Experimental Determination of Gaseous Heat Capacity via Sound Velocity Measurements

Kassandra A. Knapper*, Jeremy Jung, Andrew Pounds

Mercer University, Department of Chemistry, 1400 Coleman Ave, Macon, GA, 31207

Kassandra.A.Knapper@live.mercer.edu

KEYWORDS: Sound velocity, carbon dioxide, heat capacity

ABSTRACT:

RESULTS

Frequency data were gathered using an oscilloscope. Three trials were taken for each gaseous medium at each temperature. Trials were conducted in air and nitrogen gas as standards. The experimental values of these trials were compared to the literature in order to assess the accuracy of the setup at measuring sound velocity. Frequency data were similarly gathered for sound waves in CO_2 gas at both room temperature and lowered temperatures. Representative frequency data are displayed in Figures 1 through 4. The goal of the experiment was to provide a measured value for the heat capacity at constant volume (C_V) of carbon dioxide gas at different temperatures. This was accomplished by relating C_V to the sound velocity (μ) of a gas measured by the experimental setup using the following equations:

$$u^2 = \gamma \frac{RT}{M} = \frac{\left(\frac{C_P}{C_V}\right) RT}{M} \quad (1)$$

$$C_V = \frac{R^2 T}{\left[\left(\left(\frac{df}{dn}\right)_{CO_2} \frac{u_{N_2}}{\left(\frac{df}{dn}\right)_{N_2}}\right) M\right] - RT} \quad (2)$$

The heat capacity of CO_2 gas was experimentally determined using the frequency of sound waves at in and out of phase intervals. C_V can be theoretically determined by calculating the vibrational contribution to heat capacity (C_{vibr}) using the equations:

$$C_{vibr} = R \sum_{i=1}^{4} \frac{(cv_i/kT)^2 e^{cv_i/kT}}{(e^{cv_i/kT} - 1)^2} \quad (3)$$

$$C_v = \frac{5}{2} R + C_{vibr} \quad (4)$$

where v_i are the accepted literature values of the vibrational frequencies of CO_2,[1] R is the gas constant, T is the temperature inside of the tube, $\frac{df}{dn_{CO_2}}$ and $\frac{df}{dn_{N_2}}$ are the slopes of the graphs of the sound wave frequency versus the phase in the gaseous CO_2 and N_2 mediums, u_{N_2} is the velocity of sound waves in a gaseous N_2 medium and M is the molar mass of CO_2. For this experiment, the velocity of sound in N_2 gas was adjusted from the literature based on the average temperature at which the experiment was conducted.[2] Value for u_{N_2} was found to be $343.8834 \frac{m}{s}$.

Values for C_V were determined in the N_2 gas medium and both temperatures of CO_2 gas medium. The accepted value for C_V of N_2 gas at room temperature is $20.81 \frac{J}{mol\,K}$.[2] The experimentally determined value of C_V for N_2 gas at room temperature is $24\frac{J}{mol\,K} \pm 5$. The theoretically determined values of C_V for CO_2 gas at 295.1 K, 294.5 K, and 293.6 K were $28.69\frac{J}{mol\,K}$, $28.69\frac{J}{mol\,K}$ and $28.65\frac{J}{mol\,K}$, respectively. These values were calculated using eqs 3 and 4. The experimentally determined values of C_V for CO_2 gas at these temperatures were $26 \pm 36\frac{J}{mol\,K}$, $24 \pm 32\frac{J}{mol\,K}$ and $30 \pm 50\frac{J}{mol\,K}$, respectively. These values were calculated using eq 2. Theoretical and experimental C_v values were determined similarly for CO_2 gas at lowered temperatures. The theoretically determined values of C_V for CO_2 gas at temperatures lowered to 246.0 K, 247.0 K and 248.0K were $23.67\frac{J}{mol\,K}$, $23.67\frac{J}{mol\,K}$ and $23.67\frac{J}{mol\,K}$, respectively. The experimentally determined values of C_V for CO_2 gas at these temperatures were $26 \pm 50\frac{J}{mol\,K}$, $29 \pm 50\frac{J}{mol\,K}$ and $28 \pm 40\frac{J}{mol\,K}$, respectively.

Experimental and theoretical heat capacities are compared in Table 1.

