrodes can be used to monitor the titration of metal ions potentiometrically by EDTA. A silver electrode may be used to follow the titration of cyanide ion with a standard silver solution. The potential of the silver electrode may be expressed at 25 ^{o}C by the following equation:

$$E = E^{o} + 0.0591 \log [Ag^{+}].$$

(c) Oxidation-Reduction Titration:

Such titrations involve the transfer of electrons from the substance being oxidized to the substance being reduced. For such reaction the potential (E) acquired by the indicator electrode at 25°C is given by:

$$E = E^o + \frac{0.0591}{n} log \frac{[Ox]}{[Red]}$$

The potential is controlled by the ratio of these concentrations terms. It is possible to titrate two substances by the same titrant provided the standard potentials of the substances being titrated, and their oxidation or reduction products, differ by about 0.2 V.

(d) **Precipitation Titration:**

In this case, the titration reaction results in the formation of precipitate. A precipitation titration that involves insoluble salts of metals such as mercury, silver, lead and copper may be followed potentiometrically. The indicator electrode may be made of the metal involved in the reaction, a silver electrode for the titration of halides for instance, or may be an electrode whose potential is governed by the concentration of the anion being precipitated. The potential of the silver electrode used as a cathode with SCE as anode in the titration of potassium iodide with silver nitrate will be governed by following Nernst equation:

$$E_{Ag^+/Ag} = E^o_{Ag^+/Ag} + \frac{0.0591}{n}\log[Ag^+]$$

The concentration of silver ion is related to the concentration of iodide ion as $K_{AgI} = [Ag^+][I^-]$, where K_{AgI} is the solubility product of silver iodide. Hence, the electrode potential can be expressed in terms of the iodide ion concentration as:

$$E_{Ag^+/Ag} = E^o_{Ag^+/Ag} + 0.0591\log K_{AgI} - 0.0591\log[I^-]$$

In potentiometric titration the electrode potential over most of the titration range varies gradually, but near the equivalence point the electrode potential changes very abruptly even by the addition of small amount of titrant.

The magnitude of the potential change at the end point depends on the solubility of the substance being precipitated as well as on the concentration of the active ionic species involved. In precipitation based potentiometric titration a number of components differing in solubility product could be analyzed. For example: mixture of potassium iodide, potassium bromide and potassium chloride could be titrated with silver nitrate solution using silver electrode and silver electrode. Among three halides, the solubility product of iodide is least (10^{-16}) and of chloride is highest (10^{-10}); silver iodide precipitates first, then silver bromide and at last silver chloride. But due to co-

precipitation, adsorption the end points in halide mixture contains error.

Acid-Base Titration:

For the potentiometric acid – base titration, the indicator electrode, which responsible to hydrogen ion glass or quinhydron) is employed in order to follow the progress of titration.

Strong acids or strong bases potentiometric titration:

Titrations involving *strong acids* or *strong bases* as titrant most often have wide pH swings at the equivalence point, giving sharp end points. Yet another factor the affects the sharpness of the end point is the strength of the acid or base being titrated. For the strong acid-base reaction, the reaction is:

$$H^{+}_{(aq)} + OH^{-}_{(aq)} \rightleftharpoons H_2O_{(l)}$$

The titration curve for this type is as follows:

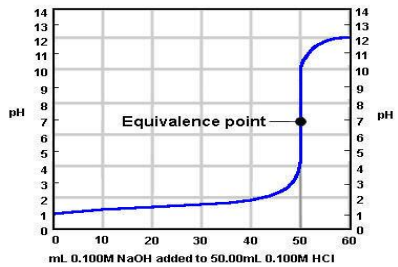


Figure 5.Titration Curve for Strong Acid with Strong Base

Example:

What is the pH when 49.00 mL of 0.100 M NaOH solution have been added to 50.00 mL of 0.100 M HCl solution?

The remaining $[H^+]$ in the solution is:

$$[(50.0 – 49.0) \times 0.1]/99.0 = 0.001 \text{ M}$$

$$\text{pH} = 3.00$$

Titration Curves of Weak Acids with a Strong Base:

The **equivalence point** for a weak acid-strong base titration has a **pH > 7.00.** For a strong acid-weak base or weak acid-strong base titration, the pH will change rapidly at the very beginning and then have a gradual slope until near the equivalence point. The gradual slope results from a buffer solution being produced by the addition of the strong acid or base, which resists rapid change in pH until the added acid or base exceeds the buffer's capacity and the rapid pH change occurs near the equivalence point. The **equivalence point** for a weak base-strong acid titration has a pH < 7.00.

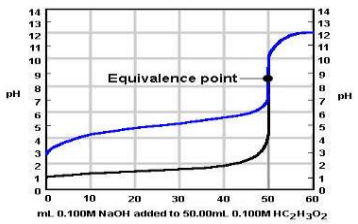


Figure 6.Titration Curve for Weak Acid with Strong Base

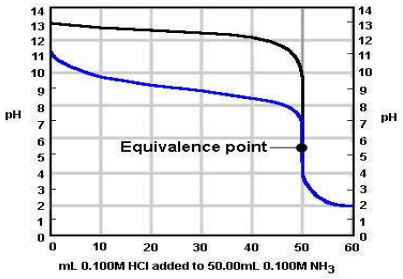


Figure 7.Titration Curve for Strong Acid with Weak Base

Example:

What is the pH when 30.0 mL of 0.100 M NaOH have been added to 50.0 mL of 0.100 M acetic acid?

Step 1: Stochiometric calculation:

The original number of moles of $HC_2H_3O_2$ in the solution is:

50.0×10^{-3} L x 0.100 M = 5.00×10^{-3} moles $HC_2H_3O_2$

Similarly, there are 3.00×10^{-3} moles of OH^- due to the NaOH solution. The reaction goes to completion:

$$OH^-_{(aq)} + HC_2H_3O_{2(aq)} \rightleftharpoons C_2H_3O^-_{2(aq)} + H_2O_{(aq)}$$

	OH^-	**$HC_2H_3O_2$**	**$C_2H_3O_2^-$**
Initial	3.00×10^{-3} mol	5.00×10^{-3} mol	0
Change	-3.00×10^{-3} mol	-3.00×10^{-3} mol	$+3.00 \times 10^{-3}$ mol
Final	0	2.00×10^{-3} mol	3.00×10^{-3} mol

The total volume is 80.0 mL.

We now calculate the resulting molarities :

$$[HC_2H_3O_2] = \{2.00 \times 10^{-3} \text{ mol } HC_2H_3O_2/0.0800 \text{ L}\} = 0.0250 \text{ M}$$

$$[C_2H_3O_2^-] = \{3.00 \times 10^{-3} \text{ mol } C_2H_3O_2^-\}/0.0800 \text{ L}\} = 0.0375 \text{ M}$$

Step 2: Equilibrium calculation, using simplification:

$$K_a = \{[H^+][C_2H_3O_2^-]/[HC_2H_3O_2]\} = 1.8 \times 10^{-5}$$

$$[H^+] = \{K_A\,[HC_2H_3O_2]/[C_2H_3O_2^-]\} =$$

$$\{(1.8 \times 10^{-5})(0.0250)/(0.0375)\} = 1.2 \times 10^{-5} \text{ M}$$

$$pH = -\log(1.2 \times 10^{-5}) = 4.92$$

It worthy to note the titration curve depends on the dissociation constant of the acid with strong base, c.f. figure 7.

