Lesson 3: Volumetric Titration-Complexometric

*Read through the lesson notes. You can write them out, print them or save them.

*Once you have tried to understand the lesson answer the questions that follow and self-evaluate your work by checking the answers.

Learning Intention

-Learn about complexometric titrations.

Background

From the previous chemistry courses, the following types of titration were studied:

1. Acid-base (focussed on neutralisation reactions).
2. Redox (focussed on redox reactions).

Titration Examples

1. A simple acid-base titration (from National 5) could be as follows:

   $HCl + NaOH \rightarrow NaCl + H_2O$

   This involves using a pH indicator (such as phenolphthalein) to determine the end point and thus the concentration of the acid or base to be calculated.

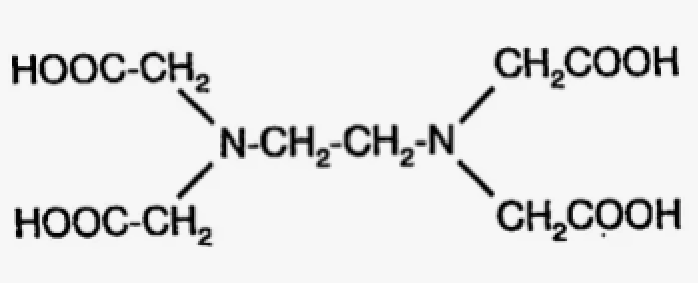
2. A simple Redox titration (from Higher) could be as follows:

   $MnO_4^- + 5Fe^{2+} + 8H^+ \rightarrow Mn^{2+} + 5Fe^{3+} + 4H_2O$

   This particular example can be used for the determination of iron (for example in iron tablets) using acidified permanganate. This titration is self-indicating due to the change in colour of the permanganate ions.

Advanced Higher Chemistry introduces a third type of titration, COMPLEXOMETRIC TITRATION. This involves reactions in which coloured complexes are formed. EDTA is possibly the most common reagent used in complexometric titrations.

EDTA (Ethylenediaminetetraacetic acid):



EDTA complexes on a 1:1 ratio with many metal ions. The use of EDTA in complexometric titrations makes it suitable for the analysis of the concentration of ions.

Examples of complexometric analysis

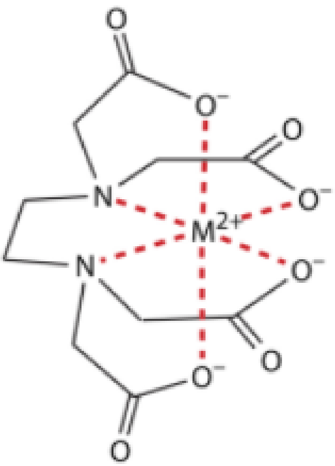
-Calcium content in milk

-Magnesium ion content to determine the “hardness” of water

-Determination of nickel content in salts

In all these examples, a suitable indicator (normally murexide) is used to determine the end point of the complexometric titration.

As the name suggests, the titration involves the formation of a complex. This occurs because EDTA acts as a hexadenate ligand, i.e. it donates six pairs of electrons to the metal being analysed.



There is no requirement to draw this complex. The diagram is just highlighting that EDTA forms a hexadentate ligand with many metals (M).

Note that the coordination number of the complex is 6.

<u>Worked Example</u>

Determine the percentage of nickel present in the salt nickel sulfate hexahydrate, $NiSO_4.6H_2O$. Compare this with the theoretical percentage of nickel that should be in the salt.

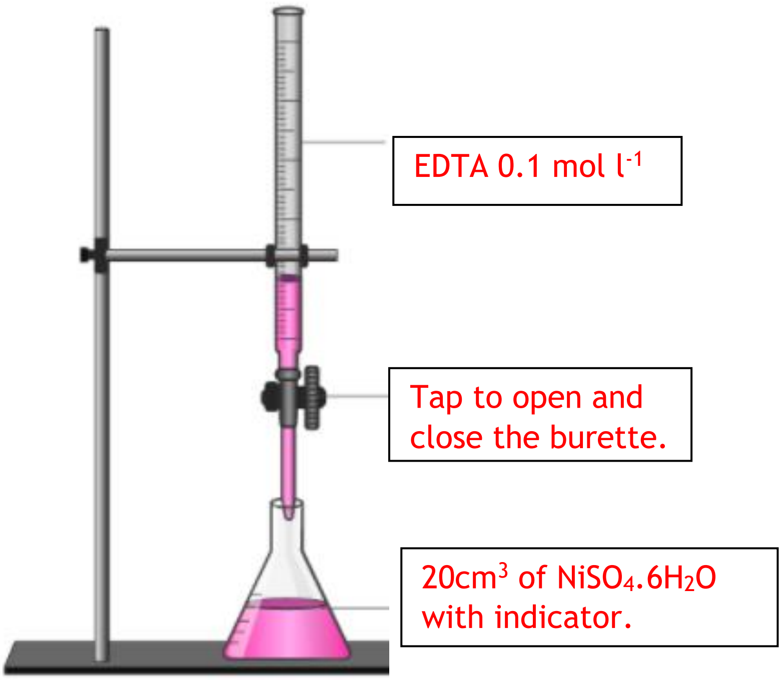
<u>Step 1</u>

Dissolve 2.63g (weighed accurately approximately) of $NiSO_4.6H_2O$ using distilled water and transfer to a 100cm^3 volumetric flask using the correct procedure to prepare a solution.

2.63g of $NiSO_4.6H_2O$ is dissolved and prepared in a 100cm^3 volumetric flask.

