

Champagne! (10 points)

Warning: Excessive alcohol consumption is harmful to health and drinking alcohol below legal age is prohibited.

Champagne is a French sparkling wine. Fermentation of sugars produces carbon dioxide (CO_2) in the bottle. The molar concentration of CO_2 in the liquid phase c_ℓ and the partial pressure P_{CO_2} in the gas phase are related by $c_\ell = k_H P_{\text{CO}_2}$, known as Henry's law and where k_H is called Henry's constant.

Data

- Surface tension of champagne $\sigma = 47 \times 10^{-3} \text{ J} \cdot \text{m}^{-2}$
- Density of the liquid $\rho_\ell = 1.0 \times 10^3 \text{ kg} \cdot \text{m}^{-3}$
- Henry's constant at $T_0 = 20^\circ\text{C}$, $k_H(20^\circ\text{C}) = 3.3 \times 10^{-4} \text{ mol} \cdot \text{m}^{-3} \cdot \text{Pa}^{-1}$
- Henry's constant at $T_0 = 6^\circ\text{C}$, $k_H(6^\circ\text{C}) = 5.4 \times 10^{-4} \text{ mol} \cdot \text{m}^{-3} \cdot \text{Pa}^{-1}$
- Atmospheric pressure $P_0 = 1 \text{ bar} = 1.0 \times 10^5 \text{ Pa}$
- Gases are ideal with an adiabatic coefficient $\gamma = 1.3$



Fig. 1. A glass filled with champagne.

Part A. Nucleation, growth and rise of bubbles

Immediately after opening a bottle of champagne at temperature $T_0 = 20^\circ\text{C}$, we fill a glass. The pressure in the liquid is P_0 and its temperature stays constant at T_0 . The concentration c_ℓ of dissolved CO_2 exceeds the equilibrium concentration and we study the nucleation of a CO_2 bubble. We note a its radius and P_b its inner pressure.

A.1 Express the pressure P_b in terms of P_0 , a and σ .

0.2pt

SOLUTION:

A.1. Laplace's law: $P_b = P_0 + \frac{2\sigma}{a}$

0.2

In the liquid, the concentration of dissolved CO_2 depends on the distance to the bubble. At long distance we recover the value c_ℓ and we note c_b the concentration close to the bubble surface. According to Henry's law, $c_b = k_H P_b$. We furthermore assume in all the problem that bubbles contain only CO_2 .

Since $c_\ell \neq c_b$, CO_2 molecules diffuse from areas of high to low concentration. We assume also that any molecule from the liquid phase reaching the bubble surface is transferred to the vapour.

A.2 Express the critical radius a_c above which a bubble is expected to grow in terms of P_0, σ, c_ℓ and c_0 where $c_0 = k_H P_0$. Calculate numerically a_c for $c_\ell = 4c_0$.

0.5pt

SOLUTION:

A.2.1. a_c is so $c_\ell = c_b$

A.2.2. $c_b = k_H P_b = k_H(P_0 + \frac{2\sigma}{a})$ and $c_0 = k_H P_0$ so $a_c = \frac{2\sigma}{P_0(c_\ell/c_0 - 1)}$

A.2.3. $a_c = 0.3 \mu\text{m}$

A.2.1. comparison (equality $c_b = c_\ell$ or inequality $c_b \leq c_\ell$)	0.1
A.2.2. exact expression $a_c = \frac{2\sigma}{P_0(c_\ell/c_0 - 1)}$	0.2
A.2.3. numerical value $a_c = 0.3 \mu\text{m}$	0.2

In practice, bubbles mainly grow from pre-existing gas cavities. Consider then a bubble with initial radius $a_0 \approx 40 \mu\text{m}$. The number of moles of CO_2 transferred at the bubble's surface per unit area and time is noted j . Two models are possible for j .

- model (1) $j = \frac{D}{a}(c_\ell - c_b)$ where D is the diffusion coefficient of CO_2 in the liquid.
- model (2) $j = K(c_\ell - c_b)$ where K is a constant here.

Experimentally, the bubble radius $a(t)$ is found to depend on time as shown in **Fig. 2**. Here $c_\ell \approx 4c_0$, and since bubbles are large enough to be visible, the excess pressure due to surface tension can be neglected and $P_b \approx P_0$.

A.3 Express the number of CO_2 moles in the bubble n_c in terms of a, P_0, T_0 and ideal gas constant R . Find $a(t)$ for both models. Indicate which model explains the experimental results in **Fig. 2**. Depending on your answer, calculate numerically K or D . 1.2pt

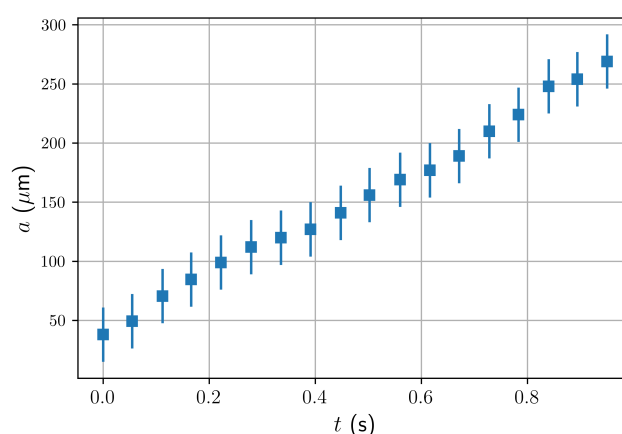


Fig. 2. Time evolution of CO_2 bubble radius in a glass of champagne (*adapted from [1]*).