The error in the experimentally determined heat capacities was determined using the equation:

$$\text{Err} = \left[\left(\frac{\delta C_V}{\delta T}\right)^2 \sigma^2 + \left(\frac{\delta C_V}{\delta\left(\frac{df}{dn}\right)_{CO2}}\right)^2 \sigma^2 + \left(\frac{\delta C_V}{\delta u_{N2}}\right)^2 \sigma^2 + \left(\frac{\delta C_V}{\delta\left(\frac{df}{dn}\right)_{N2}}\right)^2 \sigma^2\right]^{\frac{1}{2}}$$

where σ is the standard error of each respective term. The average error of each slope was calculated using the equation:

$$Err_{\frac{df}{dn}} = \sqrt{\frac{\sigma_{\frac{df}{dn_1}}^{2}+\sigma_{\frac{df}{dn_2}}^{2}+\sigma_{\frac{df}{dn_3}}^{2}}{3}} \tag{5}$$

where σ is the error in slope of the line determined using a Monte Carlo analysis technique and a 9% error in the measurements of the oscilloscope.[3] Slopes of the frequency data gathered including the error are graphically represented in Figures 1 through 4 and listed in Table 2. The error for the velocity of sound in N_2 gas was found by calculating the standard deviation of the velocities found from each trial.

FIGURES

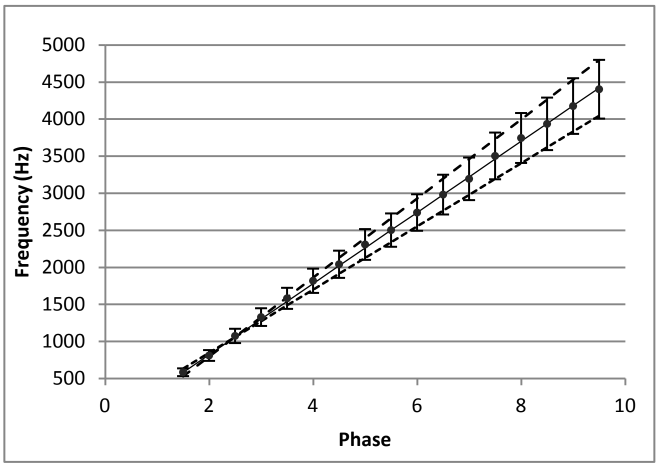

Figure 1: Sound wave frequency at phase intervals in dry air at room temperature. The frequencies of sound waves in dry air were recorded using an oscilloscope at each instance when the generated waves were in phase and out of phase with the received waves. Error bars were based on a 9% error in the oscilloscope. Maximum and minimum inclinations and regression were generated using a Monte Carlo analysis technique.[3] Similar analysis was conducted for each trial. The frequencies displayed are from trial 2. The regression and error in regression for trials 1 and 3 are found in Table 2.

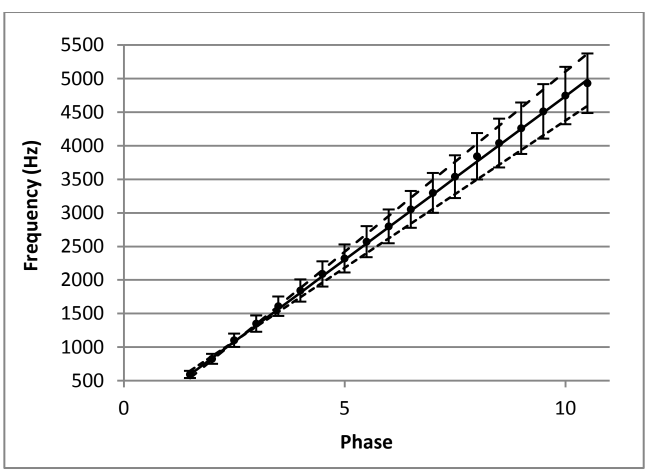

Figure 2: Sound wave frequency at phase intervals in N_2 gas at room temperature. The frequencies of the sound waves in N_2 gas were recorded using an oscilloscope at each instance when the generated waves were in phase and out of phase with the received waves. Error bars are based on a 9% error in the measurements of the oscilloscope. Maximum and minimum inclinations and a regression were generated using a Monte Carlo analysis technique.[3] Similar analysis was conducted for each trial. The frequencies displayed are from trial 1. The regression and error in the regression for trials 2 and 3 are found in Table 2.

