MODULE 2 BASIC CONCEPT OF TITRIMETRIC ANALYSIS

UNIT 1 GENERAL PRINCIPLES OF VOLUMETRIC ANALYSIS

CONTENTS

1.0 INTRODUCTION

Titrimetric analysis (Titration) is one of the core and the most useful analytical procedures that make up quantitative techniques in analytical chemistry. It is fairly rapid with good degree of accuracy. It involves measuring the volume of the reagent (titrant) needed to react with the analyte (test substance or titrand).

This unit examines the general principle of volumetric analyses which include technical terms used in describing the analytical procedure, various types of volumetric titrations and calculation in volumetric analysis.

2.0 OBJECTIVES

At the end of this unit, you should be able to:

- explain volumetric analysis;
- list and explain the various technical terms used in volumetric analysis;
- list the general requirements for volumetric titration;
- name the forms of volumetric analysis available; and
- solve fundamental calculations involved in volumetric analysis.

3.0 HOW TO STUDY THE UNIT

1. You are expected to read carefully through this unit at least twice before attempting to answer the self-assessment questions or tutor- marked assignment.
2. Do not look at the solution given at the end of the unit until you are satisfied that you have done your best to get all answers.
3. Share your difficulties with your course mates, facilitators and by consulting other related material, particularly the internet.
4. Note that if you follow the instructions you will feel self fulfilled that you have achieved the aim of studying this unit. This should stimulate you to do more.

4.0 WORD STUDY

Indicator: is a compound with a physical property (colour) which changes abruptly near the equivalence end-point.

Equivalence point: is the point in which the quantity of titrant added is the exact amount necessary for stochiometric reaction with the analyte or the titrand.

End-point: This is the actual point when a reaction is observed to be complete

5.0 MAIN CONTENT

5.1 Definition of Volumetric Analysis

Volumetric analysis is an analytical technique that deals with reactions between measured volumes of a reagent known as **titrant** against the test substance called **analyte** in a stochiometric manner. It is a quantitative study.

5.2 Principles and Technical Terms Involved in Volumetric Analysis

In a titration, the addition of the reagent solution (titrant) of known concentration to analyte continues until their reaction is complete.

Titrant is usually added from burette to the titrand or the analyte in a conical flask.
If the concentration of H^+ titrant is known, the reaction between the analyte and titrant is also known, and then the amount of the analyte can easily be calculated.

5.3 General (Basic) Requirements for Titration

i. The titration reaction should have large equilibrium constant i.e. each addition of titrant must be completely used up by the analyte.
ii. The reaction must be rapid.
iii. There should be known reaction pattern between the analyte and titrant.
iv. There should be no side or parallel reaction i.e the reaction should be specific with no interference.
v. The reaction should be quantitative.
vi. There should be distinct features in some property of the solution when the reaction is complete.
vii. The end point should coincide with the equivalence point and be reproducible.

5.4 Various Methods of Detecting Completion of a Titration Reaction

i. Observing sudden colour change in the indicator.
ii. Monitoring spectrophotometric absorbance change.
iii. Detecting a sudden change in the voltage or current between a pair of electrodes.
iv. Observation of marked change of pH in the titration of an acid with a base.

5.5 Various Technical Terms in Volumetric Analysis

These are some of the various terms used in the volumetric techniques under analytical chemistry.

a. ***Indicator***: is a compound with a physical property (colour) which changes abruptly near the equivalence end point. The change in colour is due to complete consumption of analyte near the equivalence point whose concentration is known.
b. ***Standardisation***: is a process by which the precise concentration of a solution is determined.
c. ***Primary Standard***: is the purest form of reagent which is used to prepare a standard solution. The purity is above 99.9%.
c. ***Equivalence Point***: This is the point in which the quantity of titrant added is the exact amount necessary for stochiometric reaction with the analyte or the titrand.
d. ***End point:*** This is the actual point when a reaction is observed to be complete.
e. ***Titration Error***: The difference between the equivalence point and end point. It is sometimes called indicator error, if indicator is used as a means of detecting end point.
f. ***Blank titration***: It is the type of titration in which the solution does not contain the analyte of interest. It is always carried out to estimate the amount of titration error.

g. ***Direct titration***: Is the most common form of titration in which titrant is added to the analyte until reaction is complete.

h. ***Back titration***: It is the type of titration necessary when direct titration does not give clear or sharp end point. It involves adding a known excess of the standard reagent to the analyte. Then a second standard reagent is used to titrate the excess of the first reagent so as to know the amount of first standard reagent that is consumed by analyte.

5.6 Characteristics of Standard Solution

An ideal standard solution for volumetric analysis must have the following properties.

i. Its concentration should remain constant for months or years after preparation so as to avoid the need to re -standardise

ii. Its reaction with analyte should be rapid.

iii. The reaction with the analyte must be describable by equation.

iv. A method must exist for detecting the equivalence point between the reagent and analyte.

5.7 Forms (Types) of Volumetric Procedures

i. **Acid-Basic titration**: This is the determination of the concentration of an acid or base by exactly neutralising the acid or base with acid or base of known solution. It allows for quantitative analyses of the concentration of an unknown solution.

   The most obvious application of acid-base (neutralisation) titration includes determination of innumerable inorganic, organic and biological species that possess inherent acidic or basic properties. Elemental and khjeldahl analysis are some of the other applications and they are of research and industrial importance

ii. **Oxidation-reduction (redox) titration**: This is a type of titration characterised by the transfer of electron from one substance to another (from reductant to the oxidant) with the end-point determined calorimetrically or potentiometrically. The principle is based upon reacting the analyte of interest with a standard solution of oxidizing or reducing agent.

   Various applications are known. These include determination of iron in ore and calcium in oxalate.

iii. **Precipitation titration**: is a titration in which, as it proceeds toward the end point, the substance of interest is precipitate out of the solution as an insoluble salt:

   i.e. $Ag^{+}_{(aq.unknown)} + Cl^{-}_{(aq.titrant)} \rightarrow AgCl_{(s)}$

This usually makes it difficult to determine the endpoint precisely. As a result, precipitation titrations often have to be done as "back" titrations.

iv. **Complexometric titration**: Complexometric titration (sometimes chelatometry) is a form of volumetric analysis in which the formation of a colored complex is used to indicate the end point of a titration. Complexometric titrations are particularly useful for the determination of a mixture of different metal ions in solution. An indicator capable of producing an unambiguous colour change is usually used to detect the end-point of the titration.

5.8 Volumetric Calculation

The key step is to relate the moles of titrant to the mole of analyte. In this section, a general framework would only be provided, due to space and time constraints. However, any situation (calculation) can be adapted.

Molarity is a major concept required for volumetric calculation. However, chemist also uses the equivalent weight (or the milli equivalent weight) as the basis of volumetric calculation.

Equivalent and equivalent weight are used instead of moles and formula weight.

Normal concentration depends on the particular reaction and reaction should be specified.

$$Mole = \frac{Mass\,(g)}{Molecular\ mass\,(F.w)}\ , \qquad mil\lim ole = \frac{mg}{Fw\,(molecular\ mass)}$$

$$Molar\ Concentration\,(M) = \frac{moles}{Litres} \quad or \quad M = \frac{mil\lim ole}{mL}$$

$$Normality\,(N) = \frac{equivalent}{Litre} = \frac{Meq}{mL}$$

Equivalent = mole x (no of reacting unit per molecule)
Meq = mole x (no of reacting unit per molecule)

5.8.1 Molarity

The volumetric calculation often assumes that the reaction between analyte and titrant is on 1:1 basis, hence these are valid.

$$mil\lim ole\,(mmole) = mL \times M$$
$$mg = mmole \times FW\ (molecular\ mass)$$

So based on 1:1

$$\%A = \frac{mg\ analyte \times 100\%}{mg\ sample}$$

That is,

$$\%A = \frac{M\ (mole/mL) \times F.W_{analyte}\ (mg/mole) \times 100\%}{mg\ sample}$$

Example 1

How many millilitres of 0.25M of H_2SO_4 will react with 10ml of a 0.25M solution of NaOH?

