

Introduction

The wine is the most consumed alcoholic beverage in the world. There are different winemaking methods, each one meeting the criteria desired by the producer and meeting consumer's requirements and expectations.

One of the main difficulties of this winemaking process is to control the gas exchange during all the process and especially before the bottling. There are different methods to dose, adjust the amount of gas in the wine, which are more or less expensive and efficient.

Introduced for ten years, membrane becomes an important tool in the food industry, especially for beer, soft drinks and fruit juice.

Today there was a new interest in using the membrane contactor (MC) to optimize the gas exchange in wine. A MC is a module consisting of hydrophobic hollow fiber membranes. Usually, the gas circulates inside the fibers (lumenside) while the wine circulates outside the fibers (shellside) in the opposite direction. And it is by a difference in concentrations and partial pressures of the gases on either side of the membrane that the gas exchange is done.

Firstly, it is important to measure the oxygen (O₂) and carbon dioxide (CO₂) content and to define the levels to be achieved before to adjust dissolved gases. In most cases, O₂ must be removed to prevent wine oxidation. On the contrary, CO₂ must be adjusted to a concentration appropriate to the desired wine style. In rosé and white wines, the CO₂ concentration is raised, while for the reds the CO₂ is removed (but not totally), which is often in excess.

Also the interest of the use of MC in semi-sparkling and sparkling wines (not Champagne where the bubbling is caused by a second fermentation in bottle) is more and more important, because it allows to obtain a drink with very fine bubbles and significantly different from that which can be obtained by carbonizing a wine with a simple gas injector.

So this bibliographic report aims to present MC technology allowing the control of dissolved gases in wine. It includes a whole theoretical part concerning the generalities on the gas exchanges, the flows of gas through the membrane, the resistance of the membrane, etc., then a more in-depth part on the MC and its use, on the various operating modes to follow depending on the desired objective. On the other hand, some generalities on the different applications and fields of action of MC will be mentioned, and finally a last part concerning the characteristics of the membrane.

1 Theoretical Background on Gases and Gas Exchange in Wine

1.1 Laws of Gases

1.1.1 Law of BOYLE-MARIOTTE

According to the law of BOYLE-MARIOTTE, the product of the pressure (p) and the volume (V) of ideal gases is constant:

$$P * V = const \quad (1)$$

P Pressure [Pa]

V Volume [m³]

1.1.2 Law of GAY-LUSSAC

The law of GAY-LUSSAC states that the volume (V) is proportional to the temperature (T) in K equation (2):

$$\frac{V}{T} = const \quad (2)$$

T Temperature [K]

1.1.3 Law of Ideal Gases

The Law of Ideal Gases is derived from the two gas laws cited ahead. The gas describes the relation of pressure (P), volume (V) and temperature (T) in Kelvin. This law gives a very good approximation of reality under normal conditions especially for the gases Nitrogen (N₂) and Oxygen (O₂) equations (3), (4):

$$P.V = n.R.T \quad (3)$$

$$\frac{P * V}{T} = const \quad (4)$$

R Universal gas constant [8.314 J.K⁻¹.mol⁻¹]

Solving this equation for one mole of ideal gas at normal conditions 0 °C = 273.15 K and 101.325 kPa pressure one mole gives the volume of 22.414 L (24.054 L at 20 °C) (5).

$$V_{T=0^{\circ}C} = \frac{n.R.T}{P} = \frac{1 * 8.314 * 273.15}{101325} = 22.414 L \quad (5)$$

1.1.4 Law of DALTON

DALTON's law states, that the total pressure P from a gaseous mixture is equal to the sum of partial pressures of each individual component in the gas mixture (equation (6)).

$$P = \sum_i p_i \quad (6)$$

P Total pressure [Pa]

p_i Partial pressure of the gas i [Pa]

1.1.5 Law of HENRY

HENRY's law is describing the solubility of a gas in a liquid. At a constant temperature, the amount of a given gas dissolved in a given type and volume of liquid is directly proportional to the partial pressure of that gas in equilibrium with that liquid (equation (7)).

$$p_i = H_i * C \quad (7)$$

H_i HENRY's constant of the gas i , or solubility coefficient for the gas i [Pa.m³.mol⁻¹]

C Concentration of gas i in liquid at equilibrium [mol.m⁻³]

Many different units for describing the HENRY's law constant exist; the following paragraph tries to give an overview about the units used and gives indications for conversion between the different units. All explained units can be frequently found depending on the application, one way of using the HENRY's law constant might be more useful than the other.

1.1.5.1 Henry Constant SI Unit [Pa.m³.mol⁻¹]

The given partial pressure if one mole is dissolved per m³. This unit can be directly used for the conventional HENRY's law equation (6) and is the official SI unit.

1.1.5.2 Alternative Unit [Mol.m⁻³.atm⁻¹]

The number of moles that are dissolved under a partial pressure of one atmosphere (101.325 kPa) of the gas is given by this unity.

The transfer to the SI unit can be done by the calculation (8):

$$[\text{Pa} \cdot \text{m}^3 \cdot \text{mol}^{-1}] = \frac{1 \text{ atm}}{\text{mol} \cdot \text{m}^{-3} \cdot \text{atm}^{-1}} * 101325 \text{ Pa} \quad (8)$$

This unit is frequently used as it gives a fast information on the solubility of a gas under 100% air atmosphere.

1.1.5.3 Solubility and VAN'T HOFF equation

For many compounds the solubility is expressed in mg.L^{-1} under pure air atmosphere. It can be easily transferred from $[\text{mol.atm}^{-1}]$ by multiplying with the molecular mass of the compound.

Sander (1999) uses a thermodynamic expression (equation (10)), usually associated with the name VAN'T HOFF, relates the HENRY's constant at the two absolute temperatures T_0 (reference temperature 25°C) and T (Table 1).

$$\frac{-d\ln(H_{i(T_0)})}{d(1/T)} = \frac{\Delta H_{sol}}{R} \rightarrow \frac{H_{i(T)}}{H_{i(T_0)}} = \exp\left[\left(-\frac{\Delta H_{sol}}{R}\right) * \left(\frac{1}{T} - \frac{1}{T_0}\right)\right] \quad (9)$$

$$H_{i(T)} = H_{i(T_0)} * e^{\left(-\frac{\Delta H_{sol}}{R} * \left(\frac{1}{T} - \frac{1}{T_0}\right)\right)} \quad (10)$$

Where ΔH_{sol} = enthalpy of solution.

This equation is used for systems near ambient temperature.

Table 1: Enthalpy and solubility of O_2 , CO_2 and N_2 at 20°C and 25°C in water under pure atmosphere from Sander, 1999.

At $T=20^\circ\text{C}$	Ref.	$\Delta H_{sol}/R$	ΔH_{sol}	$H_{i(T_0)}$	$H_{i(T=20^\circ\text{C})}$		Solubility
		(K)	(J/mol)		($\text{Pa.m}^3.\text{mol}^{-1}$)	($10^3.\text{Pa.m}^3.\text{kg}^{-1}$)	
O_2	¹	1700	14134	77942	71533	2235.41	45.33
	²	1500	12471		70719	2209.97	45.85
CO_2	²	2400	19954	2980	2597	59.02	1716.71
	³	2200	18291	2814	2481	56.39	1796.98
	⁴	2394	19900	2972	2592	58.901	1720.02
N_2	⁵	1300	10808	155885	144681	5167.18	19.6

¹Dean (1992), ²Lide and Frederikse (1995), ³Zhen and al. (1997), ⁴Liger-Belair (2005), ⁵Wilhelm and al. (1977)

1.1.5.4 Partition Coefficient k_i Dimensionless $[\text{L.L}^{-1}]$ or $[\text{mol.mol}^{-1}]$

The partition coefficient is defined as the number of molecules in the gas phase divided by the number of molecules in the liquid phase of the same volume under the same conditions. The coefficient is giving practical information about the distribution of a compound in the gas phase compared with the liquid phase.

The unit conversion from SI unit can be done by the following process:

- a) Calculating the volume needed for one mole in air expecting ideal gas behavior:

$$V = \frac{n * R * T}{P} \quad (11)$$

- b) One liter is containing $1/V$, mole at 20°C : $1/24.054 \text{ L} = 0.0416 \text{ mol.L}^{-1}$
 c) Dividing this by the solubility in mol.L^{-1} is giving the partition coefficient.

1.1.5.5 Bunsen Absorption Coefficient α : [-] or $[\text{L.L}^{-1}]$ or $[\text{mol.mol}^{-1}]$

The Bunsen coefficient is defined as the volume of the gas dissolved by unit volume of the solvent at the given temperature under a partial pressure of one atmosphere of the gas. The unit is dimensionless. This unit was frequently used in older publications for solubility of gases. It is different from the partition coefficient as the reference volume of the gas is in normal conditions ($1 \text{ atm}/0^{\circ}\text{C}$).

The fraction in the gas phase contains $1/22.414 \text{ L} = 0.0446 \text{ mol.L}^{-1}$ as one mole is taking 22.414 L under normal conditions (0°C ; 101.325 kPa).

Table 2 is giving an overview about the different HENRY constants and expressions for solubility for the three main gases nitrogen, oxygen and carbon dioxide in water at 20°C and under normal pressure were applicable.

