

Wine Oxidation and the Role of Cork

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The present review aims to show the state of the art of oxidation mechanisms occurring especially in white wines by taking into account knowledge from different fields in relation to the subject. It is therefore divided into three main parts. First, the mechanisms of oxidation relevant to white wine are discussed in the light of recent scientific literature. Next, the phenomenon of oxygen solubility in wine during the winemaking process, and in particular during bottling is stated theoretically as well as practically. Finally, the aspect of wine conservation after bottling is examined with respect to mass transfers which may occur through the closure, with a special emphasis on cork. Currently, specific physico-chemical properties still make cork closures the most important closure type used for the wine market, and especially for high quality wines. This final section will also include a review of studies performed on this subject, which have been analyzed in detail from a theoretical mass transfer point of view, in order to assess the extent to which the proposed scientific tools and the observed tendencies are relevant to progress in the understanding of the impact of this parameter on the behavior of a wine.

Keywords Oxygen, white wine, phenolic compounds, cork, permeability, solubility, diffusion

INTRODUCTION

The history of humans and wine goes back a long way; indeed, wine has been a part of human culture for almost 6000 years (Soleas et al., 1997). In that time, many improvements have been made in both viticulture and winemaking techniques, from the domestication of *Vitis vinifera* through the development of systematic written studies by different monastic orders beginning in the 10th century. Biological understanding of the fermentation processes occurring during winemaking took a leap forward with the remarkable work of Pasteur in the middle of the 19th century (Pasteur, 1866), when the scientist became the first to consider the importance of oxygen for wine production and ageing. Since the 1960s, researchers have collaborated with winemakers to systematically identify wine compounds, especially phenolic compounds, to better understand mechanisms of oxidation occurring in wine. These include processes from harvest through wine ageing in bottles, and are often associated with wine coloration. In subsequent literature on this subject, beginning with Ribereau-Gayon's hypothesis

on oxidation (Ribereau-Gayon, 1963; Ribereau-Gayon et al., 2004), the work of Singleton and collaborators in this field is of particular importance (Rossi et al., 1966; Singleton et al., 1976; Singleton, 1987; Tulyathan et al., 1989; Cilliers et al., 1990). However, while detrimental effects of excessive exposure are well established, little is known about the exact impact on wine quality of low levels of oxygen exposure. The first sporadic reports of white wine oxidation as a major organoleptic fault appear in the 1990s, when the problem drew attention due to increasing economic impact. The random nature of the problem makes it difficult to analyze. Research on wine oxidation has been approached on many scales; from a macroscopic point of view, modifications of sensory perceptions are considered, while work on the microscopic scale attempts to delineate the step-by-step mechanisms involved in oxidation. These more advanced explorations of oxidation phenomena in wine have been largely undertaken since the beginning of the 1990s (Cheynier et al., 1990; Atanasova et al., 2002). Experimentally, two schemes can be considered, one working on the real product and its global evolution, and the second on simplified systems in order to model what can occur in the much more complicated product. Sensory experiments in this field are most useful for assessing possible correlations with physico-chemical parameters, as, in the guise of the wine product, the

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consumer is actually buying a sensory experience (Escudero et al., 2002). While a basic understanding of key factors influencing the sensory perception of wines has been achieved, other important aspects are still not yet well understood, including the particular role of oxygen. In a more fundamental way, the molecular approach aids in clarifying the underlying mechanisms of oxidation in wine, and allows the inference of the overall impact on wine quality (Es-Safi et al., 2000; Waterhouse et al., 2006). Even as elucidation of basic wine oxidation mechanisms begins, the extreme complexity of this medium and the range of variables affecting its makeup suggest that much more work will be done before all aspects are fully understood.

The present review aims to show the state of the art of oxidation mechanisms occurring especially in white wines by taking into account knowledge from different fields in relation to the subject. It is therefore divided into three main parts. First, the mechanisms of oxidation relevant to white wine are discussed in the light of recent scientific literature. Next, the phenomenon of oxygen solubility in wine during the winemaking process, and in particular during bottling is stated theoretically as well as practically. Finally, the aspect of wine conservation after bottling is examined with respect to mass transfers which may occur through the closure, with a special emphasis on cork. Currently, specific physico-chemical properties still make cork closures the most important closure type used for the wine market, and especially for high quality wines. This final section will also include a review of studies performed on this subject, which have been analyzed in detail from a theoretical mass transfer point of view, in order to assess the extent to which the proposed scientific tools and the observed tendencies are relevant to progress in the understanding of the impact of this parameter on the behavior of a wine.

MECHANISMS OF OXIDATION IN WINE

Macroscopic Modifications and Sensorial Alteration

If wine is considered from a macroscopic point of view, the first two important sensory impressions are the color and the aroma. Browning, caused mainly by oxidation, can be perceived either as a positive aspect, in the case of sherries or sweet fortified wines such as white Ports or Rivesaltes, or as a negative aspect for dry white wines. Browning, as the name suggests, is characterized by a brown-yellow color that progressively replaces the initial (generally pale-yellow) color through the influence of oxygen, and which can be globally characterized by the absorbance at 420 nm (Singleton, 1987). On one hand, oxygen seems to have a positive effect during alcoholic fermentation or micro-oxygenation of wines. On the other hand, oxygen appears to play a negative role when sensory drifts are observed in a tank or bottle, with a loss of freshness and fruitiness, and the development of an unpleasant oxidized character. Indeed, before an easily observable chromatic change, such an oxidative aging first gives rise to typical flavors, which are generally described as “rancio” in sweet fortified wines (Cutzach et al., 1998) and as non-desirable flavors of “honey-like,” “boiled-potato,” “cooked vegetable,” “farm-feed,” “hay,” and “woody-like” in dry white wines (Escudero et al., 2002; Silva Ferreira et al., 2002, 2003). Few studies investigate the chemical modifications related to the development of such off-flavors. Table 1 reports some of the typical volatile compounds found to be responsible for this oxidized character of white wines. They include various chemical classes of compounds, including Strecker aldehydes (benzaldehyde, phenylacetaldehyde, methional), linear aldehydes ((E)-non-2-enal), hydrocarbons (1,2-dihydro-1,1,6-trimethylnaphthalene or TDN), lactones (sotolon), cyclic acetals (2,4,5-trimethyl-1,

Table 1 Typical volatile compounds, and associated perceived odor, found to be responsible of the oxidized aromatic character of white wines

Aroma compound	Odor	Type of wine	Reference
3-hydroxy-4,5-dimethylfuran-2(5H)-one (sotolon)	“Rancio”	Sweet fortified wines	(Cutzach et al., 1998)
2,4,5-trimethyl-1,3-dioxolane	—	Macabeo + Chardonnay (Spain)	(Escudero et al., 2000)
3-(methylthio)-propanal (methional)			
3-hydroxy-4,5-dimethylfuran-2(5H)-one (sotolon)			
4-allyl-2-methoxyphenol (eugenol)			
Methyl vanillate			
Benzeneacetaldehyde (phenylacetaldehyde)	“Honey-like”	Dry white wine (Alentejo, Portugal)	(Silva Ferreira et al., 2002)
3-(methylthio)-propanal (methional)	“Boiled-potato”		
1,2-dihydro-1,1,6-trimethylnaphthalene (TDN)	“Farm-feed”		
(E)-non-2-enal	“Cooked vegetable”	Macabeo (Spain)	(Escudero et al., 2002)
4-allyl-2-methoxyphenol (eugenol)			
Benzaldehyde furan-3-carbaldehyde (furfural)			
3-(methylthio)-propanal (methional)	“Honey-like”	Dry white wine (Encruzado and Assario, Portugal)	(Silva Ferreira et al., 2003)
Benzeneacetaldehyde (phenylacetaldehyde)	“Farm-feed”		
1,2-dihydro-1,1,6-trimethylnaphthalene (TDN)	“Hay”		
3-hydroxy-4,5-dimethylfuran-2(5H)-one (sotolon)	“Woody-like”		

3-dioxolane), phenols (eugenol), esters (methyl vanillate), and heterocyclic compounds (furfural). Some of them have already been identified in bottle aged white wine, such as furfural and TDN (Simpson, 1978b). Among these volatile compounds, the development of a “rancio” flavor is associated with the formation of sotolon in case of sweet fortified wines (Cutzach et al., 1998). Other off-flavors such as “honey-like,” “boiled-potato,” and “farm-feed” are reported to be linked with the presence of phenylacetaldehyde, methional, and TDN, the formation of which seems to be mainly related to two important parameters, oxygen content and temperature (Silva Ferreira et al., 2002). However, it remains difficult to associate a perceived aroma with a single compound. Escudero et al. (2002) reported a good correlation between the “cooked vegetable” odor and the quantitatively important molecules (E)-non-2-enal, eugenol, benzaldehyde, and furfural. Other important sensory descriptors such as “honey-like,” “farm-feed,” “hay,” “woody-like” have also been found to be related to the presence of methional, phenylacetaldehyde, 1,2-dihydro-1,1,6-trimethylnaphthalene and sotolon (Silva Ferreira et al., 2003). Of these molecules identified as responsible for the oxidized character of white wines, it should be noted that eugenol, which gives a woody nuance, could also be contributed by wood extraction, during barrel use. Oxidative spoilage of white wines with a modification of the organoleptic profile is thought to be the result of the degradation of precursor molecules by oxygen derivatives, in particular sensitive flavors such as enolic lactones and monoterpene alcohols, with a concurrent increase in the volatile aldehydes and ketones (Simpson, 1978a; Escudero et al., 1999). Therefore, the degree of exposure of white wine to oxygen is believed to be an important factor contributing to the formation of unwanted off-flavors (Silva Ferreira et al., 2002), with minor exposure resulting in a loss of fruity aroma, and greater exposure leading to the development of anything from the aforementioned odors up to a maderisation-like process associated with a chromatic change.

MOLECULAR OXYGEN AND CHEMICAL OXIDATION

Molecular Oxygen and the Formation of Reactive Oxygen Species

Under standard temperature and pressure, oxygen exists as a gaseous element representing 20.9% of the earth atmosphere. This diatomic molecule with the formula O_2 is commonly called oxygen, though its proper designation should be dioxygen, and it may also be called unbound oxygen or molecular oxygen. The most stable form of oxygen is known as triplet oxygen, where the two unpaired electrons in different molecular orbitals of the diradical molecule are characterized by parallel spins. This ground state of the oxygen molecule can be symbolized by the abbreviation 3O_2 . Unless it is a diradical, the triplet state is relatively unreactive and stable, in comparison to most radicals

(Hoffmann, 2004). It should be noted that the classic, simplified Lewis structure as a double bond $O=O$ does not symbolize the diradical nature of oxygen, and the two unpaired electrons are more accurately represented as follows: $\cdot O-O\cdot$. In this electron configuration, oxygen cannot directly react with most organic molecules, and cannot form bonds by accepting electron pairs. It is, however, not an inert molecule, and can enter some organic and inorganic reactions, such as reactions with other radicals to form a new radical. The conversion of oxygen to its excited singlet state forms, either chemically, thermally or by light, both weakens the $O-O$ bond and removes the spin restriction (Green et al., 1984). In fact, the absorption of a sufficient amount of energy enables it to form the singlet state, abbreviated 1O_2 , which has a pair of electrons with antiparallel spins. Though not a free radical, this molecular oxygen specie is highly reactive and electrophilic and will easily establish chemical bindings with other molecules through oxidation reactions. The reaction rate of singlet oxygen with foods is many times greater towards common organic molecules than that of triplet oxygen, due to its low activation energy (Min et al., 2002). The more reactive a molecule is, the shorter its half-life in a given medium, as for 1O_2 whose half-life is about a microsecond in water (Singleton, 1987). In an aqueous environment, the monovalent reduction of triplet oxygen by the acceptance of a single electron (which can be produced by oxidation of a catalyst, presumably a metal ion such as Fe^{2+}/Fe^{3+}) can also induce the transformation into a superoxide anion, abbreviated $O_2\cdot^-$, or represented as $\cdot O-O\cdot$. Under wine conditions, such activation is very unlikely in the absence of light, but is generally thought to be the consequence of iron catalysis (du Toit et al., 2006; Waterhouse et al., 2006). The newly-formed radical can then act either as an oxidizer or as a reducer, and exists as the protonated form of hydroperoxide radical ($HOO\cdot$) at wine pH. Not so reactive by itself, it is instead a precursor to other highly reactive oxygen species (Fig. 1), such as hydroxyl radical ($HO\cdot$). If this first step of oxygen reduction is endothermic and thus rate-limiting, the consecutive steps are exothermic and spontaneous. In the presence of metal ions, such as Fe^{2+}/Fe^{3+} or Cu^+/Cu^{2+} , the superoxide anion can then be reduced by Fe^{2+} to produce peroxide, the peroxide anion (O_2^{2-}), and readily protonated to a nonradical oxygen species, the hydrogen peroxide (H_2O_2), at wine pH (Danilewicz, 2003; Lee et al., 2004). Also, in the presence of metal ions, the Fenton reaction or the Haber-Weiss reaction can generate a hydroxyl radical ($HO\cdot$) and a hydroxide ion (HO^-) from H_2O_2 , producing a highly reactive oxygen species from a weakly reactive precursor (Khan et al., 1994; Danilewicz, 2003; Edreva, 2005; Waterhouse et al., 2006). These radical oxygen molecular species all become more reactive as their reduction level increases: *triplet oxygen* < *superoxide anion* < *hydroperoxide radical* < *peroxide anion* < *hydroxyl radical*. This last, highly reactive hydroxyl radical can be engaged in multiple pathways of radical oxidation processes through chain reactions with different organic substrates, such as between lipid radicals and oxygen, which leads to oxidative damage (Lee et al., 2004; Vanderhaegen et al., 2006).

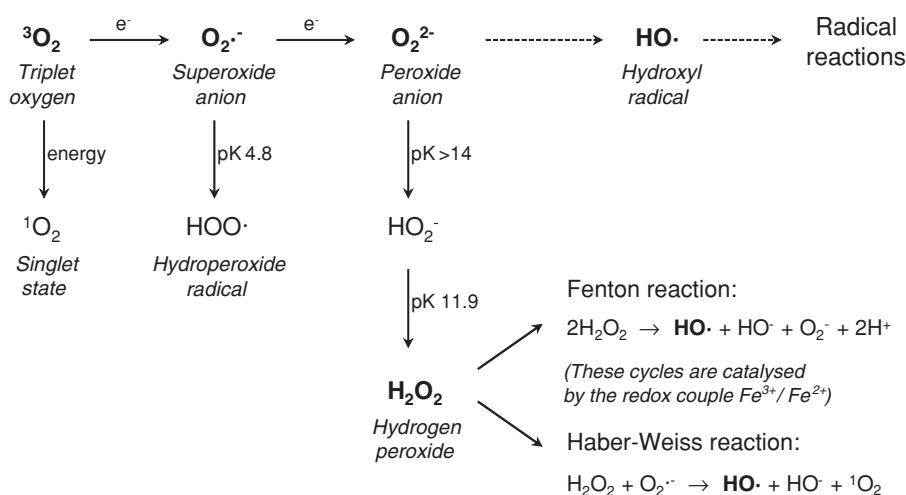


Figure 1 Successive monovalent reductions from triplet oxygen to the formation of various reactive species.

The term autoxidation generally refers to the autocatalytic chemical reaction between atmospheric oxygen and organic compounds. The reaction scheme involving free radicals is traditionally described as a three-step process including initiation, propagation, and termination. Initiation is characterized by the slow formation of new free radicals from stable species. Next, free radicals can propagate indefinitely, giving various oxidation products. Finally, termination occurs only when free radicals react with other free radicals or antioxidant molecules.

This universal scheme for the generation of reactive oxygen species is necessary to understanding the extent to which molecular oxygen could be responsible for oxidation initiation in wine. Introduction of molecular oxygen must therefore be carefully avoided in musts and wines in order to achieve maximum protection against oxidation phenomena. Under typical wine conditions, and despite its poor reactivity with organic molecules, molecular oxygen constitutes the starting point of a dramatic reductive ladder leading to highly reactive oxygen species which bear a strong oxidizing potential.

Wine Phenolic Compounds as Oxidation Substrates

Beyond the pleasure drink offered to the consumer, wine is, from a chemical point of view, a very complex fluid composed of a mixture of water, alcohols (ethyl alcohol being the major solvent of many wine compounds), organic acids (tartaric acid being an important element of wine compounds solution), phenolic compounds, sugars, amino acids, and various minerals (Waterhouse, 2002). Of these components, phenolic compounds have to be considered with special interest with respect to the oxidation process occurring during winemaking and ageing. With a typical total concentration being of about 0.01% (total weight) for white wine and 0.2% for red wine, phenols play a key role in the overall antioxidant capability of wine. Several phenolic compounds present in wine, especially red wine, have garnered scientific interest in medical applications. Procyanidins, for

example, have been identified as the main vasoactive polyphenols in red wine, and are associated with a reduction in mortality from cardiovascular diseases (Corder et al., 2006). This medicinal effect of red wine consumption is also commonly known as the “French Paradox” (Renaud et al., 1992). Some other wine polyphenols also display desirable biological properties, including nonflavonoid phenolic acids (coumaric, cinnamic, caffeic, gentisic, ferulic, and vanillic acids), trihydroxy stilbenes (resveratrol and polydatin), and flavonoids (catechin, epicatechin, and quercetin) (Soleas et al., 1997).