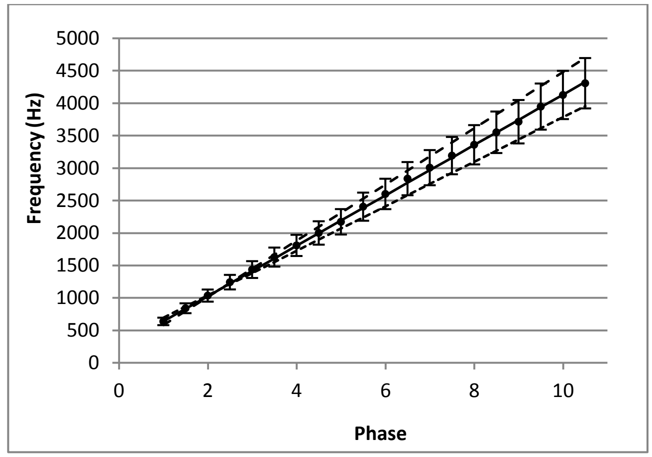

Figure 3: Sound wave frequency at phase intervals in CO_2 gas at room temperature. The frequencies of the sound waves in CO_2 gas were recorded using an oscilloscope at each instance when the generated waves were in phase and out of phase with the received waves. Error bars are based on a 9% error in the measurements of the oscilloscope. Maximum and minimum inclinations and a regression were generated using a Monte Carlo analysis technique.[3] Similar analysis was conducted for each trial. The frequencies displayed are from trial 1. The regression and error in the regression for trials 2 and 3 are found in Table 2.

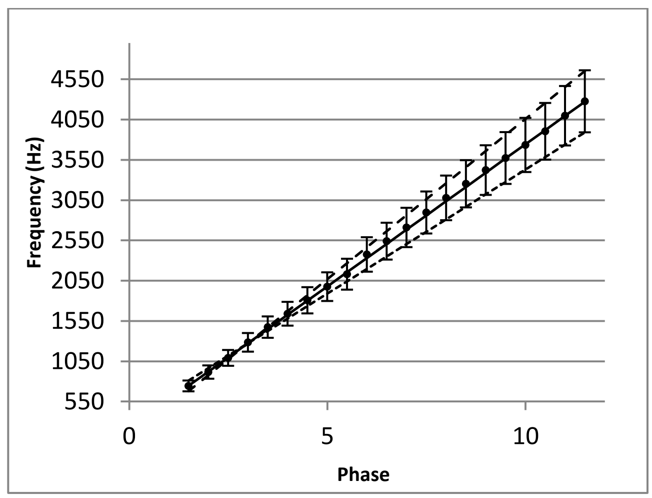

Figure 4: Sound wave frequency at phase intervals in CO_2 gas at temperatures lowered using dry ice. The frequencies of the sound waves in CO_2 gas were recorded using an oscilloscope at each instance when the generated waves were in phase and out of phase with the received waves. Error bars are based on a 9% error in the measurements of the oscilloscope. Maximum and minimum inclinations and a regression were generated using a Monte Carlo analysis technique.[3] Similar analysis was conducted for each trial. The frequencies displayed are from trial 3. The regression and error in the regression for trials 1 and 2 are found in Table 2.

TABLES

Table 1: Comparison between theoretical and experimental values for heat capacity at constant volume of CO_2 gas at different temperatures

Trial	Temperature (K)	Theoretical C_V $\left(\frac{J}{mol\ K}\right)$	Average Theoretical C_V $\left(\frac{J}{mol\ K}\right)$	Experimental C_V $\left(\frac{J}{mol\ K}\right)$	Average Experimental C_V $\left(\frac{J}{mol\ K}\right)$	Error in Experimental C_V
	Room Temperature		28.68		27	
1	295.1	28.69		26		±40
2	294.5	28.69		24		±30
3	293.6	28.65		30		±50
	Lowered Temperature		23.67		28	
1	246.0	23.67		26		±50
2	247.0	23.67		29		±50
3	248.0	23.67		28		±40

Table 2: Slopes with corresponding errors in the observed frequency of sound waves measured at in and out of phase intervals in various media[3]

Medium	Trial	$\frac{df}{dn}$ (s^{-1})	Average $\frac{df}{dn}$ (s^{-1})	Error	Average Error
Air			475		50
	1	470		50	
	2	478		50	
	3	476		50	
Nitrogen			493		60
	1	488		50	
	2	495		70	
	3	494		50	
Carbon Dioxide			387		50
Room Temperature	1	388		50	
	2	392		50	
	3	382		50	
Carbon Dioxide			353		50
Lowered Temperature	1	355		60	
	2	351		50	
	3	353		40	

REFERENCES

[1]Silbey, R. J.; Alberty, R.A.; Bawendi, M.G. Rotational and Vibrational Spectroscopy. In *Physical Chemistry,* 4th Edition; Brennan, D.; McFadden, P.; Batey, M, Eds.; John Wiley & Sons, Inc: Hoboken, NJ, 2005; p 487.

[2]CRC Handbook of Chemistry and Physics, 82th ed.; Lide, D.R.., Ed.; CRC Press: Boca Raton, FL, 2002.

[3]Pounds, A.J. Mercer University, Macon, GA. Personal Communication, 2011.