Laboratory Session 6: Kinetic theory of gases. Part I. Gas viscosity: Molecular diameter estimation

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Objectives.

- Measurement of the viscosities of two gases: nitrogen and carbon dioxide.
- Estimate the molecular diameter of each of the gases used by means of the Kinetic Theory of Gases.

Related concepts: Kinetic Gas Theory, mean free travel, transport properties, Poiseuille equation, alternative techniques.

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1. Introduction

1.1. Gas viscosity determination

The viscosity of a fluid (gas or liquid), in its simplest definition, gives us its resistance to flow. In particular, the viscosity of a gas is determined, most of the time, by the transfer rate of the moment of flow from the sheets moving faster to the slowest.

In this practice, the gas flow rate (which is inversely proportional to its viscosity) will be obtained by measuring the emptying time of a syringe through a capillary tube under a constant pressure difference.

Consider a fluid under an ideal laminar regime, with parallel planes in the x direction. The flow velocity varies linearly from the lower stationary sheet to the upper sheet that travels at the velocity v_x. The force F that compensates for the relative movement of the layered planes is proportional to the contact area A between adjacent layers of fluid and the flow velocity gradient in the fluid dv_x/dz

$$F = -\eta A \frac{dv_x}{dz} \tag{1}$$

The constant of proportionality, **η,** is the viscosity of the fluid. F/A represents the force per unit of tangential area or shear force that crosses the contour of a layer and through Newton's second law is equal to the rate of change of the moment of flow among layers.

In the experiments performed, we assume that the gas flow is laminar through the capillary cylinder which allows the gas flow velocity through the tube can be calculated using the *Poiseuille*'s equation:

$$\frac{dV}{dt}=\frac{\pi r^4\left(p_1^2-p_2^2\right)}{16 l \eta p} \tag{2}$$

where:

- dV/dt, volume flow veloctiy.
- p_1 and p_2, pressures at the beginning and end of the capillary respectively.
- r, capillary tube radius (= 0.075 mm).
- l, capillary tube length (= 98 mm).
- p, pressure at which volume is measured (p_1).

Equation 2 can be employed to calculate the absolute values of the viscosities of the gases, once the dimensions of the capillary are knowed. In addition, the differential of the constant pressure must be fixed. Thus, the velocity of emptying of the capillary is measured.

The gas pressure in the syringe is p_1 which is the atmospheric pressure (approximately 101325 Pa), while p_2 is the pressure at the end of the capillary, which it is determined through the maximum reading of the barometer coupled to the vacuum tube used p_b=−1000 mbar (p_2=p_1+p_b).

1.2. Molecular diameter estimation

A treatment of the amount of movement flow through a surface using the kinetic theory for gases of rigid spheres allows to express the viscosity in terms of the kinetic properties of the molecules that make up the gas:

$$\eta=\frac{5\pi}{32}\frac{M}{N_A}\rho\lambda\langle v\rangle \tag{3}$$

where M is the molecular weight, N_A is the Avogadro number, ρ is the gas density (particles per unit volum), λ the mean free path of the gas molecules and $\langle v\rangle$ its average translational velocity, properties all of them measured at the pressure and temperature of the experiment. For a maxwellian distribution of molecular velocities, the average molecular velocity is given by the expression:

$$\langle v\rangle=\left(\frac{8RT}{\pi M}\right)^{1/2} \tag{4}$$

being T the temperature, R the gas constant (8.31451 J K^{-1} mol^{-1}); while, in the case of a pure gas, the mean free path is:

$$\lambda = \frac{1}{\sqrt{2}\pi d^2} \frac{RT}{PN_A} \tag{5}$$

where p is the pressure and d the diameter of the rigid sphere. If we assume that in room conditions the gas behaves as ideal, and we substitute equations 4-5 in equation 3, we get an expression that relates the viscosity of the gas to the diameter of the rigid sphere, from which it is possible to clear this last magnitude, obtaining:

$$d^2 = \frac{5}{16\sqrt{\pi}} \frac{(MRT)^{1/2}}{N_A \eta} \tag{6}$$

2. Experimental Procedure

The equipment is assembled as shown in Figure 1. There are two identical assemblies, each with its corresponding gas. It should be noted that the stop piston is positioned to prevent the plunger from falling.

