The Decomposition of Hydrogen Peroxide

- To learn about Avogadro’s Hypothesis and the Ideal Gas Law.
- To learn about gas phase Stoichiometry.
- To learn about the chemistry of Peroxides.

In this laboratory exercise we will determine the percentage Hydrogen Peroxide present in a commercially available solution by measuring the volume of Oxygen gas liberated when the peroxide decomposes. Because the decomposition of dilute solutions of Hydrogen Peroxide is relatively slow, a Ferric Chloride catalyst will be used to increase the reaction rate so that the reaction goes to completion during the laboratory period.

In its pure form, Hydrogen Peroxide (H₂O₂) is a faintly bluish, syrupy liquid which boils at 150.2°C. It was first synthesized by the French chemist Louis Jaques Thenard in 1818 by acidification of Barium Peroxide (BaO₂) with Nitric Acid (HNO₃). This process was supplanted by an improved version in which the Barium Peroxide is initially treated with Hydrochloric Acid (HCl), followed by addition of Sulfuric Acid (H₂SO₄) to precipitate the Barium Ion (Ba²⁺) as Barium Sulfate (BaSO₄). This leaves a relatively pure aqueous solution of Hydrogen Peroxide:

\[
\text{BaO}_2(\text{s}) + 2 \text{HCl}(\text{aq}) \rightarrow \text{H}_2\text{O}_2(\text{aq}) + \text{BaCl}_2(\text{aq}) \quad \text{(Eq. 1)}
\]

\[
\text{BaCl}_2(\text{aq}) + \text{H}_2\text{SO}_4(\text{aq}) \rightarrow \text{BaSO}_4(\text{s}) + 2 \text{HCl}(\text{aq}) \quad \text{(Eq. 2)}
\]

When exposed to sunlight or metallic impurities, Hydrogen Peroxide rapidly decomposes to Oxygen gas:

\[
2 \text{H}_2\text{O}_2(\text{aq}) \rightarrow 2 \text{H}_2\text{O}(\text{l}) + \text{O}_2(\text{g}) \quad \text{(Eq. 3)}
\]

This is a key reaction of Hydrogen Peroxide.

Hydrogen Peroxide solutions (3-30%) are used for bleaching (pulp, paper, straw, leather, hair, etc.) and to treat wounds. Its value as an antiseptic is low, but the evolution of Oxygen when it comes into contact with clotted blood helps to loosen dirt and assists in cleansing a wound.

At higher concentrations (70-98%), the decomposition of the peroxide is accompanied by the evolution of enough heat to convert the Water to Steam. In this fashion, Hydrogen Peroxide is used as a monopropellant in rocket engines; the peroxide is passed over a Silver mesh which catalyzes the decomposition and the resulting gaseous H₂O and O₂ products are ejected through a nozzle at high velocity propelling the rocket forward. Concentrated Hydrogen Peroxide can also
be used as an oxidant with organic compounds, such as kerosene, in a bipropellant rocket engine. The German V2 Rocket of WWII used this design.

We will leverage the decomposition reaction (Eq. 3) to determine the concentration of Hydrogen Peroxide in products typically sold in the supermarket. The reaction stoichiometry allows us to use the measured amount of Oxygen (#moles $O_2$) produced to determine the amount of peroxide (#moles $H_2O_2$) initially present in the solution:

$$\text{# moles } H_2O_2 = \left( \frac{2 \text{ moles } H_2O_2}{1 \text{ mole } O_2} \right) \times \text{# moles } O_2 \quad \text{(Eq. 4)}$$

The number of moles Oxygen produced (n) by this reaction can be determined by simply measuring the volume of Oxygen gas (V) generated; the volume of a gas being related to the number of moles of its constituents by Avogadro’s Hypothesis.

