Study of Real Gas Behavior: Ideality of CO₂ Gas

Submitted: March 2, 2014 (CHEM 457, Section 2)
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Abstract

The purpose of this experiment was to determine the ideality of carbon dioxide gas (CO₂). This was done by using the virial equation of state for gases to calculate the second virial coefficient. The second virial coefficient predicts the deviation from ideality of a gas by its magnitude. When it is zero, the gas is ideal and the ideal gas law is applicable. In this experiment 1-Z versus the inverse molar volume was plotted to determine the second virial coefficient from the slope, -0.1543 ± 0.0145 L/mol, confirming CO₂’s non-ideality. A closer study at the observation of ideal and applied pressure versus the moles of CO₂ showed that at higher pressures there was increased negative deviation from ideality. This can be explained by molecular level interactions where the molecules begin to attract each other resulting in a lower actual pressure than expected ideal pressure.¹

Introduction

Gases are defined as ideal when the only interactions between molecules are elastic collisions.¹ These gases are described by the ideal gas equation (equation 1) which is a compilation Boyle’s law, Charles’ law, and Avagadro’s principle.

\[ PV = nRT \]  

(1)

In general, real gases follow this law only when they are monatomic and at low pressures and high temperatures.³ At low pressures, Boyle’s law indicates that the volume of the molecule is so small compared to the total gas volume therefore making it negligible. At high temperatures, the
molecules have very high speeds (high kinetic energy). Unfortunately, not all real gases fall under this law and therefore there needs to be a way to quantify and measure deviation from ideality. The compressibility factor is used to describe a real gas’ deviation from ideality. Represented by the variable $Z$, the compressibility factor is the ratio of molar volume of a real gas to the molar volume of an ideal gas (equation 2) with the same temperature and pressure.

$$Z = \frac{V_m}{V_m^o}$$

(2)

Equation 2 predicts what is happening at the molecular level in a non-ideal gas. If a gas is ideal, $Z$ equals one. When the molar volume of the ideal gas is greater than the molar volume of the real gas, $Z$ is less than one. In this case, attractive forces between the molecules are dominating. In the opposite case where the volume of the ideal gas is smaller, $Z$ is greater than one and repulsive forces are dominating. The farther away $Z$ is from one, the less ideal the gas is.

Since the ideal molar volume follows the ideal gas law (equation 3), equation 4 can be derived, relating $Z$ to pressure and temperature.

$$V_m = \frac{RT}{p}$$

(3)

$$PV_m = ZRT$$

(4)

In addition to the compressibility factor, there have been many models and equations derived which also express a real gas’ divergence from ideality. One of the well-known equations is the virial equation of state (equation 5) and is derived using statistical mechanics. While the equation is not the most convenient to use in its full form, its coefficients are functions of temperature where the first coefficient, $A$, is equal to one, and the second coefficient, $B$, describes the deviation from ideality.

$$PV_m = RT[1 + \frac{B}{V_m} + \frac{C}{V_m^2} + \cdots]$$

(5)
Because the second coefficient, $B$, is the most influential term, the other terms can be dropped at low pressures because they are relatively insignificant. This results in equation 6.

$$Z - 1 = \frac{B}{V_m} \quad (6)$$

By plotting values of $Z-1$ vs $1/V_m$, the second virial coefficient can be derived from the slope of the best fit line. The second virial coefficient can also be used to calculate Boyle’s temperature using another ideal gas equation, the Van der Waals equation. The Boyle temperature is seen from equation 7.

$$B = b - \frac{a}{RT} \quad (7)$$

The Boyle temperature corresponds to where the second virial coefficient is zero. In other words, where the gas exhibits quasi ideal behavior.

It is important to understand how to interpret non-ideal gases because it is something that is more likely to be found in a realistic situation. Gases have many conditions and requirements before they can be considered ideal. Real gas behavior is useful for understanding thermodynamic properties as well as interactions on a molecular scale. In this experiment carbon dioxide will be examined under different pressures in order to analyze and determine its behavior as a real gas compared to an ideal one.

