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Spontaneously expanding and shrinking soap bubbles

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Abstract. An ordinary soap bubble immersed in a pure carbon-dioxide atmosphere, created e.g. by sublimating chunks of dry ice (solid CO_2), will expand within a few minutes to a volume exceeding the original one with a factor of almost ten. Considering that the bubble simultaneously experiences a cooling of ~ 30 °C one would perhaps expect a tiny shrinkage instead. The physics behind the phenomenon, i.e. diffusion of highly soluble CO_2 through the soap film caused by the difference in the partial pressure of CO_2 between the interior and the exterior of the bubble, combined with the expansion of the active area of the bubble, is discussed. Actual data obtained from a video of an expanding bubble is combined with the simulation of the process, resulting in a fairly good agreement. The reverse experiment of a bubble filled with CO_2 under ambient conditions leads to a fast shrinkage of the bubble. Finally, a bubble filled with helium placed in a CO_2 atmosphere expands initially, reaches a maximum volume and then begins to shrink. Also this case was modeled semi-empirically. The experiments presented are suitable for upper-secondary-school pupils. Understanding the theoretical description requires first year university studies of physics or chemistry.

1. Introduction

The solubility of carbon dioxide (CO_2) in water is rather remarkable. An example of this phenomenon can be observed by measuring the pH of distilled water, where a decreasing number is observed when the container is opened to the ambient. CO_2 dissolving into the water will react to form carbonic acid, easily pushing down the pH value of the water a whole unit. In another recent experiment by one of the authors, the solubility of CO_2 was demonstrated by observing the level of a water column kept inside a closed cylinder filled with CO_2 . [1] During the experiment the water level was shown to rise to a height of 20 cm within 48 hours. Indeed, it has been suggested that films of water might be used as the active ingredient in the process of carbon capture and storage. [2, 3] Soap films and bubbles can be found in many everyday products [4] but are also an important factor to consider for example in industry [5, 6] The concept of soap bubbles are fascinating to many, and the books written by Isenberg [7] and Boys [8] can be mentioned as excellent and popular books on the subject. Soap bubbles are also popular in outreach activities [9, 10] and science education [11, 12, 13] where they have been utilized to teach even subjects such as catalysis [14] and mechanical properties of metals [15].

In this paper the solubility of CO_2 molecules in water together with interesting dynamics due to difference in permeability of gases are demonstrated using ordinary soap bubbles. The solubility of CO_2 is demonstrated via soap bubbles immersed in a carbon dioxide atmosphere (growing bubble) as well as the reversed experiment with CO_2 filled soap bubble subjected to ambient conditions (shrinking bubble). These effect has been known for some time, [16, 17] but here we present quantitative data together with phenomenological descriptions of the processes. Dry ice and carbon dioxide from a pressurized bottle were used as CO_2 sources but the demonstrations can also be facilitated using ordinary house-hold items reacting to form or simply releasing CO_2 . If dry ice is available the counter-intuitive result of bubbles expanding when cooled down adds an extra flavor to the experiment. Finally, using a combination of helium (He) and carbon dioxide the interesting phenomenon of a soap bubble undergoing both growth and shrinkage is demonstrated.

The permeability of soap films to different gases is not a new concept, and models have been developed to describe the phenomena occurring. [18, 19] However, the concept of modelling the volume as a function of time spent in a specific environment has not been presented. We hope that our approach will open up the subject to broader audiences, even though a deeper understanding requires university level knowledge of chemistry and physics.

2. Experimental

For our first experiments a few chunks of dry ice were placed in a plastic bowl with a 15 cm high rim. A single soap bubble with the initial radius of 15 mm was attached to

a plastic ring, obtained by cutting off the neck of a soda bottle, and inserted into the bowl. The soap bubble was surrounded by a CO_2 atmosphere from all directions, apart from the tiny surface in contact with the ring.

In a second set of experiments, aimed at fixing the temperature to a constant value, a glass aquarium with a transparent cover was employed, Fig. 1. The volume of the aquarium was approximately 80 litres. The walls of the aquarium were sprayed with water and the interior of the aquarium was filled with either N_2 or CO_2 gas. Soap bubbles, produced by thoroughly flushing a short stump of a garden hose with N_2 or CO_2 before dipping the end into a soap solution, were introduced into the aquarium and carefully placed on a plastic ring. The aquarium was covered and the evolution of the soap bubble was recorded using a mobile phone attached to a tripod until the bubble burst or its size remained practically constant. Using video captures the diameter of the bubble was initially read every 2 seconds using an accuracy of ± 2 pixels. Towards the latter half of the experiment the diameter was read every 4th, 8th or 10th second. The diameter of the ring was employed as a reference for measuring the diameter of the soap bubble. The gas in the aquarium and inside the soap bubble had the same temperature and the wetted walls saturated the gas with water vapor, thus restraining evaporation from the soap film, which otherwise would have led to an early demise of the bubble.