SOLUTION:

A.3.1. The number of moles of CO_2 (ideal gas) inside the bubble is $n_c = \frac{4}{3}\pi a^3 \frac{P_0}{RT_0}$

A.3.2. Equation : balance of CO_2 in the bubble

$$\text{A.3.3 } \frac{dn_c}{dt} = 4\pi a^2 \frac{da}{dt} \frac{P_0}{RT} = j4\pi a^2 \Rightarrow \frac{da}{dt} = j \frac{RT}{P_0}$$

A.3.4. Model 1: $\frac{da}{dt} = \frac{DRT}{aP_0}(c_\ell - c_0)$ so $a^2 = a_0^2 + \frac{2DRT_0}{P_0}(c_\ell - c_0)t$

A.3.5. Model 2: $\frac{da}{dt} = \frac{KRT_0}{P_0}(c_\ell - c_0)$ so $a = a_0 + \frac{KRT_0}{P_0}(c_\ell - c_0)t$

A.3.6. Experimental data : $\frac{da}{dt}$ is constant: model 2

A.3.7 Slope of the experimental data : $\dot{a} \approx 150/0.62 \approx 0.24 \text{ mm} \cdot \text{s}^{-1}$

A.3.8 $K = 1.0 \times 10^{-4} \text{ m} \cdot \text{s}^{-1}$

A.3.1. $n_c = \frac{4}{3}\pi a^3 \frac{P_0}{RT_0}$	0.1
A.3.2. any equation that that can be interpreted as a particule balance	0.1
A.3.3. equation between $\dot{a}$ (or $\dot{n}_c$) and j	0.2
A.3.4. model 1 a exact with a_0 present	0.2
A.3.5. model 2 a exact with a_0 present	0.2
A.3.6. model 2	0.1
A.3.7. value of the slope: total mark only if $\frac{da}{dt}$ is in range $[210 - 250] \mu\text{m} \cdot \text{s}^{-1}$	0.1
A.3.8. any value of K in range $[0.9 - 1.1] \times 10^{-4} \text{ m} \cdot \text{s}^{-1}$	0.2

Eventually bubbles detach from the bottom of the glass and continue to grow while rising. **Fig. 3.** shows a train of bubbles. The bubbles of the train have the same initial radius and are emitted at a constant frequency $f_b = 20 \text{ Hz}$.

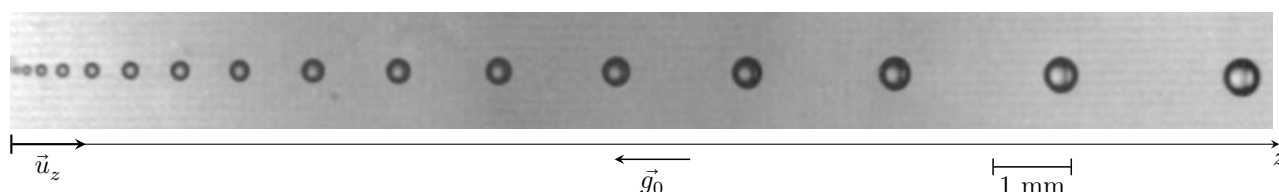


Fig. 3. A train of bubbles. The photo is rotated horizontally for the page layout (*adapted from [1]*).

For the range of velocities studied here, the drag force F on a bubble of radius a moving at velocity v in a liquid of dynamic viscosity η is given by Stokes' law $F = 6\pi\eta av$. Measurements show that at any moment in time, the bubble can be assumed to be travelling at its terminal velocity.

A.4 Give the expression of the main forces exerted on a vertically rising bubble. 0.8pt
Obtain the expression of $v(a)$. Give a numerical estimate of η using ρ_ℓ , g_0 and quantities measured on **Fig. 3**.

SOLUTION:

A.4.1. Main forces: buoyancy $\frac{4}{3}\pi a^3 \rho_\ell g_0$, drag force $6\pi\eta av$, weight is negligible: $\frac{\rho_{\text{CO}_2}}{\rho_\ell} = \frac{P_e M_{\text{CO}_2}}{RT\rho_\ell} \approx 10^{-3}$: $m_b \ll m_\ell$

A.4.2. Simplified equation is a balance between buoyancy and drag force $\frac{4}{3}\pi a^3 \rho_\ell g_0 = 6\pi\eta av$ so $v = \frac{2}{9\eta} a^2 \rho_\ell g_0$.

