



Article

Predicting CO₂ Pressure Loss in Aged Traditional-Method Sparkling Wine Bottles for Compliance with European Regulations

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Abstract

Today, billions of bottles are aging in the cellars of traditional-method sparkling wine regions prior to their release on the market. Given the fundamental role of carbon dioxide (CO₂) in both the production and sensory perception of sparkling wines, it is essential to understand and control all stages that influence its pressure and concentration in the bottle throughout the winemaking process. This study addressed the central question of how long traditional-method sparkling wine bottles can age in cellars while maintaining sufficient CO₂ pressure. By considering their capacity to retain the minimum CO₂ pressure of 3.5 bar at 20  C, as required by European regulations, a predictive formula for the shelf life of older vintages was proposed and discussed, integrating the multiple relevant parameters that govern CO₂ retention. Moreover, based on previously published datasets, a comparison was carried out between CO₂ losses measured for a range of modern crown caps and those observed in collections of older champagne vintages sealed with cork-lined crown caps. The results clearly show that modern crown caps preserve dissolved CO₂ far more effectively in traditional-method sparkling wines than the cork-lined closures commonly used during the last century, leading to substantially longer predicted shelf lives.

Keywords: sparkling wines; traditional method; carbon dioxide; pressure; aging on lees; crown caps; shelf life

1. Introduction

Driven by steadily increasing global demand, the consumption of sparkling wines has risen sharply since the turn of the century [1], now reaching nearly 2.5 billion bottles per year within a global market valued at over USD 40 billion [2–4]. With Prosecco representing the largest sparkling wine category worldwide in terms of volume, Italy is currently the leading producer of sparkling wines, followed by France and Germany [3].

The earliest written documents tracing the origin of sparkling wines date back to the early 1660s [5–8]. In December 1662, the English scientist Christopher Merret (1614–1695) presented a paper entitled *Some Observations concerning the Ordering of Wines* to the newly formed Royal Society of London [5,6]. He reported that the addition of molasses to barrels of still wines not only increased their alcohol content but also rendered them slightly effervescent. Although unaware of its significance at the time, Merret’s observation laid the foundations of what is now known as the Traditional Method for producing premium sparkling wines.



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In traditional method sparkling wines, dissolved CO₂ is generated through a secondary in-bottle fermentation initiated by the addition of yeasts and fermentable sugars to a still base wine, which is subsequently sealed in thick-walled glass bottles with either a crown cap or a cork stopper [9,10]. Today, after more than three centuries of technical refinements, sparkling wines produced in this manner are labeled *méthode traditionnelle*. This process involves several key steps, comprehensively described in the overviews by Kemp et al. [9] and Liger-Belair [10].

Furthermore, given the crucial role of CO₂ as the “reservoir of effervescence” in sparkling wines, a minimum CO₂ pressure in the bottle is legally required before traditional-method sparkling wines may be released onto the market. According to the definition established by the International Organization of Vine and Wine (OIV), which also constitutes a legal text, “sparkling wines are characterized on uncorking by the production of a more or less persistent effervescence resulting from the release of CO₂ (the excess pressure of this gas in the bottle is at least 3.5 bar at 20 °C) of exclusively endogenous origin” [3]. However, because bottle pressure and effervescence are defining features of sparkling wines, the gradual decline in both CO₂ pressure and dissolved CO₂ during aging on lees—clearly evidenced in remarkable vertical collections of Champagne bottles [11,12]—raises the fundamental question of how long traditional-method sparkling wines can be aged while still maintaining sufficient pressure and dissolved CO₂ to meet regulatory requirements.

In this article, we guide the reader step by step through the scientific principles and experimental evidence required to address this question with the highest possible level of clarity. We begin with a detailed examination of the secondary in-bottle alcoholic fermentation, the key process underlying the build-up of CO₂ pressure in sealed traditional-method sparkling wine bottles. We then introduce and explain previously published datasets documenting CO₂ pressure losses and subsequent dissolved CO₂ concentrations in exceptional collections of champagne bottles. These data provide the foundation for the development of predictive models that integrate molecular diffusion, thermodynamic equilibrium, and key physicochemical parameters. We subsequently illustrate how these models can be used to estimate the shelf life of aged traditional-method sparkling wines, with particular emphasis on compliance with European regulations requiring a minimum CO₂ pressure of 3.5 bar at 20 °C. Finally, by comparing CO₂ losses measured for a range of modern crown caps with those observed in older vintages sealed decades ago using cork-lined crown caps, we highlight the critical influence of bottle size, crown cap permeability, and aging temperature on the long-term retention of dissolved CO₂ during lees aging.

2. The *prise de mousse*: A Critical Step in Traditional-Method Sparkling Wine Production

2.1. Quantifying CO₂ in the Sealed Bottles During the *prise de mousse*

In traditional-method sparkling wines, secondary fermentation—referred to as *prise de mousse* [13]—is initiated by inoculating selected *Saccharomyces cerevisiae* strains, together with the addition of fermentable sugar (sucrose), into a blend of still wines. These base wines, typically containing approximately 11% ethanol by volume, are obtained from the first alcoholic fermentation of grape must [14–16]. The resulting blend is then transferred into thick-walled glass bottles hermetically sealed with either crown caps or natural cork stoppers, the latter being predominantly used for prestige cuvées [11]. The bottles are subsequently stored in cellars under cool temperature conditions (typically 12–14 °C), thereby facilitating a gradual secondary fermentation within a closed system. This in-bottle fermentation produces additional ethanol and carbon dioxide, the latter being responsible for the characteristic effervescence observed in the tasting glass [14–16].

With the classical addition of 25 g L⁻¹ of sucrose to the blend, a subsequent production of approximately 12.1 g L⁻¹ of ethanol is achieved, corresponding to nearly 15 mL of ethanol per liter, or an increase of roughly 1.5% by volume [13–16]. Upon completion of the *prise de mousse*, the additional ethanol produced increases the alcohol content of the bottled wine to approximately 12.5% (v/v). Moreover, adding nearly 25 g L⁻¹ of sucrose to the blend leads to the formation of about 11.9 g L⁻¹ of CO₂ during secondary fermentation (i.e., $n \approx 0.27 \text{ mol}^{-1}$ of CO₂ after completion of the *prise de mousse*, assuming a fermentation efficiency close to 95%). Considering the molar mass of CO₂ (44 g mol⁻¹) and the molar volume of an ideal gas ($\approx 24 \text{ L mol}^{-1}$ at 12 °C), this corresponds to nearly 5 L of gas-phase CO₂ physically contained in a standard 75 cL bottle [14–16].

The defining characteristic of all sparkling wines is therefore the retention of carbon dioxide (CO₂) in significant concentrations within the liquid, achieved by maintaining the wine under pressure in a sealed bottle. However, the large-scale industrial production of sparkling wines—and carbonated beverages more broadly—relies on a fundamental physical principle, called Henry’s law, which states that the concentration C_L of CO₂ dissolved in wine is directly proportional to the partial pressure of CO₂ in the gas phase in the sealed bottle, as expressed by the following relationship [17]:

$$C_L = \frac{n_L}{V_L} = k_H P_G, \quad (1)$$

where n_L denotes the moles of CO₂ dissolved in the wine, V_L the wine volume in the sealed bottle, k_H the temperature-dependent Henry’s constant for CO₂ in wine [18], and P_G the partial pressure of gas-phase CO₂.

The Henry’s constant k_H is therefore a critical parameter, as it relates the concentration of dissolved CO₂ in the beverage to the partial pressure of CO₂ in the sealed container. Over recent decades, numerous empirical and semi-empirical models have been developed to estimate the Henry’s constant of CO₂ in aqueous mixtures relevant to the sparkling beverage industry. These models encompass a broad range of systems, from simple carbonated waters to more complex alcoholic sparkling beverages, such as sparkling wines and beers [18]. In the late 1970s, based on a series of dedicated experimental studies, the following relationship was proposed, enabling the determination of the Henry’s constant of CO₂ in wine as a function of its temperature, ethanol content, and sugar concentration [19]:

$$k_H = 3.295 \times e^{(7 \times 10^{-5} a - 0.02905) T} \times e^{-(0.0179 a + 0.00111 b)}, \quad (2)$$

where k_H is expressed in g L⁻¹ bar⁻¹, T is the wine temperature (in °C), a is the ethanol content (in % v/v), and b is the sugar concentration (in g L⁻¹).

In sealed bottles, a gas-filled volume V_G (the headspace, commonly referred to as “the bubble” in the Champagne region) coexists with the liquid volume V_L of wine, as illustrated in Figure 1. Within the pressure range typically encountered in sealed bottles (a few bars, regardless of bottle size), the behavior of gaseous CO₂ in the headspace is well described by the ideal gas law,

$$P_G V_G = n_G R T, \quad (3)$$

where n_G is the mole number of moles of gas-phase CO₂ in the headspace, and R is the ideal gas constant (8.31 J K⁻¹ mol⁻¹).

