Heat Capacity of CO_2 at Varying Temperatures Generated from an Oscilloscope

Holly Burrell, Kim Lammers*, Shanna Smith, and Andrew Pounds

Mercer University, Macon, GA 31027, United States

Supporting Information Placeholder

In this experiment, a tube was connected to an oscilloscope that generated frequencies. The measured length of the tube was 90 cm. The goal of this experiment was to find the constant volume heat capacities (C_v) for CO_2 at room temperature, as well at the temperature of dry ice. Heat capacity was the observable measured experimentally. This was calculated from sound velocity measurements. Equation 1 represents the relationship between sound velocity and heat capacity. The heat capacities were calculated from Equation 2, which was derived from Equation 1.

$$u^2 = \frac{\gamma RT}{M} = \frac{(\frac{C_p}{C_v})RT}{M} \tag{1}$$

$$C_v = \frac{\frac{R^2T}{M}}{\left(\frac{u_{N_2}(\frac{df}{dn})_{CO_2}}{(\frac{df}{dn})_{N_2}}\right)^2 - \frac{RT}{M}} \tag{2}$$

The variables for Equation 2 are defined as follows: R is the gas constant (8.314 J/mol*K), T is the temperature of the tube with CO_2 gas in Kelvin (296 K for room temperature and 254 K for low temperature), M is the molar mass of CO_2 (0.04401 kg/mol), u_n is the velocity of sound in nitrogen (334 m/s)[1], $(df/dn)_{CO2}$ is the slope of frequency vs. n for CO_2 at either room temperature or dry ice (232.59 and 213.46 respectively), and $(df/dn)_{N2}$ is the slope of frequency vs. n for N_2 (303.03).

The velocity of sound in nitrogen was chosen over the velocity of sound in air to calculate the heat capacities for CO_2 in Equation 2. The velocity of sound in nitrogen was chosen over the velocity of sound in air because of the humidity in the lab. On the day of the experimentation, the humidity in lab was 40%. The air inside the tube was not dry, unlike the nitrogen gas inside the tube. Additionally, the results of the calculations of the length of the tube from the nitrogen data were more consistent with the measured value of the tube than that of the calculations of the length of the tube from the air data.

Equations 3, 4, and 5 were used to derive Equation 2 from Equation 1. Equation 3 was substituted into Equation 1 for the sound velocity, putting Equation 2 in terms of the sound velocity of N_2 and the slopes of CO_2 and N_2. Equation 4 defines the value of gamma in terms of the heat capacity at constant volume (C_v) and the heat capacity at constant pressure (C_p). Equation 5 is used to put Equation 2 in terms of heat capacity at constant volume and eliminate the variable of heat capacity at constant pressure.

$$u = \frac{u_n(\frac{df}{dn})_{CO_2}}{(\frac{df}{dn})_{N_2}} \tag{3}$$

$$\gamma = \frac{C_p}{C_v} \tag{4}$$

$$C_p = C_v + R \tag{5}$$

The slopes of CO_2 and N_2 were found by plotting the experimental data. The plots of these slopes are shown in Figure 1, Figure 2, and Figure 3. Only the plots for Trial 1 are shown for each gas. The maximum and minimum equations of the slopes according to the regression coefficients are plotted on Figure 1, Figure 2, and Figure 3 as well. There was an error of 9% with the oscilloscope used in the experiment. This error value is incorporated into the slopes.[2] The slopes for each trial from data for N_2, CO_2 at room temperature, and CO_2 at low temperature are listed in Table 1. The average slopes of all three trials are listed in Table 1 as well.