A.4.3. Time between two bubbles: $\Delta t = 1/f_b$

A.4.4. Using $\eta = \frac{2\rho_\ell g_0}{9} \times \frac{a^2}{v}$ for the penultimate bubble ($n-1$) with $a_{n-1} \approx 0.19$ mm

A.4.5. $v(t_{n-1}) = \frac{z(t_n) - z(t_{n-2})}{2 \times f_b^{-1}} = 4.5 \text{ cm} \cdot \text{s}^{-1}$

A.4.6. $\eta \approx 2 \times 10^{-3} \text{ Pa} \cdot \text{s}$

A.4.1. Expression of main forces (gravity force present or absent): fullmark	0.1
A.4.2. expression $v = \frac{2}{9\eta} a^2 \rho_\ell g_0$ (full mark on this point with or without the gravity force)	0.2
A.4.3. taking account of the time during two positions $\Delta t = 1/f_b = 5 \times 10^{-2} \text{ s}$	0.1
A.4.4. full mark for one coherent value of the radius measured on Fig.3. last bubble in [0.20 – 0.30]mm penultimate bubble : radius in [0.16 – 0.24]mm antepenultimate bubble : radius in [0.14 – 0.22]mm	0.1
A.4.5. full mark for one coherent value of the velocity measured on Fig.3. last bubble $v \in [4.3, 4.8] \text{ cm} \cdot \text{s}^{-1}$ penultimate bubble $v \in [4.2, 4.6] \text{ cm} \cdot \text{s}^{-1}$ antepenultimate bubble $v \in [3.7 - 4.2] \text{ cm} \cdot \text{s}^{-1}$	0.1
A.4.6. full mark for any value of η in range $[1.0 - 4.0]10^{-3} \text{ Pa} \cdot \text{s}$	0.2

The quasi-stationary growth of bubbles with rate $q_a = \frac{da}{dt}$ still applies during bubble rise.

A.5 Express the radius a_{H_ℓ} of a bubble reaching the free surface in terms of height travelled H_ℓ , growth rate $q_a = \frac{da}{dt}$, and any constants you may need. Assume $a_{H_\ell} \gg a_0$ and q_a constant, and give the numerical value of a_{H_ℓ} with $H_\ell = 10$ cm and q_a corresponding to **Fig. 2**. 0.5pt

SOLUTION:

A.5.1. $v = \frac{dz}{dt} = \frac{2\rho_\ell g_0}{9\eta} a^2$ and $\frac{da}{dt} = q_a$ so $\frac{dz}{da} = \frac{2\rho_\ell g_0}{9q_a\eta} a^2$

Neglecting $a(z=0)$, $z = \frac{2\rho_\ell g_0}{27q_a\eta} a^3$ so $a_{H_\ell} = \left(\frac{27q_a\eta H_\ell}{2\rho_\ell g_0} \right)^{1/3}$

A.5.2. $a_{H_\ell} = 3.9 \times 10^{-4} \text{ m}$ for $\eta = 2.0 \times 10^{-3} \text{ Pa} \cdot \text{s}$

A.5.1. $a_{H_\ell} = \left(\frac{27q_a\eta H_\ell}{2\rho_\ell g_0} \right)^{1/3}$	0.3
A.5.2. full mark if $a_{H_\ell} \in [0.36 - 0.49] \text{ mm}$	0.2

There are N_b nucleation sites of bubbles. Assume that the bubbles are nucleated at a constant frequency

f_b at the bottom of a glass of champagne (height H_ℓ for a volume V_ℓ), with a_0 still negligible. Neglect diffusion of CO_2 at the free surface.

A.6 Write the differential equation for $c_\ell(t)$. Obtain from this equation the characteristic time τ for the decay of the concentration of dissolved CO_2 in the liquid. 1.1pt

SOLUTION:

A.6.1 The rate of bubbles reaching the free surface by unit time is $N_b f_b$

A.6.2. So the volume of CO_2 released per unit time at the free surface is:

$$\frac{dV}{dt} = \frac{4}{3}\pi a_{H_\ell}^3 N_b f_b$$

A.6.3. According to A.5, $\frac{dV}{dt} = \frac{18\pi N_b f_b \eta K H_\ell}{\rho_\ell g_0} q_a$

A.6.4. With $q_a = \frac{da}{dt} = \frac{RT_0}{P_0} K (c_\ell - c_0)$ according to A3.