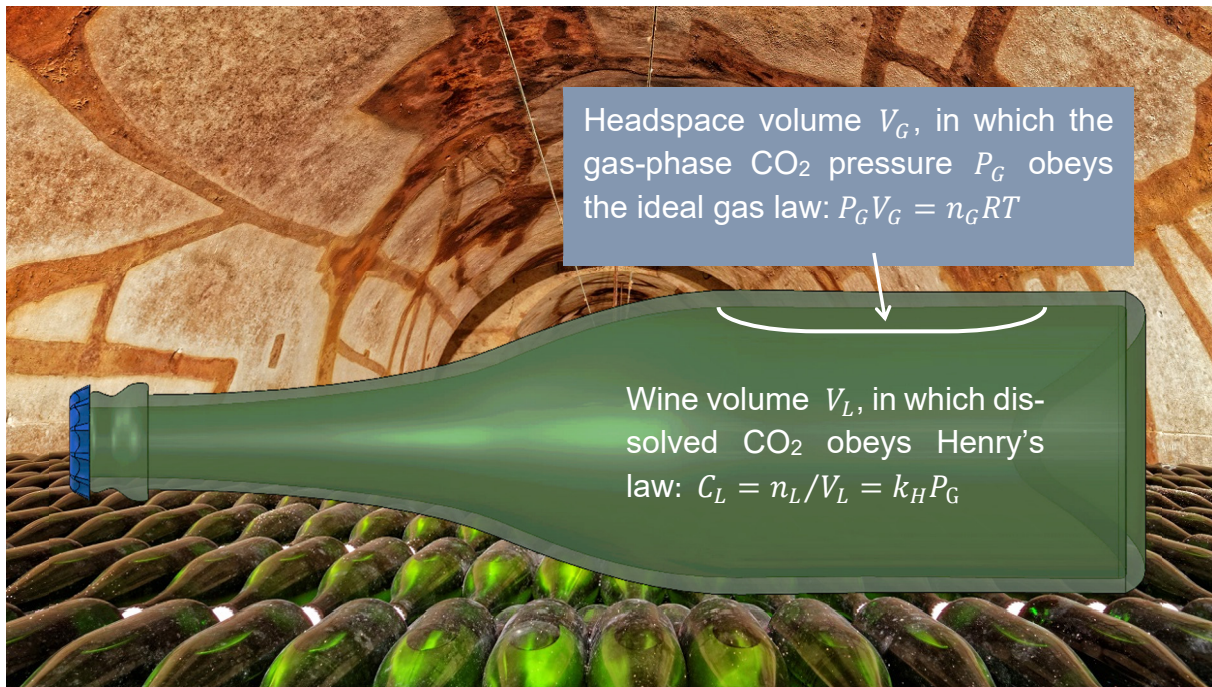


Figure 1. Schematic representation of a sparkling wine bottle sealed with a crown cap during the *prise de mousse*, illustrating the key parameters governing the thermodynamic equilibrium between dissolved and gaseous CO₂.

Otherwise, in hermetically sealed bottles, the total number of moles of CO₂ produced by yeast during the *prise de mousse* ($n_T = n_{V_L}$) is conserved and partitioned between the headspace (n_G moles) and the liquid wine (n_L moles), such that:

$$n_T = n_G + n_L. \quad (4)$$

This framework allowed the prediction of CO₂ distribution between the gas and liquid phases, providing a quantitative basis for understanding pressure development and CO₂ retention [12]. By combining the previously described equations, the gas-phase CO₂ pressure and the dissolved CO₂ concentration in the wine at the end of the *prise de mousse* (denoted C_{PDM} and P_{PDM} , respectively) can be expressed as functions of the relevant system parameters, according to the following relationships. Here x_V denotes the dimensionless ratio of the wine volume to the gaseous headspace ($x_V = V_L/V_G$), and all other parameters are expressed in SI (International System) units [12]:

$$\begin{cases} C_{PDM} \approx \frac{nk_H RT x_V}{k_H RT x_V + 1} \\ P_{PDM} \approx \frac{nRT x_V}{k_H RT x_V + 1} \end{cases}. \quad (5)$$

The *prise de mousse* is generally completed (i.e., all fermentable sugars have been consumed by the yeast) within approximately two months [9,17]. Consequently, according to Equation (2), at a cellar temperature of approximately 12 °C, the Henry's constant for CO₂ in a sugar-free wine containing 12.5% ethanol by volume is $k_H \approx 1.88 \text{ g L}^{-1} \text{ bar}^{-1} \approx 4.3 \times 10^{-4} \text{ mol m}^{-3} \text{ Pa}^{-1}$.

2.2. The Action of the Bottle Format

In traditional-method sparkling winemaking, the three bottle formats most commonly used for the *prise de mousse* are the 37.5 cL half-bottle, the standard 75 cL bottle, and the 150 cL magnum. Nevertheless, their gaseous headspace volumes V_G differ slightly, even

when all bottles are sealed with identical crown caps: 2 cL for the half-bottle, 2.5 cL for the standard bottle, and 3.3 cL for the magnum. Knowing the corresponding volume ratio x_V for each format, the system of equations described above allows the precise determination of both the dissolved CO_2 concentration (in mol m^{-3}) and the gas-phase CO_2 pressure (in Pa) at the completion of the *prise de mousse*, as a function of the relevant system parameters. For 37.5 cL half-bottles ($x_V \approx 19$), after a second in-bottle fermentation initiated at 12 °C in a blend supplemented with $25 \pm 0.5 \text{ g L}^{-1}$ of sucrose, Equation (5) yield $C_{PDM} \approx 11.3 \pm 0.2 \text{ g L}^{-1}$ and $P_{PDM} \approx 6.0 \pm 0.1 \text{ bar}$. For standard 75 cL bottles ($x_V \approx 30$), the corresponding values are $C_{PDM} \approx 11.5 \pm 0.2 \text{ g L}^{-1}$ and $P_{PDM} \approx 6.1 \pm 0.1 \text{ bar}$, whereas for 150 cL magnums ($x_V \approx 45$), the values increase slightly to $C_{PDM} \approx 11.6 \text{ g} \pm 0.3 \text{ L}^{-1}$ and $P_{PDM} \approx 6.2 \pm 0.1 \text{ bar}$. These theoretical values of pressure and CO_2 concentration are fully consistent with the experimental values measured in bottles of various sizes [10,16].

Interestingly, the larger the volume ratio x_V , the higher the resulting dissolved CO_2 concentration and the corresponding gas-phase CO_2 pressure at the completion of the *prise de mousse*, as illustrated in Figure 2.

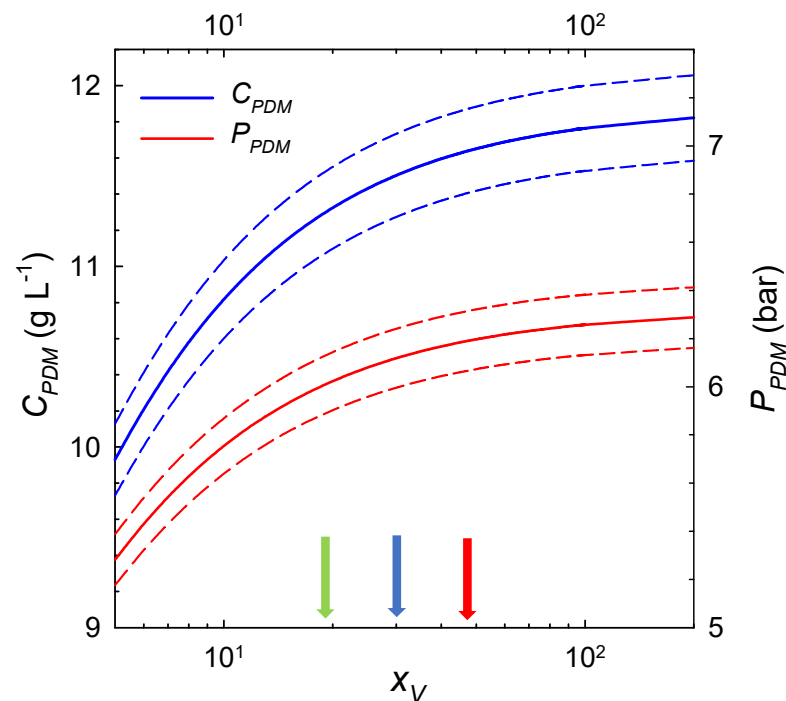


Figure 2. Concentration of dissolved CO_2 (blue solid line, with dashed line indicating uncertainty) and corresponding gas-phase CO_2 pressure (red solid line, with dashed line indicating uncertainty) at the end of the *prise de mousse* initiated with $25 \pm 0.5 \text{ g L}^{-1}$ of sucrose, plotted as a function of the dimensionless volume ratio x_V between wine and gaseous headspace; Green, blue, and red arrows indicate x_V values for the 37.5 cL half-bottle, 75 cL standard bottle, and 150 cL magnum, respectively.

3. Prolonged Aging on Lees and Shelf Life Prediction of Old Vintages

3.1. The Issue of CO_2 During Prolonged Aging

Once the *prise de mousse* is complete, traditional-method sparkling wines are not yet ready for release. A mandatory period of maturation follows, during which the wine remains in contact with the dead yeast cells—commonly referred to as “aging on lees” [20–22]. In the case of non-vintage Champagne wines, for example, this aging period must last at least 15 months, whereas vintage Champagne requires a minimum of three years of lees aging. During this aging period, the yeasts undergo autolysis. Through this process, they release a variety of organic compounds that modify the wine’s organoleptic profile, contributing to

increased roundness as well as the characteristic aromas, flavours and foaming properties associated with lees aging [20–24].

However, a common misconception persists among many wine consumers that sparkling wines should not be aged much beyond the legally mandated minimum period on lees. In reality, the most prestigious cuvées of traditional-method sparkling wines can mature in bottle for several decades, sealed either with crown caps [12] or, in some cases, with premium natural cork stoppers [11]. Yeast autolysis, which typically begins between two and four months after the second in-bottle fermentation [25], enables traditional-method sparkling wines to develop distinctive flavor and aroma profiles through a range of complex proteolytic processes [26–28]. The structural evolution of the lees in three series of traditional-method sparkling wines during long-term aging under realistic enological conditions has been investigated using high-pressure freezing combined with transmission electron microscopy [29]. It was found that the stratified structure of the yeast cell wall gradually disappeared during aging. To fully realize the beneficial effects of autolysis, extended aging on lees is necessary to develop the complex and highly sought-after aromas characteristic of traditional-method sparkling wines [21,30]. Yeast autolysis therefore represents a critical stage in the production of traditional-method sparkling wines, serving as a source of polysaccharides, mannoproteins, and proteins, as recently documented by Pons-Mercadé et al. across nine consecutive vintages [31]. Moreover, the release of proteins, polysaccharides, and mannoproteins has been shown to contribute significantly to foam stability [32–35]. In addition, polysaccharides and mannoproteins positively influence the sensory profile by enhancing mouthfeel [36], while certain peptides and proteins may also contribute to perceived sweetness [37].

Today, billions of bottles of varying sizes are aging in the cellars of traditional-method sparkling wine regions prior to release [12], including several million bottles of prestigious pre-2000 cuvées subject to prolonged lees aging [11,12]. Extended aging poses a particular challenge for exceptional vintages that may remain on lees for decades, as crown caps and corks are not completely impermeable to gas exchange [38–47]. In accordance with Fick's law, gaseous species can slowly diffuse along partial pressure gradients through the closure [32]. At the end of the *prise de mousse*, CO₂ pressure in a sealed bottle reaches nearly 6 bar at 12 °C, with slight variations depending on the ratio of wine volume to headspace and thus on bottle size (Equation (3)). During aging on lees, the high internal CO₂ pressure relative to ambient levels (≈ 420 ppm) drives slow diffusion through the closure, while thermodynamic equilibrium between gas-phase and dissolved CO₂ causes both headspace pressure and dissolved CO₂ concentration to gradually decline [42]. However, this loss of CO₂ pressure may become critical if it falls below the legal minimum of 3.5 bar at 20 °C required by European regulations.