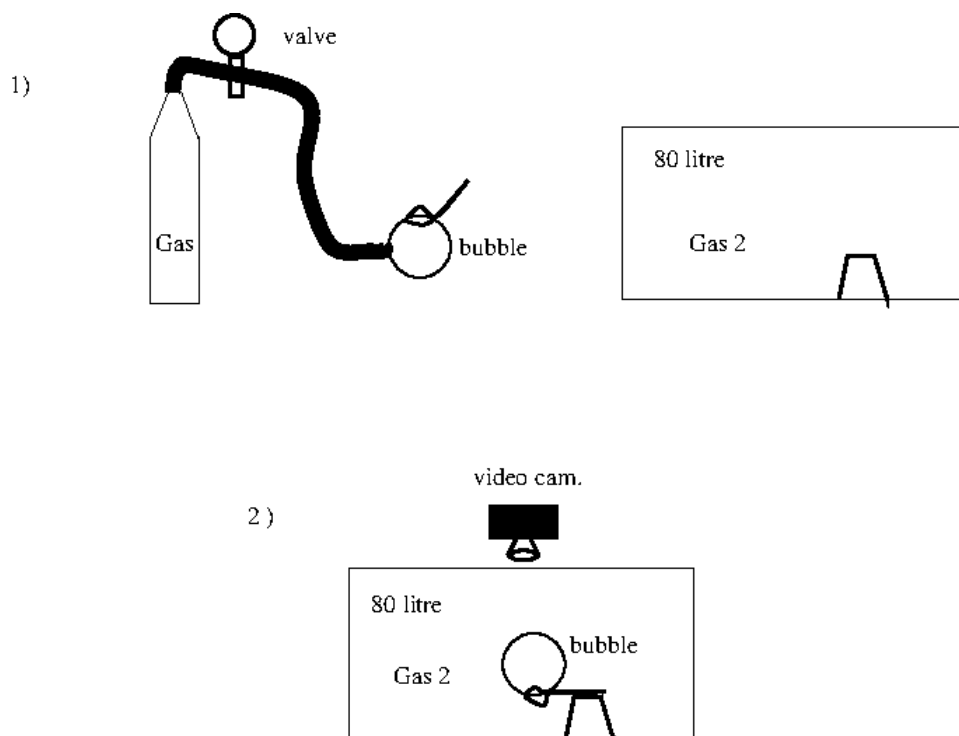


Figure 1. Sketch of experimental setup: Soap bubbles are filled with the desired gas and transferred to the aquarium filled with second gas. The dynamics of the bubble is monitored using a video camera (mobile phone).

We also introduced a helium-filled bubble to an CO_2 atmosphere to see whether the quick He atoms with rather poor solubility would escape faster than the slower, but

very soluble, CO₂ molecules entered the bubble.

3. Theory

In order to analyze the dynamics of a soap bubble we need to derive expressions for the rates at which gas from the surrounding atmosphere enters the bubble and gas from the inside of the bubble escapes into the surrounding atmosphere. The surrounding atmosphere is considered infinite and hence the escaping gas is assumed to be completely diluted, where as inside the bubble there will be a continuous evolution of the gas mixture. Gradients of concentration inside the bubble are not considered, as diffusion through the soap film is assumed to be much slower than the mixing of the gases inside the bubble. Also, due to surface tension in the soap film the interior of the bubble always has a little higher pressure than the exterior, as given by the Young-Laplace equation[20], but even for the smallest bubbles this contributes only ~ 10 Pa to the internal pressure and was neglected.

In order to model the exchange of gases we need Henry's law for the solubility H (in units of mol/m³Pa):[21]

$$H = c/p, \quad (1)$$

where c is the concentration (mol/m³) of a gas in the aqueous phase and p the partial pressure (Pa) of the gas in the atmosphere in contact with the water surface. The atmosphere on either side of the soap film may differ. Denoting the two surfaces 1 and 2 and the partial pressures surrounding the film p_1 and p_2 , we can write the difference in concentrations immediately beneath the surfaces as $\Delta c = c_2 - c_1 = H(p_2 - p_1) = H\Delta p$. We also need Fick's law of diffusion in one dimension:[22]

$$J = -D \frac{dc}{dx}, \quad (2)$$

where J is the diffusion flux vector for a gas (mol/sm²), $\frac{dc}{dx}$ the concentration gradient and D the diffusion constant (m²/s). The film of a soap bubble is rather thin. Therefore, one may assume that the concentration gradient of a specific gas is essentially determined by the difference in partial pressure Δp of the gas on either side of the film, i.e. we can write $J \propto \frac{\Delta p}{w}$, where w is the film thickness, replacing dx . The proportionality can be replaced by a proper equality by using the expression $\Delta c = H\Delta p$ derived above. Therefore,

$$J = -HD \frac{\Delta p}{w} \quad (3)$$

However, as there are continuous flows of gases and an expanding or shrinking film surface we need to take into account the dynamics of the bubble itself. Expressing the gas flow as $dN/dt = JN_A A$, i.e. total number of molecules or atoms per time unit flowing in or out of the soap bubble, where N_A is Avogadro's number and A the surface area of the soap bubble we obtain

$$\frac{dN}{dt} = N_A A H D \frac{\Delta p}{w}, \quad (4)$$

The minus sign has been dropped, as the flow direction is determined by the sign of Δp .