The equation of the reaction is $H_2SO_4 + 2NaOH \rightarrow Na_2SO_4 + 2H_2O$

Twice as many millimole of NaOH as of H_2SO_4 will react or
MH_2SO_4 x ml H_2SO_4 $= M_{NaOH}$ x ml $_{NaOH}$ x ½(mmoles H_2SO_4 /mmoles NaOH)

Therefore ml H_2SO_4 =

$$\frac{0.25mmoles/ml \times 10ml \times 1/2\ ½(\text{ mmoles } H_2SO_4 \text{ /mmoles NaOH})}{0.25mmoles/ml}$$

ml H_2SO_4 = 5.0ml

Example 2

A sample of pure salicylic acid is analysed by titration. What size of sample should be used so that percent purity is equal to five times the millilitre of 0.0500M NaOH used to titrate it?

Let y = ml NaOH; % Salicylic acid (HA) 5y

$$\%\ HA = \frac{M_{NaOH} \times ml_{NaOH} \times 1\ (mmole\ HA/mmole\ NaOH) \times f.W_{HA}\ (mg/mmole)}{mg\ of\ sample} \times 100\%$$

$$5y\ \% = \frac{0.0500M \times yml \times 1 \times 138mg/mmole}{mg\ of\ sample} \times 100\%$$

mg of sample =138mg.

However, it is now realised that not all substance react on 1:1 mole basis and so the need for a generalised formula for calculation.

Assuming $xA + yT \rightarrow P$

where A is the analyte, T is the titrant and P is the product.
Then,

M $mole_A$ = formula $\frac{\text{mmole}}{1} \times \frac{x}{y} \left(\frac{\text{A mmole}}{\text{mmole}} T\right)$

$$M\ mole_A - \frac{M\ mole}{1} \times \frac{x}{y} \left({}^{\text{Mmole A}}/_{\text{mmole T}}\right)$$

$$M\ mole_A = M_T \left({}^{\text{mmole}}/_{\text{ml}}\right) \times Ml_T \times \frac{x}{y} \left({}^{\text{mmole A}}/_{\text{mmole T}}\right)$$

$$Mg_A = mmole_A \times fw_A \left({}^{mg}/_{\text{mmole}}\right)$$

$$Mg_A = M_T \left({}^{\text{mmole}}/_{\text{ml}}\right) \times Ml_T \times \frac{x}{y} (mmole_T) \times Fe_A\ {}^{mg}/_{mm}$$

Therefore,

$$\%\ A = \frac{M \left({}^{\text{Mmole}}/_{\text{ml}}\right) \times Ml_T \times \frac{x}{y} \left({}^{mmole\ A}/_{mmole_T}\right) \times Fw \times 100\%\ {}^{Mg}/_{mmole}}{\text{Mg sample}}$$

or

$$\left(MT\ {}^{\text{moles}}/_{\text{Ml}}\right) \times Ml_T = Mmole_A \times \frac{y}{x} \left({}^{\text{mmole T}}/_{\text{mmole A}}\right) =$$

$$\frac{Mg_A}{Fw\ ({}^{mg}/_{\text{mole}})} \times \frac{y}{x} \left({}^{\text{Mmole T}}/_{\text{Mmole A}}\right)$$

$$\frac{M_T = Mg_A (Fw_A) \times \frac{y}{x} \left({}^{\text{Mmole T}}/_{\text{Mmole A}}\right)}{Ml_T}$$

5.8.2 Normality

$$\text{ef wt Acid} = \frac{F.W_{Acid}\left({}^{g}/_{\text{Mole}}\right)}{1\ \text{equivalence}\ /_{\text{mole}}} = \frac{F.W_{Acid}}{\text{No of reacting unit}}$$

$$\text{eq wt HCl} = \frac{F.W_{HCl}\left({}^{g}/_{\text{mole}}\right)}{1\ \text{equivalence}\ /_{\text{ml}}}$$

$$\text{eq wt } H_2SO_4 = \frac{F.W_{H_2SO_4}\left({}^{mg}/_{mole}\right)}{2\ {}^{equivalence}/_{ml}}$$

$$\text{eq wt } H_3PO_4 = \frac{F.W_{H_3PO_4}\left({}^{mg}/_{mole}\right)}{3\ {}^{equivalence}/_{ml}}$$

So equivalent weight is the weight of a substance in grams that will furnish one mole for the reacting unit.

$$\text{equivalence} = \frac{g}{\text{eq wt } \left({}^{g}/_{eqn}\right)} \qquad \text{meg} = \frac{mg}{\text{equit } \left({}^{mg}/_{eq}\right)}$$

$$N = \frac{equiv}{Liter} = \frac{{}^{g}/_{eg}\ wt\left({}^{g}/_{eg}\right)}{Litre}$$

$$N = \frac{Meq}{Ml} = \frac{{}^{mg}/_{g}\ wt\left({}^{mg}/_{meq}\right)}{Ml}$$

Note that the major advantage of this concept of normality is that one equivalent of substance will **ALWAYS** react with one equivalent of substance.

$$\text{Meq}_A = \frac{\text{Mg}_A}{\text{equt}_A\left({}^{mg}/_{meq}\right)} = N_T\left({}^{meq}/_{ml}\right) \text{ x } \text{Ml}_T$$

$$\text{Mg}_A = \text{Meq}_T \text{ x eq wt}_A\left({}^{mg}/_{meq}\right)$$

$$\text{Mg}_A = N_T\left({}^{Meq}/_{ml}\right) \text{ x } \text{Ml}_T \text{ x eq wt}_A\left({}^{mg}/_{meq}\right)$$

$$\% \quad A = \frac{N_T\left({}^{Meq}/_{ml}\right) \text{ x } \text{Ml}_T \text{ x eq wt}_A\left({}^{mg}/_{meq}\right)}{\text{mg Sample}} \text{x } 100\%$$

$A + B \rightarrow \text{Pr}oduct$

$$Meq_A = meq_B$$

Therefore one can calculate the volume of the two substances that react

$$N_A\left({}^{meq}/_{ml}\right) x\ Ml_A = N_t\left({}^{meq}/_{ml}\right) x\ Ml_T$$

5.9 Reacting Units in Normality Calculation

Equiv weight = $\frac{F.w}{No\ of\ reacting\ unit}$

Since there are various specific reaction, the major task is to evolve the reaction unit in each specific reactions, so as to calculate the equivalent weight from the relationship.

i. Acid-base reaction: The reaction unit for acid and bases is the proton H^+

$$eq\ wt = \frac{F.w}{No\ of\ H^+}$$

ii. Reduction – oxidation: The reacting unit of this type of reaction is electron. A reducing agent liberates electron (e^-) therefore, oxidized, while oxidizing agent takes on electron therefore, reduced.

$$eq\ wt = \frac{F.w}{No\ of\ Mole\ of\ e^-\ gaines\ or\ lost}$$

iii. Precipitation and complexometric Reaction: In this case, though there is no reacting unit exchanged but reactant merely combines, the change on cations (metal ions) is assumed to be the reacting unit.

$$eq\ wt_{m+} = \frac{Atomic\ weight}{change\ (+n)}$$

Example: A solution of sodium carbonate is prepared by dissolving 0.212g of Na_2CO_3 and diluting to 100ml. Calculate the normality of the solution (a) if it is used as monobasic acid, and (b)if t is used as dibasic acid

(a) $$\frac{N = mgNa_2CO_3/(Na_2CO_3/1)}{ml} = \frac{212mg/(106.0/1mg/meq}{100ml} = 0.02meq/ml$$

(b) $$\frac{N = mgNa_2CO_3/(Na_2CO_3/2)}{ml} = \frac{212mg/(106.0/2mg/meq}{100ml} = 0.04meq/ml$$

6.0 ACTIVITY

j. Highlight the general requirements for titrimetric analysis.
ii. Explain the following terms: (a) Blank titration (b) Back titration (c) primary standards (d) indicator error
iii. Briefly explain the various classes of volumetric analysis.
iv. How many millitre of 0.25M solution of H_2SO_4 will react with 10ml of a 0.25M solution of NaOH?

v. Calculate the number of milliequivalent of chlordane $C_{10}H_6Cl_6$ (gfw – 410) in 0.500g of the pure insecticide. Assuming that all of the chlordane present is ultimately titrated with Ag^+.

7.0 SUMMARY

In this unit, you have learnt that:

A. Volumetric titration is a very rapid and precise analytical quantitative method.
B. For titrimetric analysis to be valid, it must satisfy some requirements such as rapidity, quantitative in nature and must be presentable in equation.
C. There are various ways by which equivalence point can be detected.
D. That there are four basic types of volumetric analyses. These are acid-base, redox (oxidation-reduction), and precipitation and complexometric titrations.
E. Various technical terms that is involved in the volumetric analysis.
F. Volumetric calculations are usually done based on Molarity and normality.

