

1. Ratio of specific heats

1.1 Introduction

The purpose of this lab course is to determine the ratio κ of the heat capacities C_p at constant pressure and C_v at constant volume for various gases. To do so, we will apply two different methods.

In the first experimental part κ will be measured for argon, nitrogen and carbon dioxide out of the oscillation frequency of a piston which floats over a gas volume (method of Rüchardt and Flammersfeld). Thereby a very common experimental approach is made use of, namely the determination of a physical quantity by measuring a time. In general, a precise time measurement is already possible with relatively small effort, therefore this approach usually leads to large measurement accuracies.

In the second part of the experiment κ of air shall be determined with an alternative method of Clément-Desormes and Desormes.

The secure dealing with highly pressurized gas canisters in this experiment will be of use for other physical experiments as well.

1.2 Theoretical part

a) First law of thermodynamics

In general, when thermal energy is being supplied to a system from exterior, part of it will be stored as internal energy and part of it will be released as work to the surroundings. The first law of thermodynamics expresses this empirical fact together with the principle of energy conservation and reads

$$\delta Q = dU + \delta W, \tag{1.1}$$

where

$$\begin{aligned} \delta Q &= \text{supplied thermal energy,} \\ dU &= \text{change of inner energy,} \\ \delta W &= \text{provided work.} \end{aligned}$$

The equilibrium state of a thermodynamic system is being characterized by various state variables, e.g. the pressure p , the volume V and the temperature T . Those are connected among themselves by an equation of state. In the most simple case this is the equation of state of an ideal gas. For n moles of an ideal gas it becomes

$$p \cdot V = n \cdot R \cdot T, \quad (1.2)$$

where $R = 8.31 \text{ J Mol}^{-1} \text{ K}^{-1}$ is the universal gas constant.

b) Isothermal and adiabatic processes of ideal gases

Depending on the outer circumstances that occur during the process one distinguishes different fundamental processes of which two are of concern for this experiment.

- A process is called isothermal in case it runs at constant temperature. For ideal gases one gets, according to Eqn. 1.2, the isothermal equation of state

$$p \cdot V = \text{konstant.} \quad (1.3)$$

- Changes of state for which no thermal heat energy is being fed or discharged ($\delta Q = 0$) are called adiabatic processes. If the work done happens to be mechanical expansion of dV against the pressure p , one can write

$$\delta W = p \cdot dV \quad (1.4)$$

and the first law of thermodynamics becomes

$$dU + p \cdot dV = 0. \quad (1.5)$$

c) The specific heats C_p and C_v

As molar heat we denote the amount of thermal energy which warms up 1 mol of the regarding substance by $\Delta T = 1$. This quantity is depending on the fact, whether the heat supply happens at constant volume (isochor) or at constant pressure (isobar). Therefore, one distinguishes between

$$C_v = \left. \frac{\delta Q}{dT} \right|_{V = \text{konstant}} \quad (1.6)$$

and

$$C_p = \left. \frac{\delta Q}{dT} \right|_{p = \text{konstant.}} \quad (1.7)$$

If the volume is held constant during the heat supply, i.e. $dV = 0$, then one has $\delta W = 0$ according to Eqn. 1.4. It follows from the first law (Eqn. 1.1), that

$$C_v = \frac{dU}{dT}. \quad (1.8)$$

In the case where not the volume but the pressure is being held constant, the gas expands by dV during heat supply. Here, additional work is carried out, which has to be put up by the applied energy. Therefore, C_p is always larger than C_v for gases and by Eqn. 1.4 one has

$$C_p - C_v = \frac{\delta W}{dT} = p \cdot \frac{dV}{dT} \quad (1.9)$$

Due to Eqn. 1.2 we get $dV = \frac{R}{p} dT$ and as a consequence it holds for ideal gases, that