Equation 4 is applied for each gas with the initial soap-film thickness w_0 as the only adjustable parameter. The process of gas exchange can be rather quick, yet the gas in the bubble can be considered to be in thermodynamic equilibrium and the ideal gas law can be applied:

$$p_0V = nRT_0, \quad (5)$$

where T_0 , p_0 are the ambient temperature and pressure, n the amount of substance in moles and the ideal gas constant $R = 8.3144621 \text{ J/molK}$. However, in our modeling we are using total numbers of molecules or atoms N inside the bubble so Eq. 5 is used in the alternative form

$$p_0V = Nk_B T_0, \quad (6)$$

$k_B = 1.380649 \times 10^{-23} \text{ J/K}$ Boltzmann's constant. Only V and N change, so the derivative $\frac{dV}{dN} = \frac{k_B T_0}{p_0}$. The area of a sphere expressed by its volume is given by $A = (6\sqrt{\pi}V)^{2/3}$ and hence $dA/dV = (2/3)(6\sqrt{\pi})^{2/3}V^{-1/3}$. By replacing the volume V by the area A we obtain $dA/dV = 4\sqrt{\pi}/\sqrt{A}$. Thus, when the number of molecules changes by dN the volume changes as $V \rightarrow V + \frac{k_B T_0}{p_0} dN$ and the bubble area as $A \rightarrow A + 4\frac{k_B T_0}{p_0} \frac{\sqrt{\pi} dN}{\sqrt{A}}$. Furthermore, as the soap film contains a constant body of water with the volume wA , the thickness w decreases when the bubble expands and increases when the bubble shrinks.

Equations 4 and 5 combined with the expressions for the surface area were employed for modeling the experimentally observed expansion/shrinkage of a soap bubble. When simulating the data an initial value for $w_0 \approx 3000 \text{ nm}$ was used and it was varied until data and theoretical curves agreed. However, it was evident that the "linear" model of Eq. 4 was not capable of explaining the behavior of a helium-filled bubble that first expands and then shrinks. In order to remedy this it was assumed that whenever the difference in partial pressure for CO_2 evens out, in cases were the bubble is surrounded by this gas, a saturation effect sets in, which retards the subsequent flow of CO_2 . Experimentally the following phenomenological expression was assumed for the saturation

$$e^{[-(t/\tau_0 + k_{\text{CO}_2})]} \quad (7)$$

where the time constant τ_0 was 10-90 s and $0 \leq k_{\text{CO}_2} \leq 1$ the fractional concentration of CO_2 inside the bubble. Thus, when modeling the dynamics of the CO_2 molecules for a bubble filled with He or N_2 (and surrounded by CO_2) the right-hand side of Eq. 4 was multiplied by expression 7. There saturation effect can be justified; When CO_2 molecules enter the water containing film they react to form carbonic acid (H_2CO_3), which is a rather slow process, where as the subsequent disproportionation into H^+ and HCO_3^- is quick.[16] Hence, if the gas on one side of the film is poor in carbon-dioxide molecules the molecules are effectively vented out, which keeps the "flux running", where as a build up of CO_2 on the poorer side of the film may cause the slower of the two

chemical reactions to become a bottle neck for further CO_2 diffusion and the effective diffusion rate goes down. This effect is modeled of by expression 7.

4. Results and discussion

In Figs. 2, 3, and 4 video captures of shrinking, expanding and expanding/shrinking bubbles are shown. The captures were taken at the beginning of the experiment and immediately before ending the experiment when no expansion was detected or when the bubble became too small to retain its spherical shape on the plastic ring. The videos of



Figure 2. Video captures showing a shrinking bubble initially filled with CO_2 in a N_2 atmosphere at $t = 0$ s and $t = 30$ s.

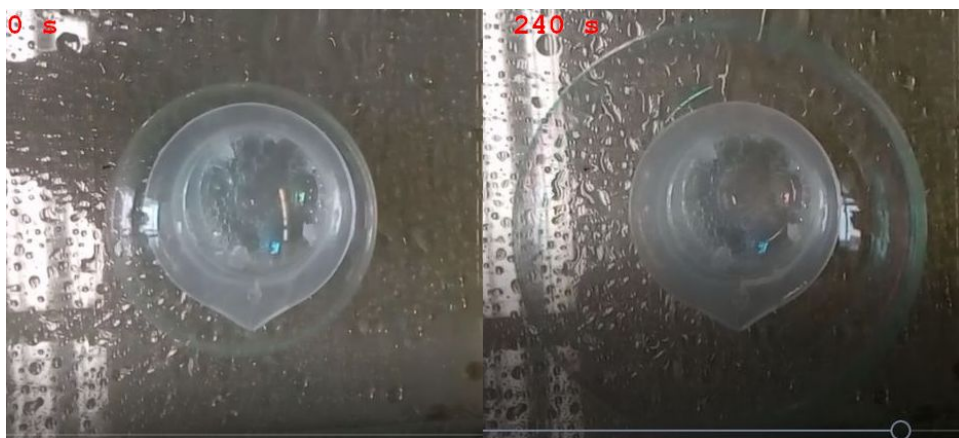


Figure 3. Video captures showing an expanding bubble initially filled with N_2 in a CO_2 atmosphere at $t = 0$ s and $t = 240$ s.

