



Flammersfeld Oscillator

Student Notes

Never Stand Still

Science

School of Physics

SKILLS GAINED

- Thermodynamics measurements
- Probe of adiabatic constants of gases
- Study of heat capacity of molecular gases

ASSUMED KNOWLEDGE

- Adiabatic process in ideal gases
- Basics of statistical physics
- Basics of mechanics

1 Experimental aim

The first aim is to discover adiabatic constants of gases. It demonstrates the importance of microscopic structure of gas molecules for macroscopic parameters such as frequency of Flammersfeld oscillator. This experiment also allows probing of vibrational modes (bending modes) of carbon dioxide that appear to be not completely frozen out. In other words, the simple oscillator can be used as an infrared spectrometer of gas molecules.

2 Background and theory

2.1 Degrees of freedom

Ideal gas is reasonable approximation of real gases with low densities away from phase transitions. In this case interaction between molecules is negligible and the molecule energy is represented by its kinetic energy. Heat capacity at the constant volume of the gas reservoir, C_V , is determined by the molecule structure and naively, it can be calculated through degrees of freedom, f , of the molecule:

$$C_V = \frac{f}{2} \quad (2.1)$$

For example, if we consider monatomic molecule of argon, Ar, it can only move along three different directions in space. Hence, the translational motion of Ar gives us three degrees of freedom. If we consider gas of diatomic molecules, for example nitrogen, N_2 , total number of degrees of freedom is $f = 3 \times 2 = 6$ because we have two atoms of N with 3 translational degrees of freedom. However, atoms are connected via chemical bond and only 3 degrees of freedom are translational here (motion of the whole molecule). Moreover, we can rotate our molecule around two axes that are perpendicular to the bond. It gives us 2 rotational degrees of freedom. Rotation of the molecule around its axis is equivalent to the identity transformation because the positions of the nitrogen atoms are the same as before the rotation. Hence, it does not change anything. So, we have one more degree of freedom left. It is called vibrational degree of freedom because we move atoms along the bond straining it. Obviously, this degree of freedom is strongly gapped because you need finite energy ω to excite the vibration. Typically, this energy expressed in Kelvins is one order of magnitude bigger than the room temperature $T = 300 K$. In other words, the vibrational mode of the nitrogen molecule (or any diatomic molecule) is totally sterile at room temperature. Then, only 5 degrees of freedom contribute to C_V .

Another important example is triatomic molecules. Total number of degrees of freedom is $f = 3 \times 3 = 9$ and three of them are translational. Further analysis depends on the geometry of a molecule. If the molecule is linear (carbon dioxide CO_2 , hydrogen cyanide HCN , etc.), i.e. all atoms are aligned, then, we have only two rotational degrees of freedom because rotation along the molecule axis is equal to identity (no rotation). It means that the linear triatomic molecule has 4 vibrational degrees of freedom. If the molecule has triangular form (H_2O , OF_2 , etc.), then all three rotations are available. It means that triangular molecule has only three vibrational degrees of freedom. Vibrational modes of H_2O and CO_2 are shown in Fig. 1 with frequencies expressed in cm^{-1} . In order to translate it into Kelvins, you need to multiply those numbers on 1.44. For example, bending mode of CO_2 has frequency $\omega = 667 \times 1.44 = 960 \text{ K}$. It is still 3 times larger than the room temperature. However, as you will see below, bending vibrations will give significant contribution to the adiabatic constant of CO_2 . You will be able to estimate experimentally frequency of bending vibrational modes of CO_2 .

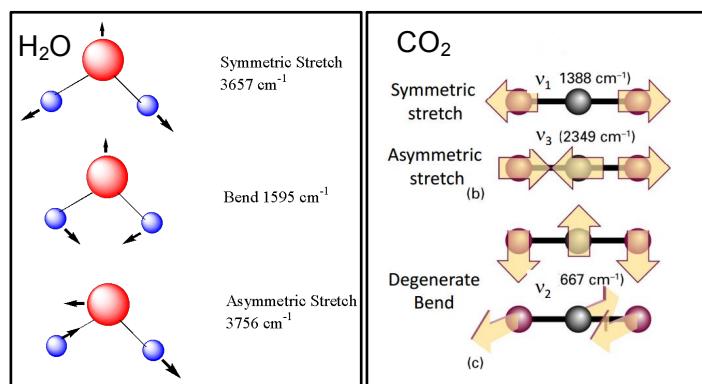


Figure 1. Vibrational modes of H_2O and CO_2 .