**Experimental**

Before beginning the experiment, the balance was calibrated using the empty vessel and weights. The vessel was placed on the balance while adding one gram each successive time until ten grams total had been added. The amount added and output reading was recorded and the calibration was performed three times for good statistics. This was done to account for variations within the balance producing a more accurate value when calculating the mass of CO₂ in the vessel.
Using a regulator, as seen in Figure 1, CO₂ was loaded into the tank at specific pressures, starting at 9 bar and decreasing by 1 bar each time until 3 bar. Before taking the mass of the vessel, five minutes were allowed for the pressure to equilibrate in the line and vessel. In between each reading, the line was purged to remove different species such as oxygen and nitrogen which could create undesired interactions with CO₂ molecules. The thermocouple temperature was maintained at a constant 21.8 °C.

![Figure 1. Experimental Setup](image)

**Results and Discussion**

The values in Table 1 were calculated from the experimental measured values in Table 2 which can be found in the Appendix. These values were used to calculate the compressibility factor, Z, as well as determine the second virial coefficient in effort to describe the non-ideality of carbon dioxide gas.
**Table 1. Tabulated Values from Experimental Data**

<table>
<thead>
<tr>
<th>Pabs (Torr)</th>
<th>T (K)</th>
<th>CO2 (mol)</th>
<th>Vm (L/mol)</th>
<th>Z</th>
</tr>
</thead>
<tbody>
<tr>
<td>7488.4481</td>
<td>294.95</td>
<td>0.2400527</td>
<td>2.337820303</td>
<td>0.951720545</td>
</tr>
<tr>
<td>6739.8483</td>
<td>294.95</td>
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<td>2.603923688</td>
<td>0.954080168</td>
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<tr>
<td>5997.2493</td>
<td>294.85</td>
<td>0.1905588</td>
<td>2.945023231</td>
<td>0.960493854</td>
</tr>
<tr>
<td>5250.1497</td>
<td>294.95</td>
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<td>0.967792038</td>
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<tr>
<td>4476.0465</td>
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<td>3763.4515</td>
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<td>2938.3415</td>
<td>294.95</td>
<td>0.0903478</td>
<td>6.211552732</td>
<td>0.992222201</td>
</tr>
</tbody>
</table>

By using the ideal gas law (equation 1), where T was the observed temperature, V was the volume of the vessel, and n was the number of moles CO$_2$ in the vessel, the ideal pressure was calculated. Figure 2 shows the graph of the actual and ideal pressures versus the moles of CO$_2$ in the vessel.

![Graph](image)

**Figure 2. Deviation of from ideality: Actual and Ideal Pressure versus Moles CO$_2$**

The plot depicts that with higher pressures, CO$_2$ deviates more from ideality. If the gas were ideal, it would show that the y-intercept was zero. This is because as defined by the ideal gas law, a plot of pressure versus moles would equal R times the temperature divided by the
volume. The actual y-intercept was 215.9 ± 16.54 torr/mol indicating that CO$_2$ does not behave as an ideal gas at high pressures. This is when molecular interactions change and attractive forces between CO$_2$ molecules begin to dominate. The y-intercept for the ideal data was 0.202 ± 1.13torr/mol which is approximately zero, expected of an ideal gas.

To better assess CO$_2$’s non-ideal behavior, the second virial coefficient was found. Figure 3 represents a plot of the compressibility factor minus one versus the inverse molar volume where the second coefficient can be derived from the slope as seen in equation 6.