In 1811, the Italian physicist Amadeo Avogadro advanced the hypothesis that equal volumes of all gases (V), measured under the same conditions of temperature (T) and pressure (P), contain the same number of molecules. As we count molecules by the mole (n), we have:

$$V \sim n \quad \text{(Eq. 5)}$$

At the time of its statement, this hypothesis made little or no impact on Avogadro’s contemporaries, in large part because his paper in the Journal de Physique contained little experimental data. Avogadro’s idea lay fallow for nearly half a century until after his death his student Stanislo Cannizzaro revived the hypothesis and showed that it resolved a number of conflicts concerning the atomic weights of the elements. Since that time, considerable evidence has accumulated to demonstrate the validity of Avogadro’s Hypothesis. Taken together with the other historical gas laws (Boyle’s, Charles’, Gay-Lusaacs’), Avogadro’s Hypothesis forms the basis of the Ideal Gas Law ($PV = nRT$). Thus, the number of moles of a gas can be determined by measuring its volume at a given temperature and pressure:

$$n = \frac{P}{RT} \times V \quad \text{(Eq. 6)}$$

As a word of caution, it must be remembered the Ideal Gas Law is a Limiting Law; it is strictly true only in the limit of zero pressure (Why?):

$$\lim_{P \rightarrow 0} PV = nRT \quad \text{(Eq. 7)}$$

At atmospheric pressures ($P \sim 760 \text{ mmHg}$), application of the Ideal Gas Law can give results which are in error by as much as 10% or more.

As an Example of the application of this procedure, consider a different decomposition reaction in which a single reaction product is gaseous:

$$2 \text{ KClO}_3(s) \rightarrow 2 \text{ KCl(s)} + 3 \text{ O}_2(g)$$
Suppose we collect 638mL of Oxygen gas at 128°C and 752mmHg. What mass of Potassium Chlorate (KClO$_3$) did we start with?

First, we convert the units of each measured quantity to those consistent with the units of the Universal Gas Constant $R = 0.08206 \, \text{L atm / K mole}$:

\[
\begin{align*}
V & = 0.638 \, \text{L} \\
T & = 401 \, \text{K} \\
P & = 0.989 \, \text{atm}
\end{align*}
\]

Second, we use the Ideal Gas Law (containing Avogadro’s Hypothesis) to determine the number of moles Oxygen produced:

\[
\begin{align*}
n & = \frac{(0.989 \, \text{atm}) (0.638 \, \text{L})}{(0.08206 \, \text{L atm / K mole}) (401 \, \text{K})} \\
& = 0.0192 \, \text{mole O}_2
\end{align*}
\]

Finally, the reaction stoichiometry is applied to determine the amount Potassium Chlorate used:

\[
\begin{align*}
\text{# moles KClO}_3 & = \left( \frac{2 \, \text{moles KClO}_3}{3 \, \text{moles O}_2} \right) \times (0.0192 \, \text{moles O}_2) \\
& = 0.0128 \, \text{mole KClO}_3
\end{align*}
\]

\[
\begin{align*}
\text{#g} & = (0.0128 \, \text{mole KClO}_3) \times (122.55 \, \text{g/mole}) \\
& = 1.57 \, \text{g}
\end{align*}
\]

Of course, in this case we could have simply weighed the amount of KClO$_3$ we started with instead of using this round-about method. However, in our case we cannot do this because the Hydrogen Peroxide is dissolved in an aqueous solution.

We must arrange our experiment such that the Oxygen gas produced is trapped so that its volume can be determined. We will do this by attaching the reaction vessel to a tank filled with Water which is itself arranged such that the Water will be pushed out as Oxygen fills the tank.
Using this arrangement, we can determine the volume Oxygen gas produced by simply measuring the volume of the displaced Water. This experimental arrangement presents us with one minor complication, however; the gas in the Collection Tank is composed of generated Oxygen and Water Vapor in equilibrium with the liquid Water. Fortunately, the presence of the Water Vapor can be accounted for using Dalton’s Law of Partial Pressures. According to Dalton’s Law:

\[ P_{\text{gas}} = \sum P_i \]  
\[ \text{(Eq. 8)} \]

where \( P_i \) represents the Partial Pressure of each gas in the mixture. For the present case, this gives us:

\[ P_{\text{gas}} = P_{O2} + P_{H2O} \]  
\[ \text{(Eq. 9)} \]

where \( P_{H2O} \) is the Vapor Pressure of the Water. Tabulated values of the Vapor Pressure of Water as a function of temperature are provided in the Appendix. This means the Partial Pressure of the Oxygen gas, \( P_{O2} \), can be determined by measuring the Pressure of the gas in the Collection Tank, \( P_{\text{gas}} \), and subtracting the Vapor Pressure of Water.

