Experimental Determination of Gaseous Heat Capacity via Sound Velocity Measurements

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The overall goal of this experiment was to independently measure the constant volume heat capacity for CO_2 at different temperatures via sound velocity measurements. The relationship between sound velocity u and constant volume heat capacity C_v is:

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

where C_p is the constant pressure heat capacity, R is the ideal gas law constant, M the molar mass and T is temperature. By rearranging Equation 1, constant volume heat capacity is expressed as:

$$C_v = \frac{R^2T}{Mu^2 - RT} \qquad (2)$$

In this experiment, the sound velocity of CO_2 was determined through sound velocity measurements with air and nitrogen. Using the literature values for u of the two gases allowed the instrument to be calibrated. Graphs were made of frequency versus n where n is 1, 2, 3, etc. for in-phase figures and n is 1/2, 3/2, 5/2, etc. for out-of-phase figures (Figure 1). Taking the derivative of the standard wave relationship (Equation 3) resulted in an equation relating slope $\frac{df}{dn}$ to the sound velocity u and length of tube l (Equation 4). Next, the equation was arranged to solve for length (Equation 5).

$$f = nuL \qquad (3)$$

$$\frac{df}{dn} = \frac{u}{L} \qquad (4)$$

$$L = \frac{u}{\frac{df}{dn}} \qquad (5)$$

The Monte Carlo method was used to determine the error in slopes since there was a 9% error associated with the observed frequency (Table 1).[1] Since the data for nitrogen and air had approximately the same error, there was not much difference in using one gas over the other to calculate C_v. In this case air was used which has a sound velocity of 343.8 m/s at 40% humidity and 297 K.[2] An average tube length of 1.16 m was calculated in comparison to the measured tube length of 0.90 m.

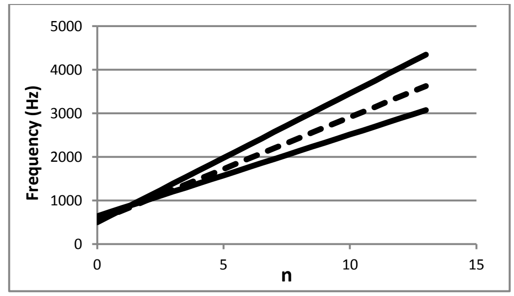

Figure 1. Sample graph of air trial using Monte Carlo Method for error analysis. The high and low boundaries are shown with the recalculated line equation in the between.

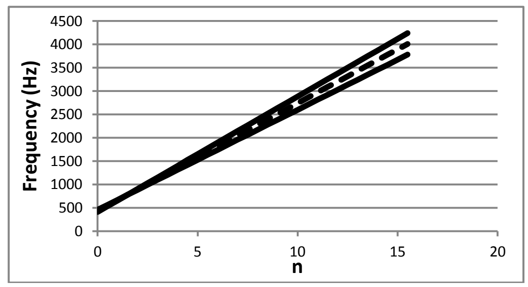

Figure 2. Sample graph of CO_2 trial at 297 K using Monte Carlo Method for error analysis. The high and low boundaries are shown with the recalculated line equation in the between.

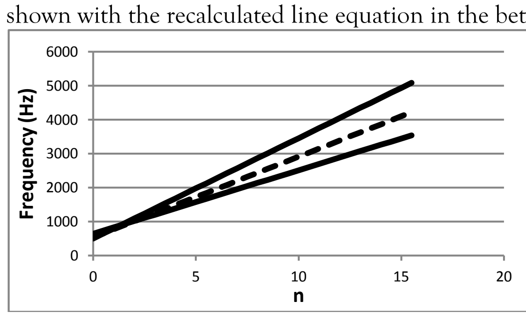

Figure 3. . Sample graph of CO_2 trial at 253.7 K using Monte Carlo Method for error analysis. The high and low boundaries are shown with the recalculated line equation in the between.

