Gas Laws

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I. Introduction

The ideal gas law is used to predict the relationship between pressure, volume, moles, and temperature of a gas. The formula for which is:

$$PV = nRT$$

Where we have P as pressure, V as volume, n as number of moles, T as temperature, and R as the gas constant. However, as the title suggests this relationship is only true for ideal gases. In practice this is a very good estimate for most gases in mild temperatures and its accuracy varies for different gases. A better description for a gas law can be found by accounting for the interaction between the molecules and their attractive forces which condense the gas through phase changes as the temperature drops. This is known as the Van der Waals Equation of State:

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

Where a and b are empirical constants that characterize the gas. This model is a much better predictor for pressure and temperature relationships observed experimentally, but once the temperature becomes closer to absolute zero it is entirely off. Here, gases tend to become an equilibrium mixture of gas and solid/liquid phases where the pressure is that of the gaseous state known as the vapor pressure. The Vapor Pressure Curve is modeled by:

$$P = Ce^{\frac{-\varepsilon}{k_B T}}$$

Where ε is the energy to take one molecule from the condensed phase to the gas phase and k_B is the Boltzmann constant. These two equations combined are great models for the relationship between temperature and pressure for gases in all ranges of temperatures. In the following experiments we will provide supporting evidence for the validity of the Van der Waals Equation of State and the Vapor Pressure Curve through a case study of helium gas and carbon dioxide.

II. Helium Gas in Temperature Baths

To hold the helium gas, we will use a copper cylinder equipped with a pressure sensor and thermocouple which will record data relevant to our studies. This copper cylinder will then be inserted carefully into various baths in order to bring the gas to a specific temperature for us to analyze its reaction. For the following experiments we will use the same technique, measuring devices, and containers and simply vary the gas held within the cylinder and the temperature of the bath it is submerged in.

The copper cylinder was filled and flushed with helium gas in order to make sure that it constained as pure helium as possible. However, it is likely that there were still other gases left in the cylinder, introducing uncertainty into our measurements. The initial voltage and pressure readings at room temperature were found to be $V = 0.204 \pm 0.001$ V and $P = 432.6 \pm 0.1$ kPa. The cylinder was then completely submerged in boiling water ($T =$

373.15 K) until the gas inside reached equilibrium. This was reached at $V = 0.993 \pm 0.001$ V and $P = 543.4 \pm 0.1$ kPa. Care was taken to not touch the cylinder to the sides of the pot holding the water, but on occasion they came into contact, meaning that the gas in the cylinder may have been at a slightly higher temperature than the boiling water as the surface of the pot was hotter than the water it contained.

The cylinder was put in a bath of room temperature water to cool it down. Once it had cooled, the cylinder was placed in a bucket of ice water ($T = 273.15$ K). The bucket was filled with ice and water to ensure that the temperature was uniformly 0 ºC. As ice floats in water, and water is at its densest at ~4 ºC, if there isn't enough water in the bath, the water at the bottom of the bucket would be warmer than the ice water at the top of the bucket, and the pressure measurements taken would be inaccurate. Care was taken to ensure that both ice and water were present all the way up the copper cylinder. Once the cylinder had reached thermal equilibrium in the ice bath, the values recorded were $V = -0.005 \pm 0.001$ V and $P = 401.0 \pm 0.1$ kPa. The measurements from this bath had uncertainty associated with them because it is unlikely that the entire surface was in contact with ice-water at exactly 0 ºC.

The cylinder was removed from the ice bath and dried it off. We then submerged the cylinder in a methanol and dry ice bath ($T = 194.6$ K), taking care to not let the methanol boil over the surface of the container. The lid was placed on the container to minimize air currents affecting the temperature reading. When equilibrium was reached, the values for voltage and pressure were found to be $V = -0.687 \pm 0.001$ V and $P = 291.1 \pm$

0.1 kPa. The methanol bath was kept at its boiling temperature with dry ice which is colder than the methanol bath. Similar to the boiling pot, a possible source of error could be that the dry ice cubes may have come into contact with the cylinder, making parts of the cylinder slightly colder than expected.