The task of understanding phenolic compounds appears rather complex when one considers their range and diversity; more than 8000 structures have been reported in plants (Bravo, 1998). The main classes of phenolic compounds traditionally found in grape and wine are shown in Table 2. For a more specific review on the chemistry of phenolic compounds, Monagas et al. (2005) reported a detailed inventory of the main types found in wine, including a well-documented collection of mass spectra data. Wine phenolic compounds can essentially be grouped into nonflavonoids and flavonoids on the basis of their carbon skeleton. Among nonflavonoids, the term “acid phenols” generally includes cinnamic acids and benzoic acids. Cinnamic acids (C6-C3) can be found either free, or more commonly, esterified to tartaric acid, or other hydroxyl-organic acids, sugars, or alcohols. Within this class, coumarins (also C6-C3 structure) are derived from cinnamic acids through intramolecular esterification of a phenolic –OH group. Volatile phenols include aroma compounds, such as vinyl-phenol and vinyl-guaiacol, typically found in white wine. Wood volatile phenols, for example guaiacol, methyl-guaiacol or syringol, are also part of this class. Another nonflavonoid molecule, tyrosol is formed during alcoholic fermentation from tyrosine amino acid synthesized by yeasts. Hydrolysable tannins such as gallic acid or ellagic acid, and stilbenes, highly antioxidant molecules, the best known of which is trans-resveratrol, also belonging to the nonflavonoids phenol class. The flavonoids, which include flavan-3-ols, flavonols, and anthocyanins, are based on a common structure, more

Table 2 Major classes of phenolic compounds in wine

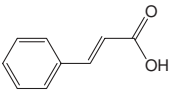
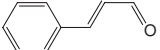
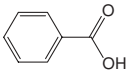
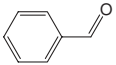
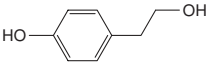

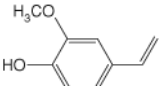
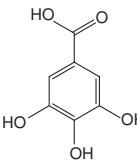
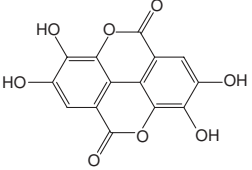
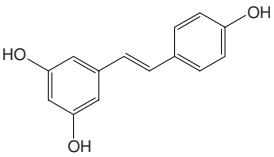
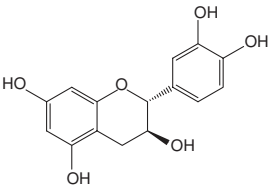
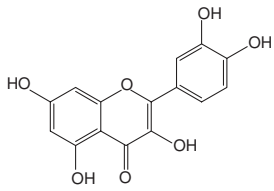
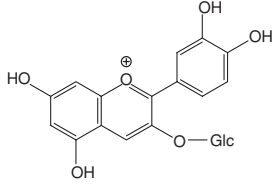
Phenol class	Typical structure	Other examples	Origin
Nonflavonoids			
<i>Cinnamates derivatives</i>	 <p>Cinnamic acid</p>  <p>Cinnamaldehyde</p>	Coumaric acid Caffeic acid Ferulic acid	G,D
<i>Low volatility benzene derivatives</i>	 <p>Benzoic acid</p>  <p>Benzaldehyde</p>	Protocatechuic acid Vanillic acid Syringic acid	D,M,G,E
<i>Tyrosol</i>			M (yeast)
<i>Volatile phenols</i>	 <p>4-Vinyl-phenol</p>  <p>4-Vinyl-guaiacol</p>	Guaiacol Methyl-guaiacol Syringol	M,D,E
<i>Hydrolyzable tannins</i>	 <p>Gallic acid</p>  <p>Ellagic acid</p>		E
<i>Stilbenes</i>	 <p>(E)-resveratrol</p>		G
Flavonoids			
<i>Flavan-3-ols (Catechins)</i>	 <p>Catechin</p>	Gallocatechin Epicatechin Epigallocatechin Procyanidins	G

Table 2 Major classes of phenolic compounds in wine (*Continued*)

Phenol class	Typical structure	Other examples	Origin*
Flavonols	 <p>Quercetin</p>	Kaempferol Myricetin	G,D
Anthocyanins	 <p>Cyanidin 3-glucoside</p>	Peonidin 3-Glc Delphinidin 3-Glc Petunidin 3-Glc Malvidin 3-Glc	G

*G = grapes; D = degradation product; M = microorganisms, yeast; E = environment; Glc = glucose.

complex than that of nonflavonoids. This group is characterized by a carbon skeleton composed of two phenol rings joined by an oxygen-containing pyran ring. Flavonoids can exist either free or polymerized with various other compounds, such as other flavonoids (forming, in the case of catechin or epicatechin, oligomers, or polymers known as proanthocyanidins or procyanidins), sugars (glycosides), nonflavonoids (acyl derivatives), proteins (macromolecular complexes), or a combination of these compounds. Flavonoid groups can be differentiated by the number of hydroxyl and/or other substituents on the benzene rings. Flavan-3-ols, also commonly known as catechins, can either exist as monomeric units, or become more or less polymerized as proanthocyanidins, also termed condensed tannins. These compounds play a fundamental role during wine maturation, when they produce a range of oligomers and polymers, from dimers to the more common four- to eight-monomer units. Among flavonoid phenolic compounds in wine, flavonols can also be distinguished by the presence of a double carbon bond and/or an additional hydroxyl group. Finally, anthocyanins are among them found in wine in the glycoside form: cyanidin, peonidin, delphinidin, petunidin, and malvidin. These exist either as aglycone moieties or as glycosides in wine, the latter being more stable.

Phenolic molecules found in wine originate mainly from the grape, where they are unequally distributed within the fruit (Macheix et al., 1991). There are important variations between white and red wines (Table 2), with the latter representing a larger source of flavonoids, about 85% of the total phenolic content, compared to white wines (about 20% of the total phenolic content). All phenolic classes occur in larger concentrations in red wines. The main nonflavonoids intrinsic to wines, stilbenes, and derivatives of hydroxycinnamic and hydroxybenzoic acids, originate primarily from grape cells and are easily extracted on crushing. In white wines, they are typically found at concen-

trations from 50 to 250 mg·L⁻¹, and normally constitute the principal phenolic molecules (Monagas et al., 2005). Mean levels of total hydroxycinnamates in finished wine are typically 130 mg·L⁻¹ in whites and 60 mg·L⁻¹ in reds (Waterhouse, 2002). In contrast, flavonols and anthocyanins are mainly found in the skins, while the main sources of flavan-3-ols (catechins) are the seeds and stems. The most important flavonoid fraction in wine is the flavan-3-ol group. In red wine, anthocyanins also represent a major compound, giving wine its color. Although flavonols are pigments located in grape skin and characterized by a yellow color, they do not participate to the color of white wines, where they are only found in trace amounts (Table 3). Collectively, the three flavonols kaempferol, myricetin, and the near-ubiquitous quercetin are reported to occur in white wine at concentrations of 1–3 mg·L⁻¹ (du Toit et al., 2006). Flavan-3-ols and anthocyanins exist in a more unpolymerized state in young wines, and they undergo different polymerization reactions during wine ageing in which oxygen plays a fundamental role (Lee et al., 2004). In red wines, for example, these reactions are typically characterized by the progressive partial disappearance of monomeric anthocyanins and the appearance of complexes of tannins and other molecules (Fulcrand et al., 2005; Monagas et al., 2005). Extrinsic sources of phenolic compounds found in wine include the barrels used in oak ageing, where small molecules are susceptible to migration from oak wood into the wine. These molecules include hydroxybenzoic acid derivatives, mostly represented by ellagic acid or gallic acid, coming from the breakdown of hydrolyzable tannins under acidic conditions of wine, or simple phenols such as cinnamaldehyde and benzaldehyde derivatives from lignin degradation (Macheix et al., 1991). It can be noted that hydrolysable tannins, also called ellagitannins, are not naturally present in grape, and their presence in wine stems from enological practices such as oak ageing and natural wood extraction, or the addition of extrinsic tannins in commercial products

Table 3 Global phenol composition estimated in Gallic Acid Equivalent ($\text{mg}\cdot\text{L}^{-1}$) for typical table wines from *Vitis vinifera* grapes (Singleton, 1982; Waterhouse, 2002)

Phenol class	White wine		Red wine	
	Young	Aged	Young	Aged
Nonflavonoids, total	175	160–260	235	240–500
<i>Cinnamates, derivative</i>	154	30	165	150
<i>Low volatility benzene, derivative</i>	10	15	50	60
<i>Tyrosol</i>	19	10	15	15
<i>Volatile phenols</i>	1	5	5	15
<i>Hydrolyzable tannins (from oak)</i>	0	0–100	0	0–260
<i>Stilbenes (Resveratrol)</i>	0.5	0.5	7	7
Macromolecular complexes				
Protein-tannin	10	5	5	10
Flavonoids, total	30	25	1060	705
<i>Catechins</i>	25	15	200	150
<i>Flavonols</i>	<i>tr</i>	<i>tr</i>	50	10
<i>Anthocyanins</i>	0	0	200	20
<i>Soluble tannins, derivative</i>	5	10	550	450
Total phenols	215	190–290	1300	955–1215

The term young refers to new wine less than six months aged not having been in contact with oak barrels, whereas aged means one year for white and two years for red, including or not oak contact.

(Moutounet et al., 2004). In addition, some wine molecules, especially volatile aroma compounds, can also be sorbed by the wood and consequently display a decreasing concentration in wine during contact with wood (Ramirez Ramirez et al., 2001; Barrera-Garcia et al., 2006). These mass transfers lead to a new equilibrium condition for the phenolic compounds of the wine, which are extremely dependant on the environmental conditions during ageing such as oxygen concentration and transfer, pH, initial phenols concentrations, temperature, ethanol concentration, SO_2 concentration, and yeast concentration.

Table 3 summarizes the most important phenolic compounds and their generalized concentrations encountered in table wines, with their evolution during ageing, as reported by Singleton (Singleton, 1982). These concentrations are presented in mg of Gallic Acid Equivalent as dictated by the Folin-Ciocalteu micro method for the determination of total phenolics in wine (Slinkard et al., 1977). Apart from the differences observed between red and white wines, the phenolic composition depends principally on three sets of parameters (Macheix et al., 1991). First, cultivar dictates considerable variations in the type and the concentration of phenolic content. While cultivar differences are magnified by the additional effects of soil and climatic conditions, viticultural practices, the state of maturity, and the quality of the grapes at harvest, it is still considered to be the determining factor for phenolic extraction. Second, winemaking techniques, and especially the transformation during the winemaking process, represent a crucial step for phenolic extraction (Budic-Leto et al., 2005; Lorenzo et al., 2005; Corder et al., 2006). For example, the influence of traditional fermentation with skin contact tends to favor the extraction of phenolic compounds, when compared to carbonic maceration or thermovinification. In addition, elements such as fruit quality (which impacts fermentation mainly through the optimization of yeast activity and concentration),

temperature, maceration duration, mixing, addition of pectolytic enzymes, and other factors determine the relative concentration of phenolic compounds in the finished wine, (Monagas et al., 2005; Sacchi et al., 2005). During the first stages of fermentation, the concentration of phenolic compounds in wine increases, favored by skin fermentation. Later, macromolecular complexes can occur between phenols and proteins or remnant from yeast walls, producing a precipitate and thus decreasing their concentration. In addition, the numerous chemical reactions that occur during ageing also contribute to different pathways of evolution for the phenolic composition of a given wine, as a function of specific intrinsic or environmental physicochemical parameters.

Enzymatic Oxidation

As in most fruit and vegetables browning (Macheix et al., 1991), enzymatic oxidation of phenolic compounds can take place very rapidly in musts, and affects color and taste equally (White et al., 1973; Moutounet et al., 1990). These first oxidation reactions can either result from polyphenoloxidase activity in healthy grapes (also known as catechol oxidase, catecholase, diphenol oxidase, o-diphenolase, phenolase or tyrosinase), or from laccase occurring in *Botrytis cinerea* infected grapes. The polyphenoloxidase enzyme first catalyzes the reactions leading to quinones from phenols in the presence of oxygen, and the quinones then undergo condensation to produce relatively insoluble brown melanin pigments, or participate in polymerization reactions with protein (Martinez et al., 1995; Friedman, 1996). Grape juice will thus brown on contact with air, and especially molecular oxygen. The most important factors that determine the rate of enzymatic browning of fruit and vegetables

are the concentrations of both active polyphenoloxidase and phenolic compounds, the pH, the temperature, and the oxygen availability (Martinez et al., 1995). For grape musts, browning is related to polyphenoloxidase enzyme concentration and the sanitary state of grapes, addition of sulfur dioxide, but also the technical route chosen, especially the choice of maceration and pressing (Moutounet et al., 1990). Assuming all extrinsic conditions are favorable in must, the susceptibility of browning is essentially related to their hydroxycinnamic acid initial concentration (Cheynier et al., 1990). These acids are mostly esterified to tartaric acid, to give caftaric acid, which is highly reactive toward white must oxidation (Cheynier et al., 1989). In an aqueous or hydroalcoholic environment, caftaric acids are colorless, but once oxidized they tend to produce a yellow color (Ribéreau-Gayon et al., 2004). Since concentrations vary as a function of grape cultivar, the rate of relative oxygen utilization also varies (White et al., 1973). The activity of polyphenoloxidase is inhibited by sulfur dioxide, requiring for most must varieties about 25 to 50 mg·L⁻¹ for complete deactivation. On the other hand, in the case of infected grapes, the laccase activity is more difficult to inhibit because of its better resistance to SO₂ and its wider spectrum of oxidation substrates. Other treatments, such as cooling white musts (down to 0°C), or enzyme removal by bentonite fining, also act to partly inhibit enzymatic activity, but to a lesser extent than with SO₂ addition to grape juice just after pressing (White et al., 1973). Heating must to 45 and 65°C has even been proposed to destroy tyrosinase and laccase respectively (Schneider, 1998). Inactivation of polyphenoloxidase in musts using moderate thermal treatments can be combined with high-pressure treatments, which act synergistically on a wide range of pressures and temperatures conditions (Rapeanu et al., 2005). Though must browning has been widely studied and largely delineated, some theories are still debated, in particular the oft-recommended idea of extensive must protection against oxygen during prefermenting stages (Cheynier et al., 1993; Moio et al., 2004; du Toit et al., 2006), versus must hyperoxidation (Vaimakis et al., 1996; Schneider, 1998). In the case of must protection, SO₂ treatment can be coupled with the use of inert gases such as N₂ or CO₂ in presses, pipes and tanks to exclude oxygen; this practice is common for fruit juice production (Martinez et al., 1995). In contrast, must hyperoxidation lowers the phenolic content of wines and thus their browning capacity, leading to a paler color. However, this process can also decrease the aroma intensity, which may be partly ameliorated by glutathione addition (Vaimakis et al., 1996). In any case, while enzymatic oxidation can induce browning in musts, the reaction is inhibited by alcohol produced during fermentation. Thus the chemical oxidation mechanism that occurs in wine is ultimately of greater importance to this discussion.

Mechanisms of Chemical Oxidation in Wine

The primary substrates for oxidation in wines are the phenolic constituents of the wine itself, which act as antioxidants

(Rossi et al., 1966; Singleton, 1987). The first aspect which must be considered regarding the oxidation of phenolic compounds in wine is the equilibrium which exists between the phenol and the phenolate anion form (loss of a proton) as a function of pH. Due to high pK_a values (9 to 10), the protonated form is favored under wine acidic conditions. Above this pH, the phenolate ion form is favored, and oxidation is much easier than with the protonated form. It is also very rapid, taking only 30 minutes to reach completion in model wine pH 11 at room temperature (23.5°C) under pure oxygen gas phase (Singleton, 1987). However, direct oxidation of phenolate ions with oxygen cannot be responsible for white wine browning, even if a small fraction of phenols remains deprotonated and thus susceptible to react (Danilewicz, 2003; Waterhouse et al., 2006). The major hydrogen-donating antioxidants are monohydroxy or polyhydroxy phenolic compounds with various ring substitutions, phenolic acids having, in general, lower antioxidant activities (Min et al., 2002). Oxidation of these phenols leads to the formation of semiquinone free radicals and quinones. The oxidation of phenolic compounds is either assumed to be catalyzed by transition metal ions (Danilewicz, 2003), or to be autocatalytic (Singleton, 1987; Waterhouse et al., 2006). The corresponding reaction schemes related to these two hypotheses are shown in Fig. 2.

In the first hypothesis, the oxidation of phenols is directly mediated by a transition metal such as ferric ions, yielding the formation of a semi-quinone radical, which is further oxidized to the corresponding quinone (Fig. 2). In a cyclic chain of radical reactions, the parallel, successive monovalent reductions involve ferrous ions oxidation to form three reactive species from the triplet oxygen: hydroperoxide radical, hydrogen peroxide, and hydroxyl radical. This last oxygen specie is very unstable and reacts very quickly. It is thus considered as a non-selective oxidation reaction, not only with phenolic compounds but also with all oxidizable wine substances, the more concentrated substances being then the more probable substrates to be oxidized. Numerous products can be formed through this oxidation mechanism (such as quinone from phenol, or dehydroascorbic from ascorbic acid). Because of its high concentration in wine, ethanol can then be oxidized by hydroxyl radicals which are then reduced to water. In a second step, the carbon radical formed from ethanol can react with an oxygen molecule to form acetaldehyde and a new hydroperoxide radical. The regeneration of such a radical perpetuates the oxidation of phenolic compounds into their respective quinone forms. A more detailed review of oxidation mechanism in wine, with special emphasis on the reduction potentials of redox couples derived from wine polyphenols and oxygen for wine conditions has been performed by Danilewicz (2003).