Various techniques adapted from food packaging and wine analysis have been applied to quantify gas permeation through crown caps and cork stoppers [40,41,43,48–53]. X-ray tomography has been used for the non-destructive visualization of internal cork defects that may increase the risk of wine leakage and to identify potential pathways for gas transfer through cork stoppers [54–56]. More recently, the diffusion of gas-phase CO₂ through macro- and micro-agglomerated corks used in Champagne and other sparkling wines has been studied using a manometric technique [44]. These studies indicate that smaller cork particle size, higher adhesive content, and greater compression enhance the stopper's gas-barrier properties.

Based on recent experimental observations, the following sections aim to highlight and provide a deeper understanding of the inevitable decrease in CO₂ during prolonged aging on lees in traditional-method sparkling wines. Furthermore, a model that integrates molecular diffusion with the ideal gas law and the thermodynamic equilibrium of CO₂ in a

sealed bottle enables a precise assessment of the contribution of each relevant parameter during lees aging.

3.2. Recent Advances from Exceptional Vertical Champagne Collections

3.2.1. A Vertical Collection of Dom Pérignon Bottles

A few years ago, measurements of dissolved CO₂ were carried out on an exceptional vertical collection of seven vintages from a prestige cuvée, spanning increasing durations of lees aging: 1, 5, 12, 15, 20, 25, and 35 years. These bottles were provided by Champagne Dom Pérignon (Épernay, France) [11]. For all seven vintages, a standard dosage of $24 \pm 0.5 \text{ g L}^{-1}$ of sucrose was added to the blend for the second in-bottle fermentation. During the *prise de mousse* and subsequent aging on lees at 12 °C, identical standard 75 cL bottles (with bottlenecks showing a narrow diameter of 26 mm) were sealed with premium traditional cork stoppers (Amorim & Irmãos, Santa Maria de Lamas, Portugal). To allow for statistical analysis, dissolved CO₂ measurements were performed on six distinct bottles for each vintage. Further details regarding this dataset are provided in ref. [11].

As shown in Figure 3, dissolved CO₂ decreased steadily during lees aging, with losses reaching approximately 6 g L^{-1} for the oldest vintage after 35 years. This decline for the prestige cuvée was well described by an exponential decay model, characterized by a timescale of $\tau \approx 48 \pm 13 \text{ years}$ [11]. It is important to note that the gradual decline in dissolved CO₂ concentration during extended aging on lees has notable sensory consequences. Specifically, this reduction results in a decreased frequency of bubble formation and smaller CO₂ bubbles in tasting glasses [57]. It is therefore noteworthy to mention that, owing to the progressive reduction in a vintage's effervescence potential over time, the so-called “carbonic bite” will gradually diminish during tasting, thereby modifying the overall processes that contribute to aroma perception [58–62].

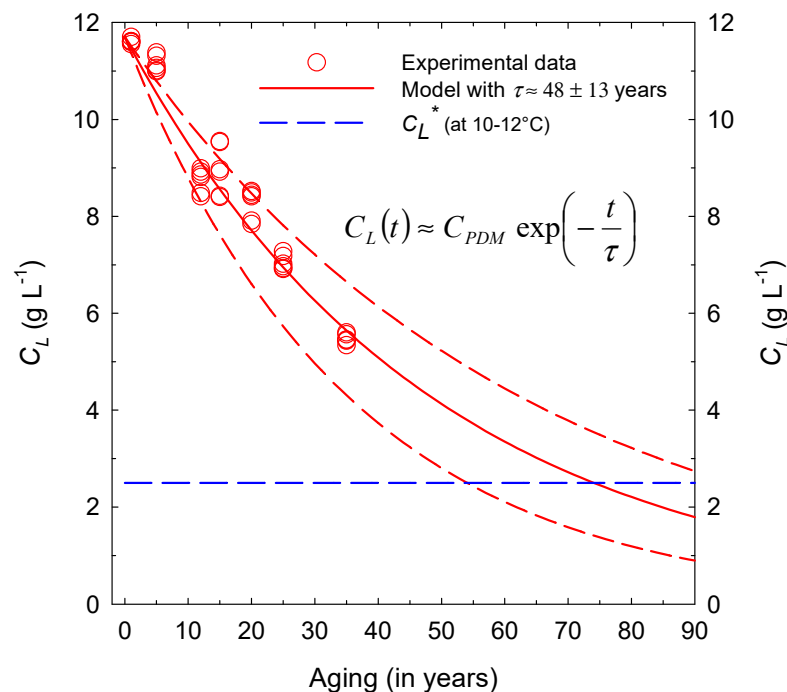


Figure 3. Decreasing concentrations of dissolved CO₂ measured in 7 vintages of Champagne Dom Pérignon that underwent progressively longer aging on lees (red circles), compared with an exponential-decay model with a characteristic timescale $\tau \approx 48 \pm 13 \text{ years}$ (red solid line, with dashed line indicating uncertainty); The horizontal blue dashed line indicates the critical dissolved CO₂ concentration below which bubble nucleation becomes thermodynamically impossible in tasting glasses at 10–12 °C (redrawn from ref. [11]).

3.2.2. A Vertical Collection of Champagne Castelnau Bottles and Magnums

Combined measurements of dissolved CO₂ concentrations and gas-phase CO₂ pressures were performed on 13 consecutive vintages of Champagne Castelnau (Reims, France), produced prior to the 2000s and aged on lees for 25 (1996) to 47 years (1974) [12]. To evaluate the influence of bottle volume, standard 75 cL bottles were compared with 150 cL magnums, except for the 1974 vintage, which was available only in 75 cL. Despite variations in base wine blends, both formats featured identical 29 mm bottlenecks and were sealed with standard crown caps fitted with agglomerated cork discs—the predominant closure for traditional-method sparkling wines before the 2000s. All bottles were aged under uniform cellar conditions (12–14 °C), and a dosage of 25 g L⁻¹ sucrose was added for the second in-bottle fermentation. To enable statistical analysis, measurements of dissolved CO₂ were carried out on three bottles and three magnums for each vintage. More details about this dataset can be found in ref. [12].

Following the second in-bottle fermentation, ethanol typically reached nearly 12.5% (*v/v*), while dissolved CO₂ concentrations were 11.5 g L⁻¹ in 75 cL bottles and 11.6 g L⁻¹ in 150 cL magnums, according to Equation (5). As shown in Figure 4, dissolved CO₂ gradually decreased during aging, with the greatest loss observed in the oldest vintage (1974 elaborated in standard 75 cL bottles), which lost nearly 9 g L⁻¹ after 47 years. A similar trend was observed in magnums, but the rate of CO₂ loss was substantially slower, demonstrating that magnums retain dissolved CO₂ more effectively during prolonged aging on lees than standard bottles.

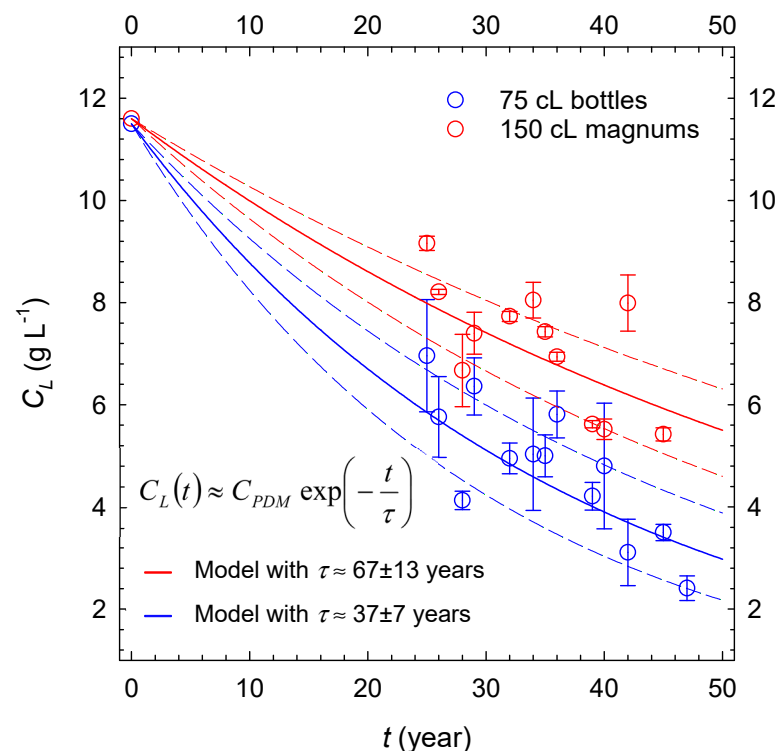


Figure 4. Decrease in dissolved CO₂ across 13 Champagne Castelnau vintages aged on lees for 25–47 years in 75 cL bottles and 150 cL magnums; dashed lines denote uncertainties in the exponential timescales (redrawn from ref. [12]); At $t = 0$, the initial dissolved CO₂ concentrations reached in bottles and magnums at the end of the *prise de mousse* were theoretically determined using Equation (3) assuming a second in-bottle fermentation initiated with 25 g L⁻¹ sucrose.

As observed for successive vintages of Champagne Dom Pérignon, the gradual decrease in dissolved CO₂ during prolonged lees aging of Champagne Castelnau is well described by exponential decay functions, albeit with markedly different characteristic

timescales depending on bottle size. In standard 75 cL bottles, the characteristic exponential timescale is $\tau_B \approx 37 \pm 7$ years, whereas in 150 cL magnums it is significantly longer, $\tau_M \approx 67 \pm 13$ years [12]. These long-term observations clearly demonstrate that bottle size plays a critical role in the gradual loss of dissolved CO₂ in traditional-method sparkling wines during aging on lees.

To better interpret these experimental results, a model describing the decay of gas-phase CO₂ pressure and dissolved CO₂ in sealed bottles is presented below, along with a discussion of the factors influencing aging duration in cellars for traditional-method sparkling wines.