<u>Step 2</u>

Pipette <u>20cm^3</u> of the dissolved $NiSO_4.6H_2O$ from the <u>volumetric flask</u> into a conical flask and titrate against 0.1 mol l^{-1} EDTA using murexide indicator to determine the end point. Repeat this until concordant results are obtained.



Sample Results and Calculation

	Rough titration	First Titration	Second titration
Initial burette reading/cm^3	0	20.7	0
Final burette reading/cm^3	20.7	40.9	20.1
Total volume EDTA added/cm^3	20.7	20.2	20.1

Average volume of EDTA required for the titration = $20.15cm^3$.

EDTA (concentration 0.10 mol l^{-1})

n= c x v

n= 0.10 x 0.02015

n= 2.015×10^{-3} moles

Ni^{2+} ions (1:1 with EDTA)

n= 2.015×10^{-3} moles (in $20cm^3$ portion for titration)

n= $2.015 \times 10^{-3} \times 5$ (in $100cm^3$ volumetric flask)

n= 1.0075×10^{-2} moles (in $100cm^3$ volumetric flask)

Mass Ni^{2+} ions = n x GFM

Mass Ni^{2+} ions = $1.0075 \times 10^{-2} \times 58.7$

Mass Ni^{2+} ions = 0.5914g

% Ni in salt = (0.5914/2.63) x 100

% Ni in salt = 22.5% (from experiment)

From the experiment is has been calculated that there is 22.5% of nickel present. However, to appreciate the purity of the salt, this value has to be compared with the theoretical percentage of nickel that should be present in the salt.

Theoretical percentage of nickel in salt:

$$\frac{\text{GFM Ni} \times 100}{\text{GFM } NiSO_4.6H_2O}$$

$$\frac{58.7 \times 100}{262.8} \longrightarrow 22.3\%$$

This compares favourably with the practical value.

→Watch the clip on Youtube.

https://www.youtube.com/watch?v=r97t1HegA94

https://www.youtube.com/watch?v=F9aSa4j-V44

→ Read Scholar Heriot-Watt/ Researching Chemistry Section 5.4.

→ Read Bright Red Advanced Higher Textbook Page 83.

→ Answer the questions from Sheet 4.3 and check the answers when you have completed them.

4.3 Complexometric Titrations

1. To determine the percentage of nickel(II) ions in nickel sulfate hexahydrate, ($NiSO_4.6H_2O$), a titration with EDTA was carried out. The procedure used was as follows:

Approximately 2·6 g of nickel(II) sulfate ($NiSO_4.6H_2O$) was weighed out accurately and made up to 100 cm^3 of solution in a volumetric flask. 20 cm^3 of this solution was pipetted into a conical flask and 5 drops of murexide indicator were added. The solution was then titrated against a primary standard solution of 0·100 mol l^{-1} EDTA. The titration was then repeated until two concordant results were obtained.

The results obtained from one such experiment are shown below.
Accurate mass of Nickel sulfate hexahydrate used = 2·58 g

Titration Number	Volume of EDTA solution used (cm^3)
1	19·9
2	19·6
3	19·5

(EDTA reacts with Ni^{2+} in a 1:1 ratio)

a) Explain the seeming contradiction in the phrase "Approximately 2·6 g of nickel (II) sulfate ($NiSO_4.6H_2O$) was weighed out accurately ".

b) Explain in detail how the nickel sulfate solution was produced.

c) Calculate the number of moles of EDTA used in the above titration.

d) Calculate the number of moles of nickel in the standard solution.

e) Calculate the mass of nickel in the standard solution.

f) Calculate the experimental percentage mass of nickel in nickel (II) sulfate hexahydrate.

2. A sample of “hard water” was analysed with EDTA. It is known that EDTA forms a complex on a 1:1 mole ratio with Ca^{2+} (aq). 10 cm^3 of the hard water was diluted to 100 cm^3 and then several 25 cm^3 samples of the diluted solution were titrated with standard 0.01 mol l^{-1} EDTA. The average titre was 24.9 cm^3.

Calculate the concentration of Ca^{2+} (aq) ions in the original hard water sample.

3. A container of impure zinc (II) sulfate was analysed using EDTA. Zinc reacts on a 1:1 mole ratio with EDTA. A 6.72g sample of the impure zinc (II) sulfate was dissolved in distilled water, filtered to remove any insoluble substances and the remaining solution made up to 250cm^3 in a standard flask. Several 25cm^3 samples of this solution were titrated with standard 0.1 mol l^{-1} EDTA. The average titre was 22.3cm^3.

a) Calculate the mass of zinc (II) sulfate in the sample taken from the container.
b) Express this as a percentage, by mass, of the original container sample.

4. In the copper (II) salt, $[Cu(NH_3)x]SO_4{\cdot}H_2O$, the copper ion is complexed with ammonia.

To determine the number of moles(x) of ammine ligands in the complex it was titrated with hydrochloric acid. One mole of ammonia will react with one mole of hydrochloric acid.

To determine the number of moles of copper in the compound it was titrated with EDTA.
(1 mole of copper ions combines with 1 mole of EDTA).

A 1·00 g sample of the salt was dissolved and made up to 100 cm^3 with distilled water. This solution was treated as follows:

(i) 50 cm^3 was titrated with 0·25 mol l^{-1} hydrochloric acid. 34·7 cm^3 of hydrochloric acid was used in the reaction.

(ii) 50 cm^3 was titrated with EDTA. The volume of 0·1 mol l^{-1} EDTA required was 21·7 cm^3.

From the experimental results above, calculate the number of moles of Cu^{2+} ions and ammine ligands present and therefore the value of x.