Determination of R: The Gas-Law Constant

PURPOSE:
To gain a feeling for how well real gases obey the ideal-gas law and to determine the ideal-gas-law constant $R$.

APPARATUS AND CHEMICALS:
- KClO$_3$
- MnO$_2$
- test tube
- ring stand
- clamp
- pinch clamp
- 8-oz wide-mouth bottle
- rubber bulb
- 250-mL beaker
- rubber stoppers
- rubber tubing
- balance
- 125-mL Erlenmeyer flask
- thermometer
- barometer
- Styrofoam cups

THEORY:
Most gases obey the ideal-gas equation, $PV = nRT$, quite well under ordinary conditions, that is, room temperature and atmospheric pressure. Small deviations from this law are observed, however, because real-gas molecules are finite in size and exhibit mutual attractive forces. The van der Waals equation,

$$\left( P + \frac{n^2a}{V^2} \right)(V - nb) = nRT$$

where $a$ and $b$ are constants characteristic of a given gas, takes into account these two causes for deviation and is applicable over a much wider range of temperatures and pressures than is the ideal-gas equation. The term $nb$ in the expression $(V-nb)$ is a correction for the finite volume of the molecules; the correction to the pressure by the term $an^2/V^2$ takes into account the inter-molecular attractions.

In this experiment you will determine the numerical value of the gas-law constant $R$, in its common units of L-atm/mol-K. This will be done using both the ideal-gas law and the van der Waals equation together with measured values of pressure, P, temperature, T, volume, V, and number of moles, n, of an enclosed sample of oxygen. An error analysis will then be performed on the experimentally determined constant.

The oxygen will be prepared by the decomposition of potassium chlorate using manganese dioxide as a catalyst:

$$2\text{KClO}_3(s) \xrightarrow{\text{MnO}_2(s)} 2\text{KCl}(s) + 3\text{O}_2(g)$$
Experiment 9: Determination of R: The Gas-Law Constant

If the KClO₃ is accurately weighed before and after the oxygen has been driven off, the weight of the oxygen can be obtained by difference. The oxygen can be collected by displacing water from a bottle, and the volume of gas can be determined from the volume of water displaced. Through use of Dalton's law of partial pressures, the vapor pressure of water, and atmospheric pressure, the pressure of the gas may be obtained. Dalton's law states that the pressure of a mixture of gases in a container is equal to the sum of the pressures that each gas would exert if it were present alone:

\[ P_{\text{total}} = \sum P_i \]

Since this experiment is conducted at atmospheric pressure, \( P_{\text{total}} = P_{\text{atmospheric}} \). Hence,

\[ P_{\text{atmospheric}} = P_{O_2} + P_{H_2O \text{ vapor}} \]

**REVIEW QUESTIONS:**

Before beginning this experiment in the laboratory, you should be able to answer the following questions:

1. Under what conditions of temperature and pressure would you expect gases to obey the ideal-gas equation?

2. Calculate the value of \( R \) in L-atm/mol-K by assuming that an ideal gas occupies 22.4 L/mol at STP.

3. Why do you equalize the water levels in the bottle and the beaker?

4. Why does the vapor pressure of water contribute to the total pressure in the bottle?

5. What is the value of an error analysis?

6. Suggest reasons, on the molecular level, why real gases might deviate from the ideal-gas law.

7. Newly devised automobile batteries are sealed. When lead storage batteries discharge, they produce hydrogen. Suppose the void volume in the battery is 100 mL at 1 atm of pressure and 25°C. What would be the pressure increase if 0.05 g H₂ were produced by the discharge of the battery? Does this present a problem? Do you know why sealed lead storage batteries have not been used in the past?

8. Why is the corrective term to the volume subtracted and not added to the volume in the van der Waals equation?

9. A sample of pure gas at 20°C and 670 mm Hg occupied a volume of 562 cm³. How many moles of gas does this represent? (HINT. Use the value of \( R \) that you found in question 2)
10. A certain compound containing only carbon and hydrogen was found to have a vapor density of 2.550 g/L at 100°C and 760 mm Hg. If the empirical formula of this compound is CH, what is the molecular formula of this compound?

11. Which gas would you expect to behave more like an ideal gas Ne or HBr Why?

PROCEDURE:

1. Add a small amount of MnO₂ (about 0.02 g) and approximately 0.3 g of KCIO₃ to a test tube.

2. Assemble the apparatus illustrated in Figure 9.1 but do not attach the test tube. Be sure that tube B does not extend below the water level in the bottle. Fill glass tube A and the rubber tubing with water by loosening the pinch clamp and attaching a rubber bulb to and applying pressure through tube B. Close the clamp when the tube is filled.

3. Mix the solids in the test tube by rotating the tube, being certain that none of the mixture is lost from the tube, and attach tube B as shown in Figure 1. WHEN YOU ATTACH THE TEST TUBE, BE CERTAIN THAT NONE OF THE KCIO₃ AND MnO₂ COMES INTO CONTACT WITH THE RUBBER STOPPER, OR A SEVERE EXPLOSION MAY RESULT. MAKE CERTAIN THAT THE CLAMP HOLDING THE TEST TUBE IS SECURE SO THAT THE TEST TUBE CANNOT MOVE.