these experiments are found in the video abstract. Figs. 5-7 present the volumes of the expanding/shrinking bubble extracted from the video material. The volume data were simulated using Eq. 4 multiplied by expression 7 when the gas surrounding the bubble was CO_2 . In table 1 literature data for each gas is presented, serving as input for Eq. 4.

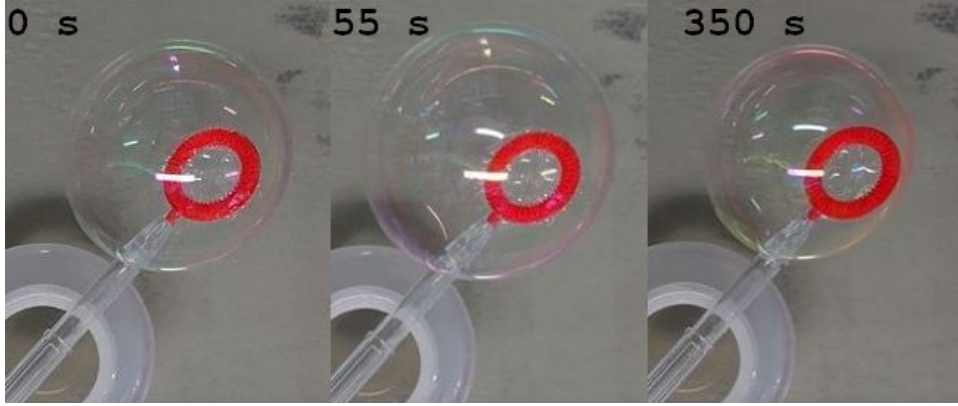


Figure 4. Video captures showing an initially expanding bubble, filled with He in a CO₂ atmosphere at $t = 0$ s, reaching a maximum at $t = 55$ s and then shrinking up to $t = 350$ s.

Table 1. Properties of gases used in the experiments

gas	H (mol/m ³ Pa)[21]	D (m ² /s)[25, 26]
N ₂	$6.4 \cdot 10^{-6}$	$1.64 \cdot 10^{-9}$
CO ₂	$3.4 \cdot 10^{-4}$	$1.77 \cdot 10^{-9}$
He	$3.9 \cdot 10^{-6}$	$6.8 \cdot 10^{-9}$

The initial wall thickness w_0 was assumed to be around 3000 nm - a value typical for soap bubbles[24]. This value was refined by iterating the simulations.

Although not easily measured it is interesting to plot the fractional concentration of gases obtained from the simulations. For the first case, where CO₂ escapes from the bubble and N₂ enters, the concentration of CO₂ in the bubble remains very high throughout the experiment, as the escaping gas immediately gets diluted, which maintains a reasonably high partial-pressure difference for CO₂, deflating the bubble before large amounts of N₂ have entered, Fig 8. In the opposite case where CO₂ molecules enter the nitrogen-filled bubble the gas contents change rather fundamentally as the original N₂ atmosphere only partially escapes and gets diluted by CO₂, Fig. 9. For the helium-filled bubble the direction of gas flows are monotonic functions of time, but the saturation effects gives rise to a knee in the inflow of CO₂ gas, causing the escaping helium gas flow to catch up with and even dominate over the CO₂ flow, Fig. 10.

Once dissolved the average time required for a CO₂ molecule to diffuse through a soap film of 3000 nm is only 2.5 ms, indicating that the interior gas could escape rather quickly. However, the process is strongly governed by the Henry solubility which brings down the flow of escaping gas to the values observed in the experiments. Henry's law deviates from the simple inverse linear form for small pressures, which was not taken into account in this work. This could partially explain the deviation between the experiment and simulation for the helium-filled bubble. We also neglected possible drainage of the water between the surfactant layers, which leads to a thinning of the soap film at the top and a thickening at the bottom of the bubble. Nevertheless, the gas flow through the