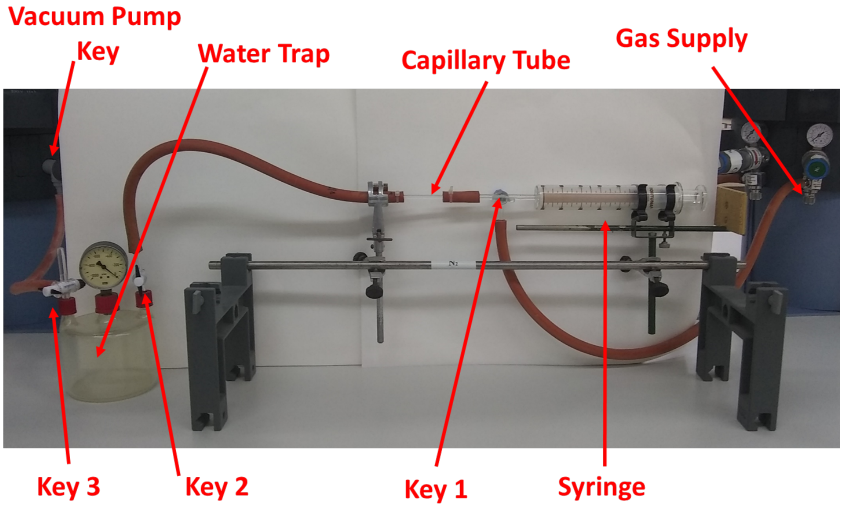

Figure 1: Experimental assembly for measuring the viscosity of a gas

First of all, it must be confirmed that the professor has connected the gas station. The three-way wrench (1) is turned so that it connects the empty syringe with the gas circuit and the rest of the line is isolated (see Figure 2 and Figure 3).

Step 1 (see Figure 2). Slightly open the pressure reducer located in the service tower (clockwise) until it marks an overpressure of approximately 0.5-1 bar. The stopcock is then opened until the syringe plunger moves to a certain volume (eg 60 mL).

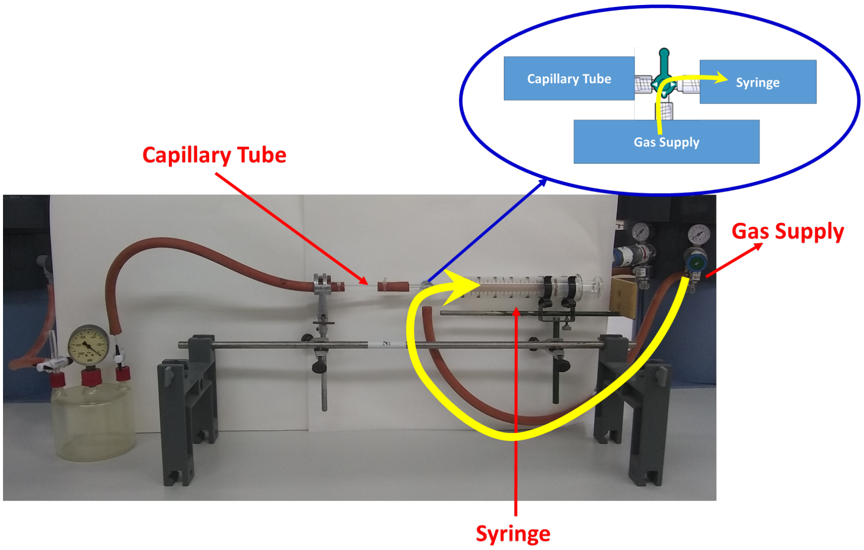

Figure 2: First step in gas viscosity determination. Lead the gas from the supply to the syringe.

Step 2 (see Figure 3): The key 2 is rotated so that it connects the flow line with the water trap and the key 3 connecting the latter to the vacuum circuit and closed to the outside. Wait for the pressure gauge to indicate a pressure difference of approximately -1000 mbar and turn the three-way wrench 1 of the syringe connecting the gas to the flow line. When the syringe stroke is empty, it will move, when it passes through a certain volume (eg 50 mL), start the stopwatch that we will stop when we reach the complete emptying of the gas inside the syringe. Once the measurement is finished, we turn the key 1 by reconnecting the syringe to the gas circuit. Repeat the emptying time measurement at least four times.

