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Slow physics: Recording the ascent and descent of a water column

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Abstract. A glass filled with carbon-dioxide gas upside down on a plate of water constitutes an excellent demonstration of the solubility of gases. If the water level on the plate is maintained the CO₂ will slowly dissolve and the column of water will rise inside the glass, without quite reaching the ceiling, before an opposite process sets in: The water level will even more slowly begin to sink in a process which will take several years. We followed the process for several months, recording images of the water column with 10-minutes to one-hour intervals. The physics of the process is discussed and modeled quantitatively.

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1. Introduction

There is a classic experiment, which is sometimes done in science classes at schools. A lit candle is placed on a plate with water. The plate is covered with a glass cup, sealing off the flow of air to the candle, which will shine for a while and then burn out. After the candle has burned out the water level inside the glass will rise. The physics behind this is simple: The air inside the glass gets heated up while the candle is burning and when the candle has burned out the air cools down, contracts and the water level will rise. A careful student may even notice some bubbles coming out of the glass in the beginning of the experiment when the air is heated. Unfortunately, even today some teachers explain the result by claiming that the candle will use up the oxygen in the air and hence the water will rise because there is only nitrogen left. This is of course wrong, as shown on several occasions.[1, 2, 3] Combustion consumes oxygen, but exhaust gases like CO_2 , H_2O and perhaps CO are released while the candle burns. The exhaust gases will replace the oxygen molecules, although some water molecules may of course condensate into liquid form. On the other hand, one O_2 molecule can lead to the formation of two H_2O or two CO molecules towards the end of the burning process, so even if some water vapor condensates into drops, the amount of gas substance in the glass does not necessarily diminish at all. If the glass, covering the candle, is left overnight a curious thing can be seen next morning: The water level will rise in the glass with perhaps 2-3 mm, even after the glass and the air inside it has cooled down properly. The air inside the glass has a high concentration of carbon dioxide, which easily dissolves into water, causing the water level to rise.

We decided to explore this process a bit further and filled the glass with pure CO_2 to see how the water level would change over a long period of time and whether it would reach the ceiling of the glass container. The comparatively fast dissolvment of CO_2 illustrates a naturally occurring process in the oceans and can perhaps be seen as demonstration of how the capture of anthropogenic greenhouse gases could be done, as CO_2 is one of the major agents in the the present climate-change process, which is a problem that has been studied for a while.[4, 5, 6]

2. Experimental

A five-liter beaker was filled almost to the rim with distilled water. The water was dyed red, using rhodamine 640 (Oriol Instruments 79156) to improve the visibility of the water column. A nominally 500-ml graduated cylinder (Hirschmann Techcolor, Germany) was filled to rim with 676 ml of the dyed distilled water and placed upside down with the opening 10 mm below the surface of the water in the beaker, Fig. 1. The height of the water column inside the cylinder was 230 mm. A computer controlled heat exchanger flushed with cold tap water maintained the water in the beaker at a temperature of 17.5 ± 0.5 °C. Styrofoam insulation around the beaker was used for reducing the heat exchange with the ambient.



Figure 1. The setup. The dyed water rises slowly inside the graduated cylinder as the CO_2 atmosphere inside the cylinder dissolves into the water. The image is one of the ~ 6000 recorded during the course of the experiment.

After fixing the position of the graduated cylinder a rubber tube was inserted inside the cylinder, the interior of which was filled and flushed with dry CO_2 gas (99.99%, AGA, Finland) replacing the water completely. Prior to the filling the rubber tube was flushed thoroughly with CO_2 . The whole setup was illuminated with a bright white LED-light source and an ordinary computer controlled web camera took photos of the cylinder with predefined intervals. During the first 48 hours images were recorded every 10 minutes, and later on with one-hour intervals. From the images the height of the water column

was read directly from the scale printed on the cylinder. Although the scale covered only a part of the cylinder the height could be read by comparing an empty cylinder with the images and extrapolating. From a plot of the height versus time the dynamics of the water column was obtained, and analyzed using a simple model, *vide infra*. The images were also combined to a video running at a speed of 6000 to 1,440,000 times faster than the actual experiment. In Fig. 1 the experiment has been running for 11 h.