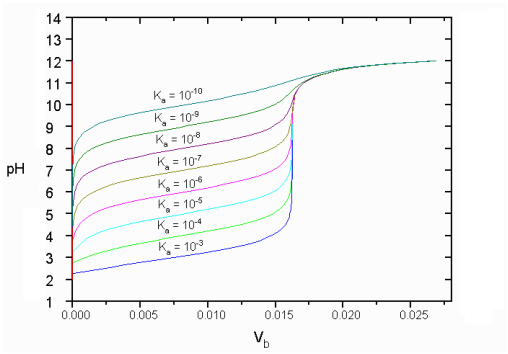
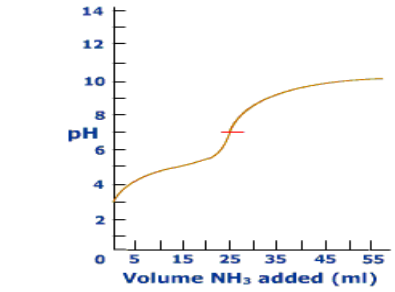


Figure 8.Titration Curves for Acids, K_a, with Strong Base

The weaker the analyte, the smaller the pH change through the equivalence point, as shown in Figure 9. The concentration of the analyte can also influence the end,

increasing (for acids) or decreasing (for bases) the starting pH as solutions become more dilute.



Titration curve of weak base (NH_4OH) and weak acid (CH_3COOH)

Fig. 9.

Potentiometric titration of a polybasic, acid:

Titration of polyprotic acids (or bases) requires more attention than titration of monoprotic ones. There are two reasons for that polyprotic acid can have more than one inflection point on the titration curve. pH change during titration is limited, that means steep part of the titration curve must be short, that the end point detection section doesn't help to achieve good accuracy of titration. Following examples are:

Sulfuric acid - while its second proton is much less acidic than the first one - is strong enough so that both protons get titrated together. There is only one, nice and high steep part of the titration curve.

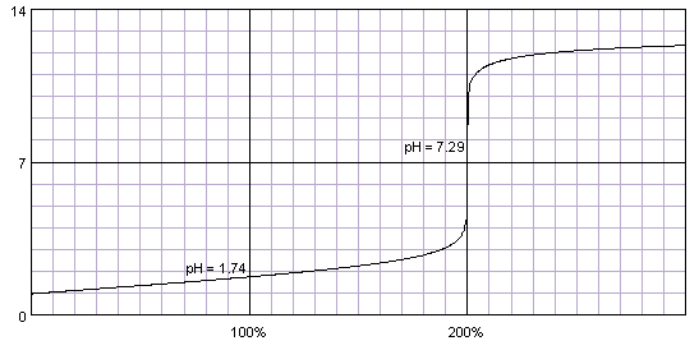


Fig. 10: Titration of 0.1M solution of sulfuric acid titrated with 0.1M solution of strong base. pK_{a1}=-3, pK_{a2}=2.

Citric acid has three relatively similar dissociation constants, thus instead of giving three (or at least two) separate end points, it has a long ramp, at which buffering effect of the first and second dissociation steps doesn't allow for fast rise of pH.

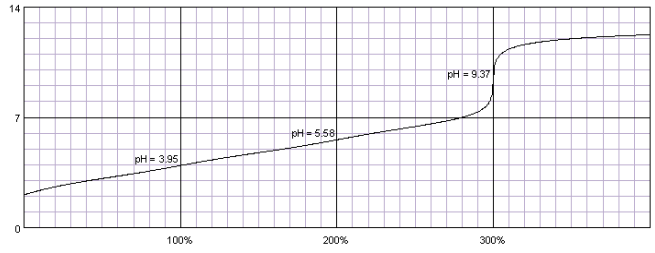


Fig. 11: Titration of 0.1M solution of citric acid titrated with 0.1M solution of strong base. pK_{a1}=3.13, pK_{a2}=4.76, pK_{a3}=6.40.

In the case of phosphoric acid give with two separate end points. Third dissociation constant is so small, that even after

adding large excess of 0.1M titrant over 20% of the acid is in the form of HPO_4^{2-}.

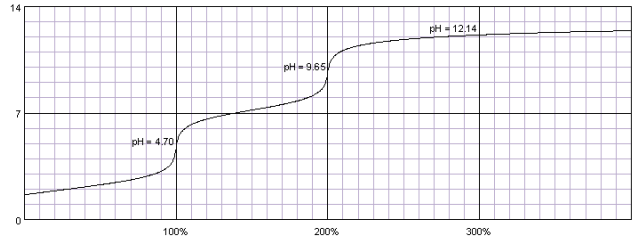


Fig. 12: Titration of 0.1M solution of phosphoric acid titrated with 0.1M solution of strong base. pK_{a1}=2.15, pK_{a2}=7.20, pK_{a3}=12.35.

While in many cases more than one end point makes the titration to be difficult, it allows simultaneous determination of NaOH and Na_2CO_3 in one solution.

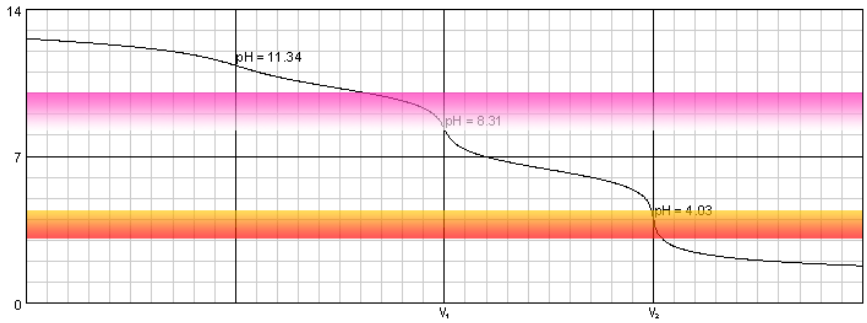


Fig. 13: Titration of solution of 0.1M Na.OH and 0.1M Na_2CO_3 titrated with 0.1M solution of strong acid. Carbonic acid dissociation constants: pK_{a1}=6.37, pK_{a2}=10.25.

Solution of sodium hydroxide and disodium carbonate contains three bases - OH^-, CO_3^{2-} and HCO_3^-. First two are much

stronger, so they are neutralized first. First equivalence point is at pH 8.31 and the second end point is at pH 4.03 to be visible.

Titration of a Dibasic Acid:

The titration curves for polyprotic, polybasic, acids show more than one equivalence point as succeeding protons are neutralized. The titration curve of a weak dibasic acid, H_2A, is essentially a composite of the titration curves of two weak acids of the same concentration and with dissociation constants K_{a1} and K_{a2}. It is important to realize that K_{a1}/K_{a2} must be greater than 1000 to see the two distinct breaks (inflection points) in the titration curve. If this is not so, the first break will be nonexistent or will be of such poor definition that it will have no analytical value.

The weak acid ***sulfurous*** acid (H_2SO_3) is much more typical. Sulfurous acid dissociates in two steps:

$$H_2SO_{3(aq)} + H_2O \rightleftharpoons HSO^-_{3(aq)} \quad K_1 = 1.4x10^{-2}$$

$$HSO^-_{3(aq)} + H_2O \rightleftharpoons SO^{2-}_{3(aq)} \quad K_2 = 6.3x10^{-8}$$

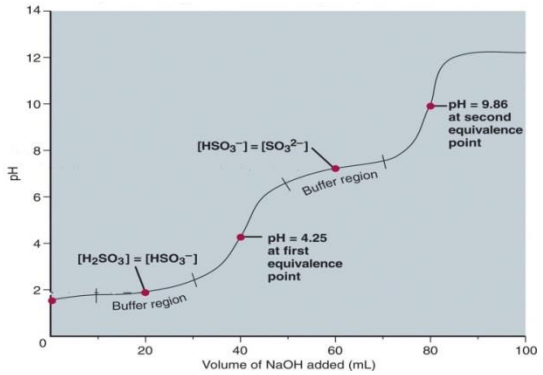


Fig. 14:Titration of 40.00 mL of 0.1000 M H_2SO_3 with 0.1000 M NaOH

For any similar system the dissociation constants are always in the relationship $K_1 > K_2$. In the case of sulfurous acid, and many others, the K values are sufficiently different that the mixture behaves during titration as though there were two acids present, but not simultaneously. Because K_2 is much smaller than K_1 there is essentially no SO_3^- present in the mixture until all of the H_2SO_3 has been converted to HSO_3^-. This would show up on a titration curve as an equivalence point. Then the "second" titration would begin with the HSO_3^-, giving a second equivalence point at the stoichiometric end of the neutralization reaction. Such a titration would give a curve as shown Fig. 8. Another example is shown in Fig. 9 for titration of oxalic acid with Strong Base, NaOH.