Table 2: HENRY constants and solubility of the three main gases at 20°C in water under pure atmosphere and 101.325 kPa pressures

Gas	Solubility [mg.L^{-1}]	H [$\text{Pa.m}^3.\text{mol}^{-1}$]	Partition coefficient	α
Oxygen	45.3	71533	30.1	32.3
Nitrogen	19.6	144681	59.4	63.7
Carbon dioxide	1797	2481	1.08	1.15

Example of solubility conversion

$$\text{Pa.m}^3.\text{mol}^{-1} \rightarrow \text{mg.L}^{-1}$$

$$\text{Solubility } (\text{Pa.m}^3.\text{mol}^{-1}) \div \text{Patm}(\text{Pa}) = \text{m}^3.\text{mol}^{-1}$$

$$\frac{1}{\dots} = \text{mol.m}^{-3}$$

$$\dots * M(\text{g.mol}^{-1}) = \text{mg.L}^{-1}$$

$$\text{Pa.m}^3.\text{mol}^{-1} \rightarrow \text{Pa.m}^3.\text{kg}^{-1}$$

$$\text{Pa.m}^3.\text{mol}^{-1} = \frac{\text{Pa.m}^3.\text{mol}^{-1}}{M(\text{kg.mol}^{-1})} = \text{Pa.m}^3.\text{kg}^{-1}$$

Transport through a dense polymer can be considered as an activated process, which can be represented by an ARRHENIUS-type equation. This implies that the temperature can have a considerable effect on the speed of transport. Equations (12) and (13) express this dependence of diffusion coefficient and solubility coefficient on temperature:

$$D = D_{(T=0^{\circ}C)} * e^{\left(\frac{-E_A}{R.T}\right)} \quad (12)$$

$$S = S_{(T=0^{\circ}C)} * e^{\left(\frac{-\Delta(H_S)}{R.T}\right)} \quad (13)$$

E_A Activation energy for diffusion

D Diffusion coefficient

R Universal gas constant [8.314 J.K⁻¹.mol⁻¹]

ΔH Dissolution heat at constant pressure and T [kJ.mol⁻¹]

T Temperature [K]

S Solubility coefficient

1.1.6 Law of FICK and Diffusion

FICK'S law is describing diffusion processes. Diffusion is the thermal motion of particles at temperatures above absolute zero. It is dependent of temperature, viscosity of the fluid and the size of the particle (Lide 2004). FICK'S first law is describing this diffusion process mathematically with the diffusion coefficient D . The flow is proportional to the diffusion coefficient D [m².s⁻¹] and the inverse of the concentration gradient $\frac{\partial c}{\partial x}$ (Equation (14)). In the second FICK'S law of diffusion it is described (equation (15)), that the change of concentration over time is dependent on the area, time and the diffusion coefficient. Some practical simplifications of the FICK'S laws are leading to a simplified model using the overall mass transfer coefficient k_L which reduces the complex diffusion process to a simple mass transfer problem, ignoring all other input factors (equation (16)). The mass transfer coefficient k_L is the constant that is typical for each combination of compounds and temperature. In some cases even further simplification is necessary as the transfer area is not precisely known and instead of the mass transfer coefficient (k_L) and area (A), the volumic transfer coefficient ($k_L a$) is used, that describes the transfer capacity of the entire system (equation (17)) (Devatine and Mietton-Peuchot 2009).

$$F = -D * \frac{\partial c}{\partial x} \quad (14)$$

$$\frac{\partial c}{\partial t} = D * \frac{\partial^2 c}{\partial^2 x} \quad (15)$$

$$F = k_L * A * (\Delta C) \quad (16)$$

$$F = k_L a * (\Delta C) \quad (17)$$

F	Flow [mol.m ⁻² .s ⁻¹]
D	Diffusion coefficient [m ² .s ⁻¹]
$\frac{\partial c}{\partial x}$	Concentration gradient [mol.m ⁻⁴]
$\frac{\partial c}{\partial t}$	Concentration change per time [mol.s ⁻¹]
k_L	Overall mass transfer coefficient [m.s ⁻¹]
$k_L a$	Volumic transfer coefficient [s ⁻¹]
A	Area [m ²]
ΔC	Difference of the concentration of the compound [mol.m ⁻²]

1.1.7 Diffusion Coefficients

For diffusion within liquids the diffusion coefficient D is used, relation equation (18), we obtain:

$$D = D_{(T=0^\circ C)} * e^{\left(\frac{\Delta H_{eq}}{R.T}\right)} \quad (18)$$

D	Diffusion coefficient [m ² .s ⁻¹]
D_0	Constant depending on the diffusion environment [m ² .s ⁻¹]
R	Universal gas constant [8.314 J.K ⁻¹ .mol ⁻¹]
ΔH	Constant standard enthalpy [kJ.mol ⁻¹]
T	Temperature [K]

The diffusion coefficient (D) of carbon dioxide in water, dependent of temperature can be expressed with the following equation (19) (Mavroudi, Kaldis, & Sakellaropoulos, 2006; Siminiceanu & Bouallou, 2008):

$$D_{CO_2} = 2.35.10^{-6} * e^{\left(\frac{2119}{T}\right)} \quad (19)$$

We can deduct using the equation (15):

$$\Delta H_{(CO_2)in\ water} = 2119 * 8,314 = 17617,38\ J.mol^{-1}$$

At 25 °C, this equals a diffusion coefficient of CO₂ 1.92.10⁻⁹ m².s⁻¹ which is the same as stated by E. L. Cussler (1997).

Table 3: Gas diffusion coefficient in water at 20, and 25 °C from the Handbook of Chemistry and Physics, 85TH Edition, 2004-2005

Gas	Diffusion coefficient [.10 ⁻⁵ cm ² .s ⁻¹]	
	20 °C	25 °C
CO ₂	1.67 ¹	1.91 ¹
O ₂	2.01 ²	2.42 ³
N ₂	-	2.0 ²

Sources: ¹Jähne, B. al., 1987; ²Himmelblau, D. M., 1964; ³Spinger-Verlag, Heidelberg, 1969.

It has been found that the diffusion of the nitrogen and oxygen gases is very close to these values. In oenology, few studies have been carried out concerning the transfer of gas in wine. According E. L. Cussler (1997), the diffusion of oxygen in pure ethanol at 29,6 °C is $D_{O_2(\text{ethanol})}(29,6\text{ °C}) = 2,64 \cdot 10^{-5} \text{ cm}^2 \cdot \text{s}^{-1}$. At the same temperature in water, $D_{O_2(\text{water})}(29,6\text{ °C}) = 2,145 \cdot 10^{-5} \text{ cm}^2 \cdot \text{s}^{-1}$, so the diffusion coefficient is nearly the same in water as in ethanol.

Wine is a far more complex media, it cannot be considered as a pure mix of ethanol and water. But there is little published research available on the diffusion coefficients of the three most important gases in wine, although this would give major advantages in the management of these gases in practice. The only available data is that of carbon dioxide in Champagne wines where the diffusion of these gases is important in the quality and size of the bubbles which is a major quality parameter of Champagne. In Champagne the carbon dioxide diffusion coefficient has been determined to be $1.41 \cdot 10^{-9} \text{ m}^2 \cdot \text{s}^{-1}$ at 20 °C this is about 15 % smaller than diffusion in water (Liger-Belair, Prost, Parmentier, Jeandet, & Nuzillard, 2003). Table 4 is summarizing some published diffusion coefficients in different media. The diffusivity of ethyl acetate in water at 20 °C is $1.0 \cdot 10^{-9} \text{ m}^2 \cdot \text{s}^{-1}$, hence it is about half that of the gases described above in water (Lide 2004). The principles for diffusion in gases are the same than that in liquids; but compared to diffusion in liquids, the diffusion in gas is much faster, for example the diffusion of carbon dioxide in nitrogen at 20 °C has been described to be $1.60 \cdot 10^{-5} \text{ m}^2 \cdot \text{s}^{-1}$ which is a 1000 larger factor than that of carbon dioxide in water (Lide 2004).

Table 4: Diffusion coefficients in $10^{-9} \text{ m}^2 \cdot \text{s}^{-1}$ of carbon dioxide, nitrogen and oxygen, ethyl acetate in water, pure ethanol and Champagne wines

Compound	Water	Ethanol	Wine /Champagne
Carbon dioxide	1.92 at 25 °C ^{1,2} 1.70 at 20 °C ² 1.67 at 20 °C ^{4,6} 1.91 at 25 °C ⁶	---	1.41 at 20 °C ³
Nitrogen	1.88 at 25 °C ¹ 2.00 at 25 °C ⁴	---	---
Oxygen	2.10 at 25 °C ¹⁶ 2.01 at 20 °C ⁴ 2.66 at 29.6 °C ² 2.42 at 25 °C ⁶	2.64 at 29.6 °C ¹	2.50 at 20 °C ⁵
Ethyl acetate	1.00 at 20 °C ⁴		

Sources: ¹Cussler, 1997; ²Mavroudi *et al.*, 2006; ³Liger-Belair *et al.*, 2003; ⁴Lide *et al.*, 2004; ⁵Devatine, 2009 .

1.2 Gases in Wine

In wine the gases oxygen (O₂), carbon dioxide (CO₂) and nitrogen (N₂) can be dissolved. O₂ and CO₂ are playing a major role because of their chemical (O₂) and sensorial (CO₂) properties. Nitrogen as an inert gas has limited effect on chemical and sensorial properties of wine, but it is the most abundant gas in air and its importance in wine is due to its use as inert gas for the protection of wine from oxygen (Boulton *et al.* 1996). Some

physical properties of these gases can be seen in Table 5, the solubility under water saturated air is shown in Table 6.

The gaseous exchanges between the wine and its atmosphere are governed by the equilibrium of the partial pressures. At constant pressure, the concentration of dissolved gas decreases exponentially with increasing temperature, where as it increases proportionally with pressure. Oxygen and nitrogen are slightly soluble gas compared to carbon dioxide.

Table 5: Properties of main gases

	CO ₂	O ₂	N ₂
Color	Uncolored	Uncolored	Uncolored
Odor	Non	Non	Non
Taste	Slightly acid	Non	Non
Molecular weight [g.mol⁻¹]	44.01	31.99	28.01
Melting point [°C]	-78	-218	-210
Boiling Point [°C]	-58	-183	-196
Mass Volume [kg.m⁻³] at 0°C	1.964	1.428	1.251
% Volumetric of air	0.0401	20.9	78.1

Table 6: Solubility in water under water saturated air at 101.325 kPa pressure and 20°C

	mg.L ⁻¹	mol.m ⁻³
N₂	15.2	0.547
O₂	9.1	0.290
CO₂	0.64	0.015

Devatine and al. (2011) learned from their observations the role of dissolved carbon dioxide against wine oxidation, and more precisely about the flow rate gases. They proposed two hypothesis which are: when the system is stable, at equilibrium there is no transfer to the liquid phase, so the gas flows of O₂ and CO₂ injected after this equilibrium stage is found in the outlet gas stream; the second one is that the liquid is perfectly mixed and the concentrations of the gases are in a thermodynamic state of equilibrium with their partial pressures in the output gas flow. The physical understanding of this phenomenon can be found in the fact that as soon as a gaseous air or pure oxygen phase in contact with carbon dioxide saturated liquid, the dissolved CO₂, which is not at equilibrium with gaseous phase, tends to escape into this gaseous phase, thereby diluting the gaseous oxygen.

