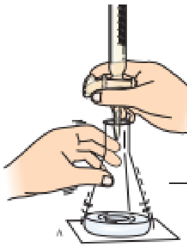
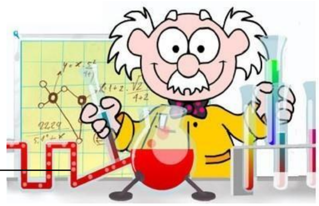


Practical Work N°3

Redox Titrations. Potassium Permanganate.



I. Introduction

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.

The titration of potassium permanganate ($KMnO_4$) against oxalic acid ($C_2H_2O_4$) is an example of redox titration. In close proximity to the endpoint, the action of the indicator is analogous to the other types of visual color titrations in oxidation-reduction (redox) titrations.

In the present experiment, potassium permanganate is a strong oxidizing agent and in the presence of sulfuric acid it acts as a powerful oxidizing agent. In acidic medium the oxidizing ability of $KMnO_4$ is represented by the following equation.

In acidic solution,

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

Solution containing MnO_4^- ions are purple in color and the solution containing Mn^{2+} ions are colorless and hence permanganate solution is decolorized when added to a solution of a reducing agent. The moment there is an excess of potassium permanganate present the solution becomes purple. Thus, ***$KMnO_4$ serves as self-indicator*** in acidic solution.

The acid used in this titration is dilute sulfuric acid. **Nitric acid** is not used as it is itself an oxidizing 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 oxidizing agent in the aqueous solution.

$2KMnO_4 + 16\ HCl \rightarrow 2KCl + 2\ MnCl_2 + 5Cl_2 + 8\ H_2O$

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

The chemical reaction at room temperature is given below.

Reduction Half reaction: $2KMnO_4 + 3H_2SO_4 \rightarrow K_2SO_4 + 2MnSO_4 + 3H_2O + 5[O]$

Oxidation Half reaction: $5(COOH)_2 + 5[O] \rightarrow 5H_2O + 10CO_2\uparrow$

The *overall reaction* takes place in the process is

Overall reaction: $2KMnO_4 + 3H_2SO_4 + 5(COOH)_2 \rightarrow K_2SO_4 + 2MnSO_4 + 8H_2O + 10CO_2\uparrow$

The ***ionic equation*** involved in the process is given below.

Reduction Half reaction: $[MnO_4^- + 8H^+ + 5e^- \rightarrow Mn^{2+} + 4H_2O] \times 2$

Oxidation Half reaction: $[C_2O_4^{2-} \rightarrow 2CO_2 + 2e^-] \times 5$

Overall Ionic reaction: $2MnO_4^- + 16H^+ + 5C_2O_4^{2-} \rightarrow 2Mn^{2+} + 10CO_2 + 8H_2O$

In these equations, MnO_4^- is reduced to Mn^{2+} and $C_2O_4^{2-}$ is oxidised to CO_2. The oxidation number of carbon in $C_2O_4^{2-}$ 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°–60°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.

Ferrous Sulphate ($FeSO_4 \cdot xH_2O$) Titration with $KMnO_4$ is another example of redox titration. In this titration Iron salt acts as a reducing agent and potassium permanganate acts as an oxidising agent. So, the reaction between Iron's salt and potassium permanganate is a redox reaction. In this redox reaction, ferrous ion gets oxidised and pink colored of manganese present in potassium permanganate, which is in the +7-oxidation state gets reduced to colorless Mn^{2+} state.

The ionic equation involved in the process is given below.

Oxidation half reaction: $[Fe^{2+} \rightarrow Fe^{3+} + e^-] \times 5$

Reduction half reaction: $MnO_4^- + 8H^+ + 5e^- \rightarrow Mn^{2+} + 4H_2O$

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

This titration is based upon oxidation-reduction titrations. When ferrous sulfate solution is titrated against potassium permanganate in the presence of acidic medium by sulfuric acid. Acidic medium is necessary in order to prevent precipitation of manganese oxide. Here $KMnO_4$ acts as a self-indicator and this titration is called permanganate titration.

II. Aims

- To determine the concentration/molarity of $KMnO_4$ solution by titrating it against a 0.1 M standard solution of oxalic acid.
- To determine the concentration/molarity of $FeSO_4.$ x H_2O solution, using a $KMnO_4$ solution prepared previously.