Figure 1. Graph of Actual, Minimum, and Maximum Slopes of N_2 Results (Trial 1)

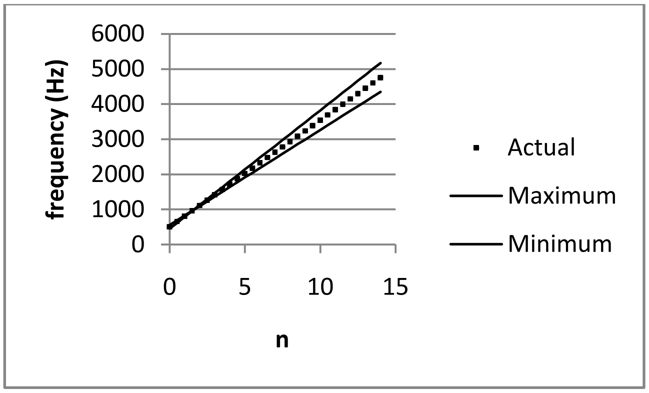

Figure 2. Graph of Actual, Minimum, and Maximum Slopes of CO_2 Room Temperature Results (Trial 1)

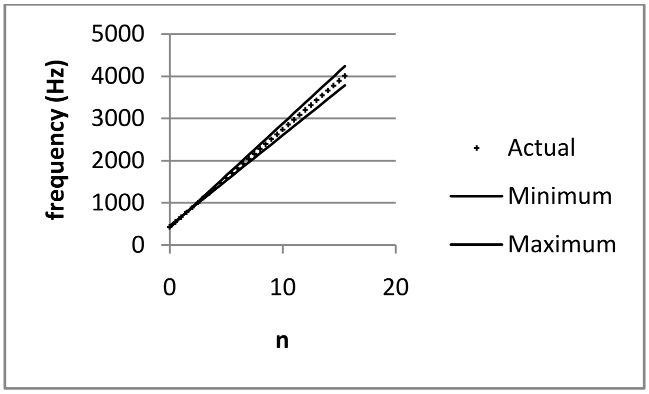

Figure 3. Graph of Actual, Minimum, and Maximum Slopes of CO_2 Dry Ice Results (Trial 1)

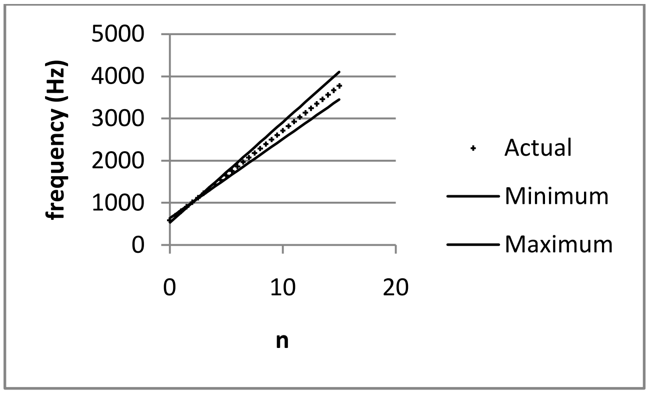

Table 1. Slopes of observables

	Trial 1	Trial 2	Trial 3	Average Slope
N_2	303.18	303.09	302.80	303.02
CO_2 (room temp)	230.69	235.92	231.16	232.59
CO_2 (low temp)	212.41	213.21	212.75	213.46

From the calculated slopes, C_v was calculated using Equation 1. The measured constant volume heat capacities (listed in Table 3) for CO_2 at 296 K and 254 K were 47.4029 J/mol*K and 47.6878 K/mol*K respectively. Theoretical heat capacities at constant volume were also calculated using Equation 6 and 7. The vibrational heat capacity must be first calculated using equation 6. The calculated vibrational heat capacities are then used to calculate the theoretical heat capacities at constant volume (Equation 7). The calculated and theoretical heat capacities are displayed in Table 3.

$$C_{vibr} = R\sum_{n=1}^{4}\frac{(\frac{hcv_i}{kT})^2 e^{hcv_i/kT}}{(e^{\frac{hcv_i}{kT}}-1)^2} \tag{6}$$

The variables for Equation 6 are defined as follows: R is the gas constant (8.314 J/mol*K), h is Plank's constant, c is the speed of light, k is Boltzmann's constant, and T is the temperature of the tube in Kelvin (296 K for room temperature and 254 K for low temperature). The vibrational nodes (v_i) are defined in Table 2.

$$C_v = C_{vibr} + \frac{5}{2}R \tag{7}$$

Table 2. Vibrational Modes (v_i)[3]

v_1	134000 m^{-1}
v_{2a}	66700 m^{-1}
v_{2b}	66700 m^{-1}
v_3	234900 m^{-1}

Table 3. Calculated and Theoretical Heat Capacities at Constant Volume of CO_2

	C_v (J/mol*K)	
	Calculated	Theoretical
CO_2 Room Temperature	47.4029	28.78696
CO_2 Low Temperature	47.6878	26.72014

The theoretical heat capacities are not compatible with the calculated capacities. The calculated heat capacities are higher than the theoretical values found. This indicates that there may be error in the experiment. The heat capacities were expected to be smaller and closer to the theoretical values.