3.3. A Simple Model for the Losses of CO₂ During Aging on Lees

Since molecular diffusion governs the transfer of gas-phase CO₂ through crown caps or cork stoppers, a model based on Fick's first law has been proposed to predict the temporal evolution of CO₂ pressure ($P_G(t)$) and the corresponding dissolved CO₂ concentration in wine ($C_L(t)$) during aging on lees [12]. Assuming that the mass transfer coefficient for gas-phase CO₂ through the bottle closure (denoted K) remains constant over time, the following multivariable exponential-decay models were developed to describe the temporal evolution of CO₂ pressure and the corresponding dissolved CO₂ concentration in sealed bottles, with all parameters expressed in SI units [12]:

$$\begin{cases} P_G(t) \approx P_{PDM} \exp\left(-\frac{t}{\tau}\right) \\ C_L(t) \approx C_{PDM} \exp\left(-\frac{t}{\tau}\right), \\ \text{with } \tau = \frac{V_G + k_H RT V_L}{K} \end{cases} \quad (6)$$

where P_{PDM} and C_{PDM} are the CO₂ pressure and dissolved CO₂ concentration in wine at the end of the *prise de mousse*, t is the aging time, and τ is the characteristic timescale of the exponential decay, determined by the properties of the bottle, wine, and closure system.

Further details regarding the stepwise determination of Equation (6) can be found in ref. [12]. Most interestingly, this system of equations indicates that experimentally determining the exponential timescales from long-term measurements of dissolved CO₂ or pressure decay in sealed bottles provides an effective indirect method for estimating the mass transfer coefficient K for CO₂ through any type of crown cap or cork stopper, according to the following relationship:

$$K = \frac{V_G + k_H RT V_L}{\tau}. \quad (7)$$

Applying this equation to the exponential timescales determined for the successive vintages of Champagne Castelnau yielded an overall CO₂ mass transfer coefficient of $K \approx 7.1 \pm 1.3 \times 10^{-13} \text{ m}^3 \text{ s}^{-1}$ for crown caps fitted with cork discs, which were commonly used prior to the 2000s [12]. Applying the same approach to the dataset from successive vintages of Champagne Dom Pérignon yielded a mass transfer coefficient of $K \approx 5.8 \pm 1.4 \times 10^{-13} \text{ m}^3 \text{ s}^{-1}$ for traditional high-quality cork stoppers, demonstrating that these closures provide a more effective barrier to CO₂ leakage during aging on lees than the crown caps with cork discs commonly used prior to the 2000s.

4. Discussion

4.1. Is There a Maximum Legal Lees-Aging Period for Aged Vintages?

4.1.1. From Lees Aging to Disgorging: Managing CO₂ Pressure in Marketable Bottles

Because European regulations require a minimum excess CO₂ pressure of 3.5 bar at 20 °C [3], the shelf life of traditional-method sparkling wine bottles can be evaluated

in terms of their ability to maintain an internal CO₂ pressure above this legal threshold (denoted P_G^*). Inevitably, due to the progressive exponential decline in pressure during aging on lees, a maximum permissible aging duration exists beyond which the pressure will inevitably fall below this limit.

Moreover, between the end of lees aging and the release of the cork-finished bottle to the market, the disgorging step induces an additional loss of CO₂ pressure, further constraining the allowable total aging time. Disgorging is the post-lees-aging process used to remove yeast sediment from the bottles. The bottle necks are first frozen—typically in a brine or glycol bath at nearly 25 °C—forming an ice plug that traps the sediment [14,15,63]. The crown caps or corks are then removed, and the internal pressure ejects the frozen plug. Finally, a specific dosage, known as the *liqueur d'expédition* and consisting of a mixture of wine and sugar [64], is added to replace the lost volume. Adding sugar at this step determines the wine's sweetness category, classified according to European regulations (in g L⁻¹) [65]:

Brut Nature: <3

Extra-Brut: 3–6

Brut: 6–12

Extra-Dry: 12–17

Sec: 17–32

Demi-Sec: 32–50

Doux: >50

From a CO₂ perspective, the gas-phase CO₂ pressure in the sealed bottle drops immediately upon opening during disgorging. Importantly, the headspace volume V_G , which initially contained CO₂ under pressure, is irreversibly lost, breaking the thermodynamic equilibrium in the bottle. When the bottle is then quickly recorked with a cork stopper, the moles of CO₂ corresponding to the evacuated headspace must be subtracted from the total CO₂ balance. Dissolved and gaseous CO₂ then re-establish Henry's equilibrium, but with a new gas-phase pressure in the recorked bottle (denoted P_{CB}) slightly lower than the pressure just before disgorging, given by [66]:

$$P_{CB} \approx P_G \left(\frac{k_H R T V_L}{V_G^{AD} + k_H^{AD} R T V_L} \right), \quad (8)$$

where P_G denotes the CO₂ pressure in the bottle after aging on lees (i.e., just before disgorging), V_G^{AD} is the new headspace volume in the bottle after dosage, and k_H^{AD} is the Henry's constant of CO₂ in the wine after dosage and recorking.

After dosage and recorking, because the cork is inserted approximately 2.5 cm into the bottleneck, the headspace volume of the recorked bottle (V_G^{AD}) is slightly smaller than the original headspace volume (V_G) present when the bottle was sealed with a crown cap during the *prise de mousse* and lees aging. In addition, the Henry's constant (k_H^{AD}) slightly differs from the previous value, as the dosage—composed of sugar and aged wine added before recorking—reduces CO₂ solubility by increasing the sugar concentration b in Equation (2). This effect of dosage on Henry's constant, and thus on CO₂ pressure in the recorked bottle, has largely been overlooked in earlier studies [9–12]. Further details on the evolution of dissolved and gas-phase CO₂ during the disgorging step can be found in a recent review by Liger-Belair [66], which also considers the consequences of moderate gushing episodes.

Moreover, aging on lees is of course not carried out at 20 °C, but rather at typical cellar temperatures closer to 12 °C. A temperature correction must therefore be applied to determine the minimum legal CO₂ pressure at cellar temperature corresponding to the

regulatory threshold of 3.5 bar at 20 °C (after disgorging). By applying Henry's law with 20 °C as the reference temperature, the relationship between the relevant parameters as a function of wine temperature T can be expressed as follows [18]:

$$\frac{P_G^{20\text{ }^\circ\text{C}}}{P_G^{T\text{ }^\circ\text{C}}} = \frac{C_L^{20\text{ }^\circ\text{C}} \times k_H^{T\text{ }^\circ\text{C}}}{C_L^{T\text{ }^\circ\text{C}} \times k_H^{20\text{ }^\circ\text{C}}}, \quad (9)$$

Nevertheless, because CO₂ is highly soluble in the liquid phase and the gaseous headspace is negligible compared with the wine volume ($V_G \ll V_L$), the total CO₂ content of a sealed bottle is dominated by the dissolved fraction ($n_G \ll n_L$). As a result, the concentration of dissolved CO₂ varies only marginally with temperature (i.e., $C_L^{T\text{ }^\circ\text{C}} \approx C_L^{20\text{ }^\circ\text{C}}$). Consequently, Equation (9) can therefore be rewritten to express the CO₂ pressure at temperature T as a function of its value at the reference temperature of 20 °C [18]:

$$P_G^{T\text{ }^\circ\text{C}} \approx \frac{k_H^{20\text{ }^\circ\text{C}}}{k_H^{T\text{ }^\circ\text{C}}} P_G^{20\text{ }^\circ\text{C}}, \quad (10)$$

According to Equation (2), at 12 °C, the Henry's constant for CO₂ in a sugar-free wine containing 12.5% (v/v) ethanol—typical of lees aging—is $k_H^{12\text{ }^\circ\text{C}} \approx 1.88 \text{ g L}^{-1} \text{ bar}^{-1}$. At 20 °C, the same equation gives $k_H^{20\text{ }^\circ\text{C}} \approx 1.50 \text{ g L}^{-1} \text{ bar}^{-1}$. Consequently, the minimum legal CO₂ pressure at 12 °C corresponds to $P_G^*(12\text{ }^\circ\text{C}) \approx (1.50/1.88)P_G^*(20\text{ }^\circ\text{C}) \approx 2.8 \text{ bar}$. Thus, taking the disgorging step into account, the critical CO₂ pressure in a bottle still sealed with a crown cap prior to disgorging (denoted P_{SB}^*), and which will result in a CO₂ pressure equal to the regulatory threshold of $P_G^* \approx 3.5 \text{ bar}$ at 20 °C in the recorked bottle after disgorging, can therefore be estimated as follows:

$$P_{SB}^*(T) \approx \left(\frac{V_G^{AD} + k_H^{AD}RTV_L}{k_HRTV_L} \right) P_G^*(T). \quad (11)$$

Thus, the shelf life of older vintages can be predicted by replacing $P_G(t)$ in Equation (6) with $P_{SB}^*(T)$ and extracting the corresponding aging time at which this critical pressure is reached. Ultimately, the maximum allowable aging time on lees at cellar temperature ($\approx 12\text{ }^\circ\text{C}$), denoted t_{CP}^* , beyond which the CO₂ pressure in the bottle would drop below the critical value of $P_G^* \approx 2.8 \text{ bar}$ after disgorging (at 12 °C), can be expressed as follows:

$$t_{CP}^* \approx \tau \ln \left(\frac{P_{PDM}}{P_{SB}^*} \right) \approx \left(\frac{V_G + k_HRTV_L}{K} \right) \ln \left(\frac{P_{PDM}}{P_{SB}^*} \right). \quad (12)$$

Using Equation (12), the shelf life of a bottle can thus be predicted from its ability to maintain, after disgorging, a CO₂ pressure above the minimum regulatory threshold ($P_G^* \approx 3.5 \text{ bar}$ at 20 °C). For second in-bottle fermentations typically initiated with 25 g L⁻¹ of saccharose, Table 1 summarizes the key parameters governing CO₂ retention in traditional-method sparkling wines produced and aged at 12 °C in 37.5 cL half-bottles, 75 cL bottles, and 150 cL magnums. All formats share identical 29 mm bottlenecks and were sealed with the same type of crown caps fitted with thin cork discs commonly used before the 2000s. Together, these parameters allow prediction of the maximum shelf life beyond which CO₂ pressure falls below the legal limit of 3.5 bar at 20 °C.