1.2.1 Oxygen (O₂)

1.2.1.1 Effect of Oxygen in Wine

Oxygen is the main compound involved in ageing reactions of wine (Waterhouse & Laurie, 2006). Contrarily to nitrogen and carbon dioxide, which do not react with wine constituents, oxygen does react with wine and is therefore consumed by its compounds. It has been identified that the main consumers are phenolic compounds; ethanol and sulfur dioxide

due to their high abundance, but all other organic compounds can also be oxidized (Elias & Waterhouse, 2010). 2 mg.L^{-1} of additional oxygen would be enough to cause significant sensory changes after a few months on white wines (Escudero, Asensio, Cacho, & Ferreira, 2002). Oxygen is therefore an important factor all along the winemaking process, from reception of the grapes, during the fermentation, storage and bottling. In some cases oxygen is considered as beneficial for wine quality, in other cases the effect is detrimental. Oxygen is considered mainly positive during fermentation (Salmon, 2006), where its effect on sterol synthesis was shown and the yeast showed a better tolerance towards alcohol at the end of the fermentation. Also red wines can benefit from low doses of oxygen, by stabilizing its color and soften the palate. Oxygen effect for must treatment like hyper oxidation in white wine can be positive or negative depending on wine style and variety, the effect of hyper oxidation is due to an early oxidation of bitter phenols and the consecutive elimination of the oxidized brown products (Schneider, 1998). After fermentation oxygen is usually considered negative for white wines as aroma compounds are oxidized and therefore quality is reduced. Oxygen can have very negative effects when it is present at the wrong moments or in too high amounts. The development of aerobic microorganisms which can lead to organoleptic defects and the degradation of color are important examples. As a very general rule, it can be estimated that a white wine can tolerate maximum 10 saturations of oxygen (80 mg.L^{-1}) during its lifetime, for red wines up to 50 saturations might not lead to problems (Boulton et al., 1996). In general, the tolerance of a wine to oxygen can be related to the level of phenolic compounds available (Boulton et al., 1996).

The most apparent development of wine after oxygen exposure is the decrease in free and total sulfur dioxide content, it has been shown that at higher oxygen exposure at bottling the SO_2 content decreased faster in bottles (Vidal & Moutounet, 2007), similar observations can be done comparing the development in glass bottles compared with wine development in Bag in Box packages that have higher oxygen transfer rates (Vidal & Moutounet, 2007). Here, the effect of higher initial dissolved oxygen was a stronger and faster decrease in SO_2 and a negative development in color. In white wines (Chardonnay and Sauvignon Blanc) it has been clearly shown, that the effect of oxygen is detrimental for wine quality, the color development, the free SO_2 and aroma compounds are affected. Even the effect of additional 25 mg.L^{-1} SO_2 could not make up for a reduction of 4 mg.L^{-1} of oxygen. Caillé et al. (2010) showed for red Grenache wines bottled with stoppers at different oxygen transfer rate that the red fruit characteristics of the wine decreased faster in wines bottled with stoppers at higher oxygen transfer rate.

The injection of oxygen can be wanted (micro/macro-oxidation, during the fermentation, barrel ageing, aerated racking), or unwanted (filtration, cold stabilization), in many cases a precise addition of oxygen is not done and is not measured (Devatine, Chiciuc, Poupot, & Mietton-Peuchot, 2007). A review (Vidal & Moutounet, 2008) is showing the major sources of oxygen uptake during the steps of winemaking. As most critical steps the conventional tartrate stabilization and the bottling process have been identified. A large variation between the oxygen uptakes at different points is shown Table 7.

Table 7: Oxygen uptake during vinification (Vidal and Moutounet, 2008)

Average uptake of oxygen by operation [mg.L ⁻¹]	VIDAL <i>and al.</i> , 2001, 2003, 2004	VALADE <i>and al.</i> , 2006	CASTELLARI <i>and al.</i> , 2004	ALINC <i>and al</i> 2008
Racking from bottom (15-20 °C)		0.3	0.37	
Racking to the top (15-20 °C)		3.1	0.37	
Racking from bottom (5-10 °C)			1.3	
Fining with removal of fining agent				1.36 – 1.47
Pumping	0.1 – 0.2		0.1	1.41
Barrel assembling			1.75	
Diatomaceous earth filtration	0.7	0.7	0.24	0.79
Plate and frame filtration	0.2	0.5	0.04	
Cartouche Filtration	0.1		0.06	
Cross Flow Filtration	1.5		0.2	
Centrifugation	1	0.95	1.2	
Refrigeration			1.3	
Heating with Heat Exchanger			0.15	
Continuous Tartrate Stabilization	2.4	1.2	4	
Tartrate Stabilization with Stabulation	2.38+5.7			
Contact Tartrate Stabilization	2.43			1.66
Electrodialysis	1.3		0.28	
Bottling	1.6	2.0 – 7.0		1
Bag in Box bottling	0.5			

The consumption of oxygen by the must or wine is not a direct reaction between oxygen in its gaseous form and the wine constituents. The reaction has to be mediated by a series of reactions, involving the production of more reacting forms of oxygen like hydrogen peroxide (Waterhouse & Laurie, 2006) (Figure 1). Recent studies significantly improved understanding of the basic mechanisms, but many pathways are still not fully understood. It is now thought that the oxidation of major wine compounds such as ethanol and tartaric acid is linked to the consumption of oxygen. This reaction is strongly influenced by the presence of catalyzing metals (iron, copper) and the presence of polyphenols as important mediators for this reaction. The polyphenols act as primary targets by the reaction of oxygen with polyphenols, oxidation of phenols to quinones and reduction of oxygen to hydrogen peroxide (as explained in Figure 2 and Figure 3). The created hydrogen peroxide is very reactive and is expected to react with a ferrous or cuprous ion in the so-called Fenton reaction to give a hydroxyl radical. This hydroxyl radical is an even more potent form of oxygen, which nonspecifically oxidizes all organic constituents in proportion relative to their abundance. The ability of SO₂ to inhibit oxidation has been partly attributed to its reactivity with hydrogen peroxide (Elias & Waterhouse, 2010).

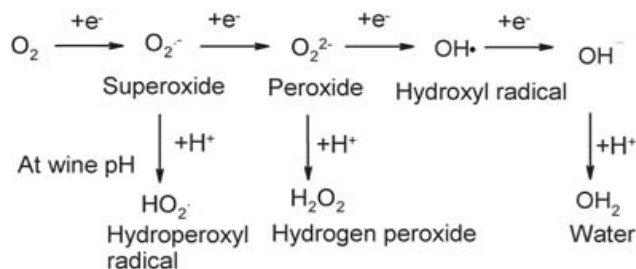


Figure 1: Radical formation in wine (Waterhouse & Laurie, 2006)

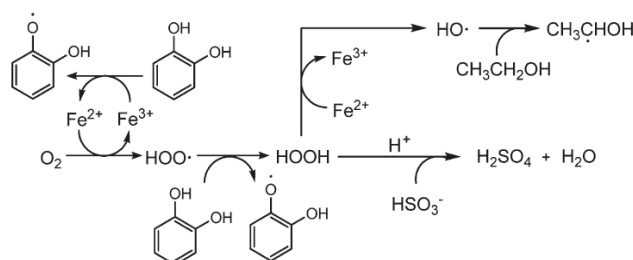


Figure 2: Oxidation reaction in wine (Elias & Waterhouse, 2010)

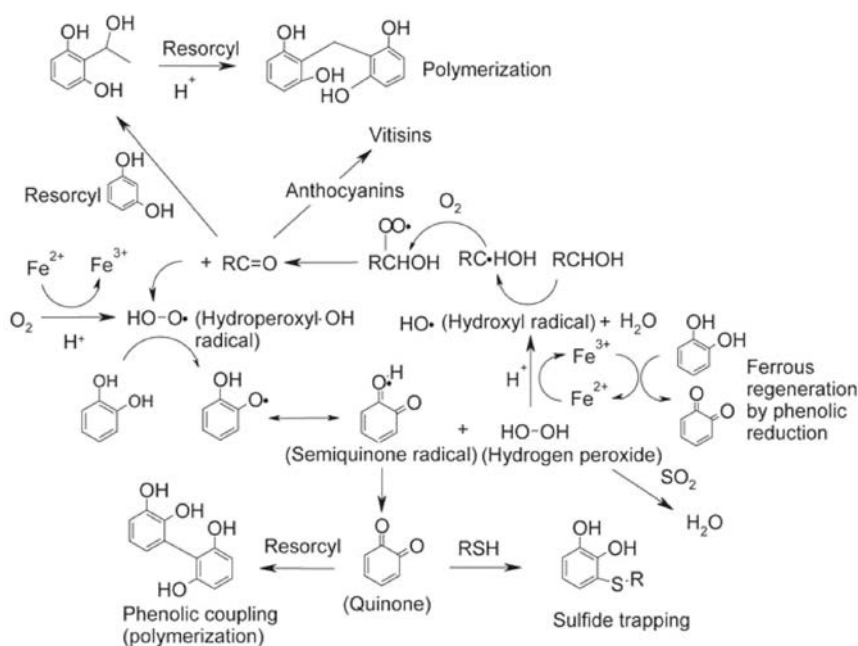


Figure 3: Wine phenolic oxidation pathway and subsequent hydroxyl radical oxidation of major wine compounds (Waterhouse & Laurie, 2006)

1.2.1.2 Precise Oxygen Management

The addition of oxygen is often involuntary and not precise (Vidal, Dufourcq, Boulet, & Moutounet, 2001). Recent developments like macro- and micro-oxidations are trying to improve this lack of precision in oxygen addition. But this task has been shown not to be easy as very low oxygen doses are used and the wine consumes this oxygen at a fast rate. So the addition of oxygen is still done empirically. Very often an addition is done by bubbling pure oxygen in a tank, but due to the low doses and the consumption the control of the dissolved or consumed oxygen is very difficult to achieve. In practice the dosing is mainly

done by sensory tasting which is often subjective and not very repeatable (Devatine and al. 2007). The presence of acetaldehyde as a measure of oxidation cannot be detected by sensorial tests before an irreversible oxidation of the wine has occurred. Only few studies were done trying to control the oxygen transfer to must or wine precisely. It has been shown that wine composition does affect the transfer of oxygen. Especially, the effect of dissolved carbon dioxide strongly reduces the transfer of oxygen (Devatine and al. 2007). With mechanistic models it can be shown that this reduced mass transfer is caused by a fast growth of the bubbles due to an uptake of carbon dioxide. This growth is leading to a faster rise of the bubble (Devatine & Mietton-Peuchot, 2009). So the effect of a shorter residence time in the bubble column combined with the dilution is leading to a weaker mass transfer in the presence of carbon dioxide.