![Compressibility Factor versus Inverse Molar Volume](image)

**Figure 3. Compressibility Factor versus Inverse Molar Volume**

From Figure 3, the second virial coefficient of carbon dioxide was determined from the slope with a value of -0.1543 ± 0.0145 L/mol. Compared to the accepted literature value of -0.1497 L/mol, with only a 3.08% error, the experiment was relatively successful in determining values that represent carbon dioxide’s deviation from an ideal gas.$^2$
Conclusion

Experimental results revealed that with higher pressures, carbon monoxide increasingly strayed from ideal behavior. The second virial coefficient also confirmed that the gas exhibited non-ideal behavior. Potential room for error in the experiment came from purging out the lines for the carbon dioxide pump. If they were not purged completely, oxygen or other molecules could have undesirable interactions which would lead to inaccurate measurements which would most likely predict greater non-ideality in CO₂. Fortunately, the observed temperature maintained relatively constant the entire time, but there was no mixer for the water bath which wouldn’t have prevented ‘hot’ or ‘cold’ spots in the bath. Since the second coefficient is a function of temperature, any variation could potentially affect the results. Overall, the experiment had success in that its findings provide a greater understanding to how carbon dioxide deviates from ideality.

References


Appendix A. Report Questions

1. It is important to account for atmospheric pressure because the pressure gauge only records the gauge pressure and for accurate calculations, the absolute pressure must be used. By adding the measured gauge pressure to the atmospheric pressure, the absolute pressure was obtained.

2. The experimental value of the second virial coefficient was determined to be \( =.1543 \pm 0.00986 \text{ L/mol} \), a 3.07 % difference from the literature value of \( -.1497 \text{ L/mol}^2 \). The literature values were recorded at a temperature of 0 °C while the experimental values were measured at 28.1± 0.1°C. The second virial coefficient is a function of temperature, and a change in temperature will affect the end result, therefore this temperature difference is a reason for discrepancies between the two values. For this reason, the thermocouple bath was strictly kept within 0.1 °C of the starting temperature during the experiment.

3. Carbon dioxide deviates from ideal behavior because of the types of interactions between molecules. At the molecular level, there are repulsive and attractive interactions between CO₂ molecules that cause it to stray from ideality. Ideal gases have zero interactions between molecules. CO₂ molecules have van der Waals forces which make them attracted and repelled from each other. While the molecule has a net dipole of zero, it still has internal dipoles between carbon and oxygen that also contributes to interactions between molecules. In this case, the compressibility factor is less than one indicating that attractive forces dominate. Because of this, with pressure changes the molecules will stick to each other more rather than bump against the wall of the vessel resulting in a lower pressure reading than would be observed in an ideal situation.
Appendix B. Additional Data

Table 2. Regression Statistics for Actual Pressure vs. Moles

<table>
<thead>
<tr>
<th>Actual Pressure vs. Moles</th>
<th>slope</th>
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<th>intercept</th>
<th>215.8610748</th>
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<td>95.637002</td>
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<td></td>
<td>r^2</td>
<td>0.9999503</td>
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<td>12.59335378</td>
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Table 3. Regression Statistics for Ideal Pressure vs. Moles

<table>
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<th>Ideal Pressure vs. Moles</th>
<th>slope</th>
<th>32774.451</th>
<th>intercept</th>
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</thead>
<tbody>
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<td>r^2</td>
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<td>0.858198474</td>
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Table 4. Regression Statistics for Z-1 vs. 1/Vm

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</thead>
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<td>r^2</td>
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Table 5. Balance Calibration Values

<table>
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<th>Output Average</th>
<th>g added</th>
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</thead>
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<td>0</td>
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Figure 4. Linear Plot of Balance Calibration Values

![Graph showing linear plot with equation $y = 0.9969x - 448.1$, $R^2 = 0.9999$]

Table 6. Regression for Balance Calibration

<table>
<thead>
<tr>
<th>Added vs. Output</th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>slope</td>
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<tr>
<td>intercept</td>
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<td>1.4317469</td>
</tr>
<tr>
<td>$r^2$</td>
<td>0.99991</td>
<td>0.0331392</td>
</tr>
</tbody>
</table>

Appendix C. Sample Calculations

1.) Mass of Carbon Dioxide in Vessel
   $y$=mass CO$_2$ in vessel $x$=mass from balance
   
