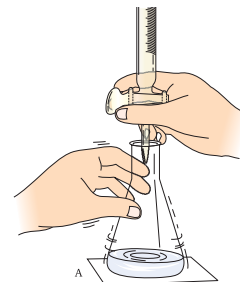


UNIT - 6

TITRIMETRIC ANALYSIS (REDOX REACTIONS)



THE oxidation and reduction reactions in aqueous solutions involve the transfer of electrons from one species to another. In the oxidation of a substance electron(s) is (are) transferred from the species and in reduction, electron(s) is (are) gained by the species. Oxidation and reduction reactions occur simultaneously. A reaction, which involves simultaneous oxidation and reduction, is called a redox reaction. The titrations involving redox reaction are called redox titrations. You know that in acid-base titrations, indicators which are sensitive to pH change are employed to note the end point. Similarly, in redox titrations there is a change in oxidation potential of the system. The indicators used in redox reactions are sensitive to change in oxidation potential. The ideal oxidation-reduction indicators have an oxidation potential intermediate between the values for the solution being titrated and the titrant and these show sharp readily detectable colour change.

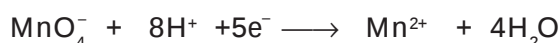
EXPERIMENT 6.1

Aim

To determine the concentration / molarity of KMnO_4 solution by titrating it against a 0.1 M standard solution of oxalic acid.

Theory

In the present experiment, potassium permanganate acts as a powerful oxidising agent. Although KMnO_4 acts as an oxidising agent in alkaline medium also, for quantitative analysis mostly acidic medium is used. The oxidising action of KMnO_4 in the acidic medium can be represented by the following equation:



The acid used in this titration is dilute sulphuric acid. Nitric acid is not used as it is itself an oxidising agent and hydrochloric acid is usually avoided because it reacts with KMnO_4 according to the equation given below to produce chlorine and chlorine which is also an oxidising agent in the aqueous solution.



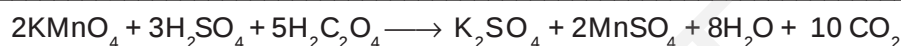
Since, oxalic acid acts as a reducing agent, it can be titrated against potassium permanganate in the acidic medium according to the following equation:

Reactions of oxalic acid

A. Chemical equations

Reduction half reaction : $2\text{KMnO}_4 + 3\text{H}_2\text{SO}_4 \longrightarrow \text{K}_2\text{SO}_4 + 2\text{MnSO}_4 + 3\text{H}_2\text{O} + 5 [\text{O}]$

Oxidation half reaction : $\text{H}_2\text{C}_2\text{O}_4 + [\text{O}] \xrightarrow{60^\circ\text{C}} 2\text{CO}_2 + \text{H}_2\text{O} \times 5$



B. Ionic equation

Reduction half reaction : $\text{MnO}_4^- + 5\text{e}^- + 8\text{H}^+ \longrightarrow \text{Mn}^{2+} + 4\text{H}_2\text{O} \quad \times 2$

Oxidation half reaction : $\text{C}_2\text{O}_4^{2-} \longrightarrow 2\text{CO}_2 + 2\text{e}^- \quad \times 5$



In these equations, MnO_4^- is reduced to Mn^{2+} and $\text{C}_2\text{O}_4^{2-}$ is oxidised to CO_2 . The oxidation number of carbon in $\text{C}_2\text{O}_4^{2-}$ changes from +3 to +4.

In these titrations, potassium permanganate acts as a self-indicator. Initially colour of potassium permanganate is discharged due to its reduction by oxalic acid. After complete consumption of oxalate ions, the end point is indicated by the appearance of a light pink colour produced by the addition of a little excess of unreacted potassium permanganate. Further, during the titration of oxalic acid against potassium permanganate, warming of oxalic acid solution ($50^\circ\text{--}60^\circ\text{C}$) along with dilute H_2SO_4 is required. This is essential because the reaction takes place at higher temperature. During the titration, first manganous sulphate is formed which acts as a catalyst for the reduction of KMnO_4 by oxalic acid. Therefore, in the beginning the reaction rate is slow and as the reaction proceeds, the rate of the reaction increases.