4. Fill the beaker about half full of water, insert glass tube A in it, open the pinch clamp, and lift the beaker until the levels of water in the bottle and beaker are identical; then close
Experiment 9: Determination of R: The Gas-Law Constant

Table 9.1 Vapor Pressure of Water at Various Temperatures

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>H₂O vapor pressure (mm Hg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>15</td>
<td>12.8</td>
</tr>
<tr>
<td>16</td>
<td>13.6</td>
</tr>
<tr>
<td>17</td>
<td>14.5</td>
</tr>
<tr>
<td>18</td>
<td>15.5</td>
</tr>
<tr>
<td>19</td>
<td>16.5</td>
</tr>
<tr>
<td>20</td>
<td>17.5</td>
</tr>
<tr>
<td>21</td>
<td>18.6</td>
</tr>
<tr>
<td>22</td>
<td>19.8</td>
</tr>
<tr>
<td>23</td>
<td>21.1</td>
</tr>
<tr>
<td>24</td>
<td>22.4</td>
</tr>
<tr>
<td>25</td>
<td>23.8</td>
</tr>
</tbody>
</table>

the clamp, discard the water in the beaker, and dry the beaker. The purpose of equalizing the levels is to produce atmospheric pressure inside the bottle and test tube.

5. Set the beaker with tube A in it on the desk and open the pinch clamp. A little water will flow into the beaker, but if the system is airtight and has no leaks, the flow will soon stop, and tube A will remain filled with water. If this is not the case, check the apparatus for leaks and start over again.

6. Leave the water that has flowed into the beaker in the beaker; at the end of the experiment, the water levels will be adjusted, and this water will flow back into the bottle.

7. Heat the lower part of the test tube gently (be certain that the pinch clamp is open) so that a slow but steady stream of gas is produced, as evidenced by the flow of water into the beaker. When the rate of gas evolution slows considerably, increase the rate of heating, and heat until no more oxygen is evolved.

8. Allow the apparatus to cool to room temperature; being certain that the end of the glass tube in the beaker is always below the surface of the water. Equalize the water levels in the beaker and the bottle as before and close the clamp.

9. Weigh a 125-mL Erlenmeyer flask to the nearest 0.01 g and empty the water from the beaker into the flask. Weigh the flask with the water in it.

10. Measure the temperature of the water, calculate the volume of the water displaced. This is equal to the volume of oxygen produced.

11. Remove the test tube from the apparatus and accurately weigh the tube plus the contents. The difference in weight between this and the original weight of the tube plus MnO₂ and KCIO₃ is the weight of the oxygen produced.
12. Record the barometric pressure. The vapor pressure of water at various temperatures is given in Table 9.1.

13. Calculate the gas-law constant, $R$, from your data, using the ideal-gas equation. Calculate $R$ using the van der Waals equation $(P + n^2a/V^2)(V - nb) = nRT$ (for $O_2$, $a = 1.360 \text{ L}^2\text{atm/mol}^2$, and $b = 31.83 \text{ cm}^3/\text{mol}$). Be sure to keep your units straight.

QUESTIONS:

1. Does your value of $R$ agree with the accepted value within your uncertainty limits?

2. Discuss possible sources of error in the experiment; indicate the ones that you feel are most important.

3. Which gas would you expect to deviate more from ideality, $H_2$ or $HBr$. Explain your answer?

4. How does the solubility of oxygen in water affect the value of $R$ you determined? Explain your answer?

5. Calculate the van der Waals correction terms to pressure and volume for $C_1\text{}_2$ at STP. The values of the van der Waals constants $a$ and $b$ are $6.49 \text{ L}^2\text{atm/mol}^2$ and $0.0562 \text{ L/mol}$, respectively, for $C_1\text{}_2$. At STP, which is the major cause of deviation from ideal behavior, the volume of the $C_1\text{}_2$ molecules or the attractive forces between them? Why?

6. How much potassium chlorate is needed to produce 20.0 mL of oxygen gas at 670 mm Hg and 20$^\circ$C?

7. If oxygen gas were collected over water at 20$^\circ$C and the total pressure of the wet gas were 670 mm Hg, what would be the partial pressure of the oxygen?

8. An oxide of nitrogen was found by elemental analysis to contain 30.4 % nitrogen and 69.6 % oxygen. If 23.0 g of this gas were found to occupy 5.6 L at STP, what are the empirical and molecular formulas for this oxide of nitrogen?

9. The gauge pressure in an automobile tire reads 32 pounds per square inch (psi) in the winter at 32$^\circ$F. The gauge reads the difference between the tire pressure and the atmospheric pressure (14.7 psi). In other words, the tire pressure is the gauge reading plus 14.7 psi. If the same tire were used in the summer at 110$^\circ$F and no air had leaked from the tire, what would be the tire gauge reading in the summer?
# Experiment 9: Determination of R: The Gas-Law Constant

## DATA SHEET

### Determination of R: The Gas-Law Constant

<table>
<thead>
<tr>
<th>Description</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Student’s Name</td>
<td></td>
</tr>
<tr>
<td>Date:</td>
<td></td>
</tr>
<tr>
<td>Laboratory Section/Group No</td>
<td></td>
</tr>
<tr>
<td>Assistant’s Name and Signature</td>
<td></td>
</tr>
</tbody>
</table>

1. Weight of test tube + KClO₃ + MnO₂                                      | .......... g |
2. Weight of test tube + contents after reaction                           | .......... g |
3. Weight of oxygen produced                                               | .......... g |
4. Weight of 125-mL flask + water                                          | .......... g |
5. Weight of 125-mL flask                                                  | .......... g |
6. Weight of water                                                         | .......... g |
7. Temperature of water                                                     | .......... °C |
8. Density of water                                                         | .......... g/mL |
9. Volume of water ........ mL = volume of O₂ gas ........ L                 |           |
10. Barometric pressure                                                     | .......... mm Hg |
11. Vapor pressure of water                                                 | .......... mm Hg |
12. Pressure of O₂ gas                                                      | .......... mm Hg |
14. R from the van der Waals equation                                       | .......... L-atm/mol-K |
15. Accepted value of R ..........(Source of R value) ......................... |           |