Phenolic oxidation can also result from the reduction of oxygen to the hydroperoxide radical (involving Fe²⁺ oxidation to Fe³⁺) which can then oxidize a phenol into a semiquinone radical (Fig. 2). Phenolics are good hydrogen donors, and consequently enable hydroperoxide radicals to abstract protons from hydroxyl groups. The hydroperoxide radical thus becomes

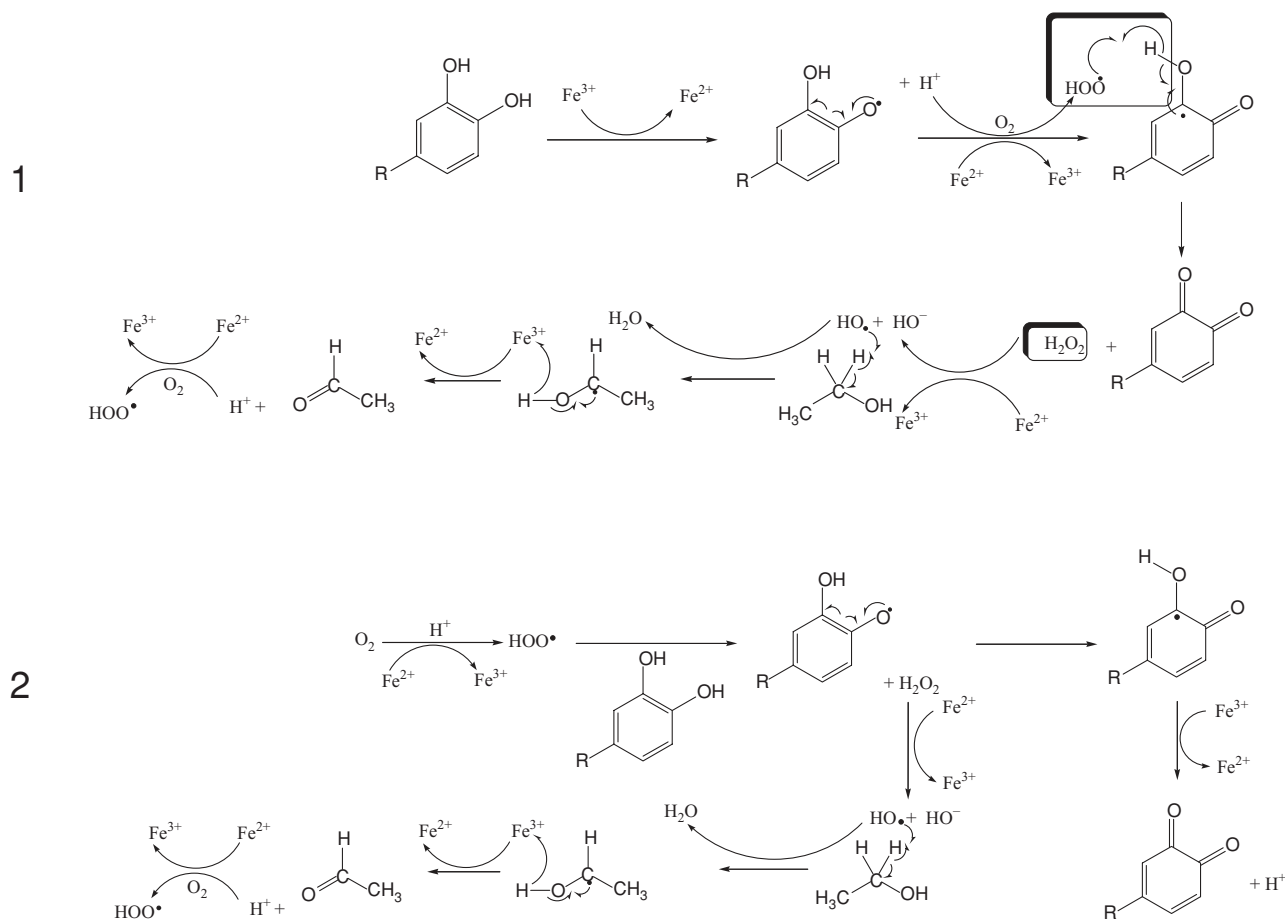


Figure 2 General scheme for oxidation of phenolic compounds involving reduction of oxygen and oxidation of ethanol. The first reaction process is based on the hypothesis of a direct role of the iron redox couple, whereas the second one assumed a two-step phenomenon with firstly the formation of an oxygen reactive specie, iron mediated, and secondly the oxidation of phenols.

reduced into hydrogen peroxide through acceptance of the hydrogen radical. It can then be reduced to the highly reactive specie of hydroxyl radical through the participation of a transition metal ion, in the same manner, for example, as previously described in ethanol oxidation. The hydrogen peroxide effect is suspected to be the coupled product of phenolic compound oxidation, leading to further oxidation reactions (Wildenrad et al., 1974). With about 2 moles of hydrogen peroxide reacting with each mole of gallic acid, the oxidation in highly alkaline solution leads to the consumption of 4.9 atoms of oxygen per molecule of gallic acid oxidized (Tulyathan et al., 1989). The hydroxyl radical appears to be of great importance in wine oxidation, as suggested by the two hypotheses supporting the reaction mechanisms detailed in Fig. 2 (Danilewicz, 2003; Waterhouse et al., 2006). It can, in particular, lead to the formation of various aldehydes and ketones via this oxidative pathway from alcohols or organic acids.

As shown by these mechanisms of oxidation, the antioxidant properties of wine are clearly dependant on the phenolic content (Manzocco et al., 1999). The products of the reaction, semiquinones, display resonance stabilization of the delocalized electrons in the ortho- and para-positions of the aromatic ring,

which make them susceptible to participation in other radical reactions (Singleton, 1987). In this way, two semiquinone free radicals can form a covalent bond by sharing the two unpaired electrons, giving rise to a new, oxidizable dimer which can further react with oxygen. Trimer, tetramer, or even larger molecules can also be generated by such an association between two semiquinones, or by reaction between a quinone and a phenol. This process is the so-called regenerative polymerization (Singleton, 1987). In addition, the brown color given by quinone molecules increases as long as polymerization occurs.

Acetaldehyde, produced by ethanol oxidation (Fig. 2), also plays an important role in the structural modification involving wine phenolics and oxygen during the ageing (Dallas et al., 1996; Atanasova et al., 2002; Jones et al., 2004). In particular, it can favor the reactions between anthocyanins and flavanols which form new polymeric phenols (Fulcrand et al., 1996; Saucier et al., 1997). Glyoxylic acid, produced from the oxidation of tartaric acid, can also participate into these polymerization reactions as a bridging molecule between phenolic compounds (Drinkine et al., 2005). Such condensation reactions, with anthocyanins and tannins in particular, contribute to the formation of stable polymeric pigments in solution, which,

in turn, tend to stabilize color in red wines (Singleton et al., 1992; Es-Safi et al., 1999; Monagas et al., 2005). The lack of polymeric phenols in white wines made by the red vinification method, in which prolonged skin contact during fermentation occurs, has been explained by the lack of anthocyanins to complex with the tannins (Singleton et al., 1992). The subsequently lower amount of such complexes of increased solubility leads to a deficiency in tannins and astringency. The higher concentration of proteins in white wines could also play a role in polymer adsorption and precipitation. In white wines (Chardonnay, Sauvignon blanc, and Sherry) exposed to increased amounts of oxygen, a significant decrease in total phenols occurs, in which the flavonoid fraction remains stable and only the non-flavonoid fraction decreases (Singleton et al., 1979). In this case the oxygen consumption is evaluated at 4 mL of oxygen per 10 mg of Gallic Acid Equivalent under standard temperature and pressure. The chemical structures of wine phenolics, such as flavonoids, confer varying antioxidant activities as peroxyl radical scavengers. Oxidative browning in wine displays a particularly good correlation with some flavanols, mainly catechin and epicatechin (Fernandez-Zurbano et al., 1995; Sioumis et al., 2006), with cinnamate derivatives also playing a minor role (Cilliers et al., 1990; Fernandez-Zurbano et al., 1998). Oxidation reactions involving mainly catechin, one of the most common grape flavanols, and a procyanidins constituent, lead to colorless and yellow pigments (Simpson, 1982). Indeed, from studies on wine model solutions, Es-Safi et al. (2000) identified the formation of two types of yellow pigments showing visible absorption maxima at 440 and 460 nm, respectively xanthylum salt pigments and ethylester of xanthylum salts, both derived from flavanol oxidation and polymerization. With an absorption maximum in the region of 400–500 nm, these pigments directly contribute to white wine browning during ageing. This reaction, and thus the extent of browning, is accelerated in model wine solution with the addition of iron and copper, which probably act as catalysts to form intermediate oxidation products. For example, the oxidation of tartaric acid to produce glyoxylic acid can further link two catechin units and lead to the formation of xanthylum cations (Oszmianski et al., 1996; Vivas et al., 1998; Clark et al., 2003; Es-Safi et al., 2003). Manganese is also found to catalyze these reactions, and has been found to act in synergy with iron to change susceptibility of sherry wines to browning (Benitez et al., 2002a). The presence of copper may result from the use of vineyard treatments and from the use of copper sulphate in wine to remove hydrogen sulphide and other sulphide compounds. It is difficult not only to clearly identify intermediate reaction products, but also to determine the sensory modification related to the formation of new, pigmented oligomers or larger polymers during wine ageing. Further characterization of these compounds should be pursued.

Other factors, both intrinsic and environmental are key in determining the extent of browning oxidation in white wine. In addition to the effect of grape variety (Caputi et al., 1965; Peterson et al., 1967), the region of origin and degree of maturity at time of harvest, Berg et al. (1956) showed that increasing

temperature, oxygen content or pH (between 3 and 4) increase the browning rate (as measured by the change in optical density at a wavelength of 425 nm). An excess of ultraviolet and visible radiation also produces significant oxidative changes in the volatile and polyphenolic content during storage, with a higher visual browning (as measured by absorbance at 420 nm), as it has been observed in “Fino” sherry wine (Benitez et al., 2003). For white wines, Cartagena et al. (1994) found the color stability is more dependent upon light exposure than upon oxygen concentration at 20°C, whereas at 45°C their respective effects become equal. High pH and high temperature are also found to affect a pronounced increase in browning. The increase in pH makes the concentration of the phenolate ions increase relative to the phenol form, thus increasing oxidation rates by about nine times between pH 3 and 4 (Singleton, 1987). However, it should be noted that the different factors implied in oxidation of white wines during storage (temperature, oxygen, pH, light) act as a whole on wine oxidation rate, and the isolated effect of each parameter remains very difficult to study.

On the whole, the oxygen absorption capacity of a wine is positively related to its total phenol content, among which the catechin fraction appears to contribute significantly to oxidative browning (Rossi et al., 1966).

Antioxidant Potential of Wine

Operating under the hypothesis that wine phenolic compounds provide the major contribution to the antioxidant capacity of a wine studies are currently underway to investigate this antioxidant potential. It has been determined that the redox potential of a wine gives an instantaneous representation of the global state of reduction or oxidation of wine (Vivas et al., 1995), but this value provides only a relative indicator, as wine is a complex mixture of various redox species with their own redox potential (Danilewicz, 2003). It is useful to correlate variations in redox potential to oxygen consumption by phenolic compounds, and to follow its evolution during winemaking and ageing in order to use it as a discriminating variable for a specific sample (Vivas et al., 1993; del Alamo et al., 2006). Applied to wine by Singleton et al. (1999), the total phenols assay by Folin-Ciocalteu reagent measures the reducing capacity of a sample. Various other methods for determining the antioxidant activity of a given compound are described in the literature, all of which involving the measure antioxidant effectiveness by monitoring the inhibition of oxidation of a suitable substrate (Robards et al., 1999). These methods are based on the kinetics study of a reaction in which a free radical is generated, and on the quantification of its inhibition by the addition of the compound, the antioxidant power of which is then determined, either by determining the inhibition time at fixed inhibition level or the inhibition extent at a fixed time. The Total Radical-trapping Antioxidant Parameter, or TRAP assay, developed by Wayner et al. (1985) was first used as a comparative test for antioxidant properties, as determined from a lipid peroxidation reaction, and

standardized with reference to Trolox, a water-soluble vitamin E analogue. The TRAP method has been mostly replaced by another, quicker standardized test, originally called the TEAC method, for Trolox Equivalent Antioxidant Activity. TEAC was proposed by Rice-Evans et al. (1994), and later improved by Alonso et al. (2000) for wine. More commonly known as the ABTS method, it is based on the use of methylmyoglobin/2,2'-azino-bis(3-ethylbenzthiazoline-6-sulfonic acid) (or ABTS) and the generation of the highly stable, chromophoric ABTS radical cation, which can be detected by UV/vis absorption at 414 nm. The delay, or intensity decrease of the latter, can be related to the antioxidant activity of the tested compound. The semi-automated method of Oxygen Radical Absorbance Capacity (ORAC) method is also widely used for measuring antioxidant power in wine, and expresses inhibition time and the extent of inhibition in a single value, as a quantity of Trolox equivalent (Prior et al., 1999; Caldwell, 2001; Davalos et al., 2004). Some other methods applied to wine include, to a lesser extent, electron spin resonance (ESR) spectroscopy (Gardner et al., 1999; Kocherginsky et al., 2005), the DPPH method involving the 1,1-diphenyl-2-picrylhydrazyl substrate (Larrauri et al., 1999) and the FRAP (Ferric Reducing/Antioxidant Power) method (Jamroz et al., 2001). Some of these methods have been compared in the Prior et al.'s review (1999), considering application to biological systems such as plasma and serum. For wines, whatever the method used, wines with a high overall polyphenol content show a general tendency towards a higher antioxidant activity (Fuhrman et al., 2001; Alonso et al., 2002; Fernandez-Pachon et al., 2004), with, for example, obvious differences between grape juice and wine (Davalos et al., 2005), as well as between white and red wines (Fuhrman et al., 2001; Fernandez-Pachon et al., 2004). Fernandez-Pachon et al. (2004) also reported the best correlation coefficients between total phenolic content and antioxidant activity for the ORAC method, in comparison to the ABTS or DPPH method. In another study (Fernandez-Pachon et al., 2006) they showed that different phenolic compounds contributed in various amounts to the total antioxidant activity of the wine, depending on the method used for determination. In any case, the limitation of each method should be considered, especially when using a single for analysis (Prior et al., 1999), and the determined antioxidant value should be regarded as a relative value or a tendency more than an absolute indication of the real antioxidant efficiency of the tested sample. Moreover, as noted by Robards et al. (1999), in analysis depending on free radical oxidation by a metal ion, the chemistry of phenolic compounds, and particularly their ability to bind metal ions, may also introduce a discrepancy on the real efficiency of the tested molecule to interact with the free radical. As mentioned previously, the evolution of wine phenolics with ageing can also lead to the formation of new species having different antioxidant activities, and possible synergism between compounds (Singleton, 1987; Arnous et al., 2001). Therefore, the sum of the overall antioxidant activity of all species is therefore the result of a slow but permanent evolution encompassing the disappearance of some compounds and

concurrent appearance of others. For this reason, the reactions of phenolic compounds in wine are still only partly known, even as general schemes are clarified.

Reaction Order and Modeling

In order to predict the antioxidant properties of white wines, Singleton et al. (1976) proposed the use of a standardized, accelerated test to measure their browning capacity. Indeed, various arbitrarily chosen conditions can be found in literature to test oxidative browning, variations of which include oxygenation conditions of the sample, temperature, or the wavelength measurement of browning. Singleton proposed using a bentonite treatment under nitrogen to precipitate proteins or polypeptides that could interfere in browning measurement, and to incubate the sample with 25% headspace of oxygen or nitrogen, for 5 days at 55°C. Subsequent absorbance measurements at 420 nm will then indicate the wine capacity of browning. Even if some brown wines display absorbance spectra with a broad maximum near 445 nm, the use of the 420 nm wavelength is preferred, to avoid interference with the possible pinking of leucoanthocyanins. The ultraviolet spectrum at 320 nm also correlates to oxidation exposure, with a marked absorbance increase as phenols are oxidized to quinones (Singleton et al., 1979). This standardized test has been used by other researchers for different types of studies relative to oxidation phenomena (Fernandez-Zurbano et al., 1998). Another accelerated test for browning, based on the electrochemical oxidation of wine, has been proposed recently by Palma et al. (2002). This analysis correlates well with the natural evolution of wines; in the analyses of the phenolic content of different Fino sherries, for example, higher oxidizable contents have been found to yield to higher browning. One must be cautious, however, in applying the data from accelerated, high temperatures tests to wine stored at lower temperatures. Such test results may not correlate with the long-term evolution of the wine under traditional storage conditions, as the temperature is one of the many parameters controlling the oxidation rate (Caputi et al., 1965).

Another interesting attempt at predicting the oxidation rate involves analyzing the overall reaction and determining reaction kinetics; this method makes the choice of the indicator more important. Considering the oxidation process in wine as first-order kinetics, which results from the global reaction between oxidizable phenolic compounds and dissolved oxygen to form condensed polyphenols, researchers estimate the oxidation rate as dependent on a kinetic constant of $1 \times 10^{-4} \text{ h}^{-1}$ at 20°C for sherry wines over ten days old, from absorbance measurements at 470 nm (Palacios et al., 2001b). The process is very slow at this temperature. It was also shown that the effect of temperature on oxidation phenomena follows an Arrhenius type relation. On the other hand, Sioumis et al. (2006) found browning kinetics of white wines (measured by absorbance changing at 420 nm) to obey zero-order kinetics, with kinetic constants ranging from $15 \text{ to } 75 \times 10^{-3} \text{ day}^{-1}$, over ten days under accelerated test

Table 4 Solubility of various gases in water compared to oxygen (assuming the same partial pressure to that of oxygen in the air)

Substance	Solubility in water (mg·L ⁻¹)				Henry's law constant (*) k_H (mol·m ⁻³ ·Pa ⁻¹)	Enthalpy of solution (*) $\Delta_{sol}H$ (KJ · mol ⁻¹)
	0°C	10°C	20°C	30°C		
O ₂	14.2	11.4	9.3	7.7	1.28×10^{-5}	14.13
CO ₂	633.3	464.2	347.5	265.2	3.36×10^{-4}	19.95
N ₂	5.5	4.6	4.0	3.4	6.42×10^{-6}	10.81
SO ₂	40311.4	26987.9	18569.7	13096.5	1.18×10^{-2}	25.77

*Sander (1999).

conditions. Perez-Zuniga et al. (2000) also used a combined model of zero-order and first-order kinetics, which correctly described the browning reaction rate in white wines, assuming the color evolution of white wines (measured by absorbance changing at 425 nm) results from a combination of the formation of colored polymeric compounds (described by a zero-order kinetic) on one hand, the loss of color intensity due to polymer dissociation (described by a first-order kinetic) on the other.