Contrarily, the other direction i.e. the effect of reducing oxygen has not been studied so precisely. The focus of the research for this field was done to avoid any uptake of oxygen. This is usually done by inerting all equipment in contact with wine with inert gases like carbon dioxide or nitrogen or mixes thereof. For this process high amounts of gases are necessary and time is a major limiting factor (Falkenburg, 1986; Wilson, 1985). For example by the loading of a transport truck a fast loading is very important and there is not enough time for a sufficient inerting of the receiving tank.

The usual method to strip excess amounts of oxygen in wine is the stripping with nitrogen bubbles. The oxygen diffuses into the bubbles and leaves the tank. This method has been already described by Cant (1960) and has been used since then to avoid browning reactions in wine. An inert gas purge can be done in the tank, but this bubbling is more effective during transfer operations. Wilson (1985) explains the efficiency of gas transfer using inert gas purge by porous injectors. It is shown that oxygen is reduced, but also the levels of carbon dioxide decreases when nitrogen is used as purging gas. Hence, Falkenburg (1986) proposed the use of gas mixes to adjust to certain carbon dioxide content. The problem of these methods is that additionally many other aroma compounds are said to dissolve in the bubbles and are lost. Allen (1994) is showing different ways of injecting strip gas for oxygen removal, he is showing that due to different bubble diameters and bubble distribution the transfer for oxygen is better using an ejector for oxygen removal than the standard practice of a porous diffuser, but oxygen removal is quite effective for both treatments.

In a study on alcohol removal, CO₂ stripping has been studied. It was shown that there is a significant loss in aroma compounds due to this stripping (Aguera, Bes, Roy, Camarasa, & Sablayrolles, 2010). A reduction in 20 % ethanol causes a reduction of up to 43 % in other volatiles. For these stripping trials, very high amounts of gas has been used (6 hours at 50 m³.h⁻¹ for 100 L Tanks (3000 L Gas/ L Wine)).

A newly developed method is the gas stripping using selective hydrophobic membranes (Schmidt, Vidal, & Waidelich, 2010). This method is more selective, nevertheless in an experiment volatile esters were reduced up to 40 %, especially the most hydrophobic esters like ethyl-octanoate, ethyl-hexanoate, isoamyl-acetate and hexyl-acetate were said to

show a high affinity toward this membrane and showed high losses. The further study presented here is the follow up of the essays since 2008 at the INRA Experimental Unit of Pech-Rouge.

1.2.1.3 Solubility of Oxygen

The solubility of oxygen in wine is very important for describing the physical processes involved. The solubility of oxygen in water at 20 °C is in the order of 9.34 mg.L⁻¹ under normal conditions at 20 °C, 101.325 kPa at 20.95 % O₂ in air (Boulton and al. 1996). As for other gases the solubility decreases with rising temperatures.

The solubility can be calculated according to the following formula. The solubility of oxygen under 100 % oxygen atmosphere is about five times higher than this value (equation (20)) according to Boulton and al. (1996).

$$C_{O_2}[\text{mg.L}^{-1}] = \exp\left[-3.606 + \frac{1713}{T + 273.15}\right] \quad (20)$$

Sander (1999), in his compendium of Henry constants, proposes the following calculation for the solubility in Pa.m³.mol⁻¹ (equation (21)) according to the VAN'T HOFF relation (equation (9)):

$$C_{O_2} = 77942 * \exp(1500 * -\left(\frac{1}{T + 273.15} - \frac{1}{298.15}\right)) \quad (21)$$

Devatine and al. (2007), determined the Henry constant of oxygen in wine (12 % vol - Ethanol at 19 °C) as 2.72 MPa.L.g⁻¹ this equals a saturation of oxygen at 8.2 mg.L⁻¹ under air and 39.2 mg.L⁻¹ under pure oxygen atmosphere.

The mole fraction of oxygen in the output gas flow $y_{O_2}^S$ is given by the ratio of the partial molar flow rates, which values are identical to those of the input flow:

$$y_{O_2}^S = \frac{N_{O_2}^S}{N_{air}^S + N_{CO_2}^S} = \frac{N_{O_2}^e}{N_{air}^e + N_{CO_2}^e} = \frac{0,2 * N_{air}^e}{N_{air}^e + N_{CO_2}^e} \quad (22)$$

$y_{O_2}^S$ Mole fraction of oxygen in the output gas flow

$N_{O_2}^S$ Partial molar flow rate of O₂ in the output gas flow (e: input gas flow) [mol.s⁻¹]

N_{air}^S Partial molar flow rate of air in the output gas flow (e: input gas flow) [mol.s⁻¹]

$N_{CO_2}^S$ Partial molar flow rate of CO₂ in the output gas flow (e: input gas flow) [mol.s⁻¹]

The equilibrium concentrations are:

$$C_{O_2}^f = \frac{y_{O_2}^s * P_T}{H_{O_2}} = \left(\frac{0,2 * N_{air}^e}{N_{air}^e + N_{CO_2}^e} \right) * \frac{P_T}{H_{O_2}} \tag{23}$$

$C_{O_2}^f$ Dissolved O_2 final concentration in the liquid phase [mg.L⁻¹]

P_T Total pressure [Pa]

H_{O_2} O_2 Henry's constant [Pa.m³.kg⁻¹]

When the dissolved CO_2 concentration is at zero, the equilibrium oxygen value corresponds at the saturation in the air (7.9 mg.L⁻¹).

$$C_{O_2} = - \frac{C_{O_2}^*|_{air}}{C_{CO_2}^*} * C_{CO_2} + C_{O_2}^*|_{air} \tag{24}$$

The value of Henry's constant depends on the liquid temperature, the gas used and on the composition of the liquid phase, when the temperature increases.

Table 8: Henry's constant of O_2 and CO_2 versus temperature and O_2 saturation concentration for a gas phase (air ambient) and CO_2 saturation concentration for a gas phase (pure CO_2) (Devatine and al. 2007)

T (°C)	H_{O_2} [Pa.m ³ .kg ⁻¹]	$C_{O_2}^* _{air}$ [mg.L ⁻¹]	H_{CO_2} [Pa.m ³ .kg ⁻¹]	$C_{CO_2}^*$ [mg.L ⁻¹]
20	2.24x10 ⁶	9.3	5.60x10 ⁴	1745.6
25	2.44x10 ⁶	8.5	6.41x10 ⁴	1511.5

During winemaking:

$$C_{O_2} = - \frac{C_{O_2}^*|_{air}^{in\ wine}}{C_{CO_2}^*|_{in\ wine}} * C_{CO_2} + C_{O_2}^*|_{air}^{in\ wine} \tag{25}$$

With:

$$C_{O_2}^*|_{air}^{in\ wine} = \frac{0.2095 * 1.013 * 10^5}{H_{O_2}|_{in\ wine}} \tag{26}$$

Table 9: Numerical values of coefficients as a function of temperature (Devatine and al. 2007)

T (°C)	$C_{O_2}^* _{air}^{in\ wine}$ (mg.L ⁻¹)	$C_{O_2}^* _{pure\ O_2}^{in\ wine}$ (mg.L ⁻¹)	$C_{CO_2}^* _{in\ wine}$ (mg.L ⁻¹)
20	7.7	36.7	1550.0
25	7.2	34.1	1342.1

The equilibrium value is dependent on the amount of CO_2 production rate and the air flow rate that were in contact with the liquid. Experiences of Devatine et al. (2011)

demonstrated that in the case where there is no CO₂ production but when there is a high initial dissolved CO₂ concentration present in the liquid, the protective effect acts only by reducing the rate of oxygen transfer like explained before. When the gaseous air or pure oxygen phase is in contact with carbon dioxide saturated liquid, the dissolved CO₂, which is not at the equilibrium with the gaseous phase, tends to escape. Thus two gases cannot be treated independently when they are simultaneously present in the liquid.

1.2.1.4 Oxygen Conversion

For the calculations during this work the solubility of oxygen in water according to Huber et al. (2006) is used. The instruments PreSens luminescent probe and Varian μGC are calibrated for gaseous and not for dissolved oxygen, although displaying values in mg.L⁻¹ these values are calculated based on the Henry constants for oxygen in water. The following equations are only valid in aqueous solutions and humidified air, showing the unit transfer and the solubility of oxygen in water.

The unit transfer is done according to the calculations proposed by Huber et al. (2006) in equations (27)-(32) ((PreSens, 2006):

- % Oxygen saturation:

$$\%O_2 = \%air - saturation * \frac{20.95}{100} \quad (27)$$

20.95 = Volume percent of oxygen in air

- Partial pressure of oxygen [hPa]:

$$p_{O_2} = P_{abs} * \%O_2 \quad (28)$$

p_{O_2} Partial pressure of oxygen [hPa]

P_{abs} Absolute pressure [hPa]

With:

$$P_{abs} = P_{atm} - p_{w(T)} \quad (29)$$

P_{atm} Actual atmospheric pressure [hPa]

$p_{w(T)}$ Vapor pressure of water at temperature $T_{(K)}$ (equation (35)) [hPa]

So:

$$p_{O_2} = (P_{atm} - p_{w(T)}) * \frac{\%air - saturation}{100} * 0.2095 \quad (30)$$

- Calculation of oxygen solubility in air at a given temperature:

$$C_{O_2} = \frac{p_{O_2}}{p_N} * \alpha(T) * 1000 * \frac{M(O_2)}{V_M} \quad (31)$$

C_{O_2}	Oxygen concentration [mg.L ⁻¹]
p_N	Standard pressure (1013 mbar)
p_{O_2}	Equation (30)
%O ₂	Equation (27)
$\alpha(T)$	Bunsen absorption coefficient at temperature T [cm ³ O ₂ .cm ⁻³]
$M(O_2)$	Oxygen's molecular mass [32 g.mol ⁻¹]
V_M	Molar Volume [22.414 L.mol ⁻¹]

According to the equation (28), we have:

$$C_{O_2} = \frac{p_{atm} - p_w(T)}{p_N} * \frac{\%air - saturation}{100} * 0.2095 * \alpha(T) * 1000 * \frac{M(O_2)}{V_M} \quad (32)$$

- Water vapor pressure:

As shown in equation (27) and (30), the water vapor pressure p_w influences the oxygen partial pressure of air saturated water and water-vapor saturated air.

