



035 exercise

Titration of Hydrogen Peroxide Solutions

SUSB-035

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purpose

We will use a volumetric titration method to determine the concentration of a solution of hydrogen peroxide that you provide.

concepts

titration • end point • oxidizing agents • reducing agents • oxidation-reduction reactions • standardization • primary standard • relative reactivity • ideal gas law (pre-lab)

[Background Information]

Peroxy compounds, i.e., those including oxygen-oxygen bonds in covalent molecules, or O_2^{2-} ions in ionic substances, are well known and used for a variety of purposes. The simplest covalent compound containing the oxygen-oxygen bond (other than O_2) is hydrogen peroxide, H_2O_2 , which in dilute aqueous solution (typically 3%) finds use as a common topical antiseptic and disinfectant. Hydrogen peroxide in more concentrated solutions is used to bleach hair. In very concentrated solution (90%), hydrogen peroxide has been used as an oxidizer for rocket propulsion. More complex peroxy compounds, such as benzoyl peroxide, are used in pharmaceutical preparations to treat certain skin conditions as well as in the plastics industry to make polymers. Peroxy compounds are also an unwanted product that slowly forms when certain other oxygen containing compounds, such as ethers, are oxidized under the action of atmospheric oxygen.

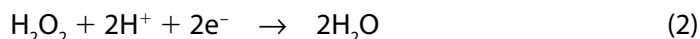
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The chemical property that best accounts for the widespread use of peroxy compounds is that, like the parent oxygen molecule from which they derive, they are all **oxidizing agents**—i.e., they are able, under a wide range of conditions, to accept electrons from other substances. The loss of one or more electrons by a molecule or ion to another molecule or ion is generally called an oxidation reaction. When an oxidizing agent oxidizes another substance, it is itself reduced.

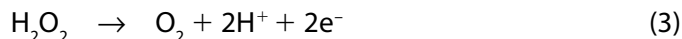
A simple way to think of the **reduction** of H_2O_2 by the acceptance of electrons is through the half reaction:



If, instead, we wish to consider this half reaction in an acidic environment, we can add 2H^+ to both sides of the above reaction, observe that $\text{H}^+ + \text{OH}^- \rightarrow \text{H}_2\text{O}$ and rewrite it as



In the presence of a stronger oxidizing agent, H_2O_2 can itself be oxidized. Imagining H_2O_2 as containing the O_2^{2-} ion, one should not be surprised that the oxidation (loss of electrons) could result in O_2 , molecular oxygen. The half reaction for the **oxidation** of H_2O_2 in acidic aqueous solution is:



Indeed, with traces of a catalyst, H_2O_2 can undergo simultaneous oxidation and reduction (a process sometimes called auto-oxidation) through the balanced (overall, not half) reaction:



Almost certainly, the commercial hydrogen peroxide solution that you are asked to use in this exercise has a trace of “stabilizer” (acetanilide or phosphoric acid are often the substances) added to it to extend its shelf life and prevent the decomposition of the product. Concentrated solutions of hydrogen peroxide are dangerous to handle for the very reason that the auto-oxidation can produce large amounts of free oxygen which can cause materials that do not burn in the normal atmosphere to ignite spontaneously. Hydrogen peroxide plays an increasingly important role in industrial processes that require oxidizing agents. Since the product of its reaction with many materials is water, it is an environmentally preferred agent.

The analytical procedure we use in this exercise uses the fact that in acidic aqueous solutions, potassium permanganate, KMnO_4 , is a stronger oxidizing agent than H_2O_2 and reacts quantitatively with it according to the reaction:



Dilute solutions of potassium permanganate are sometimes used as topical disinfectants, particularly for fungal diseases of the skin. Note that in this process, molecular oxygen is liberated and a considerable amount of hydrogen ion is consumed. Potassium permanganate is intensely purple, even in dilute aqueous solution. Manganous ion Mn^{+2} , is almost colorless at the same concentrations. It is therefore expected that if we add permanganate to a solution of hydrogen peroxide, the violet color will disappear as long as there is any H_2O_2 to react with the permanganate. Once the H_2O_2 is consumed, the purple color of any additional permanganate is expected to persist. This feature makes it **unnecessary to use an indicator** to signal the end point of the reaction—the permanganate ion is the indicator. The solution will turn from clear to purple when the first drop of excess KMnO_4 is added to the titration container.