PREVENTION OF OXIDATION IN WINE

Use of Antioxidants

In order to protect musts and wines against oxidation, sulfur dioxide is used from pressing to bottling, especially for white wines. Its empiric use began in the 18th century. In addition to antiseptic properties, sulfur dioxide acts as an inhibitor of enzymatic and chemical oxidation and therefore has a positive effect in decreasing the browning rate (Berg et al., 1956; Sioumis et al., 2005). Sulfur dioxide is highly soluble in water and ethanol as compared to oxygen or other gases (Table 4); solubilities are high and increases with decreasing temperature. Sulfur dioxide is also highly volatile, with a solubility coefficient of 1.2×10^{-2} mol·m⁻³·Pa⁻¹ (Sander, 1999). Concentrations of added sulphur dioxide to wine generally vary from 50 to 200 mg·L⁻¹, and are of greater importance for sweet wines.

In wine, there is an equilibrium between the molecular and ionic forms of sulfur dioxide. At wine pH, it can exist in the molecular form, SO₂, but is more commonly present (94 to 99% at wine pH) or in the ionic form as the bisulfite ion, HSO₃⁻ (SO₂ + H₂O → H⁺ + HSO₃⁻, pK_a = 1.91). The sulfite ion, SO₃²⁻, only appears at a higher pH (pK_a = 6.91), and is thus present at very low concentrations at wine pH. Once in solution in wine medium, sulfur dioxide may bind with several wine constituents such as acetaldehyde, anthocyanins, pyruvic acid, glutaric acid, glucose, or certain phenolic compounds; of which ethanal, pyruvic acid, and 2-oxoglutaric acid appear to react with particular efficiency (Boulton et al., 1996b; Barbe et al., 2000). Some binding agents, such as aldehydes, quinones, or keto acids, may derive from oxidation reactions (Fig. 2). Thus, these two fractions of SO₂ present in wine are respectively referred to as “free SO₂,” referring to HSO₃⁻ and SO₂, and “bound SO₂,” indicating sulfur dioxide bound mainly to unsaturated compounds. Only free SO₂ is active against oxidation; however,

below 10 mg·L⁻¹ of free SO₂ in wine, this protective effect is no longer efficient (Chatonnet et al., 2003).

SO₂ in wine plays an important role against oxidation, not in direct oxygen scavenging (Jacobs, 1976), but by reacting with hydrogen peroxide, which subsequently decreases the oxidation potential (Manzocco et al., 1999; Danilewicz, 2003). The reaction involves a nucleophilic displacement of HSO₃⁻ by H₂O₂ to form sulfuric acid, HSO₄⁻, as an endproduct (McArdle et al., 1983). In this way, sulfur dioxide can inhibit the aldehyde-forming reaction (Fig. 2) by competing for hydrogen peroxide (Wildenradt et al., 1974). However, the considerably larger concentration of ethanol, compared to that of sulfur dioxide, makes its oxidation possible (to ethanal) even in the presence of SO₂. It is generally thought that a concentration at or above approximately 10 mg·L⁻¹ of free SO₂ is necessary to ensure acceptable protection against oxidation (Godden et al., 2005). SO₂ is also thought to play an important role in reducing quinones, formed during the oxidation process product, back to their phenol form (Waterhouse et al., 2006).

The effect of oxidation mechanisms in wine on the SO₂ concentration during wine bottle ageing is discussed in more detail at the end of this paper, with the context of mass transfers coupled to oxidation mechanisms.

Ascorbic acid, the L-enantiomer of which is commonly known as vitamin C, is used widely in the food industry as an antioxidant and could be applicable in wine production. This water soluble organic acid is a 6-carbon lactone ring structure with a 2,3-enediol functional group that confers antioxidant properties. It is, indeed, a good electron donor, as it is easily converted into semi-dehydroascorbic acid, and then into dehydroascorbic acid, via the donation of a hydrogen atom and an electron in each step of the oxidation process (Lee et al., 2004). The reaction rate can be very rapid for the electron transfer to reactive oxygen species. As with SO₂, it is also assumed that ascorbic acid reduces the oxidized phenolic compound, quinone back to its original form (phenol), in addition to acting as an oxygen scavenger (Peng et al., 1998; Bradshaw et al., 2001).

In light of these properties, the use of ascorbic acid as an antioxidant in white wines first appears as a viable solution. In fact, the reduction potential of ascorbic acid has been found to be higher than sulfur dioxide (Oliveira et al., 2002). Skouroumounis et al. (2005b) demonstrated that for two white wines, a Riesling and a wooded Chardonnay, the addition of ascorbic acid at bottling when free SO₂ levels were between

20 and 30 mg/L, produced no significant differences or less oxidized wines for a five year storage period.

However, the effect of ascorbic acid used in combination with sulfur dioxide to protect white wines against oxidation is not clearly evident, especially for long storage. In particular, Oliveira et al. (2002) observed no synergistic effect between these two antioxidants for the quantities currently employed in wine-making. The reduction in browning measured by absorbance at 420 nm is also not evident when ascorbic acid is used in combination with SO₂ after disgorgement for sparkling wines (Marks et al., 1993).

Other studies, however, suggest that ascorbic acid could favor wine browning. First, Ribereau-Gayon (1963) observed that in still wines the use of ascorbic acid alone produces unfavorable oxidations. Later, Peng et al. (1998) found anti-oxidative or pro-oxidative effects of acid ascorbic addition in white wines (*Chardonnay*, *Colombard*) depending on the duration of storage (up to five years). The pro-oxidative effect only appeared after an initial period of anti-oxidant activity, as measured by the redox potential, SO₂ consumption and browning (at 420 nm). This hypothesis of crossover from anti-oxidative to pro-oxidative activity is supported by Bradshaw et al. (Bradshaw et al., 2001, 2002, 2003, 2004) who showed a similar lag time, followed by an increasing rate of browning, in a model wine containing (+)-catechin to which ascorbic acid was added. It would appear, then, that browning is induced by a degradation product of ascorbic acid. As one of the oxidation products of ascorbic acid in oxygen scavenging reactions (Nanni et al., 1980), H₂O₂ can take part to some extent in browning reactions, if there is not enough sulfur dioxide to fully disable it. These authors also suggested that additional oxidation products of ascorbic acid under wine conditions include acetaldehyde, 2,3-diketo-L-gulononic acid, L-threonic acid, oxalic acid, L-threo-2-pentulosonic acid, 4,5,5,6-tetrahydroxy-2,3-diketohexanoic acid and furfural, all of which could take part in browning reactions with wine phenolic compounds, and in binding SO₂ to aldehydic functional groups.

Some other products have been tested for antioxidant activity. These include citric acid, which is known to complex iron and to decrease browning rates (Berg et al., 1956); quercetin and 2,4,5-trihydroxybutyrophenone, which act as chelating agents for metallic cations; cystein, which can combine with quinones to form a stable complex and thus limit their polymerization; and glutathione, which can trap oxygen radical species and chelate metals (Vivas et al., 2001).

As an alternative to sulfur dioxide, or for complementary use, ascorbic acid is not a satisfactory antioxidant despite its excellent capabilities as oxygen scavenger. In particular, the oxygen present in the headspace and its ingress through the closure could lead to the observed crossover from anti-oxidative to pro-oxidative activity, with a subsequent loss of sulfur dioxide. For this reason, sulfur dioxide remains the only antioxidant additive for wine producers to use efficiently against oxidative spoilage (Eschenbruch, 1987); moreover, its anti-microbial activity continues to make essential in wine production.

Other Strategies

Winemaking practices have also a considerable effect on the tendency of wine to brown, and impact this parameter with every processing step from pressing to bottling. This impact is particularly pronounced during white wines pressing, where a delicate balance must be maintained. On one hand, pressing renders the juice very sensitive to enzymatic oxidation, which can generally be controlled by careful pressing, settling, fining, sulfiting, and temperature control. On the other hand, the quantity of phenolic compounds extracted during this unit operation depends on the press level, crushing and destemming, skin contact, and detanninizing treatments. For this reason, some general precautions are commonly applied to white wines in order to obtain less oxidizable musts, and may include soft pressing, minimum handling, no skin contact, removal of stems, sulfur dioxide addition, and use of fining treatments (Macheix et al., 1991; Ribereau-Gayon et al., 2004). Other general recommendations include limiting contact with the air through manipulations such as pumping, the use of inert gases, favoring contact with yeast lees, and processing in large volumes as much as possible.

An opposite school of thought considers phenolic compounds, especially flavanoids, as substrates for oxidation, and favors initial oxidization without anti-oxidant additions, then the precipitation and the elimination of formed compounds. This limits the amount of oxidation in the final product, as it does not contain enough substrates for further oxidation. This technique is known as must hyperoxidation (Muller-Spath, 1990; Schneider, 1998), and basically consists of adding small quantities of oxygen to must prior to the fermentation, without sulfur dioxide, in order to let enzymatic oxidation occur. This leads to the precipitation of the more oxidizable fraction of phenolic compounds as insoluble brown pigments. Some researchers report that wines produced from oxidized musts appear to be more resistant to oxidative browning during ageing (Nagel et al., 1988; Schneider, 1998), less bitter and astringent, and subject to a slower evolution (Schneider, 1998). Nevertheless, in a previous study led on dry white table wines made from Chardonnay, Chenin Blanc, French Colombard, and Semillon grapes, Singleton et al. (1980) reported that while wines produced from deliberate oxidation of musts exhibited no browning increased resistance to further oxidation, they were also less fruity. Wines produced with moderate amounts of initial SO₂ (around 50 mg·L⁻¹ for a good sanitary state of grapes) were found to exhibit better overall sensory characteristics. Ough and Crowell (1987) also compared the effect of pretreatment of the juice of various common cultivars used for white wines with air, with nitrogen or with sulfur dioxide, and found that the best wines, as evaluated by sensory analysis, were made using SO₂ both in the juice and in the wine.

The removal of polyphenols, including those responsible for browning, can also be achieved to some extent at the end of the fermentation with wine stabilizers such as PVPP (polyvinylpolypyrrolidone) (Gopal et al., 1999), potassium caseinate, activated charcoal, or even chitosans (Spagna et al.,

2000). Sorption properties of yeast cell walls can also be used to adsorb oxidized browning products, depending on the yeast specie (Merida et al., 2005). The use of yeast as fining treatment to decrease wine polyphenol content, and especially brown color, has been proposed by several authors as an alternative to classical preventive or remedial treatments (Bonilla et al., 2001; Razmkhab et al., 2002; Languet et al., 2005; Lopez-Toledano et al., 2006). During wine ageing on lees, it is also thought that yeasts can preferentially consume oxygen and thus protect oxidizable wine substrates (Fornairon et al., 1999; Salmon, 2006).

Other authors argued that the higher the phenolic compounds concentration is, the greater the capacity for the wine to resist oxidation (Singleton, 1987; Villano et al., 2006; Gomez-Miguez et al., 2007). In this case, hard pressing or skin contact is used to increase the extraction of flavonoids, which act as effective free radical scavenger.

Another strategy for preventing oxidative browning attempts to eliminate the metallic cations which play an essential role in oxidation reactions, as exemplified by the recent study of Danilewicz (2007). For iron to act as a catalyst for oxidation, it appears that manganese has also to be present, and the concentrations of both elements have thus to be reduced (Benitez et al., 2002a). To address this, Palacios et al. (2001a, 2001b) and Benitez et al. (2002b) proposed the use of ion exchange techniques for the removal of iron, copper and manganese from white wines. This treatment is very effective in lowering the metal content of wines (more than 90% decrease in both studies) as well as concentration of phenols. This subsequently reduces susceptibility to browning. It was found, however, that this treatment significantly alters the wine's organoleptic qualities (Benitez et al., 2002b).

Ultimately, with the possible exception of hyperoxidation, wine should be protected against oxygen throughout processing, and sulfur dioxide is, for now, the only efficient antioxidant additive (Désert et al., 2002). Oxygen interaction can occur at any point during the wine elaboration process, as well as during bottle aging as a result of oxygen ingress through the closure.

OXYGEN UPTAKE DURING WINEMAKING

Oxygen and Solubility

Throughout the elaboration process, wine can be brought in contact with oxygen existing in the surrounding atmosphere. It is therefore important to understand the laws that govern the transfer of gases, and oxygen in particular, into the liquid phase.

Air, the earth's atmosphere, is a mixture of gases containing approximately 78% nitrogen (volume fraction), 20.9% oxygen, 0.9% argon, 0.04% carbon dioxide, trace amounts of other gases (Ne, He, NO, CH₄, Kr, H₂), and a variable amount of water vapor (averaging around 1%). The standard atmospheric pressure is an established constant, with a value of 1013 hPa, approximately equal to the air pressure at earth mean sea level. The dry atmosphere consists of approximately 20.9% oxygen (O₂). Its

partial pressure is thus close to 212 hPa, as given by the following equation, derived from Dalton's law, which states that the total pressure of gaseous mixture is equal to the sum of its partial pressures:

$$p_{O_2} = x_{O_2} \cdot p \quad (1)$$

Where x_{O_2} is the molar fraction of oxygen in air, equal to its volumetric fraction (= 0.209); p_{O_2} is the partial pressure of oxygen in the air (Pa); p is the total pressure of the gas mixture in the air (Pa).

As the atmosphere surrounding water or wine can be considered saturated by water vapor, the partial pressure of oxygen at equilibrium must take into account the vapor pressure of water, 23 hPa at 20°C (Lide, 2005), and thus becomes $(1013-23) \times 0.209 = 207$ hPa, at 20°C under standard pressure.

At a constant temperature, Henry's law describes the relationship between the concentration of a given gas dissolved in a liquid phase and its partial pressure in the gas phase in equilibrium with the liquid. For oxygen, this can be expressed as:

$$C_{O_2} = k_H \cdot p_{O_2} \quad (2)$$

Where C_{O_2} is the concentration of oxygen in the aqueous phase ($\text{mol} \cdot \text{m}^{-3}$); p_{O_2} is the partial pressure of oxygen in the gas phase (Pa); k_H is the Henry's law constant for oxygen ($\text{mol} \cdot \text{m}^{-3} \cdot \text{Pa}^{-1}$).

k_H is also termed the solubility coefficient (S), as it represents the capacity of a given gas to be dissolved in a liquid at a given temperature and pressure. The greater the coefficient for Henry's law is, the greater the solubility. As a function of the gas partial pressure and its concentration in the liquid phase, the partition could be volatilization, the transfer from the liquid to the gas phase, or, more commonly for wine and oxygen, solubilization, involving the transfer from the gas to the liquid phase. The phenomena occurring in a headspace sparged with inert gas follow the opposite pattern.

For example, at 20°C, with k_H equal to $1.4 \times 10^{-5} \text{ mol} \cdot \text{m}^{-3} \cdot \text{Pa}^{-1}$ (Sander, 1999), the concentration of dissolved oxygen in water obtained at equilibrium under atmospheric conditions is $0.29 \text{ mol} \cdot \text{m}^{-3}$, obtained from Eq. 2, or $9.3 \text{ mg} \cdot \text{L}^{-1}$, using the molar mass of oxygen ($32 \text{ g} \cdot \text{mol}^{-1}$).

As stated by Henry's law, the quantity of the gas dissolved in the liquid phase at equilibrium is directly proportional to the pressure of the gas above the liquid. Figure 3 clearly displays this relationship in the case of water at 20°C as a function of the oxygen volumetric fraction in the surrounding atmosphere, which ranges from 0 (inert atmosphere) to 21% (standard conditions).

In addition to gas phase composition, the solubility of oxygen in wine also depends on temperature. The effect of temperature on Henry's law constant can be described by the following equation:

$$k_H = k_H^\theta \cdot e^{\left[-\frac{\Delta_{sol}H}{R} \left(\frac{1}{T^\theta} - \frac{1}{T}\right)\right]} \quad (3)$$

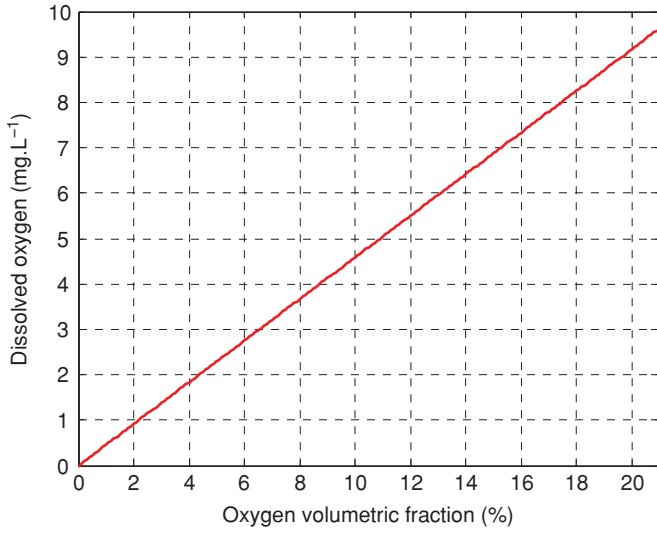


Figure 3 Effect of oxygen volumetric fraction on the equilibrium dissolved concentration in water at 20°C, calculated from Henry's law.