Material Required

	• Measuring flask (250 mL):	One		• Oxalic acid	: As per need
	• Burette (50 mL)	: One		• Potassium permanganate solution	: As per need
	• Burette stand	: One		• 1.0 M Sulphuric acid	: As per need
	• Pipette	: One			
	• Conical flask	: One			
	• Funnel	: One			
	• Weighing bottle	: One			
	• Glazed tile(white)	: One			
	• Burner	: One			
	• Wire gauze	: One			
	• Chemical balance	: One			

Procedure

A. Preparation of 0.1 M standard solution of oxalic acid

Prepare 0.1M oxalic acid solution as mentioned in experiment 2.1(Unit 2, Class XI, Laboratory Manual)

Oxalic acid



Potassium permanganate



Sulphuric acid



B. Titration of oxalic acid solution against potassium permanganate solution

- Rinse and fill a clean burette with potassium permanganate solution. Remove the air bubble, if any, from the nozzle of the burette by releasing some solution through it. The burette used in the permanganate titration must have a glass stop cock as rubber is attacked by permanganate ions.
- Take 10 mL of 0.1 M oxalic acid solution in a conical flask and add half of the test tube full (5 mL) of 1.0 M H_2SO_4 to it to prevent the formation of any precipitate of manganese dioxide during the course of the titration.
- Heat the oxalic acid solution upto $50^\circ - 60^\circ\text{C}$ before titrating it with potassium permanganate solution taken in the burette. To increase the visibility of the colour change, place the conical flask containing the solution to be titrated over a white glazed tile kept below the nozzle of the vertically fitted burette.
- Note the initial reading of the volume of permanganate solution in the burette and add it in small volumes to the hot oxalic acid solution while swirling the contents of the flask gently. The violet colour of permanganate solution is

discharged on reaction with oxalic acid. The end point is indicated by the appearance of permanent light pink colour due to a slight excess of permanganate solution.

- (v) Repeat the titration till three concordant readings are obtained. Since the solution of KMnO_4 is of dark colour, the upper meniscus should be considered for noting the burette readings.
- (vi) Record the readings as shown in observation Table 6.1 and calculate the strength of potassium permanganate solution in mols/litre.

Table 6.1 : Titration of potassium permanganate solution against standard oxalic acid solution

Sl. No.	Volume of Oxalic acid in mL	Burette readings		Volume (V) of KMnO_4 used $V = (y-x)$ mL
		Initial (x)	Final (y)	

Calculations

- (i) The strength of the unknown solution in terms of molarity may be determined by the following equation.

$$a_1 M_1 V_1 = a_2 M_2 V_2 \quad (6.1)$$

For oxalic acid vs potassium permanganate titration:

$a_1 = 2$, (the number of electrons lost per formula unit of oxalic acid in a balanced equation of half cell reaction)

$a_2 = 5$, (the number of electrons gained per formula unit of potassium permanganate in the balanced equation of half cell reaction)

M_1 and M_2 are the molarities of oxalic acid and potassium permanganate solutions used in the titration.

V_1 and V_2 are the volumes of oxalic acid and potassium permanganate solutions.

On putting the value of a_1 and a_2 in equation 6.1 we get

$$\begin{array}{ccc} \text{Oxalic acid} & & \text{KMnO}_4 \\ 2M_1V_1 & = & 5M_2V_2 \\ M_2 & = & \frac{2M_1V_1}{5V_2} \end{array} \quad (6.2)$$

We can calculate the molarity of potassium permanganate solution by using equation 6.2. Strength of the solution is given by the following equation:

$$\text{Strength} = \text{Molarity} \times \text{Molar mass}$$

Result

- (i) Molarity of KMnO_4 solution is _____.
- (ii) Strength of KMnO_4 solution is _____.

Precautions

- (a) Always rinse the burette and the pipette with the solutions to be taken in them.
- (b) Never rinse the conical flask with the experimental solutions.
- (c) Remove the air gaps if any, from the burette.
- (d) Never forget to remove the funnel from the burette before noting the initial reading of the burette.
- (e) No drop of the liquid should hang at the tip of the burette at the end point and while noting reading.
- (f) Always read the upper meniscus for recording the burette reading in the case of all coloured solutions.
- (g) Never use pipette and burette with a broken nozzle.
- (h) Lower end of the pipette should always remain dipped in the liquid while sucking the liquid.
- (i) Do not blow out the last drop of the solution from the jet end of the pipette.
- (j) The strength of the solution must be calculated up to the fourth decimal place.
- (k) Do not forget to heat the mixture of oxalic acid and H_2SO_4 solutions between $50^\circ\text{--}60^\circ\text{C}$ while titrating it against potassium permanganate.



Discussion Questions

- (i) What specific name is given to the permanganate titrations?
- (ii) Which indicator is used in the permanganate titration?

- (iii) Why is a burette with pinch-cock regulator not used for the permanganate titration ?
- (iv) Why do we heat oxalic acid solution containing sulphuric acid up to 50–60°C in the permanganate titration?