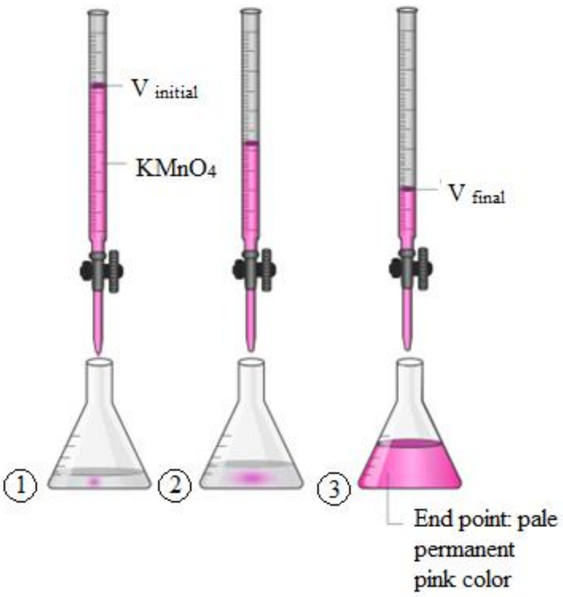
III. Materials Required:

Materials 	Chemicals 
✓ Burette (50 mL) with burette stand and clamp. ✓ Pipette (10 mL) ✓ Graduated cylinder ✓ Conical flask ✓ Hotplate magnetic stirrer ✓ Funnel	✓ An unknown solution of potassium permanganate ($KMnO_4$). ✓ 0.1 mol/L Oxalic acid ($H_2C_2O_4$) solution ✓ 0.1 mol/L Sulfuric acid(H_2SO_4) solution ✓ An unknown solution of ($FeSO_4.x\ H_2O$) ✓ Distilled water

IV. Experimental Procedure.

Apparatus Setup:

1. In burette – $KMnO_4$ solution
2. In Conical flask – 2,5 ml of oxalic acid + sulfuric acid
3. Indicator – Self indicator ($KMnO_4$)
4. End Point – Appearance of permanent pale pink color.



Titration of Oxalic Acid with $KMnO_4$

(a)Titration of potassium permanganate solution against standard oxalic acid solution:

1. Rinse the burette with the potassium permanganate solution and fill the burette with potassium permanganate solution.
2. Fix the burette in the burette stand
3. Pipette out 2,5 ml of 0.1N standard oxalic acid solution in a conical flask.
4. Add a 2,5 ml of sulfuric acid (H_2SO_4) in order to prevent oxidation of manganese to form manganese dioxide.
5. Heat the mixture up to 60°C before titrating with potassium permanganate.
6. Note down the initial reading in the burette before starting the titration.
7. The hot solution is titrated against potassium permanganate solution and simultaneously swirl the solution in the flask gently.
8. Initially the purple color of $KMnO_4$ is discharged with oxalic acid. The appearance of permanent pink color reveals the end point.

9. Repeat the titration twice.
10. Note down the upper meniscus on the burette readings. Record the reading in the **observation table** given below in order to calculate the molarity of $KMnO_4$ given.

Observation table:

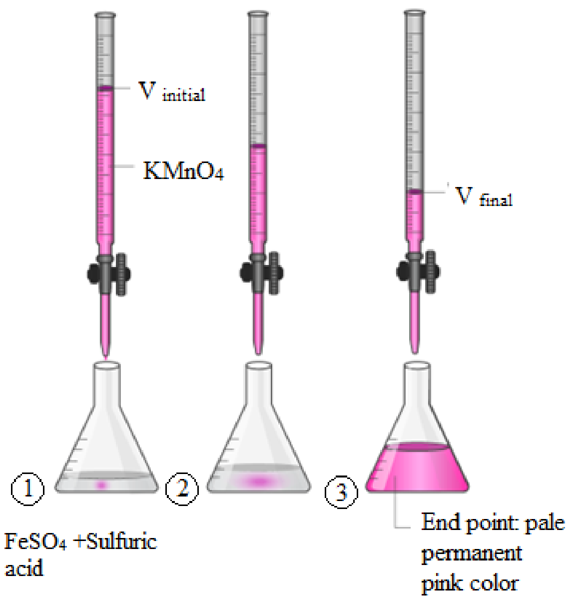
S. N°	Volume of oxalic acid in ml	Burette Reading		Volume(V) of $KMnO_4$ used V = (y-x) ml
		Initial(x)	Final(y)	
Titration 1				
Titration 2				

(b). Titration of potassium permanganate solution against unknown Fe (II) solution.

1. Using a 10 mL pipet, transfer exactly 5 mL of an unknown solution into an Erlenmeyer flask.
2. Using a graduated cylinder, add 2,5 mL of 1 M H_2SO_4 to the flask.
3. Fill your burette with the **$KMnO_4$** solution and drain out enough so that the liquid level is just below the upper calibration mark and the burette tip is full. Read the initial volume from the calibration scale on the burette. The color of potassium permanganate is so deep that you hardly can see the lower meniscus. Use the upper one to read the volumes.
4. Titrate the iron solution in the flask. The pinkish color produced by the first drop of excess **$KMnO_4$** signals the end point for the titration. Obtain the final volume reading from the calibration scale on the burette.
5. Repeat step 4 twice.

Apparatus Setup:

1. In burette – $KMnO_4$ solution
2. In Conical flask – 5 ml of Ferrous Sulfate + Sulfuric acid
3. Indicator – Self indicator ($KMnO_4$)
4. End Point – Colorless to permanent pale pink colour.



S. Nº	**Volume of ferrous sulfate used**	**Burette Reading**		**Volume(V) of $KMnO_4$ used V = (y-x) ml**
		Initial(x)	**Final(y)**	
Titration 1				
Titration 2				