- Oxygen partial pressure in dry air:

$$P_{O_2} = P_{atm} * 0.2095 \quad (33)$$

- Oxygen partial pressure in air-saturated water and water-vapor saturated air:

$$P_{O_2}' = (P_{atm} - p_w(T)) * 0.2095 \quad (34)$$

Water vapor pressure is strongly affected by temperature variations and so, influences the oxygen partial pressure as shown in equation (34).

$$p_w = f(T)$$

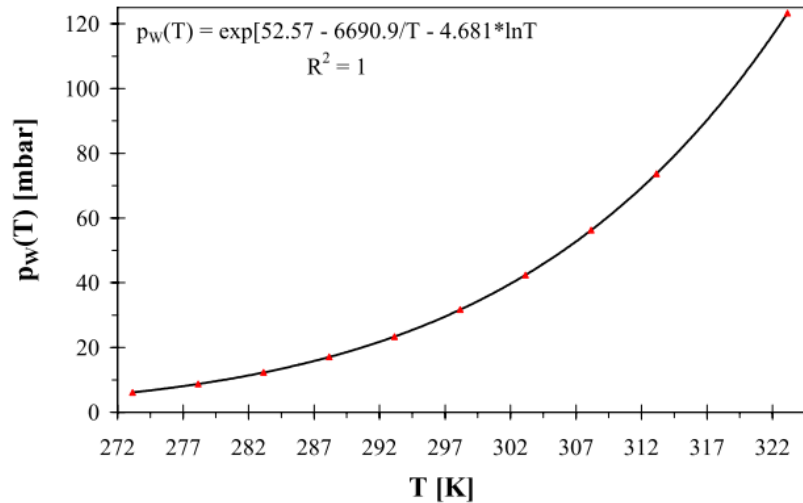


Figure 4: Variation of water vapor pressure with temperature (PreSens, 2006)

The water vapor pressure increase with the temperature, an expression of the variation of water vapor pressure with temperature is obtained:

$$p_w = \exp \left[52.57 - \frac{6690.9}{T} - 4.681 * \ln(T) \right] \quad (35)$$

The solubility of oxygen can be described by the Bunsen absorption coefficient $\alpha(T)$. This coefficient determines the partition between gas and liquid phase. (PreSens, 2006)

- Bunsen Absorption Coefficient α :

$$\alpha(T) \cdot 10^3 = 48.998 - 1.335 * T + 2.755 \cdot 10^{-2} * T^2 - 3.220 \cdot 10^{-4} * T^3 + 1.598 \cdot 10^{-6} * T^4 \quad (36)$$

This is giving a solubility of 44.27 mg.L⁻¹ under pure O₂ atmosphere and a solubility of 9.1 mg.L⁻¹ under air saturated water at the reference temperature of 20 °C. This overestimates the O₂ content in wine by about 10 %, but Henry constants for wine are usually not determined.

Numerical application example:

Solubility of O₂ under air saturated water at the reference temperature of 20 °C

$$C_{O_2} = \frac{p_{atm} - p_w(T)}{p_N} * 0.2095 * \alpha(T) * \frac{M(O_2)}{V_M}$$

$$p_w = \exp \left[52.57 - \frac{6690.9}{T} - 4.681 * \ln(T) \right]$$

$$p_w = \exp \left[52.57 - \frac{6690.9}{(20+273,15)} - 4.681 * \ln(20 + 273,15) \right] = \mathbf{23,3 \text{ mbar}}$$

$$\alpha(T).10^3 = 48.998 - 1.335 * T + 2.755.10^{-2} * T^2 - 3.220.10^{-4} * T^3 + 1.598.10^{-6} * T^4$$

$$\alpha(20^\circ\text{C}).10^3 = 48.998 - 1.335 * 20 + 2.755.10^{-2} * 20^2 - 3.220.10^{-4} * 20^3 + 1.598.10^{-6} * 20^4 = \mathbf{31.01}$$

$$P_{atm} = P_N = 1013 \text{ mbar}$$

$$M(O_2) = 32 \text{ g.mol}^{-1}$$

$$V_M = 22.414 \text{ L mol}^{-1}$$

$$C_{O_2} = \frac{1013 - 23.3}{1013} * 0.2095 * 0.03101 * \frac{32}{22.414} = \mathbf{9.1 \text{ mg/L}}$$

Solubility of O₂ under pure oxygen atmosphere at the reference temperature of 20 °C

$$\frac{P_{O_2}}{P_N} = \mathbf{1 \text{ mbar}}$$
 with $P_w = 0$ under pure oxygen atmosphere

$$\text{So } C_{O_2} = 0.03101 * \frac{32}{22.414} = \mathbf{44.27 \text{ mg/L}}$$

1.2.2 Carbon Dioxide (CO₂)

CO₂ is a primary fermentation product. In wine it is mainly produced during this winemaking step (ca. 80-100 g.L⁻¹), another source of CO₂ is the malolactic fermentation. Most of the CO₂ is lost during fermentation because of its relative low partial pressure in air.

1.2.2.1 Carbon Dioxide Effect on Wine

The effect of carbon dioxide in wine is mainly sensorial. In early released white and rosé wines carbon dioxide is used to enhance fruit flavor. It is said that carbon dioxide is perceptible at levels from 200 mg.L⁻¹ in water and in wine from about 700 mg.L⁻¹. At levels from 900 mg.L⁻¹ to 1300 mg.L⁻¹ the differences needs to be higher than 300 mg.L⁻¹ to be detectable in sensorial comparisons (Zoecklein and al. 1994). Carbon dioxide is claimed to enhance the acidity and hereby reinforce the tannin and bitterness effects of a wine. Furthermore it is stated that CO₂ reduces the sweetness perception in certain wines (Zoecklein

and al. 1994). In white and rosé wines an elevated CO₂ level is considered as positive, because of its refreshing effect. In red wines, especially those used for ageing, the effect of CO₂ is described as aggressive, sour and therefore negative.

For white wines, it is explained that contents between 600 and 800 mg.L⁻¹ are usually considered positive (see also Table 10), for certain wines a carbon dioxide content up to 1000 mg.L⁻¹ can create a lively refreshing palette. Research on the German market has shown that consumers prefer a lively refreshing wine taste and rate this positively, contradicting this, it is reported that consumers of the British market are much more sensitive to carbon dioxide and usually rate its perception as negative (Singleton V.L, 1987), Figure 5. For red wines CO₂ levels should be smaller than 500 mg.L⁻¹ to create a full, smooth palette. Due to carefully chosen winemaking techniques these values are often achieved without further intervention. The carbon dioxide loss in cold stored stainless steel tanks for white wine is very limited. The warm fermentation and the following storage in barrels for red wines are having the opposite effect in which carbon dioxide is reduced naturally (Boulton and al. 1996). The following Table 10 is showing the recommended carbon dioxide contents for different wines according to Devatine and Mietton-Peuchot 2009.

As the use of alimentary grade carbon dioxide is permitted by the OIV and the EU, the levels of carbon dioxide can be adjusted to a desired level. Like for the introduction of oxygen in micro or macro-oxygenation this is usually done by bubbling pure CO₂ in the tank or during transfer into the wine. The reduction of carbon dioxide can be done by stripping with another gas or by stirring the liquid in an open tank. The insertion or the removal of carbon dioxide with these methods is usually done empirically. With traditional methods there is not a very good precision in adjusting the carbon dioxide content, therefore precise adjustments are often not done. Further precision can only be achieved by using mix-gases according to (Lonvaud-Funel & Ribéreau-Gayon, 1977). As shown before, traditional practice is leading to high levels of CO₂ in white wines and low levels in red wines as it is required from a sensorial point of view. There are some cases where this goal is not achieved naturally. First, for red wines that are bottled early or that just underwent malolactic fermentation short time before bottling, the concentration of carbon dioxide is close to saturation and might cause sensorial problems, this requires a reduction in carbon dioxide content. Second for white and rosé wines the concentrations might be too low (Figure 5). This low concentration could be due to storage in warm conditions, many transfer operations or other reasons. Those wines have the need to be adjusted in carbon dioxide content.

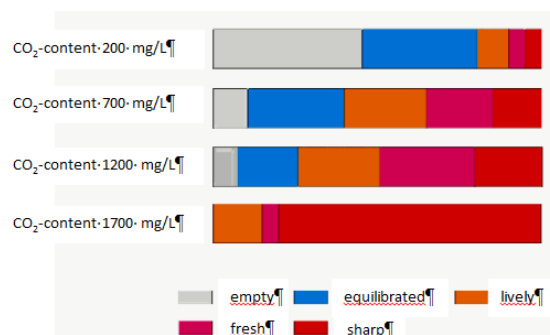


Figure 5: Sensory descriptors for white wine in a German consumer study (reference?)

Table 10: Desired amounts of CO₂ [mg.L⁻¹]

	BLANKENHORN, 2002	DEVATINE <i>et al.</i> , 2009
Red wine	400 – 800	300
White wine	700 – 1 500	800 – 1 000
Rosé wine	700 – 1 200	800 – 1 000

1.2.2.2 Solubility of CO₂ in Water

Carbon dioxide is very soluble in water cause of its polarity. The solubility is around 30 times higher than that of oxygen. In water CO₂ dissolves to the weak acid H₂CO₃; in wine at a pH 3; 99 % of the CO₂ is present in the anhydride the gaseous form (Liger-Belair, 2005). According to DALTON'S law the partial pressure of CO₂ in water can be calculated by using the volume proportion of CO₂ in air, the total pressure (101.325 kPa) and the saturated vapor pressure of water at 20 °C (2.3311 kPa). The CO₂ concentration in air in 2005 is approximately 380 ppm, growing at a rate of 1.6 ppm per year (IPCC, 2007). For further calculations, the value of 408 ppm is taken for the year 2017 (<https://fr.co2.earth/daily-co2>).

