# Determination of Vibrational Heat Capacity of $CO_2$ by Sound Velocity Measurements

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*KEYWORDS: Vibrational Heat Capacity ($C_v$), temperature, sound velocity*

**ABSTRACT:**

RESULTS:

Sound velocity values were experimentally acquired for air at room temperature, $N_2$ at room temperature, $Co_2$ at room temperature, and $CO_2$ cooled by dry-ice to about -71.0 □C. The collected data was then used to calculate the constant volume heat capacity for $CO_2$ ($C_v$) at different temperatures.

During experimentation, the lab conditions were as follows: the room temperature was 19.5 □C (292.65 K), atmospheric pressure was 754.4 mmHg, and the relative humidity was 47%. The frequencies at which the sound waves in phase and out of phase were recorded with reference to their appropriate phase numbers. The linear portion of each data set was used in the following calculations. The Monte Carlo method was used to determine the error in the slope of the experimental data sets. The following figures include the raw data points used with their regression coeffients , which is the average slope of the data. The figures also include the maximum and minimum inclination according to the 9% error due to the instrumentation. Accepted data from trial 1 of the $N_2$ trials with the aformentioned data analysis is displayed below in Figure 1 as a representative set from the conducted trials. Figure 2 is a plot of the accepted data from trial 1 from the air trials. Figure 3 and 4 display the data of trials 1 of the room-temperature and dry-ice trials of $CO_2$, respectively, in the same manner as was done for the air and $N_2$ trials. Table 1 displays the regression coefficients for each trial.