Where $\Delta_{sol}H$ is the enthalpy of solution, and the index θ refers to standard temperature (293 K). $\frac{\Delta_{sol}H}{R}$ is a constant, equal to 1700 K for oxygen (Sander, 1999).

The effects of temperature on the capacity of water to dissolve oxygen are illustrated in Fig. 4, which shows a temperature range corresponding to the extremes that can be encountered in oenological conditions for wine storage. Lower temperatures clearly lead to higher oxygen solubility. Under standard conditions of temperature and pressure, the oxygen concentration in the liquid phase also depends on ethanol concentration, the solubility being slightly reduced until 30% (v/v) and highly increased beyond, and on the concentration of solutes, which tend to increase oxygen solubility. Nevertheless, for a 10% (v/v) hydroalcoholic solution, the oxygen solubility remains in the

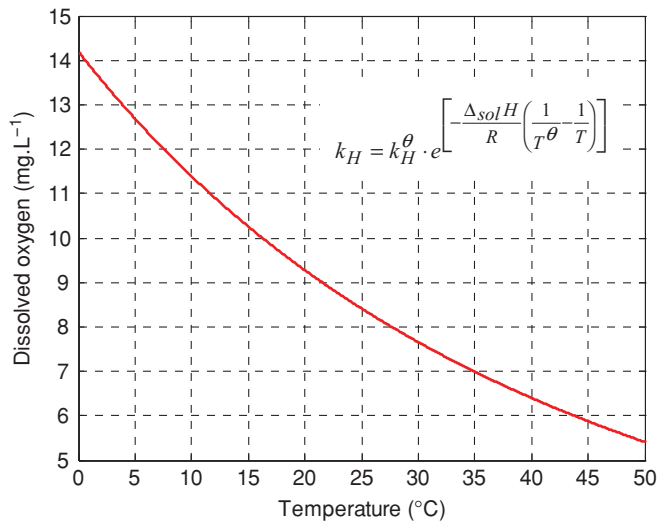


Figure 4 Effect of temperature on oxygen solubility in water under standard pressure.

same order of magnitude as water (Moutounet et al., 2001). As shown in Fig. 4, this means that cellar temperatures (between 12 and 20°C), a wine saturated with O₂ contains between 9 and 11 mg·L⁻¹ O₂, as reported by Singleton (1987). Compared to other gases, oxygen is slightly soluble in aqueous medium, slightly more so than nitrogen, but much less than carbon dioxide or sulphur dioxide (Table 4).

The solubilization rate of oxygen from air into aqueous or hydroalcoholic media depends mainly on two mechanisms: convection and diffusion. The natural diffusion process of oxygen from air to water is very slow (Lewis et al., 1924). Three main mass transfer models have been proposed to quantify the absorption of gases into turbulent liquids in the absence of chemical reaction: the two film theory (Lewis et al., 1924), the penetration theory (Higbie, 1935) and the surface renewal theory (Dankwerts, 1951). In its simplest form this rate of solubility, or global absorption flux per unit of liquid volume, is stated as follows (Adeney et al., 1919):

$$\Phi = F \cdot a = \frac{dC}{dt} = k_L \cdot a \cdot (C_i - C) = \frac{D}{e} \cdot a \cdot (C_i - C) \quad (4)$$

Where Φ = absorption flow per volume unit (mol·m⁻³·s⁻¹); F = absorption flow per interfacial area unit (mol·m⁻²·s⁻¹); a = interfacial gas-liquid area per volume unit (m⁻¹); C = concentration (mol·m⁻³); C_i = concentration at equilibrium with the partial pressure of the gas, at the interface liquid-gas (mol·m⁻³); k_L = mass transfer coefficient in the liquid phase (m·s⁻¹), which mainly depends upon the temperature and the degree of turbulence, and is equivalent to a resistance to the transfer; D = diffusion coefficient of the gas dissolved in the liquid (m²·s⁻¹); e = stagnant liquid film thickness (m).

In a wine bottle with a headspace containing air, the surface area available for oxygen mass transfer clearly influences the absorption flow through the a parameter of Equation (4). Compared to vertical storage, horizontal storage creates a larger surface area in contact with the headspace, and thus increases the absorption flow of oxygen in wine. When wine is stored in tank under stagnant conditions without agitation, the dissolved oxygen concentration gradient only occurs within the first ten centimeters of liquid (Moutounet et al., 2001).

The diffusivity of oxygen in water at 25°C is 2.5×10^{-9} m²·s⁻¹. It is approximately 10000 times lower than it is in air (1.76×10^{-5} m²·s⁻¹ in air) (Liley et al., 1997). The mass transfer rate, therefore, is limited by the diffusion coefficient of the liquid phase.

In addition, there are oxidation reactions that play an important role in oxygen disappearance in wine. As previously seen in the section relating reaction order and modelling for oxygen in wine, the kinetic order of this reaction must also to be considered when using the above mentioned solubilization model (Roizard et al., 1997).

Table 5 Oxygen addition to wine for the different winemaking operations

Unit operation	Oxygen addition (mg·L ⁻¹)			References*
	Min	Mean	Max	
Pumping	<0.1	0.1 to 0.2	1	1
Transport in full tank		0.4 to 1.1		4
Transport in broached tank		1.2 to 6.6		4
Racking (bottom tank pumping)	0.1	0.3	0.5	4
Racking (top tank pumping)	2.1	3.1	4.4	4
Centrifugation		1		1
Tangential filtration	0.6	1.5	2.2	1
Diatomaceous earth filtration	0.1	0.7	1.7	1
	0.1	0.7	2.0	4
Perpendicular flow polymeric membrane filtration	0.1	0.5	0.8	4
Continuous tartaric stabilization	0.1	1.2	2.6	4
		2.4		2
Membrane filtration	0.6	1.3	2.1	2
		0.1		3
Plate filtration		0.2		3
Bottling on moving line	0.6	1.4	2	3
Bottling on fixed line	0.2	1.6	3.9	3
		2 to 7		5

*1 = Vidal et al., 2001; 2 = Vidal et al., 2003; 3 = Vidal et al., 2004; 4 = Valade et al., 2006; 5 = Valade et al., 2007.

Effect of Winemaking Operations

During winemaking, the different unit operations may integrate oxygen from the atmosphere into the wine. Operations particularly prone to oxygen integration include pumping, transport, racking, centrifugation, filtration, stabilization, and bottling, as reported in Table 5, and as observed by Vivas et al. (1995).

Continuous pumping leads to a small amount of added oxygen, especially during the initiation and completion of pumping (Vidal et al., 2001). Agitation effects can be minimized by decreasing pump speed at these beginning and end of the operation. During filtration, the greatest risk for oxygen addition occurs during the first step of the operation, when the wine makes initial contact with the dead volume of the system, and the air included in filtration products such as kieselguhr (Valade et al., 2006). In consequence, the most important parameter is the wine volume; bigger volumes giving lesser enrichment with oxygen, as it is the case in most other unit operations. Tartaric stabilization can also lead to high oxygen addition (Vidal et al., 2003), as it generally combines cooling and mixing. As mentioned in Table 5, reported measures of dissolved oxygen addition in wine during bottling is variable, ranging from 0.2 to 7 mg·L⁻¹. For this operation, oxygen integration can be limited by minimizing the dead volume of the system, and using inert gases instead of air, especially at the beginning and the end of each cycle (Vidal et al., 2004). Filling, in particular, is responsible for 30 to 70% of oxygen added during bottling for fixed or moving bottling lines, respectively (Vidal et al., 2004). Except for specific winemaking practices, the addition of oxygen during blending or bottling is directly attributable to unit operations (without considering storage phases). They have been estimated to range from 0.5 to around 10 mg·L⁻¹. However, it must be

remembered that during winemaking, between these different unit operations, wine comes into contact with air, which can lead to different dissolved oxygen concentrations. In particular, the container size determines the total amount of dissolved oxygen in the liquid, which can in turn influence the oxidation rate (Palacios et al., 2001b). The initial dissolved oxygen concentration at each step of the process also has an effect on the transfer rate during the unit operations. As described by Fick's law (Equation 6) the higher the concentration gradient, the higher the transfer rate; consequently, the lower the dissolved oxygen concentration in wine, the greater capacity to absorb oxygen during the unit operations when direct contact occurs with air.

It is also important to consider the instantaneous dissolved oxygen concentration from the beginning to the end of a unit operation, which represents a balance between chemical reactions and solubilization. Unless these operations take place successively, the final dissolved oxygen concentration after a unit operation probably differs from the initial dissolved oxygen concentration at the beginning of the next unit operation. In the mean time, some chemical reactions involving oxygen certainly occur, and are possibly coupled to a mechanism of solubilization if contact with air occurs. The total cumulative capacity of oxygen absorption by wines, including reactions with wine constituents, is around 85 mg·L⁻¹ for white wines and 260 mg·L⁻¹ for red wines (Singleton, 1987). After that point, the organoleptic characteristics indicating oxidation begin to appear. The kinetics of dissolved oxygen consumption by chemical reaction with wine constituents, from saturation down to undetectable levels in wine, is about a week at room temperature for red wines (Singleton, 1987; Boulton et al., 1996a) and three times lower for white wines (Ribéreau-Gayon et al., 2004). Increasing pH highly increases these kinetics, probably due to the greater proportion of phenolate ions being oxidized.

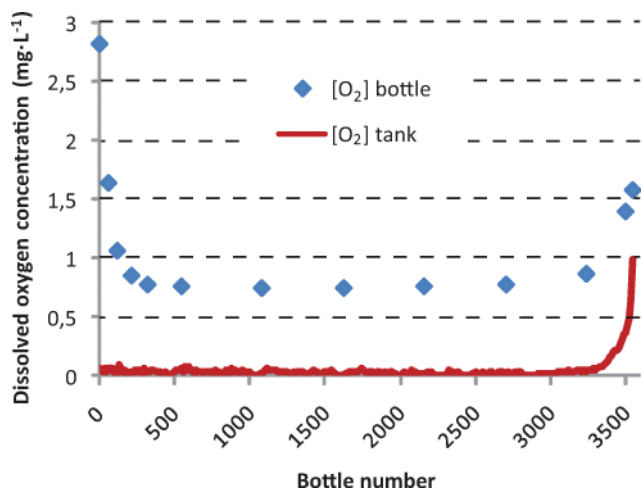


Figure 5 Effect of bottling on oxygen addition during the whole unit operation (Standard deviation is contained between each point).

As previously reported, the effect of bottling is of particular importance, and could lead to large amounts of oxygen entering wine. The exact amount of oxygen added appears to be dependent on the operating system of the bottling line. Figure 5 displays the results observed in 2006 by the BIVB (Bureau Interprofessionnel des Vins de Bourgogne) in a study of bottling lines in Burgundy (France). On an isobaric bottling filler with gravity filling, with corking done under low pressure (-0.8 bar), at 18°C (± 1), the dissolved oxygen was continuously measured at the tank and in the bottle after filling and corking. The oxygen addition was found to be around $0.7\text{ mg}\cdot\text{L}^{-1}$ during steady state of bottling. At the beginning and the end of the bottling process, however, higher amount of oxygen are added up to 2.8 and $1.6\text{ mg}\cdot\text{L}^{-1}$, respectively, for a wine containing less than $0.1\text{ mg}\cdot\text{L}^{-1}$ initial dissolved oxygen. For the first 150 bottles, the mean oxygen addition was around $1.7\text{ mg}\cdot\text{L}^{-1}$, mainly caused by the dead volume of the system and air dissolution. The mean value was around $1.3\text{ mg}\cdot\text{L}^{-1}$ for the last 250 bottles, due to oxygen dissolved near to the wine surface at the top of the tank, as displayed by Fig. 5 with a good correlation between $[\text{O}_2]$ bottle and $[\text{O}_2]$ tank. The oxygen content in the final bottles could also be due to turbulence and contact with air at the end of the bottling cycle. In both cases, the use of an inert gas, such as nitrogen, could lead to a considerable decrease of oxygen addition during bottling, especially for bottling small wine volumes.

As bottling is a source of oxygen enrichment, the degree of oxygen addition has to be controlled. The empty bottle itself contains 750 mL of air, or over 200 mg O_2 , which is mixed with wine during bottling under turbulent conditions, unless the bottle has previously been flushed with an inert gas such as nitrogen. Figure 6 also displays the oxygen quantity present in bottle headspace for different filling heights at 20°C . Headspace height depends on the wine filling level (55 to 63 mm) and on the length of the cork stopper (38 , 44 , 49 , or 53 mm). Generally, a 15 mm height is maintained to avoid partial cork ejection in

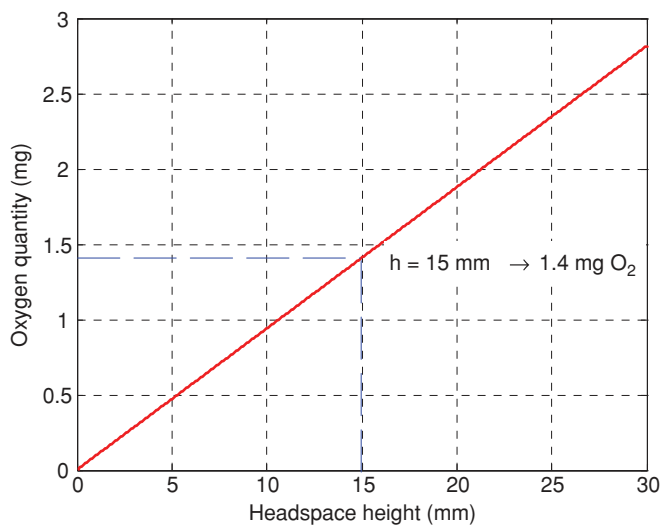


Figure 6 Oxygen quantity present in bottle headspace for different filling height at 20°C , assuming a standard diameter of 18.5 mm .

the case of headspace gas compression caused by thermal expansion of the liquid. This corresponds to 1 to 2 mg of oxygen available for dissolution in wine (or 1.3 to $2.7\text{ mg}\cdot\text{L}^{-1}$), if any vacuum has been drawn in the neck of the bottle. Relatively to the consumption ratio of 4 mg SO_2 per mg of O_2 (Boulton et al., 1996b), this means around 10 mg SO_2 could be lost oxidatively ($2\text{HSO}_3^- + \text{O}_2 \rightarrow 2\text{H}^+ + 2\text{SO}_4^{2-}$). During the corking operation itself, the closure goes down into the bottleneck, compressing the headspace atmosphere between the closure and the liquid. If no vacuum is drawn during the corking operation, this displacement creates a potential increase of oxygen dissolution into wine, following Henry's law (Fig. 7), and could lead to a four-fold increase of oxygen uptake. It should also be noted that cork contains between 80 and 85% of air in its cellular structure. Thus, a classical closure, with pre-compression dimensions of 44 mm length \times 24 mm diameter, already contains about 4.8 mg of oxygen. Consequently, it represents a potential source of oxygen by slow diffusion rate from the porous cellular structure into the headspace, even if the headspace has been sparged with inert gas.

Once in the bottle, three mechanisms can modify the dissolved oxygen concentration: chemical reaction with wine constituents, absorption by dissolution from the gas phase, and permeation through the closure. Thus, any measurement of the concentration of dissolved oxygen in wine represents a transient state of the system, which is the result of the relative importance of these combined phenomena. Sometimes confusion exists when from dissolved O_2 concentration presented as an equilibrium data; since this measurement represents relative information, such applications are misleading. It is useful, for example, for comparing two measurements with knowledge of events that occurred in between. Temperature is also a confusing variable: on one hand, high temperatures accelerate chemical reaction kinetics, following roughly a Q_{10} of 2 : when temperature increases by 10°C the reaction rate doubles (Boulton et al.,

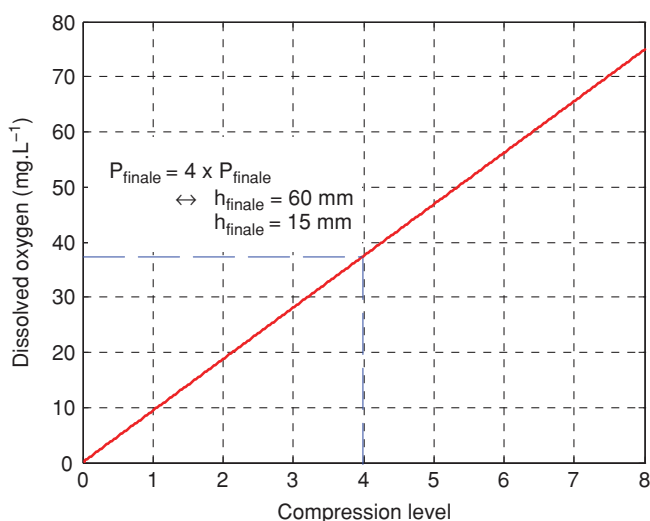


Figure 7 Effect of pressure (equivalent to the air compression in the headspace during bottling) on the equilibrium oxygen dissolved concentration in water at 20°C.

1996a). On the other hand, higher temperatures result in lower gas solubility. Currently, the most important questions about oxygen addition are first, how to predict the capacity of a specific wine to resist oxidation, and second, how much oxygen can be optimally added during wine processing.

ROLE OF THE CLOSURE

The main function of a wine bottle closure is to ensure a good seal, in order to prevent any organoleptic deterioration of the wine during storage. Unlike the glass bottle, however, the cork closure is not an inert material, and its permeability can lead to mass transfer of various small molecules, such as oxygen or water.