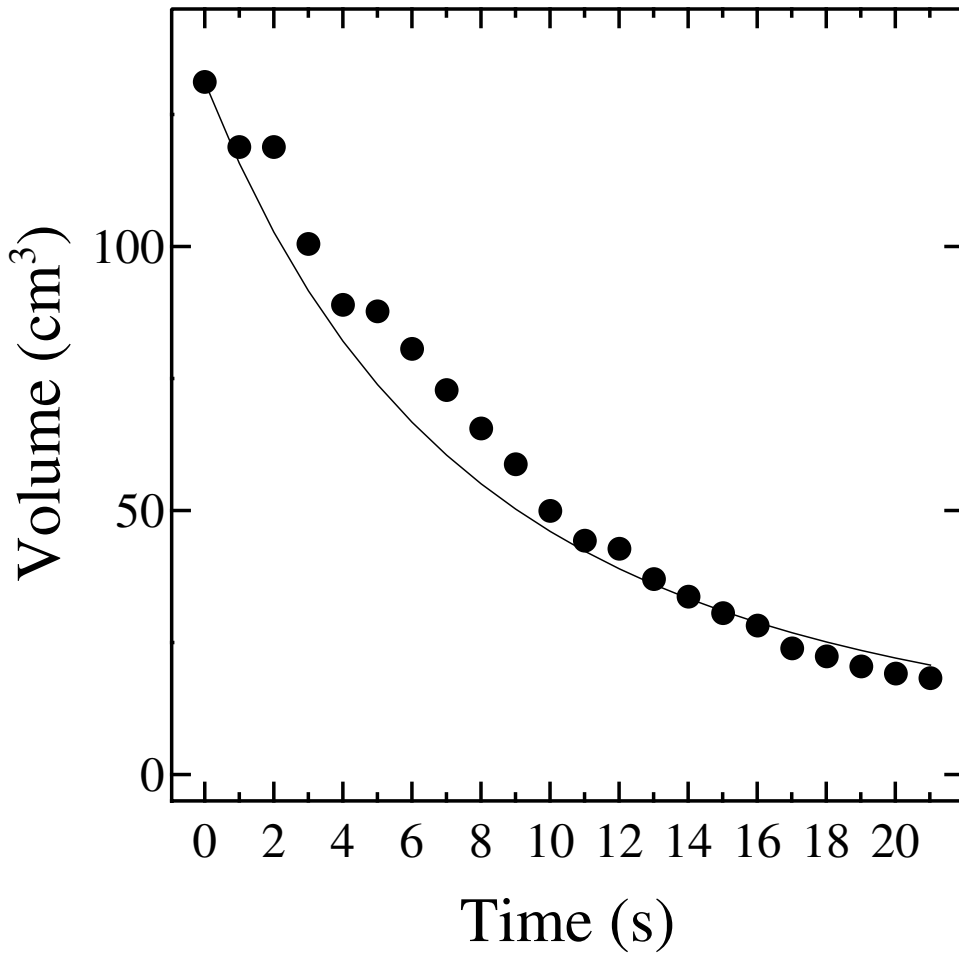


Figure 5. Volume versus time of a soap bubble initially filled with CO_2 shrinking in a nitrogen atmosphere. The theoretical curve is based on Eq. 4 with the initial thickness $w_0 = 1080$ nm. The statistical errors are the same size as the symbols along the volume axis and the time axis.

walls of soap bubbles could be described by rather simple equations capturing the fast expansion/shrinkage of the bubble fairly well. More detailed simulations would probably require the use of molecular dynamics and proper inclusion of water and carbon-dioxide chemistry. Also the surfactant molecules from the soap, neglected in this work, will have an impact on the absorption of the gases.[27] The present experiments could possibly be used for a non-optical method of measuring the wall thickness of a soap bubble, after first calibrating the thickness by examining the interference fringes in the films using a suitable light source.

5. Conclusions

Soap bubbles filled with, or surrounded by a carbon-dioxide atmosphere will spontaneously shrink or expand on a time scale of 10-300 s and constitute excellent demonstrations of the high solubility of CO_2 gas in water. The dynamics of these