   $y = 0.9969x - 448.1 = 0.9969(460.091) - 448.1 = 10.565g$

2.) Moles of Carbon Dioxide in Vessel

   $Moles\text{CO}_2\text{(mol)} = \frac{\text{Mass}_{\text{CO}_2}}{MW_{\text{CO}_2}} = \frac{10.565(g)}{44.0098\left(\frac{g}{mol}\right)} = 0.240mol$
3.) Molar Volume

\[ V_m(\text{L/mol}) = \frac{\text{Volume}_{\text{vessel}}}{\text{Moles}_{\text{CO}_2}} = \frac{0.5612 \text{(L)}}{0.240 \text{(mol)}} = 2.338 \text{L/mol} \]

4.) Compressibility Factor

\[ Z = \frac{PV_m}{RT} = \frac{(7488 \text{ Torr})(2.338 \text{ L/mol})}{(62.36367 \text{ L/Torr/mol K})(294.95 \text{ K})} = 0.952 \]

5.) Ideal Pressure

\[ P_{abs, \text{Ideal}}(\text{Torr}) = \frac{RT}{V_m} = \frac{(62.36367 \text{ L/Torr/mol K})(294.95 \text{ K})}{(2.338 \text{ L/mol})} = 7867 \text{Torr} \]

6.) Percent Error of Second Virial Coefficient

\[ \% \text{Error} = \frac{\text{(Accepted)} - \text{(Experimental)}}{\text{(Accepted)}} \times 100\% = \frac{(-0.1497) - (-0.1543)}{(-0.1497)} \times 100\% = 3.07\% \]

Appendix D. Standard Error

1.) Mass of Carbon Dioxide in Vessel Uncertainty

\[ y = \text{mass CO}_2 \text{ in vessel} \quad x = \text{mass from balance} \]

Uncertainty from regression statistics

\[ y = 0.9969x - 448.1 = 0.9969(460.091) - 448.1 = 10.565 \pm 1.432 \text{g} \]

2.) Moles of Carbon Dioxide in Vessel Uncertainty

\[ \Delta \text{Moles}_{\text{CO}_2} = (\text{Moles}_{\text{CO}_2}) \left( \frac{\Delta \text{Mass}_{\text{CO}_2}}{\text{Mass}_{\text{CO}_2}} \right) = (0.240 \text{ mol}) \left( \frac{4 \times 10^{-4} \text{ g}}{10.565 \text{ g}} \right) = 9.09 \times 10^{-6} \text{ mol} \]

3.) Molar Volume Uncertainty

\[ \Delta V_m = V_m \times \left( \frac{\Delta (\text{mol}_{\text{CO}_2})}{\text{mol}_{\text{CO}_2}} \right) = (2.338 \text{ L/mol}) \times \left( \frac{9.09 \times 10^{-6} \text{ mol}}{0.240 \text{ mol}} \right) = 8.85 \times 10^{-5} \text{ L/mol} \]

4.) Compressibility Factor Uncertainty
\[ \Delta Z = Z \sqrt{\frac{\Delta^2(P_{abs})}{(P_{abs})^2} + \frac{\Delta^2(V_m)}{(V_m)^2} + \frac{\Delta^2(T)}{(T)^2}} \]

\[ = (0.950) \sqrt{\frac{(3\text{Torr})^2}{(7488)^2} + \frac{(8.85 \times 10^{-5} \text{ L/mol})^2}{(2.338 \text{ L/mol})^2} + \frac{(0.1K)^2}{(295.49K)^2}} = 5.26 \times 10^{-4} \]

5.) Ideal Pressure Uncertainty

\[ \Delta P_{abs, Ideal} = (P_{abs, Ideal}) \sqrt{\frac{\Delta^2(T)}{T^2} + \frac{\Delta^2(V_m)}{V_m^2}} \]

\[ = (7867\text{Torr}) \sqrt{\frac{(0.1K)^2}{(295.49K)^2} + \frac{(8.85 \times 10^{-5} \text{ L/mol})^2}{(2.338 \text{ L/mol})^2}} = 2.68\text{Torr} \]