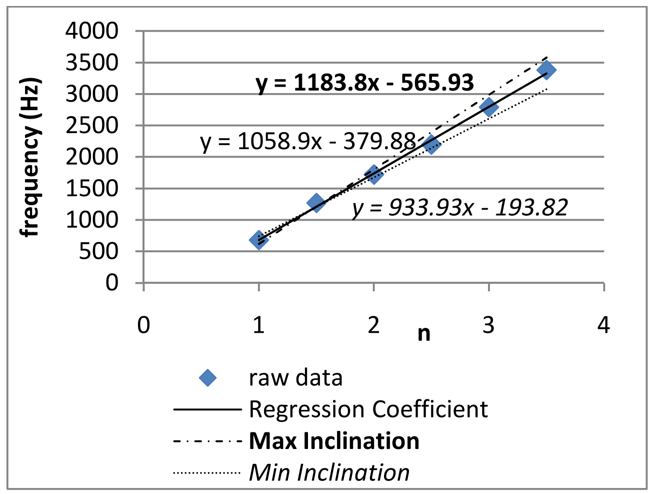


Figure 1. $N_2$ at room temperature as gas medium - Trial1

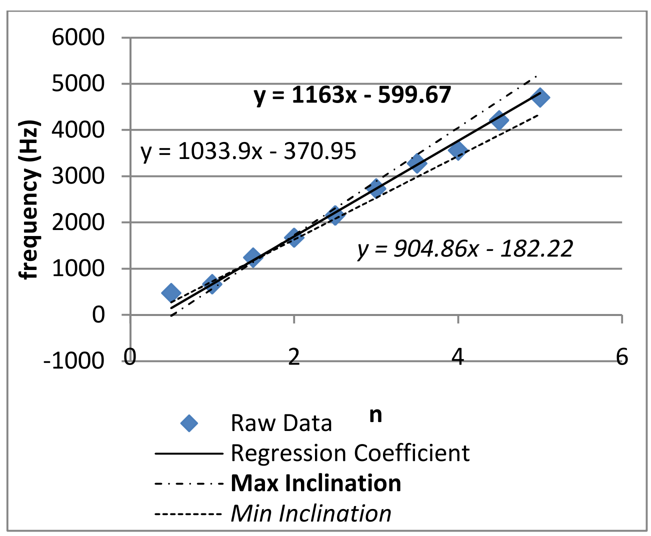

Figure 2. Air at Room Temperature as gas medium-Trial 1

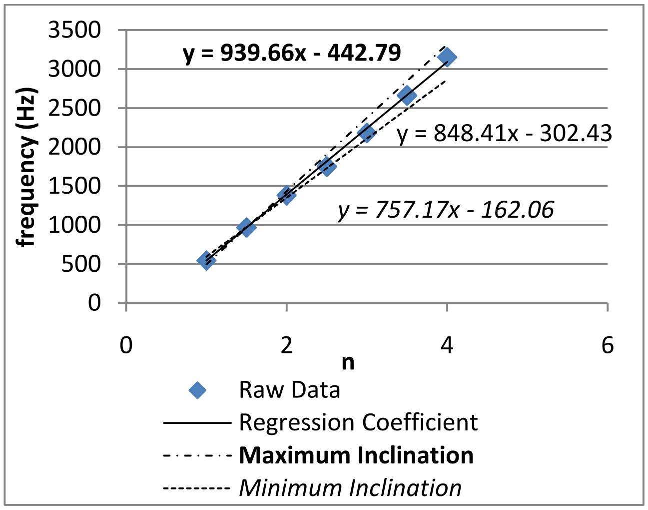


Figure 3. $CO_2$ at Room Temperature as gas medium-Trial 1

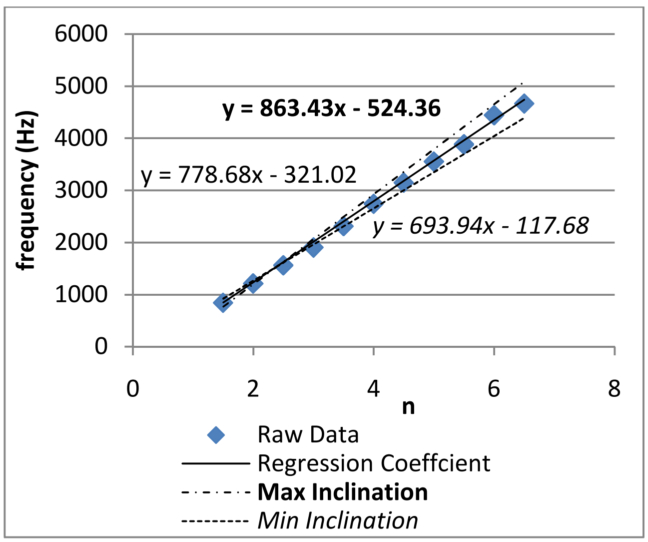


Figure 4. $CO_2$ cooled with dry-ice as gas medium-Trial 1

Table 1. Regression Coefficients $\left(\frac{df}{dn}\right)$ [1/s]

| | Trial 1 | Trial 2 | Trial 3 |
|---|---|---|---|
| $N_2$ | 1058.88 | 1061.29 | 1060.76 |
| Air | 1033.94 | 1032.83 | 1033.40 |
| $CO_2$ at RT | 848.41 | 850.16 | 849.33 |
| $CO_2$ at -71.0 □C (202.15 K) | 778.68 | 778.41 | 777.84 |

Table 2 below displays the average slopes for each condition with their associated error. This initial calculation of error was done using the equation $Err_{avg} = \sqrt{err_{T1}{}^2 + err_{T2}{}^2 + err_{T3}{}^2}$.

Table 2. Average slopes $\left(\frac{df}{dn}\right)$ with associated error

| | Slope with error |
|---|---|
| $N_2$ | 1060.31 +/- 72.82 |
| Air | 1033.39 +/- 74.48 |
| $CO_2$ at RT | 849.30 +/- 52.95 |
| $CO_2$ at -71.0 □C (202.15 K) | 778.31 +/- 48.74 |

The data from either the air or $N_2$ could have been used for this calculation of the experimental tube length. Arbitrarily, the $N_2$ data sets were used for the calculations. The slopes from the $N_2$ trials $\left(\left(\frac{df}{dn}\right)_{N_2}\right)$ were used with literature values of the velocity of sound in $N_2$ to mathematically determine the length of the tube used throughout the experiments. The literature value for the speed of sound in nitrogen $(u_{N_2})$ is 334 m/s [1]. This value was corrected for the difference in temperature using the following equation.

$$u = \sqrt{\frac{RT\gamma}{M}} \qquad (1)$$

where $R$ is the gas constant 8.314 J/ mol*K, $T$ is temperature in Kelvin, $\gamma$ is 7/5 for $N_2$, and $M$ is the molar mass in kilograms. The corrected velocity was determined to be 349.45 m/s.

The corrected velocity using (1) and the experimental slopes $\left(\left(\frac{df}{dn}\right)_{N_2}\right)$ were used to calculate the length of the tube using the equation

$$L = \frac{u}{\left(\frac{df}{dn}\right)_{N_2}} \qquad (2)$$

The calculated lengths for each $N_2$ trial was averaged to get a tube length of 0.330 m. The tube length was measured in lab to be approximately 0.283 m. The calculated tube length was then use as a known value for further calculations of vibrational heat capacity $(C_v)$ involving the $CO_2$ data.