Physico-Chemical Properties of Cork

Cork, commonly used for wine stoppers comes from the bark of the oak tree *Quercus suber L.* The first known use of cork as a closure dates back to the fifth century BC, when it was used with Greek amphora. Nevertheless, the rise of cork started at the fifteenth century with the beginning of glass wine bottles. For several centuries, cork was the stopper of choice for various alcoholic beverages, due to its supposedly inert nature, impermeability to liquids and gases, and flexibility (Gibson et al., 1981; Maga et al., 2005).

Cork harvesting only takes place every nine to twelve years, and the first harvest of useable quality generally occurs on 40- to 50-year-old trees. Once harvested cork planks are stored for six months to two years. The next step is to boil the cork in water for at least one hour in order to tighten cells and produce uniform cell structure by gas expansion, and at the same time reduce the

microorganism population (Maga et al., 2005; Silva et al., 2005). After drying and several weeks of storage under controlled conditions of temperature and relative humidity, cork is then graded and cut into strips. The quality grading is based on visual analysis of transverse and tangential sections of cork planks, taking into account the three main types of defects: pores (lenticular channels), physiological anomalies (nails, clay), and pathogenic anomalies (insect galleries) (Gonzalez-Adrados et al., 2000). The stoppers are finally punched from strips of acceptable quality, and the remaining material is commonly used for agglomerate stoppers. After cutting to proper size and cleaning, cork stoppers are visually sorted into grades of different quality, depending on the extent of holes or imperfections. Then, they may be printed and the surface treated with either silicone or paraffin, in order to improve insertion and removal from the bottleneck (Fugelsang et al., 1997). In addition to the visual control, most finished cork stoppers undergo a set of standard analyses (ISO-9727), which include dimensional measurements (diameter, length, ovalization), mass and apparent density, moisture content (optimally between 4 to 8%), diameter recovery after compression, maximum extraction force, liquid tightness, dust content, and in some cases peroxide residue and organoleptic tests (Riboulet, 2000).

The physical structure of cork can be considered in terms of its three axes: axial (vertical, parallel to the center of the tree), radial (horizontal), and tangential (perpendicular to the axial-radial plane). Cork stoppers are punched out along the axial dimension. When viewed from a radial perspective, cork cellular structure is a homogeneous tissue of thin-walled cells orientated in an alveolar, honeycomb type pattern of hexagonal sections with no intercellular spaces. When viewed from an axial or a tangential perspective, the cells appear as rectangular prisms, stacked base to base, parallel to the radial axis (Silva et al., 2005). Average cork cells are 45 μm tall with a hexagonal face of 20 μm and with a thickness of 1 μm (Gibson et al., 1981). The density of cork can vary from 120 and 240 $\text{kg}\cdot\text{m}^{-3}$, with 10 to 40 million cells per cubic centimeter (Silva et al., 2005). Cork always contains lenticular varying numbers of lenticular channels running radially, which are hollow and approximately cylindrical, and constitutes macroscopic porosity. The volume and number of these channels varies significantly according to different types of cork, and is directly related to its industrial quality.

The composition of cork as described in literature is relatively variable, but can be summarized as follows (Silva et al., 2005):

- Suberin: 33–50% (w/w)
- Lignin: 13–29%
- Polysaccharides: 6–25%
- Waxes: 2–8%
- Tannins: 6–7%
- Extractables: 8–24%
- Ash: 2–3%
- Others: 6–7%

Pereira (1988) also indicated the existence of variation in the composition within the tree and a large variability between trees. Nevertheless, the main constituents are suberin and lignin, with somewhat smaller percentages of polysaccharides and waxes. Lignin is thought to be the main constituent of the thin internal primary cork cell wall, which is surrounded by alternating suberin and wax lamella in the thick secondary wall, which is in turn contained by the thin tertiary wall composed of polysaccharides (Silva et al., 2005). The chemical structure of suberin and lignin in cork has not yet been fully deciphered. Suberin is thought to be a macromolecular network of aliphatic polyesters, with various long-chain fatty acids and phenolic moieties (Cordeiro et al., 1998). Although covalently linked, the poly(aliphatic) and poly(phenolic) domains appear to be spatially distinct. Suberin is assumed to play an important physiological role of water retention, and also acts as an antimicrobial barrier (Bernards, 2002). It is also indicated in the low permeability of cork to liquids. Its surface properties as measured by goniometry give a contact angle $\theta = 84^\circ$ at $t = 0$ for water on cork substrate, a mean surface tension $\gamma_S = 32 \text{ mN}\cdot\text{m}^{-1}$ and a polarity γ_S^P/γ_S around 0.25 (Gomes et al., 1993). Cork therefore displays a low-energy surface, with a low polarity, similar to those low density polyethylene or polypropylene packaging films (Karbowiak et al., 2006).

While its status as a natural product is desirable, the cork's reputation for chemical inertness has come into question, and along with it the quantity of potential extractables. Mazzoleni et al. (1988) reported more than a hundred volatile compounds identified from cork. While the interactions of these aromatic components with wine remain largely unknown, Conde et al. (1997) also identified, after ether extraction, various low molecular weight phenolic compounds, most of them described in oak wood and wine: mostly ellagic acid (over 200 ppm), but also (in order of decreasing concentration, and less than 50 ppm) protocatechuic acid, vanillic acid, gallic acid, vanillin, scopoletin, caffeic acid, coniferaldehyde, ferulic acid, protocatechuic aldehyde, aesculetin, and sinapaldehyde. These authors reported a high variability in composition, which could be attributed to the age of the tree and to the distance of the samples from the base of the tree. No significant difference in extract concentration has been found between natural cork stoppers and agglomerated cork stoppers (Varea et al., 2001). Moreover, during the stages of cork production, the concentration of these compounds tends to decrease (Pena-Neira et al., 1999). Ellagic and gallic acids concentrations, in particular, are affected strongly by the boiling step in processing, which suggests hot water extraction, and by beaching with H_2O_2 . These low molecular weight phenolic compounds found in cork may be formed by the breakdown of lignin and suberin, caused either physically or chemically by the manufacturing process, or by microorganism biodegradation. These compounds can have a direct influence on the organoleptic characteristics of the wine, and, subsequently, either positive or negative effects on wine quality.

The washing and disinfection steps of cork processing can affect wine by affecting the sorption properties of cork. For

instance, Michellod et al. (1990) studied the effect of cleaning treatment products; namely, aqueous solutions of chlorine-based compounds or hydrogen peroxide. They reported a positive oxidative effect for corks with peroxide residues, but no significant effect with chlorine residues. This difference could be due to the basic pH used for the peroxide treatment, which may lead to suberin saponification and penetration of the peroxide residues into the cork, while chlorine residues remain at the surface of the material. Other less contaminating treatments, such as ozone disinfection techniques, are now considered (Molinier et al., 2005).

A more widely studied aspect of the release of organic compounds from cork closures is the transfer of those volatiles implicated in cork taint, and particular chloroanisoles (mainly 2,4,6-trichloroanisole) and chlorophenols (Sefton et al., 2005). Some technical agglomerated cork stoppers are treated to protect against these compounds using supercritical fluid extraction with carbon dioxide (Lumia et al., 2005), which decontaminates cork stoppers and also significantly reduces the aromatic compounds present in cork giving it a neutral organoleptic profile (Bobé et al., 2006). In addition, most corks undergo surface treatment with silicone or paraffin; these hydrophobic compounds could also enhance the retention of non-polar taint compounds (Sefton et al., 2005).

Contrariwise, sorption properties of cork must also be considered. As a function of the concentration gradient between cork and wine, mass transfer can indeed occur from the cork to the wine as well as from the wine to the cork. A lot of other chemical species can also be sorbed by cork. In addition to water (Gil et al., 1998) and ethanol, also all compounds present in wine having an affinity to cork also may be sorbed by the closure. Although less studied, this aspect should be considered in relation to long-term interactions between wine and cork during wine aging in bottle. Cork stoppers may also sorb compounds from the environment: 2,4,6-trichloroanisole, for example, has been shown to be easily sorbed by cork in the vapor phase, but sorption is mainly confined in the outer 2 mm of the cork cylinder with some slight migration towards the interior after 24 hours of exposure to the contaminant (Barker et al., 2001). Moreover, permeation of this compound through cork seems to be a very slow process, confined to the outer portion of the closure after three years (Capone et al., 2002). More recently, the understanding of sorption properties of cork has mostly been studied with a view to use cork powder waste as a potential biosorbent of pollutants, as it can easily be incinerated afterwards. The removal of heavy metals from aqueous solutions via biosorption on cork powder has been particularly studied for chromium (Machado et al., 2002), copper, nickel (Villaescusa et al., 2000) and zinc (Chubar et al., 2003). The adsorption of metal ions generally showed a pH-dependent profile, revealing the important role of the carboxylic groups in binding through ion exchange mechanism. Cork has also been tested for the removal of biphentrin, a pyrethroid (Domingues et al., 2005), and even uranium (Psareva et al., 2005). The sorption isotherms can, in most of these cases, be described by the non-competitive Langmuir adsorption model.

Under standard conditions of temperature and pressure, cork contains 7% water on average. Heating at 100°C leads to a water mass loss of 4%: the 3% remaining is eliminated at a lower rate between 100 and about 200°C (Rosa et al., 1988b). Up to 250°C, it is interesting to note that no irreversible changes in cork composition occur. The water desorption process requires an activation energy of about 58 kJ·mol⁻¹ (Dionisio et al., 1995). It gives an endothermic peak close to the peak corresponding to the melting of waxes at 75°C, as measured by differential scanning calorimetry. Desorption of water molecules from the cork structure, associated with a possible anti-plasticization effect, gives rise to a modification of the dielectric properties (Dionisio et al., 1995) and mechanical properties of cork (Mano, 2002), as these two relaxation processes are related to molecular mobility in the system.

At bottling, cork stoppers are compressed horizontally, in the radial-tangential plane. The diameter is reduced by about 25%, from 24 to 18.5 mm, resulting in a 45% reduction in volume. Before closing, the ideal compression diameter is estimated to range between 15.5 and 16 mm, to avoid either too much cell damages or a strong piston effect. It is interesting to note that the mechanical characteristics of cork are roughly isotropic in the plane perpendicular to the radial axis, as dictated by its special shape and cell structure (Gibson et al., 1981). It is, however, anisotropic in the two other planes, as revealed by compression studies (Rosa et al., 1988a). As a consequence of this material anisotropy, the best seals for mechanical properties would theoretically be obtained by punching out stoppers radially in the isotropic plane. Unfortunately, lenticels also run in the radial direction, and act as preferential pathways for liquids and gases, cork's elastic properties are characterized by a low Young modulus (~20 MN·m⁻², roughly two times greater along the radial axis than along the other two directions) but also a low bulk modulus; this leads to high deformability, which could be explained in terms of cell-wall deformation recovery through bending or buckling (Gibson et al., 1981). Furthermore, due to the existence of lenticels, the deformation of cork is not uniform and mainly occurs near these lenticular channels, which are irregularly dispersed within the material and cause local variability in mechanical properties (Gameiro et al., 2007). Despite these irregularities, cork is assumed to retain some degree of resilience for 5 to 10 years (Maga et al., 2005).

Mass Transfer Mechanisms Applied to Cork Closure

The first systematic studies on mass transfer, originally in gas and then in liquids, were performed by the chemist Thomas Graham from 1828 to 1833. Doctor Adolf Fick, following the same principle as Fourier's law for heat (1822) or Ohm's law for electricity, then postulated mathematic laws. By analogy, he stated that mass flux is directly proportional to the concentration gradient, by a factor qualified as "constant depending on the nature of substances."

Interpretation of diffusion processes is based on the continuous and anarchic displacement of the particles, and is related to

mass transport. It is designated as Brownian motion, named after the botanist Thomas Brown, who first discovered and reported these phenomena in 1828 after observing the erratic motions of small particles in pollen through the microscope. It was only in 1905, however, that Einstein formulated the laws of Brownian motion, by linking a phenomenological variable, the diffusion coefficient, to a microscopic quantity, the quadratic mean displacement of the particle. The macroscopic migration of chemical species in a medium thus results from diffusion, occurring through the effect of thermal agitation, which can also be associated to the effect of a chemical force, in the presence of a chemical potential gradient.

Depending on the structure of the material in question, transfer mechanisms may be described by several laws. Darcy's law describes a fluid mass transfer through an open porous system. It supposes the existence of preferred open pathways from one side of the material to the other. A porous medium is, indeed, considered to be a continuous medium, either cohesive or not, the interior of which presents a volume fraction accessible to a fluid. This "empty" volume fraction, composed of pores, constitutes the porosity of the medium. The fluid flow rate through the medium, Q (m³·s⁻¹), depends on the pressure difference from one side of the porous material to the other, Δp (Pa), its thickness L (m), its section A (m²), the dynamic viscosity of the fluid η (Pa·s), and a proportionality coefficient z (m²) related to the resistance of the medium to the flow. It is expressed by the following equation:

$$Q = \frac{z \Delta p}{\eta L} A \quad (5)$$

Application of this law, however, requires specific conditions necessary for fluid flow, in particular the existence of open pores, or channels, through the material. For condensed vapor, the partial pressure must be high enough to achieve condensation. If cork can be considered as porous, this model appears inappropriate, as pores never cross over the entire length of the closure. Further, the applied pressure on the material, once inserted in the bottleneck, greatly reduces the pore volume within the cork.

The most commonly used model to describe mass transfer phenomena in a dense, homogeneous, and isotropic material is the simple diffusion model described by Fick's law. In an isotropic, immobile medium with constant volume, this law states that the unidirectional flow of diffusing matter is proportional to the concentration gradient:

$$F = -D \frac{\partial C}{\partial x} \quad (6)$$

Where F (kg·m⁻²·s⁻¹) is the flow density, D (m²·s⁻¹) is the diffusion coefficient, or diffusivity of the penetrant in the system, assumed to be constant in all points, C is the concentration (kg·m⁻³) and x is the thickness coordinate (m).

At constant temperature, as previously seen, Henry's law describes the relation between the penetrant concentration and

its partial pressure ($C = S \cdot p$) through the sorption coefficient (S) in the material. Assuming that the quantity solubilized in the material is a linear function of the partial pressure, the flow density can be written as follows:

$$F = -D \cdot S \frac{\partial p}{\partial x} \quad (7)$$

Where $\partial p = p_2 - p_1$ is the partial pressure gradient from one side of the material to the other. For dense materials, permeation of small molecules through thin layers implies a molecular diffusion due to a chemical potential differential between the two sides of the layer (Chao et al., 1988).

Thus, for a water flow in a dense material, it can be expressed as a function of the water activity gradient ($a_w = p/p_0$):

$$F = -D \cdot S \cdot p_0 \frac{\partial a_w}{\partial x} \quad (8)$$

From this model, we can see that the mass transfer through the material depends on:

- one extrinsic parameter: the chemical potential difference, expressed in partial pressure for gases, or in activity (e.g., a_w for water);
- two intrinsic parameters: the sorption coefficient, which represents the affinity of the material for the sorbate (water) at equilibrium (thermodynamic parameter), and the diffusion coefficient, which gives information on the mobility of the diffusing molecule in the system (kinetic parameter).

In the absence of chemical interactions between the sorbent and the sorbate, the product of these last two parameters gives the permeability of the material, P :

$$P = D \cdot S \quad (9)$$

Permeation, defined by the transmission of molecules in a gaseous state through a dense material (Rogers, 1985), is described as a three-steps process (Fig. 8):

1. adsorption (either coupled, or not, to condensation) of the diffusing molecule onto the surface of the material;
2. diffusion through the material due to the difference in chemical potential;
3. desorption (either coupled, or not, to evaporation) from the other surface of the material.

Transport or barrier properties of packaging towards small molecules are generally based on the permeability value. Standard test methods have been developed for water (ASTM-Standard-E96) and oxygen (ASTM-Standard-F1927). This gravimetric method is based on mass gain measurements of these volatile molecules through a permeation cell sealed with

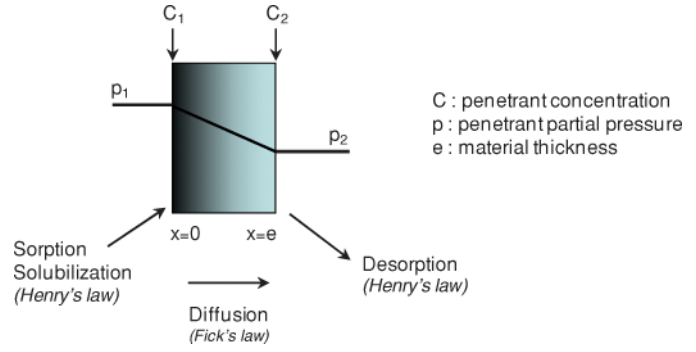


Figure 8 Simplified mechanism of permeation through a membrane, under steady state.

the tested material, under steady state, in well-defined experimental conditions (system geometry and homogeneity, temperature, absence of boundary layer, chemical potential gradient). The transmission rate (in $\text{kg} \cdot \text{m}^{-2} \cdot \text{s}^{-1}$) corresponds to the flow going through the material, or the mass transferred (Δm) per unit of time (Δt) and surface (A):

$$\text{Transmission rate} = \frac{\Delta m}{A \cdot \Delta t} \quad (10)$$

This flow also depends on partial pressure conditions applied from one side of the material to the other. Permeance establishes a relationship between the transmission rate and the partial pressure gradient $\Delta p = p_2 - p_1$ (Pa). Finally, permeability (P , in $\text{kg} \cdot \text{m}^{-1} \cdot \text{s}^{-1} \cdot \text{Pa}^{-1}$) is the product of permeance and material thickness (e):

$$\text{Permeance} = \frac{\text{Transmission rate}}{p_2 - p_1} \quad (11)$$

$$\text{Permeability} = \frac{\Delta m \cdot e}{A \cdot \Delta t \cdot (p_2 - p_1)} \quad (12)$$

Where Δm is the mass variation (kg) during Δt (s), e the material thickness (m), A the surface exposed to mass transfer (m^2) and Δp the partial pressure difference from one side of the material to the other.