The cylinder was removed from the methanol, dried off, and slowly submerged into the liquid nitrogen bath ($T = 77.3$ K). This was done very carefully as the nitrogen bubbles vigorously as it boils off. The recorded values at this temperature were $V = -1.418 \pm 0.001$ V and $P = 115.8 \pm 0.1$ kPa. The cylinder was removed from the nitrogen, disconnected from the computer, and run under water until it returned to room temperature.

There are a few sources of uncertainty in these measurements. Firstly, the recorded thermal equilibrium was reached by the gas in the cylinder without knowing the internal temperature. It is possible that data requisition was stopped too soon as the temperature changed very slowly when approaching the temperature of the bath. To minimize this, the cylinder was kept in the bath for ~30 seconds until thermal equilibrium had evened out to ensure that the readings remained stable. Additionally, the equipment used to measure the temperature and pressure have some offset from the correct values. However, the corrections needed to be made are shown by the following formula, where α, V_0, and V_s are all known values associated with the instruments, and P, T, and T_0 are the measured values:

$$P_{corr} = P \frac{1 + \alpha(T - T_0) + \frac{V_s T}{V_0 T_0}}{1 + \frac{V_s}{V_0}}$$

Using these empirical values, we can create a graph of the corrected pressure vs. bath temperature for the helium gas. Using the slope of this line we can determine the accuracy of the ideal gas law. The graph is shown in Figure 1 and least-squares regression fit in Table 1.
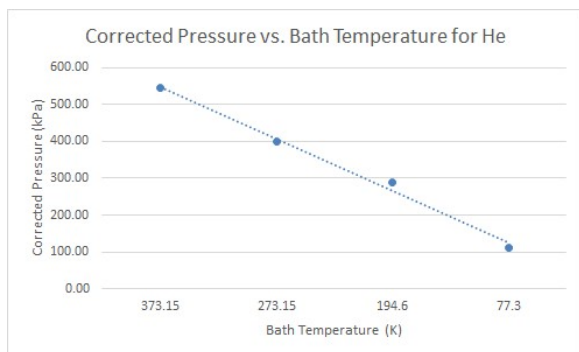

Corrected Pressure vs. Bath Temperature for He

Figure 1: Corrected Pressure vs. Bath Temperature for Helium gas

	Slope	Intercept
Value	1.460134	0.742473
Error	0.009496	2.410233
Correlation	0.999915	2.05698

Table 1: Least-squares regression fit for corrected pressure vs. bath temperature for helium gas

The slope predicted by the ideal gas law is $P_0/T_0 = 1.4682 \pm 0.0028$ and intercept at 0. This aligns very closely to the experimental data obtained in the above experiment modeled by the equation $y = 1.4601x + 0.74$ as the slope is off by 0.5% and intercept is effectively the same as the prediction from the ideal gas law. This shows that the ideal gas law is a very good description for the relationship between temperature and pressure for a wide range of temperatures.

III. Carbon Dioxide Gas in Temperature Baths

The helium gas was flushed from the cylinder and filled with carbon dioxide gas, making sure to flush and fill the cylinder multiple times as in the first experiment. The measured voltage and pressure at room temperature for the CO_2 were $V = 0.249 \pm 0.001$ V and $P = 424.7 \pm 0.1$ kPa. The exact same procedures outlined above in the previous experiment were followed for the boiling water; ice water; and methanol and dry ice baths. The procedure for the liquid nitrogen bath was slightly different as the geometry of the cylinder does not allow you to completely submerge the cylinder. If instantly submerged, a plug of frozen CO_2 could form at the top of the cylinder in the stem tube, preventing proper pressure measurements. Thus, the internal pressure had to drop to almost 0 before completely submerging the cylinder in the bath.