$$C_p - C_v = R \quad (1.10)$$

d) The adiabatic equation for ideal gases

Involving Eqn. 1.8, the first law (Eqn. 1.5) becomes

$$C_v \cdot dT + p \cdot dV = 0 \quad (1.11)$$

or specifically for one mol ($n = 1$) of an ideal gas according to Eqn. 1.2

$$C_v \cdot \frac{dT}{T} + R \cdot \frac{dV}{V} = 0. \quad (1.12)$$

By integrating this equation one gets

$$C_v \cdot \ln \frac{T}{T_0} + R \cdot \ln \frac{V}{V_0} = \ln \left(\frac{T}{T_0} \right)^{C_v} + \ln \left(\frac{V}{V_0} \right)^R = \text{konstant} \quad (1.13)$$

referred to an arbitrary state T_0, V_0 of the gas, or

$$T^{C_v} \cdot V^R = \text{konstant}. \quad (1.14)$$

Due to $R = C_p - C_v$, with $\kappa = C_p/C_v$ one can write

$$p \cdot V^\kappa = \text{konstant}, \quad (1.15)$$

where Eqn.1.2 has been applied, the C_v -th root has been taken, multiplied by R . Because of the proportionality of the isobaric as well as the isochoric heat capacity to the number of particles n , Eqn. 1.15 holds generally for arbitrary amounts of substances.

When measuring the pressure and the volume for two states, that are connected to each other via an adiabatic process, one can determine κ from Eqn. 1.15.

1.3 Experimental part

In this experiment one shall determine $\kappa = C_p/C_v$ for the gases argon (Ar), nitrogen (N₂) and carbon dioxide (CO₂) with the method of Rüchardt/Flammersfeld and for air with the method of Clément-Désormes.

a) Experimental set-up for the method of Rüchardt/Flammersfeld

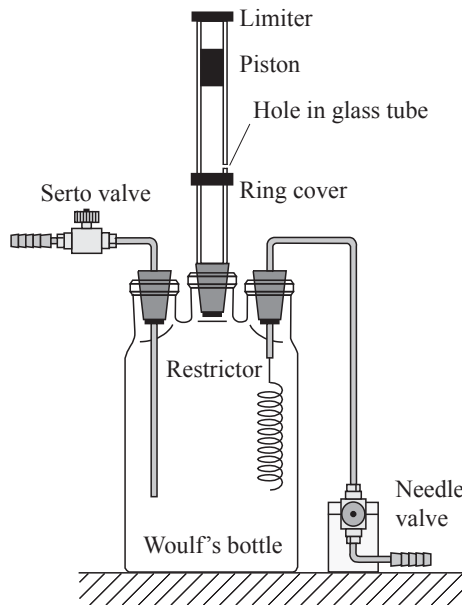


Figure 1.1: Set-up for the method of Rüchardt/Flammersfeld

The gas, which we going to investigate on, is being poured into a so-called Wouff bottle through a long, thin tube. A cylindrical, vertical glass tube is being connected to the bottle. It features a small drilling in the middle and holds a well fitting, slightly movable piston. Due to the incoming gas, the pressure in the bottle raises and the piston gets elevated until it frees the drilling in the glass tube. Thereby the pressure drops again and the piston sinks. By the use of the continuous gas current one can maintain an undamped oscillation of the piston. Because of the fast movement of the piston no heat exchange between the gas and the environment takes place in the short time in which the piston performs an oscillation. Therefore, the process runs adiabatically to a very good approximation. For the following observation we denote the following symbols:

- m_1 = Mass of the piston [kg],
- d = Diameter of the piston [m],
- V = Volume of the Wouff bottle,
including the volume of the glass pipe up to the drilling [m³],
- b = Barometer reading [Pa],
- g = Gravitational acceleration = 9.81 m/s².

The piston in the pipe is in equilibrium, if

$$p = b + \frac{4 m_1 \cdot g}{d^2 \cdot \pi}. \quad (1.16)$$

When the pressure in the bottle changes by Δp , the piston gets moved due to a force $F(x)$ by a distance x from the initial equilibrium position. The equation of motion for the piston becomes

$$m_1 \cdot \ddot{x} = F(x) = A \cdot \Delta p = \pi \frac{d^2}{4} \cdot \Delta p. \quad (1.17)$$

