

## PHYS3113 – Flammersfeld Oscillator

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This experiment using Flammersfeld Oscillations predicts the adiabatic constants for Air,  $N_2$  and  $CO_2$  and predicts the contribution of vibrational modes of  $CO_2$  to the heat capacity. The experimental values of adiabatic constants were  $\chi_{Air} = 1.375 \pm 0.014$ ,  $\chi_{N_2} = 1.4104 \pm 0.0099$  and  $\chi_{CO_2} = 1.2966 \pm 0.0052$  all within their theoretical range. The experimental value of vibrational contribution to  $C_V$  was  $\delta C_V = 0.872 \pm 0.059$  was within 1.9% of the theoretical value and the experimental value for the bending mode of  $CO_2$ ,  $\omega = 675 \pm 31 \text{ cm}^{-1}$  was within 1.2% of the theoretical value.

### INTRODUCTION

The aim of this experiment is to find the adiabatic constant of various gases/gaseous combinations as well as finding the vibrational contribution to  $C_V$  of  $CO_2$ . The Flammersfeld Oscillation experiment sets up a frictionless oscillating mass which oscillates with a period proportional the adiabatic constant. Given a static mass, the pressure equilibrium of the mass is (all derivation sourced from Student Notes [1]);

$$p = p_0 + \frac{mg}{\pi r^2}, \quad [1]$$

and by letting a small displacement of the mass be  $x(t)$ , the equation of motion of the mass is;

$$m \frac{d^2 x}{dt^2} = \pi r^2 \delta p(x). \quad [2]$$

Since the oscillation is relatively quick, we can take the process as being adiabatic. For a single gas, by differentiating the adiabatic equation w.r.t  $x$ ;

$$pV^\chi = \text{const}, \quad [3]$$

the small change in pressure due to the small displacement can be expressed as;

$$\delta p(x) = -\chi p \frac{\delta V(x)}{V}, \quad [4]$$

where  $\delta V(x) = \pi r^2 x$  is the small change in volume due to the small displacement. By substituting equation [4] into equation [2], the equation of motion can be expressed as;

$$\frac{d^2 x}{dt^2} + \Omega^2 x(t) = 0, \quad [5]$$

where the frequency of oscillation can be expressed as;

$$\Omega = \pi r^2 \sqrt{\frac{\chi p}{mV}}. \quad [6]$$

The final expression for adiabatic constant  $\chi$  can then be expressed as;

$$\chi = \frac{4mV}{\pi r^4 \tau^2}. \quad [7]$$

If multiple gases are present with partial pressures and adiabatic constants,  $p_1, p_2, \chi_1, \chi_2$ , then the expression for total  $\chi$  can also be expressed as;

$$\chi = \frac{p_1 \chi_1 + p_2 \chi_2}{p_1 + p_2}. \quad [8]$$

The value of  $\chi$  equated through the gases degrees of freedom is given by the equation;

$$\chi = 1 + \frac{2}{f}. \quad [9]$$

The value of  $f$  is dependent on temperature as the vibrational modes of molecules quantified by their frequency  $\omega$ , become active at certain temperatures. The affect this has on the heat capacity at a specific temperature  $T$  is described by the equation (perfectly derived in section 2.3 of the Student Notes [1]);

$$\delta C_V = \frac{\omega^2}{T^2} \frac{e^{\frac{\omega}{T}}}{\left(e^{\frac{\omega}{T}} - 1\right)^2}. \quad [10]$$

At high temperatures where  $T \gg \omega$ ,  $\delta C_V \approx 1$  and at low temperatures where  $T \ll \omega$ , the vibrational contribution vanishes exponentially. The total  $C_V$  is described by;

$$C_V = (C_V)_0 + \delta C_V. \quad [11]$$

To find the value of  $\delta C_V$  experimentally, the value is determined through the equation;

$$\delta C_V = \frac{1}{\chi - 1} - (C_V)_0, \quad [12]$$

and to find the value of  $\omega$  experimentally, the value of  $\frac{\omega}{T}$  is read from FIG. 1;

