EXPERIMENT 24C

Quantitative Redox Reactions Involving Permanganate Ion

A common laboratory oxidizing agent is the permanganate ion, MnO_4^-, which is usually provided by the compound potassium permanganate, $KMnO_4$. It is especially useful for quantitative redox reactions because the permanganate in solution is an intense purple color, but when reduced all the way to the 2+ state in Mn^{2+} becomes virtually colorless, thereby acting as its own indicator. A sample of a reducing agent can therefore be titrated with $KMnO_4$ solution, and the faint purple color that remains even after the solution is swirled makes the completion of the reaction apparent. You may think that $KMnO_4$ will not be highly accurate in showing the completion of the reaction, since it must be left over to be seen as a purple color. However, its color is very intense; the 0.020*M* solution you will be using is a very dark purple, and its color can still be detected when 1 mL of the solution is added to 2 L of water, that is, when $[MnO_4^-] = 1.0 \times 10^{-5} M$. This figure represents only 0.05% of the original concentration, which is certainly accurate enough for most situations.

Potassium permanganate is obtainable in analytical reagent quality, so a solution of it can be made up to accurate concentration from a known mass of crystals. However, the solution should be freshly prepared because after a time, any potassium permanganate solution decomposes to a certain extent, and a brown coloration of MnO_2 appears on the side of the container.

The Mn in the permanganate ion has an oxidation number of 7+; in the manganese(II) ion it has an oxidation number of 2+. It has still other common oxidation states; 6+ in the manganate ion (MnO_4^{2-}), which is green, and 4+ in manganese dioxide, which is brown. In order to make sure that all the permanganate ion is reduced completely to Mn^{2+} and not some other state, you must follow the instructions in the experiment carefully. In Part I of the procedure you will look in a qualitative way at the conditions which result in these different compounds, before you go on to use $KMnO_4$ quantitatively in Parts II and III. In Part II you will determine the $[Fe^{2+}]$ in an unknown solution (or the molar mass of an unknown iron compound), then in Part III you will determine the concentration of a solution of hydrogen peroxide, H_2O_2. Your teacher will provide you with a solution of potassium permanganate of known concentration.

OBJECTIVES: (copy these out!)

1. to determine the conditions under which $KMnO_4$ is reduced completely to Mn^{2+}
2. to determine the ? e molar mass of g/mol
   an unknown compound containing Fe^{2+}

MATERIALS

Apparatus

buret (50 mL)
stand
buret clamp
Erlenmeyer flask (250 mL)
3 test tubes (18 mm × 150 mm)
test-tube rack
beaker (250 mL)
beaker (100 mL)
pipet (25 mL)
suction bulb
graduated cylinder (10 mL)
centigram balance
medicine dropper
filter funnel
safety goggles
lab apron

Reagents

standard solution of $KMnO_4$ (approx. $0.02M$)
$0.050M$ Na_2SO_3
$3M$ H_2SO_4
$6M$ $NaOH$
unknown Fe^{2+} solution (or unknown solid containing Fe^{2+})
hydrogen peroxide solution (approx. 3%)

PROCEDURE: (Parts I + II in flow chart form)

Part I Preliminary Investigation of $KMnO_4$ as an Oxidizing Agent

1. Put on your lab apron and safety goggles.
2. Obtain in a 250 mL beaker about 150 mL of the solution of $KMnO_4$ provided. Note its concentration. (record value)
3. Obtain three 18 mm × 150 mm test tubes and place them in the rack. To each add 1 mL of the $KMnO_4$ solution.
4. Next, to one test tube add 2 mL of $3M$ H_2SO_4, to the second add 2 mL of water, and to the third add 2 mL of $6M$ $NaOH$.
5. To each test tube add 2 mL of $0.05M$ Na_2SO_3. Record your observations in your copy of Table 1 in your notebook.

CAUTION: Potassium permanganate ($KMnO_4$) solution is a strong irritant, and will stain skin and clothing. Wash any spills with plenty of water.

CAUTION: Sulfuric acid is very corrosive. Do not get any on your skin, in your eyes, or on your clothing. Wash any spills with plenty of water, and call your teacher.

CAUTION: Sodium hydroxide solution (especially the 6M concentration used here) is very caustic. Do not get any on your skin or in your eyes. Wash any spills immediately with plenty of water. Call your teacher.

CAUTION: Sodium sulfite solution (Na_2SO_3) is a strong irritant to skin and eyes. Wash any spills with plenty of water.

Part II Determining the Concentration of a Solution of Fe^{2+}

1. Using the filter funnel, pour about 15 mL of $KMnO_4$ solution into your buret. Rinse and discard.
2. Fill up the buret with the $KMnO_4$, and allow some to drain in order to fill the tip. Read the volume. and record

3. Go to step number 8

HAZARD

CAUTION: Ingestion of Fe^{2+} solution can cause intestinal disorders. Always use a suction bulb on your pipet. Do not get any in your mouth. Do not swallow any.