It is known that with only CO_2 in the cylinder, the pressure at 77 K is extremely low, corresponding to a very high vacuum much lower pressure than can be achieved with a mechanical vacuum pump. We used this pressure value, P_{77}, for CO_2 as an instrumental correction P_{vac}. We can use the values recorded for the various temperature baths shown in Table 2 to plot the corrected pressure vs. bath temperature.

Table 2: CO2 in Temperature Baths		
Bath	Temperature (K)	Pressure (kPa)
Boiling Water	373.15 ± 0.1	543.4 ± 0.1
Ice Water	273.15 ± 0.1	386.2 ± 0.1
Methanol	194.6 ± 0.1	123.1 ± 0.1
Liquid Nitrogen	77.3 ± 0.1	1.53 ± 0.10

We know that the Van der Waals equation only works for CO2 above 250 K. To test its accuracy in this range we can perform a similar analysis as in experiment 1 by plotting the pressure vs. temperature as

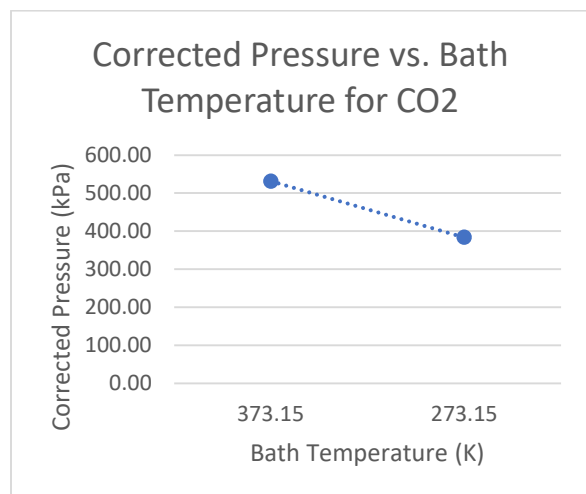shown in Figure 2 with relevant least-squares regression fit shown in Table 3.

Figure 2: Corrected pressure vs. bath temperature for CO2 above 250K

	Slope	Intercept
Value	1.476967	-19.3946
Error	0	0
Correlation	1	0

Table 3: Least-squares regression data for corrected pressure vs. bath temperature for CO2 above 250K

Compared with the predictions of the ideal gas law and Van der Waals equation, we expect a straight-line variation for temperatures above ~250 K. The slope predicted by the ideal gas law is $P_0/T_0 = 1.4414 \pm 0.0028$ and intercept should be 0. The slope predicted by the Van der Waals equation is 1.44 and intercept prediction is -10.8. The equation for the experimental line above is y = 1.4770x -19.39. The slope calculated using the ideal gas law and the Van der Waals equation is a little bit off from the experimentally found value by 2.5% for both slopes. Errors here are likely because we have only two points with which to create a least-squares estimate. With more experimental values, the slope and intercept would likely be closer to the expected values.

Comparing the lower temperature values against the Vapor Pressure Curve we can see that they are similar qualitatively. The experimental values are plotted in Figure 3 and theoretical Vapor Pressure Curve in Figure 4.
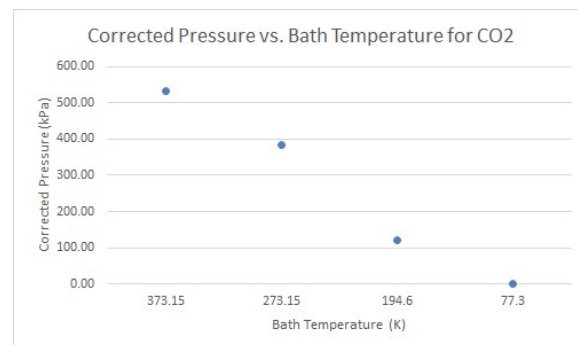