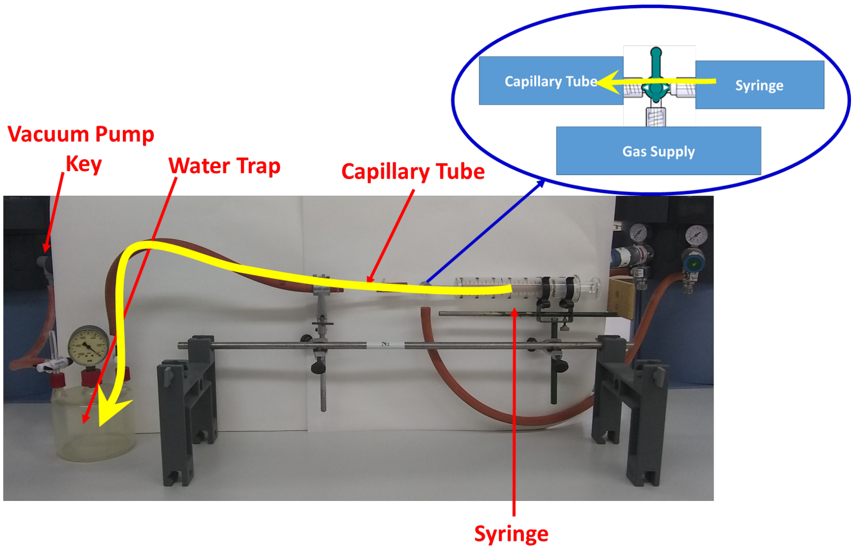

Figure 3: Second step in gas viscosity determination. Lead the gas from the syringe to the vacuum trap trough the capillary tube.

At the end of all measurements, the vacuum key is closed and the key 3 is opened outside. Change assembly (adjacent workstation) to measure the remaining gas. The ambient temperature of the laboratory and the atmospheric pressure must be recorded.

Observations: Generally, the first measure can leave the remaining ones either due to lack of familiarity with the handling of the equipment or due to air pollution inside it.

3. Results

3.1 Determination of the viscosity of the gases N_2 and CO_2 gases

Using equation 2, calculate the viscosity with its random error of the different gases studied. Compare the values obtained with those that appear in the bibliography and calculate the absolute error. Express the magnitude with its error.

3.2 Determination of the molecular diameter of N_2 and CO_2 gases

Obtain the molecular diameter of the used gases employing the equation 6. Compare the values obtained with those that appear in the bibliography including the complete reference and calculate the absolute error. Express the magnitude with its error and discuss the validity of the gas kinetic model in your study.

3.3 Determination of the thermal conductivity and diffusion coefficient of N_2 and CO_2 gases.

Using the molecular diameters obtained with equation 6, calculate the thermal conductivity and diffusion coefficient for each of the gases used. Compare the values obtained with those that appear in the bibliography, including the complete reference, and calculate the absolute error. Express the magnitude with its error and discuss the validity of the gas kinetic model for the gases studied.

Part II. Determination of the molecular mass using the law of ideal gases

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Objectives

- Determination of the molecular mass of two gases: nitrogen and carbon dioxide.
- Verification of the validity range of the ideal gas law for these two cases.

Related Concepts: Gases ideales y reales. Ecuaciones de estado.

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1. Introduction

In the first approximation, the behavior of the gases can be described by the equation of state of the ideal gases, which relates the pressure (p), volume (V), temperature (T) and amount of substance (n) of one particular gas.

$$P\bar{V} = RT \qquad (7)$$

$$\bar{V} = \frac{V}{n} \qquad (8)$$

The amount of gas n, is expressed as the number of moles and is equal to m/M, where m is the mass of the gas present and M is the mass of one mol of gas. Thus, if the volume occupied by a known mass of gas is measured at a given pressure and temperature, the ideal gas equation (7), can be employed to estimate the molecular mass (molecular weight) of the gas.