3. Obtain about 85 mL of unknown Fe^{2+} solution from your teacher. Use a 100 mL beaker. Write down any identifying letter or number if more than one unknown is provided.
4. Using a suction bulb on your pipet, withdraw about 5 mL of the Fe^{2+} solution, and rinse inside the pipet with it. Discard. Refill the pipet to the 25 mL mark with more Fe^{2+} solution, and transfer to a 250 mL Erlenmeyer flask.
5. Add 10 mL of $3M$ H_2SO_4 to the flask, then allow the $KMnO_4$ solution to run into the flask, swirling constantly.
6. When the purple color starts to take a longer time to disperse, slow down the addition of the $KMnO_4$ until you add it a drop at a time. Record the volume in the buret when the faint purple color first stays in the flask.
7. Repeat once or twice if necessary, to obtain consistent results. Record your observations in your copy of Table 2.
8. If instead of using an unknown solution you are instructed to use a approximatkly 0.28 grams ~~particular mass~~ of an unknown solid containing Fe^{2+}, then measure the mass accurately, dissolve the solid in about 30 mL of water, add 10 mL of $3M$ H_2SO_4, and carry out the titration in the same manner as described above.

Part III Determining the Concentration of an H_2O_2 Solution

HAZARD

CAUTION: Hydrogen peroxide is corrosive. It causes burns and is an irritant to skin. Wash any spills with plenty of water.

DO NOT DO THIS SECTION

1. Obtain in a clean, dry test tube about 5 mL of hydrogen peroxide (H_2O_2) solution, labelled 3% or "10 volume". (This is the type available in drug stores as an antiseptic.)
2. Obtain a clean, dry 250 mL flask and measure its mass.
3. Using a medicine dropper, place 20 to 30 drops of hydrogen peroxide in the flask (about 1 mL to 1.5 mL) and again measure the mass.
4. Add about 30 mL of water and 10 mL of $3M$ H_2SO_4.
5. Read the volume of $KMnO_4$ in the buret (after refilling if necessary), then run the solution in as before to the first appearance of a pale purple color. Record the volume in your copy of Table 3.
6. Repeat 1 or 2 more times, as necessary, to obtain consistent results. Record all observations in Table 3.
7. Before you leave the laboratory, wash your hands thoroughly with soap and water; use a fingernail brush to clean under your nails.

In the fume hood

REAGENT DISPOSAL

Place any unused solutions of $KMnO_4$ and Fe^{2+} in the designated waste containers. Solutions left in the flask after the titrations may safely be rinsed down the sink with copious amounts of water.

POST LAB DISCUSSION (read this!)

In order to calculate the results for this experiment, you first need to work out the balanced overall redox equation for each reaction. Then you will use the mole relationships in each equation to relate the quantities that are reacting.

The following are the half-reactions occurring in this experiment:

Reduction of MnO_4^-:

In acid:	$MnO_4^- + 8H^+ + 5e^-$	$\rightarrow Mn^{2+} + 4H_2O$
In neutral solution:	$MnO_4^- + 4H^+ + 3e^-$	$\rightarrow MnO_2 + 2H_2O$
In base:	$MnO_4^- + e^-$	$\rightarrow MnO_4^{2-}$
Oxidation of SO_3^{2-}:	$SO_3^{2-} + H_2O$	$\rightarrow SO_4^{2-} + 2H^+ + 2e^-$
Oxidation of Fe^{2+}:	Fe^{2+}	$\rightarrow Fe^{3+} + e^-$
Oxidation of H_2O_2:	H_2O_2	$\rightarrow O_2 + 2H^+ + 2e^-$

Remember that the titrations in Parts II and III were done in acidic solution. !

DATA AND OBSERVATIONS: (use ruler + pen!)

It would be a good idea to have these tables ready in your notebook before coming to the laboratory.

Part I Preliminary Investigation of $KMnO_4$ as an Oxidizing Agent

Table 1 Preliminary Investigation of $KMnO_4$ as an Oxidizing Agent

TYPE OF SOLUTION	COLOR	ION OR MOLECULE PRESENT
Acidic (3*M* H_2SO_4)	COMPLETE IN YOUR NOTEBOOK	COMPLETE IN YOUR NOTEBOOK
Neutral (water)		
Basic (6*M* NaOH)		

Part II Determining the Concentration of a Solution of Fe^{2+}

Table 2 i Volume of $KMnO_4$ to React with the Fe^{2+} Solution

$[KMnO_4]$ = ? *M*	TRIAL 1	TRIAL 2	TRIAL 3 (if necessary)
Initial volume of $KMnO_4$ (mL)	COMPLETE IN YOUR NOTEBOOK		COMPLETE IN YOUR NOTEBOOK
Final volume of $KMnO_4$ (mL)			
Volume of $KMnO_4$ required (mL)			
Average Volume			

