

Experiment no: 1

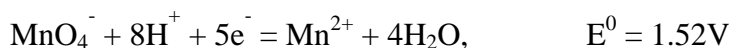
Redox titration (Titration of ferrous ion by potassium permanganate)

Introduction

Iron is the second most abundant metal in the earth's crust of which it accounts for about 5%. Iron ions Fe^{2+} and Fe^{3+} readily combine with oxygen and sulphur containing compounds to form oxides, hydroxides, carbonates and sulphides. Iron is most commonly found in nature in the form of its oxides. In drinking water supplies, iron (II) salts are unstable and are precipitated as insoluble iron (III) hydroxide, which settles out as a rust-coloured sludge. Anaerobic ground waters contain iron (II) at concentrations of up to several milligrams per litre without discoloration or turbidity in the water when directly pumped from a well, although turbidity and colour may develop in piped systems at iron levels above 0.05-0.1 mg/litre. High concentrations of dissolved iron can result in poor tasting and also stains both plumbing fixtures and clothing. Vegetables cooked in iron-rich waters become unappetizing. Iron is present in drinking water as a result of natural earth processes or corroded pipes.

Principle

Permanganometry is one of the techniques of redox titration used in quantitative analysis in chemistry. It involves the use of permanganates and is required to measure the amount of analyte present in unknown chemical samples. A redox reaction (oxidation-reduction reaction) is a reaction in which electrons are transferred between species. There is loss of electrons by a species (or increase of oxidation number) during oxidation. Reduction involves the gain of electrons by a species or decrease of oxidation number. Permanganometric titration involves two steps: the standardization of potassium permanganate and the titration of the analyte with the potassium permanganate solution. Depending on the reaction conditions, the permanganate ion can be reduced to Mn^x , where $x = +2, +3, +4$ and $+6$. In most cases, where permanganometry is performed in high acidic solutions, the following reaction occurs:



KMnO_4 in acidic medium is a very strong oxidizing agent and can oxidize Fe^{2+} ($E^0_{\text{Fe}^{3+}/\text{Fe}^{2+}} = 0.77\text{V}$), Sn^{2+} ($E^0_{\text{Sn}^{4+}/\text{Sn}^{2+}} = 0.20\text{V}$), Cl^- ($E^0_{\text{Cl}_2/\text{Cl}^-} = 1.36\text{V}$) etc. In weak acidic medium MnO_4^- accepts only 3 electrons and forms $\text{MnO}_2(\text{s})$ by the following electrochemical reaction:



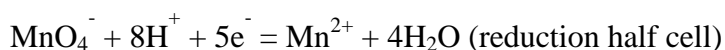
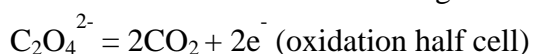
Potassium permanganate is not a primary standard. It is difficult to obtain in perfectly pure form and completely free from manganese dioxide. Moreover, ordinary distilled water contains reducing substances (traces of organic matter etc) which will react with the potassium permanganate to form manganese dioxide. The presence of manganese dioxide catalyzes the auto decomposition of permanganate solution on standing.



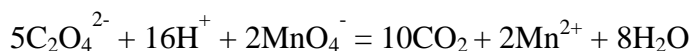
Potassium permanganate is unstable in presence of Mn (II) ions:



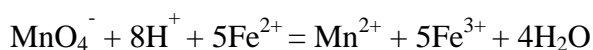
This reaction is slow in acidic medium but very rapid under neutral medium. For these reasons, a freshly prepared potassium permanganate solution is boiled for 15-30 minutes, allowed to cool at room temperature and the solution is filtered through a sintered glass crucible after 2-3 days. Sodium oxalate ($\text{Na}_2\text{C}_2\text{O}_4$) is used as the primary standard for the standardization of potassium permanganate. Sodium oxalate and potassium permanganate react in an acid medium according to the following two half cell reactions.



The two half cell reactions are combined to obtain the complete redox reaction:



From this balanced equation, we can see that there is 5:2 stoichiometric ratio between the moles of oxalate and that of permanganate. During the titration of iron (II) solution with potassium permanganate, an acid mixture containing sulphuric acid and phosphoric acid is added. Phosphoric acid complexes with Fe(III) to lower the concentration of free Fe^{3+} helping to drive the titration to completion.



<i>Apparatus required</i>		<i>Chemicals required</i>	
A1.1	Burette with burette stand	C2.1	Potassium permanganate
A1.2	Pipette (10 mL, 25 mL)	C1.2	Sulphuric acid
A1.3	Conical flask (Erlenmeyer's flask) (250 mL)	C2.2	Sodium oxalate
A1.4	Beaker (1500 mL)	C2.3	Phosphoric acid
A1.5	Graduated measuring cylinder (1000 mL)		
A1.6	Standard flask (250 mL)		
A1.7	Volumetric flask (250 mL)		
A1.8	Wash Bottle		
A1.9	Funnel		
A2.1	Dark brown coloured bottle (1000 mL)		

Procedure

P2.1 Preparation of 1000 mL of ~ 0.02 (M) potassium permanganate solution

A 1500 mL beaker was cleaned out. It was washed with soap solution, and then rinsed with tap water to remove all the soap. Finally, it was rinsed with several small portions of distilled water. Then 250 mL of distilled water was placed in the beaker. About 3.2-3.5 gm of reagent grade potassium permanganate was taken and transferred to the beaker. 750 ml of distilled water was then added and beaker was covered with a clock glass. The solution was heated to boiling, gently for 15-30 minutes and solution was allowed to cool to laboratory temperature. The solution was filtered through a sintered-glass crucible or funnel with a glass wool. The filtrate was collected and transferred it into a clean, stoppered dark brown coloured 1 litre glass bottle and kept in dark or diffuse light except in use. Diffuse daylight causes no appreciable decomposition, but bright sunlight slowly decomposes even pure solutions.