Under certain conditions the previous equation does not describe the behavior of gases correctly, being necessary to resort to state equations that take into account the interactions among the molecules that compose it. Two of the most used equations to describe the behavior of real gases are the virial equation (9) and the van der Waals equation (10),

$$\frac{P\bar{V}}{RT} = 1 + \frac{B(T)}{\bar{V}} + \frac{C(T)}{\bar{V}^2} + \ldots \qquad (9)$$

$$\left(P+\frac{a}{\bar{V}^2}\right)\left(\bar{V}-b\right)=RT \tag{10}$$

2. Experimental Procedure

There are two assemblies like the one shown in Figure 4, one connected to a nitrogen cylinder and the other to a carbon dioxide cylinder.

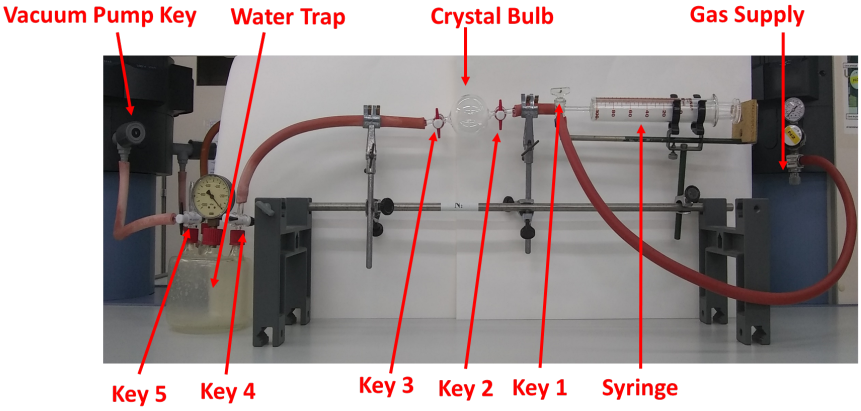

Figure 4: Experimental assembly for measuring the molecular mass of a gas.

Step 1 (see Figures 4 and 5): In order to calculate the mass of the glass bulb, it must be weighed. For this, the vacuum pump is connected to the clock-switch located in the central service tower and the vacuum key located in the lateral service tower is opened. The three-way key 4 must be turned so that it connects the circuit to the water trap and the key 5 must connect the trap to the pump. With the key 2 closed and the key 3 open the bulb is evacuated by pumping for a period of 1 to 2 minutes. Afterwards, the keys 3 and 4 are closed. The bulb is disconnected from the vacuum line and weighed, previously cleaning the outer surface of the bulb before weighing. Once the mass of the empty bulb is determined, it is reconnected to the vacuum line.

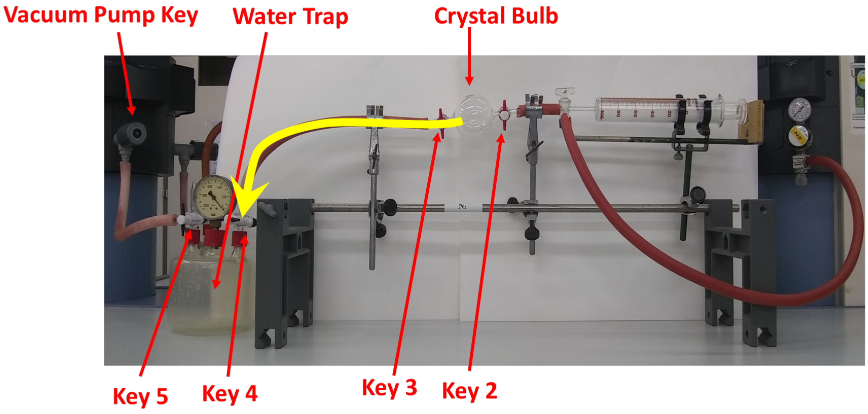

Figure 5: First step in gas weight determination. Procedure to empty the glass bulb.

Before filling the bulb with the corresponding gas, verify that the professor has connected the gas station. The vacuum is done for 1 more minute, checking that the keys 3 and 4 are open and key 2 is closed (see previous paragraph). Once the vacuum is done, we close again keys 3 and 4.