Question 1: How many vibrational modes does the methane molecule CH_4 has? PS: the molecule shape is tetrahedron with C at the centre and H at the vertices.

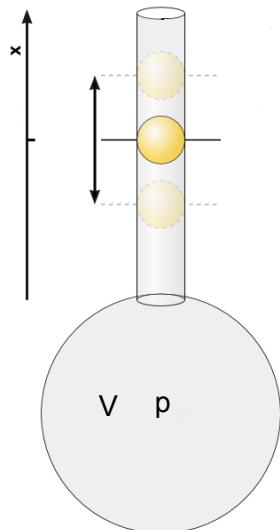


Figure 2. Simplified diagram of the experimental setup.

2.2 Flammersfeld oscillator

The primitive setup is shown on Fig. 2. It consists of a narrow neck bottle filled with a gas under consideration. The bottle is hermetically corked with a ball or cylinder of mass m . The volume of reservoir in equilibrium (when the cork is not moving) is V . Equilibrium pressure reads

$$p = p_0 + \frac{m g}{\pi r^2} \quad (2.2)$$

where p_0 is the atmospheric pressure, r is the radius of the bottle neck, $g = 9.8 \text{ m s}^{-2}$ is the free fall acceleration. Let us hit the cork to initiate oscillations. We neglect friction in our equations because real setup you will work with is modified in a way to maintain steady oscillations without damping. In other words, oscillations will be excited by a resonant force. Let $x(t)$ be a small displacement of the cork from its equilibrium position. Then, the equation of frictionless motion reads:

$$m \frac{d^2x}{dt^2} = \pi r^2 \delta p(x) \quad (2.3)$$

where $\delta p(x)$ is the difference of internal gas pressure from the equilibrium value p when the ball's displacement equals x . Of course, we consider small oscillations when $\delta p \ll p$. In order to find $\delta p(x)$, let us differentiate the adiabatic equation

$$p V^\chi = \text{const} \quad (2.4)$$

where χ is the adiabatic coefficient. Differentiation yields

$$\delta p(x) = -\chi p \frac{\delta V(x)}{V} \quad (2.5)$$

where $\delta V(x) = \pi r^2 x$ is the change of volume after the cork's displacement. Substitution of (2.5) to (2.3) results in the oscillator equation

$$\frac{d^2x}{dt^2} + \Omega^2 x(t) = 0 \quad (2.6)$$

with frequency

$$\Omega = \pi r^2 \sqrt{\frac{\chi p}{m V}} \quad (2.7)$$

The final formula for the adiabatic coefficient can be rewritten through the period of motion $\tau = 2\pi/\Omega$ as follows

$$\chi = \frac{4 m V}{p r^4 \tau^2} \quad (2.8)$$

This is the equation you will use to find adiabatic coefficients of different gases.

Question 2: During the derivation we used the adiabatic equation (2.4). Explain why this process is adiabatic.

Question 3: Think how the Eq. (2.8) should be modified if you have a mixture of two gases with partial pressures p_1 , p_2 and different adiabatic constants χ_1 , χ_2 . In other words, what is χ expressed in terms of χ_1 , χ_2 , p_1 , p_2 ? PS: total pressure $p = p_1 + p_2$.

Question 4: Imagine that you measure the adiabatic constant χ_1 of the gas 1 using Eq. (2.8). However, there is unexpected admixture of a gas 2 with $\chi_2 = \chi_1$. Using results of the previous question, answer whether the measured value is less, equal or bigger than χ_1 ? What if $\chi_2 > \chi_1$? What if $\chi_2 < \chi_1$?

From the other hand, the adiabatic coefficient can be expressed in terms of degrees of freedom of gas molecules. As you remember from a thermodynamics course, the adiabatic coefficient is the ratio $\chi = C_p/C_V$ where $C_p = C_V + 1$ for ideal gases (Mayer's relation). Using Eq. (2.1) we get the desirable equation

$$\chi = 1 + \frac{2}{f} \quad (2.9)$$

Eq. (2.9) will be used to compare with your experimental value (2.8).

2.3 Vibrational contributions to the heat capacity

This experiment allows you to measure χ with uncertainty less than 5%. In particular, you will be able to estimate the excitation energy of bending vibrational modes of CO₂. This is the trickiest part but just think about it. The simple oscillator works here as infrared spectrometer for CO₂ molecules! In this part we will calculate the contribution of vibrational degrees of freedom to the heat capacity C_V .