8.0 ASSIGNMENT

i. Give concise meaning of the following terms
(a) back titration
(b) standard solution
(c) titration error
(d) equivalence point.
ii. Differentiate between the following pairs
a. End-point and equivalence point.
b. Molarity and normality
iii. Write briefly on four known classes of volumetric analysis.
iv. A solution of sodium carbonate is prepared by dissolving 0.420g of Na_2CO_3 and diluting to 100mL. Calculate the normality of the solution
(a) If it is used as a monoacidic base,
(b) If it is used as an acidic base.

9.0 REFERENCES/FURTHER READING

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UNIT 2 ACID-BASE TITRATION

CONTENTS

1.0 INTRODUCTION

Acid-base titration is one of the types of volumetric analyses. It is the most commonly used throughout the realm of chemical analysis. Through the use of titration curve, both acidic and basic component of a material (sample) can be determined. In this unit, how to select a suitable indicator for detecting completion of titration reaction, preparation of standard acid or base solution (medium) are part of the areas covered.

2.0 OBJECTIVES

At the end of this unit, you should be able to:

- explain correctly acid-base titration;
- define some basic technical terms in acid- base titration;
- outline the basic concepts and principles involved in acid - base titration;
- use acid-base titration curve to determine components of a given sample;
- explain the principle of selecting a suitable indicator; and
- prepare standard acid and base solutions.

3.0 HOW TO STUDY THE UNIT

1. You are expected to read carefully through this unit at least twice before attempting to answer the self-assessment questions or tutor- marked assignment.
2. Do not look at the solution given at the end of the unit until you are satisfied that you have done your best to get all answers.
3. Share your difficulties with your course mates, facilitators and by consulting other related material, particularly the internet.
4. Note that if you follow the instructions you will feel self fulfilled that you have achieved the aim of studying this unit. This should stimulate you to do more.

4.0 WORD STUDY

Amphiprotic: solvents that have both basic and acidic properties.
Aprotic: solvents that is neither appreciably acidic nor basic. They are weakly polar in nature e.g. benzene tetrachloride.
Hasselbalch equation: is equations which express pH of a buffer solution as a function of the concentration of the weak acid or base and the salt component of the buffer system.

5.0 MAIN CONTENT

5.1 Acid-Base Titration

It is a volumetric analytical method which relates acid and base stochiometrically till reaction is completed. It is a very simple, reproducible and accurate analytical technique.

Acids and bases have been described by various theories which are:

i. **Arrhenius theory**: describes an acid as any substance that ionises partially or completely in water to give hydrogen ion, while base is any substance which ionises partially or completely in water to give hydroxyl ions.
ii. **Bronsted-Lowry theory:** describes an acid as a substance that can donate a proton and a base as any substance that can accept a proton.

There is a medium (solvent) necessary for the titration reaction to occur which can be aqueous or non aqueous.

5.2 Solvents Classification

The solvents may be classified into three groups based on certain principles.

(i) Amphiprotic: those solvents that have both basic and acidic properties e.g. water, ethanol. These solvents can ionise.

(ii) Aprotic: those solvents that are neither appreciably acidic nor basic. They are weakly polar in nature e.g. benzene tetrachloride.
(iii) Basic but not acidic: these solvents are extremely weak bases. They are non-ionisable e.g. ether and ketone.

5.3 Varity of Acid-Base System/Monitoring pH Change

For the study of various acid-base titrations to be comprehensive and goal oriented, the study would monitor trends of change in pH as titrant is added to the analyte. The stages to cover are:
(i) Before equivalence point
(ii) At equivalence point and
(iii) After equivalence point.

5.3.1 Titration Strong Acid against Strong Base

The reaction is a neutralisation. This type of acid-base titration is always a strong acid on a strong base.

The first step is to write a comprehensive ionic equation of the reaction.

Example: Titrating HCl against NaOH.

The exercise in the system is $H^+ + Cl^- + Na^+ + OH^- \dashrightarrow H_2O + Na^+ + Cl^-$

The ionic equation is $H^+ + OH^- \rightarrow H_2O$. This is otherwise known as titration reaction. The equation can also help in determining/calculating the composition and pH after each addition of titrant.

V_x (ml) (Molarity of x) = V_y (ml) (Molarity of y)

$$V_x = \frac{V_y M_y}{m_x}$$

Where x is for the acid and y is for the base

At V_x the equivalence point is reached. Prior to this V_x point, there will be excess of OH^- and after the V_x point, there will be excess of H^+. Therefore, in plotting titration curve pH versus the volume y of the titrant (x), there are three variable regions, Viz:

i. Before reaching the equivalence point, the pH is determined by the excess of OH in the solution.
ii. At equivalence point, the H^+ is just sufficient to completely react with all OH^-. So the pH is determined by dissociation of water, while $K_W = 10^{-14}$. So the reaction goes to completion.

iii. After reaching the equivalence point, pH is determined by the excess H^+ in the solution.

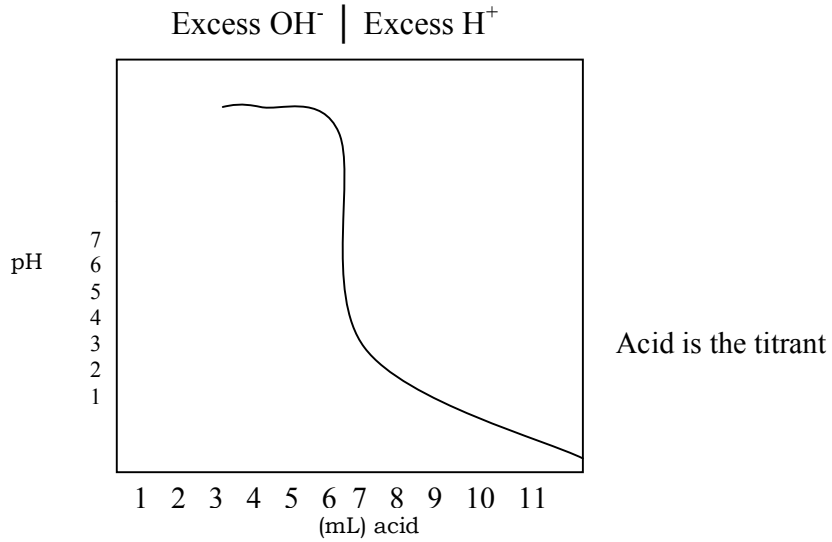


Fig. 2.1 The titration curve of H^+ being added to OH^-

The magnitude of the break (end point) depends on the concentration of both titrant and analyte.

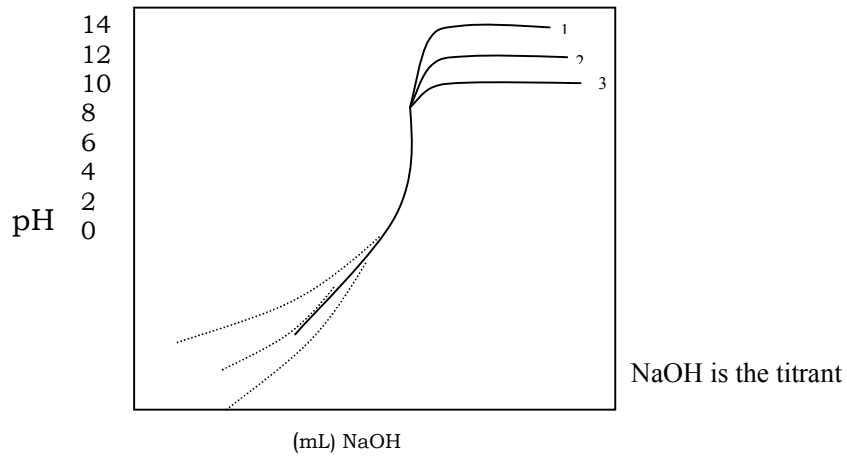


Fig. 2.2 The titration curve of 0.1M HCl against 0.1M NaOH (Curve 1), 0.01M HCl against 0.01M NaOH (Curve 2), 0.01M HCl against 0.01M

5.3.2 Titration of Weak Acid against Strong Base

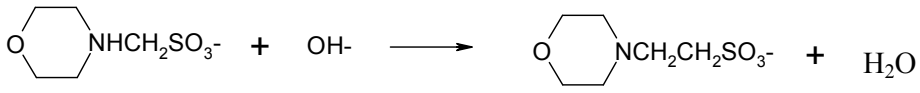
The titration is a neutralization reaction. Strong base is the titrant while the weak acid is the analyte.