A.6.5. In the bubble, $c_b \approx c_0$. Using the ideal gas law, the total number n of CO_2 moles in V_ℓ verifies:

$$\frac{dn}{dt} = -\frac{P_0}{RT_0} \frac{dV}{dt} = -\frac{18\pi N_b f_b \eta K H_\ell}{\rho_\ell g_0} (c_\ell - c_0)$$

With $c_\ell = \frac{n}{V_\ell}$, we get a first order linear ODE $\frac{dc_\ell}{dt} = \frac{1}{V_\ell} \frac{dn}{dt} = -\frac{18\pi N_b f_b \eta K H_\ell}{\rho_\ell g V_\ell} (c_\ell - c_0)$

A.6.6. Exponential decay with characteristic time: $\tau = \frac{\rho_\ell g V_\ell}{18\pi N_b f_b \eta K H_\ell}$

A.6.1. Correct count of bubbles reaching the free surface by unit time: $N_b f_b$	0.1
A.6.2. Balance at the free surface: $\frac{dV}{dt} = \frac{4}{3}\pi a_{H_\ell}^3 N_b f_b$	0.2
A.6.3. Exact expression of $\frac{dV}{dt} = \frac{18\pi N_b f_b \eta K H_\ell}{\rho_\ell g_0} q_a$ using A.5.	0.1
A.6.4. $q_a = \frac{da}{dt} = \frac{RT_0}{P_0} K (c_\ell - c_0)$	0.2
A.6.5. First order linear differential equation $\frac{dc_\ell}{dt} + \frac{18\pi N_b f_b \eta K H_\ell}{\rho_\ell g_0 V_\ell} (c_\ell - c_0) = 0$. If an homogeneous mistake has been made at a previous task, but the differential equation is first order and coherent, fullmark.	0.3
A.6.6. Exponential decay with characteristic time: $\tau = \frac{\rho_\ell g_0 V_\ell}{18\pi N_b f_b \eta K H_\ell}$ full mark if the numerical coefficient is absent or different of $1/18\pi$ (reasonable solution)	0.2

Part B. Acoustic emission of a bursting bubble

Small bubbles are nearly spherical as they reach the free surface. Once the liquid film separating the bubble from the air thins out sufficiently, a circular hole of radius r forms in the film and, driven by surface tension, opens very quickly (**Fig. 4.** left). The hole opens at constant speed v_f (**Fig. 4.** right). The film outside the rim remains still, with constant thickness h .

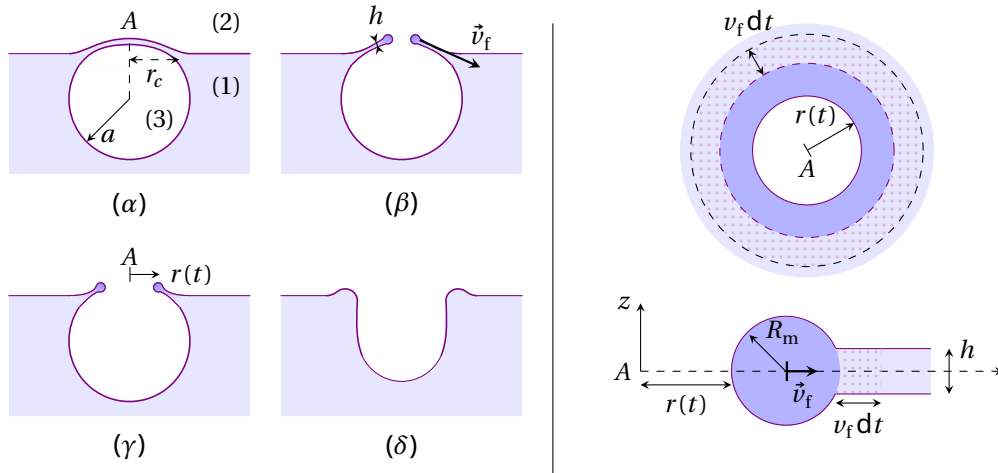


Fig. 4. (Left) (α) Bubble at the surface: (1) liquid, (2) air at pressure P_0 and (3), CO_2 at pressure P_b , (β) and (γ) retraction of the liquid film, where the rim is in dark blue, (δ) bubble collapse. (Right) Retraction of the liquid film at time t . Top: sketch of the pierced film seen from above. Bottom: cross-section of the rim and the retracting film. During dt the rim accumulates nearby liquid (dotted).

Due to dissipative processes, only half of the difference of the surface energy between t and $t + dt$ of the rim and the accumulated liquid is transformed into kinetic energy. We further assume that the variation of the surface of the rim is negligible compared to that of the film.

B.1 Express v_f in terms of ρ_ℓ, σ and h .

1.1pt

SOLUTION:

B.1.1. and 1.2. Variation of kinetic energy: system : the rim (perimeter $\ell = 2\pi r$) and the volume $\delta V = h\ell dt = h2\pi r v_f dt$ $\delta V = h\ell v_f dt = h2\pi r v_f dt$; during dt the volume δV get a kinetic energy $dE_c = \frac{1}{2}\rho_\ell \delta V v_f^2 = \frac{1}{2}\rho_\ell h\ell v_f^2 dt = \pi r \rho_\ell h v_f^2 dt$ $dE_c = \frac{1}{2}\rho_\ell \delta V v_f^2 = \frac{1}{2}\rho_\ell h\ell v_f^2 dt = \pi r \rho_\ell h v_f^2 dt$.

B.1.3. surface tension energy: $E_s = \sigma S$ for a surface S

B.1.4. $\delta E_s = -2\sigma \ell v_f dt = -4\sigma \pi r v_f dt$.