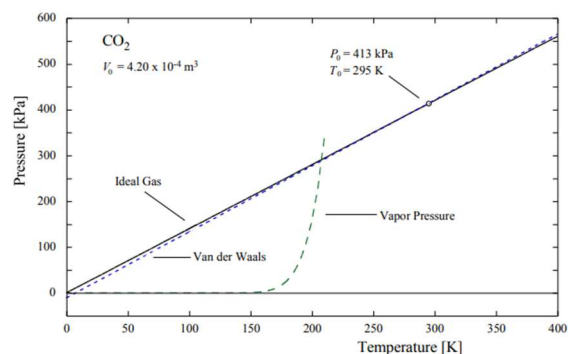Figure 3: Corrected Pressure vs. Bath Temperature for CO2

Figure 4: Theoretical predicting curves

As the procedures for Experiment 2 were identical to the procedures of Experiment 1, the sources of error were largely the same, and the same care was taken for both experiments to reduce these uncertainties as much as possible. Additional uncertainty was introduced by there being less of each liquid in each bath as noticeable amounts of each substance had boiled off in the first experiment. This meant that it was more difficult to completely submerge the cylinder in the liquid. This was especially relevant in the methanol and dry ice bath because the temperature inside the cylinder dropped too low when it touched the dry ice. When the cylinder was

lifted slightly, keeping it submerged in the methanol but removing its contact with the dry ice, the temperature and pressure started increasing slightly, meaning the thermal equilibrium had to be located from the other direction.

IV. Warming of CO_2 from 77K to Room Temperature

Immediately following the previous experiment, the rate at which measurements were changed to being taken by the computer to be one sample every 10 seconds, rather than every second. The cylinder was removed from the liquid nitrogen bath and started recording. Samples were recorded for about an hour as the cylinder slowly warmed up to room temperature.

Uncertainty in the values measured in this experiment could come from fluctuations in the temperature of the room. Nearby the warming cylinder was the cooling pot of boiling water. The heat radiating off the pot could cause the temperature of the air around the cylinder to vary, which could affect how quickly the cylinder warmed up. Figure 5 shows the two plots of voltage and pressure as functions of time for the hour-long thaw out.
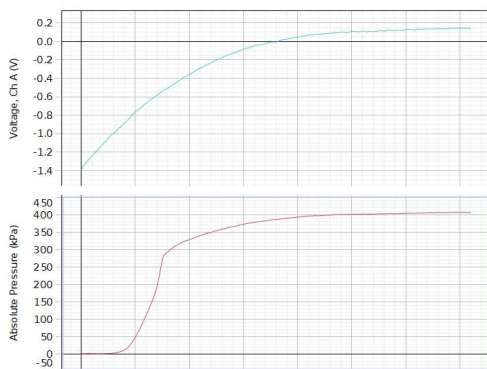

Figure 5: Graphs of the temperature and pressure of the cylinder as a function of time as the cylinder warmed to room temperature

The objectives here are to compare the very detailed measurements taken for the pressure with the Van der Waals equation at temperatures above 250 K (the ice bath and boiling water) and with the vapor pressure curve at low temperatures (methanol and liquid nitrogen). The thermocouple voltage is given by $v = g\,(V_T - V_{273})$ where $g = -5.829$ mV / $(V_{77} - V_{273})$. The temperature in Kelvin can then be calculated with

$$T = 273.15 + M_1 v + M_2 v^2 + M_4 v^4 + M_5 v^5$$

Where $M_1 = 25.665$, $M_2 = -0.4304$, $M_4 = -0.00680$, and $M_5 = 0.003444$. Calculating the temperature and correcting the pressure for each sample recorded over the hour, we can plot corrected pressure as a function of temperature as shown in Figure 6.
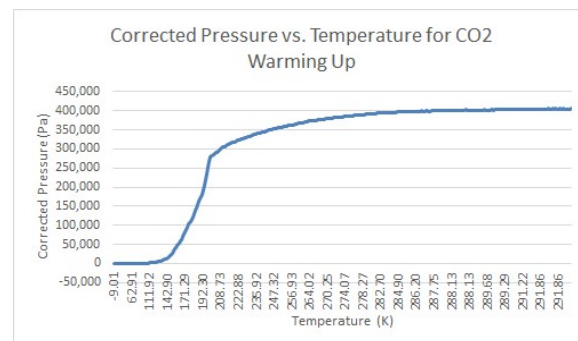