In order to compensate for natural evaporation ~ 80 ml of distilled water was carefully poured into the beaker twice a week. Additionally, during the first 24 h of the experiment it was necessary to compensate for the ascending water column by automatically filling the beaker. For this purpose a second (150 ml) cylinder filled with distilled water was kept submerged barely 2 mm below the surface of the water level in the beaker. The second cylinder can be seen on the right edge of Fig. 1. The cylinder was carefully removed after it had emptied itself after the first day of the experiment. In order to prevent the formation of potentially diffusion-hemming algae in the water, which could form from organic dust contamination 10 g of sodium azide (NaN_3) dissolved into 80 ml of distilled water was carefully poured into the beaker after the experiment had been running for two months.

In a second experiment the first part, i.e the dissolvment of CO_2 , was repeated with a pH-meter (PASCO[®] Chemistry sensor) immersed in container of the distilled water. The pH-meter was connected (via a PASCO[®] PS-2009A sparklink) to a computer. The pH of the water was initially recorded with 1-s intervals and then with 60-s intervals after the CO_2 gas had been introduced into the cylinder and the acidity of the water had stabilized.

3. Theory

In order to analyze the dynamics of the water column we developed a simple model based on the partial pressures of the gases inside the cylinder, and the mass-transfer rates of CO_2 and air. There are two gas-water interfaces: One inside the cylinder and the other between the 5-litre beaker and the ambient, Fig 2. These two surfaces were not modelled separately, as we assumed that the mass transfer of gases is a steady state process. Obviously the mass transfer rates are dependent on the surface areas of the interfaces. The atmospheric pressure (P_0), and the temperature (T_0) of the water and the gas column were assumed to be constant during the experiment. Naturally, the pressure varies with meteorological conditions, while the gas temperature is expected to vary less, as the gas column is in contact with the temperature-controlled water. The relative humidity of the ambient varies with the seasons, but this is not considered in the model. Inside the cylinder the relative humidity is assumed to be 100%.

The height of the water column is denoted with h , while the pressure and volume of the gas column are denoted P and V , respectively. The hydrostatic pressure (ρgh) and pressure in the gas column are related as:

$$P + \rho gh = P_0, \tag{1}$$

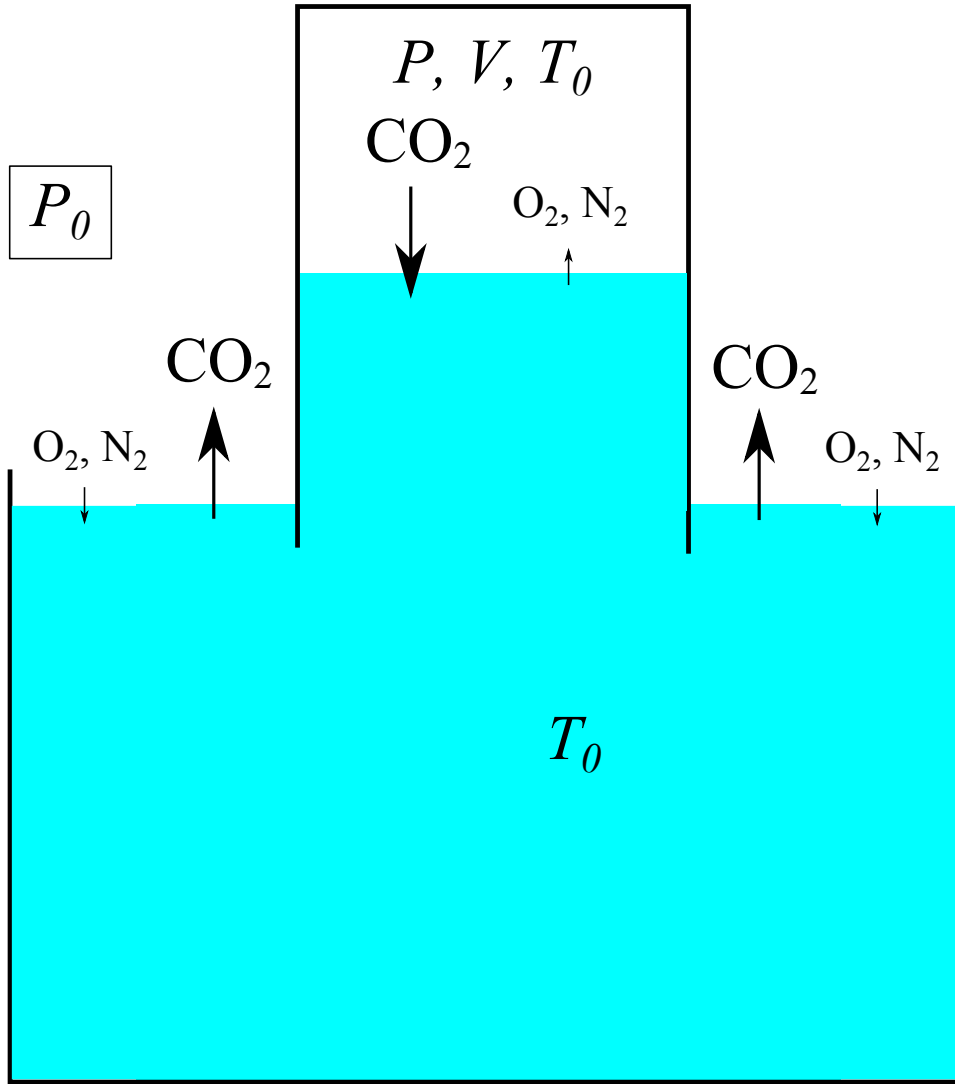


Figure 2. A schematic flow diagram of the gases into and from the cylinder.

where the density of water and acceleration of free fall are denoted by ρ and g , respectively. When the column height is h the amount of substance in the gas column is n . Later on when the column height is h' , the pressure has changed to $P' = P_0 - \rho gh'$, i.e the change in pressure is given by

$$\Delta P = \rho g(h - h') = -\rho g \Delta h. \quad (2)$$

The process of dissolving gas is slow. Hence the gas in the cylinder can be considered to be in thermodynamic equilibrium and the ideal gas law can be applied:

$$PV = nRT_0, \quad (3)$$

where

$$V = A(h_0 - h) \quad (4)$$

is the volume of the gas expressed as a product of the cross section A and height h_0 of the empty cylinder. $R = 8.3145 \text{ J/molK}$ is the ideal gas constant. Differentiating the

ideal gas law at constant temperature we get $V\Delta P + P\Delta V = \Delta nRT_0$. Upon inserting Eqs. 2,3 and differentiating Eq. 4: $\Delta V = -A\Delta h$ we get

$$-\rho gV\Delta h - \frac{nRT_0}{V}A\Delta h = RT_0\Delta n, \quad (5)$$

Solving for Δh yields:

$$\Delta h = \frac{RT_0\Delta n}{\rho gA(h_0 - h) + \frac{nRT_0}{h_0 - h}}. \quad (6)$$

By dividing Eq. 6 with a time interval Δt and taking the limit $\Delta t \rightarrow 0$ a differential equation for the height change dh/dt is obtained as a function of the changing amount of gas substance dn/dt :

$$\frac{dh}{dt} = \frac{RT_0}{\rho gA(h_0 - h) + \frac{nRT_0}{h_0 - h}} \frac{dn}{dt}. \quad (7)$$

At any given time the atmosphere of the gas column consist of CO_2 , air, and H_2O , so that

$$n = n_{\text{CO}_2} + n_{\text{air}} + n_{\text{H}_2\text{O}}. \quad (8)$$

The solubility of CO_2 in water is good, but depends on the partial pressure of the gas, the purity of the water and the surface of the interface between the liquid and the gas.[7] In the present quasi-static experiment there is no stirring and the decrease in the amount of CO_2 substance is simply modelled as:

$$\frac{dn_{\text{CO}_2}}{dt} = -\alpha_{\text{CO}_2} \frac{n_{\text{CO}_2}}{n}, \quad (9)$$