The stoichiometry of reaction (5) shows that 2 moles of MnO_4^- will react with 5 moles of H_2O_2 . If we know the concentration of the KMnO_4 solution, we can calculate the number of moles of H_2O_2 that were present in the titration container. How shall we determine the concentration of the KMnO_4 ? While in many exercises in this course you are provided with the precise concentrations of the titrants, in this case that is not practical. Stock solutions of KMnO_4 in water decompose slowly, but significantly. It therefore becomes essential for you to establish the concentration of the KMnO_4 as near as possible to the time that you use it. This is done through a process called **standardization**.

Standardization of a solution of a reagent is accomplished through the reaction of the reagent with a substance whose composition is known with high precision, which is stable against typical laboratory storage conditions and which reacts in a clean and consistent way with the reagent in question—a **primary standard**. For potassium permanganate, the primary standard of choice is sodium oxalate, $\text{Na}_2\text{C}_2\text{O}_4$. Sodium oxalate is the sodium salt of oxalic acid. Oxalic acid is a moderately strong diprotic organic acid. It and its salts are naturally occurring constituents of many vegetables, notably spinach and rhubarb. Both the acid and its salts are moderately toxic.

The reaction between permanganate ion and oxalate ion in acidic aqueous solution is described by the following equation:



Note once again that the products of the reaction are colorless so that the end point in the standardization will also be the appearance of the purple color due to the first drop of excess potassium permanganate added to the oxalate solution. As with hydrogen peroxide, the stoichiometry shows that 2 moles of permanganate react with 5 moles of oxalate. This time, CO_2 is liberated and 8 moles of hydrogen ion are consumed for every mole of permanganate ion. This reaction is initially slow, so we heat the solution to speed up the reaction.

The exercise will be in two parts—titration of hydrogen peroxide with potassium permanganate and standardization of the potassium permanganate with sodium oxalate. The titration involves volumetric manipulations to prepare the hydrogen peroxide solutions. The standardization requires weighing. You should note that it does not matter in which order these two parts are done.

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As a secondary objective in this exercise, we hope to collect and post data for each subsection showing the following:

NAME OF ANALYST	MANUFACTURER	EXPIRATION DATE	NOMINAL CONCENTRATION (%)	ACTUAL CONCENTRATION (%)	AVERAGE DEVIATION (%)

You should comment on any systematic variations you observe in these data.

CAUTION

Sulfuric acid is corrosive. Hydrogen peroxide is a bleach and can discolor fabrics. Potassium permanganate is toxic and can cause discoloration of skin or fabrics. Sodium oxalate is toxic.

procedure

You are required to work individually.

Preliminary Activities

- Remember that the burets are only as clean as they were left by the last user. Clean the buret thoroughly. If the stopcock shows brown stains, consult your TA about cleaning the stopcock before proceeding.
- Obtain the reagents in the amount you will need, namely:

~0.025 M KMnO_4 Solution	Take only ~200 mL —Use a clean, dry beaker
4 M H_2SO_4	Take only ~70mL —Use a clean beaker
$\text{Na}_2\text{C}_2\text{O}_4$	Will be dispensed to you individually in vials

- Rinse the buret with about 5 mL of the KMnO_4 stock solution. Be sure to rinse the tip as well. Drain the buret. If the buret drains properly, fill it with the KMnO_4 stock solution.
- Before proceeding with either the standardization or the titration of the hydrogen peroxide, you should do the following to establish the appearance of the end point of the reaction.
- Place 10 mL of 4 M sulfuric acid in an Erlenmeyer flask and add about 50 mL of water. Deliver one drop of the stock solution of KMnO_4 to the solution and swirl to insure complete mixing. Note the color of the solution. This should be the color at the end point.