Figure 6: Corrected pressure vs. temperature for CO2

Comparing this to the graph shown in Figure 4, we can see that the experimental data follows the Vapor Pressure Curve until about 200K, at which point it smoothens into the Van der Waals equation. Comparing only the pressures above 250K we can compare the plot to the Van der Waals equation to find its accuracy. This experimental graph is shown in Figure 7 and least squares regression fit in Table 4.
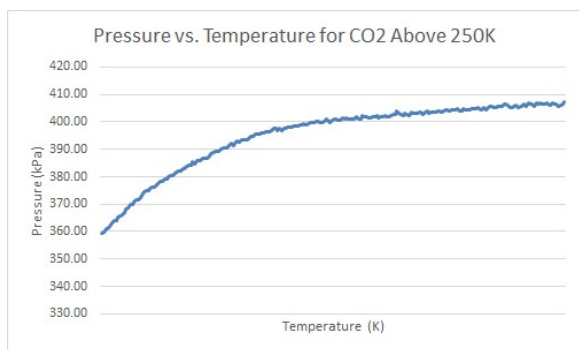
Figure 7: Pressure vs. temperature for CO2 warming up above 250K

	Slope	Intercept
Value	1.13587	74.73664
Error	0.00276	0.779299
Correlation	0.998655	0.453522

Table 4: Least-squares regression fit for pressure vs. temperature for CO2 warming up above 250K

The equation for the regression line above is $y = 1.1359x + 74.74$. The Van der Waals equation predicts a slope of 1.44, which is also quite far from the experimentally found slope. The source of this error is due to the length of the experiment. Had it lasted for a longer period of time, the measurements would have more closely approximated a line. Additionally, the curve does not appear to flatten into a line until about $T = 275K$. Using this data, we calculate values for the gas characteristics of CO2 $a = 0.00239$ and $b = -6.32$. These are quite off from the expected values of a = 3.66 x 10^{-1} and b = 4.29 x 10^{-5}. This is either due to a unit/calculation error or error in calculating the slope of the graph for the pressure vs. temperature for CO2 warming up. However, the data collected qualitatively agrees with the expected values and we will continue with the analysis. Using the following equation, we can calculate the radius of a CO2 molecule:

$$r = \left(\frac{3b}{4\pi N_A}\right)^{1/2}$$

We obtain $r = 1.36$ x 10^{-8} for the radius of a CO2 molecule.

Plotting the natural log of the corrected pressure vs the inverse of the temperature should give us a straight line which we can use to calculate the value ε for the Vapor Pressure Curve modeled by:

$$P = Ce^{\frac{-\varepsilon}{kT}}$$

Our calculated ε comes out to be $\varepsilon = 6.19$ x 10^{-25} J which does not align with the expected value of $\varepsilon = 4.18$ x 10^{-20} J. This is likely due to the same errors made in the previous calculation and again we will continue with our conclusions following qualitative analysis.

V. Conclusion

In these experiments we have shown the relationship between temperature and pressure of a gas can follow several different theoretical predictions. As we saw in experiment 1, for certain gases such as helium, the ideal gas law and corrected Van der Waals equation hold as models for pressure as a function of temperature. This is where the idea for the ideal gas law came from, as it was observed in a few gases and generalized. However, for a gas like CO2, we saw in experiment 2 that as the temperature reached below 250K, both the ideal gas law and the corrected Van der Waals equation do not hold. This new activity is instead modeled by the Vapor Pressure Curve which we saw in the second part of experiment two. To get a more complete view of a gas curve, we performed experiment 3 which mapped out a full transition of CO2 gas from 77K to room temperature at about 300K. Although our calculations were vastly out of proportion, we can qualitatively observe the curve shown in Figure 6 to see the full relationship of pressure and temperature for a gas.