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

**OBJECTIVE:** To gain a feeling for how well real gases obey the ideal-gas law and to determine the ideal-gas-law constant, \( R \).

**Apparatus**
- balance
- Bunsen burner and hose
- test tube
- 250-mL beaker
- 8-oz wide-mouth bottle
- rubber stoppers (2)
- pinch clamp
- clamp
- barometer
- glass tubing with 60-degree bends (2) and straight pieces (2)
- 125-mL Erlenmeyer flask
- rubber tubing
- thermometer
- Styrofoam cups
- ring stand

**Chemicals**
- KClO₃
- MnO₂

Most gases obey the ideal-gas equation, \( PV = nRT \), quite well under ordinary conditions, that is, at 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 VanderWaals equation,

\[
(P + \frac{n^2a}{V^2})(V - nb) = nRT
\]

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 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 \( n^2a/V^2 \) takes into account the intermolecular attractions.

In this experiment you will determine the numerical value of the gas-law constant \( R \), in its common units of \( \text{L-atm/mol-K} \). This will be done using both the ideal-gas law and the VanderWaals equation together with measured values of pressure, \( P \), temperature, \( T \), volume, \( V \), and number of moles, \( n \), of enclosed sample of oxygen. Then you will perform an error analysis on the experimentally determined constant.

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

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

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. The pressure of the gas may be obtained through use of Dalton’s law of partial pressures, the vapor pressure of water, and the atmospheric pressure. 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:

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

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

\[
P_{\text{atmospheric}} = P_{\text{O}_2} + P_{\text{H}_2\text{O \; vapor}}
\]

**PROCEDURE:**

Add a small amount of MnO₂ (about 0.02 g) and approximately 0.3 g of KClO₃ to a test tube and accurately weigh to the nearest 0.001 g. Your instructor will demonstrate how to insert the glass tubing into the rubber stoppers. Be extremely careful to follow his or her instructions. Assemble the apparatus illustrated in Figure 14.1, but do not attach the test tube. Be sure to fill glass Tube A and the rubber tubing with water by loosening the pinch clamp and blowing air to apply pressure through Tube B. Close the clamp when the tube is filled.

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 14.1. **(CAUTION: when you attach the test tube, be certain that none of the KClO₃**
and MnO₂ comes out 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.)

![Diagram of apparatus for determination of R.]

**Table 14.1 Density of Pure Water at Various Temperatures**

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>Density (g/mL)</th>
</tr>
</thead>
<tbody>
<tr>
<td>15</td>
<td>0.999099</td>
</tr>
<tr>
<td>16</td>
<td>0.998943</td>
</tr>
<tr>
<td>17</td>
<td>0.998774</td>
</tr>
<tr>
<td>18</td>
<td>0.998595</td>
</tr>
<tr>
<td>19</td>
<td>0.998405</td>
</tr>
<tr>
<td>20</td>
<td>0.998203</td>
</tr>
<tr>
<td>21</td>
<td>0.997992</td>
</tr>
<tr>
<td>22</td>
<td>0.997770</td>
</tr>
<tr>
<td>23</td>
<td>0.997538</td>
</tr>
<tr>
<td>24</td>
<td>0.997296</td>
</tr>
<tr>
<td>25</td>
<td>0.997044</td>
</tr>
<tr>
<td>26</td>
<td>0.996783</td>
</tr>
<tr>
<td>27</td>
<td>0.996512</td>
</tr>
<tr>
<td>28</td>
<td>0.996232</td>
</tr>
</tbody>
</table>

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 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.

Set the beaker with the 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 full of water. If this is not the case, check the apparatus for leaks and start over. 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.

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 evidence by the flow of water into the beaker. When the rate of gas evolution slows considerably, increase the rate if heating, and heat until no more oxygen is evolved. Allow the apparatus to cool to room temperature; making 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. Weigh a 125-mL Erlenmeyer flask to the
nearest 0.001 g and empty the water from the beaker into the flask*. Weigh the flask* with the water in it. Measure the
temperature of the water and, using the density of water in Table 14.1, calculate the volume of the water displaced. This
is equal to the volume of oxygen produced. Remove the test tube from the apparatus and accurately weigh the tube plus
the contents. The difference in mass between this and the original mass of the tube plus MnO₂ and KClO₃ is the mass of
the oxygen produced.

Record the barometric pressure. The vapor pressure of water at various temperatures is given in Table 14.2.

**Waste Disposal Instructions** KClO₃ is a powerful oxidizing agent and must not be disposed of in a waste paper basket!
Do not attempt to clean out the residue that remains in the test tube. Return the test tube to the instructor or follow his
instructions for disposal of its contents.

**Calculations**

Calculate the gas-law constant, \( R \), from your data, using the ideal-gas equation. Calculate \( R \) using VanderWaals equation
\[
(P + n^2a/V^2)(V-nb) = nRT \quad \text{for O}_2, \quad a = 1.360 \, \text{L}^2\text{atm/mol}^2, \quad \text{and} \quad b = 31.38 \, \text{cm}^3/\text{mol}.
\]
Be sure to keep your units straight.