Step 2 (see Figure 6): The key 1 is then placed in the position of connecting the xyringe with the gas circuit. To do this, first open the pressure reducer located in the service tower (turning clockwise) until it marks an overpressure approx. 0.5-1 bar. Then the stopcock is opened by carefully filling the gas syringe up to 100 mL. The stopcock is closed. The bulb is filled by turning key 1 so that it connects with the syringe and opening key 2.

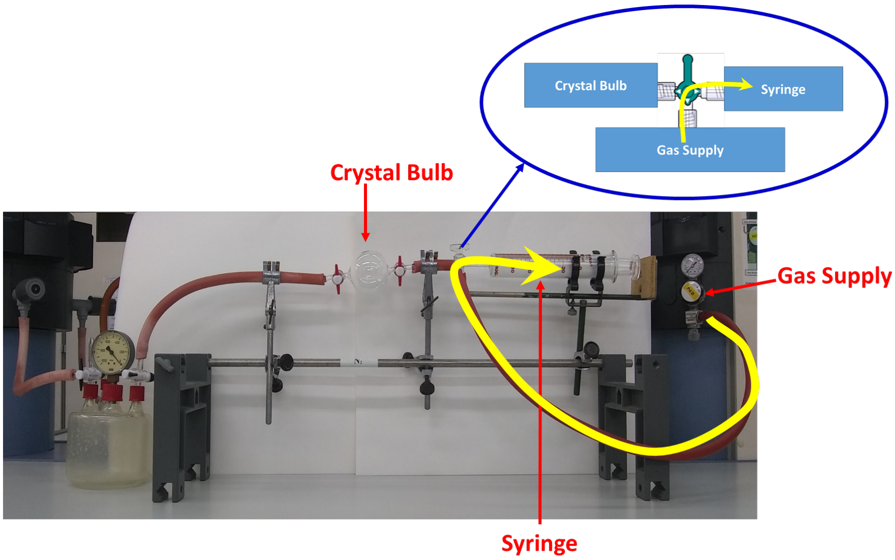

Figure 6. Second step in gas weight determination. Lead the gas from the supply to the syringe

Step 3 (see Figure 7): Once the syringe is emptied, it closes key 2 quickly, the vacuum line key closes, opens 5 to eliminate the vacuum, and finally the bulb is disconnected from the line to proceed to weighing. Weighing should be performed by previously cleaning the external surface of the bulb before weighing.

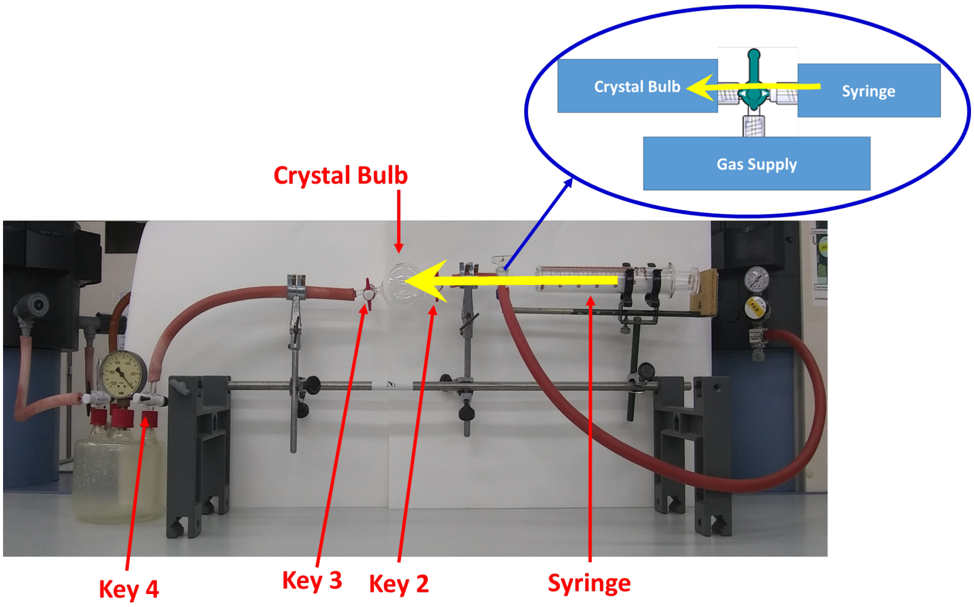

Figure 7. Third step in gas weight determination. Lead the gas from the syringe to the crystal bulb (in vacuum)

The bulb is replaced and the procedure is repeated three times before measuring the next gas.