Table 1. For prolonged aging on lees at 12 °C in 37.5 cL half-bottles, 75 cL standard bottles, and 150 cL magnums (all sealed with identical crown caps fitted with a thin cork disc), the table compares the relevant parameters that govern CO₂ loss and ultimately determine the predicted shelf life beyond which the CO₂ pressure drops below the minimum 3.5 bar at 20 °C required by European regulations. These predictions apply here to standard *Zero Dosage* traditional-method sparkling wines after disgorging (i.e., without added sugar in the liqueur d’expédition, implying $k_H^{AD} \approx k_H$).

Parameters of the Bottle, Wine, and Crown Cap and Corresponding CO ₂ Variables During Aging on Lees at 12 °C.	Half-Bottles (37.5 cL)	Standard Bottles (75 cL)	Magnums (150 cL)
V_G (cL)	2	2.5	3.3
V_L (cL)	37.5	75	150
$x_V = V_L/V_G$	≈19	30	45
Neck diameter (mm)	29	29	29
k_H (g L ⁻¹ bar ⁻¹)	1.88	1.88	1.88
C_{PDM} (g L ⁻¹)	11.3	11.5	11.6
P_{PDM} (bar)	6.0	6.1	6.2
K (×10 ⁻¹³ m ³ s ⁻¹)	7.1 ± 1.3	7.1 ± 1.3	7.1 ± 1.3
$\tau = \frac{V_G + k_H RT V_L}{K}$ (year)	18 ± 4	35 ± 7	70 ± 13
V_G^{AD} (cL)	1.5	2.0	2.8
P_{SB}^* (bar)	2.9	2.9	2.9
$t_{CP}^* \approx \tau \ln\left(\frac{P_{PDM}}{P_{SB}^*}\right)$ (year)	13 ± 3	26 ± 5	53 ± 10

As clearly shown in Table 1, the potential shelf life of older vintages is strongly influenced by bottle size—an essential parameter that traditional method sparkling wine makers must consider when crafting prestigious cuvées intended for release many decades later. Notably, owing to their superior ability to retain CO₂ above the minimum pressure mandated by European regulations, traditional-method sparkling wines produced in 150 cL magnums can sustain more than twice the maximum aging time on lees compared with those produced in standard 75 cL bottles.

4.1.2. The Combined Influence of Temperature and Crown Cap Permeability

Today, modern crown caps used to seal traditional-method sparkling wines during secondary fermentation no longer contain cork liners, thereby eliminating the potential risk of cork taint and providing a more hermetic seal than crown caps fitted with cork liners commonly used prior to the 2000s. Several manufacturers currently produce crown caps with synthetic liners for the secondary alcoholic fermentation and the subsequent lees aging of traditional-method sparkling wines [67].

In most studies on traditional-method sparkling wines, the CO₂ permeability of crown caps during lees aging is expressed as the volume of CO₂ lost per day (cm³ day⁻¹), measured at 1 bar and 20 °C. The relationship between the volumetric CO₂ gas loss and the CO₂ mass transfer coefficient of the crown cap can be determined using the equation below, derived from Fick’s law:

$$\frac{dn_T}{dt} \approx -K \frac{(P_G - P_{ATM}^{CO_2})}{RT}, \tag{13}$$

where $\frac{dn_T}{dt}$ denotes the rate at which the number of CO₂ moles escapes from the sealed bottle during lees aging in response to the difference in CO₂ partial pressure between the bottle (P_G) and the cellar atmosphere ($P_{ATM}^{CO_2}$).

Combining the latter equation with the ideal gas law leads to the following relationship between the volumetric CO₂ gas loss, denoted $\frac{dV_T}{dt}$, and the CO₂ mass transfer coefficient K of the crown cap:

$$\frac{dV_T}{dt} \approx -K \frac{(P_G - P_{ATM}^{CO_2})}{P_0}, \tag{14}$$

where P_0 is the ambient pressure in the cellar (usually close to 1 bar if not too far above seal level).

Finally, with $P_{ATM}^{CO_2}$ being negligible compared with the partial pressure of CO₂ in the sealed bottle, the CO₂ mass transfer coefficient of can easily be determined as follows (in m³ s⁻¹):

$$K \approx 1.16 \times 10^{-11} \left(\frac{P_0}{P_G} \frac{dV_T}{dt} \right), \tag{15}$$

where the numerical factor 1.16×10^{-11} accounts for the conversion to m³ s⁻¹ of the volumetric CO₂ gas loss, which is usually expressed in cm³ day⁻¹ by most crown cap manufacturers.

Recently, a study has been conducted in collaboration between our laboratory at the University of Reims Champagne-Ardenne and the crown cap manufacturer PE.DI (Dizy, France), which offers a wide range of crown caps with different CO₂ permeabilities [47]. For the first time, the volumetric CO₂ fluxes through different crown cap models were determined in situ by tracking the mass loss of several batches of standard 75 cL bottles sealed with synthetic-liner crown caps of varying permeability (called TOP, TOP+3, TOP+, TOP Z and TOP S) during five years of lees aging. Thollin et al. [47], in their description of this collaborative study, reported a cellar temperature of 13 °C during lees aging. Consequently, the CO₂ mass transfer coefficient K of crown caps must be determined using Equation (15), by taking into account the CO₂ partial pressure reached at the end of the secondary fermentation (for a tirage containing 25 g L⁻¹ sucrose and a cellar temperature of 13 °C). Applying Equation (5) shows that a CO₂ partial pressure P_G of 6.3 bar is reached once the *prise de mousse* is completed in standard 75 cL bottles. Table 2 summarizes the corresponding CO₂ mass transfer coefficients for these closures.

Table 2. Bottle and wine parameters used to determine the CO₂ mass transfer coefficients of various crown cap models from experimentally measured volumetric CO₂ fluxes in batches of standard 75 cL bottles (all with 29 mm neck diameters) sealed with different crown cap models from PE.DI (Dizy, France) and aged on lees for five years in a 13 °C cellar.

Bottle and Wine Parameters (at 13 °C) Needed to Determine the CO₂ Mass Transfer Coefficients K of the Various Crown Cap Models from Equation (15)	TOP	TOP+3	TOP+	TOP Z	TOP S
V_G (cL)	2.5	2.5	2.5	2.5	2.5
V_L (cL)	75	75	75	75	75
$x_V = V_L/V_G$	30	30	30	30	30
k_H (g L ⁻¹ bar ⁻¹)	1.83	1.83	1.83	1.83	1.83
P_G (bar)	6.3	6.3	6.3	6.3	6.3
dV_T/dt (cm ³ day ⁻¹)	0.27 ± 0.01	0.16 ± 0.01	0.09 ± 0.01	0.07 ± 0.01	0.04 ± 0.02
K (×10 ⁻¹³ m ³ s ⁻¹)	5.0 ± 0.2	2.9 ± 0.2	1.7 ± 0.2	1.3 ± 0.2	0.7 ± 0.4

It is worth noting that, based on the volumetric CO₂ gas losses derived from the data reported by Thollin et al. [47], the resulting CO₂ mass transfer coefficients of modern crown caps with synthetic liners are consistently lower than those of crown caps with cork liners commonly used prior to the 2000s. It is also important to note that the CO₂ mass transfer coefficients, K , given in Table 2 clearly depend on the permeability of the liner but are

assumed to be independent of wine temperature. The resulting volumetric CO₂ gas losses during lees aging, as given in Equation (14), are temperature-dependent only because the CO₂ partial pressure in the bottle (P_C) is indeed temperature-dependent (but not K).

Having determined the CO₂ mass transfer coefficients for each crown cap model presented in Table 2, the maximum lees-aging durations beyond which the CO₂ pressure falls below the critical threshold required by European regulations after disgorging can now be estimated, using Equation (12), for each cap model as a function of cellar temperature T during aging. To this end, the temperature dependence of the Henry's law constants of CO₂ in wine, both before and after disgorging (i.e., k_H and k_H^{AD}), must also be taken into account by correctly using Equation (2).

Ultimately, by combining Equations (2), (5) and (10)–(12), the maximum allowable lees-aging time (t_{CP}^*) for each cap model, as a function of cellar temperature (T), can be determined. Beyond this duration depending on both temperature and crown cap permeability, the CO₂ pressure in the bottle would fall below the critical value of 3.5 bar at 20 °C after disgorging, as shown in Figure 5.

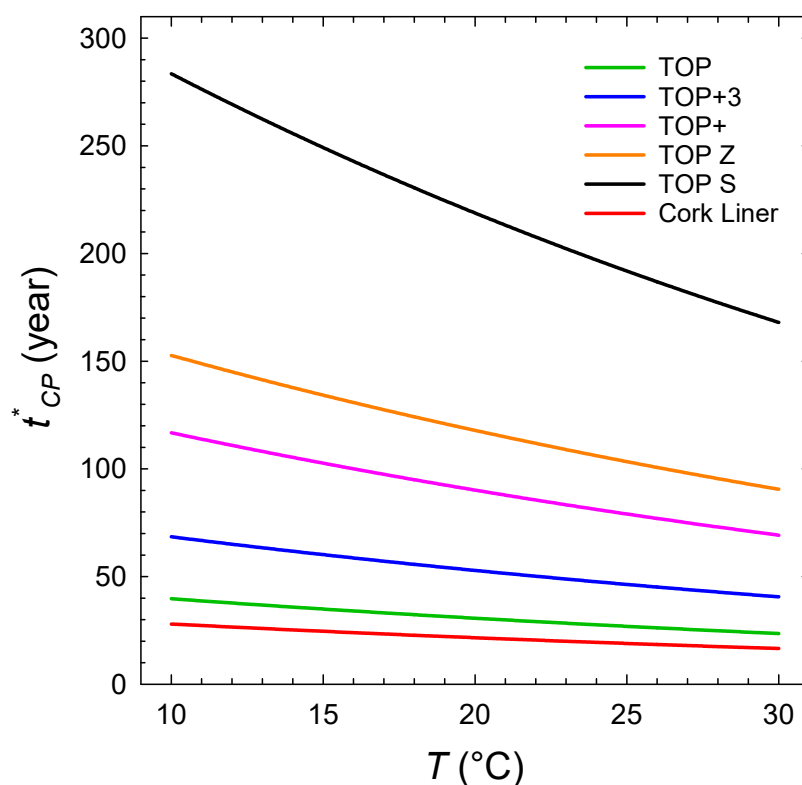


Figure 5. Predicted shelf life (in years) beyond which the CO₂ pressure falls below the minimum threshold of 3.5 bar at 20 °C required by European regulations, as a function of cellar temperature during lees aging and crown cap type (from the PE.DI collection). These predictions apply here to standard *Zero Dosage* traditional-method sparkling wines after disgorging (i.e., without added sugar in the liqueur d'expédition, implying $k_H^{AD} \approx k_H$).