1st step – write the ionic equation

If we are titrating MES against NaOH

MES ⟹ 2 - (N-morphline) ethanesulfonic acid.
It is a weak acid with pKa = 6.15

Titration Equation:



From the reaction

V_m (ml) (molarity M_m) = V_n (ml) (Molarity M_n)

$$V_m = \frac{V_n M_n}{M_m}$$

It is helpful to calculate Vm needed to reach equivalence.

where m = strong base (titrant)
n = weak acid (analyte)
The titration calculation is then divided into four stages which is also reflected in the titration curve.

1. Before any base is added, the solution contains just HA in water. It is a weak acid problem in which pH is determined by the equilibrium

$$HA \underset{}{\overset{K_a}{\rightleftharpoons}} H^+ + A^-$$

2. From the first addition of NaOH until before the equivalence point, there exist a mixture of unreacted HA and the A^- produced by the reaction. Henderson – Hasselbalch equation can be used to find the pH.
Hasselbalch equation is equations which express pH of a buffer solution as a function of the concentration of the weak acid or base and the salt component of the buffer system.

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

3. At equivalence point 'all' of the HA has been converted to A^-. The problem is the same as if the solution had been made by merely dissolving A^- in water. pH can be determined by the reaction.

$$A^- + H_2O \rightleftharpoons HA + OH^-$$

4. Beyond the equivalence point, excess NaOH is being added to a solution of A^- to a good approximation the pH is determined by strong base. We calculate the pH as if we simply add excess NaOH to water

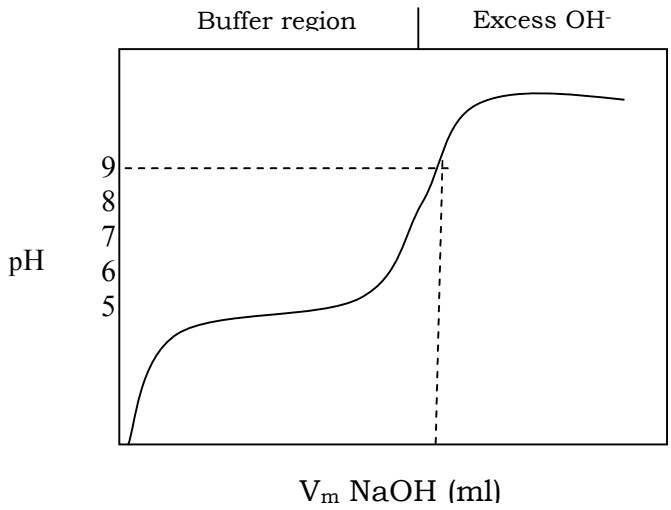


Fig 2.3 Titration curve of a strong base against weak acid

Before the titration reaction started at all, we have only weak acid in the medium, and so pH is calculated as for weak acid. At the commencement of titration, some HA is converted to A^- and so buffer system is set up. As the titration continues, the pH slowly increases as the ratio of A^- : HA changes.

At the mid-point of the titration [OAc]=[HOAc] and pH is equal to pK_a.
The pH of equivalence point will be alkaline.

The weaker the acid (the smaller K_a), the longer the positive K_b of the salt and the more alkaline the equivalence point.

5.3.3 Titration of Weak Base against Strong Acid

It is also a neutralisation reaction. It is just the opposite of the case of weak acid against strong Base.

The titration reaction is $B + H^+ \rightarrow BH^+$.

The reaction goes to completion after each addition of acid. There are also four stages shown in the titration curve.

1. Before acid is added, the solution contains only the weak base in water.
   The pH is determine by the K_b reaction

   $B+H_2O \rightleftharpoons BH +OH^-$

2. After the commencement of titration up to equivalence point there is a mixture of **B** and BH^+. That is, Buffer system is set up. K_b can easily be determined from the titration curve.

3. At the equivalence point. B has been converted into BH^+, a weak acid. The pH is calculated by the consideration of dissociation of acid BH^+

$BH^+ \overset{k_b}{\rightleftharpoons} B + H^+$ $\qquad Ka = \frac{Kw}{Kb}$

The formal concentration of BH^+, F, is not the same as the original formal concentration of B, because of some dilution that has occurred. Because the solution contains BH^+ at the equivalence point, it is acidic. The pH at the equivalence point must be below 7.

4 After the equivalence point, there is excess of H^+ in the solution.

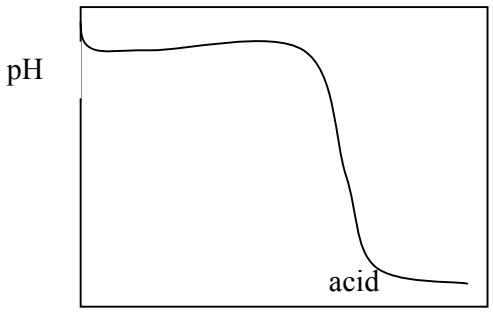


Fig. 2.4 Titration curve after the equivalent point

5.3.4 Titration of Polyprotic Systems

There are some bases that hydrolyse in more than one step, thereby having more than one dissociation constant. Generally, the principle developed for the titration of monoprotic systems readily applies to them.

For example, consider titration of base (B) against Acid (H) in which the base is dibasic.

The titration equation

$B + H \longrightarrow BH^+$ …… a
$BH^+ + H^+ \longrightarrow BH_2^{2+}$ …….. b

The titration curve shows reasonable sharp breaks at both equivalence points.

From equation (a)

$V_b \times n_b = V_a \times n_a$

Where "b" is for the base and "a" is for the acid

$$V_a = \frac{V_b \times n_b}{n_a}$$

The volume of the acid required to reach 1st equivalence point is Va_1

Going by equation (b), the volume of acid to reach 2nd equivalence point is 2 x Va_1
So, $Va_2 = 2\ Va_1$

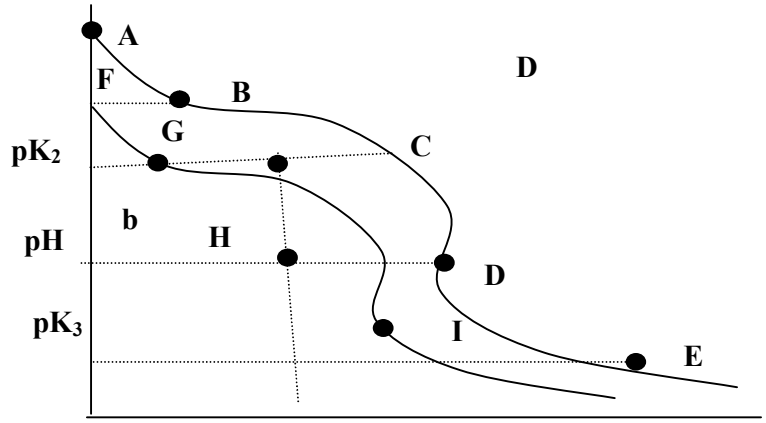


Fig 2.5 Titration curve of polyprotic systems

Point C and E are the two equivalence points while point B and D are the half-neutralisation points whose values equal pKa_2 as pK_1 respectively. The titration curve is in the following phases.

Point A. Before any acid is added, the solution contains just B, a weak base whose pH can be found as follows.

is $\underset{y-x}{B} + H_2O \xrightarrow{k_b} \underset{x}{B^+} + \underset{x}{OH^-}$

y = Original volume of B in the system

$$[H^+] = \frac{Kw}{x} = pH$$

Point B. Between point A and C, we have buffer system established containing B and BH^+. B is half way to equivalence point. So [B] = $[BH^+]$, pH is calculated using Henderson- Hasselbalch for weak acid whose dissociation constant is Ka_2 for BH_2^{2+}

$$Ka_2 = \frac{Kw}{Kb_1}$$

To calculate pH at B

$$pH = pKa + \frac{Log[B]}{[BH^+]}$$

Point C. This is the first equivalence point .B has been converted to BH^+, the intermediate form of diprotic acid BH_2^{2+}.

$$[H^+] = \sqrt{\frac{K_1K_2F + K_1K_w}{K_1 + F}}$$

where F is the formal concentration of BH^+

$pH = ½ [pK_1 + pK_2]$

Point D_1. At any point between C and E, we can consider the solution to be buffer containing BH^+ and BH_2^{2+}

$$pH = pKa_1 + \log\frac{[BH^+]}{BH_2^{2+}}$$

Point E: Point E is the second equivalence point at which solution is formerly the same. The pH is determined by the acid dissociation reaction of BH_2^{2+}.

$$\underset{F-x}{BH_2^{2+}} \rightleftharpoons \underset{x}{BH^+} + \underset{x}{H^+}$$

5.4 Detecting the End Point with Indicator

The use of an acid-base indicator to find end point is a more convenient method. It involves adding small amount of acid-base indicator, itself an acid or base, whose various protonated species have different colours.