B.1.5. Kinetic energy theorem: the lost energy is $\delta E_s/2 < 0$ so $dE_c + \delta E_s = \delta E_s/2$

B.1.6. $v_f = \sqrt{2\sigma/\rho_\ell h}$

If partial answer: $v_f = \sqrt{\sigma/\rho_\ell h}$ obtained only by dimensional analysis: 0.2 pt to the question

B.1.1. Any expression of kinetic energy	0.1
B.1.2. Variation of kinetic energy (differential or finite variation accepted)	0.2
B.1.3. Expression of a surface energy or a variation.	0.1
B.1.4. Exact expression of δE_s	0.3
B.1.5. Kinetic energy balance (without sign mistake). If the candidate forget the energy loss, it is treated as a small mistake (-0.1pt)	0.2
B.1.6. exact expression of v_f	0.2

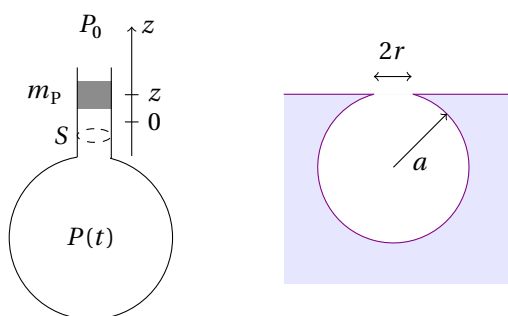


Fig. 5. (Left) a Helmholtz resonator. (Right) a bubble as an oscillator.

When the film bursts, it releases internal pressure and emits a sound. We model this acoustic emission by a Helmholtz resonator: a cavity open to the atmosphere at P_0 through a bottleneck aperture of area S (**Fig. 5.** left). In the neck, a mass m_p makes small amplitude position oscillations due to the pressure forces it experiences as the gas in the cavity expands or compresses adiabatically. The gravity force on m_p is negligible compared to pressure forces. Let V_0 be the volume of gas under the mass m_p for $P = P_0$ as $z = 0$.

B.2 Express the frequency of oscillation f_0 of m_p . Hint: for $\varepsilon \ll 1$, $(1 + \varepsilon)^\alpha \approx 1 + \alpha\varepsilon$. 1.1pt

SOLUTION:

B.2.1. Pressure forces on m_p : $F_z = P(t)S - P_0S$

B.2.2. Volume $V(t) = V_0 + Sz$

B.2.3. Adiabatic and reversible compression for an ideal gas: $PV(t)^\gamma = P_0V_0^\gamma$ so $P(t) = P_0 \left(\frac{V_0}{V_0 + Sz} \right)^\gamma = P_0 \left(\frac{1}{1 + Sz/V_0} \right)^\gamma$

B.2.4. Approximation: $P(t) \approx P_0(1 - \gamma \frac{Sz}{V_0})$

B.2.5. Pressure force: $F_z = -\gamma S^2 P_0 \frac{z}{V_0}$

B.2.6. Newton's 2nd law: $m_p \ddot{z} = -\gamma S^2 P_0 \frac{z}{V_0}$ so $m_p \ddot{z} + \gamma S^2 P_0 \frac{z}{V_0} = 0$

B.2.7. Harmonic oscillator of angular frequency $\omega_0^2 = S^2 \frac{P_0 \gamma}{m_p V_0}$

B.2.8. $f_0 = \frac{1}{2\pi} \sqrt{\frac{S^2 P_0 \gamma}{m_p V_0}}$

B.2.1. Pressure force with P_0	0.1
B.2.2. Expression of volume $V(t)$	0.1
B.2.3. Expression of $P(t)$ with adiabatic reversible process for an ideal gas	0.2
B.2.4. Approximate pressure	0.2
B.2.5. Exact linearized pressure force	0.1
B.2.6. Law of motion	0.1
B.2.7. Harmonic oscillator, angular frequency	0.2
B.2.8. Expression of f_0	0.1

The Helmholtz model may be used for a bubble of radius a . V_0 is the volume of the closed bubble. From literature, the mass of the equivalent of the piston is $m_p = 8\rho_g r^3/3$ where r is the radius of the circular aperture and $\rho_g = 1.8\text{ kg}\cdot\text{m}^{-3}$ is the density of the gas (**Fig. 5.** right). During the bursting process, r goes from 0 to r_c , given by $r_c = \frac{2}{\sqrt{3}}a^2\sqrt{\frac{\rho_\ell g_0}{\sigma}}$. At the same time, the frequency of emitted sound increases until a maximum value of 40kHz and the bursting time is $t_b = 3 \times 10^{-2}$ ms.