**Error Analysis**

Determine the maximum and the minimum value of \( R \) consistent with the experimental reliability of your data from the
ideal-gas law:
\[
\frac{PV}{nT} = \frac{(32.00 \, \text{g/mol})PV}{mT}.
\]
Assume that the reliabilities for the various measured quantities in this experiment are as follows:

\[
P = \pm 1 \, \text{mmHg} \quad \quad T = \pm 1^\circ \text{C}\n\]
\[
V = \pm 0.0001 \, \text{L} \quad \quad m = \pm 0.001 \, \text{g}
\]

To determine the maximum value of \( R \), use the maximum values for your pressure and volume and the minimum values
for mass and temperature. Similarly, calculate the minimum value of \( R \) from the minimum values of \( P \) and \( V \) and the
maximum values for mass and \( T \). Determine the average value of \( R \) and assign an uncertainty range to the average value.

**EXAMPLE 14.1** Assume that the measured quantities were as follows: \( P = 705.5 \, \text{mm Hg}; \quad T = 20^\circ \text{C}; \quad V = 242.9 \, \text{mL}; \quad \text{and} \quad m = 0.3002 \, \text{g} \). What would be the maximum and minimum values of \( R \), and the uncertainty range to be assigned to this
average value?

**SOLUTION:** First put the measured quantities into proper units as follows:

\[
P = \frac{705.5 \, \text{mm Hg}}{760 \, \text{mm Hg/ atm}} = 0.928 \, \text{atm}
\]
\[
V = 242.9 \, \text{mL} = 0.2429 \, \text{L}
\]
\[
m = 0.302 \, \text{g}
\]
\[
T = (20^\circ \text{C} + 273)K = 293K
\]

Therefore,
\[
Maximum \quad R = \frac{0.056 \, \text{mm Hg} / (760 \, \text{mm Hg/ atm}) \cdot (0.2430 \, \text{L})(32.00 \, \text{g/mol})}{(0.301 \, \text{g})(292K)} = 0.0823 \, \text{L-atm/mol-K}
\]
\[
Minimum \quad R = \frac{0.054 \, \text{mm Hg} / (760 \, \text{mm Hg/ atm}) \cdot (0.2428 \, \text{L})(32.00 \, \text{g/mol})}{(0.303 \, \text{g})(294K)} = 0.0816 \, \text{L-atm/mol-K}
\]

The average value for \( R \) is, therefore,
\[
Average \quad R = \frac{0.0823 + 0.0816}{2} \, \text{L-atm/mol-K} = 0.0820 \, \text{L-atm/mol-K}
\]

Note that the minimum and maximum values of \( R \) differ from the average by 0.0004. Consequently, the uncertainty in \( R \)
can be written as \( + \) or \( - 0.0004 \, \text{L-atm/mol-K} \) and the data would be reported as
\[
R = 0.0820 \pm 0.0004 \, \text{L-atm/mol-K}
\]
**Data Table**

<table>
<thead>
<tr>
<th>Mass of test tube + KClO₃ + MnO₂</th>
<th>g</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mass of test tube + contents after reaction</td>
<td>g</td>
</tr>
<tr>
<td>Mass of Oxygen produced</td>
<td>g</td>
</tr>
<tr>
<td>Mass of 125-mL flask* + water</td>
<td>g</td>
</tr>
<tr>
<td>Mass of 125-mL flask*</td>
<td>g</td>
</tr>
<tr>
<td>Mass of water</td>
<td>g</td>
</tr>
<tr>
<td>Temperature of water</td>
<td>°C</td>
</tr>
<tr>
<td>Density of water</td>
<td></td>
</tr>
<tr>
<td>Volume of water and volume of O₂ gas</td>
<td>mL</td>
</tr>
<tr>
<td>Barometric pressure</td>
<td>mm Hg</td>
</tr>
<tr>
<td>Vapor pressure of water</td>
<td></td>
</tr>
<tr>
<td>Pressure of O₂ gas (show calculations)</td>
<td>mm Hg</td>
</tr>
<tr>
<td>Gas-law constant, R, from ideal-gas law (show calculations)</td>
<td></td>
</tr>
<tr>
<td>R from the Van der Waals equation (show calculations)</td>
<td></td>
</tr>
<tr>
<td>Accepted value of R and source of R value</td>
<td></td>
</tr>
<tr>
<td>Uncertainty in R (show calculations)</td>
<td></td>
</tr>
</tbody>
</table>

**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, H₂ or HBr? Explain your answer.
4. How does the solubility of oxygen in the water affect the value of R you determined? Explain your answer.
5. Under what conditions of temperature and pressure would you expect gases to obey the ideal-gas equation?
6. Why do you equalize the water levels in the bottle and the beaker?
7. What is the value of an error analysis?
8. Suggest reasons why real gases might deviate from the ideal-gas law on the molecular level.
9. At present, 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 were not used in the past?
10. Why is the corrective term to the volume subtracted and not added to the volume in the VanderWaals equation?
11. How much potassium chlorate is needed to produce 20.0 mL of oxygen gas at 670 mm Hg and 20°C?
12. If oxygen gas were collected over water at 20°C and the total pressure of the wet gas were 670 mm Hg, what would be the partial pressure of the oxygen?