The colour of the ionised form is different from the unionised form. One form may be coloured, the other form may be colourless.

$$\underset{\text{Red}}{HIn} \rightleftharpoons H^+ + \underset{\text{Blue}}{In^-}$$

The unionised form is red while the ionised form is blue. Then the Henderson-Hasselbalch equation gives.

$$pH = pKIn + \log\frac{[In^-]}{[HIn]}$$

Note that since the indicator is a weak acid or base, the amount added should be kept minimal so that it does not contribute appreciably to the pH. Moreover, the smaller the quantity of the indicator added, the sharper the colour changes.

There are other methods though not as simple as the use of indicator, through which end point can be detected. These include:

- the use of pH electrode
- the use of derivatives and
- the use of graph plot.

6.0 ACTIVITY

i. Define the following terms
   (a) Monoprotic acid-base system
   (b) Polyprotic acid-base system
   (c) Indicator
ii. Highlight various stages of acid-base titration curve.
ii. Briefly explain how an indicator works.

7.0 SUMMARY

In this unit, you have learnt that:

i. Definition and fundamental principle of acids-base trimetric method.
ii. Classification of solvent need as to act as a medium for the titration.
iii. Various phases of titration survey of (a) strong acid versus strong base (b) Strong acid versus weak base, (c) weak acid verses strong acid, (d) Polyprotic system.
iv. The use of indicator to defect end-point.
v. Other methods of detecting end-point.

8.0 ASSIGNMENT

1 Highlight various phases of acid-base titration curve
2 Consider the titration of 40.0ml of 0.20M malonic acid with 0.100MNaOH. Calculate the pH at each point listed and sketch the titration curve when Vb = 0.0, 8.0, 12.5, 19.3, 25.0, 37.5, 50.0 and 56.3ml
3 Make a short note on the classification of solvents in acid-base system
4 Write short note on pH:
   (a) before equivalent point
   (b) at equivalence point; and
   (c) after equivalence point of strong acid versus strong base system.

9.0 REFERENCES/FURTHER READING

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UNIT 3 OXIDATION REDUCTION TITRATION

CONTENT

1.0 INTRODUCTION

Oxidation – Reduction titration (redox) is one of the main types of volumetric analytical techniques. It is based on oxidation – reduction reaction in which electrons are transferred from one substance to another. It helps in determining the component of many substances qualitatively. This unit covers balancing redox reaction equations as well as principles of electrochemical cell and how electrode potential can be used to predict which oxidizing and reducing agent might get involved in the reaction. It also includes construction and use of Redox titration curve.

2.0 OBJECTIVES

By the end of this unit, you should be able to:

- explain the mechanism of redox titrations;
- explain the technical terms and principles involved in the titration of redox components;
- illustrate the principle of Electrochemical cells; and
- use of redox titration curves to predict component of given substance.

3.0 HOW TO STUDY THE UNIT

1. You are expected to read carefully through this unit at least twice before attempting to answer the self-assessment questions or tutor- marked assignment.
2. Do not look at the solution given at the end of the unit until you are satisfied that you have done your best to get all answers.
3. Share your difficulties with your course mates, facilitators and by consulting other related material, particularly the internet.
4. Note that if you follow the instructions you will feel self fulfilled that you have achieved the aim of studying this unit. This should stimulate you to do more.

4.0 WORD STUDY

Oxidizing agent: is the substance(s) that tend to take up an electron(s) and get reduced to lower oxidation state.
Reducing agent: is the substance(s) that tend to give up electron(s) and get oxidized to higher oxidation state.
Galvanic cell: This is the type of electrochemical cell in which a chemical reaction spontaneously occurs to produce electrical energy.
Electrolytic cell: It is the type of chemical cell in which electrical energy under the influence of an external source of power produces chemical energy.

5.0 MAIN CONTENT

5.1 Definition and General Principle

Oxidation – Reduction reaction is a reaction which involves the movement of electrons from one point to another, in a reaction between analyte and titrant. The general principle of Redox reaction lies in the fact that reaction occurs between a reducing agent and an oxidizing agent.

5.2 Review of Technical Terms in Redox Reaction

1. ***Oxidation:*** simply defined as loss of electron(s) to give higher oxidation state. The oxidation electrode is always more positive.
2. ***Reduction*****:** Is gain of electron(s) to give lower oxidation state. The reduction electrode is always more negative.
3. ***Oxidizing agent:*** is the substance(s) that tend to take up an electron(s) and get reduced to lower oxidation state.
4. ***Reducing agent:*** is the substance(s) that tend to give up electron(s) and get oxidized to higher oxidation state.

$$\underbrace{Ox_1}_{\text{oxidizing agent}} + \underbrace{\text{Re}\,d_2}_{\text{Reducing agent}} \rightleftharpoons \text{Re}\,d_1 + Ox_2$$

The tendency to oxidise or reduce depends on the reduction potential of a substance. The course of monitoring redox titration by potentiometry requires the need to review and understand very well the fundamental of electrochemical cells and electrode potential.

5.3 Electrochemical Cell

It is a device in which electrolysis of solution takes place. It is a compartment where electrochemical reaction occurs. There are basically two types of cells.

Galvanic cell: This is the type of electrochemical cell in which a chemical reaction spontaneously occurs to produce electrical energy.

Electrolytic cell: It is the type of chemical cell in which electrical energy under the influence of an external source of power produces chemical energy. A typical cell is made up of electrolyte, electrodes and salt bridge.

Electrodes are strip of metals that are conducting in nature. There are two types of electrodes Anode, where oxidation takes place and; Cathode where reduction takes place.

Electrolyte: is a liquid or molten subtance (solution) that can allow the passage of electrical current. They are conducting in nature.

Salt bridge: This is often made up of KCl crystals. They connect two reacting systems (beaker) together, thus allowing movement of electron from one beaker to another thereby preventing overconcentration of electron in beaker. However, it disallows any other substance from passing through it.

$E_{cell} = E_{right} - E_{left} = E_{cathode} - E_{anode} = E^{+} - E^{-}$

Nernst Equation: This is the equation that relates the standard potential of a system with the concentration of both oxidized and reduced forms when they are expressed in unit activity.

$$aOx + ne^{-} \rightleftharpoons bRed.$$

By Nernst **equation:** $$E = E^{0} - \frac{2.2320RT}{nf} \rightarrow \log \frac{(\mathrm{Re}d)^{b}}{(Ox)^{a}}$$

Where; E is the electrode potential
E^0 is the standard electrode potential
n is the number of electron transfer
F is the Faraday's constant
R is gas constant
T is the temperature

Each electrode has the tendency to loose or gain electron when in reaction, the tendency of each electrode is referred to as electrode potential. The electrode potential is more often the function of its makeup which has great impact on the cell reaction.
Note that:

The more positive the electrode potential, the greater the tendency of the oxidized form to be reduced e.g. $Ce^{4+} + e^- \rightarrow Ce^{3+}$ $E^o = +1.70V$ .Therefore, Ce^{+4} is a strong oxidizing agent while Ce^{3+} is a very weak reducing agent.

The more positive the electrode potential, the stronger the oxidising power of the oxidised form and the weaker the reducing power of the reducing form.

The more negative the reduction potential, the weaker the oxidising power of the oxidised form and the stronger the reducing power of the reduced forms.
e.g. $Zn^{2+} + 2e^- \rightarrow Zn$, $E^o = -0.76V$ is very negative. So, Zn^{2+} is a weak oxidizing agent while Zn is a strong reducing agent.

5.4 Redox Titration Curve

The course of redox titration is monitored by the use of a potentiometer. Potentiometer measures in voltage, the concentration of species in solution.