We have one last hurdle to overcome; how do we measure \( P_{\text{gas}} \)? We employ a trick! If the surface of the Displaced Water is arranged so that it is leveled with the surface of the Water in the Collection Tank, then the pressure of the gas in the Collection Tank is equivalent to the atmospheric pressure, \( P_{\text{atm}} \):

\[ P_{\text{gas}} = P_{\text{atm}} \]  
\[ \text{(Eq. 10)} \]

This is important because the atmospheric pressure can be easily measured using a relatively simple barometer. Thus, the partial pressure of Oxygen in the Collection Tank can be determined by:

\[ P_{O2} = P_{\text{atm}} - P_{H2O} \]  
\[ \text{(Eq. 11)} \]

Finally, we should consider the role of the Ferric Chloride (FeCl₃) catalyst in the decomposition reaction. In the absence of a catalyst, Hydrogen Peroxide is quite stable, decomposing only very slowly. (Otherwise you would not be able to buy it in the supermarket.) However, when any of a number of catalysts is present, the decomposition reaction proceeds very rapidly. And, many of these catalysts take advantage of the fact that this reaction is a Disproportionation; the Hydrogen Peroxide is both Oxidized and Reduced. Peroxides are unique in that the Oxygen exists in a -1 oxidation state (\( O^{-1} \)), which lies between the usual states of \( O^{0} \) and \( O^{2-} \). Thus, the Hydrogen Peroxide can disproportionate to both \( O^{0} \) and \( O^{2-} \) according to:
This, coupled with the fact that Iron can exist in two different oxidation states, Fe$^{2+}$ (Ferrous) and Fe$^{3+}$ (Ferric), allows the catalyst to break the reaction into two different redox steps, each of which has a lower energy barrier to completion than the uncatalyzed reaction:

\[
\begin{align*}
2 \text{H}_2\text{O}_2(\text{aq}) + 2 \text{Fe}^{3+}(\text{aq}) & \rightarrow \text{O}_2(\text{g}) + 2 \text{Fe}^{2+}(\text{aq}) + 2 \text{H}^+(\text{aq}) \quad (\text{Eq. 12}) \\
\text{H}_2\text{O}_2(\text{aq}) + 2 \text{Fe}^{2+}(\text{aq}) + 2 \text{H}^+(\text{aq}) & \rightarrow 2 \text{H}_2(\text{l}) + 2 \text{Fe}^{3+}(\text{aq}) \quad (\text{Eq. 13})
\end{align*}
\]

Note the first step in the catalyzed reaction involves reduction of the Ferric Ion (Fe$^{3+}$) to the Ferrous Ion (Fe$^{2+}$), which is then re-oxidized to Ferric Ion in the second step. Hence, on net, the catalyst is not consumed during the course of the decomposition.

Transition Metals like Iron (Fe) are not the only possible catalysts for this reaction. Because Hydrogen Peroxide is harmful biologically, a number of enzymes, large protein molecules that catalyze biologically important reactions, also catalyze this reaction. Catalase, present in the blood and liver of mammals, is an example of such an enzyme. The active site of Catalase, the point at which the reaction takes place, contains an Fe$^{3+}$ ion attached to a Heme group embedded in the protein. Catalase most likely catalyzes the decomposition of Hydrogen Peroxide via a mechanism that is very similar to that used by Ferric Chloride. (Take Home Expt Idea: The next time you have liver for dinner, try grinding up a bit of the raw liver and add it to a solution of Hydrogen Peroxide. You should see an immediate fizzing due to the production of Oxygen gas. The liver must be ground in order to break apart the cells and release the Catalase.)