As shown in Figure 5, for a given crown cap model, the higher the cellar temperature, the shorter the potential shelf life beyond which the CO₂ pressure falls below the minimum threshold of 3.5 bar at 20 °C required by European regulations. This can be explained by the fact that increasing cellar temperature raises the CO₂ pressure in the sealed bottle (through a decrease in the Henry's law constant of CO₂), thereby enhancing CO₂ losses due to a greater difference in CO₂ partial pressure between the bottle and the cellar atmosphere.

Moreover, it clearly emerges from Figure 5 that modern crown caps retain CO₂ far more effectively in traditional-method sparkling wines than crown caps fitted with cork

liners used in the last century (which still seal tens of thousands of prestigious bottles stored in the cellars of major Champagne and sparkling wine houses).

4.2. The Issue of Dissolved CO₂ in Tasting Glasses

With effervescence being the defining sensory hallmark of sparkling wine [57,68], the shelf life of aged Champagne and other traditional-method vintages can also be assessed based on their ability to generate CO₂ bubbles and provide a pleasing mouthfeel when served. However, bubble formation is fundamentally determined by the concentration of dissolved CO₂. This raises a key question: *What is the dissolved CO₂ concentration in a bottle that has just reached the minimum legal pressure of 3.5 bar at 20 °C following disgorging, recorking, and preparation for market release and tasting?*

Just before tasting, and while the bottle is still corked, the concentration of dissolved CO₂ in the wine follows Henry's equilibrium and may be written as $C_{CB} \approx k_H^{AD} P_G^*$. Consider, for example, a Brut-labelled sparkling wine with 12.5% ethanol by volume and 6 g L⁻¹ of residual sugar after dosage. From Equation (2), the Henry's constant for CO₂ in such a wine at 20 °C is $k_H^{AD} \approx 1.49 \text{ g L}^{-1} \text{ bar}^{-1}$. Therefore, once the bottle has reached the minimum legal pressure of 3.5 bar required by European regulations, the dissolved CO₂ concentration is $C_{CB} \approx 1.49 \times 3.5 \approx 5.2 \text{ g L}^{-1}$. However, serving sparkling wine in a glass induces significant losses of dissolved CO₂. When 100 mL of a standard commercial Champagne are poured at a tasting temperature close to 12 °C into a vertically oriented flute, approximately 30% of the dissolved CO₂ is lost due to flow-induced turbulence during the pour [69]. As a result, after service in the glass, the dissolved CO₂ concentration drops to $C_L \approx 0.7 \times 5.2 \approx 3.6 \text{ g L}^{-1}$.

As widely documented, bubbles in sparkling wines, beers, and other carbonated beverages repeatedly originate from preexisting gaseous nuclei trapped in particles suspended in the liquid or in micro-crevices on the glass wall intentionally created by the glassmaker to promote heterogeneous bubble nucleation [10,57,68,70–72]. However, below a critical dissolved CO₂ concentration C_L^* (expressed hereafter in the SI units), these preexisting nuclei become thermodynamically unable to nucleate CO₂ bubbles during tasting [10–12]:

$$C_L^* \approx k_H \left(P_0 + \frac{2\gamma}{r} \right), \quad (16)$$

with P_0 being the ambient pressure (in Pa), γ being the surface tension of the wine (in N m⁻¹), and r being the radius of curvature of gaseous germs acting as bubble nucleation sites (in m).

If the level of dissolved CO₂ drops below C_L^* , the entrapped air bubble cannot overcome the Laplace pressure barrier and thus fails to nucleate CO₂ bubbles during tasting. Although C_L^* depends on tasting temperature, ambient pressure, and the initial radius of the preexisting gaseous nucleus, we consider here typical tasting conditions: 12 °C, near sea level (ambient pressure close to 1 bar $\approx 10^5$ Pa), and with pre-existing gaseous nuclei of characteristic radius $r \approx 5 \text{ }\mu\text{m}$ [10,11]. Under these conditions, the critical concentration is $C_L^* \approx 2.5 \text{ g L}^{-1}$. In a tasting glass, the dissolved CO₂ concentration must therefore exceed this threshold to sustain heterogeneous bubble nucleation.

It is worth emphasizing that this critical concentration $C_L^* \approx 2.5 \text{ g L}^{-1}$ required to trigger visible effervescence in sparkling wines, should not be confused with the minimum dissolved CO₂ concentration of approximately 1.2 g L⁻¹ needed for the sensory perception of carbonation and "bite," as highlighted by McMahon et al. [73]. With a dissolved CO₂ concentration of about 3.6 g L⁻¹ after serving, a bottle that has reached the minimum legal pressure of 3.5 bar at 20 °C therefore still comfortably exceeds the 1.2 g L⁻¹ sensory

threshold, and also remains well above the 2.5 g L^{-1} limit required for effervescence to occur in a tasting glass.

5. Limitations

It is worth noting that the various parameters appearing in the exponential timescale τ of Equation (6) are assumed to remain constant during aging. As a first approximation, it is reasonable to assume that the cellar temperature, as well as the volumes of wine and gaseous headspace in sealed bottles, remain constant throughout the aging on lees. Nevertheless, slight seasonal temperature variations of 2–3 °C may occur. Over very long aging periods, minor evaporation from the bottles can also lead to small changes in wine volume and headspace, which may slightly affect the validity of this approach.

Furthermore, the mass transfer coefficient (K) of a crown cap or cork stopper may also change over time. Indeed, the overall appearance of corks visibly evolves during aging. Corks sealing the youngest vintages retain a characteristic mushroom shape, with the lower portion largely regaining its original diameter after insertion into the bottleneck, demonstrating the resilience of cork cells. In contrast, corks sealing older vintages show little ability to recover their original shape and have completely lost their natural elasticity. Liger-Belair et al. [11] reported that the oldest corks used to seal a 35-year-old vintage even appeared to have shrunk into the bottleneck. Such structural changes during aging on lees could affect the transport of gaseous CO_2 from the bottle headspace to the ambient air, either through the cork cells themselves or via the interface between cork and bottleneck. Similarly, prolonged aging may induce structural changes in crown cap seals, potentially modifying their gas permeability and ultimately impacting the validity of the present model.

6. Conclusions and Prospects

This study addresses how long traditional-method sparkling wines can age while maintaining sufficient CO_2 pressure and dissolved CO_2 . A predictive formula for the shelf life of older vintages was developed, integrating all relevant parameters to ensure compliance with the minimum CO_2 pressure of 3.5 bar at 20 °C required by European regulations. Furthermore, the broad applicability of the exponential-decay model for CO_2 pressure and dissolved CO_2 developed here should be emphasized. Regardless of bottle format or the type of crown cap or cork used during the second in-bottle fermentation and subsequent aging on lees, precise knowledge of the CO_2 mass transfer coefficient K , together with other key bottle and wine parameters, enables accurate prediction of the progressive CO_2 loss before the bottles reach the market.

Based on the comparison between CO_2 losses for a range of modern crown caps and those measured in bottles from older vintages sealed with cork-lined crown caps, it clearly emerges that modern crown caps retain CO_2 far more effectively in traditional-method sparkling wines than cork-lined crown caps used in the last century. Otherwise, because effervescence defines the sensory identity of sparkling wine, the shelf life of aged traditional-method vintages was also assessed by their ability to maintain CO_2 bubbles and the characteristic carbonation mouthfeel when served.

In future complementary research, the model will also be confronted with additional analytical datasets from other wine libraries in order to further assess its performance with respect to wine aging temperature, as well as the choice between crown caps and cork closures used to seal bottles during the secondary fermentation and lees aging of traditional-method sparkling wines.

The next stage of this work on the aging of traditional-method sparkling wines on their lees will be to model accurately, in situ, the gradual ingress of oxygen through crown

caps or cork stoppers—an ingress that accompanies CO₂ losses and drives the progressive evolution of wine aroma through slow oxidative processes.

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Conflicts of Interest: Virginie Thollin runs her own consulting company (SARL VT). She contributed to the writing and conceptual development of certain parts of this work. It is clear that the involvement of Virginie Thollin in this work did not, in any way, affect the authenticity or objectivity of the experimental results, the interpretation of data, the writing of this article or the decision to submit it for publication. Moreover, we certify that SARL VT has not provided any financial compensation to Clara Cilindre, Gérard Liger-Belair, or their laboratory.