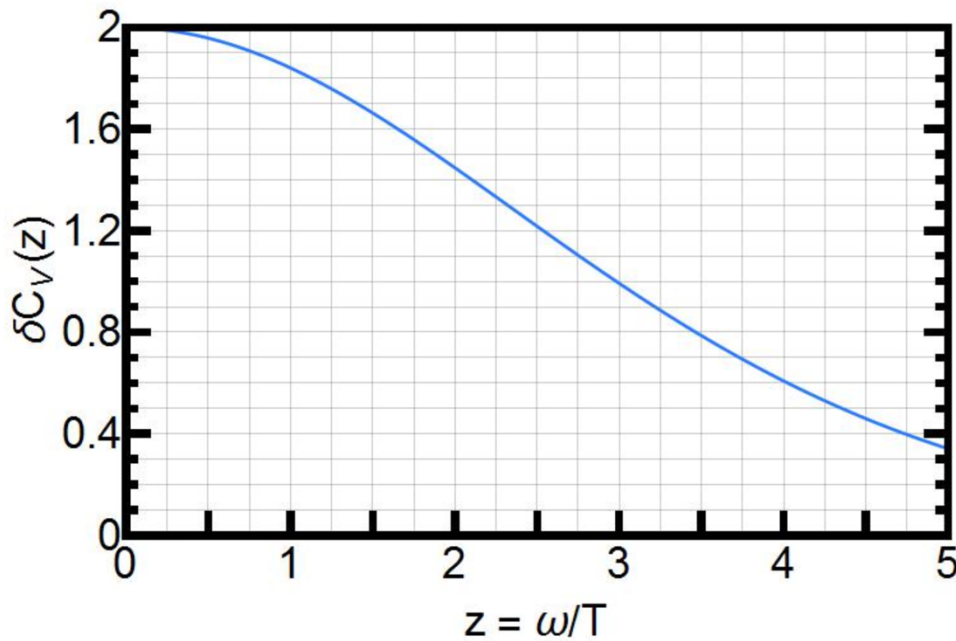


FIG. 1: Vibrational contribution to the heat capacity of  $\text{CO}_2$  (seen in section 2.3 of the Student Notes [1].)

Uncertainties for calculations were estimated to 2.d.p using the independent uncertainty formula for a function  $f(a, b, c, \dots)$ ;

$$\Delta f(a, b, c, \dots) = \sqrt{\left(\Delta a \times \frac{\partial f}{\partial a}\right)^2 + \left(\Delta b \times \frac{\partial f}{\partial b}\right)^2 + \left(\Delta c \times \frac{\partial f}{\partial c}\right)^2 + \dots}, \quad [13]$$

and values were taken to the decimal place of its uncertainty.

## METHOD

### Experiment 1: Air

1. Adjust the counter emitter in such a way that the optical path crosses the bottle neck at the position of the hole.
2. Insert the red cylinder (oscillator mass) in the bottle neck.
3. Plug the aquarium pump into the power socket. This will make the pump turn on.
4. Adjust the valve in order to get the right air flow to the Flammersfeld bottle such to get steady oscillations.
5. Press the “set” button of the counter and record the time it to count 300 oscillations.
6. Repeat the Step 5 three times.
7. Once finished, unplug the aquarium pump.

### Experiment 2: $N_2$ and $CO_2$

1. Select a  $N_2$  using the gas selector valve.
2. Reset the fine control valve to closed then rotate it anticlockwise by 1/4-1/2 a turn.
3. Reset the aspirator bottle valve to closed then rotate it anticlockwise by 3-5 turns.
4. Insert the red cylinder (oscillator mass) in the bottle neck.
5. Open the gas regulator knob clockwise until the oscillator starts to go up.
6. Using the aspirator bottle valve, adjust gas flow to get steady oscillations.
7. Let the  $N_2$  flow through the system for about 10 minutes to ensure any previous gas is purged from the system.
8. Press the “set” button of the counter and record the time it to count 300 oscillations.
9. Repeat the Step 8 three times.
10. When finished, reduce the pressure to zero by turning the regulator knob slowly.
11. Repeat steps 1-10 using  $CO_2$  gas.

## RESULTS & ANALYSIS

Environmental and experimental constants;

$$T = 295.95K, \quad P_0 = 101.84kPa, \quad V = 1.155 L, \quad r_0 = 5.95 \times 10^{-3} m, \quad m_0 = 4.5784 g. \quad [14]$$

All uncertainty for the environmental and experimental constants are taken to half their absolute accuracy.