The equation to determine $C_v$ was derived from the equation

$$u^2 = \frac{\gamma RT}{M} = \frac{\left(\frac{C_p}{C_v}\right) RT}{M} \qquad (3)$$

where $M$ is the molar mass in kg. $C_p = C_v + R$ therefore (3) can be rewritten in terms of $C_v$ as follows

$$C_v = \frac{R^2 T}{(u_{CO_2}{}^2 * M) - RT} \qquad (4)$$

Equation (2) was substituted into the equation $u_{CO_2} = \left(\frac{df}{dn}\right)_{CO_2} * \text{L}$ to form the equation

$$u_{CO_2} = \left(\frac{df}{dn}\right)_{CO_2} * \left(\frac{u_{N_2}}{\left(\frac{df}{dn}\right)_{N_2}}\right) \qquad (5)$$

(4) and (5) were then used to derive the equation

$$C_v = \frac{R^2 T}{\left(-RT + \frac{M(\frac{df}{dn})_{CO_2}^{\;2} * u_{N_2}}{(\frac{df}{dn})_{N_2}^{\;2}}\right)} \qquad (6)$$

This equation was then used to calculate the $C_v$ for $CO_2$ at both room temperature and cool by dry ice.

The following values were used in the calculation of $C_v$.

Table 3. $C_v$ calculation values

| | Room Temp $CO_2$ | Dry Ice $CO_2$ |
|---|---|---|
| M | 0.04401 kg | 0.04401 kg |
| T | 292.65 K | 202.15 K |
| $u_{N_2}$ | 349.45 m/s | 349.45 m/s |
| $(\frac{df}{dn})_{CO_2}$ | 849.30 $s^{-1}$ | 778.31 $s^{-1}$ |
| $(\frac{df}{dn})_{N_2}$ | 1060.31 $s^{-1}$ | 1060.31 $s^{-1}$ |
| $C_v$ | 19.93 J/K | 11.50 J/K |

The error in the temperature values were calculated using the equation

$$Err_T = 0.01 * T \qquad (7)$$

Table 4 displays the error terms for both $CO_2$ conditions for the various components of the $C_v$ calculations.

Table 4. Error components of $C_v$ calculations

| | $CO_2$ at RT | $CO_2$ at -71.0 □C |
|---|---|---|
| $(\frac{df}{dn})_{CO_2}$ | +/- 52.95 | +/- 48.74 |
| $(\frac{df}{dn})_{N_2}$ | +/- 72.82 | +/- 72.82 |
| $u_{N_2}$ | +/- 1.747 | +/- 1.747 |
| T | +/- 2.927 | +/- 2.022 |

These values were used in the equation

$$Err_{C_v} = Sqrt\left[\left(\frac{dC_v}{d\left(\frac{df}{dn}\right)_{CO_2}}\right)^2 * \left(err\left(\frac{df}{dn}\right)_{CO_2}\right)^2 + \left(\frac{dC_v}{d\left(\frac{df}{dn}\right)_{N_2}}\right)^2 * \left(err\left(\frac{df}{dn}\right)_{N_2}\right)^2 + \left(\frac{dC_v}{du_{N_2}}\right)^2 * (err u_{N_2})^2 + \left(\frac{dC_v}{d\text{T}}\right)^2 * (err\text{T})^2\right]$$

(8)

The error in $C_v$ was calculated to be +/- 12.60 for RT and +/- 5.11 for dry ice.

The theoretical value of $C_v$ was calculated with the equation

$$C_v = \left(\frac{5}{2}\right)R + C_{vib} \qquad (9)\ [3]$$

and $C_{vib}$ was calculated using the equation with the vibrational constant provided in Table 5.

$$C_{vib} = R * \sum_{i=1}^{i=4} \frac{\left(\frac{hcv_i}{KT}\right)^2 * e^{\frac{hcv_i}{KT}}}{\left(e^{\frac{hcv_i}{KT}} - 1\right)^2} \qquad (10)$$

Table 5. Vibrational constant values for $CO_2$ [2]

| Vibrational mode number | Value ($cm^{-1}$) |
|---|---|
| $v_1$ | 1330 |
| $v_2$ | 667 |
| $v_3$ | 2349 |
| $v_4$ | 2349 |

The theoretical $C_v$value was solved for using the $C_{vib}$ value in (10). The values are complied in Table 6.

Table 6. Calculated $C_v$ values, associated error and Theoretical $C_v$ values

| | $C_v$ | $C_v$ error | Theo $C_v$ |
|---|---|---|---|
| Room Temp $CO_2$ | 19.93 | +/- 12.60 | 32.20 |
| Dry Ice $CO_2$ | 11.50 | +/- 5.11 | 25.75 |

This analysis shows that the experimental values for room temperature are acceptable, but the dry ice values fell slighly short of the theoretical values.

## REFERENCES

[1] CRC Handbook of Chemistry and Physics, $70^{th}$ ed., Boca Raton, FL, 1990. E44 & E47.

[2] http://www.uotechnology.edu.iq/appsciences/physics/lecture/physics/four_class/spectral%20analysis/3.pdf. Sept 30, 2011.

[3] Pounds, A. Lab Manual: Experimental Determination of Gaseous Heat Capacity via Sound Velocity. 2011

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