The sorption process, the distribution of molecules between different phases, includes a variety of possible actions, including adsorption and absorption, trapping in microvoids, the formation of aggregates or clustering, and other mixing phenomena (Rogers, 1985). Sorption represents a thermodynamic equilibrium property of the sorbent-sorbate complex, which depends on their mutual affinity. Sorption includes adsorption, or sorption of sorbate molecules on the sorbent surface, and absorption, when molecules are sorbed into the material, but also desorption. The sorption isotherm of a sorbent-sorbate complex gives the solubility of the sorbate in the sorbent as a function of the partial pressure of the sorbate (Sing et al., 1985).

The diffusion phenomenon describes the mechanism by which molecules move from one place to another, generally

Pore diameter (μm)	Flow ($\mu\text{L}/\text{year}$)
0.001	5×10^{-10}
0.01	5×10^{-7}
0.1	5×10^{-4}
1	0.5
10	500

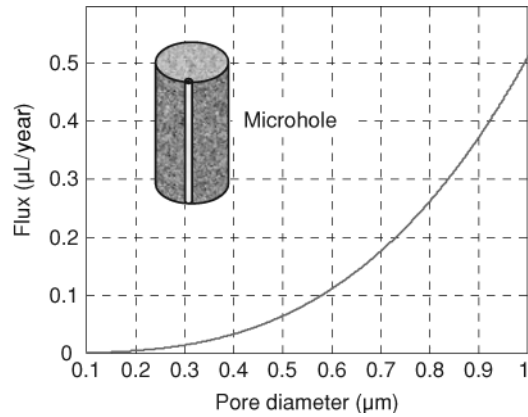


Figure 9 Oxygen flow at 20°C through a microhole, which could exist in cork material, as a function of the pore diameter, assuming Knudsen diffusion.

in a succession of random molecular motions in all space directions (Crank, 1975). Molecular diffusion can be explained by the free volume theory, in which molecules move by jumping from one equilibrium position to another within adjacent free volumes (Vrentas et al., 1976). A cohesive network needs a higher energy level for the creation of void spaces, thereby limiting this process. Crystalline regions within a material have to be bypassed by diffusing molecules (Rogers, 1985). In addition, diffusion is dependent on the medium viscosity, as expressed by the Stokes-Einstein relationship. This involves both translational diffusion, D_{trans} , the diffusion under a chemical potential (or concentration) gradient, and rotational diffusion, D_{rot} , the frequency of molecular reorientation. These diffusions can be written as follows (Le Meste et al., 1988):

$$D_{\text{trans}} = \frac{kT}{6\pi\eta r} \quad (13)$$

$$D_{\text{rot}} = \frac{kT}{8\pi\eta r^3} \quad (14)$$

Where D_{trans} = translational diffusion coefficient ($\text{m}^2 \cdot \text{s}^{-1}$); D_{rot} = rotational diffusion coefficient (s^{-1}); k = Boltzmann constant ($\text{m}^2 \cdot \text{kg} \cdot \text{s}^{-1} \cdot \text{K}^{-1}$); T = temperature (K); η = dynamic viscosity ($\text{Pa} \cdot \text{s}$ or $\text{kg} \cdot \text{m}^{-1} \cdot \text{s}^{-1}$); r = hydrodynamic radius of the diffusing molecule (m).

If it is important to determine the solubility of gases in aqueous or hydroalcoholic media, it is also crucial to experimentally assess the rate of mass transfer, expressed by the apparent diffusivity. To calculate the diffusion of oxygen in water at 25°C, for example, where $k = 1.38 \times 10^{-23} \text{ m}^2 \cdot \text{kg} \cdot \text{s}^{-1} \cdot \text{K}^{-1}$, $\eta = 10^{-3} \text{ kg} \cdot \text{m}^{-1} \cdot \text{s}^{-1}$ and $r = 1.73 \times 10^{-10} \text{ m}$, it is possible to use the Stokes-Einstein relationship that gives:

$$D_{O_2} = \frac{k \cdot T}{6 \cdot \pi \cdot \eta \cdot r} = 1.26 \times 10^{-9} \text{ m}^2 \cdot \text{s}^{-1}$$

From a macroscopic point of view, mass transfer is generally considered in terms of a chemical potential gradient, which is

the driving force behind transport process. Migration of chemical species can then be quantified as an apparent translational diffusion, D_{app} . From a steady state, mass flow can be generally described by Fick's law, as presented in Equation (6). The integration of the law of conservation of mass, which expresses the concentration (C) variation in the system, leads to the following equation in the case of a unidirectional transfer:

$$\frac{\partial C}{\partial t} = \frac{\partial}{\partial x} \left(D \frac{\partial C}{\partial x} \right) \quad (15)$$

Which can be written as $\frac{\partial C}{\partial t} = D \frac{\partial^2 C}{\partial x^2}$ when diffusivity is constant.

Nevertheless, the determination of diffusion in complex media, by imposing a chemical potential gradient to the system in order to generate a mass transfer, often includes multiple phenomena such as capillary migration, Knudsen diffusion in porous media, or the effect of gravitational forces. The diffusivity is then described by an apparent diffusion coefficient. This parameter corresponds to the kinetics of the transfer, and represents the ability of the penetrant molecule to move as a function of physico-chemical properties of the medium.

In the case of cork, the calculation of diffusivity and transfer rate through micro holes can also be determined from Knudsen equations. Since microholes are equivalent to tubular-cylindrical pores, and if the mean free path of the molecules, λ , is higher than the pore diameter, d_{pore} ($d_{\text{pore}}/\lambda < 0.2$), then the gas transfer rate (or flux) can be calculated by the Knudsen diffusion laws (which take into account the collision of gas molecules with the pore walls).

The adimensional Knudsen number, K_n , is described as the ratio of the mean free path of the molecules, λ (m), which depends on the nature of gas molecules, and the pore diameter, d_{pore} (m):

$$K_n = \frac{\lambda}{d_{\text{pore}}} \quad (16)$$

The mean free path of the gas molecules λ is the mean distance traveled between two consecutive intermolecular collisions. It is described as follows:

$$\lambda = \frac{k_B \cdot T}{p \cdot \sqrt{2} \cdot \pi \cdot d_m^2} \quad (17)$$

Where k_B is the Boltzman constant ($1.38 \times 10^{-23} \text{ J}\cdot\text{K}^{-1}$), T the temperature (K), p the partial pressure of the diffusing gas (Pa), and d_m the diameter of the diffusing molecule in accordance with the rigid sphere model (m).

As an example, d_m for oxygen is $2.98 \times 10^{-10} \text{ m}$ ($\sim 0.3 \text{ \AA}$), and the mean free path of the molecules is:

$$\begin{aligned} \lambda_{\text{oxygen}} &= \frac{1.38 \times 10^{-23} \times 293}{101325 \times \sqrt{2} \times \pi \times (2.98 \times 10^{-10})^2} \\ &= 5 \times 10^{-7} \text{ m} = 0.5 \text{ \mu m} \end{aligned}$$

If $K_n \gg 1$, or $d_{\text{pore}} < 0.1 \text{ \mu m}$, small particles undergo erratic displacements, for which kinetics are governed by collisions between gas molecules and pore walls. At this point, they can be characterized by the kinetic theory of gases. The Knudsen diffusion coefficient D_K is directly related to the pore diameter and to the mean velocity of gas particles:

$$D_K = \frac{d_{\text{pore}}}{3} \bar{v} \quad (18)$$

The mean velocity of gas particles \bar{v} is only dependent on temperature and is given by the following relation:

$$\bar{v} = \left(\frac{8 R \cdot T}{\pi M} \right)^{1/2} \quad (19)$$

Where M is the molar mass of the diffusing gas ($\text{kg}\cdot\text{mol}^{-1}$) and R the ideal gas constant ($= 8.314 \text{ N}\cdot\text{m}\cdot\text{kg}^{-1}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$)

The mean molecular velocity of the gas can be calculated either by the mean molecular velocity of the same gas at a different temperature, or using the mean molecular velocity of another gas at the same temperature:

$$\bar{v}_{atT_1} = \bar{v}_{atT_2} \cdot \left(\frac{T_1}{T_2} \right)^{1/2} \quad (20)$$

$$\bar{v}_A = \bar{v}_B \cdot \left(\frac{M_B}{M_A} \right)^{1/2} \quad (21)$$

Where the indices A and B refer to two distinct gas molecules.

The mean molecular velocity of oxygen at 20°C is $440 \text{ m}\cdot\text{s}^{-1}$.

The molar transfer rate of a gas through a pore is generally described as follows:

$$J = -D_K \frac{dC}{dx} \quad (22)$$

Where J is the flow density of gas molecules ($\text{mol}\cdot\text{m}^{-2}\cdot\text{s}^{-1}$), D_K is the Knudsen diffusion coefficient ($\text{m}^{-2}\cdot\text{s}^{-1}$), C is the molar concentration ($\text{mol}\cdot\text{L}^{-1}$), and x is the axial distance in the pore or microhole (m).

This generalized Knudsen equation can also be written:

$$J = -\frac{d}{3} \bar{v} \cdot \frac{dC}{dx} \quad (23)$$

After integration, the Knudsen molar flow through a pore of area A (m^2) is:

$$F = A \frac{D_K}{R \cdot l \cdot T} (p_{\text{int}} - p_{\text{ext}}) \quad (24)$$

Where A is the pore area (m^2) and l the pore length or the thickness of the material that includes it (m).

Then, the gas flow ($\text{mL STP}\cdot\text{s}^{-1}$) through the pore becomes:

$$F = 706 \cdot d^3 \cdot \bar{v} \frac{(p_{\text{int}} - p_{\text{ext}})}{l \cdot T} \quad (25)$$

From this equation, the volume of oxygen that permeated through a pore of 0.1 \mu m diameter in cork at 20°C can be estimated. As displayed in Fig. 9, when the pore size is doubled, the flow is increased tenfold. In addition, for pore sizes greater than 1 \mu m , the effect on oxygen mass flow becomes non-negligible in regard to potential oxidation reactions with wine constituents. Such large pores could be the result of a structural defect in the cork, either inherent to the cork material itself, or produced by the compression jaws at bottling, or even due to a structure defect of the glass bottle.

Kinetic Properties of Cork and Comparison to other Closure Systems

To ensure an appropriate seal, permeability properties of the closure are very important. These properties are obviously related to the physical properties, discussed above, that determine the quality of the cork stopper. In the field of food packaging, the permeability of materials to water or oxygen is commonly used as a means of evaluating barrier efficiency, and is often listed by suppliers as technical information. However, it should be noted that various ambiguous or confusing terms may appear in manufacturer publications. The permeability has been previously defined as the mass transfer for a given surface, thickness and partial pressure difference. The permeation rate represents

the permeability without taking into account the partial pressure difference. The permeance is the permeability with no reference to the film thickness; it is thus the inverse of the resistance to the transfer. For oxygen, the gas flow is often referred to as OTR for Oxygen Transmission Rate, which is dependent on both the thickness of the material and the partial pressure gradient.

Natural cork stoppers constitute a natural food packaging material with specific properties. As a natural product, its main drawback lies in its heterogeneity, as previously mentioned, especially in chemical composition. Other alternatives to cork, produced from various synthetic materials classically used for food packaging have been investigated during the last thirty years, especially since the 1990s. Synthetic stoppers include those obtained by injection molding (Aegis, Auscork, Beta-corque, Integra, Supremecorq, Tage) and by extrusion or co-extrusion (Néocork™, NuKork, Nomacorc®). They can be made of various olefinic thermoplastic elastomers, complexed with various additives, such as antiblocking agents, antioxidant agents, antistatic agents, lubricants, surface treatments, plasticizers, hardening agents, coloring agents, and foaming agents, which improve their mechanical properties and physico-chemical stability (Chatonnet et al., 2005). Other closures, termed technical stoppers, are formed from agglomerate or composition cork, or associate natural cork and synthetic materials (Altec® and Diam®, Neutrocork®, Twin Top®). Some of these technical stoppers (Diam®) are made of cork powder with agglomerating agents, and are moreover using supercritical fluid extraction in order to eliminate odorous compounds responsible for cork taints (Lumia et al., 2005). Another type of closure, first introduced in the 70s in Switzerland and Australia, is the metal screw cap (Stelvin®, Supervin). It consists of an aluminum outer shell and a liner composed of synthetic barrier materials such as polyvinylidene chloride, aluminum and polyethylene. Unlike other alternative closures, the screw cap requires the use of a specially designed bottle.

In terms of oxygen barrier properties of closures, it is interesting to compare the permeability to oxygen of the different closure materials, whether synthetic or natural. Table 6 summarizes oxygen permeability values, measured for various food packaging, to enological packaging materials, in the decreasing order of their oxygen barrier performance (Greener Donhowe et al., 1993; Sanchez et al., 1998; Massey, 2003). Permeabilities range from $1.6 \times 10^{-21} \text{ kg}\cdot\text{m}^{-1}\cdot\text{s}^{-1}\cdot\text{Pa}^{-1}$ for ethylene vinyl alcohol, the most impermeable material, to $5.5 \times 10^{-11} \text{ kg}\cdot\text{m}^{-1}\cdot\text{s}^{-1}\cdot\text{Pa}^{-1}$ for natural cork. These values are usually obtained in reference to the active standard (ASTM-Standard-F1927) which requires the use of a coulometric sensor to determine the oxygen transmission rate through a dry package at 23°C temperature, 0% relative humidity and a 0–100% oxygen gradient. In order to compare the oxygen permeability of various materials, it is critical to run analyses under identical environmental conditions. As clearly displayed in Table 6, oxygen permeability measured under standard conditions is very low for EVOH or PVDC, around $10^{-21} \text{ kg}\cdot\text{m}^{-1}\cdot\text{s}^{-1}\cdot\text{Pa}^{-1}$. Other classical synthetic materials, such as PC, PP, PE, PVC, and

PET, display oxygen permeability in the range 10^{-17} to $10^{-19} \text{ kg}\cdot\text{m}^{-1}\cdot\text{s}^{-1}\cdot\text{Pa}^{-1}$. Natural cork stoppers or technical stoppers show rather high oxygen permeability values compared to these synthetic packaging materials. Nevertheless, permeability measurements could be highly dependent on the environmental conditions. The increase of the relative humidity from 0 to 100% (which better corresponds to an application of moist products) only leads to a slight modification of the oxygen permeability of hydrophobic materials, such as PET, but has a considerable effect on the increase of the oxygen permeability of hydrophilic materials, such as EVOH or cellophane. Water is indeed the most widespread plasticizer and tends to favor the loosening of polymer networks. Temperature is another external factor which can lead to a decrease or increase of the permeability of packaging materials.

While the oxygen barrier properties of synthetic materials appear to be better than those of cork, the closures made from these materials often do not perform well, and generally lead to more rapid oxidation of wines (Godden et al., 2005). The reproduction of a cellular structure similar to that of cork, which exhibits the closely-linked attributes of appropriate impermeability and mechanical properties is not so trivial to achieve.

Oxygen permeability values obtained by Sanchez et al. (1998) on natural cork and technical stoppers using pressure measurements, showed a high heterogeneity for natural cork compared to technical stoppers, even for stoppers of a same batch. Such variability could be a possible explanation for the seemingly random oxidation observed in white wines. The permeability of technical stoppers lies in the lowest end of the permeability range of natural cork stoppers. As this permeability describes the rate at which oxygen can migrate through the cork matrix, it can be used in Eq. 12 ($\text{Flux} = \frac{\text{Permeability} \times \Delta p_{O_2}}{\text{thickness}}$), to calculate oxygen flux through the stopper material, assuming an oxygen gradient $\Delta p_{O_2} = 0\% - 21\% \text{ O}_2$, a diameter of 20 mm diameter and a thickness of 45 mm. The flux of natural cork stoppers, with a permeability range between 8.1×10^{-14} and $5.5 \times 10^{-11} \text{ kg}\cdot\text{m}^{-1}\cdot\text{s}^{-1}\cdot\text{Pa}^{-1}$, can be estimated between 3.9×10^{-8} to $2.6 \times 10^{-5} \text{ kg}\cdot\text{m}^{-2}\cdot\text{s}^{-1}$, which is equivalent to 33 mg to 21 g oxygen for a 30 day-period for the cork surface exposed to the transfer. In practice, this translates anywhere from an irrelevant to considerable quantity of oxygen transferred over the course of one year, between 0.4 and 256 g. Nevertheless, this permeability value is susceptible to variation during normal use, as a natural cork stopper operates under high relative humidity conditions, and with a high compression level, once inserted in the bottleneck.