B.3 Find the radius a and the thickness h of the champagne film separating the bubble from the atmosphere. 1.1pt

SOLUTION:

Determination of a

B.3.1. The maximal value of f_0 is $f_0 = 40\text{ kHz}$ is obtained for $r = r_c$

B.3.2. Exact expression of f_0 with $m = \frac{8r^3}{3}\rho_g$ and $S = \pi r_c^2$: $f_0 = \frac{1}{2\pi}\sqrt{\frac{3r_c\pi^2 P_0 \gamma}{8\rho_g V_0}}$ so $f_0 = \frac{1}{2\pi}\sqrt{\frac{\gamma P_0}{\rho_g}}\sqrt{\frac{3\sqrt{3}\pi}{16a}\sqrt{\frac{\rho_\ell g_0}{\sigma}}}$

$$\text{or } a = \frac{3\sqrt{3}}{64\pi}\frac{\gamma P_0}{\rho_g f_0^2}\sqrt{\frac{\rho_\ell g_0}{\sigma}}$$

B.3.3. $a = 0.53\text{ mm}$

Determination of h

B.3.4. $r_c = \frac{2}{\sqrt{3}}a^2\sqrt{\frac{\rho_\ell g_0}{\sigma}}$ and $r_c = 0.15\text{ mm}$ so $v_f = \frac{r_c}{t_b} = 5.0\text{ m}\cdot\text{s}^{-1}$

$$\text{B.3.5. } h = \frac{2\sigma}{\rho_\ell v_f^2} = \frac{3t_b^2}{2a^4}\sqrt{\frac{\sigma^3}{\rho_\ell^3 g_0}} \quad h = \frac{2\sigma}{\rho_\ell v_f^2} = \frac{3t_b^2\sigma^2}{2a^4\rho_\ell^2 g_0}$$

B.3.6. Numerical value $h = 3.7\text{ }\mu\text{m}$

B.3.1. Use of r_c for f_0	0.1
B.3.2. Exact expression of f_0 in terms of $a, \rho_g, \sigma, g_0, \rho_\ell, P_0$ or expression of a	0.3
B.3.3. Exact numerical value between 0.5 mm and 0.6 mm	0.2
B.3.4. Relationship between t_b, v_f and r_c or a	0.2
B.3.5. Expression of h in terms of σ, ρ_ℓ and v_f (or a and t_b)	0.1
B.3.6. Numerical value $h = 3.7 \mu\text{m}$	0.2

Part C. Popping champagne

In a bottle, the total quantity of CO_2 is $n_T = 0.2 \text{ mol}$, either dissolved in the volume $V_L = 750 \text{ mL}$ of liquid champagne, or as a gas in the volume $V_G = 25 \text{ mL}$ under the cork (**Fig. 6.** left). V_G contains only CO_2 . The equilibrium between both CO_2 phases follows Henry's Law. We suppose that the fast gaseous CO_2 expansion when the bottle is opened, is adiabatic and reversible. Ambient temperature T_0 and pressure $P_0 = 1 \text{ bar}$ are constant.

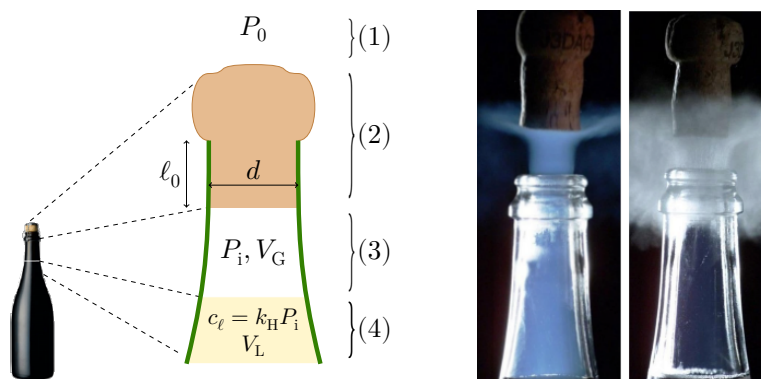


Fig. 6. *Left:* traditional bottleneck: (1) surrounding air, (2) cork stopper, (3) headspace, (4) liquid champagne. *Right:* Two phenomena observed while opening the bottle at two different temperatures (adapted from [2]).

C.1 Give the numerical value of the pressure P_i of gaseous CO_2 in the bottle for $T_0 = 6^\circ\text{C}$ and $T_0 = 20^\circ\text{C}$. 0.4pt

SOLUTION:

C.1.1. Conservation of CO_2 molecules: $n_T = n_V + n_L = n_V + k_H(T_0)P_iV_L$

C.1.2. Ideal gas law: $n_V = \frac{P_i V_G}{RT_0}$

$$P_i = \frac{n_T}{V_L k_H(T_0) + \frac{V_G}{RT_0}} = \frac{\frac{n_T RT_0}{V_G}}{1 + RT_0 k_H(T_0) \frac{V_L}{V_G}}$$

C.1.3. For $T_0 = 6^\circ\text{C}$: $P_i = 4.81 \text{ bar}$

C.1.4. For $T_0 = 20^\circ\text{C}$: $P_i = 7.76\text{ bar}$

C.1.1. Conservation of CO_2 molecules	0.1
C.1.2. Litteral expression of P_i	0.1
C.1.3. For $T_0 = 6^\circ\text{C}$: $P_i = 4.81\text{ bar}$	0.1
C.1.4. For $T_0 = 20^\circ\text{C}$: $P_i = 7.76\text{ bar}$	0.1

Another step of champagne production (not described here) leads to the following values of P_i that we will use for the next questions: $P_i = 4.69\text{ bar}$ at $T_0 = 6^\circ\text{C}$ and $P_i = 7.45\text{ bar}$ at $T_0 = 20^\circ\text{C}$.