Standardization

(Keep in mind that this step can be done after the titration of the H_2O_2)

- How much sodium oxalate will be required?** The concentration of the KMnO_4 is *nominally* 0.025 M. Remember that in order to make use of the full precision of the buret, we wish to use between 20 and 30 mL of potassium permanganate in each titration. In the pre-lab exercise, you calculated the amount of sodium oxalate required to react with 25 mL of 0.025 M KMnO_4 . If the number you calculated is not close to 160 mg, consult your teaching assistant.
- Weigh a sample of sodium oxalate of the appropriate weight into a clean (but not necessarily dry) 250 mL Erlenmeyer flask. The weighing should be done using the analytical balance and should be done **by difference**. I.e., weigh the vial + the sodium oxalate and record the initial weight in your notebook. Transfer an amount of sodium oxalate directly into the flask. Weigh the vial + sodium oxalate again. If the difference in weight is not the amount desired, repeat the process. When the final weight of the vial + sodium oxalate is less than the initial weight by approximately the desired weight, record the final weight. *[The advantage of this weighing method is that the sample is never in contact with an intermediate container (such as a watch glass or weighing paper) and, therefore, the chances of losing some solid in the transfer process are minimal. This technique also avoids spills on the balance pan since the transfer is done outside the balance case.]*
- Add 50–60 mL of water and 10 mL of 4 M H_2SO_4 to the flask. Swirl until the sodium oxalate dissolves completely, heat the sample on a hotplate to a temperature of 80°C without permitting boiling (sodium oxalate decomposes in boiling water). If you use a thermometer to measure the temperature, be sure to rinse the thermometer into the flask with a small amount of water from your wash bottle.
- Remove the solution from the heat, carefully, and move it quickly to the buret stand.
- Titrate the **hot** solution with the potassium permanganate solution. Since the solution is deeply colored, you will not be able to read the meniscus. In such cases, the buret is read (consistently) at the top of the liquid level. Record the initial buret reading (**not 0.00**). Add the KMnO_4 dropwise initially and be sure to swirl the solution. When the purple color of the drops fades quickly, you can add the KMnO_4 more rapidly until you approach the end point. Be sure to swirl the solution to insure that the reactants are always well mixed. If a brown color develops where the KMnO_4 is added, you are probably adding the KMnO_4 too rapidly. When the purple color of the permanganate begins to persist for a few seconds after its addition, add the KMnO_4 solution dropwise and slowly. The end point will be signaled by the light pink color of the permanganate that persists for 15 seconds. Be sure to record the final volume in your notebook (and later, on the data sheet as well) with the appropriate precision.
- Compute the concentration of the potassium permanganate solution (to the appropriate number of significant figures) and record this value in your notebook.

SAMPLE CALCULATION

$$\text{Weight of Na}_2\text{C}_2\text{O}_4 = 0.1974 \text{ g} (= 197.4 \text{ mg})$$

$$\text{Volume of KMnO}_4 = 31.34 \text{ mL}$$

$$\text{Mmoles of Na}_2\text{C}_2\text{O}_4 (\text{weight (mg)}/134.00) [= 197.4/134.0] = 1.473 \text{ mmoles}$$

$$\text{Mmoles of KMnO}_4 (2/5 \times \text{mmoles Na}_2\text{C}_2\text{O}_4) [= 2 \times 1.473/5] = 0.5892 \text{ mmoles}$$

$$\text{Molarity of KMnO}_4 (\text{mmol KMnO}_4/\text{mL KMnO}_4) [= 0.5892/31.34] = 0.01880 \text{ M}$$

Repeat the standardization titration (steps 7 – 11).

