

## Statement

To demonstrate that air weights, and to measure its density, the following experiment is performed. We have an aluminium sphere  $250\pm 1$  mm in diameter, with a valve that allows it to be connected to a vacuum pump. Initially, when full of air at  $20\pm 1$  °C and  $95\pm 0.5$  kPa, the vessel (sphere with valve) has a mass of  $219\pm 1$  g. After making some vacuum, and waiting to thermal equilibrium, the mass is  $214\pm 1$  g at  $50\pm 0.5$  kPa, and  $210\pm 1$  g at  $5\pm 0.5$  kPa. To do:

- Find the air density from the extreme measurements, indicating the uncertainty, and comparing with the ideal gas model.
- Indicate the goodness of the ideal gas model, and how to increase the experimental accuracy.
- Based on density, molar mass and Avogadro's number, find the average distance between air molecules.

Se desea comprobar que el aire pesa y medir su densidad, para lo que se realiza el experimento siguiente. Se tiene una esfera de  $250\pm 1$  mm de diámetro exterior, de aluminio, con una válvula que puede conectarse a un equipo de vacío. Inicialmente, conteniendo aire a  $20\pm 1$  °C y  $95\pm 0,5$  kPa, la esfera con la válvula tienen una masa de  $219\pm 1$  g. Después de aspirar algo de aire y esperar al atemperamiento, cuando la presión interior es  $50\pm 0,5$  kPa la masa es  $214\pm 1$  g, y para  $5\pm 0,5$  kPa  $210\pm 1$  g. Se pide:

- Determinar la densidad del aire a partir de las medidas extremas, indicando la incertidumbre y comparándola con el modelo de gas ideal.
- Indicar si el modelo de gas ideal es apropiado, y cómo se podría mejorar la exactitud experimental.
- Calcular la separación media entre las moléculas del aire, en función de la densidad, masa molar y número de Avogadro.

## Solution

- Find the air density from the extreme measurements, indicating the uncertainty, and comparing with the ideal gas model.

First a sketch to help visualise the system:

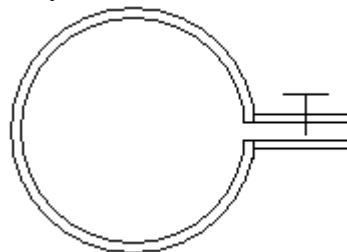


Fig. 1. Hollow sphere with control valve.

Density, or specific mass, is mass divided by volume. We start by assuming that the mass remaining at 5 kPa is negligible (we can correct for that once we found the mass dependence with pressure), and consider also negligible the solid volume of the sphere. With that we get:

$$\rho = \frac{m}{V} = \frac{m_{full} - m_{void}}{\pi D^3 / 6} = \frac{0.219 - 0.210}{\pi 0.25^3 / 6} = \frac{0.009}{0.008} = 1.10 \frac{\text{kg}}{\text{m}^3}$$

with a relative uncertainty:

$$\frac{\sigma_\rho}{\rho} = \sqrt{\left(\frac{\sigma_m}{m}\right)^2 + \left(\frac{\sigma_V}{V}\right)^2} = \sqrt{\left(\frac{\sigma_m}{m}\right)^2 + \left(3\frac{\sigma_D}{D}\right)^2} = \sqrt{\left(\frac{0.001}{0.009}\right)^2 + \left(3\frac{0.001}{0.250}\right)^2} = 0.1$$

i.e., the measured density is the range 1.0..1.2 kg/m<sup>3</sup>.

Now the comparison of this experiment with the ideal-gas-model (IGM) prediction:

$$\rho = \frac{p}{RT} = \frac{95 \cdot 10^3}{287 \cdot 293} = 1.19 \frac{\text{kg}}{\text{m}^3}$$

where the  $R$ -value for air,  $R \equiv R_u/M = 8.3/0.029 = 287 \text{ J}/(\text{kg}\cdot\text{K})$ , which should be memorised in a Thermodynamic course, has been directly substituted. As for the relative uncertainty:

$$\frac{\sigma_\rho}{\rho} = \sqrt{\left(\frac{\sigma_p}{p}\right)^2 + \left(\frac{\sigma_R}{R}\right)^2 + \left(\frac{\sigma_T}{T}\right)^2} = \sqrt{\left(\frac{0.5 \cdot 10^3}{95 \cdot 10^3}\right)^2 + 0 + \left(\frac{1}{293}\right)^2} = 0.006 \approx 0.01$$

i.e., the measured density is the range 1.18..1.20 kg/m<sup>3</sup>. Notice that we neglect the uncertainty in  $R$ , which is not zero but difficult to guess (the effect of the actual 'air' mix used relative to the standard dry air).

b) Indicate the goodness of the ideal gas model, and how to increase the experimental accuracy.

