

Oxidation-Reduction Titration and Analysis of an Unknown Mixture

PURPOSE OF EXPERIMENT: Standardize a solution of KMnO_4 , and determine the percent by mass of $\text{Na}_2\text{C}_2\text{O}_4$ in an unknown mixture.

The process of titration may be used for the standardization of solutions of oxidizing and/or reducing agents, provided a suitable method for observing the endpoint of the reaction is available. When potassium permanganate, KMnO_4 , is used as a titrant, the endpoint is easily apparent. The intensely purple colored MnO_4^- in acidic solution produces the manganese(II) ion, which is very pale pink in color, but dilute solutions are practically colorless. Thus, as MnO_4^- is initially added to a solution of a colorless reactant, the resulting solution will remain essentially colorless. After excess MnO_4^- has been added, the solution will have a pink color.

In this experiment you will prepare a dilute solution of MnO_4^- and standardize it by titration with an acidified solution of ferrous ammonium sulfate hexahydrate, $\text{Fe}(\text{NH}_4)_2(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$. During standardization, MnO_4^- reacts very rapidly at room temperature with iron(II) in acidic solution to produce solutions of manganese(II) and iron(III). You will then use your standardized solution of MnO_4^- to analyze a mixture of sodium oxalate, $\text{Na}_2\text{C}_2\text{O}_4$, and a second component, potassium sulfate, K_2SO_4 , which does not react with MnO_4^- . The oxalate ion reacts slowly in dilute acidic solutions with MnO_4^- to produce carbon dioxide and manganese(II) ion. Since this reaction is slow at room temperature, the solution containing the oxalate ion will be heated and titrated at 55°C . In addition, the rate of reaction will be enhanced by the formation of manganese(II) because manganese(II) is an autocatalyst. In autocatalysis, a product of the reaction acts as a catalyst of the reaction. By knowing the balanced chemical equation and the number of moles of MnO_4^- which react, the number of moles of oxalate ion and the number of moles of sodium oxalate can be calculated. The number of moles of sodium oxalate can, in turn, be used to calculate the percent composition by mass of sodium oxalate in the unknown mixture.

REFERENCES

- (1) Kotz, J. C., and Purcell, K. F., Chemistry and Chemical Reactivity, Saunders College Publishing, Philadelphia, 1987, sections 1.3, 2.5, 2.12, 3.1, 3.2, 3.4, 4.4, and 25.1.
- (2) Masterton, W. L., Slowinski, E. J., and Stanitski, C. L., Chemical Principles, 6th ed., Saunders College Publishing, Philadelphia, 1985, sections 1.6, 2.5, 2.6, 3.6, 3.7, 12.2, 23.2, 25.2, and 25.3.

EXPERIMENTAL PROCEDURE

(Study this section and the PRE-LABORATORY QUESTIONS before coming to the laboratory. Wear safety goggles when performing this experiment.)

A. Standardization of a Potassium Permanganate Solution

Clean your buret, a 100-mL graduated cylinder, three 250-mL Erlenmeyer flasks, a 100-mL beaker, and a 500-mL Florence flask.

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Prepare a dilute solution of potassium permanganate, KMnO_4 , by mixing in your 500-mL Florence flask about 25 mL of the concentrated KMnO_4 solution, provided on the reagent table, and 275 mL of distilled water. Shake or swirl the flask thoroughly to mix the solution. Determine the concentration of this solution by titrating it against a known quantity of iron(II) by the following procedure.

Label the three Erlenmeyer flasks 1, 2, and 3. Using your analytical balance (Laboratory Methods C), weigh onto weighing paper the ferrous ammonium sulfate hexahydrate, $\text{Fe}(\text{NH}_4)_2(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$, as calculated in PRE-LABORATORY QUESTION 3. (It is not necessary to have exactly the calculated mass, but you must know the mass precisely.) Record the masses in TABLE 30.1A. Place this sample in flask 1. Weigh two more samples, put them into flasks 2 and 3, and record the masses in TABLE 30.1A. Dissolve each sample of the salt in 30. mL of distilled water (Laboratory Methods K), and add 10. mL of 3 M sulfuric acid, H_2SO_4 , solution.

Make a rapid preliminary titration of sample 1 with your KMnO_4 solution to gain experience with the procedure. Place a white sheet of paper under the flask so that the color of the solution may be seen clearly. Add the KMnO_4 solution from the buret, swirling the sample constantly, until the last drop leaves a permanent pink color. Rinse the walls of the flask with distilled water from your wash bottle to make sure all the Fe^{2+} reacts. The first appearance of a permanent pink color from MnO_4^- indicates the endpoint of the titration. Record the initial and final volumes in TABLE 30.1A.

Titrate samples 2 and 3, adding the first 20. mL of KMnO_4 rapidly and then approaching the endpoint with care. Record your initial and final volumes in TABLE 30.1A.

B. Analysis of $\text{Na}_2\text{C}_2\text{O}_4$ in an Unknown Solid Mixture

Obtain an unknown from your instructor. Clean two 250-mL Erlenmeyer flasks, and rinse them with distilled water. Using your analytical balance, weigh onto weighing paper two samples of unknown of approximately 0.25 g each, record your masses in TABLE 30.1B, and put the samples into the flasks, labeling them 1 and 2.