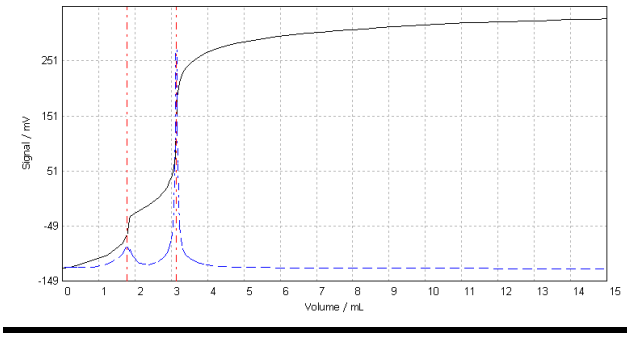


Figure 15: Titration curve of dibasic, Oxalic Acid, with NaOH

For weak diprotic acids in which K_1 is about 10^4 times (or more) greater than K_2 the relationships are valid. For the general case of H_2A titrated with NaOH, the neutralization reaction could be written as:

$$H_2A_{(aq)} + 2\ NaOH_{(aq)} \leftrightharpoons Na_2\ A_{(aq)} + 2\ H_2O$$

At that point the "first" neutralization is complete:

$$H_2A_{(aq)} + NaOH_{(aq)} \leftrightharpoons HA^-_{(aq)} + H_2O$$

and moles of base added do indeed equal the moles of acid originally present. Once the first equivalence point has been reached, the important equilibrium in the mixture becomes:

$$HA^- + H_2O \leftrightharpoons A^{2-} + H_3O^+$$

Titration of Tribasic Acid, Phosphoric acid

Some acids react with water in steps; a well-known example is Phosphoric Acid. During the titration H_3PO_4 reacts with hydroxide in three steps. The pH values at the two equivalence points are:

At the first equivalence point: pH = 4.7

$$H_3PO_{4(aq)} + OH^-_{(aq)} \leftrightharpoons H_2PO^-_{4(aq)} + H_2O_{(l)}$$

At the second equivalence point: pH = 9.3

$$H_2PO^-_{4(aq)} + OH^-_{(aq)} \leftrightharpoons HPO^{2-}_{4(aq)} + H_2O_{(l)}$$

Neutralization of the third proton of phosphoric acid does not produce an appreciable break in the titration curve. The basicity (proton accepting ability) of the phosphate ion is large, and it undergoes hydrolysis producing hydroxide ion.

$$HPO^{2-}_{4(aq)} + OH^-_{(aq)} \leftrightharpoons PO^{3-}_{4(aq)} + H_2O_{(l)}$$

$$PO^{3-}_{4(aq)} + H_2O_{(l)} \leftrightharpoons HPO^{2-}_{4(aq)} + OH^-_{(aq)} \quad \text{(hydrolysis)}$$

The first reaction will occur first until all of the acid H_2A is used up. Then the second reaction will begin and will continue until all of the H_2A^- is gone. Then the third reaction will occur until all of the HA^{2-} is gone. This will only be true when the successive dissociation constants are different by a large enough factor and when all of the acidic species are strong enough. For example, phosphoric acid has K_a values that are different by a large enough factor to allow it to react with a strong base in a stepwise fashion, however, the last proton of phosphoric acid is extremely difficult to remove, and the reaction of phosphoric acid that is analogous to the final reaction essentially will not occur in aqueous solution.

The titration curve for the polybasic acid such as phosphoric acid will have the form shown in Figure 16. Its K_a

values are approximately 10^{-3}, 10^{-8} and 10^{-13}. The first point on the curve corresponds to a solution of phosphoric acid only. The pH at this point is due solely to the phosphoric acid in the solution. As soon as some base is added, some $H_2PO_4^-$ is produced. The solution now contains both phosphoric acid (a weak acid) and its conjugate base dihydrogen phosphate, and thus it is a buffer. This will be the situation from the initial point to the first equivalence point, and therefore this region of the curve is called the first buffer zone. The pH of the point midway between the first and second equivalence points is equal to the negative logarithm of K_{a1}, pK_{a1}. At the first equivalence point, all of the H_3PO_4 has been neutralized and only $H_2P0_4^-$ is present in the solution. When more base is added, some of the $H_2P0_4^-$ is neutralized and some $HP0_4^{2-}$ is produced. This solution contains both dihydrogen phosphate (a weak acid) and its conjugate base hydrogen phosphate, and thus is a buffer. At all points between the first and second equivalence points, the solution will contain these two species, and therefore this portion of the curve is called the second buffer zone. The pH of the solution at the point halfway between the second and third equivalence points is equal to pK_{a2}. At the second equivalence point the only species in the solution is HPO_4^{2-}.

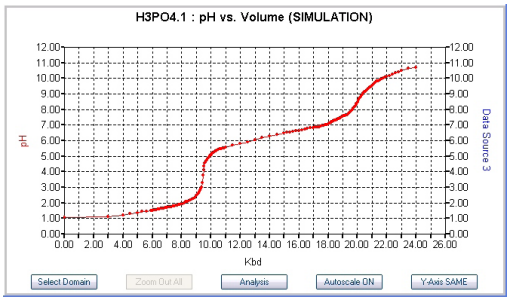


Fig. 16:Titration curve of H_3PO_4, with strong base

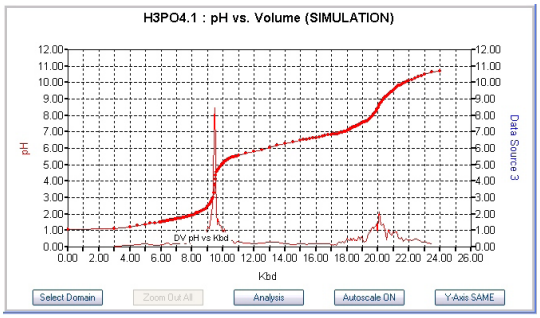


Fig. 17: Titration curve of with strong base and first derivative plot.

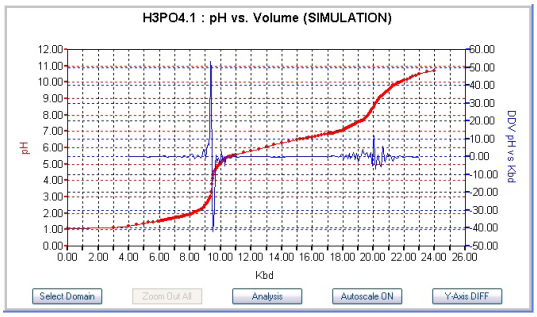


Fig. 18: Titration curve of H_3PO_4, with strong base and second derivative.

The Potentiometric Titration of an Acid Mixture:

Mixtures of two acids can be determined in one titration if there is a significant difference in pKa value. The strongest acid

is titrated first, resulting in the first endpoint, the second endpoint can represent the weaker acid. If the difference in pK is too small no separate endpoints will be found, only the sum of the acids can be determined.