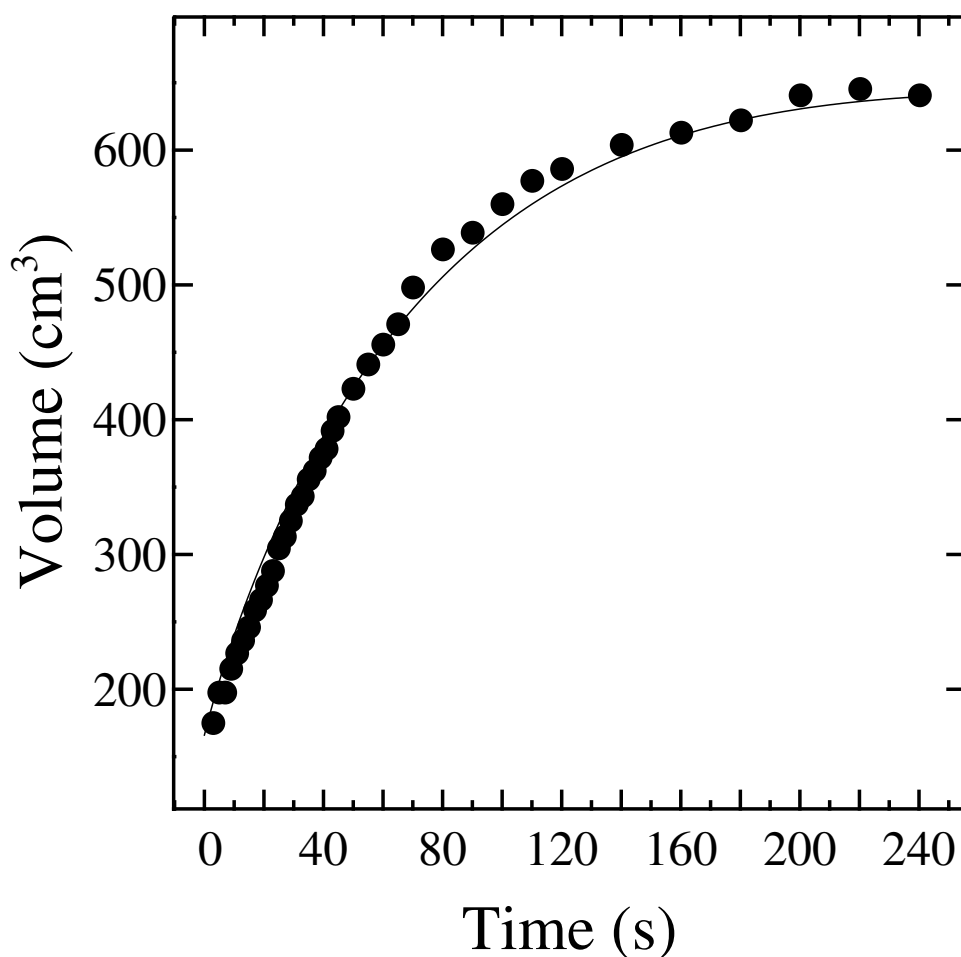


Figure 6. Volume versus time of a soap bubble initially filled with nitrogen expanding in a CO_2 atmosphere. The theoretical curve is based on Eq. 4, with the initial thickness $w_0 = 2400$ nm, and multiplied by expression 7 with $\tau_0 = 90$ s. The statistical errors do not exceed the size of the symbol along the time- nor the volume axis.

processes were successfully simulated using Henry's law of solubility and the diffusion law as starting points. The demonstrations are fairly easy to reproduce in a class room if CO_2 gas and a suitable transparent vessel are available. The experiments can be varied by the use of various gases and combinations of gas inside the bubble versus the atmosphere surrounding it.

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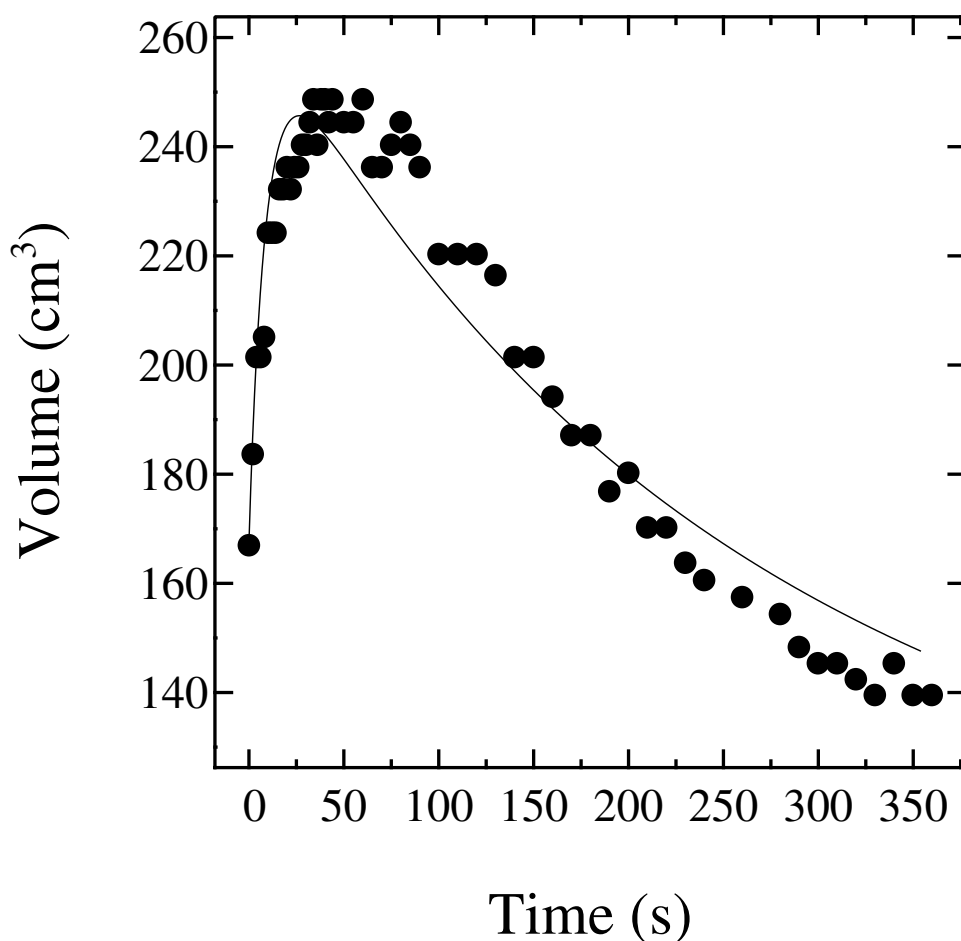


Figure 7. Volume versus time of a soap bubble initially filled with helium in a CO_2 atmosphere. After expanding for a while the bubble begins to shrink. The theoretical curve is based on Eq. 4, with the initial thickness $w_0 = 1800$ nm, and multiplied by expression 7 with $\tau_0 = 10$ s. The statistical errors are 2-3 times the size of the symbol along the volume axis.