As the process proceeds adiabatically up to a very good approximation, one has $p \cdot V^\kappa = \text{constant}$. Furthermore, the changes of pressure and volume, Δp and ΔV , are small compared to the pressure p and the volume V , such that we can write as a good approximation:

$$\frac{\Delta p}{\Delta V} \approx \frac{dp}{dV} = \frac{\kappa \cdot p}{V} \rightarrow \Delta p = -\frac{\kappa \cdot p \cdot \Delta V}{V} = -\frac{\kappa \cdot p \cdot \pi d^2 \cdot x}{4V}. \quad (1.18)$$

Hence, Eqn. 1.17 can be written as follows:

$$m_1 \cdot \ddot{x} + \frac{\kappa \cdot p \cdot \pi^2 d^4}{16V} \cdot x = 0. \quad (1.19)$$

The solutions of those differential equations are harmonic oscillations with a circular frequency of

$$\omega = \frac{2\pi}{t_s} = \sqrt{\frac{\kappa \cdot p \cdot \pi^2 d^4}{16V \cdot m_1}} \quad (1.20)$$

and an oscillating period of $t_s = 2\pi/\omega$. Hence

$$\kappa = \frac{64 m_1 \cdot V}{d^4 \cdot p \cdot t_s^2}. \quad (1.21)$$

Due to the fact that the gas in the pipe joins the movement of the piston, one has to replace m_1 by

$$m = m_1 + \frac{\pi d^2}{4} \cdot l \cdot \left(\frac{\rho_L + \rho_G}{2} \right), \quad (1.22)$$

where l is the length of the glass pipe, ρ_L the density of air and ρ_G the density of the used gas. Therefore one has

$$\kappa = \frac{64 m \cdot V}{d^4 \cdot p \cdot t_s^2}. \quad (1.23)$$

b) Carrying out of the experiment following the method of Rüchardt/Flammersfeld

Before starting the measurement, you should check the following points together with the assistant:

1. Are the rubber clasps plugged into the bottleneck of the Woulff bottle up to the affixed markers?
2. Is the glass tube standing vertically?

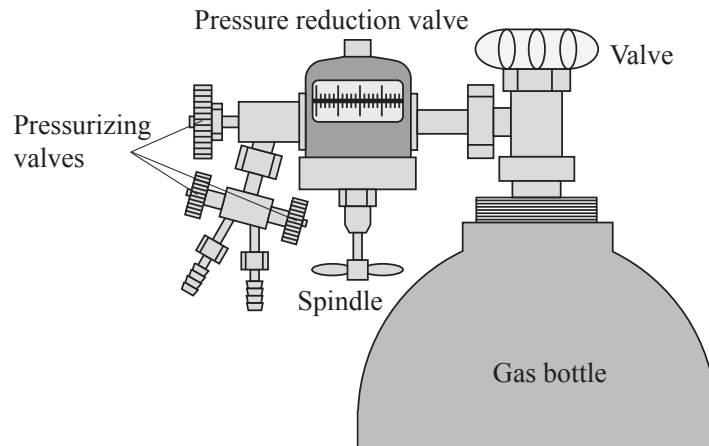


Figure 1.2: Gas bottle and valves.

3. Is the piston able to oscillate freely or is it stuck?
4. Is the serto valve closed completely?

Warning:

- **The needle valve must never be closed completely!** (*Damage of the needle valve*).
- *The piston is very sensitive to mechanical damage.*

Due to danger of accident, the following operations 1 to 5 and 7 are only allowed to be executed supervised by the responsible assistant (cf. Fig. 1.1 and 1.2).

1. Slowly open the gas bottle valve, with the pressure reducing valve being relaxed and the distributor valves being closed.
2. Slowly screw the spindle on the pressure reduction valve inwards, until the low pressure manometer displays a pressure of 0.4 bar. Flush the pipes shortly.
3. Connect the pressure reduction valve with the serto valve and the needle valve with tubes. Open both distributor valves. Open the needle valve for approx. 30 seconds completely, then, open the serto valve just a little bit. As a result, the piston in the glass tube gets elevated and can be removed with the confining ring.
4. Open the serto valve completely and flush the bottle for about 30 seconds. Close the serto valve, reinstall the piston and secure it with the confining ring.
5. Adjust the needle valve and the cover ring at the glass tube in such a way, that the lower edge of the piston oscillates as symmetrically as possible around the drilling in the glass tube. The amplitude of the oscillation should account for 30 mm.
6. Measure the oscillation period t_s as an average over 10 series, each of which contain 20 oscillations.