Nomenclature

a	Level of ethanol in the liquid phase (i.e., in the wine), in % by volume
b	Concentration of sugar in the liquid phase (i.e., the wine), in g L ⁻¹
C_L	Concentration of dissolved CO ₂ in the liquid phase (i.e., the wine), in mol m ⁻³
C_{CB}	Concentration of dissolved CO ₂ in the recorked bottle, after disgorging and dosage, in mol m ⁻³
C_{PDM}	Concentration of dissolved CO ₂ after the prise de mousse is completed, in mol m ⁻³
C_L^*	Critical concentration of dissolved CO ₂ in the liquid phase required to enable bubble nucleation from a gas cavity, in mol m ⁻³
k_H	Henry’s constant of CO ₂ in wine (i.e., its solubility), in mol m ⁻³ Pa ⁻¹
k_H^{AD}	Henry’s constant of CO ₂ in wine in the recorked bottle after dosage and disgorging, in mol m ⁻³ Pa ⁻¹
K	Mass transfer coefficient for gas-phase CO ₂ through the closure system used to seal the bottle during on lees, in m ³ s ⁻¹
n	CO ₂ mole number produced per liter of wine in the sealed bottle, following Equation (1), after the prise de mousse is achieved, in mol L ⁻¹
n_T	Total CO ₂ mole number trapped in the sealed bottle, in mol
n_L	Mole number of dissolved CO ₂ in the liquid phase, in mol
n_G	Mole number of gas-phase CO ₂ in the bottle headspace, in mol
P_G	Gas-phase CO ₂ pressure in the bottle headspace, in Pa

P_G^*	Minimum gas-phase CO ₂ pressure required by European regulations in the sealed bottle after disgorging, ≈ 3.5 bar at 20 °C (3.5×10^5 Pa)
P_{SB}^*	Minimum gas-phase CO ₂ pressure required by European in the bottle sealed before disgorging, in Pa
P_{PDM}	Gas-phase CO ₂ pressure in the bottle headspace after the prise de mousse is completed, in Pa
P_{CB}	Gas-phase CO ₂ pressure in the recorked bottle, after disgorging and dosage, in Pa
$P_{ATM}^{CO_2}$	Gas-phase CO ₂ pressure in the atmosphere of the cellar where bottles and magnums have aged for several decades, in Pa
r	Radius of curvature of the pre-existing air bubble immersed in the liquid phase and acting as a bubble nucleation site, in m
R	Ideal gas constant, = $8.31 \text{ J K}^{-1} \text{ mol}^{-1}$
t	Time, in s
t_{CP}^*	Maximum aging duration on lees beyond which the CO ₂ pressure in the bottle would drop below the critical pressure P_G^* after disgorging, in s
T	Temperature, in K
V_G	Volume of gas phase found in the headspace in the sealed bottles during the second in-bottle fermentation, in m ³
V_G^{AD}	Gaseous headspace volume in the recorked bottle, after disgorging, in m ³
V_L	Volume of the liquid phase in the sealed bottle (i.e., volume of wine), in m ³
V_M	Molar volume of an ideal gas (RT/P_0), in m ³ mol ⁻¹
x_V	Dimensionless ratio of the wine volume to the gaseous headspace ($x_V = V_L/V_G$)
τ	Time scale of the exponential decay-type model, in s
γ	Surface tension of wine, $\approx 45\text{--}50 \text{ mN m}^{-1}$ (for a wine with 12–13% ethanol by volume) [10]

References

- Perpetuini, G.; Tofalo, R. Editorial: Sparkling wines: Current trends and future evolution. *Front. Microbiol.* **2023**, *14*, 1199578. [CrossRef]
- Alexandre, H. Production Methods. In *New Frontiers in Sparkling Wine Production*; Tofalo, R., Alexandre, H., Eds.; Nova Science Publishers: Hauppauge, NY, USA, 2024; pp. 1–25.
- OIV Focus: The Global Sparkling Wine Market. Available online: https://www.oiv.int/sites/default/files/2024-04/OIV_STATE_OF_THE_WORLD_VINE_AND_WINE_SECTOR_IN_2023.pdf (accessed on 5 July 2025).
- Cravero, M.C. Innovations in Sparkling Wine Production: A Review on the Sensory Aspects and the Consumer's Point of View. *Beverages* **2023**, *9*, 80. [CrossRef]
- Stevenson, T. *Christies World Encyclopedia of Champagne and Sparkling Wines*; Absolute Press: Bath, UK, 1998.
- Liger-Belair, G. *Uncorked, the Science of Champagne*, rev. ed.; Princeton University Press: Princeton, NJ, USA, 2013.
- Phillips, R. *Alcohol: A History*; University of North Carolina Press: Chapel Hill, NC, USA, 2014.
- Gonzales Viejo, C.; Torrico, D.D.; Dunshea, F.R.; Fuentes, S. Bubbles, foam formation, stability and consumer perception of carbonated drinks: A review of current, new and emerging technologies for rapid assessment and control. *Foods* **2019**, *8*, 596. [CrossRef] [PubMed]
- Kemp, B.; Alexandre, H.; Robillard, B.; Marchal, R. Effect of production phase on bottle-fermented sparkling wine quality. *J. Agric. Food Chem.* **2015**, *63*, 19–38. [CrossRef] [PubMed]
- Liger-Belair, G. Effervescence in Champagne and sparkling wines: From grape harvest to bubble rise. *Eur. Phys. J. Spec. Top.* **2017**, *226*, 3–116. [CrossRef]
- Liger-Belair, G.; Carvajal-Pérez, D.; Cilindre, C.; Facque, J.; Brevot, M.; Litoux-Desrues, F.; Chaperon, V.; Geoffroy, R. Evidence for moderate losses of dissolved CO₂ during aging on lees of a champagne prestige cuvee. *J. Food Eng.* **2018**, *233*, 40–48. [CrossRef]
- Liger-Belair, G.; Khenniche, C.; Poteau, C.; Bailleul, C.; Thollin, V.; Cilindre, C. Losses of yeast-fermented carbon dioxide during prolonged champagne aging: Yes, the bottle size does matter! *ACS Omega* **2023**, *8*, 22844–22853. [CrossRef]
- Valade, M. La prise de mousse: Historique. *Vign. Champen.* **1999**, *120*, 63–77.
- Duteurtre, B. *Le Champagne: De la Tradition à la Science*; Lavoisier: Paris, France, 2016.
- Liger-Belair, G. *Un Monde de Bulles: Le Champagne ou la Science de L'effervescence*; Ellipses: Paris, France, 2020.
- Liger-Belair, G.; Cilindre, C. Recent progress in the analytical chemistry of champagne and sparkling wines. *Annu. Rev. Anal. Chem.* **2021**, *14*, 21–46. [CrossRef]

17. Smith, F.L.; Harvey, A.H. Avoid Common Pitfalls when using Henry's Law. *Chem. Eng. Prog.* **2007**, *103*, 33–39.
18. Liger-Belair, G. Carbon dioxide solubility in sugar and water-ethanol solutions for applications to sparkling drinks. *ACS Food Sci. Technol.* **2025**, *5*, 36–49. [[CrossRef](#)]
19. Lonvaud-Funel, A.; Matsumoto, N. The solubility coefficient of carbonic acid in wines. *Vitic* **1979**, *18*, 137–147.
20. Leroy, M.J.; Charpentier, M.; Duteurtre, B.; Feuillat, M.; Charpentier, C. Yeast Autolysis during Champagne Aging. *Am. J. Enol. Vitic.* **1990**, *41*, 21–28. [[CrossRef](#)]
21. Alexandre, H.; Guilloux-Benatier, M. Yeast autolysis in sparkling wines: A review. *Aust. J. Grape Wine Res.* **2006**, *12*, 119–127. [[CrossRef](#)]
22. Alexandre, H. Yeasts and Sparkling Wine Production. In *Yeasts in the Production of Wine*; Springer: New York, NY, USA, 2019; pp. 395–432.
23. Moreno-Arribas, M.V.; Pueyo, E.; Nieto, F.J.; Martin-Avarez, P.J.; Polo, M.C. Influence of the polysaccharides and the nitrogen compounds on foaming properties of sparkling wines. *Food Chem.* **2000**, *70*, 309–317. [[CrossRef](#)]
24. Nunez, Y.P.; Carrascosa, A.V.; Gonzalez, R.; Polo, M.C.; Martinez-Rodriguez, A.J. Effect of accelerated autolysis of yeast on the composition and foaming properties of sparkling wines elaborated by a champenoise method. *J. Sci. Food Agric.* **2005**, *53*, 7232–7237. [[CrossRef](#)]
25. Todd, B.E.N.; Fleet, G.H.; Henschke, P.A. Promotion of autolysis through the interaction of killer and sensitive yeasts: Potential application in sparkling wine production. *Am. J. Enol. Vitic.* **2000**, *51*, 65–72. [[CrossRef](#)]
26. Gnoinski, G.B.; Schmidt, S.A.; Close, D.C.; Goemann, K.; Pinfold, T.L.; Kerslake, F.L. Novel methods to manipulate autolysis in sparkling wines: Effects on yeast. *Molecules* **2021**, *26*, 387. [[CrossRef](#)] [[PubMed](#)]
27. Babayan, T.L.; Bezrukov, M.G. Autolysis in Yeasts. *Acta Biotechnol.* **1985**, *5*, 129–136. [[CrossRef](#)]
28. Marti-Raga, M.; Martin, V.; Gil, M.; Sancho, M.; Zamora, F.; Mas, A.; Beltran, G. Contribution of yeast and base wine supplementation to sparkling wine composition. *J. Sci. Food Agric.* **2016**, *96*, 4962–4972. [[CrossRef](#)]
29. Tudela, R.; Gallardo-Chacón, J.J.; Rius, N.; López-Tamames, E.; Buxaderas, S. Ultrastructural changes of sparkling wine lees during long-term aging in real enological conditions. *FEMS Yeast Res.* **2012**, *12*, 466–476. [[CrossRef](#)]
30. Buxaderas, S.; López-Tamames, E. Sparkling wines: Features and trends from tradition. *Adv. Food Nutr. Res.* **2012**, *66*, 1–45. [[PubMed](#)]
31. Pons-Mercadé, P.; Giménez, P.; Vilomara, G.; Conde, M.; Cantos, A.; Rozès, N.; Ferrer, S.; Canals, J.M.; Zamora, F. Monitoring yeast autolysis in sparkling wines from nine consecutive vintages produced by the traditional method. *Aust. J. Grape Wine Res.* **2022**, *28*, 347–357. [[CrossRef](#)]
32. Martínez-Rodríguez, A.J.; Carrascosa, A.V.; Barcenilla, J.M.; Pozo-Bayón, M.A.; Polo, M.C. Autolytic capacity and foam analysis as additional criteria for the selection of yeast strains for sparkling wine production. *Food Microbiol.* **2001**, *18*, 183–191. [[CrossRef](#)]
33. Cilindre, C.; Fasoli, E.; D'Amato, A.; Liger-Belair, G.; Righetti, P.G. It's time to pop a cork on champagne's proteome! *J. Proteom.* **2014**, *105*, 351–362. [[CrossRef](#)]
34. Condé, B.C.; Bouchard, E.; Culbert, J.A.; Wilkinson, K.L.; Fuentes, S.; Howell, K.S. Soluble protein and amino acid content affects the foam quality of sparkling wine. *J. Agric. Food Chem.* **2017**, *65*, 9110–9119. [[CrossRef](#)] [[PubMed](#)]
35. Kemp, B.; Condé, B.; Jégou, S.; Howell, K.; Vasserot, Y.; Marchal, R. Chemical compounds and mechanisms involved in the formation and stabilization of foam in sparkling wines. *Crit. Rev. Food Sci. Nutr.* **2019**, *59*, 2072–2094. [[CrossRef](#)]
36. Gawel, R.; Smith, P.A.; Cicerale, S.; Keast, R. The mouthfeel of white wine. *Crit. Rev. Food Sci. Nutr.* **2018**, *58*, 2939–2956. [[CrossRef](#)] [[PubMed](#)]
37. Marchal, A.; Marullo, P.; Moine, V.; Dubourdieu, D. Influence of yeast macromolecules on sweetness in dry wines: Role of the *Saccharomyces cerevisiae* protein Hsp12. *J. Agric. Food Chem.* **2011**, *59*, 2004–2010. [[CrossRef](#)]
38. Vasserot, Y.; Jacopin, C.; Jeandet, P. Effect of bottle capacity and bottle-cap permeability to oxygen on dimethylsulfide formation in Champagne wines during aging on the lees. *Am. J. Enol. Vitic.* **2001**, *52*, 54–55. [[CrossRef](#)]
39. Bunner, D.; Landrieux, A.; Valade, M.; Langleron, E.; Tribaut-Sohier, I.; Moncomble, D.; Viaux, L.; Bourdelet Walter, L.; Chaperon, V.; Gouez, B. La mesure de l'oxygène dans les bouteilles par chimiluminescence. *Vign. Champen.* **2010**, *131*, 84–101.
40. Karbowski, T.; Gougeon, R.D.; Alinc, J.-B.; Brachais, L.; Bebeaufort, F.; Voilley, A.; Chassagne, D. Wine oxydation and the role of cork. *Crit. Rev. Food Sci. Nutr.* **2010**, *50*, 20–52. [[CrossRef](#)]
41. Faria, D.P.; Fonseca, A.L.; Pereira, H.; Teodoro, O. Permeability of cork to gases. *J. Agric. Food Chem.* **2011**, *59*, 3590–3597. [[CrossRef](#)] [[PubMed](#)]
42. Liger-Belair, G.; Villaume, S. Losses of dissolved CO₂ through the cork stopper during champagne aging: Toward a multiparameter modeling. *J. Agric. Food Chem.* **2011**, *59*, 4051–4056. [[CrossRef](#)]
43. Lequin, S.; Chassagne, D.; Karbowski, T.; Simon, J.-M.; Paulin, C.; Bellat, J.-P. Diffusion of oxygen in cork. *J. Agric. Food Chem.* **2012**, *60*, 3348–3356. [[CrossRef](#)] [[PubMed](#)]
44. Crouvisier Urion, K.; Bellat, J.-P.; Liger-Belair, G.; Gougeon, R.D.; Karbowski, T. Unravelling CO₂ transfer through cork stoppers for Champagne and sparkling wines. *Food Packag. Shelf Life* **2021**, *27*, 100618. [[CrossRef](#)]