3. Results

3.1 Determination of the molecular mass using the ideal gas law

The mass of the gas contained in the bulb is determined from the difference between the average mass of the filled and empty bulb.

From this data and the volume it occupies at the working pressure determine the molecular mass of the gas using equation 7. Compare the results obtained with the values of the atomic mass tables. Determine possible sources of error.

Table 1. Molecular mass determined using ideal gas law

GAS	V (mL)	Mass empty (tare) (g)	Mass Filled (gross weigth) (g)	Mass gas (net) (g)	M (g.mol-^{1})
N_2					
Average					
CO_2					
Average					

3.2 Determination of the molecular mass by means of the virial equation of state

Check the accuracy provided by the ideal gas equation (7) in the working conditions (room temperature), recalculating the molecular mass through the equation of the virial (9) truncated in its second term. The value of B (T) can be obtained by means of this expansion:

$$B\left(cm^3/mol\right) = \sum_i a_i \left[\frac{298.15}{T(K)} - 1\right]^{i-1} \qquad (11)$$

The coefficients a_i for nitrogen and carbon dioxide are shown in table 2.

Table 2. Coefficients a_i in cm^3/mole, of the expansion of B(T) for N_2 and CO_2.

Gas	a_1	a_2	a_3
N_2	-4	-56	-12
CO_2	-127	-288	-118

3.3 Determination of the molecular mass by means of the van der Waals equation of state

Repeat the previous section but using the van der Waals equation (10). The constants of this equation for nitrogen and carbon dioxide are shown in table 3

Table 3. Constants of van der Waals equation for N_2 and CO_2.

Gas	a (bar L^2 mol^{-2})	b (L mol^{-1})
N_2	1.370	0.0387
CO_2	3.658	0.04286

4. Questions

4.1. Preliminary Questions

1- Deduce equation (6) from (3) using (4) and (5).

2- Look for the expressions that relate the thermal conductivity and the diffusion coefficient in gases with the diameter of the rigid sphere.

3- Deduce the Poiseuille equation for the flow rate of a fluid through a capillary tube of radius r.

4- The Poiseuille equation was deduced for an incompressible fluid. Can it be applied to gases? How is this fact taken into account? (Compare the equation used for liquids and gases).

5- Search in the bibliography the values of viscosities, molecular diameters, thermal conductivities and diffusion coefficients of N_2 and CO_2 gases in the closest conditions to those of the laboratory. Present in a table the values and the bibliographical reference.

4.2. Post-laboratory Questions

1. Calculate the average translational velocity, <v>, of the N_2 and CO_2 molecules under the conditions of the experiment.
2. Calculate the collision frequency, z, for N_2 molecules and also for the CO_2 molecules under the conditions of the experiment.
3. Calculate the mean free path, λ, for the N_2 and CO_2 molecules under the experimental conditions.
4. Considering the diameters obtained in practice and the calculated parameters λ discuss the validity of the gas kinetic model for N_2 and CO_2 in this study.
5. We can get an idea of the validity interval of the ideal gas equation (7) at room temperature, calculating the pressure at which the second term of the virial equation (9) introduces a significant correction, for example, 1% with respect to the value of the PV/RT ratio of the ideal gas. Calculate this pressure for the two gases used in this practice and explain the relative values based on the magnitude of the intermolecular forces put into play in each of the gases.

Apendix A. Material

- H shaped base support.
- Rod support, l=759 mm.
- Syringe holder for gas with brake.
- 100 mL gas syringe with three way wrench.
- Glass capillary tube, d=0.15 mm, l=98 mm and 100 mL balloon.
- Water trap.
- Vacuum pump.
- Digital stopwatch , 1/100 s.
- Barometer.
- Thermometer.
- Pressurized nitrogen.
- Pressurized carbon dioxide.

References

[1] Handbook of Chemistry and Physics. 77 edition CRC Press. 1996.

[2] I.N. Levine. Fisicoquímica. McGraw-Hill, Madrid, 4 edition, 1996.

[3] W.J. Moore, Química Física, URMO, Bilbao, 2ª ed. 1978.