Analysis of H₂O₂ solutions

12. Rinse a 25 mL pipet twice with about 5 mL of your hydrogen peroxide solution.
13. Transfer 25.00 mL of the solution into a clean 250.0 mL volumetric flask using a 25 mL transfer pipet. Add water up to the lower neck of the volumetric flask. Cap the flask and mix the solution thoroughly. When the solution is mixed, dilute with additional water to the mark on the volumetric flask (use a dropper if necessary). Mix again.

This represents a ten-fold dilution (10.00 ×). 25.00 mL of the dilute solution contains only 2.500 mL of the original solution of hydrogen peroxide.

14. Transfer 25.00 mL of the **diluted** hydrogen peroxide solution into a clean, but not necessarily dry, 125 mL Erlenmeyer flask. Add 10 mL of 4 M H₂SO₄ using a 10 mL graduated cylinder.
15. Titrate the solution with potassium permanganate. In this case, **no heating of the solution is required.**

Repeat above procedure (steps 14–15) twice more. Note that each titration is performed on the same volume of hydrogen peroxide solution. Therefore, if the concentration of the hydrogen peroxide solution is uniform and the pipet has been used properly, the volume of potassium permanganate required should be the same in each titration.

Determination of the concentration of the hydrogen peroxide solution

16. Once you have completed both the standardization of potassium permanganate and titration of hydrogen peroxide solutions, compute the concentration of the hydrogen peroxide. The concentrations of hydrogen peroxide solutions are normally given a percent by weight. We assume that the densities of these dilute solutions of hydrogen peroxide are the same as that of pure water (1.000 g / mL).

SAMPLE CALCULATION OF CONCENTRATION OF HYDROGEN PEROXIDE

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Concentration of KMnO_4 (from standardization) = 0.01893 (**use your own value**)

	Sample 1	Sample 2	Sample 3
Volume of H_2O_2 solution titrated	25.00 mL	25.00 mL	25.00 mL
Volume of original H_2O_2 solution titrated	2.500 mL	2.500 mL	2.500 mL
Volume of KMnO_4 used	26.58 mL	26.15 mL	26.97 mL
<i>[Avg vol of KMnO_4]</i>		26.57 mL	
<i>Deviations</i>	0.01 mL	0.42 mL	0.40 mL
<i>Average deviation</i>		0.28 mL	
<i>Percent deviation</i>		1.0 %	
Mmoles of KMnO_4 used (vol. \times molarity (0.01893))	0.5032 mmol	0.4950 mmol	0.5105 mmol
Mmoles of H_2O_2 ($5/2 \times$ mmoles of KMnO_4)	1.258 mmol	1.238 mmol	1.276 mmol
Weight of H_2O_2 (mmoles \times 34.02 mg/mmmole)	42.80 mg	42.12 mg	43.41 mg
Volume of original H_2O_2 solution	2.500 mL	2.500 mL	2.500 mL
Weight of original H_2O_2 solution	2.500 g	2.500 g	2.500 g
Percent H_2O_2 (weight H_2O_2 /weight solution)	1.712 %	1.685 %	1.736 %
Average weight percent of H_2O_2		1.711 %	
Deviation from average	0.001	0.026	0.025
Average deviation		0.017	
Percent deviation		1.0 %	

The percent deviation of the result is the same as the percent deviation of the volumes of KMnO_4 used because the same volume of H_2O_2 was used in each run.

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[Data Sheet 1]