where α_{CO_2} is the mass-transfer coefficient of CO_2 for the present setup. The increase in the amount of air substance in the column is assumed to follow the expression

$$\frac{dn_{\text{air}}}{dt} = \alpha_{\text{air}} \frac{P_0 - P_{\text{air}}}{P_0}, \quad (10)$$

where α_{air} is the mass-transfer coefficient of air for the present setup. The partial pressure of water is assumed to be 20 mbar, a number valid for a relative humidity of 100% at a temperature of 17.5 °C.[8] The corresponding relative substance of gaseous water $n_{\text{H}_2\text{O}}/n$ in the gas column was kept constant in the model. Equations 7,9 and 10 were solved numerically with a dedicated computer program and after each step h , $P = P_{\text{air}} + P_{\text{CO}_2} + P_{\text{H}_2\text{O}}$ and n were updated self-consistently. The presence of CO_2 (and other trace gases) in the ambient air was not taken into account, but the decrease of n_{CO_2} in the cylinder was stopped when the relative portion of it in the gas column reached equilibrium with the ambient, *i.e* 400 ppm.

4. Results and discussion

In Fig. 3 a plot of the pH vs. time on half-logarithmic scale is plotted. The initial descent of the pH is due to the fact that atmospheric CO_2 dissolves into the distilled water, causing the pH plunge well below 7. Then, filling of the cylinder with CO_2

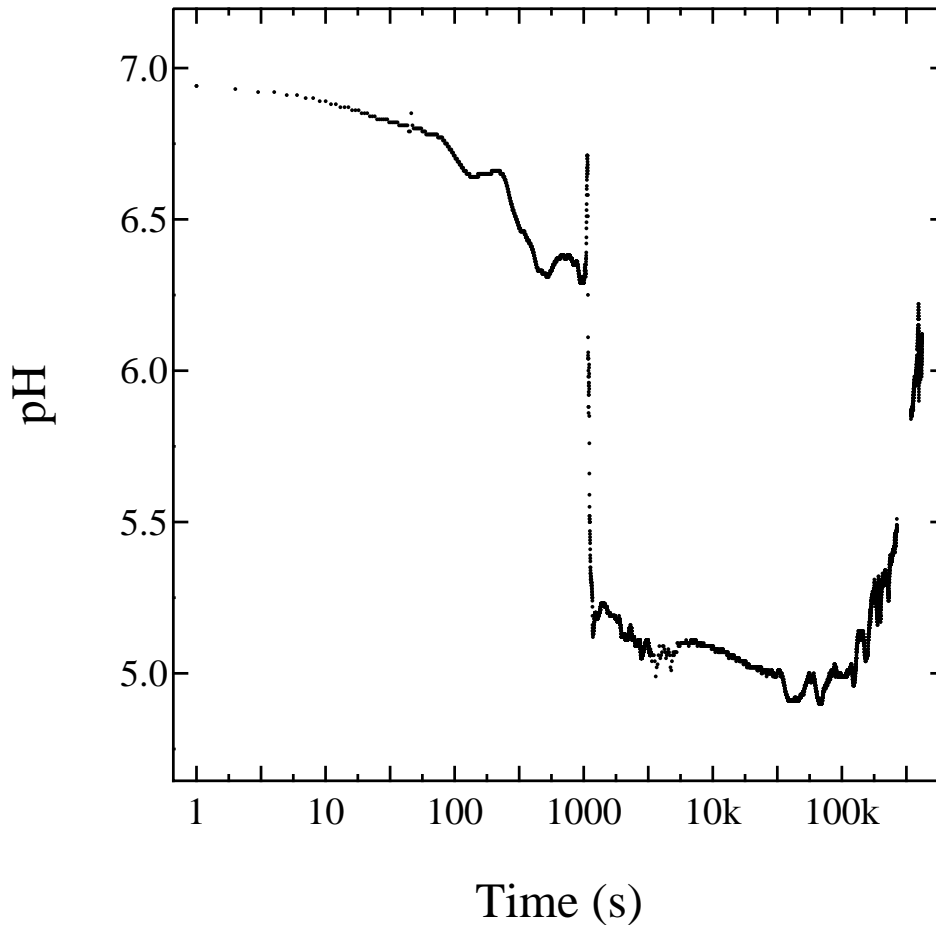


Figure 3. Acidity of the water, expressed with pH, vs. logarithm of time as the cylinder is first filled with CO_2 gas, which then dissolves into the water.