Several conclusions can be drawn from the previous work:

- Measure and model are congruent in the sense that their ranges intersect.
- IGM prediction is more precise (less relative uncertainty), but that does not mean the IGM is more accurate (i.e. better represents reality; the model might be wrong or not applicable to this case).
- In case of conflict (i.e. non-overlapping ranges), direct measurement should prevail over any model, in spite of precision; the ultimate check of any model is experiment.
- A model worths a thousand experiments; we have measured here air density just at one temperature and one pressure, whereas the IGM predicts it for any temperature and any pressure (and any composition). But, again, the ultimate check of any model is experiment.
- Much more information can be obtained from a series of experiments than from a single measurement: first of all, redundancy decreases the uncertainty, and second, a parametric study (here in terms of internal pressure) serves to find trends.

If we approximate the tare as the final mass, and subtract it to all the mass-measurements, we can represent the measured points and the IGM predictions for comparison:

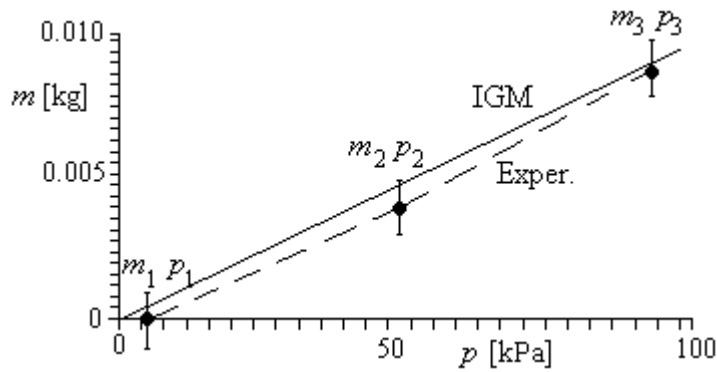


Fig. 2. Mass of air inside the sphere; experimental results versus ideal gas model.

Experiments are thus coherent with the linear dependence of trapped mass with pressure. Now, how to increase the accuracy? There are many options; from simpler to more difficult:

- Take much more measures, not just a three points (one is already redundant); cost/benefit is low for this process, and statistical averaging decreases the uncertainty.
- Use better measuring instruments, if possible. Here, the uncertainty analysis teaches a lot: do not go for better thermometers but for a better balance, whose impact on uncertainty is much larger.
- Try direct measurements instead of indirect ones; e.g. try to measure the actual volume occupied by air, instead of assuming that the sphere is perfect and a single diameter measurement is enough, and that the spherical-shell volume is negligible, etc.
- Try to enhance the relative uncertainty by working with larger values; e.g. you may fill the vessel over ambient pressure, or decrease the surrounding temperature (and its uncertainty) by submerging the vessel in icy water. This is a similar case as when one measures the mass or thickness of a sheet of paper by using a stack instead of a single sheet.
- Try to slightly modify the set-up so as to decrease the relative uncertainties; e.g. for a given wall thickness, tare increases with the square of size, but air mass with the cube of size.
- Try to completely modify the set-up so as to drastically change one measure (e.g. measuring the volume of air extracted, balancing the tare with an appropriate counterweight, etc.) or going to a different experimental concept (most accurate density measurements today rely on resonant vibration processes instead of weighting).

- c) Based on density, molar mass and Avogadro's number, find the average distance between air molecules.

The volume of one mole of molecules is  $v = M/\rho = 0.029/1.19 = 0.024 \text{ m}^3$  (Avogadro was the first to notice that any one mole of ideal gas occupies 22.4 L at 0 °C and 101 kPa). One may then ascribe a volume  $v_0 = v/N_A$  to each molecule, and consequently an average distance between particles  $d = v_0^{1/3} = (0.024/(6.02 \cdot 10^{23}))^{1/3} = 3 \cdot 10^{-9} \text{ m}$ , i.e. a few nanometres.

This is about one order of magnitude larger than the size of molecules (e.g.  $0.152 \cdot 10^{-9} \text{ m}$  is the H-H distance in the water molecule  $\text{H}_2\text{O}$ ), which could be worked out from the density of solid matter (three orders of magnitude larger than that of room air).