Table 2 ii Mass of Fe^{2+} compound

	Trial 1	Trial 2	Trial 3
Mass Fe^{2+} used			
Average mass			

Part III Determining the Concentration of an H_2O_2 Solution

Table 3 Volume of $KMnO_4$ to React with H_2O_2 Solution

$[KMnO_4]$ = M	TRIAL 1	TRIAL 2	TRIAL 3 (If necessary)
Mass of empty flask (g)			
Mass of flask + H_2O_2 (g)			
Mass of H_2O_2 (g)			
Initial volume of $KMnO_4$ (mL)			
Final volume of $KMnO_4$ (mL)			
Volume of $KMnO_4$ used (mL)			

COMPLETE IN YOUR NOTEBOOK

ANALYSIS: (Show all previous calculations before answering these)

(QUESTIONS AND CALCULATIONS)

Part I Preliminary Investigation of $KMnO_4$ as an Oxidizing Agent

1. Write the overall redox equation for MnO_4^- reacting with SO_3^{2-} to give Mn^{2+} and SO_4^{2-} in acidic solution.
2. Write the overall redox equation for MnO_4^- reacting with SO_3^{2-} to give MnO_2 and SO_4^{2-}. (This occurred in neutral solution, but H^+ ions will appear in the final equation.
3. Write the overall redox equation for MnO_4^- reacting with SO_3^{2-} to give MnO_4^{2-} and SO_4^{2-} (in basic solution).
4. Explain why titrations using permanganate are performed in acid solution.

Part II Determining the Concentration of a Solution of Fe^{2+}

1. Write the balanced overall redox equation for MnO_4^- reacting with Fe^{2+} in acid solution to give Mn^{2+} and Fe^{3+}.
2. From the average volume of MnO_4^- used and the molarity of the solution provided by your teacher, calculate the number of moles of MnO_4^-.
3. Using the mole relationship given by the balanced equation, calculate the number of moles of Fe^{2+} used.
4. ~~Calculate the $[Fe^{2+}]$ from the number of moles and the volume of the solution (in liters). (If you used a solid sample~~, calculate the molar mass or percent of Fe instead, as directed by your teacher.)

molar mass determination:
= average mass used ÷ moles used

Part III Determining the Concentration of an H_2O_2 Solution

1. Write the balanced overall redox equation for MnO_4^- reacting with H_2O_2 in acid solution to give Mn^{2+} and O_2.
2. For the first titration, calculate the number of moles of MnO_4^- from the volume and the molarity.
3. Using the mole relationship given by the balanced equation, calculate the number of moles of H_2O_2 oxidized, and convert to grams using the molar mass of H_2O_2.
4. Using the calculated mass of H_2O_2 above and the mass of the solution from Table 3, calculate the percent of H_2O_2 in the solution.
5. Repeat questions 2 to 4 for each of the other titrations performed, and average your answers for the percent of H_2O_2 in the solution.

DISCUSSION: (in full sentences!)

FOLLOW-UP QUESTIONS

1. A bottle containing a standard solution of $KMnO_4$ is found to have brown stains on the inside. Why will this $KMnO_4$ be of no further use for quantitative experiments?
2. Hydrogen peroxide is usually labelled 3%, meaning 3 g/100 mL. Assuming that the solution has a density of 1 g/mL, what is the percent deviation between your calculated concentration and the stated 3% figure?
3. Hydrogen peroxide breaks down easily to give water and oxygen as follows:

$$2H_2O_2(aq) \rightarrow 2H_2O(l) + O_2(g)$$

Bottles of hydrogen peroxide are sometimes labelled as 10 volume as well as 3%. This means the volume of oxygen that can be liberated is 10 times the volume of the solution. Remembering that 1 mol of gas occupies 22.4 L at STP, calculate the volume of oxygen at STP that could be produced from 1 L of a 3% solution. Is 10 L a good approximation to your answer?

4. Many different materials can catalyze the breakdown of H_2O_2. (If your dropper is not clean, you may find bubbles of oxygen forming in the dropper!) However, high temperature alone can cause sufficient pressure to build up because of released oxygen to explode a glass container. For this reason, hydrogen peroxide is usually purchased in plastic bottles which often have a venting cap to allow gas to escape. Under what conditions should hydrogen peroxide be stored?

Sources of error: (don't forget this!)

CONCLUSION:

- QUANTITATIVE RESULT FIRST
- OTHER OBJECTIVES SECOND
- CONNECTION TO EVERYDAY LIFE (unique)