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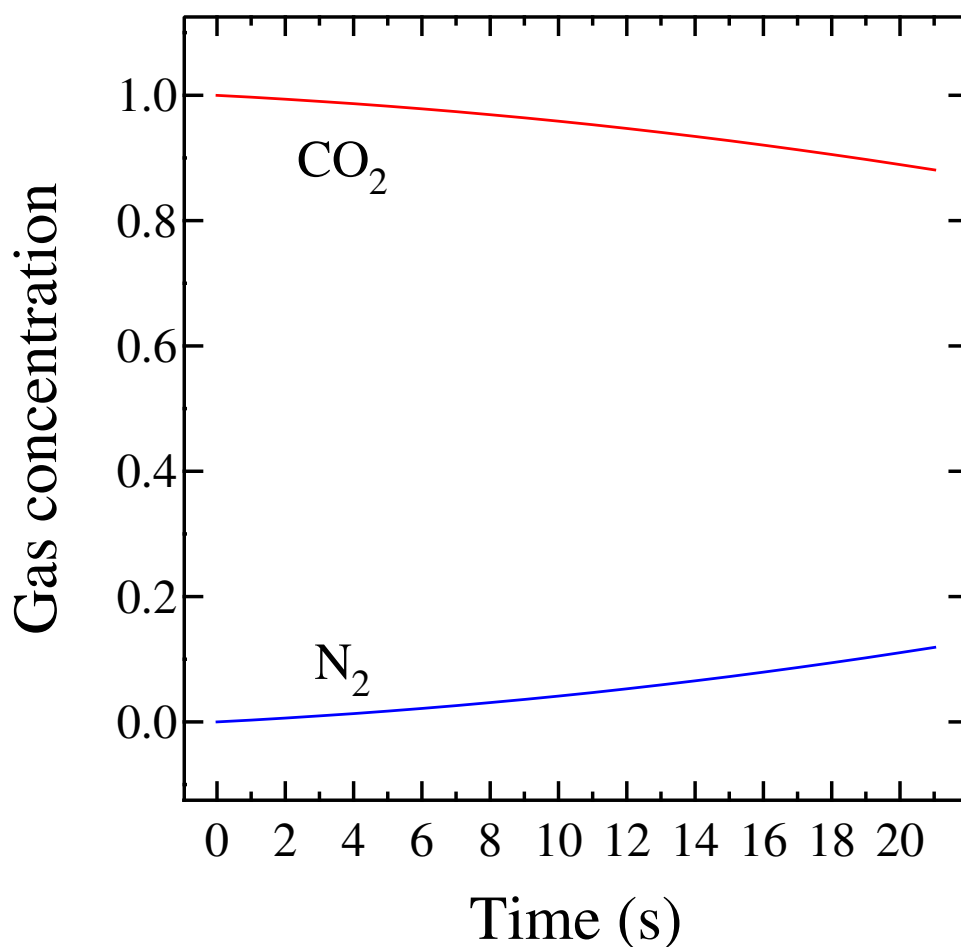


Figure 8. Simulated fractional concentrations of CO₂ and N₂ for the bubble initially filled with CO₂ in a N₂ atmosphere.