EXPERIMENT 6.2

Aim

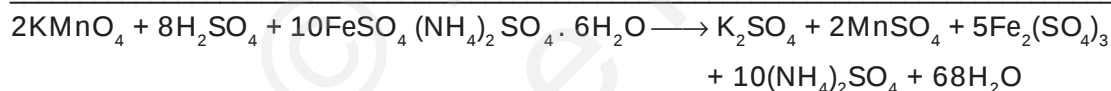
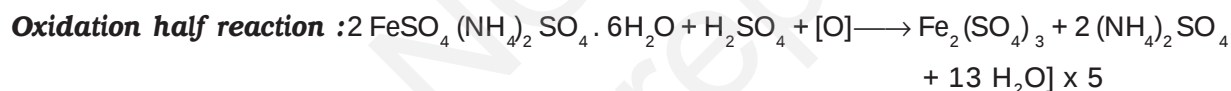
To determine the concentration / molarity of KMnO_4 solution by titrating it against standard solution of ferrous ammonium sulphate.

Theory

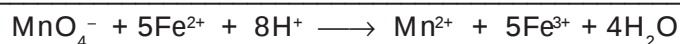
Like oxalic acid, ferrous ammonium sulphate also acts as a reducing agent in the titration against potassium permanganate.

The reaction which takes place is given below :

(a) Chemical equation



(b) Ionic equation



The oxidation number of iron in Mohr's salt is +2. Iron is oxidised during the reaction and its oxidation number changes from +2 to +3. In this titration heating of ferrous ammonium sulphate solution is not required because reaction rate is very high even at room temperature. Also, at high temperatures, ferrous ions may be oxidised to ferric ions by oxygen of air and error may be introduced in the experiment.

Material Required



- Measuring flask (250 mL) : One
- Burette (50 mL) : One
- Burette stand : One
- Pipette : One
- Conical flask : One
- Glazed tile (white) : One
- Funnel : One
- Weighing bottle : One



- Potassium permanganate solution : As per need
- Dilute sulphuric acid : As per need
- Ferrous ammonium sulphate : As per need

Procedure

Potassium permanganate



Sulphuric acid



A. Preparation of 0.05 M, standard solution of ferrous ammonium sulphate

(Molar mass of $\text{FeSO}_4(\text{NH}_4)_2\text{SO}_4 \cdot 6\text{H}_2\text{O} = 392 \text{ g mol}^{-1}$).

- (i) Weigh 4.9000 g of ferrous ammonium sulphate and transfer it into a 250 mL measuring flask through a funnel.
- (ii) Transfer the solid sticking to the funnel with the help of distilled water into the flask and add dilute H_2SO_4 into the flask drop wise to get the clear solution.
- (iii) Shake the flask till the substance dissolves and make the solution upto the mark.

B. Titration of ferrous ammonium sulphate against potassium permanganate solution

- (i) Rinse and fill the clean burette with potassium permanganate solution. Remove air bubbles if any, from the burette tip by releasing some solution through it.
- (ii) Take 10 mL of 0.05 M ferrous ammonium sulphate solution in a conical flask and add half test tube ($\approx 5 \text{ mL}$) full of (1.0 M) H_2SO_4 to it.
- (iii) Titrate the above solution with potassium permanganate solution till the colour of the solution changes to permanent pink. Swirl the content of the flask during the titration.
- (iv) Repeat the titration, until three concordant readings are obtained.
- (v) Record the readings as shown in observation Table 6.2 and calculate the strength of potassium permanganate solution in mols/litre.

Table 6.2 : Titration of potassium permanganate solution against standard ferrous ammonium sulphate solution

Sl. No.	Volume of ferrous ammonium sulphate solution used for each titration in mL	Burette Readings		Volume (V) of KMnO_4 used $V = (y-x)$ mL
		Initial (x)	Final (y)	

Calculations

The strength of unknown solution in terms of molarity may be determined by the following equation :

$$a_1 M_1 V_1 = a_2 M_2 V_2$$

M_1 and M_2 are the molarities of ferrous ammonium sulphate and potassium permanganate solutions and V_1 and V_2 are volumes of ferrous ammonium sulphate and potassium permanganate solutions, respectively.

$a_1 = 1$, (the number of electrons lost per formula unit of ferrous ammonium sulphate in the half cell reaction)

$a_2 = 5$, (the number of electrons gained per formula unit of potassium permanganate in a half cell reaction)

Strength can be calculated by the formula given below :

$$\text{Strength} = \text{Molarity} \times \text{Molar mass}$$

Result

The strength of the given potassium permanganate solution is ____ g/L.

Precautions

- Always use a fresh sample of ferrous ammonium sulphate to prepare its standard solution.
- Other precautions are same as that in Experiment 6.1.



Discussion Questions

- (i) Why is ferrous ammonium sulphate solution not heated before titration?
- (ii) Why is nitric acid or hydrochloric acid not used in permanganate titration? Explain.
- (iii) Why is dilute sulphuric acid added while preparing a standard solution of ferrous ammonium sulphate?
- (iv) How will you prepare 100 mL of 0.1 M standard solution of ferrous ammonium sulphate?
- (v) Why is KMnO_4 not regarded as a primary standard?
- (vi) What type of titrations are given the name redox titrations? Name some other redox titrations?