Potentiometric Titrations for Precipitation Reactions

Precipitation potentiometric titration is based upon reactions that yield ionic compounds of limited solubility. A reaction in which the analyte and titrant form an insoluble precipitate also can form the basis for a titration. Titration curves for a single anion are derived in a way completely analogous to another titration methods. The only difference is that the solubility product of the precipitate is substituted to for the ion-product constant for water. The change in p-function value at the equivalence point becomes grater as the solubility products become smaller – that is, as the reaction between the analyte and precipitant becomes more complete. Ions forming precipitates with solubility products much larger than about 10^{-10} do not yield satisfactory end point.

The titration curve for a precipitation titration follows the change in either the analyte's or titrant's concentration as a function of the volume of titrant.

Potentiometric Titrations of Silver Ions

Potentiometric titrations of silver ions, indicator electrode is a **silver electrode**. For a silver electrode at 25 °C, the electrode reaction is represented by the following equation:

$$Ag^{+}_{(aq)} + e^{-} \leftrightharpoons Ag_{(s)} \qquad ; E° = +0.799 \text{ V}$$

Therefore the electrode potential is given approximately by the following Nernest equation:

$$E = 0.799 \text{ V} + 0.0592 \text{ V} \log [Ag^{+}]$$

More important is the approximation of using $[Ag^{+}]$ in place of the Ag^{+} ***activity***. The relationship between concentration and activity is accurate expressions for this relationship exist for only very dilute solutions.

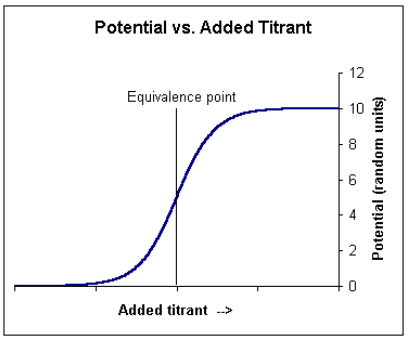


Fig. 19: Typical potentiometric titration curve for Ag^{+} against Cl^{-}.

Potentiometric Titration of Iodide ion Solution:

The amount of iodide ion contained in a sample is determined by titration of the iodide ion solution with a standard

solution of silver nitrate through following electrode reaction equation:

$$AgI_{(s)} + e^- \leftrightharpoons Ag_{(s)} + I^-_{(aq)} \quad E^o = -0.151 \text{ volt} \quad (1)$$

The course of this titration can be monitored or determined through **silver electrode** as indicator. The end point can be determined by observing the change in potential of the indicator electrode. The Nernest equation for theis electrode at at 25 ^oC is represented by the following equation:

$$E_{AgI/Ag} = E^o_{AgI/Ag} - 0.0591 log a_{I^-}$$

Substitution of the value of $E^o_{AgI/Ag}$ and at low concentrations, the Nernest equation is as follows:

$$E_{AgI/Ag} = -0.151 - 0.05916 \log [I^-]$$

Example:

Titration of Iodide ions by Ag^+, the electrode reaction is:

$$AgI_{(s)} + e^- \leftrightharpoons Ag_{(s)} + I^-_{(aq)} \quad E^o = -0.151 \text{ volt} \quad (1)$$

Since K_{sp} is so small ($K_{sp} = 3.8 \times 10^{-17}$), each addition of Ag^+ reacts completely with I^-. At equivalence point, sudden increase in Ag^+ concentration is seen. Consider the titration of 25.00 mL of 0.050 M NaI solution with concentration of 0.10 M $AgNO_3$. The volume of $AgNO_3$ to equivalence point is calculated to be:

$$25.0 \times 0.05 = 0.01 \times V$$

$$= 12.5 \text{ mL of } AgNO_3$$

Three distinct regions in titration curve are shown:

Before the Equivalence Point:

Concentration of iodide ions is governed by K_{sp},. After addition of 12.0 mL of $AgNO_3$, the concentration of iodide ions is $[I^-] = 0.00135$ M. On application of Nernst equation

$$E_{ind} = E^o - 0.0591 \log[I^-]$$

$$E_{ind} = -0.151 - 0.0591 \log[I^-]$$

$$E_{ind} = -0.151 - 0.0591 \log[0.00135]$$

$$E = 39 \text{ mV}$$

At Equivalence Point:

On addition of ***exactly*** enough titrant, $AgNO_3$, solution to the iodide solution, the titrant reacts completely with *all* I^- ions, $[I^-]$ is not depend of the original concentrations of NaI, but depends on K_{sp}. Thus, the remaining $[I^-]$ can be calculated from the value of solubility product, K_{sp}, as follows:

$$[I^-] = \sqrt{K_{sp}} = \sqrt{8.30x10^{-17}} = 9.11x10^{-9}\ M$$

On substitution;

$$E_{ind} = -0.151 - 0.0591 \log[9.11x10^{-9}]$$

$$E = 324\ mV$$

After Equivalence Point:

After equivalence point, the concentration of silver ions appears and the electrode reaction is expressed by the following equation:

$$Ag^{+}_{(aq)} + e^{-} \leftrightharpoons Ag_{(s)} \qquad ; E° = +0.799\ V$$

From Nernst equation at 25 °C:

$$E = E_0 - \frac{RT}{F} ln \frac{a_{Ag}}{a_{Ag^+}}$$

$$E = E_o + 0.0591\ log\ [Ag^+]$$

$$E = 0.799 + 0.0591\ log\ [Ag^+]$$

Concentration of silver ions after equivalence point, on addition of 13.0 mL of silver nitrate solution is calculated to be 0.00256 M. Thus,

$$E = 0.799 + 0.0591 log[0.00256]$$

$$E = 647\ mV$$

Shape of Titration Curve:

Titration curve strongly depends on the solubility constant of the precipitate salt at equivalence point. The following curves represent this dependence for different ions, c.f. Fig. 20.

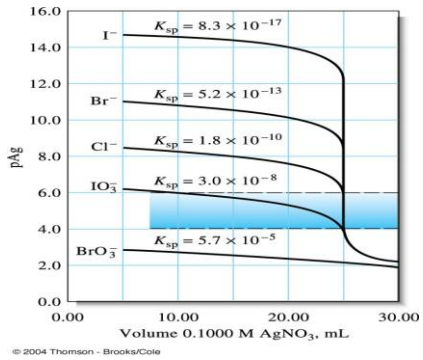


Fig. 20.

Potentiometric titration of a mixture of Chloride and Bromide Ions

The sample solution of a mixture of chloride and bromide ions will be titrated against a silver nitrate solution using a silver indicator electrode. Ag^+ ions react with halide ions (X^-) to form sparingly soluble salts, AgX:

$$X^-_{(aq)} + Ag^+_{(aq)} = AgCl_{(s)}$$

The solubility constants are 5.2×10^{-13} for AgBr and 1.8×10^{-10} for AgCl. Therefore, if the sample contains both Cl^- and Br^-, AgBr precipitates first and Ag^+ concentration is increased gradually until all Br^- turns into AgBr. Then, the Ag^+ concentration increases suddenly to a higher level which is determined by AgCl solubility and AgCl starts to form. Ag^+ ions concentration jumps again when AgCl precipitation was completed and free Ag^+ ions accumulate in the solution (see Fig. 2). It results that the progress of the titration can be monitored by checking Ag^+ concentration. This can be accomplished by means of an **indicator silver electrode**. When dipped in a Ag^+ containing solution, the electrode assumes an electric potential which is a function of Ag+ concentration according to Nernst equation:

$$E = E^o + 2.303RT/F \log [Ag^+] = E^o - 2.303RT/F \, pAg$$

Measurement of *E* provides therefore information about the change of Ag^+ concentration during the titration. In order to

perform *E* measurements, the indicator electrode should be combined with a reference electrode. Such an electrode contains as rule a concentrated KCl solution which can leak and contaminate the sample with additional amounts of Cl^-, leading to a positive error in Cl^- determination. Contamination can be prevented if the reference electrode is dipped into another solution which is connected to the sample by means of an electrolyte bridge, like the Agar bridge. The voltage of this cell will be measured by a mV-meter and plotted against the added silver nitrate volume to obtain the titration curve (Fig. 21) using either the initial data (upper curve) or its derivative (lower curve). Calculation of the derivative is illustrated by Fig 21. The derivative provides a more reliable estimation of the equivalence volumes, (V_e).