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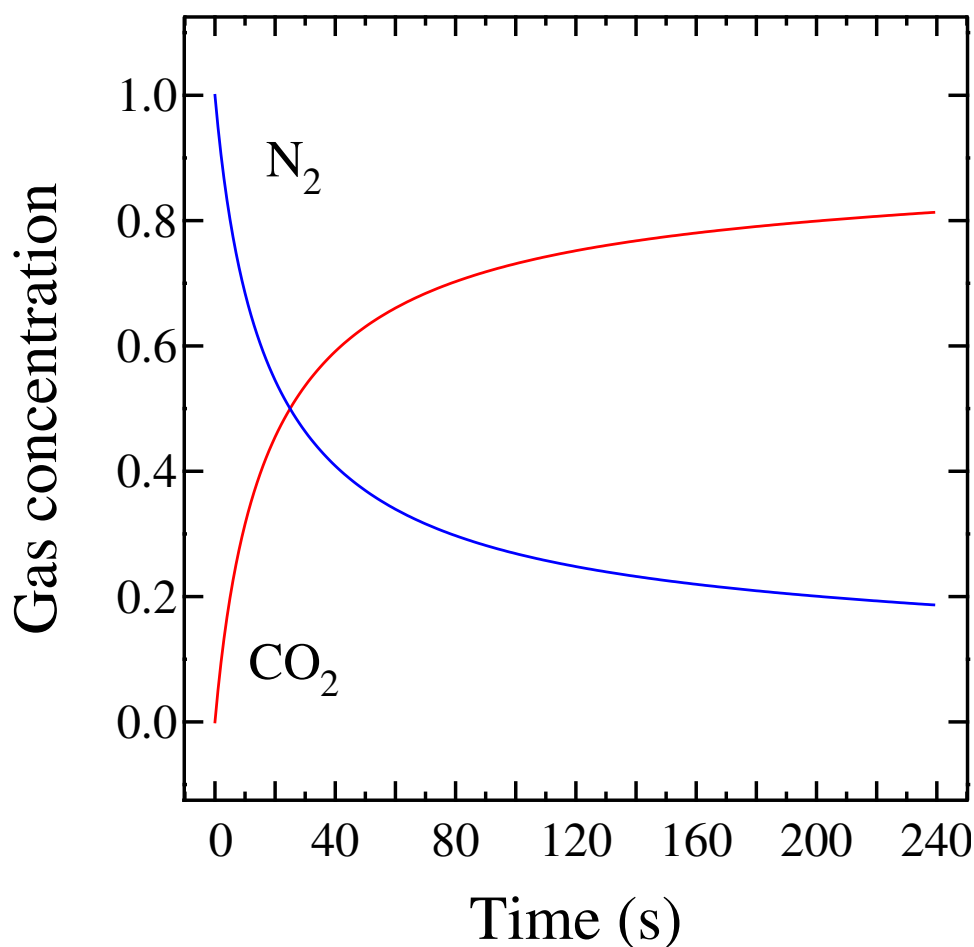


Figure 9. Simulated fractional concentrations of CO₂ and N₂ for the bubble initially filled with N₂ in a CO₂ atmosphere.

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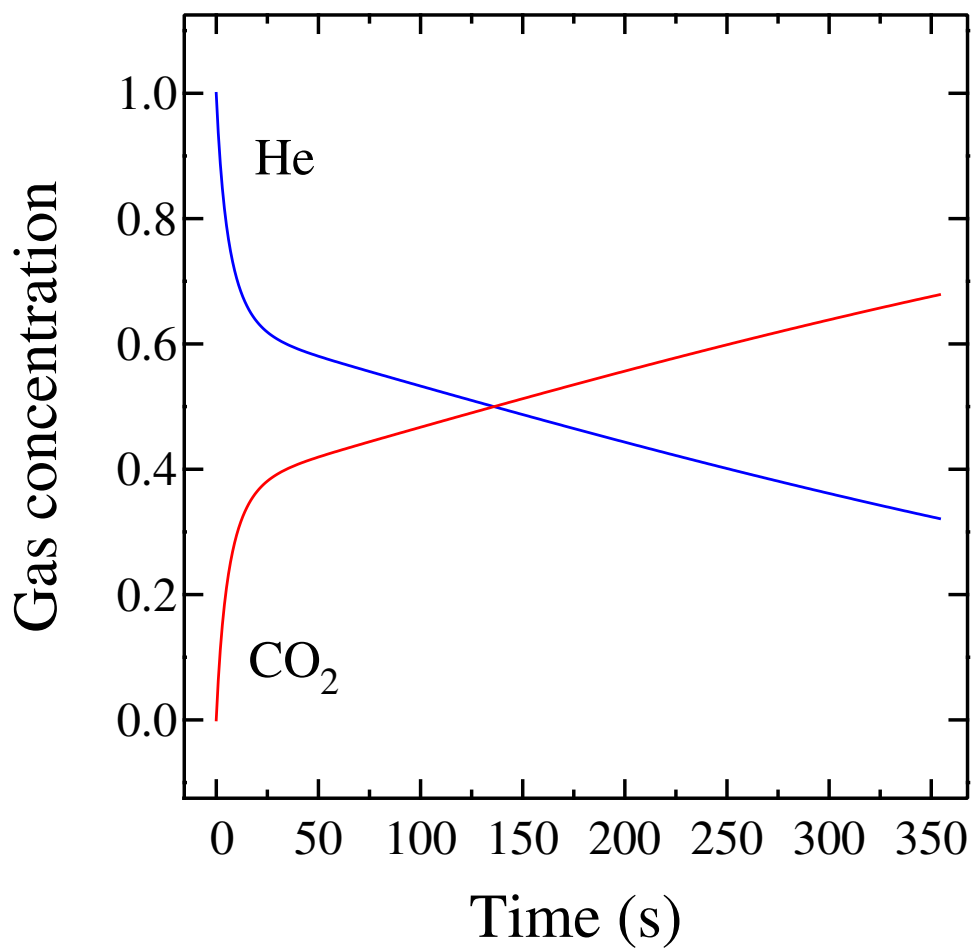


Figure 10. Simulated fractional concentrations of CO₂ and He for the bubble initially filled with He in a CO₂ atmosphere.