Numerical Applications:

At a vapor pressure of 0.0404 kPa the solubility is 0.69 mg.L⁻¹, and under pure CO₂ atmosphere about 1742 mg/L (see following equations).

$$p_{CO_2} = (p_{atm} - p_{w(T=20^\circ C)}) * C_{CO_2}$$

$$= (101.325kPa - 2.351kPa) * 0.000408 = 0.0404kPa$$

The solubility of CO₂ in water under normal conditions at 20°C is:

$$p_{CO_2} = H_{CO_2} \times C_{CO_2} \quad (37)$$

p_{CO_2} Partial Pressure of CO₂ [Pa]

C_{CO_2} Concentration of dissolved CO₂ [g.L⁻¹]

H_{CO_2} Henry's constant for CO₂ in water [Pa.L⁻¹.mol⁻¹]

P_w Saturated water vapor at 20°C (p28)

Versteeg and Van Swaij proposed in 1998, the dimensionless HENRY'S law coefficient for carbon dioxide in pure water according equation (10):

$$H_{CO_2} = 2.8249 \cdot 10^{-6} * e^{\left(\frac{-2044}{T}\right)} \quad (38)$$

Sander (1999) proposed an equation (10) according to the VAN'T HOFF equation (10) and with a Henry's constant of CO₂ in water at 298.15 K (25°C).

$$H_{CO_2} = 2814 \times e^{\left(2200 \cdot \left(\frac{1}{298,15} - \frac{1}{T+273,15}\right)\right)} \quad (39)$$

2814 is the HENRY's constant for CO₂ in water at 298.15K in Pa.m³.mol⁻¹ (= 3.5.10⁻²mol.L⁻¹.atm⁻¹ = 3.45.10⁻⁷mol.L⁻¹.Pa)

C_{CO_2} Concentration of dissolved CO₂ [g.L⁻¹]
 p_{CO_2} Partial pressure of CO₂ [Pa]

Temperature corrections for Henry constants are usually done with Van't Hoff equation like equations following the form in equation (40) (Sander 1999). In tables, the dissolution enthalpy ΔH_{diss} is often already divided by the gas constant R which gives the dimensionless factor $\frac{\Delta H_{diss}}{R}$.

According to Sander (1999), this factor $\frac{\Delta H_{diss}}{R}$ equals 2200 in water.

Numerical Applications:

$$H_{CO_2}^{(20^\circ C)} = 2815 \times e^{\left(2200 \cdot \left(\frac{1}{298,15} - \frac{1}{(20+273,15)}\right)\right)} = 2482 \text{ Pa} \cdot \text{m}^3 \cdot \text{mol}^{-1} \quad (40)$$

$$\Delta H_{CO_2 \text{ diss water}} = 2200 * 8,314 = 18290,8 \text{ J} \cdot \text{mol}^{-1}$$

$\Delta H_{CO_2 \text{ diss}}$ Dissolution enthalpy [J.mol⁻¹]
 T Absolute temperature [K]
 R Universal gas constant [8.314 J.K⁻¹.mol⁻¹]

Under Air conditions at 20 °C:

$$C_{CO_2} = \frac{p_{CO_2}}{H_{CO_2}} = \frac{40.4}{2.56 \cdot 10^6} = 1.58 \cdot 10^{-5} \text{ mol} \cdot \text{L}^{-1} = 0.69 \text{ mg} \cdot \text{L}^{-1} \quad (41)$$

And under pure CO₂ Atmosphere (101.325 kPa, 20 °C):

$$C_{CO_2} = \frac{P_{atm}}{H_{CO_2}} = \frac{101325}{2.56 \cdot 10^6} = 0.0396 \text{ mol} \cdot \text{L}^{-1} = 1742 \text{ mg} \cdot \text{L}^{-1} \quad (42)$$

1.2.2.3 Solubility of CO₂ in Wine

Because of the hydrophilic properties of CO₂, its properties cannot be directly transferred from water to wine. Hence, several propositions have been made to calculate the solubility of carbon dioxide. The following extract is trying to summarize some of these attempts. Table 11 gives an overview of the published solubility data at 20°C. Furthermore Figure 5 is showing the effect of the temperature according to different formulas.

Lonvaud-Funel and Ribéreau-Gayon (1977) demonstrated the effect of wine composition on CO₂ solubility. It was shown that with increasing alcohol and sugar levels the solubility decreases as expected from their chemical properties. The solubility can therefore be calculated using the tables created by Agabaliantz. In 1979, Lonvaud-Funel and Matsumoto presented a more comprehensive formula for the direct calculation of the maximum solubility (equation (43)). The calculated Bunsen solubility coefficient α is taking into account the effect of ethanol (E), sugar (S) and temperature (T) (equation (44)). The solubility in mg.L⁻¹ can be calculated by multiplying α with 1977 mg.L⁻¹ (equation (45)).

Formula of Lonvaud-Funel and Matsumoto (1979):

$$P_{CO_2} = f(E, S, T)$$

$$\ln(P_{CO_2}) = (7.10^{-5} * E - 0.02905) * T - 0.0179 * E - 0.00111 * S + 4.34497 \quad (43)$$

P_{CO_2} Partial pressure of CO₂ in wine at T [mg.L⁻¹]

E Ethanol [%vol]

S Sugar [g.L⁻¹]

T Temperature [°C]

$$\ln(\alpha_{wine}^T) = (7.10^{-5} * E - 0.02905) * T - 0.0179 * E - 0.00111 * S + 0.519767 \quad (44)$$

$$C_{CO_2(T=C)} = \alpha_{wine}^T * 1977 \quad (45)$$

C_{CO_2} CO₂ concentration [mg.L⁻¹]

α_{wine}^T Bunsen absorption coefficient of CO₂ in wine at temperature T (°C) [L.L⁻¹]

E Ethanol [%vol]

1977 Weight in mg of a liter of CO₂ at 0 °C.

The OIV Compendium of International Methods of Must and Wine Analysis proposed a formula to calculate dissolved CO₂ at 20°C (MA-E-AS314-01-DIOCAR, 2008). This formula can be rearranged to calculate the solubility at 1 atm = 101.325 kPa. The calculation of CO₂ solubility according to OIV Reference Method at 20°C is equation (46):

$$C_{CO_2}^{20^\circ C} = P_{CO_2}^{20^\circ C} * 1.951.10^{-2} * (0.86 - 0.01 * E) * (1 - 0.00144 * S) \quad (46)$$

$C_{CO_2}^{20^\circ C}$ CO₂ concentration at 20 °C [mg.L⁻¹]

E Ethanol [%vol]

S Sugar [g.L⁻¹]

With:

$$P_{CO_2}^{20^\circ C} = \frac{\%CO_2}{100} * (P_{abs} - P_w) \quad (47)$$

$$P_{abs} = P_{atm} + P_r \quad (48)$$

- P_{abs} Measured pressure compared to absolute vacuum ≥ 0 [Pa]
- P_r Relative pressure defines to P_{atm} at the moment of measurement. ≥ 0 if $P_r > P_{atm}$ and ≤ 0 if $P_r < P_{atm}$ [Pa]
- P_w (equation (54))

In the review on physical properties of carbon dioxide (Liger-Belair, 2005), they correlated the temperature correction factor according to the data of Agabalianz, he showed that in champagne the dissolution enthalpy for CO_2 ($\Delta H_{diss} = 24800 J.mol^{-1}$) is higher than in water ($\Delta H_{diss} = 19900 J.mol^{-1}$). Although, this correlation differs from the data presented by Lonvaud-Funel and Matsumoto (1979), the author states that this is the first correction for temperature derived from actual wine data. The temperature correction is significantly higher than that from water, indicating a higher temperature dependency of carbon dioxide solubility in wine than in water. Equations (50) are showing the temperature correction for wine at 20°C, according the VAN'T HOFF relation (equation (9)).

$$C_{i(T)} = C_{i(20^\circ C)} * e^{\left(\frac{\Delta H_{diss}}{R} * \left(\frac{1}{T+273.15} - \frac{1}{293.15}\right)\right)} \tag{49}$$

$$C_{CO_2} = C_{CO_2;20^\circ C} * e^{\left(2984 * \left(\frac{1}{T+273.15} - \frac{1}{293.15}\right)\right)} \tag{50}$$

With $\frac{\Delta H_{diss}}{R} = \frac{24800}{8.314} = 2984 K^{-1}$

Figure 6 and Table 11 are summarizing the proposed formula for carbon dioxide solubility in wine and water.

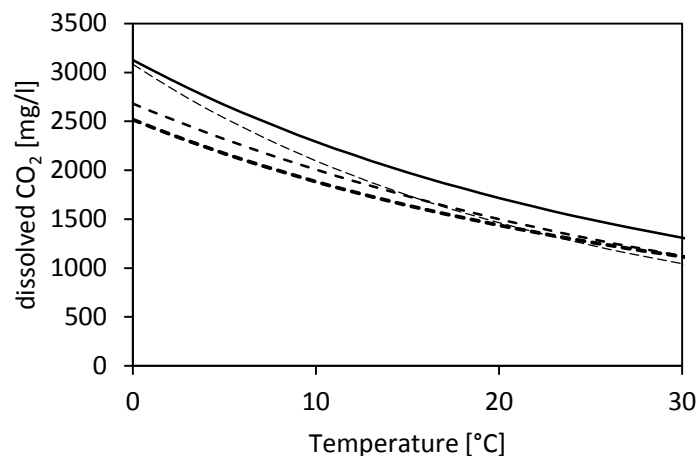


Figure 6: Dissolved CO_2 at 101.3 kPa calculated from (Lonvaud-Funel & Ribéreau-Gayon, 1977) (short dash), and Boulton et al. 1996 (points) Sander, 1999 (solid line), and the OIV Reference Formula (long dashed)

Table 11: Solubility of CO₂ in wine and water at 20°C

	Author	Composition	Solubility 100% CO ₂ (101.3kPa) [mg.L ⁻¹]	Solubility under air* [mg.L ⁻¹]
Wine	ABERGALLIANTZ, 1976	12% Eth, 2g/L S.	1477	0.59
	DEVATINE and al. 2011	12% Eth pH = 3.5	1550	0.62
	OIV REFERENCE METHOD	12% Eth, 2g/L S.	1458	0.58
	LONVAUD-FUNEL and MATSUMOTO, 1979	12% Eth, 2g/L S.	1470	0.58
	LONVAUD-FUNEL and MATSUMOTO, 1979	10% Eth, 50g/L S.	1440	0.57
	OIV REFERENCE METHOD	10% Eth, 50g/L S.	1394	0.56
	LONVAUD-FUNEL and MATSUMOTO, 1978	Wine 0 % Eth, 0g/L S.	1796	0.71
	OIV REFERENCE METHOD	Wine 0 % Eth, 0g/L S.	1700	0.64
Water	SANDER, 1999	Water	1742	0.69
	DEVATINE and al. 2011	Water	1746	0.69

* Air at normal pressure 101.3 kPa, saturated with water vapor, and containing 404 ppm CO₂ ($p_{CO_2} = 0.404$ hPa)

1.2.2.4 Utilization of Mixed Gases:

According to FICK'S Law of diffusion a wine always tends to achieve the partial pressure of the atmosphere around it. This means that under normal air conditions a wine will always lose its indigenous CO₂ till equilibrium of the partial pressure in air and wine is reached. Hence, in adjusting the percentage of the CO₂ in the headspace it is possible to adjust a precise CO₂ concentration in the wine ((Lonvaud-Funel & Matsumoto, 1979)).