However, a problem appears due to the relatively low difference in solubility between AgBr and AgCl, the coprecipitation action and the adsorption of the halide ions on the silver electrode. This makes AgCl precipitation to starts up before the complete precipitation. These effects brig about a slight deviation from the stoichiometric ratio.

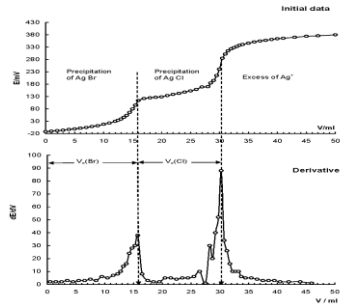


Fig. 21: Titration curve for Cl^- and Br^- ions mixture: initial data (up) and derivative (down).

Oxidation-Reduction Potentiometric Titration

Another type of titration is the oxidation-reduction titration which is also called Redox titration and is used to determine the oxidizing agent (oxidant) or reducing agent (reductant) in a solution. When performing redox titrations, either the reducing or oxidizing agent will be used as the titrant against the other agent. The purpose of this titration is to determine the transfer of electrons from one substance to the other, similar to that of a redox reactions, in order to determine the reductant or oxidant. There are numerous applications for the redox titration in chemistry, pharmaceutical preparations, environmental analysis, agriculture and many more.

It is well known that Nernst equation relates a solution's potential to the concentrations of reactants and products participating in the redox reaction. The reaction's standard

potential, E^o_{cell} , is the difference between the standard potentials for each half-reaction.

$$E^o_{cell} = E^o_B - E^o_A,$$

Where A and B are the analyte's oxidized form and the titrant's reduced form. After each addition of titrant the reaction between the analyte (titrand) and the titrant reaches a state of equilibrium. Because the potential at equilibrium is zero, the analyte's and the titrant's reduction potentials are identical :

At equilibrium and at any point during titration:

$$E_{cell} = E_B - E_A = 0.0$$

$$E_A = E_B$$

This is an important observation because one can use either half-reaction to monitor the changes of potential during titration. Before the equivalence point the titration mixture consists of appreciable quantities of the analyte's oxidized and reduced forms. The concentration of unreacted titrant, however, is very small. The potential, therefore, is easier to calculate if one apply the Nernst equation for the analyte's half-reaction.

$$E = E_A = E^o_A - \frac{0.0591}{n_A} log \frac{[A_{Ox}]}{[A_{Red}]}$$

Note that at the middle of the titration where half of $[A_{Ox}]$ is converted to $[A_{Red}]$ which means $[A_{Ox}] = [A_{Red}]$ and if the half

reaction of the analyte is symmetrical, the potential of the titration solution equal to the standard potential of the analyte.

$$E = E_A = E_A^o - \frac{0.0591}{n_A} log \frac{[A_{Ox}]}{[A_{Red}]} = E_A^o - \frac{0.0591}{n_A} log 1 = E_A^o$$

After the equivalence point, it is easier to calculate the potential using the Nernst equation for the titrant's half-reaction.

$$E = E_B = E_B^o - \frac{0.0591}{n_B} log \frac{[B_{Ox}]}{[B_{Red}]}$$

If the titrant half reaction is symmetrical, the potential of the titration solution will be equal to the standard potential of the titrant after adding double its equivalent amount i.e $[B_{OX}]$ = $[B_{RED}]$, then, $E = E_B^o$.

At equivalent point: From the balanced redox reaction equation one can say that at the equivalent point, n_A moles of B_{ox} have been added to n_B moles of A_{red}. The electrode potential at equivalent point can be calculated either by using the above two equations.

In the simplest electrochemical experiment, **platinum** is used as the indicator electrode. These ions can be interconverted by adding an electron to Fe^{3+} (reduction) or removing an electron from Fe^{2+} (oxidation). Platinum electrode is used as a source or sink for a very small number of electrons allowing this interconversion to take place. The following dynamic equilibrium is thus established on the surface of the metal,

without measurably perturbing the Fe^{3+} and Fe^{2+} concentrations in solution.

$$Fe^{3+}_{(aq)} + e^{-}\ (metal) \leftrightharpoons Fe^{2+}_{(aq)}$$

If the equilibrium lies to the left, favouring the formation of $Fe^{3+}_{(aq)}$, then the electrode will bear a slight negative charge and the solution a slight positive charge, and vice versa. There is thus a charge separation, and hence a potential difference, between the metal and the solution. An *electrode potential* is established on the metal wire relative to the solution phase. Qualitatively, the position of the equilibrium and hence the electrode potential will depend on the relative concentrations of Fe^{2+} and Fe^{3+}. Quantitatively the potential difference for a couple is given by the *Nernst Equation:*

$$E = E^{o}_{Fe^{2+}/Fe^{3+}} - 0.0591 log \frac{[Fe^{2+}]}{[Fe^{3+}]}$$

E and $E^{o}_{Fe^{2+}/Fe^{3+}}$ are the potential and standard potential of the electrode assuming ideal behaviour. More correctly the Nernst equation should be expressed in terms of activities. However in fairly dilute solutions it is common to assume that the activity of a species is equal to its concentration; one shall make that approximation in the following discussion. It is evident that electrode potentials must be measured relative to some reference. In practice, the saturated calomel reference electrode (SCE) is used. The potential of a calomel electrode relative to a

standard hydrogen electrode is +0.242V, so if measurements are made using a calomel electrode, this value must be added to the measured voltage.

Potentiometric titration of Fe^{2+} with Ce^{4+}

On titrating ferreous ions, Fe^{2+}, against ceric ions, Ce^{4+}, platinum electrode is used as indicator. The potential developed on the indicator electrode (measured against the SCE) is plotted as a function of the volume of Ce^{4+} added. The half equations for this redox reaction are as follows:

$$Fe^{+3}{}_{(aq)} + e^{-}{}_{(aq)} \leftrightharpoons Fe^{+2}{}_{(aq)} \qquad E^{o} = 0.771\ V$$

$$Ce^{4+}{}_{(aq)} + e^{-} \leftrightharpoons Ce^{3+}{}_{(aq)} \qquad E^{o} = 1.700\ V$$

The redox potential of the Ce^{4+}/Ce^{3+} couple is much more positive than that of the Fe^{3+}/Fe^{2+} couple, so if Ce^{4+} is added to a solution containing Fe^{2+}, effectively all of the Ce^{4+} reacts to oxidize Fe^{2+} to Fe^{3+} and the overall reaction is as follows.

$$Fe^{2+}{}_{(aq)} + Ce^{4+}{}_{(aq)} \rightarrow Ce^{3+}{}_{(aq)} + Fe^{3+}{}_{(aq)}$$

Shape of a Redox Titration Curve:

Titration curve has three regions:

Before the Equivalence Point, At the Equivalence Point and After the Equivalence Point.