Titration reaction is

$$\underset{\text{Titrant}}{Ce^{4+}} + \underset{\text{Analyte}}{Fe^{2+}} \rightarrow Ce^{3+} + Fe^{3+}$$

However note that at each electrode, the following half reactions occur. Ka

$Fe^{3+} + e^- \rightleftharpoons Fe^{2+}$ $E^o = +0.77V$
$Ce^{4+} + e^- \rightleftharpoons Ce^{3+}$ $E^o = +1.61V$

At the calomel reference electrode, the half reaction is
$2Hg^+ + 2Cl^- \rightarrow HgCl_2 + 2e^-$

Therefore the cell reaction can be in other ways.

i. $2Fe^{3+} + 2Hg + 2Cl^- \rightleftharpoons 2Fe^{2+} + Hg_2Cl_2$

ii. $2Ce^{4+} + 2Hg + 2Cl \rightleftharpoons 2Ce^{3+} + Hg_2Cl_2$

The titration curve is divided into three phases (stages).

Before equivalence point: Each aliquot of Ce^{4+} added is consumed and create equal mole of Ce^{3+} as Fe^{3+}. Prior to the equivalence point excess Fe^{2+} remain in the solution, therefore, calculating the E of the cell is ensure through the activity of Fe^{2+}.

The potential therefore is calculated using Nernst equation.

NB: $E^{+} = E^{0} - 2.3026RT \log \frac{[\mathrm{Re}\,d]}{[Ox]}$

$E = 0.767 - 0.05916 \frac{[Fe^{2+}]}{[Fe^{3+}]}$ 0.241=Potential for Calomel electrode

Potential for Fe^{3+} reduction in 1M $HClO_4$

$$E = 0.5266 - 0.059.6 \log \frac{[Fe^{2+}]}{[Fe^{3+}]}$$

At the equivalence point, enough Ce^{4+} has been added to react with all Fe^{2+}.

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

all Ce^{4+} are converted to $Ce^{3,+}$ while Fe^{2+} are converted to Fe^{3+}

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

$$E_f = 0.767 - 0.05916 \log \frac{[Fe^{2+}]}{[Fe^{3+}]} \quad .....(1)$$

$$E^{+} = 1.70 - 0.05916 \log \frac{[Ce^{3+}]}{[Ce^{4+}]} \quad .....(2)$$

Neither the equation 1 nor equation 2 alone is enough to calculate E^{o} of the cell, but combination of the two equations.

$$2E^{+} = 0.767 + 1.70 - 0.05916 \log \frac{[Fe^{2+}]}{[Fe^{3+}]} - 0.05916 \frac{[Ce^{3+}]}{[Ce^{4+}]}$$

$2E^{+} = 2.46V$

$E_{+} = 2.46/2 = 1.23V$

$E = E^{+} - E_{calomel}$

$E = 1.23 - 0.241 = 0.99V.$

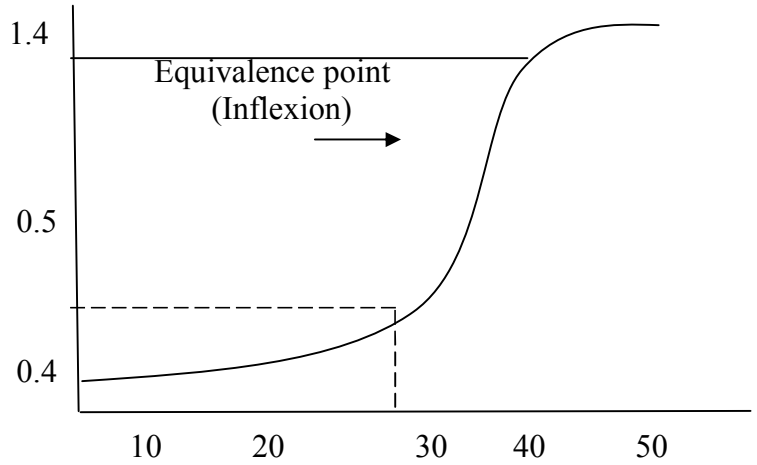

Fig. 3.1 Redox Titration curve

After the Equivalence Point

Almost all Fe^{2+} are now in form of Fe^{3+} while the excess Ce^{4+} remained in the system. So the E of cell is formed from the activity of Ce^{4+}.

$$E = E^{+} - E_{calomel} = 1.70 - 0.05916 \log \frac{[Ce^{3+}]}{[Ce^{4+}]} - 0.24$$

$$E_{+} = 1.70$$

$$E_t = E^o \frac{Ce^{4+}}{Ce^{3+-}} - 0.241$$

$$E = 1.216V$$

5.5 Detecting Redox End Point

The end point of the redox titration can be determined by the use of electrode to measure potential and is plotted against the volume of titrant. Three visual indicators are commonly used.

(i) ***Self Indicator***

This is when the titrant is highly coloured. The colour changes may be used to detect the end point.

Example: Titration of acidified $KMnO_4$ against freshly prepared $FeSO_4$ solution. $KMnO_4$ which is deep blue/purple converts to colourless at end point.

(ii) ***Starch Indicator***
Starch indicator is often used when the titration involves iodine /starch complex, which is blue colour but at the end point turns colourless but addition of drops of starch turns it back to blue.

(iii) ***Redox Indicators***
These are highly coloured dyes. They are weak reducing or oxidizing agent. They are potential dependent. Example is Ferroin whose colour changes from pale blue to red and is potential dependent.

5.6 Iodimetry and Iodometry

Both are analytical techniques that involve the use of iodine [I_2] but of different status.

(i) Iodine is a moderately strong oxidizing agent and can be used to titrate reducing agent. Titration with I_2 as oxidizing agent is called iodimetric analysis. It is performed in neutral or mildly alkaline (pH = 8) medium.

(ii) Iodine is also a weak reducing agent and will reduce oxidizing agent so when an excess iodine is added to a solution of an oxidizing agent, I_2 is produced in an amount equivalent to the oxidizing agent present. Such analytical method is known as iodometric method

6.0 ACTIVITY

i. What is (a) an oxidizing agent, (b) a reducing agent? Give two examples in each case.
ii. Differentiate between Iodimetry and Iodometry.
iii. Explain the following terms: (a) Galvanic cell, (b) Electrolyte, (c) Salt bridge.

7.0 SUMMARY

In this unit, you have learnt that:

a. Definition of redox titration and various technical terms.
b. Electrochemical cell and cell potential
c. How to use Nearnst equations to monitor by the use of a potentiometer, the activity of species at, before and after the equivalence point.
d. Redox indicator.

8.0 ASSIGNMENT

ia. Differentiate between the two major types of electrochemical cells known
b. Explain the following terms:
(i) Reducing agent (ii) Oxidizing agent (iii) Electrode potential (iv) Salt bridge

ii. Calculate the potential of half reaction of solution of 10^{-3}M in $Cr_2O_7^{2-}$ and 10^{-2}M in Cr^{3+} of pH 2.0
iii. Differentiate between Iodometry and Iodimetry
iv. Name the various types of indicators often used in Redox titration. Write briefly about each of the named indicators.

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UNIT 4 COMPLEXOMETRIC AND PRECIPITATION TITRATIONS

CONTENTS

1.0 INTRODUCTION

Some metal ions form slightly soluble salts or slightly dissociated complexes. The formation of these complexes can be the basis for accurate, more precise and convenient titrimetric determination for such metal ions. Titration based on these complexes is known as complexometric-titrimetric method.

This unit reviews some fundamentals of the complexing agents called chelate, their effects and their equilibrium. Titration curves of complexometric and precipitation titrations are also discussed.

2.0 OBJECTIVES

At the end of this unit, you should be able to:

- explain the principle of complex ion formation;
- explain the working principle of EDTA in complexometric titrations using appropriate indicators;

- use titration curves to illustrate both the complexometric titration and precipitation titrations; and
- list the applications of complexometric titration and precipitation titrations.

3.0 HOW TO STUDY THE UNIT

1. You are expected to read carefully through this unit at least twice before attempting to answer the self-assessment questions or tutor- marked assignment.
2. Do not look at the solution given at the end of the unit until you are satisfied that you have done your best to get all answers.
3. Share your difficulties with your course mates, facilitators and by consulting other related material, particularly the internet.
4. Note that if you follow the instructions you will feel self fulfilled that you have achieved the aim of studying this unit. This should stimulate you to do more.

4.0 WORD STUDY

Ligands: are complexing agents that bind with the metal ions to form complexes.
Metal-ion indicator: is a compound which changes when it binds to a metal ion.