Table 1.1: Details for the experimental set-up after Rüchardt/Flammersfeld

Volume of bottle 1	$V = (5.420 \pm 0.005) \text{ l}$
Volume of bottle 2	$V = (5.595 \pm 0.005) \text{ l}$
Mass of the piston	$m_1 = 5 - 10 \text{ g}$ (precise information are written down at the experimental spot)
Inner diameter and length of the glass tube	$d = (14.00 \pm 0.02) \text{ mm}$ $l = (170.0 \pm 1.0) \text{ mm}$

7. After completion of the experiment, close all pressure bottle valves and relieve the pressure reduction valves.
8. Read the pressure value from the precision barometer in the lab. As usual in meteorology the barometer is calibrated for the altitude and the reading refers to sea level. Calculate the absolute pressure in the lab using the following formula for the altitude of $h = 473 \text{ m}$:

$$p(h) = p_0 \cdot \left(1 - \frac{6.5h}{2.88 \times 10^5}\right)^{5.255}, \quad (1.24)$$

where

$$\begin{aligned} p(h) &= \text{pressure at altitude } h \text{ [Pa]}, \\ p_0 &= \text{pressure at sea level [Pa]}, \\ h &= \text{altitude [m]}. \end{aligned}$$

9. Calculate κ of the three gases with the help of Eqn. 1.23 and estimate the error on κ . The relevant parameter are arranged in table 1.1.

c) Experimental set-up for the method of Clément-Desormes

With the help of bellows one can pump air into a gas container (see Fig. 1.3).

The gas container is connected to a simple fluid manometer. By shortly opening the valve one can reduce the pressure in the container.

d) Carrying out of the experiment following the method of Clément-Desormes

The quantity κ is being determined in three steps.

In the first step the molar volume of the initial state is being determined. To do so, you will pump air into the gas container. After the air has adopted ambient temperature (wait for approx. 5-10 minutes), determine the associated state variables for this condition:

$$\text{Pressure } p_1 = p_0 + \rho_{Fl} \cdot g \cdot h_1, \text{ where:}$$

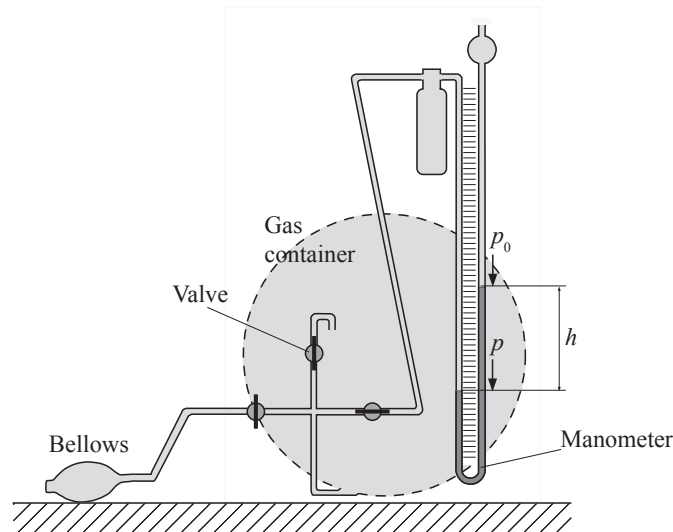


Figure 1.3: Experimental set-up for the Methode von Clément-Desormes

p_0 = External pressure,

$\rho_{Fl} = 1.0 \times 10^3 \text{ kg m}^{-3}$ = Density of the fluid in the manometer,

h_1 = Height, indicated on the manometer h ,

Volume $V_1 = V$ = Volume of the gas container,

Temperature $T_1 = T$ = Room temperature,

Number of moles $n_1 = \frac{p_1 \cdot V}{R \cdot T}$,

Molar volume $v_1 = \frac{V}{n_1} = \frac{R \cdot T}{p_1}$.