Consider the Titration Reaction:

$$Fe^{2+}{}_{(aq)} + Ce^{4+}{}_{(aq)} \rightarrow Ce^{3+}{}_{(aq)} + Fe^{3+}{}_{(aq)}$$

The two electrodes established through the titration are:

$$Pt//Fe^{3+}/Fe^{2+} \text{ and } Pt//Ce^{4+}/Ce^{3+}$$

Region 1: Before the Equivalence Point

Each aliquot of Ce^{4+} creates with an equal number of moles of Ce^{3+} and Fe^{3+}. Excess unreacted Fe^{2+} remains in solution. Amounts of Fe^{2+} and Fe^{3+} are known, use to determine cell voltage. Residual amount of Ce^{4+} is unknown. Use iron half-reaction the active electrode at this point is $Pt//Fe^{3+},Fe^{2+}$. Thus, measurements of the electrode potential for the Fe^{3+}/Fe^{2+} couple is as follows:

$$Fe^{+3}{}_{(aq)} + e^{-}{}_{(aq)} \leftrightharpoons Fe^{+2}{}_{(aq} \qquad E^{o} = 0.771 \text{ V}$$

$$E = 0.771 - 0.05916 \log\left(\frac{[Fe^{2+}]}{[Fe^{3+}]}\right)$$

A special point when V = 1/2 V_e, where V_e is the volume of titrant to the end point. At this point $[Fe^{3+}] = [Fe^{2+}]$. Thus, on substitution:

$$E = E^{o} = 0.771V.$$

Region 2: At the Equivalence Point:

On addition of enough Ce^{4+}, it reacts with all Fe^{2+}, primarily only Ce^{3+} and Fe^{3+} present. Tiny amounts of Ce^{4+} and Fe^{2+} are present at equilibrium. From the reaction:

$$Fe^{2+}{}_{(aq)} + Ce^{4+}{}_{(aq)} \rightarrow Ce^{3+}{}_{(aq)} + Fe^{3+}{}_{(aq)}$$

$$[Ce^{3+}] = [Fe^{3+}]$$

$$[Ce^{4+}] = [Fe^{2+}]$$

Both Reactions are in equilibrium at the Pt electrode, Thus:

$$E_{+} = 0.771 - 0.05916\log\left(\frac{[Fe^{2+}]}{[Fe^{3+}]}\right)$$

$$E_{+} = 1.700 - 0.05916\log\left(\frac{[Ce^{3+}]}{[Ce^{4+}]}\right)$$

On addition:

$$2E_{+} = 0.767 + 1.70 - 0.05916\log\left(\frac{[Fe^{2+}]}{[Fe^{3+}]}\right) - 0.05916\log\left(\frac{[Ce^{3+}]}{[Ce^{4+}]}\right)$$

Since:

$$[Ce^{3+}] = [Fe^{3+}]$$

$$[Ce^{4+}] = [Fe^{2+}]$$

$$2E_{+} = 2.47 - 0.05916\log\left(\frac{[Fe^{2+}]}{[Fe^{3+}]}\frac{[Ce^{3+}]}{[Ce^{4+}]}\right)$$

Thus, E = 1.235 V.

Region 3: After the Equivalence Point:

It is opposite situation compared to before the equivalence point. Equal number of moles of Ce^{3+} and $Fe^{3+}$are found. Thus, no Fe^{2+} remains to be oxidized by the Ce^{4+}, so measurements are made on the Ce^{4+}/Ce^{3+} couple and the active electrode is Pt/ Ce^{4+}, Ce^{3+}. Excess unreacted Ce^{4+} remains in solution. Amounts of Ce^{3+} and Ce^{4+} are known and used to determine the electrode potential. From the cerium half-reaction:

$$Ce^{4+} + e^{-} \leftrightharpoons Ce^{3+} \qquad E^{o} = 1.700 \text{ V}$$

$$E = \left[1.700 - 0.05916\log\frac{[Ce^{3+}]}{[Ce^{4+}]}\right]$$

This change in potential can be used to measure the concentration of the test solution, c.f. Fig. 22.

Potentiometric titration of Fe^{2+} with Cr^{6+}

On titration of Fe^{+2} ions with $K_2Cr_2O_7$ in the test solution, the following two half-cell-reactions take place.

$$Cr_2O_7^{-2}{}_{(aq)} + 14H^+_{(aq)} + 6e^-_{(aq)} \leftrightharpoons 2Cr^{3+}_{(aq)} + 7H_2O_{(l)} \quad E^o = 1.232 \text{ volt}$$

$$Fe^{3+}_{(aq)} + e^-_{(aq)} \leftrightharpoons Fe^{2+}_{(aq)} \qquad E^o{}_{L2} = 0.771 \text{ volt}$$

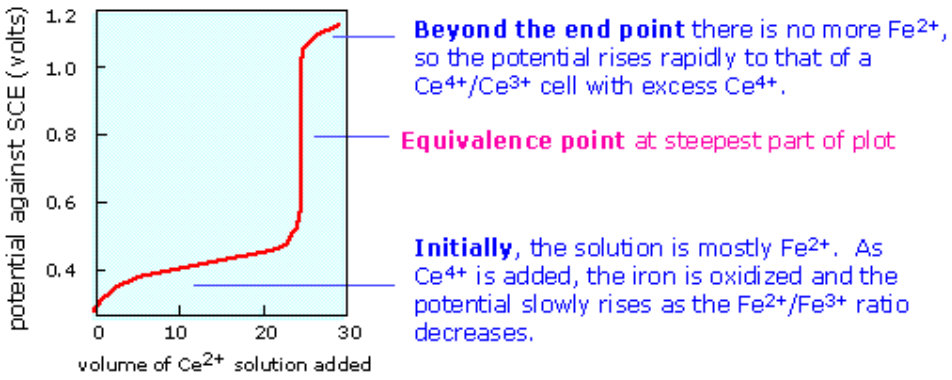


Fig. 22: Titration Curve for Fe^{2+} ions against standard C^{4+} ions.

These two half-reactions are combined to form the following overall reaction.

$$6\,Fe^{2+}_{(aq)} + Cr_2O_7^{-2}{}_{(aq)} + 14H^+_{(aq)} \leftrightharpoons 2Cr^{3+}_{(aq)} + 6Fe^{3+}_{(aq)} + 7H_2O_{(l)} \quad E^o{}_2 = 0.461 \text{ volt} \quad (7)$$

As $K_2Cr_2O_7$ is added to the solution, a proportional amount of Fe^{+2} is oxidized to Fe^{+3}. If sufficient $K_2Cr_2O_7$ titrates with the Fe^{+2} ions, all Fe^{+2} ions will convert to Fe^{+3}. The point, where the amount of $K_2Cr_2O_7$ added is sufficient to completely convert Fe^{+2}

to Fe^{+3} is the equivalence point of the titration. At the equivalence point, the amount of $K_2Cr_2O_7$ added to the solution is used to calculate the original amount of $FeSO_4$ in the solution. When $K_2Cr_2O_7$ is added incrementally to the solution and the potential of the solution measured after each addition, a titration curve of potential versus.

At the equivalence point, Fe^{+2} is entirely converted to Fe^{+3}. The active electrode is Pt/Fe^{+2}, Fe^{+3} is established and the electrode equation is as above. The addition of another aliquot of titrant will cause a dramatic jump in the measured potential of the system due to the switch of dominant cell reaction. Upon identifying the equivalence point, the original concentration of ferrous sulfate is calculated using the stoichiometric coefficient of the equation, the concentration of dichromate titrant, and the volume of titrant used.

Another application of potentiometric titration is that it allows the computation of the concentration of each species at various points in the titration using the Nernst equation and the measured potential. Referring to Figure 2, a titration curve consists of three regions important to this discussion: the buffer region, equivalence point, and over titration region.