The kinetic theory of gases serves to explain the ideal gas law in terms of momentum exchange with the walls and mean kinetic energy of the random molecular motion (equivalent to temperature in an ideal gas), and also shows that gas molecules randomly move with a root-mean-square of  $\sqrt{3RT/M} = \sqrt{3 \cdot 8.3 \cdot 293 / 0.029} = 500$  m/s here, colliding in the average every  $10^{-10}$  s after having travelled some  $10^{-7}$  m in the average, i.e. a length two order of magnitude larger than their average separation, or three orders larger than their size. Those are figures that, although no longer used in the engineering exercises following, are worth to keep in mind for a proper understanding of both basic and applied physics.

## Comments

First of all, a definition from the 3rd CGPM held in 1901:

**Weight is the force experienced by a mass at a point in Earth-surface when measured under vacuum. Conversely, weight is the force that, if applied to an isolated body, would impose on it an acceleration similar to its free fall under vacuum. By extension, it may be applied to weight over different heavenly bodies.**

With this definition, a given mass (e.g. the standard kilogramme in Paris) would weight differently at different latitudes, longitudes, altitudes and times, due to geodesic and centripetal variations, and a kilogramme of cotton would seem to weight more than a kilogramme of cotton if weighted in air (similarly, if a mass of gold weights the same than a mass of silver in the atmosphere, the former will be heavier if weighted under water). The answer to the old quiz of "Is a kilogramme of metal heavier than a kilogramme of cotton?" have to be "No, if performed according to international standards; yes, if performed as usual, although the difference is below 1%". The standard weight of a body is the product of its mass and the standard gravitational acceleration,  $\vec{F}_{\text{weight}} \equiv m\vec{g}_0$  ( $g_0=9.80665$  m/s<sup>2</sup>).

Notice that space weightlessness (e.g. astronauts floating around) is not the lack of weight but the balancing of weight by acceleration, as in free fall (gravitational attraction at the usual 400 km of space stations is only 11% less than at sea level on ground).

It might appear that the former definition of weight has equal grounds as the one defining weight as measured within the ambient air, as usual, but this exercise points to the key difference: with the second definition, air has no weight, and it would be embarrassing to explain how we weighted it here. One may call 'apparent weight' to the force experienced by a mass on Earth when measured within an ambient fluid like air or water, but it is better to avoid confusion and just keep to the standard weight,  $\vec{F}_{\text{weight}} \equiv m\vec{g}_0$ . Modern electronic balances used in Analytical Chemistry are calibrated using standard weights, made of a material with density  $\rho_0$ , and every measure is corrected for air buoyancy in the way  $m=m_0(1-\rho_{\text{air}}/\rho_0+\rho_{\text{air}}/\rho)$ , where  $m$  is the corrected mass,  $m_0$  the indicated mass,  $\rho_{\text{air}}$  the density of ambient air, and  $\rho$  the density of the sample being weighted; notice that, without this correction, the relative error when weighting water would be of  $10^{-3}$  instead of the  $10^{-5}..10^{-6}$  presently achievable (to reach that precision, the sample must be at room temperature to avoid additional buoyancy due to convective air currents, changes in density of trapped-air, and changes in sample density with time).

Measuring the weight of air is not a Byzantine question. Aristotle in the 300s b.C. postulated that earth and water have weight, whereas air and fire have levitation force. It was Galileo in the early 1600s the first to investigate the weight of air (he measured its density by differential weighting of an evacuated bottle, finding  $\rho \approx 2 \text{ kg/m}^3$ ). In 2004 it has been found that air is 0.01% heavier than the NIST standard.

At high pressure, the weight of air in a vessel becomes apparent; e.g. a typical scuba (self-contained underwater breathing apparatus) compressed-air aluminium bottle with 10 L capacity (0.18 m in diameter by 0.64 m in length), holds 2.4 kg of air at the standard 20 MPa filling, with a tare of 16 kg.

A final comment is that the order of magnitude for the density of any substance should be learned by heart: all condensed matter has a density around  $10^3 \text{ kg/m}^3$  (from  $0.07 \cdot 10^3 \text{ kg/m}^3$  for liquid hydrogen to  $23 \cdot 10^3 \text{ kg/m}^3$  for osmium), whereas gases at room conditions have a density around  $1 \text{ kg/m}^3$  (from 0.07 for hydrogen to  $6 \text{ kg/m}^3$  for sulfur hexafluoride).

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