In summary, we will measure the volume of Oxygen gas produced, at a given temperature and pressure, as a result of the Ferric Chloride catalyzed decomposition of Hydrogen Peroxide in a commercial solution. The measured volume will allow us to determine the number of moles Oxygen produced. The reaction stoichiometry will then be used to determine the number of moles Hydrogen Peroxide in the starting solution. This information can then be used to determine the percentage Hydrogen Peroxide in the solution.
Procedure

1. Assemble the Reaction Apparatus as diagramed above. Use a 500 mL Erlenmeyer flask for the Reaction Vessel. Use an 800mL Beaker to collect the Displaced Water.

2. Clean and dry the Beaker used to collect the Displaced Water.

3. Measure out 30.0mL of commercial Hydrogen Peroxide solution in a graduated cylinder and pour it into the Reaction Vessel. (Record the exact volume used, the Brand and the reported percentage Hydrogen Peroxide.)

4. Measure ~6mL of the catalyst (FeCl$_3$) into a small test tube. Make sure none of it contaminates the outside of the test tube. Slide the test tube into the flask so that it does not spill into the H$_2$O$_2$ solution.

5. **Your instructor will demonstrate the following step!** Fill the Oxygen Collection Tank until its almost full of Water. With the pinch clamp on the delivery tube open, and the Reaction Vessel unstoppered, establish a siphon from the Collection Tank to the Displaced Water beaker. (A simple Pipette Bulb can be used to “push” the Water through the system from the Reaction Vessel side of the Collection Tank.) Be sure and remove all air bubbles in the delivery tube. Collect ~200 mL of Water in the Beaker, enough to completely cover the delivery tube. Now, close the pinch clamp.

6. Connect the Oxygen delivery tube to the Reaction Vessel and make sure the Vessel is stoppered tightly.

7. Open the pinch clamp and level the Water in the Collection Tank with the Water in the Displaced Water beaker. (Recall, this is done to ensure the gas’s pressure $P_{\text{gas}}$ in the closed system is the same as the atmospheric pressure $P_{\text{atm}}$.) Close the pinch clamp when this is the case.

8. Carefully lower the Beaker and remove the delivery tube from the beaker so as to not lose the siphon. (If you do lose the siphon, you will have to start the leveling procedure all over again.) Pour out all the Water in the Displaced Water beaker, dry the beaker and replace it. Again, this must be done such that your siphon is not lost. Open the pinch clamp. If done correctly, a little Water will dribble into the Displaced Water beaker as the siphon tries to re-establish itself. However, the Water flow should cease almost immediately. If it does not, you have a leak in the system. If this is the case, check to make sure all the connections are tight and re-level the system. (**Why do we not need to subtract this bit of Water from the volume of Water collected after the evolution of the Oxygen gas is complete?**)
9. Tip the Reaction Vessel so that the catalyst flows into the Hydrogen Peroxide solution. Swirl the mixture. You should observe the production of a gas after a few moments. About half-way through the reaction (~7 minutes) swirl the system again to make sure the reaction goes to completion.

10. When the reaction is complete (~15 minutes), the level of the Water in the Collection Tank will remain unchanged. At this point, again level the water in the two containers. Close the pinch clamp.

11. Record the temperature of the Water in the Displaced Water beaker. This will be assumed to be approximately the temperature of the gas in the Collection Jar.

12. Measure the volume of Water displaced using a large graduated cylinder.

13. Record the barometric pressure. Your laboratory instructor will show you how to correctly read the barometer.
**Data Analysis**

1. Determine the Partial Pressure of the Oxygen gas collected, $P_{O_2}$.

2. Determine the number of moles Oxygen gas collected.

3. Determine the number of moles Hydrogen Peroxide present in the initial solution. Convert this to the mass of Hydrogen Peroxide.

4. Calculate the mass of the initial Solution. The density of a dilute Hydrogen Peroxide solution near Room Temperature is 1.03 g/mL.

5. Determine the percentage Hydrogen Peroxide in the commercial solution.

6. What is the percentage difference between your determination and that reported by the manufacturer?

7. Comment on which measurement or procedure has the largest error. How might you improve this measurement?
Post Lab Questions

1. Hydrazine (NH$_2$NH$_2$) is considered the Group 5A cousin of Hydrogen Peroxide and is also used as a rocket fuel, particularly as a fuel in ICBM’s. Draw the Lewis Structures of Hydrazine and Hydrogen Peroxide.