P2.2 Preparation of 250 mL of ~0.02 (M) standard sodium oxalate solution

0.65 gms of sodium oxalate was weighed and the weighed sample was transferred to a 250 mL volumetric flask. The sodium oxalate was dissolved in about 100 mL of distilled water. The solid has completely dissolved and then diluted to the mark with distilled water, mixed thoroughly and labelled.

P2.3 Preparation of 100 mL of ~6(M) sulphuric acid solution

16 mL of concentrated sulphuric acid was poured in 50 mL of distilled water in a graduated 250 mL standard flask and then diluted to 100 mL with distilled water and then the solution was mixed thoroughly by a glass rod.

P2.4 Standardization of potassium permanganate solution

At first, the burette is cleaned with distilled water. Then the burette is rinsed with two 5 mL portions of KMnO_4 solution. The burette was filled with KMnO_4 solution making sure no air remains in the tip. The initial burette reading was recorded. Now, 10 mL of sodium oxalate solution was pipetted out into a 250 mL conical flask (Erlenmeyer's flask). 60 mL of distilled water and 12 mL of 6(M) sulphuric acid solution was then added. The solution was heated to 55-60°C. It was then titrated with KMnO_4 solution until a faint pink colour remains at least 30 seconds. The first few drops of permanganate added to the acidified oxalate solution are not decolorized immediately. Mn^{2+} ion produced in the reaction acts as catalyst and reacts with KMnO_4 to form intermediate oxidation states of manganese. These states, in turn, then react rapidly with oxalate to give the products. KMnO_4 acts as its own indicator since pink colour being distinguishable even in very dilute solution. Therefore no indicator is used in this reaction. The final burette reading is recorded. The difference between initial and final readings gives the volume of required KMnO_4 solution. The titration was repeated to get at least three concordant readings.

Table 1**Standardization of potassium permanganate solution vs. standard sodium oxalate solution**

No. of titrations	Volume of standard sodium oxalate solution taken in mL	Volume of potassium permanganate solution required in mL			
		Initial reading V_i	Final reading V_f	Difference $V_f - V_i$	Average x
1	10	0	x1	x1	x
2	10	0	x2	x2	
3	10	0	x3	x3	

P2.5 Estimation of amount of Fe^{2+} in the given sample by permanganometry

25 mL of the given Fe^{2+} sample solution was pipetted out in a 500 ml conical flask. 8 mL 6(M) H_2SO_4 and 3 ml of syrupy phosphoric acid (H_3PO_4) was then added to the solution. Now, the solution was then titrated with the potassium permanganate solution running from the burette until the colour turns faint pink and persists for 30 seconds. The initial and final readings were noted. The titration was repeated with at least two more samples of the given Fe^{2+} sample solution and three concordant readings were recorded.

Table 2**Titration of Fe^{2+} sample solution vs. potassium permanganate**

No. of titrations	Volume of Fe^{2+} sample solution taken in ml	Volume of potassium permanganate solution required in ml			
		Initial reading V_i'	Final reading V_f'	Difference $V_f' - V_i'$	Average y
1	25	0	y1	y1	y
2	25	0	y2	y2	
3	25	0	y3	y3	

Calculations

The molarity of potassium permanganate solution is calculated using the formula:

$$M_1V_1 = M_2V_2;$$

M_1 = Molarity of standard sodium oxalate solution;

V_1 = Volume of standard sodium oxalate solution (10 mL);

M_2 = Molarity of potassium permanganate solution;

V_2 = Volume of potassium permanganate solution required (x)

Now, $M_2 = [M_1V_1] \times V_2 = [0.02 \times 10]/x = M_2$ (M) = Strength of KMnO_4 solution

Titration result of $\text{KMnO}_4 \equiv y$ mL of M_2 (M) KMnO_4

1000 mL of 1(M) $\text{KMnO}_4 \equiv 55.85$ gm Fe^{2+}

y mL of M_2 (M) $\text{KMnO}_4 \equiv [55.85 \times y \times M_2]/1000$ gm Fe^{2+}

Therefore, 25 mL of the Fe^{2+} sample solution contains $[55.85 \times y \times M_2]/1000$ gm Fe^{2+}

1000 mL of the Fe^{2+} sample solution contains

$[55.85 \times y \times M_2]/25$ mg $\text{Fe}^{2+} = A$ mg Fe^{2+}

1 L Mohr's Salt solution contains A mg Fe^{2+} .

Result

Therefore the amount of Fe^{2+} present in the given sample is A mg/L

Lab Precautions

1. The burette and pipette was washed with distilled water and then rinsed with the working liquid before use
2. Potassium permanganate solution was added directly into the oxalate solution at 55-60°C and flask was swirled constantly
3. The surface of permanganate solution was used to measure titrant volumes
4. Titration of the given Fe^{2+} solution was carried out at room temperature and never heated.
5. Partial decomposition of permanganate to MnO_2 may occur if it remains in the burette for a long time. Clean the burette with a dilute sodium bisulfate solution
6. Potassium permanganate is a strong oxidizing agent and can be damaging to eyes and clothing. So, it was handled with care
7. If sulphuric acid or phosphoric acid is spilled on skin, it was washed immediately and the instructor was informed