During bottle opening, two different phenomena can be observed, depending on T_0 (Fig. 6. right).

- either a blue fog appears, due to the formation of solid CO_2 crystals (but water condensation is inhibited);
- or a grey-white fog appears, due to water vapor condensation in the air surrounding the bottleneck. In this latter case, there is no formation of CO_2 solid crystals.

The saturated vapor pressure $P_{\text{sat}}^{\text{CO}_2}$ for the CO_2 solid/gas transition follows : $\log_{10}\left(\frac{P_{\text{sat}}^{\text{CO}_2}}{P_0}\right) = A - \frac{B}{T + C}$ with T in K, $A = 6.81$, $B = 1.30 \times 10^3\text{ K}$ and $C = -3.49\text{ K}$.

- C.2** Give the numerical value T_f of the CO_2 gas at the end of the expansion, after opening a bottle, if $T_0 = 6^\circ\text{C}$ and if $T_0 = 20^\circ\text{C}$, if no phase transition occurred. Choose which statements are true (several statements possible): 0.7pt
1. At $T_0 = 6^\circ\text{C}$ a grey-white fog appears while opening the bottle.
 2. At $T_0 = 6^\circ\text{C}$ a blue fog appears while opening the bottle.
 3. At $T_0 = 20^\circ\text{C}$ a grey-white fog appears while opening the bottle.
 4. At $T_0 = 20^\circ\text{C}$ a blue fog appears while opening the bottle.

SOLUTION:

C.2.1. The adiabatic reversible expansion goes from P_i to P_0 .

C.2.2. $T_f = T_0 \left(\frac{P_i}{P_0}\right)^{(1/\gamma)-1}$

C.2.3. For $T_0 = 6^\circ\text{C}$: $P_i = 4.69\text{ bar}$ and $T_f = 195.3\text{ K} = -77.8^\circ\text{C}$.

C.2.4. For $T_0 = 20^\circ\text{C}$: $P_i = 7.45\text{ bar}$ and $T_f = 184.3\text{ K} = -88.8^\circ\text{C}$.

C.2.5. *First method*: comparison $P_{\text{sat}}(T_f)$ and $P_f = P_0$.

Second method: evaluation of the transition temperature at P_0 and comparison with T_f .

C.2.6. *First method*: $P_{\text{sat}}^{\text{CO}_2}(T_f = 6^\circ\text{C}) = 1.07\text{ bar} > P_0$. As the solid-liquid frontier has a positive slope in P, T state-diagram, the final state of CO_2 is gaseous. $P_{\text{sat}}^{\text{CO}_2}(T_f = 20^\circ\text{C}) = 0.41\text{ bar} < P_0$. As the solid-gas frontier has a positive slope in P, T state-diagram, the final gaseous state hypothesis is inconsistent and a phase transition has occurred in the latter case.

Second method: $T_{\text{trans}} = \frac{B}{A - \log_{10}\left(\frac{P_0}{P_0}\right)} - C$. $T_{\text{trans}} = 194.4\text{ K} = -78.8^\circ\text{C}$. For $T_0 = 6^\circ\text{C}$: $T_f = 195.3\text{ K} > T_{\text{trans}}$; the

final state of CO_2 is gaseous. For $T_0 = 20^\circ\text{C}$: $T_f = 184.3\text{ K} < T_{\text{trans}}$; the final gaseous state hypothesis is

inconsistent and a phase transition has occurred.

C.2.7. The true statements are: 1 and 4.

C.2.1. Final pressure of the expansion.	0.1
C.2.2. Litteral expression of T_f .	0.1
C.2.3. For $T_0 = 6^\circ\text{C}$: $P_i = 4.69\text{ bar}$ and $T_f = 195.3\text{ K}$;	0.1
C.2.4. For $T_0 = 20^\circ\text{C}$: $P_i = 7.45\text{ bar}$ and $T_f = 184.3\text{ K}$;	0.1
C.2.5. Idea of comparison between P_{sat} and P_0 or evaluation of the transition temperature at P_0 and idea of comparison with T_f .	0.1
C.2.6. Numerical comparison.	0.1
C.2.7. True statements (all or nothing).	0.1

During bottle opening, the cork stopper pops out. We now determine the maximum height H_c it reaches. Assume that the friction force F due to the bottleneck on the cork stopper is $F = \alpha A$ where A is the area of contact and α is a constant to determine. Initially, the pressure force slightly overcomes the friction force. The cork's mass is $m = 10\text{ g}$, its diameter $d = 1.8\text{ cm}$ and the length of the cylindrical part initially stuck in the bottleneck is $\ell_0 = 2.5\text{ cm}$. Once the cork has left the bottleneck, you can neglect the net pressure force.