It is also of note that surface treatments classically used for stoppers, or agglomerating agents, have lower oxygen permeabilities than cork. For this reason, unless there are defects in the surface coating, mass transfers are more likely to occur through the cork itself. This has been illustrated by Keenan et al. (1999) who concluded that the permeability of macrocrystalline paraffin wax film of 17 μm thickness, applied on cork as a uniform coating layer would not allow enough oxygen ingress to obtain the oxidation phenomena observed by following SO_2

Table 6 Oxygen permeability for various synthetic materials classically used as food packaging, and comparison of their barrier performance to materials used for stoppers in the enological field

Classical food packaging materials	Enological materials	$P_{O_2}(\text{kg}\cdot\text{m}^{-1}\cdot\text{s}^{-1}\cdot\text{Pa}^{-1})$	$T(^{\circ}\text{C})$	RH (%)
EVOH (biaxially oriented)	—	1.6×10^{-21}	20	65
		2.4×10^{-20}	20	100
		2.0×10^{-22}	5	0
		1.6×10^{-21}	23	0
		1.6×10^{-21}	35	0
PVDC	—	4.9×10^{-21}	50	0
		1.6×10^{-21} to 7.7×10^{-20}	23	75
Cellophane	—	3.3×10^{-20} to 5.1×10^{-20}	20	65
		1.3×10^{-19}	20	100
Epoxy thermoplastic (epoxy resin)	—	5.1×10^{-20}	23	0
		1.5×10^{-19} to 3.9×10^{-19}	25	0
PET (oriented)	—	1.9×10^{-19}	20	65
		1.9×10^{-19}	20	100
		4.2×10^{-20}	5	0
		1.5×10^{-19}	23	0
		3.3×10^{-19}	35	0
PVC (rigid)	—	1.1×10^{-18}	50	0
		3.2×10^{-19} to 1.3×10^{-18}	23	50
PVC (plasticized)	—	1.7×10^{-18} to 1.3×10^{-16}	23	50
HDPE	—	7.2×10^{-18} to 1.2×10^{-17}	23	0
LDPE	—	2.4×10^{-17} to 3.3×10^{-17}	23	0
OPP	—	1.0×10^{-17}	23	0
PP	—	1.6×10^{-17}	23	0
PC	—	1.5×10^{-17} to 2.0×10^{-17}	23	0
—	Macrocrystalline wax	6.2×10^{-18}	22	55
—	Microcrystalline wax	2.5×10^{-17}	25	0
Olefinic Thermoplastic Elastomers	—	2.1×10^{-17}	23	50
Polyurethane	—	1.3×10^{-17}	25	0
Polyether	—	2.1×10^{-16} to 2.6×10^{-15}	23	0
—	Silicone	6.4×10^{-16} to 3.2×10^{-15}	25	0
—	Technical stopper	8.4×10^{-14} to 2.2×10^{-13}	25	0
—	Natural cork stopper	8.1×10^{-14} to 5.5×10^{-11}	25	0

EVOH = Ethylene vinyl alcohol; PVDC = polyvinylidene chloride; PET = polyethylene terephthalate; PVC = polyvinyl chloride; HDPE = high density polyethylene; LDPE = low density polyethylene; OPP = oriented polypropylene; PP = polypropylene; PC = polycarbonate.

References: Massey (2003), Greener Donhowe et al. (1993) for waxes, and Sanchez et al. (1998) for stoppers.

consumption over time (assuming a direct relationship with oxygen permeation).

How should Kinetic Properties of the Closure, and the Effect of Environmental Parameters, be Assessed?

The oxygen permeability of cork closures has been investigated by different means, including both direct methods and indirect methods using reactive reference molecules. Some confusion can arise, however, if all experimental conditions (mainly environmental) are not rigorously specified, or when the resulting data represents a flux rather than actual permeability. As recommended by the active standard (ASTM-Standard-F1927), it is possible to use a coulometric sensor to determine the oxygen transmission rate. This rate is only defined for dry packaging, however, which means a 0% relative humidity environment. This is obviously not the case for closure in contact with the wine, and even when the headspace remains in vertical storage, the relative humidity is at or around 100%. For this reason, such permeability data are useful for comparison measurements be-

tween different closures, but are invalid for predicting oxygen barrier performance in a moist environment. This is especially true for materials susceptible to water adsorption, since the liquid can act as a plasticizer even in small amounts.

Using the ASTM method, Godden et al. (2005) found permeation rates ranging between 0.0001 and 0.1753 mg/day—a thousand-fold variation—with a mean around 0.0256 mg/day for a natural cork closure. In contrast, permeation rates ranged only from 0.0010 to 0.0019 mg/day for a technical cork closure. For comparison, Keenan et al. (1999) estimated the permeation rate of a cork closure at around 0.0024 mg/day for a natural cork closure, calculated from the loss of sulfur dioxide in wine. This estimation is also questionable to an extent, since sulfur dioxide can be consumed by multiple chemical reactions pathways in wine, and is not solely lost through reactions with reactive oxygen species resulting from oxygen permeation through the cork closure (Boulton et al., 1996b). Lopes et al. (2005) developed a non-destructive colorimetric method to determine the permeation rate of oxygen through closures into bottles during the postbottling period. This method is based on the color change (from yellow to indigo blue) of an aqueous solution of indigo

carmines, initially reduced and then re-oxidized by oxygen introduction into the bottle through the closure. Using appropriate calibration and a color measurement, it is possible to estimate the quantity of oxygen that has passed through the closure, and to thereafter calculate a permeation rate. The detection limit, which does not produce detectable color change, is below $1 \text{ mg}\cdot\text{L}^{-1}$ of dissolved oxygen, or a total of 0.75 mg of oxygen, permeating through the closure into the bottle. In data taken for natural cork closures, permeation rates ranged from 0.0001 up to 0.0643 mg/day (Lopes et al., 2005; Lopes et al., 2006), which remains highly variable, but in the same order of magnitude as previously cited studies. This analysis is very useful, in that it allows the determination of oxygen transfer through cork closures in conditions very similar to those found in everyday use. However, if the solution used has a high relative humidity, it may be very different from wine which contains numerous solutes and volatiles. In this case, the wine may modify the oxygen barrier properties of the closure, either by formation of crystals on the closure surface, or by sorption of other volatile compounds into the material. In addition, these two direct methods (coulometric or colorimetric) give an overall permeation rate of oxygen through the closure, but the mechanism of oxygen permeation that could result from sorption, diffusion, or both phenomena still has to be investigated.

An interesting aspect of oxygen transfer through cork is its evolution over time post-bottling. Using the method described previously, Lopes et al. (2006) showed that the rate of transfer through natural cork stoppers depends on time, with measurements varying from 0.0357 to 0.0643 mg/day during the first month of storage, from 0.0001 to 0.0087 mg/day between the 2nd and 12th month, and from 0.0001 to 0.0063 mg/day between the 12th and the 36th month. This suggests a decrease in the permeability of the cork closure over time. It could be inferred that the high permeability observed during the initial period is due to a rapid diffusion of the oxygen initially contained in the cork closure, and not to permeation through the cork. Brajkovich et al. (2005) reported a similar tendency looking at the decrease of total and free SO_2 of wine (Sauvignon Blanc) over time as a function of the closure type. The decrease in the antioxidant concentration was found to be higher during the first four months than during the following 4th to 10th months and the 10th to 23rd months. The comparison is not exact, however, as an additional parameter is involved; the initial concentration of dissolved oxygen in wine can have a positive effect on the SO_2 consumption during the first aging period, but is irrelevant in permeability measurements.

Another parameter to consider during the postbottling period is the position of the bottle during storage. Horizontal or vertical storage leads to mass transfer either in the gaseous or liquid state, respectively. While several studies on this subject exist, observations differ. First, it should be noted that the relative humidity in the vapor phase above water is close to one, and should thus be similar to a liquid water contact. For some materials, however, a difference exists between adsorption from the saturated vapor and from pure liquid of the same solvent. A good

example of this phenomenon, known as Schroeder's paradox, is the sorption of 2-propanol by silicon (Vallieres et al., 2006). Sorption of wine is even more complex. If there is no direct contact, as in vertical storage, only volatile organic compounds can move through the liquid-gas interface into the headspace and reach the gas-solid interface between headspace and cork. In the case of horizontal storage, when direct contact occurs, there is potential for both interaction at the liquid-solid interface and transfer into the gaseous state within the cork itself. In addition, other nonvolatile compounds can migrate from wine to cork and from cork to wine. In a study on wine storage, Puech et al. (2006) focused on the effect of three parameters, bottle position, light, and temperature on red wine oxidation (as measured by SO_2 analysis), and showed that temperature seems to be the only relevant parameter influencing oxidation. Lopes et al. (2006) also found no significant differences in the oxygen permeation rate through natural cork closures for bottles in horizontal or vertical positions during 36 months of storage. In another study, Skouroumounis et al. (2005a) also reported no significant effect of bottle orientation during storage on the composition and sensory properties of Riesling and Chardonnay wines over a five-year period. In contrast, using chemical and sensory analysis performed along 24 months, Mas et al. (2002) concluded that wines were best preserved when bottles were stored horizontally rather than vertically. Thus, at present, there is no consensus on the effect of the bottle position on oxygen mass transfer and wine aging over time.

The permeation property of a sealing system is sometimes difficult to assess, but some indicators that correlate to oxidation phenomena may be useful for characterization. In white wines, for instance, the absorbance at 420 nm gives a good idea of the overall oxidation state (Singleton et al., 1976; Manzocco et al., 1999). This oxidation level, as estimated by color (extent of browning at 420 nm), also correlates linearly with the decrease of SO_2 concentration in the wine (Waters et al., 1996; Chatonnet et al., 2003; Godden et al., 2005). It remains, however, an overall measurement of specific consequences of oxidation reactions occurring in wine. In addition to the reaction between SO_2 and oxygen in the liquid phase, the loss of total SO_2 also involves different parallel reactions or transfer schemes; these include loss as vapor through the closure, the formation of strongly bound compounds (such as with aldehydes, quinones, or keto acids), and the slow oxidation of SO_2 by previously oxidized phenols (Boulton et al., 1996b). Thus, in addition to the absorbance at 420 nm, the total SO_2 level in white wines acts as an additional measurement indicating the progress of oxidation. Chatonnet et al. (2003) reported no evident relationship between the oxidative process, as measured by the loss of SO_2 and the total thiol content, although thiols are highly reactive towards radical oxygen species. There is, however, a suspected correlation between the loss of SO_2 and the increase in furanic derivatives and in sotolon. In addition, various sensory attributes correlate strongly with both the SO_2 concentration and the absorbance at 420 nm. For a dry white Semillon wine, for example, high ratings for overall fruit and

Table 7 Oxygen transmission rate, expressed in mg of oxygen permeating per stopper and per year, for different types of closures used for wine bottling, including natural cork, technical stopper, synthetic stopper, screw cap and bottle cap

Type of closure	Oxygen Transmission Rate (mg O ₂ /stopper/year)	O ₂ gradient (%)	Time	Method (detection)	T (°C)	RH (%)	References*
Natural cork	40.67 to 43.28	—	—	Coulometric	23	Ambient	5
Natural cork	2.19 (±1.46) to 4.56 (±2.74)	0–21	Over 2 to 12 months	Colorimetric	20	65	3
Natural cork	0.05 to 1.41	0–21	Over 2 to 24 months	Colorimetric	20	65	4
Natural cork	0.87	0–21	Over 22 months	Loss of SO ₂	13 to 31	—	2
Natural cork	9.33 (0.05 to 64)	—	After 36 months postbottling	Coulometric	—	—	1
Technical cork "Altec"	0.52 (0.37 to 0.68)	—	After 36 months postbottling	Coulometric	—	—	1
Technical cork (agglomerate)	0.09 (± 0.18)	0–21	Over 2 to 12 months	Colorimetric	20	65	3
Technical cork "Neutrocork"	0.91 (± 0.18)	0–21	Over 2 to 12 months	Colorimetric	20	65	3
Technical cork "Twin Top"	0.18 (± 0.09)	0–21	Over 2 to 12 months	Colorimetric	20	65	3
Technical cork (agglomerate)	0.05 to 0.47	0–21	Over 2 to 24 months	Colorimetric	20	65	4
Synthetic "Supremecorq"	13.69 (± 3.10)	0–21	Over 2 to 12 months	Colorimetric	20	65	3
Synthetic "Supremecorq"	5.94 to 6.36	0–21	Over 2 to 24 months	Colorimetric	20	65	4
Synthetic "Namacorc"	7.76 (± 2.28)	0–21	Over 2 to 12 months	Colorimetric	20	65	3
Synthetic "Namacorc"	4.07 to 4.69	0–21	Over 2 to 24 months	Colorimetric	20	65	4
Synthetic (without diaphragm)	15.64 to 19.81	—	—	Coulometric	23	Ambient	5
Synthetic (with double diaphragm)	7.82 to 8.86	—	—	Coulometric	23	Ambient	5
Screw cap "ROTE"	0.61	0–21	Over 22 months	Loss of SO ₂	13 to 31	—	2
Screw cap "ROTE"	0.26 (0.10 to 0.42)	—	After 36 months postbottling	Coulometric	—	—	1
Bottle cap (Champagne)	1.20 to 2.19	—	—	—	—	—	7
Bottle cap (Champagne)	0.31 to 0.99	0–21	—	Coulometric	—	—	6
Bottle cap (Champagne)	1.51 to 4.69	0–100	—	Coulometric	—	—	6

T = Temperature; RH = Relative Humidity; — = unknown.

*References: 1 = Godden et al., 2005; 2 = Keenan et al., 1999; 3 = Lopes et al., 2005; 4 = Lopes et al., 2006; 5 = Silva et al., 2003; 6 = Valade et al., 2007; 7 = Vasserot et al., 2001.

citrus aromas correlate with high SO₂ concentrations and low absorbance values; in contrast, oxidized aromas correspond to low SO₂ concentrations and high absorbance values (Godden et al., 2005). All of these techniques, however, result in the destruction of the cork closure, with the exception of absorbance measurements made through the bottle (Skouroumounis et al., 2003). The Nuclear Magnetic Resonance spectroscopy appears to be a promising non-destructive means for identification and quantification of certain compounds present in an unopened wine bottle, and has been used successfully to measure acetic acid in bottled wine (Weekley et al., 2003).

A comparison of the oxygen barrier performances between closing systems, including natural cork stoppers, agglomerated

cork stoppers, synthetic closures, and screw cap closures, has been reported by several authors. Table 7 displays an overview of the primary studies in this field. Even when synthetic materials, such as polyethylene, present efficient oxygen barriers when used in thin sheets (Table 6), the processing necessary to produce a synthetic stopper of the same material results in modified permeability properties. As displayed in Table 7, synthetic stoppers are the worst barriers to oxygen transfer when compared to the other types of wine bottle closures. Due to the potential for high rates of oxygen transfer, it is generally thought that synthetic stoppers are only useful for wines consumed less than two years after bottling. While natural cork is less permeable to oxygen, as a biological product its

composition is highly variable, as shown in measurements performed both in different studies, and on different batches during a single experiment (Table 7). This high variability in permeability of natural cork stoppers from various origins, and even within a given batch of cork, could explain the variability and sporadic nature of the observed oxidation phenomena of bottled wine (Caloghiris et al., 1997). Ultimately, the best barriers to limit oxygen transfer into wine through the closure are bottle caps and screw caps, and with technical cork stoppers ranking second. This theory has been confirmed by Godden et al. (2005) and to a lesser extent by the works of Mas et al. (2002), Chatonnet et al. (2003) and Brajkovich et al. (2005), all of which showed the same classification for closure performance according to the decrease in the SO₂ level and the increase of the absorbance at 420 nm. The near-complete oxygen barrier provided by bottle and screw caps can, however, create additional problems, and may lead to negative sensory attributes such as the rubber and flint aroma associated with reduction phenomena. As technical materials offer the best homogeneity, it is likely that they will be key elements for the development of new barrier or functional packaging materials specifically designed for wine.

CONCLUSION

The wide spectrum of chemical species present in wine makes it a very complex media with the potential for numerous complex interactions. A step-by-step identification, using simple model systems, of the mechanisms implicated in chemical oxidation processes has been underway for at least three decades, with particular emphasis on phenolic compounds, especially flavonoids and their subsequent polymers. The complexity of this phenomenon makes it difficult to identify and to characterize all intermediate reaction products involved in oxidation processes, even in simplified model wine solutions. In addition to the usual parameters influencing oxidation rate, such as temperature, light, and pH, the presence of metallic cations in wine has been specifically identified as playing an important catalytic role. Further, as the global oxidation mechanism occurring in wine is not only the sum of individually identifiable chemical reaction pathways, it remains difficult to extrapolate to such a higher level of complexity. Several studies have approached the problem of oxidation measurement from a more holistic point of view, investigating the influence of various parameters on the rate of the oxidation process as determined by more universal measurements. From a practical point of view, oxygen mass transfer has been analyzed throughout the wine elaboration process, and for each distinct winemaking operation. While wine can never be completely protected from oxygen, most researchers advocate maximum protection of must and wine during the processing throughout, and especially during bottling, which can be a critical time for oxygen ingress. In terms of oxygen solubility and mass transfer post-bottling, multiple factors must be considered, such as temperature and its effects on solubility and reaction rate, fill height, and gas

composition in the headspace. It is, however, extremely difficult to estimate the aging potential of wine as a function of, for example, its composition or other physico-chemical parameters. Determining the amount of oxygen needed by a given wine type would represent a huge step towards improving wine quality, and would involve finding a specific, measurable molecular parameter in wine which can be correlated to sensory scale ranging from reductive to oxidative. The oxygen barrier property of a closure is also very difficult to assess. While knowledge of this parameter is limited and few studies have been performed, oxidation reactions are assumed to play a dominant role in wine aging, and seem to be related to measured values of oxygen transfer through various types of closures. As a natural material, cork characteristically shows high variability in terms of oxygen permeability. Cork evinces superior sealing properties, the mechanics of which are not completely understood, but it is known to be considered favorably by the consumer, and even conveys the perception of wine quality (Marin et al., 2007). Overall, wine closures must be considered a unique type of food packaging, and it may be of interest to investigate, in a more detailed way, the relationship of a closure's permeability properties and the chemical reactions occurring in wine. This would allow the efficiency of each closure to be extrapolated through the use of mathematical modeling (Barron et al., 1993), and could include, in an integrated approach, other important factors such as temperature. Ultimately, such work would be key to obtaining a predictive tool to improve wine production and quality.

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