5.0 MAIN CONTENT

5.1 Definition

Complexometric titration is an analytical method which is used to determine larger number of metals that form soluble salt or slightly dissociated complexes.

Almost all metals on the periodic table form complex with electron donating agent (ligand) (e.g. O, N, and S atoms) which are capable of satisfying the coordination number of such metal. The metals are lewis acids, (electron accepting species), while the ligands are lewis bases (election pair donors).

5.2 Ligands

Ligands are complexing agents that bind with the metal ions to form complexes. The number of ligand that form complexes with metal ions depends on the coordination number of the metal. Hence there are two types of ligands.

i. **Monodentate Ligands**: are those ligands that bind with the metal ion through only one atom (the carbon atom) e.g CN^-, NH_3
ii. **Multidentate Ligands**: These are the types of ligands that attach to metal ion through more than one ligand atom. *Example* is EDTA (ethylenediaminetetraacetic acid) called Chelating Ligand. ATP (adenosine triphosphate) is another important tetra dentate ligand.

5.3 Formation Constant

Most of the ligands except, perhaps, nitrilotriacetic acid (NTA), form complexes with metal ions in the stochiometric 1:1 (ligand: metal ion) ratio regardless of the charge on the ion.

The equilibrium constant for the reaction of a metal ion with a ligand is called the formation constant K_f – It is also called stability constant K_s or K_{stab}.

$$K_f = \frac{[\text{Pr}oduct]}{[\text{Re}ac\,\text{tan}ts]}$$

e.g. $Ag^+ + 2NH_3 \rightleftharpoons Ag(NH_3)_2^+$

$$K_f = \frac{[Ag(NH_3)_2^+]}{[Ag^+][NH_3]^2}$$

However, equilibria could also be written in reverse direction as dissociation. The constant is then called instability constant K_i , or dissociation constant, K_d.

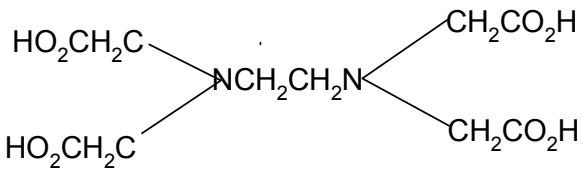
$$Ag(NH_3)_2^+ \longrightarrow Ag^+ + 2(HN_3)$$

$$K_d = \frac{[Ag^+][NH_3]^2}{[Ag(NH_3)_2]}$$

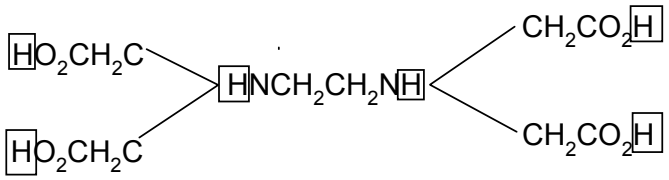
Hence, $K_d = \frac{1}{K_f}$

5.4 EDTA Titrations

EDTA is the most widely used chelator in the field of analytical chemistry, through direct titration or indirect sequence of reactions. It has a sharp end-point corresponding to the stochiometric complex formed. The ligand is called chelating agent, while the complex formed with metal ion is called chelate. EDTA is a hexaprotic system designated as H_6Y^{2+} with the exact structure.



EDTA is a hexaprotic H_6Y^{2+}, because the number of acidic hydrogen atom lost upon complete metal complex formation is six. The first four that are lost apply to carboxyl protons while the last two are of ammonium protons.



However, the neutral acid is tetraprotic which is designates by H_4Y, all the 4H referring to proton from carboxyl proton, with different pKa values.
EDTA has four pKa values corresponding to the step wise dissociation of the four protons.

$$H_4Y \rightleftharpoons H^+ + H_3Y^- \qquad Ka_1 = 1.0 \times 10^{-2} \frac{[H^+][H_3Y^-]}{H_4Y}$$

$$H_3Y^- \rightleftharpoons H^+ + H_2Y^{2-} \qquad Ka_2 = 2.2 \times 10^{-3} \frac{[H^+][H_2Y^{2-}]}{[H_2Y^-]}$$

$$H_2Y^{2-} \rightleftharpoons H^+ + HY^{-3} \qquad Ka_3 = 6.9 \times 10^{-7} \frac{[H^+][HY^{-3}]}{[H_2Y^{2-}]}$$

$$HY^{3-} \rightleftharpoons H^+ + Y^{4-} \qquad Ka_4 = 5.59 \times 10^{-11} \frac{[H^+]\ [Y^{4-}]}{[HY^{3-}]}$$

Anion is the ligand species in complex formation, the complex formed are markedly affected by the pH. H_4Y has low solubility in water, hence the commonly used reagent is disodium salt, ($Na_2H_2Y_2.2H_2O$).

The fraction [α] for each species is the fraction of EDTA in that form.

Example $\alpha\ Y^{4-}$ is the fraction of EDTA in the form of

$$\alpha\ Y^{4-} = \frac{[Y^{4-}]}{[H_4Y] + [H_3Y^-] + [H_2Y^{2-}] + [HY^{3-}] + [Y^{4-}]}$$

$$\alpha\ Y^{4-} = [Y^{4-}] \frac{\quad}{[EDTA]}$$

Where [EDTA] is the total concentration of all free EDTA species in the solution.

Free EDTA means EDTA that does not form a complex with the metal ion. Formation constant, K_f, of metal - EDTA complex is the equilibrium constant for the reaction.

Example $M^{n+} + Y^{4-} \rightleftharpoons MY^{n-4}$

$$K_f = \frac{[MY^{n-4}]}{[M^{n+}]\ [Y^{4-}]}$$

$$Ca^2 + Y^{4-} \rightleftharpoons CaY^{2-}$$

$$K_f = \frac{[CaY^{2-}]}{[Ca^{2+}][Y^{4-}]}$$

5.4.1 Conditional Formation Constant

Due to the fucntionability of pH on the equilibrium, the fraction of EDTA is not all Y^{4-} at pH below 10.24. Species such as HY^{3-}, HY^{2-} predominate at lower pH.

Therefore to conveniently express the fraction of free EDTA, there is the need for a substitution and rearrangement as follows:

Substitute $\alpha\ Y^{4-}\ [Y^1]$ or $\alpha\ Y^{4-}\ [EDTA]$ as $[Y^4]$

$$K_f = \frac{[MY^{n-4}]}{[M^{n+}]\ \alpha\ Y^{4-}\ [Y^-]} \quad \text{or} \quad \frac{[MY^{A-4}]}{[M^{n+}]\ \alpha\ Y^{4-}\ [EDTA]}$$

K^1 = conditional formation constant

Rearranging gives

$$K_f\ \alpha\ Y^{4-} = K^1 \qquad \frac{[MY^{n-4}]}{[M^{n+}]\ [Y^-]} \quad \text{or} \quad \frac{[MY^{A-4}]}{[M^{n+}]\ [EDTA]}$$

This equation can be used to calculate the equilibrium concentration of the different species at a given pH. It is also called effective formation constant.

5.4.2 EDTA Titration Curve

The concentration of the metal ion can be calculated easily during the course of complexometric titration of metal ion and EDTA in which chelating agent (titrant) is added to the sample containing metal (analyte). The titration is analogous to that of a strong acid metal ion and weak base (EDTA).

The titration reaction is

$$M^{n+} + EDTA \rightleftharpoons MY^{N-4}$$

$$K_f^1 = \alpha\ Y^{4-}\ K_F$$

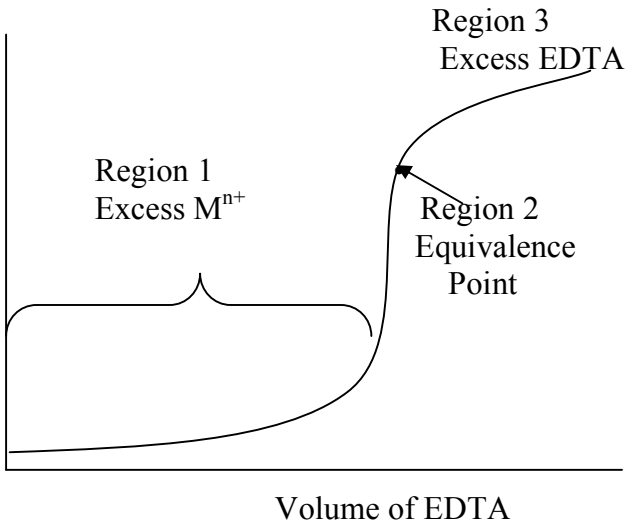


Fig. 4.1 EDTA Titration Curve

If K_f^1 is large, then the reaction is considered to be complete at each point of titration. The titration curve is usually divided into three phases.