acidifies the water almost instantaneously at $t = 1000$ s. The pH remains roughly constant between 1000 and $1.6 \cdot 10^5$ s, which is the time it takes for the water column to rise to within millimeters of its maximum height. This indicates that the mass transfer rate from the CO_2 column to the water remains a steady-state process, which gives justification to our simplified mass-transfer model, Eq. 9, 10 and the omission of the separate mass-transfer processes at the two gas-water interfaces.

In Fig. 4 the height of the column is plotted as a function of time. The data points were obtained directly from the image data. The zero level is taken from the submerged edge of the cylinder. Minute small-amplitude oscillations with several-day-long periods can be observed in the water level during the descent. These are probably caused by variations in the atmospheric pressure P_0 , i.e. the water column works as a very crude barometer. It turned out that the red dye used for enhancing the contrasts was not stable, causing the water column to fade from a bright purple to a faint pink during the course of the experiment. Despite of this the level of the water column remained clearly visible in the image data.

The theoretical curve was obtained by numerically solving Eq. 7, with experimental mass transfer coefficients of $\alpha_{\text{CO}_2} = 2.17 \cdot 10^{-7}$ mol/s and $\alpha_{\text{air}} = 3.47 \cdot 10^{-9}$ mol/s as free parameters. The dissolvment of CO_2 into water is pressure dependent. Here we

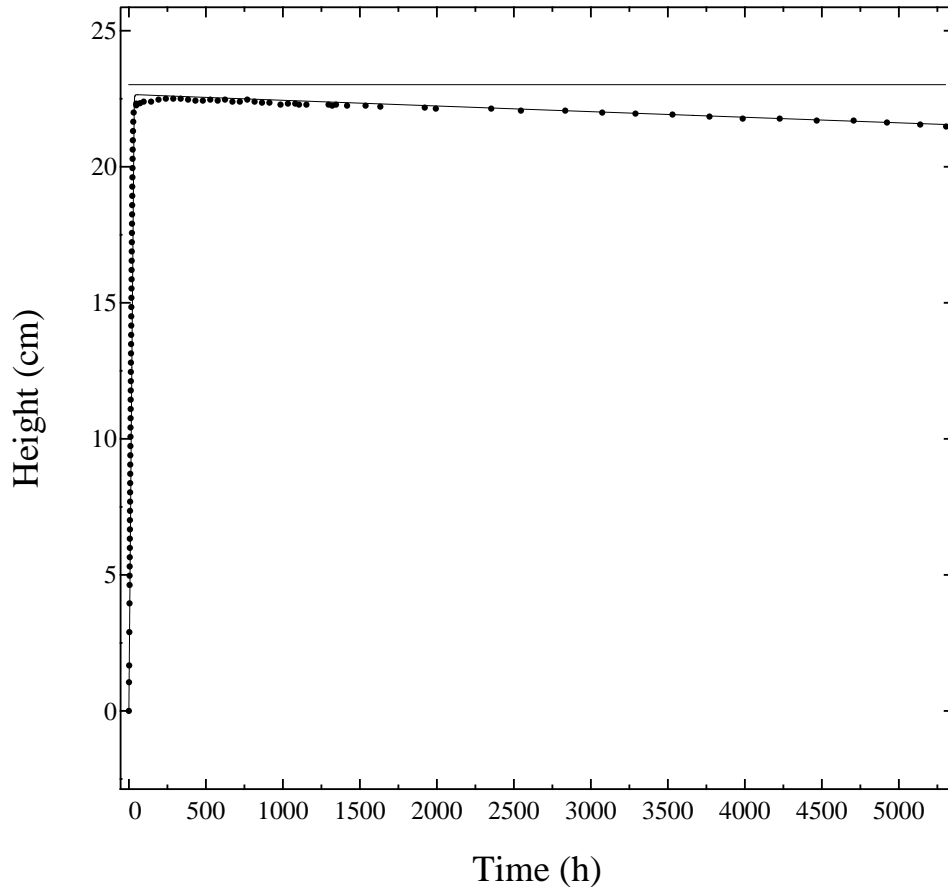


Figure 4. Height of water column in the graduated cylinder, during the first 5400 hours when CO_2 first dissolves, after which the descent commences. The experimental data was fitted using eq. 7 numerically, see text. The horizontal line denotes the height of the cylinder.