It is possible to calculate the solubility according to the partial pressure (application of DALTON'S law equation (51) :

$$p_{CO_2} = \%CO_2 \times \frac{101325}{100} \quad (51)$$

Now, the concentration which is dissolved at a given partial pressure can be calculated using equation (52): it is dependent on temperature, ethanol and sugar content and the percentage of CO₂ in the mix. The quantity that is dissolved can be calculated dividing the percentage by the solubility under pure atmosphere condition.

$$c_{CO_2}(T, E, S, \%mix) = \frac{\%CO_2}{c_{CO_2,max}(T, E, S)} \quad (52)$$

1.2.3 Nitrogen (N₂)

Nitrogen is a gas that does not react with wine and therefore it has not been intensively studied therein. Nitrogen is often used to inert containers or gaseous atmospheres that are in contact with wine in order to minimize oxygen uptake. In wine the influence from nitrogen on the sensorial properties has not been studied and is considered as negligible.

In beer it has been reported that low concentrations of nitrogen do not exert a sensorial impact (Bamforth, 2004). Nevertheless, it is well established, that nitrogen is a major factor in stabilizing the foam of a beer by ensuring a more uniform size of the bubbles. These uniform size bubbles are more stable than disproportional bubbles.

This effect has also not been studied in wine, as wine does not tend to foam due to its low carbon dioxide content. For the foaming of wine in filters and during bottling the nitrogen content might play a role as it has an effect on total saturation and might stabilize the foam formed, which might lead to problems during bottling, but this has not been studied. In carbonated wine of the type Prosecco Frizzante, nitrogen does play a role. In this carbonated wine, the total carbon dioxide content is limited to 2.5 bars overpressure by law. If more than 2.5 bars are formed in the bottle the beverage cannot be sold. For this regulation it is estimated that the pressure in the bottle is mainly due to carbon dioxide.

This is true, but the nitrogen content is also playing a minor, but existing role as DALTON'S law does apply, where the total pressure is the sum of the partial pressures (Equation (6)).

Two extreme examples:

- (1) If a wine is saturated with nitrogen under 100 % nitrogen, only 2.5 of CO₂ saturations = 3645 mg.L⁻¹ (with CO₂ saturation = 1458 mg.L⁻¹, Table 11, OIV reference) can be added to attain 2.5 bars overpressure.
- (2) If no other gases except CO₂ are present in the wine for 2.5 bars overpressure 3.5 saturations can be present and still not exceeding the legal limit (3.5 x 1458 = ca. 5103 mg.L⁻¹).

As this is a major difference from a sensorial point of view, it is important to adjust nitrogen levels in this type of wine. For further explanation, the following example at the end of the section is shown (Figure 7).

The solubility of N₂ in water can be expressed in the form presented by Sander (1999) (Equations (53)). According to the model of equation (10):

$$H_{N_2}(\text{mol. dm}^{-3} \cdot \text{atm}^{-1}) = 6,5 \cdot 10^{-4} \times \exp\left(1300 \times -\left(\frac{1}{T + 273,15} - \frac{1}{298,15}\right)\right) \quad (53)$$

With:

T *Temperature [K]*

ΔH_{N_2} $\Delta H_{N_2} = 1300 * 8,314 = 10808,2 \text{ J. mol}^{-1}$. According to the equation (9).

Thus at 20 °C and under pure nitrogen the solubility is of 19.9 mg.L⁻¹. Under water saturated air at 20 °C a solubility of 15.2 mg.L⁻¹ can be calculated. The solubility of nitrogen in wine has not been determined so solubility in water is used here.

A wine with 12% vol. of ethanol and 2 g/L of sugar is stored in an almost full pressure tank under atmospheric conditions 20°C 101.3kPa, the gases of the headspace are in equilibrium with the wine.

First case:

The following liquid and gas concentrations are measured:

$$[\text{O}_2] = 4 \text{ mg.L}^{-1} \quad \rightarrow \quad P_{\text{O}_2} = 9.2 \text{ kPa} \quad \text{according to the Equation (31).}$$

$$[\text{N}_2] = 7.3 \text{ mg.L}^{-1} \quad \rightarrow \quad P_{\text{N}_2} = 37.6 \text{ kPa} \quad \text{according to the Equation (53).}$$

$$[\text{CO}_2] = 780 \text{ mg.L}^{-1} \quad \rightarrow \quad P_{\text{CO}_2} = 54.5 \text{ kPa} \quad \text{according to the Equation (46).}$$

$$\Sigma \text{ partial pressures} = P_{\text{O}_2} + P_{\text{N}_2} + P_{\text{CO}_2} = 101.3 \text{ kPa}$$

Now the tank is closed and CO₂ is added till an equilibrium pressure of 3 bars absolute pressure is reached.

So to have $P_{tot} = 300 \text{ kPa}$, we need to add 198.7 kPa ($300 - 101.3 = 198.7$) of CO₂, which means 2860 mg.L⁻¹ of CO₂ is added.

After add CO₂, we have:

$$P_{\text{CO}_2} = 54.5 + 198.7 = 253.2 \text{ kPa} \quad \rightarrow \quad [\text{CO}_2] = 3645 \text{ mg.L}^{-1}.$$

Hence, at a CO₂ concentration of 3645 mg.L⁻¹ this 300 kPa pressure is reached.

Second case:

Before applying pressure the gases O₂ and N₂ are completely removed by sparkling the tank with large amounts of CO₂ without applying counter pressure.

The following dissolved gas concentrations are measured:

$$[\text{O}_2] = 0 \text{ mg.L}^{-1} \quad \rightarrow \quad P_{\text{O}_2} = 0 \text{ kPa} \quad \text{according to the Equation (31).}$$

$$[\text{N}_2] = 0 \text{ mg.L}^{-1} \quad \rightarrow \quad P_{\text{N}_2} = 0 \text{ kPa} \quad \text{according to the Equation (53).}$$

$$[\text{CO}_2] = 1458 \text{ mg.L}^{-1} \quad \rightarrow \quad P_{\text{CO}_2} = 101.3 \text{ kPa} \quad \text{according to the Equation (46).}$$

$$\Sigma \text{ partial pressures} = P_{\text{O}_2} + P_{\text{N}_2} + P_{\text{CO}_2} = 101.3 \text{ kPa}$$

Now the tank is closed and CO₂ is added till an equilibrium pressure of 3.5 bars is reached.

So to have $P_{tot} = 350 \text{ kPa}$, we need to add 248.7 kPa ($350 - 101.3 = 248.7$) of CO₂, which means 3580 mg.L⁻¹ of CO₂ is added.

After add CO₂, we have:

$$P_{\text{CO}_2} = 101.3 + 248.7 = 350 \text{ kPa} \quad \rightarrow \quad [\text{CO}_2] = 5039 \text{ mg.L}^{-1}$$

Hence, at a CO₂ concentration of 5039 mg.L⁻¹ this 350 kPa pressure is reached.

Figure 7: Exemple for pressure in tank dependant on gas concentration

1.2.4 Water Vapor

Water is also present in the gas phase above a wine. It is in equilibrium between the vapor and liquid phases depending on the temperature. But contrarily to the gases mentioned above it is present in undiluted form, so HENRY'S law is not applicable. The saturated water vapor pressure at a certain temperature can be expressed with the CAMPBELL equation (54) in the following form (Huber et al., 2006); this is showing a very good correlation with the tables presented by (David R, 2004).

$$p_w(T) = \exp\left(A - \frac{B}{T} - C \times \ln T\right) \quad (54)$$

Using the constants: A: 52.57; B: 6690.9; C: 4.681.

T Temperature [K]

p_w Saturated vapor pressure [hPa = mbar]

Table 12: Saturated vapor pressure against temperature

θ [°C]	0	5	10	15	20	25	30	35	40	50
T [K]	273.15	278.15	283.15	288.15	293.15	298.15	303.15	308.15	313.15	323.15
$p_w(T)$ [mbar]	6.16	8.78	12.36	17.15	23.51	31.85	42.67	56.54	74.16	123.99

1.2.5 Ethanol Vapor

Similar to water, ethanol vapor is also present in the gas phase above a wine. Comparable to the estimation of saturated water vapor, the saturated ethanol vapor of pure ethanol can be calculated: In this case formulas proposed by Williams and Boulton 1983 for the calculation of ethanol loss during fermentations can be used: the ANTOINE'S equation (55) is expressing the saturated vapor pressure of ethanol as using the constants A: 8.20147; B: 1642.89 and C: 230.3. One has to be aware care, that using these constants the pressure is given in [mm Hg] and the temperature in [°C].

$$\log_{10} p^0 = A - \frac{B}{T + C} \quad (55)$$

Wine does not contain 100% ethanol; thus for the calculation of the vapor pressure of an ethanol/water mixture, RAOULT'S law has to be applied. RAOULT'S law states that the vapor pressure of a compound is proportional to its molar fraction (x_i) in the liquid of an ideal mixture. As water/ethanol mixtures do not behave ideally (Williams and Boulton 1983) used a modified RAOULT'S law in which an activity coefficient (γ_i) has been added (equation (56)).

$$p_i = p_i^0 \times \gamma_i \times x_i \quad (56)$$

Williams and Boulton 1983 suggest using equation (57) for the calculation of these activity coefficient (γ_i) in wine at mole fractions between (0-0.046) and temperatures under 50 °C.

$$\ln \gamma_{EtOH} = a - b \left[\frac{1}{T + 273} - \frac{1}{323,15} \right] \tag{57}$$

$$a = 1,6027 \times e^{-2,8235x_e}$$

$$b = 982,27 - 6861,39 * x_e$$

The following Figure 8 is showing the calculated saturated vapor pressures of pure water, pure ethanol and a mixture of 12 %vol ethanol as an example calculation for wine.