Error was calculated first for the average slopes of frequency vs. n for N_2, CO_2 at room temperature, and CO_2 at low temperature. The averages of the slopes was found using Equation 8 (tabulated in Table 1). Error was then found using Equation 9. The error terms were found in the corrected, actual slopes from the Monte-Carlo Exploration Method (Table 4).[2] The error for the slopes is displayed in Table 5.

$$(\frac{df}{dn})_{avg} = \frac{(\frac{df}{dn})_1 + (\frac{df}{dn})_2 + (\frac{df}{dn})_3}{3} \tag{8}$$

$$\sigma_{(\frac{df}{dn})_{avg}} = \frac{1}{3}\sqrt{\left(\sigma_{(\frac{df}{dn})_1}{}^2\right) + \left(\sigma_{(\frac{df}{dn})_2}{}^2\right) + \left(\sigma_{(\frac{df}{dn})_3}{}^2\right)} \tag{9}$$

Table 4. Slope Error Terms from Monte-Carlo Exploration Method[2]

N_2	Trial 1	32.57
	Trial 2	32.81
	Trial 3	32.72
CO_2 (room temp)	Trial 1	16.3
	Trial 2	28.59
	Trial 3	16.98
CO_2 (low temp)	Trial 1	25.32
	Trial 2	24.44
	Trial 3	25.87

Table 5. Slope Error for N_2 and CO_2

N_2	303.02 ± 20
CO_2 (room temperature)	210 ± 10
CO_2 (low temperature)	230 ± 10

From the slope errors, error of the heat capacities was found using Equation 10. Error from the slopes of CO_2 at room temperature and low temperatures, error from the slopes of N_2, and error from the thermometer factor into the error of C_v. Each of these elements of error is a part of Equation 10. The error for the slopes of CO_2 and N_2 came from Table 5. The error from temperature was based on the accuracy of the thermometer. The accuracy of the thermometer was ± 1% up to 1°C. For the temperature at 296 K, the error was 0.24. The partial derivatives with respect to slope of CO2, slope of N2, and temperature were found from Equation 2. For the temperature at 254 K, the error was 0.19. The calculated error for heat capacity is displayed in Table 6.

$$\sigma_{C_v} = \sqrt{\left((\frac{\partial c_v}{\partial (\frac{df}{dn})_{CO_2}})^2 * \sigma_{(\frac{df}{dn})_{CO_2}}{}^2 \right) + \left((\frac{\partial c_v}{\partial (\frac{df}{dn})_{N_2}})^2 * \sigma_{(\frac{df}{dn})_{N_2}}{}^2 \right) + \left((\frac{\partial c_v}{\partial T})^2 * \sigma_T{}^2 \right)} \quad (10)$$

Table 6. Heat Capacity with Calculated Error

CO_2 Room Temp	47 ± 50 J/mol*K
CO_2 Low Temperature	48 ± 60 J/mol*K

REFERENCES

(1) The Handbook of Chemistry and Physics. Weast, Robert C., Ed.; The Chemical Rubber Company: Boca Rato, FL, 1990; Vol. 70, pp E44.

(2) Pounds, A. J. Mercer University, Macon, GA. Personal communication, 2011.

(3) Silbey, Robert J.; Aberty, Robert A.; Bawendi, Moungi, G. Rotational and Vibrational Spectroscopy. In *Physical Chemistry,* 4th ed.; Brennan, Deborah, McFadden, Patricia, Batey, Martin, Eds.; Wiley: Hoboken, 2005; 487.