have assumed that it is linearly proportional to the relative partial pressure of the gas or rather the molar ratio, which is almost the same thing. Close to the maximum height of Fig. 7 the fit curve describes poorly the data and this is probably where our simple linear model fails. Later on, when the CO_2 is more or less completely dissolved, the descent is dominated by Eq. 10. However, Eq. 10 contributes also strongly during the ascent, when the partial pressure of air is close to zero, which makes the ratio $(P_0 - P_{\text{air}})/P_0$ large in Eq. 10. This is why the water column never reaches the top: During the first 36-45 hours when the column ascends rapidly, some air is also transferred into the cylinder, and in the ensuing time interval the water column remains practically motionless as the remaining CO_2 slowly dissolves and air, driven by the now very small pressure difference, is transferred into the cylinder. Visually, actual descent is observed only after 500-1000 h.

It is instructive to plot the predicted CO_2 , air and H_2O contents in the cylinder, Fig. 5

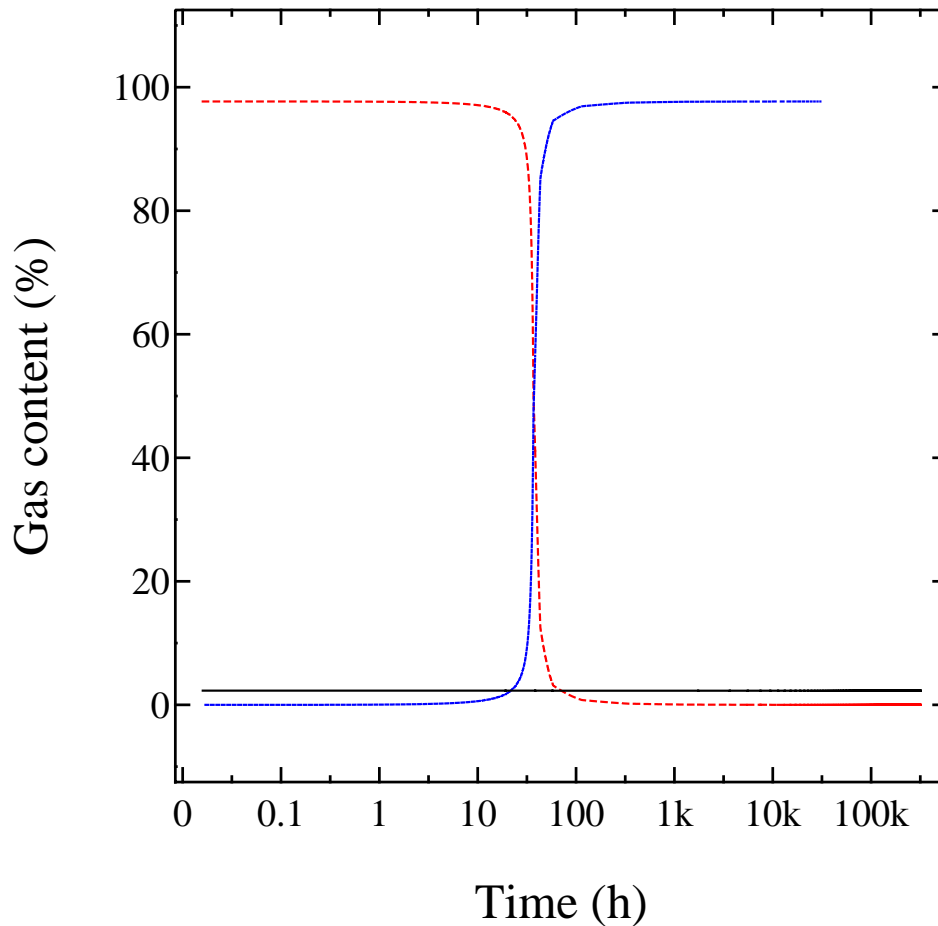


Figure 5. Predicted gas contents in the column obtained from Eqs. 9, 10 as n_{CO_2}/n and n_{air}/n : CO_2 (red dashed line), air (blue continuous line), and H_2O (black horizontal line).