In the second step, one lets the trapped gas in the container expand adiabatically. For this purpose, let some gas escape the container by shortly opening the valve, such that the head of liquid in the manometer drops for about 5 to 10 cm. The gas is in a new state (2) immediately after the closing of the valve, which is characterized by the following quantities:

Pressure $p_2 = p_0 + \rho_{Fl} \cdot g \cdot h_2$

Volume $V_2 = V$ = Volume of the gas container

Temperature $T_2 = n$

Number of moles $n_2 = \text{unknown}$

Molar volume $v_2 = \frac{V}{n_2} = \text{unknown}$

For the exact determination of h_2 , check appendix a)!

The new number of moles n_2 and the temperature T_2 is not known a priori. The equation of state $p_2 \cdot V = n_2 \cdot R \cdot T_2$ yields only the product of these quantities.

In the third step, the molar volume of the final state will be determined. In order to do so, wait until the remaining gas has adopted room temperature once more. For this state (3) one has:

$$\begin{aligned}
\text{Pressure } p_3 &= p_0 + \rho_{Fl} \cdot g \cdot h_3 \\
\text{Volume } V_3 &= V = \text{Volume of the gas container} \\
\text{Temperature } T_3 &= \text{Room temperature} \\
\text{Number of moles } n_3 &= \frac{p_3 \cdot V}{R \cdot T} \\
\text{Molar volume } v_3 &= \frac{V}{n_3}
\end{aligned}$$

Since no gas escaped in the transition between states (2) and (3), one has

$$n_2 = n_3 = \frac{p_3 \cdot V}{R \cdot T} \quad (1.25)$$

and therefore

$$v_2 = v_3 = \frac{R \cdot T}{p_3} \quad (1.26)$$

Finally κ shall be determined. For the adiabatic transition from state (1) to state (2) Eqn. 1.15 holds, so

$$p_1 \cdot V_1^\kappa = p_2 \cdot (V_1 + \Delta V)^\kappa, \quad (1.27)$$

where ΔV (outside the container) is unknown. For the molar volume in state (2) one has:

$$\frac{V_1 + \Delta V}{n_1} = \frac{V_2}{n_2} = v_2$$

and thereby

$$p_1 \left(\frac{V_1}{n_1} \right)^\kappa = p_2 \cdot \left(\frac{V_1 + \Delta V}{n_1} \right)^\kappa = p_2 \cdot v_2^\kappa. \quad (1.28)$$

After the extension with $(RT)^\kappa$ for the states (1) and (3) and with Eqn. 1.25 and 1.26 one gets:

$$p_1 \cdot \left(\frac{1}{p_1} \right)^\kappa = p_2 \cdot \left(\frac{1}{p_3} \right)^\kappa. \quad (1.29)$$

Thereby, with the reference pressure p_0 , it holds that

$$\kappa = \frac{\ln \left(\frac{p_2}{p_1} \right)}{\ln \left(\frac{p_3}{p_1} \right)} = \frac{\ln \left(\frac{p_2}{p_0} \right) - \ln \left(\frac{p_1}{p_0} \right)}{\ln \left(\frac{p_3}{p_0} \right) - \ln \left(\frac{p_1}{p_0} \right)}. \quad (1.30)$$

On the other hand, it holds that

$$p_i = p_0 + \rho_{Fl} \cdot g \cdot h_i, \quad (1.31)$$

such that

$$\kappa = \frac{\ln \left(1 + \frac{\rho_{Fl} \cdot g \cdot h_2}{p_0} \right) - \ln \left(1 + \frac{\rho_{Fl} \cdot g \cdot h_1}{p_0} \right)}{\ln \left(1 + \frac{\rho_{Fl} \cdot g \cdot h_3}{p_0} \right) - \ln \left(1 + \frac{\rho_{Fl} \cdot g \cdot h_1}{p_0} \right)}. \quad (1.32)$$

With the power series expansion $\ln(1 + \varepsilon) = \varepsilon - 1/2 \varepsilon^2 + \dots$ it follows for $\varepsilon = \frac{\rho_{Fl} \cdot g \cdot h_i}{p_0} \ll 1$ that

$$\kappa = \frac{h_2 - h_1}{h_3 - h_1}. \quad (1.33)$$

Therewith, κ can be calculated only with the values from the height measurement of the manometer. The temperatures and the molar volume are not need to be known.