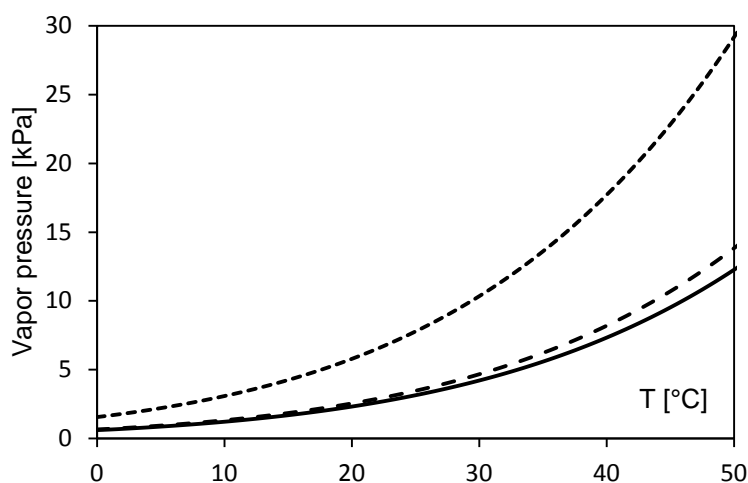


Figure 8: Vapor pressure of pure ethanol (short dash), water (solid line) and ethanol water mixture (12%vol long dash) as a function of temperature

It might be interesting to know the amount of ethanol in the gas phase in function of the ethanol in the liquid phase. For the following example the calculation for a wine with 12 %vol ($d_{ethanol} = 0.789$ so $\rho_{ethanol} = 0.12 * 0.789(\frac{kg}{L}) = 94.7 g.L^{-1}$) ethanol is chosen at 25 °C under normal pressure (101.3 kPa).

Example: calculation of the ethanol vapor amount in the headspace over a wine at 12 %vol at 25°C and 101.3 kPa

a) The mole fraction (x_e) of Ethanol in Water ($\rho_{H_2O} = 1000 \text{ g.L}^{-1}$) is calculated:

($M_{(\text{ethanol})}=46.07 \text{ g.mol}^{-1}$, $M_{(\text{water})}=18.02 \text{ g.mol}^{-1}$)

$$x_e = \frac{n_{C_2H_5O}}{n_{C_2H_5O} + n_{H_2O}} = \frac{[C_2H_5O]}{[C_2H_5O] + [H_2O]} = \frac{94.7/46.07}{(94.7/46.07) + (1000 - 94.7)/18.02} = 0.039$$

b) The activity coefficient γ_{EtOH} of Ethanol under the given conditions is calculated:

Equation (57)

$$\ln \gamma_{EtOH} = 1,6027 \times e^{-2,8235 \times x_e} - 982,27 - 6861,39 * x_e \left[\frac{1}{25 + 273,15} - \frac{1}{323,15} \right]$$

$$\gamma_{EtOH} = 3.49$$

c) The pure component vapor pressure is calculated (A 8.20147, B 1642.89 and C 230.3)

$$\log_{10} p^0 = 8.20147 - \frac{1642.89}{25+230.3} \text{ with } p^0 \text{ in mmHg so } p_{EtOH}^0 = 58.39 \text{ mmHg} = 7.785 \text{ kPa}$$

d) The vapor pressure of the ethanol in the dilution is estimated according to modified RAOULT'S law (equation (59)):

$$p_{EtOH} = p_{EtOH}^0 \times \gamma_{EtOH} \times x_{EtOH} = 7.785 \times 3.49 \times 0.039 = 1.059 \text{ kPa}$$

e) At 101.325 kPa and 25 °C the moles per L gas can be calculated using the ideal gas law:

$$n = \frac{p \times V}{RT} = 0.0409 \text{ mol}$$

f) Now, the proportion of ethanol in the gas can be calculated:

$$\frac{p_{EtOH}}{p} = \frac{1.059}{101.325} = 0.0104 = 1.04 \%$$

g) The ethanol mass in the gas can therefore be calculated *mol* and *mg*:

$$0.0104 \times 0.0409 = 4.25 * 10^{-4} \text{ mol} = 4.25 * 10^{-4} * 46.07 = 19.59 \text{ mg}$$

As a result of calculation it can be proved that in a headspace of one liter saturated with ethanol vapor of a 12 %vol wine one may find 19.59 mg ethanol. For a headspace of 1L gas per liter wine this content is negligible comparing with that present in the liquid (0.0196 g.L⁻¹ in gas per 94.7 g.L⁻¹ in liquid). Even for bigger headspaces, this equilibrium stays strongly on the liquid side and the mass in the gas phase remains negligible, as there is also a loss in water of similar volume (3.1 kPa at 25°C corresponding to 22.54 mg.L⁻¹_{gas}). As there is very little loss of ethanol and water there is negligible change in ethanol concentration and negligible losses of volume.

Aguera et al. 2010, conducted trials on alcohol reduction via stripping during alcoholic fermentation. They reduced the alcohol content of a fermenting wine at 6 %vol to 4 %vol by nitrogen stripping using about 3000 L N₂ gas / L wine. Applying the formulas described above is predicting an alcohol loss of ca. 18.3 g.L⁻¹ ≈ 2.3 %vol.

1.2.6 Further Compounds in Vapor Phase

Like the described gases, water and ethanol, all other compounds can be found in the gas phase above the liquid, as all these compounds are creating an equilibrium between liquid and gas phase according to HENRY'S law or RAOULT'S law. The abundance of these compounds in the gas phase is dependent from their concentrations in the liquid phase and their volatility. As shown in the previous chapters, the gases are found in high concentrations in the volatile form and only some milligrams can be dissolved, contrarily to water and ethanol which are in very high concentration (ca. 900 g.L⁻¹ for water, 100 g.L⁻¹ ethanol) in the wine only show limited pressures in the gaseous form.

Very few studies exist on the volatility/solubility of aroma compounds like esters and higher alcohols in wine. In water these volatilities are often known. The hydrophobic properties of the aroma compounds lead to a better solubility, meaning lower volatility in ethanol. Wine as a mixture of water and ethanol is estimated to have a solubility that is in between that water and pure ethanol. As there is also an influence of the matrix of the wine the solubility of these aroma compounds are not very well known (Diban et al. 2008).

Table 13 is summarizing the solubility, typical high and low concentrations found in wine, the sensory description of some important esters and higher alcohol as well as their Henry constants in wine and water. The descriptors for esters are ranging from positive attributes like pineapple, fruit towards negative attributes like solvent, glue characteristics (Francis & Newton, 2005).

In Table 14 the volatilities of some compounds found in wine are summarized as partition coefficients, meaning the dimensionless ratio gas/liquid of the molecules, where data for wine could not be found, partition coefficients in water are presented. Using carbon dioxide as a reference, nitrogen is more than 40 times more volatile, oxygen is more than 20 times more volatile than carbon dioxide. Contrarily the aroma compounds like esters and higher alcohols are much less volatile. It can be seen that the very volatile ester iso-amylacetate is factor 177 times less volatile than the gas carbon dioxide in wine. The higher alcohol iso-amylalcohol has a volatility that is almost 9000 times lower than that of carbon dioxide. Acetaldehyde is rather volatile; its partition coefficient is in the order of the esters presented here. The partition coefficients of the acids typically found in wine are several orders of magnitude lower than those of the other compounds presented here. Even the so called volatile acidity acetic acid is less volatile than the higher alcohol iso-amylalcohol. As the data presented here is determined on water and the volatility of this acid is pH dependent a higher volatility in wine is very likely, but even a 1000 fold higher order of volatility would not change the conclusion.

Table 14 is showing the calculated corresponding headspace concentration for a wide range of compounds found in wine. The liquid concentrations are chosen to be realistic values

for wine, for esters and higher alcohols the high concentration given by Francis and Newton 2005 were chosen. It can be seen, that the concentrations in the headspace are dependent on the different partition coefficients and very different initial concentration. It can be seen that the concentrations in the gas phase are negligible for most of the compounds compared to that in liquid phase.

An aroma compound with a very negative aroma descriptor is hydrogen sulfide; it is very volatile compared to the esters and higher alcohols presented here. Although there is only data available for water (Sander, 1999a), which is suggesting a volatility that is three times lower than that of CO₂. Due to the complex matrix of wine, this volatility might be significantly different but the order of magnitude should stay in a similar range. For other aroma compounds, the partition coefficients or HENRY constants have not been determined or could not be found during this research.

Sulfur dioxide, which is used to preserve wine from oxidation and microbiological spoilage, is another important volatile compound. Due to its acidic behavior in water and wine its solubility is highly dependent on the pH. Only molecular SO₂ is volatile, this part of molecular SO₂ in wine is very small at about 4 % at pH 3.2 and 0.6 % at pH 4. Precise published Henry constants for SO₂ cannot be found and is likely to differ strongly from wine to wine. The value for water where it is ten times less volatile than H₂S (partition coefficient K_i=0.03 (Sander, 1999a) is presented here, but a lower pH is indicating a higher volatility in wine than in water.

There are much more known and studied compounds in wine and hence in the atmosphere around wine, (Francis & Newton, 2005). As volatilities and Henry constants are not often studied for these compounds in wine we want to focus here on the esters and higher alcohols that could be determined in our laboratory with the methods available.

Table 13: Properties of some selected esters and higher alcohols in wine

Compound	n° CAS*	M [g/mol]	C _{Low} [mg/L]	C _{High} [mg/L]	Odor threshold [mg/L]	Descriptor	H _i ^{25°C} Water [Pa/m ³ mol]	H _i ^{25°C} Wine [Pa/m ³ mol]
Source			FRANCIS and NEWTON, 2005				DIBAN <i>et al.</i> , 2008	
Ethyl acetate	141-78-6	88.1	22.5	208	12.26	Pineapple	14.6	9.25
Ethyl butyrate	105-54-4	116.15	0.18	0.7	0.020	Apple		
Ethyl hexanoate	123-66-0	144.21	0.28	1.02	0.014	Apple, pear, fruit	30.24	21.94
Isoamyl acetate	123-92-2	130.18	0.163	4.74	0.030	Banana	32.55	20.35
iso-butanol	78-83-1	74.12	32	108	40.0	Wine, solvent, bitter		
isoamyl alcohol	123-51-3	88.14	109	357	30.0	Whiskey, malt, burnt	0.9	0.41

*Chemical Abstract Service registry number