The time for the mass to complete 300 oscillations and the average period for a single oscillation for each gas are;

**Table 1: Experimental values of period for each gas.**

Gas	$t_{300} (s)$	$\tau (s)$
Air	$103.96 \pm 0.52$	$0.3465 \pm 0.0017$
$N_2$	$102.64 \pm 0.34$	$0.3421 \pm 0.0011$
$CO_2$	$107.05 \pm 0.08$	$0.3568 \pm 0.0003$

By substituting values from equation line [14] into equation [1] the pressure on the mass can be found;

$$p = (101.84 \pm 0.005 \times 10^3) + \frac{(4.5784 \pm 0.00005 \times 10^{-3})(9.8 \pm 0.05)}{\pi(5.95 \pm 0.005 \times 10^{-3})^2}, \quad [15]$$

$$= 102.2434 \pm 0.0054 kPa. \quad [16]$$

Uncertainties of  $p$  were calculated using equation [13];

$$\Delta p(P_0, m_0, g_0, r_0) = \sqrt{\left(\Delta P_0 \times \frac{\partial p}{\partial P_0}\right)^2 + \left(\Delta m_0 \times \frac{\partial p}{\partial m_0}\right)^2 + \left(\Delta g_0 \times \frac{\partial p}{\partial g_0}\right)^2 + \left(\Delta r_0 \times \frac{\partial p}{\partial r_0}\right)^2} \Bigg|_{P_0, m_0, g_0, r_0}. \quad [17]$$

Using equation [7], the experimental values for the adiabatic constant  $\chi$  can be found;

$$\chi_{Air} = 1.375 \pm 0.014, \quad \chi_{N_2} = 1.4104 \pm 0.0099, \quad \chi_{CO_2} = 1.2966 \pm 0.0052. \quad [18]$$

Uncertainties of  $\chi_i$  were calculated using equation [13];

$$\Delta \chi_i(m_0, V_0, p, r_0, \tau_i) = \sqrt{\left(\Delta m_0 \times \frac{\partial p}{\partial m_0}\right)^2 + \left(\Delta V_0 \times \frac{\partial p}{\partial V_0}\right)^2 + \left(\Delta p \times \frac{\partial p}{\partial p}\right)^2 + \left(\Delta r_0 \times \frac{\partial p}{\partial r_0}\right)^2 + \left(\Delta \tau_i \times \frac{\partial p}{\partial \tau_i}\right)^2} \Bigg|_{m_0, V_0, p, r_0, \tau_i}. \quad [19]$$

Gases  $N_2$  and air which is majorly composed of 78%  $N_2$ , 21%  $O_2$  are diatomic thus have degrees of freedom of  $f = 6$  of which 1 is vibrational and  $CO_2$  is triatomic with degrees of freedom  $f = 9$  of which 4 are vibrational. At the temperature of the experiment, all of the vibrational degrees of freedom should be mostly sterile (check further into the report to quantify this statement). Using equation [9] the theoretical value range of  $\chi$  for each gas can be found;

$$\chi_{Air} = \chi_{N_2} = [1.33, 1.40], \quad \chi_{CO_2} = [1.22, 1.40]. \quad [20]$$

The lower limits in equation line [20] presumes all vibrational degrees of freedom are active and the converse for the upper limit. The vibrational mode of  $N_2$  and  $O_2$  are high thus their adiabatic constant should be close to the top of their range which is seen by comparing equation line [18] and [20] (The vibrational mode of  $O_2$  is lower than that of  $N_2$  thus  $\chi_{Air}$  should theoretically be lower than that of  $\chi_{N_2}$  but not to the degree of which is exhibited experimentally). 2 of  $CO_2$ 's vibrational modes are bending modes which are comparably lower, thus could have some effect on  $\chi_{CO_2}$  and thus sits closer to its lower limit which is again seen by comparing equation line [18] and [20].

To quantify the effect the partly active vibrational modes have on  $CO_2$ 's adiabatic constant experimentally, substitute the value for  $\chi_{CO_2}$  into equation [12] where  $(C_V)_0 = \frac{f_T + f_R}{2} = \frac{5}{2}$ ;

$$\delta C_V = \frac{1}{(1.2966 \pm 0.0052) - 1} - \frac{5}{2}, \quad [21]$$

$$= 0.872 \pm 0.059. \quad [22]$$

Uncertainties of  $\delta C_V$  were calculated using equation [13];

$$\Delta \delta C_V(\chi_{CO_2}) = \sqrt{\left( \Delta \chi_{CO_2} \times \frac{\partial p}{\partial \chi_{CO_2}} \right)^2} \bigg|_{\chi_{CO_2}} . \quad [23]$$

The value of  $\frac{\omega}{T}$  are read from FIG. 1 (was read to pixel accuracy seen in Annex (1));

$$\frac{\omega}{T} = 3.29. \quad [24]$$

As uncertainties are difficult to read off a graph, the value was also estimated through numerical methods (uncertainty taken as biggest difference in value from inputting the uncertainty of  $\delta C_V$ ) which produced the value of;

$$\frac{\omega}{T} = 3.29 \pm 0.15. \quad [25]$$

The values of the two estimation methods are extremely close so the uncertainty found through numerical methods will be used.