e) Exercises

- Verify the assumption $\varepsilon = \frac{\rho_{FL} g \cdot h_i}{p_0} \ll 1$.
- Calculate the amount of moles of gas inside of the container.
- Compare the experimentally acquired values from Eqn. 1.23 and 1.33 with the expected values after Eqn. 1.38 (appendix b) and literature values for κ at 20 °C:

$$- \kappa (\text{Ar}) = 1.668, \quad \kappa (\text{N}_2) = 1.404, \quad \kappa (\text{O}_2) = 1.404 \quad \text{and} \quad \kappa (\text{CO}_2) = 1.304$$

1.4 Appendix

a) For the determination of pressure changes at the adiabatic expansion from state (1) to (2)

Due to inevitable oscillations of the fluid manometer, a direct read off of the pressure in state (2) is not possible until quite some time after the escape of the gas. At this time, the gas has again warmed a little bit, such that the transition can't be assumed to be adiabatic any more. In the following it is shown, how one can extrapolate backwards from subsequent measurements to the correct initial value h_2 .

Open the valve at the time $t = 0$ shortly and read off the height h_t of the head of liquid in the manometer at times $t = 10, 20, 30, 40, 50$ and 60 s as well as the final value h_∞ after 5 and 10 minutes ($h_\infty = h_3$).

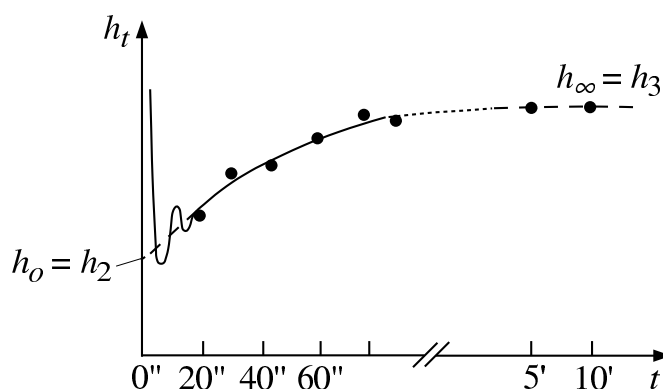


Figure 1.4: Measurement of the height as a function of time

From the graphically represented measurements one could basically directly extrapolate to the searched value $h_0 = h_2$ at time $t = 0$ (see Fig. 1.4). Nevertheless, the extrapolation is easier and produces a more accurate result if a representation can be found, where the pressure history is described as a straight line.

For that to happen, one makes the obvious assumption that the warming per second is proportional to the difference in temperature between the gas in the container and the environment, i.e.

$$\frac{dT}{dt} \propto T - T_2 = T_3 - T_2. \quad (1.34)$$

Since for an ideal gas after Eqn. 1.2 at constant volume one has $p \propto T$, it holds for the temporal change of the manometer read-off $h(t)$ ($k = \text{constant}$) that

$$\frac{dh_t}{dt} = k \cdot (h_\infty - h_t). \quad (1.35)$$

The solution of this differential equation for h_t is

$$h_\infty - h_t = (h_\infty - h_0) \cdot e^{-kt}. \quad (1.36)$$

Finding the logarithm of this equation yields

$$\ln(h_\infty - h_t) = \ln(h_\infty - h_0) - kt, \quad (1.37)$$

where all heights have to be divided by the same (arbitrary) reference value (e.g. 1 cm) before taking the logarithm.

Therefore, plotting $\ln(h_\infty - h_t)$ instead of the measured values as a function of time t , one expects a linear connectedness.