Obviously the time scales involved in the experiment differ a lot: the relatively fast dissolving of CO_2 , causes the water column to ascend and reach its peak practically within 1-2 days, while the very slow descent of the water column when air diffuses into the column takes years, Fig. 6. Yet, as the water column never reaches the ceiling the process of air intake starts immediately. As a classroom demonstration only the first part of the experiment is easy to perform, while the second part requires attention during a prolonged time. A considerably higher cylinder and a beaker with a larger surface area should speed up both the ascent and the descent. If carbon dioxide is not available, *e.g.* carbonized soda water can be used instead. By shaking the soda-water bottle the released CO_2 gas can be collected.

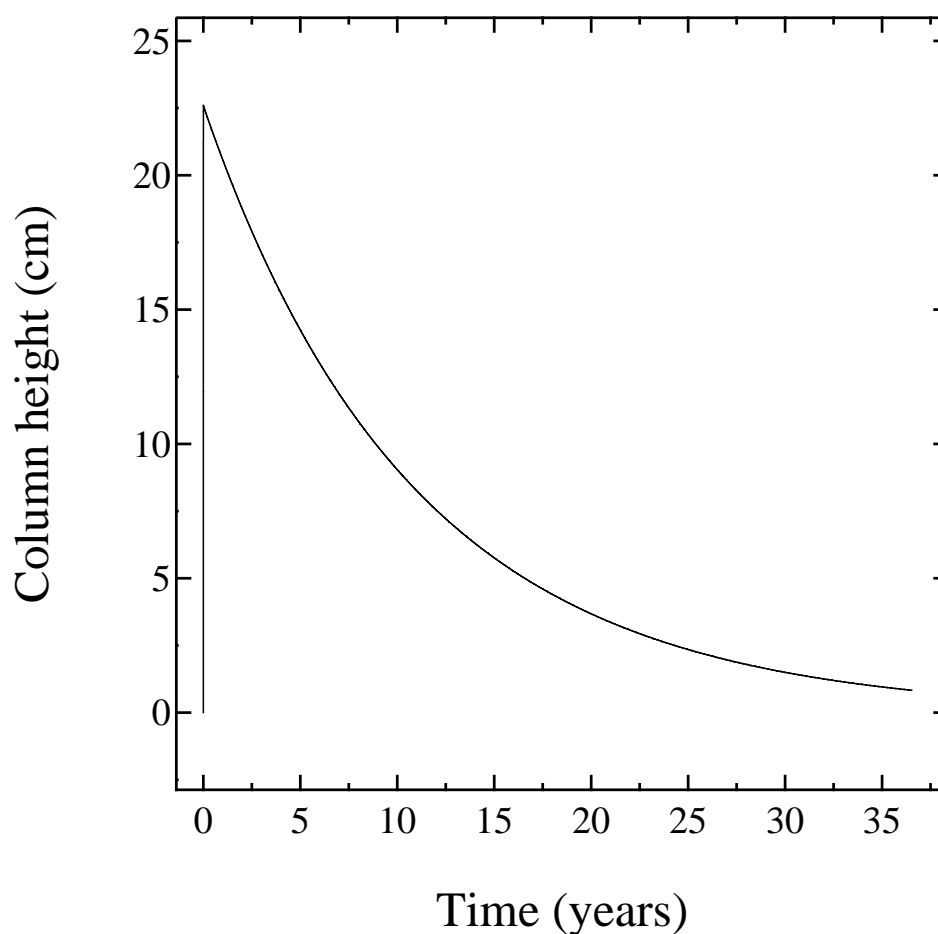


Figure 6. Predicted long-term evolution of the height of the water column.

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