The concentration of the iron species in the buffer region can be computed using the Nernst equation for Fe^{+2}/Fe^{+3}. *(All the solutions in the Nernst equations are assumed ideal)*

$$E = 0.771 - .0592 \log \frac{[Fe^{+2}]}{[Fe^{+3}]}$$

At the beginning of titration, no significant levels of $Cr_2O_7^{-2}$ exist because it is assumed the entire aliquot of $Cr_2O_7^{-2}$ reacts with Fe^{+2} to form Fe^{+3}. The equation took only into account the effects of iron on the electrode. The dichromate reaction is not taken into account, dominant reaction is the conversion of Fe^{+3} into Fe^{+2}. The potential at the equivalence point is calculated using the Nernst equation. The Nernst equations at the equivalence point are:

$$E_{eq} = 0.771 - \frac{0.0592}{1} \log \frac{[Fe^{+2}]}{[Fe^{+3}]}$$

$$E_{eq} = 1.232 - \frac{0.0592}{6} \log \frac{[Cr^{+3}]^2}{[Cr_2O_7^{-2}][H^+]^{14}}$$

By adding these equations one gets an expression that relates the equivalence point to all the reactants in the system.

$$7E_{eq} = 6.59\text{V} - \log \frac{[Fe^{+2}][Cr^{+3}]^2}{[Fe^{+3}][Cr_2O_7^{-2}][H^+]^{14}}$$

The equivalence point that the following relationships between Fe^{+2}, Fe^{+3}, $Cr_2O_7^{-2}$, and $Cr^{+3}$is the following:

$$[Fe^{+2}] = 6[Cr_2O_7^{-2}]$$
$$[Fe^{+3}] = 3[Cr^{+3}]$$

With these relationships applied, the result is an expression that can be used to compute the electric potential at equivalence point.

$$E = .942\text{V} - \frac{0.0592}{7}\log\frac{2[Cr^{+3}]}{[H^{+}]^{14}}$$

On assumption that all solutions to be ideal and the reaction goes to completion, the equation shows that the potential at the equivalence point is a function of the concentration of Cr^{+3} and H^{+} only. These assumptions apply best when the solutions of interest are very dilute solutions. Furthermore, the equation requires the concentration of H^{+} ion to stay constant at 1 M. This assumption only applies when H^{+} ion presented in the solution is in great excess compared the other reaction species.

Potentiometric titration of a Mixture:

It is possible to titrate simultaneously two reducing forms with standard solution of oxidizing form if there is a sufficient difference in their standard potentials. For example Fe^{2+} (E^{o} = 0.771) and Sn^{2+} (E^{o} = 0.15) can be titrated with MnO_4^{-}, where Sn^{2+} will react first because it is stronger as a reducing agent than Fe^{2+}.The result is two well separated equivalent points, c.f. 23.

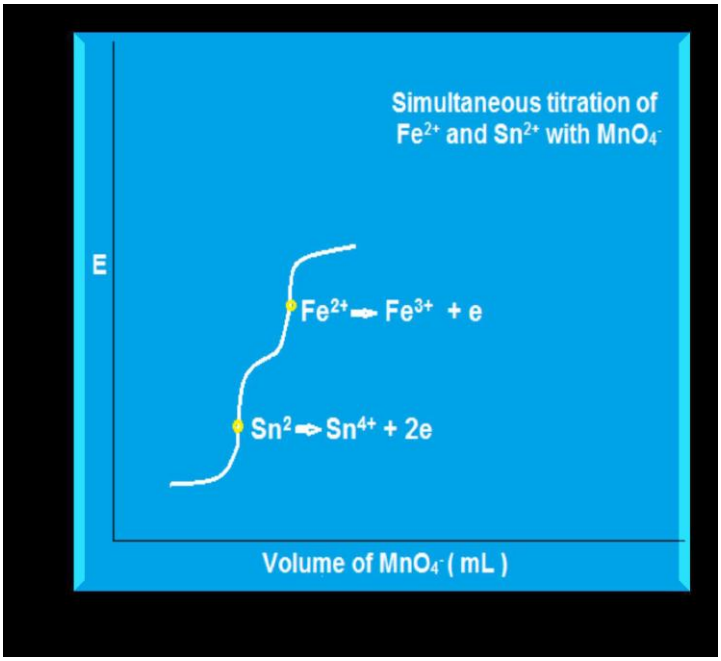


Fig. 23: Titration of a mixture of Fe^{2+} and Sn^{2+} with a standard solution of MnO_4 ions.

Likewise, two oxidants e.g. Ag^+ ($E^o = 0.8$) and Ce^{4+} ($E^o = 1.44$) can be titrated with a standard solution of a reducing agent e.g. Sn^{2+} ($E^o = 0.15$). Note that if the difference between the standard potential of the mixture substances is not sufficient then the two equivalent point will overlap giving one equivalent point.

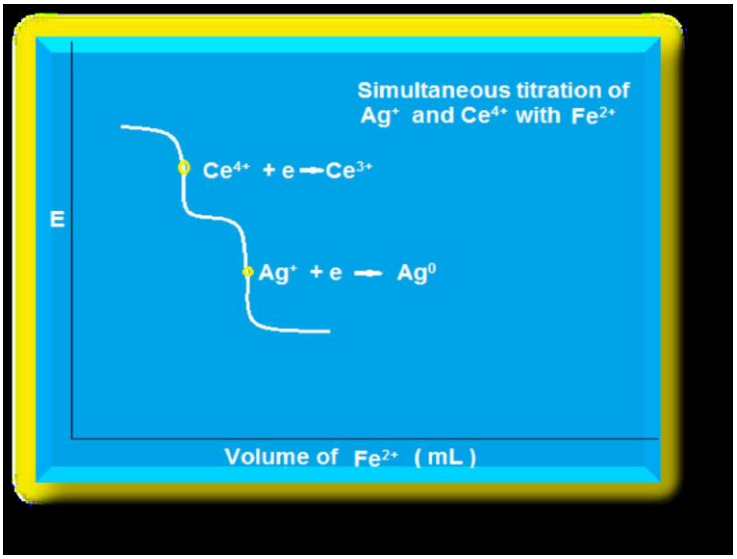


Fig. 24: Titration of a mixture of Ag^{+} and Ce^{4+} with a standard solution of Sn^{2+}.

Complexometric titration:

A technique of volumetric analysis, in which the formation of a coloured complex is used to indicate the end point of titration is known as complexemetry. Also it is known as chelatometry. Complexiметric titration is a type of titration based on complex formation between the analyte and titrant. Complexometric titrations are particularly useful for determination of a mixture of different metal ions in solution.

Any complexation reaction can in theory be applied as a volumetric technique provided that:

1. The reaction reaches equilibrium rapidly following each addition of titrant.

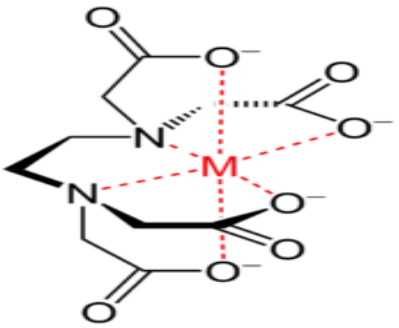
2. Interfering situations do not arise (such as stepwise formation of various complexes resulting in the presence of more than one complex in solution at significant concentration during the titration process). In practice, the use of EDTA as a titrant is well established.

Complexometric titration with EDTA

Metal-EDTA complex

EDTA, ethylenediaminetetraacetic acid, has four carboxyl groups and two amine groups that can act as electron pair donors, or Lewis bases. The ability of EDTA to potentially donate its six lone pairs of electrons for the formation of coordinate covalent bonds to metal cations makes EDTA a hexadentate ligand. However, in practice EDTA is usually only partially ionized, and thus forms fewer than six coordinate covalent bonds with metal cations. Disodium EDTA, commonly used in the standardization of aqueous solutions of transition metal cations, only forms four coordinate covalent bonds to metal cations at pH values less than or equal to 12 as in this range of pH values the amine groups remain protonated and thus

unable to donate electrons to the formation of coordinate covalent bonds.