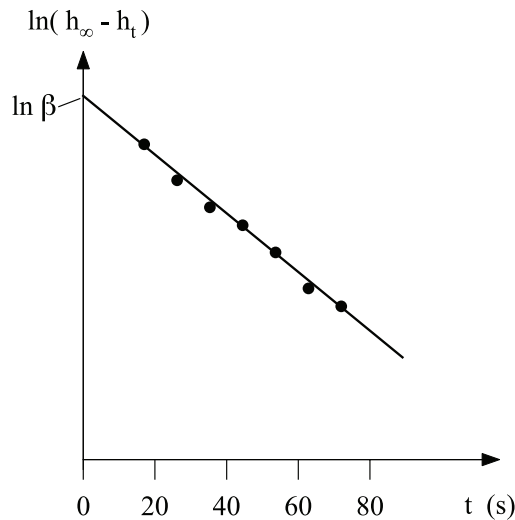


Figure 1.5: Linearisation and extrapolation for $t = 0$.

Fit the best straight line through the points and extrapolate it until reaching $t = 0$. From the section of the abscissa $\ln(h_\infty - h_0)$ determine the desired initial value $h_0 = h_2$.

b) On the gas kinetic interpretation of κ

Since no forces act in between molecules of an ideal gas, no potential energy can be stored. Therefore, C_v corresponds to the increase of kinetic energy of one mole of gas for an increment of temperature of 1 K.

According to the equipartition law, for each mole of the gas an energy of $\frac{1}{2} R \cdot T$ falls on each (fully excited) “degree of freedom” of the gas molecules. The number f of degrees of freedom is determined by the possibilities of translation, rotation and eventual oscillations of the concerning molecules.

Having $R = C_p - C_v$, it follows for ideal gases with f degrees of freedom that

$$\kappa = \frac{C_p}{C_v} = \frac{C_v + R}{C_v} = \frac{\frac{f}{2} \cdot R + R}{\frac{f}{2} \cdot R} = 1 + \frac{2}{f}. \quad (1.38)$$

Since the angular momentum L can only embrace certain, discrete values (quantum mechanics), namely $L = n \cdot \frac{h}{2\pi}$, the associated rotational energy is quantised as well:

$$E_{rot} = \frac{L^2}{2J} = \frac{n^2 \cdot h^2}{8\pi^2 \cdot J} \quad (1.39)$$

Here, h is the Planck's constant and J the moment of inertia of the molecule.

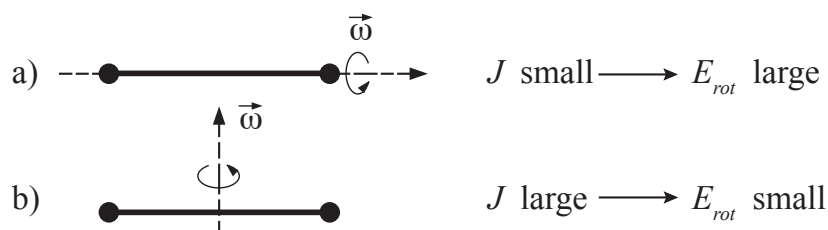


Figure 1.6: Moments of inertia and degrees of freedom of a 2-atomic molecule

At room temperature, the average kinetic energy is too small to excite rotations such as shown in Fig. 1.6a). Hence the three degrees of freedom don't play a role for one-atomic gases and for linear molecules the rotation around the connecting axis can be neglected as a degree of freedom. Similar considerations hold for the degrees of freedom of vibrations, since the oscillation energy of a molecule is much greater than the rotational energy and therefore vibrations are frozen at room temperature and do not contribute to the number of degrees of freedom.

For example the number of degrees of freedom for the linear CO_2 -molecule is composed of

$$f = 3 \text{ (Translation)} + 2 \text{ (Rotation)} + 1 \text{ bis } 4 \text{ (Vibration, depending on the temperature)}.$$

In general, the number of degrees of freedom under standard conditions amounts to:

- one-atomic gases: $f = 3 \Rightarrow C_v = \frac{3}{2} R \cdot T \Rightarrow \kappa = \frac{5}{3}$
- two-atomic gases: $f = 3 + 2 \Rightarrow C_v = \frac{5}{2} R \cdot T \Rightarrow \kappa = \frac{7}{5}$
- three-atomic gases: $f = 3 + 3 \Rightarrow C_v = \frac{6}{2} R \cdot T = 3 R \cdot T \Rightarrow \kappa = \frac{4}{3}$