Notebook Grade: _____

Safety Grade: _____

Name _____

Date _____

Course/Section _____

1. Standardization of KMnO_4

	Run 1	Run 2
Initial weight of vial + $\text{Na}_2\text{C}_2\text{O}_4$	_____ g	_____ g
Weight of vial after transfer	_____ g	_____ g
Weight of $\text{Na}_2\text{C}_2\text{O}_4$	_____ g	_____ g
Weight of $\text{Na}_2\text{C}_2\text{O}_4$	_____ mg	_____ mg
Mmoles of $\text{Na}_2\text{C}_2\text{O}_4$ (weight (mg)/134.00)	_____ mmol	_____ mmol
Final buret reading, KMnO_4	_____ mL	_____ mL
Initial buret reading, KMnO_4	_____ mL	_____ mL
Volume KMnO_4 delivered	_____ mL	_____ mL
Mmoles of KMnO_4 ($2/5 \times$ mmoles $\text{Na}_2\text{C}_2\text{O}_4$)	_____ mmol	_____ mmol
Molarity of KMnO_4 (mmol KMnO_4 /mL KMnO_4)	_____ M	_____ M
Average Molarity of KMnO_4	_____ M	_____ M
Deviation of Molarity from average	_____ M	_____ M
Average deviation of Molarity of KMnO_4	_____ M	
Percent Deviation of Molarity of KMnO_4	_____ %	
Average Molarity of KMnO_4	_____ M	
Deviation of Molarity from average	_____ M	_____ M
Average deviation of Molarity of KMnO_4	_____ M	
Percent Deviation of Molarity of KMnO_4	_____ %	

[Data Sheet 2]

2. Titration of H₂O₂

	_____ M		
	Run 1	Run 2	Run 3
Volume of commercial solution diluted (mL)	25.00	25.00	25.00
Volume of H ₂ O ₂ after dilution (mL)	250.0	250.0	250.0
Volume of diluted H ₂ O ₂ titrated (mL)	25.00	25.00	25.00
Final buret reading, KMnO ₄ (mL)	_____	_____	_____
Initial buret reading, KMnO ₄ (mL)	_____	_____	_____
Volume KMnO ₄ delivered (mL)	_____	_____	_____
Mmoles of KMnO ₄ (vol. × molarity, from above) (mmol)	_____	_____	_____
Mmoles of H ₂ O ₂ (5/2 x mmol KMnO ₄) (mmol)	_____	_____	_____
Weight of H ₂ O ₂ (mmoles H ₂ O ₂ × 34.02 mg/ mmole) (mg)	_____	_____	_____
Weight of H ₂ O ₂ (grams)	_____	_____	_____
Weight of commercial solution titrated (Vol. of original solution × 1.000 g/mL) (g)	_____	_____	_____
Percent H ₂ O ₂ by weight (%)	_____	_____	_____
Average percent H ₂ O ₂ by weight (%)		_____	
Deviation of percent H ₂ O ₂ from average(%)	_____	_____	_____
Average deviation of percent H ₂ O ₂ by weight (%)		_____	
Percent deviation of percent H ₂ O ₂ by weight (%)		_____	

Characterization of the commercial H₂O₂ titrated:

Brand: _____

Nominal Percentage: _____

Expiration Date: _____

[Pre-laboratory Questions]

Name

Date

Course/Section

1. The concentration of the potassium permanganate (KMnO_4) solution provided in this exercise is approximately 0.025 M.
 - a. What is the molar mass of potassium permanganate?

 - b. What is the molar mass of sodium oxalate?

 - c. What weight of sodium oxalate ($\text{Na}_2\text{C}_2\text{O}_4$) is required to consume 25 mL of this potassium permanganate solution?

2. If 0.2640 g of sodium oxalate requires 30.74 mL of potassium permanganate solution in a titration, what is the concentration of the potassium permanganate?

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3. A student dilutes 10.00 mL of commercial hydrogen peroxide (H_2O_2) to 100.0 mL with water. Titration of 25.00 mL of the diluted solution requires 34.58 mL of the potassium permanganate solution from Question 2.
- How many mmols of KMnO_4 were consumed in the titration.
 - How many mmols of H_2O_2 were in the titrated sample?
 - What was the weight of the H_2O_2 in the titrated sample?
 - What was the weight of commercial H_2O_2 in the titrated sample (density = 1.000 g / mL)?
 - What was the percentage by weight of H_2O_2 in the original commercial hydrogen peroxide?
4. Commercial 3% H_2O_2 is sometimes called "10 volume strength." Calculate what volume of oxygen at 25°C and 1 atm is liberated by 1 mL of 3% H_2O_2 when it decomposes. Assume the density of 3% H_2O_2 is 1 g/mL.