2. The decomposition of KClO$_3$ is another example of a disproportionation:

   \[ 2 \text{KClO}_3(s) \rightarrow 2 \text{KCl}(s) + 3 \text{O}_2(g) \]

   Determine the oxidation states for the Chlorine and Oxygen in each of the above species and identify the Oxidation and Reduction half-reactions.

3. We have indicated the oxidation state of the Oxygen in H$_2$O$_2$ is O$^{-1}$, midway between the extremes of O$^0$ and O$^{-2}$. Hence, Hydrogen Peroxide can act as an Oxidizing Agent and a Reducing Agent. In practice, Hydrogen Peroxide is a powerful Oxidizing Agent and only a weak Reducing Agent. In the following reaction it is acting as an Oxidizing Agent:

   \[ \text{H}_2\text{O}_2(\text{aq}) + 2 \text{I}^- (\text{aq}) + 2 \text{H}^+ (\text{aq}) \rightarrow 2 \text{H}_2\text{O} + \text{I}_2(\text{aq}) \]

   Determine the oxidation States for the Oxygen and Iodine in each of the above species and identify the Oxidation and Reduction half-reactions.

4. Which ion acts as a “Spectator” in (Eq. 1) and (Eq. 2)

5. When collecting Oxygen gas over Water, we have to correct the gas pressure by subtracting out the vapor pressure of Water because we know some Water vaporizes into the gas phase. We also know Oxygen gas will dissolve, to some extent, in liquid Water. Why do we not have to correct our results for the solubility of Oxygen in the Water in the Collection Tank?
Appendix  - Some Physical Properties of Water

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Addendum

A Reaction of Sodium Peroxide

In this short exercise, we will treat a mixture of Sodium Peroxide (Na$_2$O$_2$) and Sulfur (S) with Water. This results in the production of aqueous Hydrogen Peroxide which then oxidizes the Sulfur.

\[
\text{Na}_2\text{O}_2(s) + 2 \text{H}_2\text{O}(l) \rightarrow 2 \text{H}_2\text{O}_2(aq) + 2 \text{NaOH}(aq) \quad \text{(Eq. A1)}
\]

\[
2 \text{H}_2\text{O}_2(aq) + \text{S}(s) \rightarrow 2 \text{H}_2\text{O}(l) + \text{SO}_2(g) \quad \text{(Eq. A2)}
\]

We can see the Hydrogen Peroxide is acting as an Oxidizing Agent in reaction (Eq. A2) by explicitly assigning appropriate oxidation numbers to the relevant species:

\[
\begin{align*}
\text{O}^{-1} + \text{e}^{-} & \rightarrow \text{O}^{2-} & \text{Reduction} \\
2 \text{H}_2\text{O}_2 & + \text{S} & 2 \text{H}_2\text{O} + \text{SO}_2 \\
\text{S}^{0} & \rightarrow \text{S}^{4+} + 4 \text{e}^{-} & \text{Oxidation}
\end{align*}
\]

Procedure

The steps in this procedure must be followed very carefully. The Sodium Peroxide can detonate prematurely if not handled with caution. If you are unsure of what to do, have your instructor help you do this experiment. Do this experiment in a Fume Hood!

1. Wearing gloves, obtain ~1.0g Sodium Peroxide (Na$_2$O$_2$) that has been previously weighed out. Sodium Peroxide is a strong Oxidizing Agent. Avoid getting on your skin or clothing. It is also Water sensitive, so do not place your sample into anything that is damp.

2. Also obtain ~0.1g of Sulfur (S) that has also been previously weighed out. In a very dry evaporating dish gently mix these solids together with your spatula to form a uniform powder.

3. Form the powder into a small pile in the middle of the evaporating dish. Make a slight depression in the top of the pile.

4. Add 1-2 drops of water to the depression and quickly step back. Observe the results.