Metal-EDTA complex

In analytical chemistry the shorthand "Na_2H_2Y" is typically used to designate disodium EDTA. This shorthand can be used to designate any species of EDTA. The "Y" stands for the EDTA molecule, and the "H_n" designates the number of acidic protons bonded to the EDTA molecule.

EDTA forms an octahedral complex with most 2 metal cations, M^{2+}, in aqueous solution. The main reason that EDTA is used so extensively in the standardization of metal cation solutions is that the formation constant for most metal cation-EDTA complexes is very high, meaning that the equilibrium for the reaction:

$$M^{2+} + H_4Y \rightleftharpoons MH_2Y + 2H^+$$

removes H^+ as it is formed, which also favors the formation of the EDTA-metal cation complex reaction product. For most purposes it can be considered that the formation of the metal cation-EDTA complex goes to completion, and this is chiefly why EDTA is used in titrations/ standardizations of this type.

Compexometric titration of Ca^{2+} and Mg^{2+} in drinking water

Chlating Agent:

Complexometric titration using chelating agent Y (comprising n complexing groups) is far more advantageous than titration with monodendate ligand L (of the same type), for two reasons:

(1) The chelate MY is more stable than the ML_n complex due to thermodynamic considerations. The free energy change, ΔG,

$$\Delta G = \Delta H - T\Delta S$$

is characterized by similar ΔH values, but very different ΔS values, were ΔH is the enthalpy and ΔS is the entropy. More disorder is created by the dissociation of ML_n with the formation of n+1 species, compared to two species for the chelate.

(2) Stepwise complexation with monodendate ligands is usually characterized with successive formation constants relatively close to each other. Thus, there are several types of complexes in the vicinity of the end point, compared to a chelate, where a single 1:1 complex is usually formed.

One of the most widely used chelating agents is EDTA. EDTA titrations have been applied to the determination of most metal cations with the exception of the alkali metal ions. Selectivity is obtained by controlling the pH. Ca^{2+} and Mg^{2+} have however close formation constants ($K_f = 5.0 \cdot 10^{10}$ and $4.9 \cdot 10^{8}$ respectively), unsuitable for separate detection. Titrating with EDTA, the total concentration of Ca^{2+} and Mg^{2+} is determined.

Indicator mercury electrode,

Hg/HgY, MY, M^{n+}

The mercury electrode can serve as an indicating electrode for complexometric titrations when it is used as an electrode of the third kind.

Let us consider a mercury electrode dipped in a solution containing the following relevant species: Hg^{2+}, M^{2+} (metal ions), Y^{4-}, HgY^{2-}, MY^{2-}.

The following processes are to be considered:

$$Hg^{2+} + 2e^{-} \leftrightharpoons Hg$$

$$E_{eq} = E^{o}_{Hg^{2+}/hg} + \mathrm{RT/nF} ln[Hg^{2+}]$$

$$Hg^{2+} + Y^{4-} \leftrightharpoons HgY^{2-}$$

$$K'_{f,HgY^{2-}} = \frac{[HgY^{2-}]}{[Hg^{2+}][Y^{4-}]}$$

$$M^{2+} + Y^{4-} \leftrightharpoons MY^{2-}$$

$$K'_{f,MY^{2-}} = \frac{[MY^{2-}]}{[M^{2+}][Y^{4-}]}$$

where K'_f is the conditional formation constant The expression for the equilibrium potential is obtained,

$$E_{eq} = E^0_{Hg^{2+}/Hg} + \frac{RT}{2F}\ln\frac{K'_{f,MY^{2-}}}{K'_{f,HgY^{2-}}} + \frac{RT}{2F}\ln\frac{[HgY^{2-}]}{[MY^{2-}]} + \frac{RT}{2F}\ln[M^{2+}]$$

combining the previous equations.

The potential of the mercury electrode varies with the variation of the concentrations of HgY^{2-}, MY^{2-} and M^{2+}. Around the equivalence point, however, $[MY^{2-}]$ is almost constant (why?); $[HgY^{2-}]$ is virtually constant when the condition $K'_{f,HgY}{}^{2-} >> K'_{f,MY}{}^{2-}$ is fulfilled (why?). Since HgY^{2-} forms a very stable complex, the inequality is fulfilled for most metal ions. The concentration of M^{2+} varies by several orders of magnitude around the equivalence point.

Since the first three terms on the right-hand of the last equation are almost constant around the equivalence point, the

electrode potential serves as reliable indicator for the variation of the concentration of the uncomplexed metal ion. Thus the electrode is an efficient tool for the end-point detection of complexometric titrations.

According to the above thermodynamic treatment, the presence of Hg(II) species is imperative for the proper functioning of the electrode. This is a reason that a small amount of the EDTA complex of Hg(II) is introduced into the solution in complexometric titrations (why Hg(II) in the complex form and not as Hg^{2+} is used?).

The Titration Curve has three distinct regions:

Before the equivalence point (excess M^{n+})

At the equivalence point ([EDTA]=[M^{n+}]

After the equivalence point (excess EDTA)

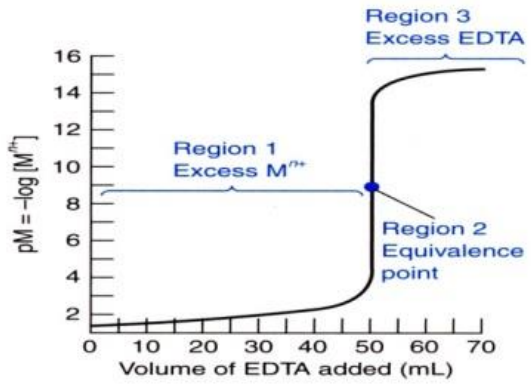


Fig. 25: Titration of EDTA with metal ions.

pH is an important factor in setting the completeness and selectivity of an EDTA titration.

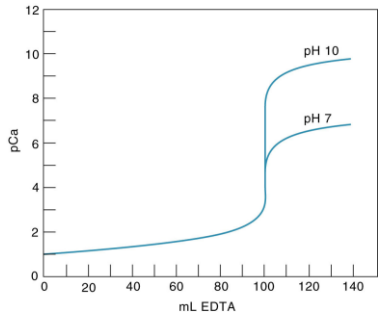


Fig. 26: Titration curves for Ca^{2+} versus Na_2EDTA at pH 7 and 10.

Questions:

1-Complete:

In potentiometric titration of silver nitrate solution:

The Indicator Electrode is

The electrode reaction before end point is

The electrode reaction after end point is

2-Complete:

In potentiometric titration of a mixture of acetic and hydorchloric acids using quinehydrone electrode

The quinehydrone electrode reaction is

The Nernest equation for quinehydrone electrode is:

3-Complete:

In potentiometric titration of sodium chloride solution:

The Indicator Electrode is

The electrode reaction before end point is

The electrode reaction after end point is

4-Complete:

In potentiometric titration of ferrous solution:

The Indicator Electrode is

The electrode reaction before end point is

The electrode reaction after end point is

5-Complete:

$Q_{(aq)} + 2e^- + 2H^+_{(aq)} \rightleftharpoons$

Oxidation-reduction potentail of qouinone-hydroquenone equilibrium depends on the solution pH, write the equilibrium equation and write the electrode reaction, Nernst equation.

6-Discuss:

The electrode potential of Calomel electrode depends on its anion concentration.