	Trial 1	Trial 2	Trial 3
Air	300±30	300± 30	300 ± 30
N_2	300±30	300±30	300±30
CO_2 at 297K	230 ±20	240±30	230±20
CO_2 at 253.7 K	210 ±30	210±20	210± 30

Table 1. Slopes of air, N_2 and CO_2 trials with associated error calculated from the Monte Carlo Method.

For CO_2, experiments were done at 297K and 253.7 K. Graphs of frequency and phase were plotted again (Figures 2 and 3), and the average length from the previous section was used to calculate an average slope. With the average length and the average slope calculated, it was possible to derive an equation for sound velocity for CO_2 which was then substituted into Equation 2 to give:

$$C_v = \frac{R^2T}{M*\left(\frac{1}{9}\left(\frac{u_{air}}{\left(\frac{df}{dn}\right)_{air1}}+\frac{u_{air}}{\left(\frac{df}{dn}\right)_{air2}}+\frac{u_{air}}{\left(\frac{df}{dn}\right)_{air3}}\right)*\left(\left(\frac{df}{dn}\right)_{CO_{2,1}}+\left(\frac{df}{dn}\right)_{CO_{2,2}}+\left(\frac{df}{dn}\right)_{CO_{2,3}}\right)\right)^2 - RT} \quad (6)$$

where the subscript associated with $\frac{df}{dn}$ refers to the trial number.

The associated slope for C_v was also calculated for both CO_2 experiments, as determined by:

$$Error = \left[\left(\frac{\partial C_v}{\partial\left(\frac{df}{dn}\right)_{air1}}\right)^2 (\sigma)^2 + \left(\frac{\partial C_v}{\partial\left(\frac{df}{dn}\right)_{air2}}\right)^2 (\sigma)^2 +\right.$$

∂𝐶𝑣∂𝑑𝑓𝑑𝑛𝑎𝑖𝑟32𝜎2+∂𝐶𝑣∂ 𝑑𝑓𝑑𝑛𝐶𝑂2,12𝜎2+∂𝐶𝑣∂ 𝑑𝑓𝑑𝑛𝐶𝑂2,12𝜎2+∂𝐶𝑣∂ 𝑑𝑓𝑑𝑛𝐶𝑂2,22𝜎2+∂𝐶𝑣∂ 𝑑𝑓𝑑𝑛𝐶𝑂2,32𝜎2+∂𝐶𝑣∂𝑇2𝜎212

In which each σ is the error associated with the preceding variable in the equation. For temperature, the listed error was 1% of the observed temperature in Celsius.

For CO_2 at 297K and 253.73K, the C_v was 30±20 J/mol K and 30 ±30 J/mol K respectively (Table 2).

The empirical C_v was compared to the theoretical value by using $C_v = \frac{5}{2}R + C_{vibr}$, given that $C_{vibr} = R\sum_{i=1}^{4}\frac{\left(\frac{hcv_i}{kT}\right)^2 e^{\frac{hcv_i}{kT}}}{\left(e^{\frac{hcv_i}{kT}}-1\right)^2}$ and v_i refers to the four normal vibrational frequencies for CO_2.[3] The theoretical values for CO_2 at 297K and 253.73K, the C_v was 28.7 J/mol K and 26.7 J/mol K respectively.

	Measured C_v (J/mol K)	Theoretical C_v (J/mol K)
CO_2 at 297 K	30±20	28.7
CO_2 at 253.7 K	30 ±30	26.7

Table 2. Measured and theoretical Cv values for CO_2 at 297 K and 353.7 K.

REFERENCES

1. Pounds, A.J. Mercer University, Macon, GA. Personal Communication, 2011.
2. CRC Handbook of Chemistry and Physics; 7th ed. Boca Raton, FL, 1990; pp E44-E46.
3. Silbey, R.J.;Alberty, R.A.; Bawendi, M.G. Physical Chemistry. 4th ed. Wiley Hoboken, NJ,2004;pp 487.