(1) Before the equivalence point: Each addition of EDTA is consumed completely at this stage, so there is excess of M^{n+} left. The concentration of free metal ion is equal to the concentration of excess, unreacted M^{n+}. The dissociation of MY^{n-4} is negligible.

(2) At the equivalence point: The concentration of EDTA is exactly as that of metal ion in the solution. The solution is treated as if it is dissolving pure MY^{n-4}

$$MY^{n-4} \rightarrow M^{n+} + EDTA$$

So at equivalence point M^{n+} = EDTA

(3) After the equivalence point: Now there is excess of EDTA while the entire metal ion has been virtually consumed and all metal ions in form of MY^{n-4}. The concentration of free EDTA can be equated to the concentration of excess EDTA added after the equivalence point.

5.4.3 Detection of End-Point

There are methods involved when trying to detect the end point in complexometric titrations. These methods include:

(i) The use of metal ion indictor
(ii) Use of mercury electrode
(iii) Glass (pH) electrode
(iv) Ion -selective electrode.

However, the use of metal ion indicator appears the most convenient and efficient.

5.4.4 Metal Ion Indicator

A metal-ion indicator is a compound which changes when it binds to a metal ion. It is important to note that.

"For a metal-ion indicator to be useful, it must bind metal less strongly than EDTA does".

There are so many different types of metal - ion indicators, which include Erichrome Black T, Calmagite, murexide, xylenol, pyridylazonephthol, etc. A typical example is the using of Erichrome Black T in the titration of Mg^{2+} with EDTA.

$$\underset{Red}{MgIn} + \underset{Colourless}{EDTA} \rightarrow \underset{Colourless}{MgEDTA} + \underset{Blue}{In}$$

$In = Indicator$

Most metal ion indicators are acid-base indicator. If the metal-indicator does not dissociate easily to release metal to EDTA to form metal-EDTA complex, the metal is said to be blocked.

However, the blocked EDTA can be titrated through back titration. Example, excess EDTA (standard) can be added to Cu^{2+}. The indicator is added and excess EDTA is back-titrated with Mg^{2+}.

5.4.5 EDTA Titration Techniques

There are many types of titration methods involved with EDTA. This is probably due to large number of elements that can be titrated through EDTA. The techniques include:

i. ***Direct titration***: In this type of titration, analyte is titrated with standard EDTA. The analyte is buffered to an appropriate pH at which conditional formation constant is larger and free indicator has a distinct colour. Addition of auxiliary complexing agent such as ammonia, tartarate, and citrate is added to prevent metal ion from, precipitating in the absence of EDTA.

ii. ***Back-Titration***: a known excess of EDTA is added to the analyte. The excess EDTA is then titrated with standard solution of a second metal ion.
Back titration is useful if the metal ion precipitate in the absence of EDTA. The metal ion used in the back titration must not displace the analyte metal ion from its EDTA sample.

iii. ***Displacement Titration:*** It is a type of titration in which analyte is usually treated with excess $Mg(EDTA)^2$ to displace Mg^{2+}, which is later titrated with standard EDTA. Displacement titration is often used when metal ions do not have satisfactory indicator.

$$M^{n+} + MgY^{2-} \rightarrow MY^{n-4} + Mg^{2+}$$

iv. ***Indirect Titration*:** Anions that form precipitate with certain metal ion can be analysed with EDTA by indirect titration.
Example SO_4^{2-} precipitate with excess Ba^{2+} at pH 1.0 .$BaSO_4$ is filtered, washed and boiled with excess EDTA at pH 10, to bring back Ba^{2+} into solution as Ba $[EDTA]^{2-}$. The excess EDTA is back titrated with Mg^{2+}.

v. ***The Use of Masking Agent*:** This is used to prevent the element from interfering in the analysis of another element. Masked element can however be demasked after the analysis of element of interest by reacting with anion that has stronger affinity with the masked element, after which it is then titrated.

5.5 Precipitation Titration

This type of titration is very useful in determining the concentration of analyte which precipitates with the anion or titrant. It is useful, provided that equilibrium are rapid and a suitable means of detecting the end-point is available.

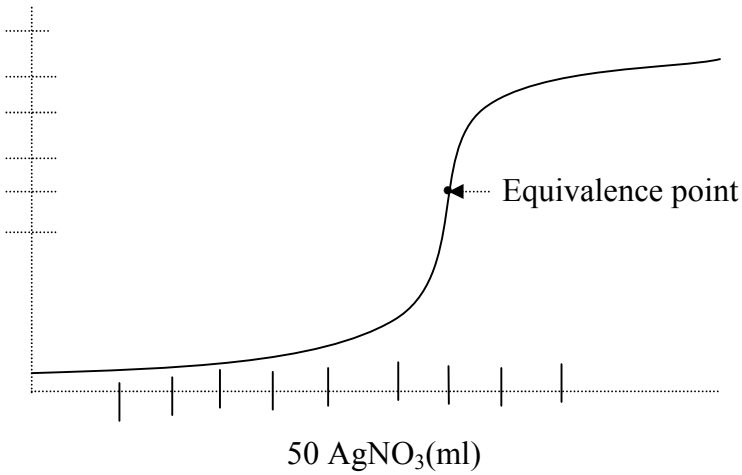


Fig. 4.2 Titration curve

Consider Cl^- being titrated with $AgNO_3$ which is similar to acid-base titration. Prior to the equivalence point, part of the Cl^- is consumed by $AgNO_3$ to precipitate AgCl. The pH is determined by the remaining Cl^- in the system.

At the equivalence point, there is saturated solution with AgCl. The Cl^- is almost exactly the same with $AgNO_3$ added, while at points beyond the equivalence point, this is determined from the concentration of Ag^+ and K_{sp} values.

The smaller the K_{sp}, the larger the break at equivalence point.

5.5.1 Detection of End-Point

End point can be detected by either with the use of potentiometer with an appropriate electrode. Indicator can also conveniently be used. There are two major types of indicators.

a. **The *first type*** of indicators are those that forms a coloured compound with the titrant when it is in excess.
Example 1: In Mohr method for determining Cl^- which is titrated with $AgNO_3$, chromate (CrO_4^{2-}), soluble salt is the indicator. This produces yellow solutions. When Cl^- precipitate is complete, the first excess Ag^+ reacts with indicator to precipitate red Ag_2ClO_4.
In Volhard Titration, F^{2+} (Ferrion) is added as indicator which forms soluble complex with the first excess of titrant.
$Fe^{2+} + SCN \rightarrow Fe(SCN)^{2+}$

c. ***The second type*** of indicator is adsorption indicator. The indicator becomes adsorbed on the precipitate at the equivalence point. The colour of the indicator changes when it is adsorbed. *Example* is in Fajans method. Fluorescien is used as an indicator for halides at pH 7.

6.0 ACTIVITY

i. Explain the following terms: (a) Ligand, (b) Formation constant and (c) Conditional formation constant.
ii. Give the mathematical expressions for the various formation constant in the complete dissociation of EDTA.
iii. Write briefly about the types of complexometric titrations known.
iv. Calculate the concentration of Mg^{2+} and show shape of titration curve for reaction of 50.0mL of 0.020 M Mg^{2+} (buffered to pH 10) with 0.020M EDTA.

7.0 SUMMARY

In this unit, you have learnt about:

a. The definition and basic principle in complexometric titration
b. The underlying principle in precipitation titration
c. Ligands and their formation
d. Detailed structure and properties of EDTA
e. Different phases and application of titration curve for complexometric and precipitation titrations
f. Various types of complexometric titrations
g. Types of indicators in both titrations.

8.0 ASSIGNMENT

i. Differentiate between monodentate and multidentate ligands.
ii. Explain briefly types of complexometric titrations you know.
iii. Suppose that 0.01M Fe^{2+} is titrated with 0.002M EDTA at pH 2, what is the concentration of free Fe^{3+} at the equivalence point and beyond equivalence point.
iv. What is a masking agent? Give three examples.

9.0 REFERENCES/FURTHER READING

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