Let us consider one vibrational mode with excitation frequency ω . The vibrations are thermally excited and, in principle, any integer number of quanta of this vibration can be created. However, the more quanta you create the more energy you need and these high energy excitations are suppressed by a Boltzmann factor $e^{-E_n/T}$, where $E_n = n \omega$ is the energy of n quanta, T is the temperature. In our case, $T \approx 300 K$ (you will check the actual

temperature in a laboratory at the day of experiment). The Boltzmann constant is disregarded here as we measure ω in Kelvins, so the relation ω/T is dimensionless. Let us calculate the average vibrational energy by summing up all possible configurations when we have 1 quantum, 2 quanta, 3 quanta etc.

$$E_v(\omega, T) = \frac{\omega e^{-\frac{\omega}{T}} + 2\omega e^{-\frac{2\omega}{T}} + 3\omega e^{-\frac{3\omega}{T}} + \dots}{1 + e^{-\frac{\omega}{T}} + e^{-\frac{2\omega}{T}} + e^{-\frac{3\omega}{T}} + \dots} \quad (2.10)$$

The denominator here is merely a normalization coefficient which is called statistical sum Z . In our case, Z is geometric series and summation is straightforward

$$Z = 1 + e^{-\frac{\omega}{T}} + e^{-\frac{2\omega}{T}} + e^{-\frac{3\omega}{T}} + \dots = \frac{1}{1 - e^{-\frac{\omega}{T}}} \quad (2.11)$$

It is convenient to rewrite Eq. (2.10) in terms of Z

$$E_v(\omega, T) = -\frac{\partial \ln Z}{\partial \beta} = \frac{\omega}{e^{\frac{\omega}{T}} - 1} \quad (2.12)$$

where $\beta = 1/T$. One can get Eq. (2.12) right away if one notices that $1/(e^{\frac{\omega}{T}} - 1)$ is Bose-Einstein distribution of bosonic quanta which is nothing but the average number of quanta at given temperature T . Multiplying the average number of quanta to the energy ω of one quantum, we get Eq. (2.12).

The vibrational contribution to the heat capacity then reads

$$\delta C_V = \frac{\partial E_v(\omega, T)}{\partial T} = \frac{\omega^2}{T^2} \frac{e^{\frac{\omega}{T}}}{\left(e^{\frac{\omega}{T}} - 1\right)^2} \quad (2.13)$$

At small temperatures $T \ll \omega$ the vibrational contribution vanishes exponentially, $\delta C_V \approx \frac{\omega^2}{T^2} e^{-\frac{\omega}{T}}$. At big temperatures $T \gg \omega$, $\delta C_V \approx 1$. Comparing it with Eq. (2.1), we conclude that each unfrozen vibrational mode yields 2 degrees of freedom.

Question 5: Why?

However, the room temperature is much smaller than the vibration energy ω and naively, we can forget about Eq. (2.13). Indeed, if $\omega/T = 10$, then $\delta C_V = 0.0045 \ll 1$ and this is the case for diatomic molecules, their vibrational mode is sterile. However, the bending modes of CO₂ are much softer and yield $\omega/T \approx 3$ which results in $\delta C_V \approx 0.5$. In other words, such vibrations are half unfrozen and significantly contribute to the heat capacity.

CO₂ has two degenerate bending modes, Fig. 1, that equally contribute to C_V . Other modes are sterile due to much bigger activation energy. Hence, the vibrational contribution to C_V for CO₂ gas is the following

$$\delta C_V \left(\frac{\omega}{T} \right) = 2 \frac{\omega^2}{T^2} \frac{e^{\frac{\omega}{T}}}{\left(e^{\frac{\omega}{T}} - 1\right)^2} \quad (2.14)$$

δC_V as the function of $z = \omega/T$ is represented at Fig. 3. You will use it in order to find ω from the experimental data.

In order to extract the experimental value of δC_V , we use that $\chi = 1 + 1/C_V$, see the paragraph before Eq. (2.9), and $C_V = C_V^{(0)} + \delta C_V$, where $C_V^{(0)} = \frac{5}{2}$ is the heat capacity without vibrational contribution for any of gases you will consider. Hence, the experimental formula for δC_V is the following

$$\delta C_V = \frac{1}{\chi - 1} - C_V^{(0)} = \frac{1}{\chi - 1} - 2.5 \quad (2.15)$$

You use experimental value of the adiabatic constant χ and Eq. (2.15) in order to find the experimental value of δC_V . After that you use Fig. 3 in order to find the corresponding value

of parameter $z = \omega/T$ which gives you the experimental value of bending mode excitation energy in CO_2 .