C.3 Give the numerical value of H_c if the external temperature is $T_0 = 6^\circ\text{C}$.

1.3pt

SOLUTION:

C.3.1. Let us evaluate the work of the friction force. $\vec{F} = -\alpha \pi d(l_0 - z)\vec{u}_z$. Initially, this force slightly compensates the pressure force: $F = \pi \alpha d \ell_0 = \pi \frac{d^2}{4} (P_i - P_0)$ so $\alpha = (P_i - P_0) \frac{d}{4\ell_0}$

C.3.2. $\vec{F} = -(P_i - P_0) \pi d^2 \frac{(\ell_0 - z)}{4\ell_0} \vec{u}_z$ The total work is therefore: $W_f = -\alpha \pi d \frac{\ell_0^2}{2} = -\frac{(P_i - P_0) \pi d^2}{8} \ell_0$

C.3.3. and C.3.4. Work of the internal pressure force:

First method: the variation of internal energy of the gas is:

$$\Delta U_g = \frac{n_V R}{\gamma - 1} (T_f - T_0) = \frac{n_V R}{\gamma - 1} T_0 \left(\frac{1}{\left(1 + \frac{\pi d^2 \ell_0}{4 V_G}\right)^{\gamma - 1}} - 1 \right) = \frac{P_i V_G}{\gamma - 1} \left(\frac{1}{\left(1 + \frac{\pi d^2 \ell_0}{4 V_G}\right)^{\gamma - 1}} - 1 \right)$$

As its expansion is adiabatic: $\Delta U_g = W_{\text{cork} \rightarrow \text{CO}_2} = -W_{\text{CO}_2 \rightarrow \text{cork}}$ The cork stopper receives therefore a work from this gas equals to $-\Delta U_g$.

$$W_{\text{CO}_2 \rightarrow \text{cork}} = \frac{P_i V_G}{\gamma - 1} \left(1 - \frac{1}{\left(1 + \frac{\pi d^2 \ell_0}{4 V_G}\right)^{\gamma - 1}} \right)$$

Second method: let us write P the internal pressure during the expansion. The work received by the cork is:

$$W_{\text{CO}_2 \rightarrow \text{cork}} = \int_{V_G}^{V_F} P dV, \text{ where } V_F = V_G + \frac{\pi d^2 \ell_0}{4} \text{ and } P_0 V_F^\gamma = P_i V_G^\gamma.$$

The integration leads to the same result.

C.3.5. The work due to the external pressure P_0 is: $W_e = -P_0 \cdot \frac{\pi d^2}{4} \ell_0$

C.3.6. Energy balance. The cork stopper has an initial kinetic energy: $E_c = -\Delta U_g + W_f + W_e$

(The work of the weight is negligible and should not be taken into account).

At $T_0 = 6^\circ\text{C}$: $P_i = 4.69\text{ bar}$. $W_f = -1.17\text{ J}$; $W_e = -0.64\text{ J}$; $\Delta U_g = -2.57\text{ J}$; $E_c = 0.76\text{ J}$

C.3.7. The maximum height reached by the cork stopper is therefore: $H_c = \frac{E_c}{mg_0} = \frac{-\Delta U_g + W_f + W_e}{mg_0}$.

C.3.8. $H_c = 7.7\text{ m}$

If the candidates assumed a constant pressure P_i for the gaseous CO_2 during its expansion, they would find a work done by CO_2 on the cork equal to: $P_i(\pi \ell_0 d^2 / 4) = 3\text{ J}$ instead of 2.56 J and finally $H_c = 12\text{ m}$. The difference is not negligible!

C.3.1. Correct expression of α (all or nothing). If α is not correct (contribution of P_0 forgotten for example), 0 point but the following items are evaluated with this uncorrect α .	0.2
C.3.2. Expression of the friction work (all or nothing)	0.2
C.3.3. Consequences of the adiabatic reversible expansion (1st principle with $Q = 0$ or $PV^\gamma = P_i V_G^\gamma$)	0.1
C.3.4. Exact expression of the work (all or nothing) <i>Partial points</i> : if P is considered constant during the expansion, 0 point for C.3.4. but all points for the following items if coherent with the incorrect work expression.	0.3
C.3.5. Work due to external pressure correct. If this item is forgotten by the candidate, 0 point.	0.1
C.3.6. Correct E_c with the 3 contributions (even if errors in the writing of the contributions). If the candidate has forgotten the contribution of the external pressure, 0 point.	0.1
C.3.7. Correct energy balance during the free flight or use of Newton's second law.	0.2 <u>0.1</u>
C.3.8. Correct numerical value of H_c . If the candidate has forgotten the contribution of the external pressure in C.3.5 but H_c is coherent, fullmark.	0.2

[1] Liger-Belair *et al*, Am. J. Enol. Vitic., Vol. 50, No. 3 (1999).

[2] Liger-Belair *et al.*, Sc. Reports **7**, 10938 (2017).