Add 25 mL of distilled water and 25 mL of 3 M sulfuric acid, H_2SO_4 , solution to flask 1. **CAUTION: Dilute sulfuric acid is corrosive and causes burns on your skin or holes in your clothing. If any spills or splatters occur onto your skin or clothing, wash the affected area thoroughly with water.** Swirl the mixture to hasten dissolution. (You should remember that H^+ reacts with $\text{C}_2\text{O}_4^{2-}$ to form $\text{H}_2\text{C}_2\text{O}_4$.) Fill your buret with your standard KMnO_4 solution, and record the initial reading of the buret in TABLE 30.1B. Add rapidly about 15 mL of KMnO_4 , swirl the mixture, and let the solution stand until the pink color of MnO_4^- disappears. This should occur in less than five minutes. Heat the solution to between 55°C and $60.^\circ\text{C}$ (Laboratory Methods D), and complete the titration by adding MnO_4^- solution slowly. (At temperatures below 55°C the reaction between MnO_4^- and $\text{H}_2\text{C}_2\text{O}_4$ is too slow to give a good endpoint, but above $60.^\circ\text{C}$ the oxalic acid decomposes.) Therefore, temperature control is very important. The pink color of MnO_4^- should persist for 30. seconds at the endpoint. Record the final buret reading in TABLE 30.1B.

Dissolve your sample 2 in 25 mL of distilled water and 25 mL of 3 M H_2SO_4 . Heat the solution to between 55°C and $60.^\circ\text{C}$. Then titrate, adding the KMnO_4 very rapidly up to about 2 mL of the volume you estimate will be needed on the basis of your titration of sample 1. Then slowly add more MnO_4^- solution until you reach the endpoint. Record your initial and final volumes in TABLE 30.1B.

Perform the calculations in TABLE 30.2 including the sample calculations for one run on the back of TABLE 30.2.

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Section _____ Date _____

Instructor _____

DATA

TABLE 30.1. Masses and volumes for oxidation-reduction titrations.

	Run 1	Run 2	Run 3
A Mass of weighing paper (g)			
Mass of $\text{Fe}(\text{NH}_4)_2(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$ and weighing paper (g)			
Initial reading of buret (mL)			
Final reading of buret (mL)			
	Run 1	Run 2	
B Mass of weighing paper (g)			
Mass of unknown and weighing paper (g)			
Initial reading of buret (mL)			
Final reading of buret (mL)			

Instructor's initials _____

Name _____
 Student ID number _____
 Section _____ Date _____
 Instructor _____

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CALCULATIONS

TABLE 30.2. Molarity of KMnO_4 solution and percent $\text{Na}_2\text{C}_2\text{O}_4$ by mass.

		Run 2	Run 3
A	Mass of $\text{Fe}(\text{NH}_4)_2(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$ which reacted with MnO_4^- (g)		
	Moles of iron(II) which reacted with MnO_4^- (mol)		
	Moles of MnO_4^- which reacted with iron(II) (mol)		
	Volume of MnO_4^- solution which reacted with iron(II) (mL)		
	Molarity of KMnO_4 solution (M)		
	Average molarity of KMnO_4 (M)		
		Run 1	Run 2
B	Volume of MnO_4^- which reacted with oxalic acid (mL)		
	Moles of MnO_4^- which reacted with oxalic acid (mol)		
	Moles of oxalic acid which reacted with MnO_4^- (mol)		
	Moles of $\text{Na}_2\text{C}_2\text{O}_4$ present in unknown sample (mol)		
	Mass of $\text{Na}_2\text{C}_2\text{O}_4$ present in unknown sample (g)		
	Mass of unknown sample (g)		
	Percent by mass of $\text{Na}_2\text{C}_2\text{O}_4$ in unknown sample (%)		
	Average percent by mass of $\text{Na}_2\text{C}_2\text{O}_4$ (%)		

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Sample calculations for Run 2

A Moles of iron(II) which reacted with MnO_4^-

Moles of MnO_4^- which reacted with iron(II)

Molarity of KMnO_4 solution

B Moles of MnO_4^- which reacted with oxalic acid

Moles of oxalic acid which reacted with MnO_4^-

Moles of $\text{Na}_2\text{C}_2\text{O}_4$ present in unknown sample

Mass of $\text{Na}_2\text{C}_2\text{O}_4$ present in unknown sample

Percent $\text{Na}_2\text{C}_2\text{O}_4$ by mass in unknown sample

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d. Your instructor made your unknown from $\text{Na}_2\text{C}_2\text{O}_4$ and KCl rather than K_2SO_4 .

e. You added 50. mL of 3 M H_2SO_4 rather than the required 25 mL of 3 M H_2SO_4 .

2. What is the meaning of the term, autocatalytic reaction? How could you prove experimentally that a reaction was "autocatalytic"?

3. What is the color of each of the following?

a. $\text{KMnO}_4(\text{s})$.

b. $\text{Na}_2\text{C}_2\text{O}_4(\text{s})$.

c. $\text{Mn}^{2+}(\text{aq})$.