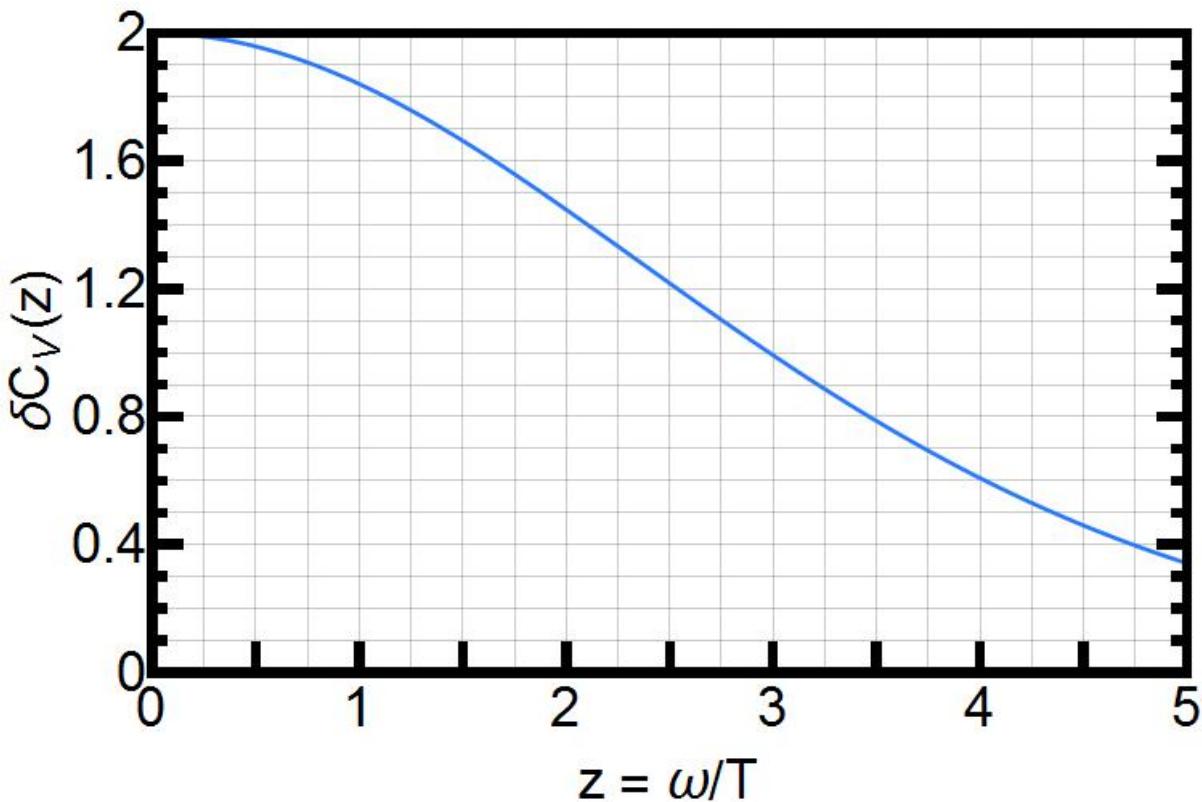


Figure 3. Vibrational contribution to the heat capacity of CO_2 , see Eq. (2.14).

3 Prework

This is very easy work but it yields beautiful results. There are some simple things you will probably need to know in order to complete the work successfully.

1. The oscillator equation that you know from the first year physics.
2. Adiabatic equation for ideal gas, heat capacity and adiabatic coefficient.
3. There is no necessity to fully understand the derivation of Eq. (2.14) but you still need to get that vibrational modes can contribute to the heat capacity even if the temperature is smaller (but not much smaller) than the vibrational excitation energy ω . Moreover, Fig. 3 demonstrates that $2 < \omega/T < 4$ is the optimal interval to probe ω .
4. In order to get reasonable result for ω , you have to be careful performing the experiment with CO_2 . Probably, it is better to start with air and nitrogen in order to understand how to perform the CO_2 experiment with smaller uncertainties.
5. As the work is straightforward and simple for third year physics, you will have to calculate carefully uncertainties for χ and ω . So, you will probably need to remember how to do it quickly.

3.1 Experimental plan

Much of what needs to be done to get this experiment to work is discussed in the Operating Instructions. Make sure you have read those carefully in advance and understand what the plan is.

The only important thing here is to let the gas flow some time before you insert the oscillator. It is essentially important in CO_2 measurements. So, make sure that you perform measurements with CO_2 but not with its mixture with air.