Thus, the experimental value of the vibrational mode in  $K$  is;

$$\omega = (3.29 \pm 0.15)(295.95 \pm 0.05), \quad [26]$$

$$= 973 \pm 44 \text{ K}, \quad [27]$$

$$= 675 \pm 31 \text{ cm}^{-1}. \quad [28]$$

Uncertainties of  $\omega$  were calculated using equation [13];

$$\Delta \omega \left( \frac{\omega}{T}, T \right) = \sqrt{\left( \Delta \frac{\omega}{T} \times \frac{\partial p}{\partial \frac{\omega}{T}} \right)^2 + \left( \Delta T \times \frac{\partial p}{\partial T} \right)^2} \bigg|_{\frac{\omega}{T}, T} . \quad [29]$$

The theoretical value for  $\omega$  for the bending modes of  $CO_2$  (found in section 2.1 of Student Notes [1]);

$$\omega = 667 \text{ cm}^{-1}. \quad [30]$$

Using  $T$  from equation line [14] and  $\omega$  from equation [30], the theoretical value for  $\frac{\omega}{T}$  is;

$$\frac{\omega}{T} = 3.245. \quad [31]$$

By substituting  $\frac{\omega}{T}$  into equation [10] and doubling as there are 2 identical bending modes of  $CO_2$ , the theoretical value of the total vibrational contribution of the bending modes of  $CO_2$  is;

$$\delta C_V = 2(3.245)^2 \frac{e^{(3.245)}}{(e^{(3.245)} - 1)^2} = 0.8886. \quad [32]$$

## DISCUSSION

The predictions of the adiabatic constants for each gas were very accurate all falling within the range of the theoretical ranges. The adiabatic constant for the triatomic gas  $CO_2$  was expectedly lower than that of the 2 diatomic gases. This is due to some vibrational modes being active where in the diatomic molecules the temperature was not high enough. The adiabatic constants for  $N_2$  and Air (combination of  $N_2$  and  $O_2$ ) are theoretically meant to be the same but they do differ. The vibrational mode of  $O_2$  is  $\omega \approx 2000 \text{ cm}^{-1}$  where the vibrational mode of  $N_2$  is  $\omega \approx 2700 \text{ cm}^{-1}$  thus there should be a higher proportion of vibrational contribution in  $O_2$  but this could not cause a quantifiable difference in adiabatic constants. The difference is produced by error most likely due to the difference in gas application. The Air was put into the system by a pump which could have more variance in flow rate where the  $N_2$  was placed into the system through a regulator. This can be seen in the uncertainty of each period value where that of Air is almost twice as large.

The prediction for  $\delta C_V$  and for the bending mode of  $CO_2$  were very accurate having a difference of 1.9% and 1.2% respectively. The values were extremely accurate, but the uncertainty ranges of the values were approximately 5% each thus the abnormal accuracy must be analysed carefully. This accuracy is most likely due to the 'idealisation' of the apparatus. The hole in the tube neck turns a static system into a steady flow system but where the flow is extremely slow. In doing so the apparatus negates the damping of friction while introducing minimal error itself which for air and  $N_2$  can be ignored completely but for  $CO_2$  can be significant but the small gas flow ensures this is kept to a minimum.

## CONCLUSION

The experiment was successful in predicting the adiabatic constants for Air,  $N_2$  and  $CO_2$  and was successful in predicating the contribution of vibrational modes of  $CO_2$  to the heat capacity. The experimental values of adiabatic constants were  $\chi_{\text{Air}} = 1.375 \pm 0.014$ ,  $\chi_{N_2} = 1.4104 \pm 0.0099$  and  $\chi_{CO_2} = 1.2966 \pm 0.0052$  all within their calculated range. The experimental value of vibrational contribution to  $C_V$  was  $\delta C_V = 0.872 \pm 0.059$  was within 1.9% of the theoretical value and the experimental value for the bending mode of  $CO_2$ ,  $\omega = 675 \pm 31 \text{ cm}^{-1}$  was within 1.2% of the theoretical value.

## REFERENCES

- [1] UNSW, "Flammersfeld Oscillator Student Notes".

## APPENDIX

(1) Method of reading  $\frac{\omega}{T}$  off FIG. 1.