45. Jolly, N.; Minnaar, P.; Booyse, M.; Gerber, P. Bottle fermented sparkling wine: Cork or crown closures during the second fermentation? *S. Afr. J. Enol. Vitic.* **2021**, *42*, 136–153. [[CrossRef](#)]
46. Thollin, V.; Liger-Belair, G.; Cilindre, C.; Di Crescenzo, R. Champagne et vins effervescents: La première capsule de tirage dopée aux sulfites. *Rev. Oenol.* **2021**, *181*, 50–53.
47. Thollin, V.; Robillard, B.; Di Crescenzo, R.; Barbier, J.E.; Cilindre, C.; Liger-Belair, G. Une première approche in situ de la perméabilité aux échanges gazeux des capsules de tirage pour vins effervescents. *Rev. Fr. D'Œnol.* **2024**, *320*, 26–31.
48. Lopes, P.; Saucier, C.; Teissedre, P.-L.; Glories, Y. Main routes of oxygen ingress through different closures into wine bottles. *J. Agric. Food Chem.* **2007**, *55*, 5167–5170. [[CrossRef](#)]
49. Lagorce-Tachon, A.; Karbowiak, T.; Paulin, C.; Simon, J.M.; Gougeon, R.D.; Bellat, J.-P. Diffusion of oxygen through cork stopper: Is it a Knudsen or a Fickian mechanism? *J. Agric. Food Chem.* **2014**, *62*, 9180–9185. [[CrossRef](#)] [[PubMed](#)]
50. Teodoro, O. The permeation of cork revisited. *J. Agric. Food Chem.* **2016**, *64*, 4182–4184. [[CrossRef](#)]
51. Crouvisier Urion, K.; Bellat, J.-P.; Gougeon, R.D.; Karbowiak, T. Gas transfer through wine closures: A critical review. *Trends Food Sci. Technol.* **2018**, *78*, 255–269. [[CrossRef](#)]
52. Karbowiak, T.; Crouvisier Urion, K.; Lagorce-Tachon, A.; Ballester, J.; Geoffroy, A.; Roullier-Gall, C.; Chanut, J.; Gougeon, R.D.; Schmitt-Kopplin, P.; Bellat, J.-P. Wine aging: A bottleneck story. *npj Sci. Food* **2019**, *3*, 14. [[CrossRef](#)]
53. Chanut, J.; Bellat, J.-P.; Gougeon, R.D.; Karbowiak, T. A key to wine conservation lies in the glass–cork interface. *PNAS Nexus* **2023**, *2*, pgad344. [[CrossRef](#)]
54. Lagorce-Tachon, A.; Karbowiak, T.; Loupiac, C.; Gaudry, A.; Ott, F.; Alba-Simionesco, C.; Gougeon, R.D.; Alcantara, V.; Mannes, D.; Kaestner, A.; et al. The corked viewed from the inside. *J. Food Eng.* **2015**, *149*, 214–221. [[CrossRef](#)]
55. Oliveira, V.; Lopes, P.; Cabral, M.; Pereira, H. Influence of cork defects in the oxygen ingress through wine stoppers: Insights with X-ray tomography. *J. Food Eng.* **2015**, *165*, 66–73. [[CrossRef](#)]
56. Crouvisier Urion, K.; Chanu, J.; Lagorce-Tachon, A.; Winckler, P.; Wang, Z.; Verboven, V.; Nicolai, B.; Lherminier, J.; Ferret, E.; Gougeon, R.D.; et al. Four hundred years of cork imaging: New advances in the characterization of the cork structure. *Sci. Rep.* **2019**, *9*, 19682. [[CrossRef](#)]
57. Liger-Belair, G.; Lecasse, F. Decoding the visual aesthetics of bubble trains in sparkling drinks. *Curr. Opin. Food Sci.* **2025**, *66*, 101360. [[CrossRef](#)]
58. Cain, W.S.; Murphy, C.L. Interaction between chemoreceptive modalities of odour and irritation. *Nature* **1980**, *284*, 255–257. [[CrossRef](#)]
59. Cometto-Muñiz, J.E.; Garcia-Medina, M.R.; Calviño, A.M.; Noriega, G. Interactions between CO₂ oral pungency and taste. *Perception* **1987**, *16*, 629–640. [[CrossRef](#)]
60. Wise, P.M.; Wysocki, C.J.; Radil, T. Time-intensity ratings of nasal irritation from carbon dioxide. *Chem. Senses* **2003**, *28*, 751–760. [[CrossRef](#)]
61. Dunkel, A.; Hofmann, T. Carbonic anhydrase IV mediates the fizz of carbonated beverages. *Angew. Chem. Int. Ed. Engl.* **2010**, *49*, 2975–2977. [[CrossRef](#)]
62. Wise, P.M.; Wolf, M.; Thom, S.R.; Bryant, B. The influence of bubbles on the perception carbonation bite. *PLoS ONE* **2013**, *8*, e71488. [[CrossRef](#)] [[PubMed](#)]
63. Valade, M.; Humbert, F. *Comment met-on les bulles dans le champagne?* Editions France Agricole: Paris, France, 2020.
64. Kemp, B.; Hogan, C.; Xu, S.; Dowling, L.; Inglis, D. The Impact of Wine Style and Sugar Addition in *liqueur d'expédition (dosage)* Solutions on Traditional Method Sparkling Wine Composition. *Beverages* **2017**, *3*, 7. [[CrossRef](#)]
65. UMC: Union des Maisons de Champagne Depuis 1882. Available online: <https://maisons-champagne.com/en/> (accessed on 5 July 2025).
66. Liger-Belair, G. A new perspective on carbon dioxide in the production of traditional-method sparkling wines. *ACS Food Sci. Technol.* **2026**, *6*, 890–900. [[CrossRef](#)]
67. Tribaut-Sohier, I.; Valade, M.; Moncomble, D. Les capsules de tirage: Leur caractérisation par mesure des transferts d'oxygène par chimiluminescence. *Vign. Champen.* **2014**, *135*, 32–50.
68. Liger-Belair, G.; Cilindre, C.; Beaumont, F.; Polidori, G. Understanding the tasting of champagne and other sparkling wines from a scientific perspective. *Food Res. Int.* **2024**, *191*, 114678. [[CrossRef](#)] [[PubMed](#)]
69. Liger-Belair, G.; Bourget, M.; Villaume, S.; Jeandet, P.; Pron, H.; Polidori, G. On the losses of dissolved CO₂ during champagne serving. *J. Agric. Food Chem.* **2010**, *58*, 8768–8775. [[CrossRef](#)]
70. Uzel, S.; Chappell, M.A.; Payne, S.J. Modeling the cycles of growth and detachment of bubbles in carbonated beverages. *J. Phys. Chem. B* **2006**, *110*, 7579–7586. [[CrossRef](#)] [[PubMed](#)]
71. Lee, W.T.; McKechnie, J.S.; Devereux, M.G. Bubble nucleation in stout beers. *Phys. Rev. E* **2011**, *83*, 051609. [[CrossRef](#)]

72. Beaumont, F.; Bogard, F.; Murer, S.; Polidori, G. New Insights on the Effect of Forced Laser-Etched Nucleation on the Unsteady Evolution of Two-Phase Flow in a Beer Glass. *Exp. Tech.* **2024**, *48*, 31–39. [[CrossRef](#)]
73. McMahon, K.M.; Culver, C.; Ross, C.F. The production and consumer perception of sparkling wines of different carbonation levels. *J. Wine Res.* **2017**, *28*, 123–134. [[CrossRef](#)]

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