THE PROTECTIVE ROLE OF DISSOLVED CARBON DIOXIDE AGAINST WINE OXIDATION: A SIMPLE AND RATIONAL APPROACH

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Abstract

Aims: During wine making, oxygen and carbon dioxide are often simultaneously present in the liquid phase. We propose a simple rational approach, based on usual chemical engineering and thermodynamic principles, to provide understanding and practical rules for controlling the effects of these two dissolved gases, and especially their inter-relationship. Furthermore, this study proposes an explanation for the "protective" effect against oxidation, which is reported when high concentrations of carbon dioxide are present in musts and wines.

Methods and results: The theoretical quantitative relation, termed "binary gas equilibrium line", between the maximum possible concentration of dissolved oxygen in respect to dissolved carbon dioxide was derived and, in our experiments, corresponded to $C_{O_{2max}} \cong -0{,}005\ C_{CO_2} + 7{,}9\ mg.L^{-1}$. Specific saturation experiments using simultaneous injection of air and gaseous carbon dioxide were performed and the experimental results allowed us to validate this theory in the case of gas bubbling in a liquid.

Conclusion: It is shown that complete protection is only obtained when carbon dioxide is generated by the fermentation in the liquid. An interesting parallel conclusion is that micro-oxygenation is totally inefficient in such periods. In the case where there is no production of CO_2 but where a high initial dissolved carbon dioxide concentration is present, the "protective" effect acts only by reducing the rate of oxygen transfer.

Significance and impact of the study: The physical understanding of this phenomenon can be found in the fact that as soon as a gaseous air or pure oxygen phase is in contact with a carbon dioxide saturated liquid, the dissolved carbon dioxide, which is not at equilibrium with the gaseous phase, tends to escape into this gaseous phase. This study points out the complexity of the gas-liquid equilibrium when two dissolved gases are simultaneously present in a liquid and its implication in the winemaking process.

Key words: dissolved gases, micro-oxygenation, carbon dioxide, oxygen, wine making

Résumé

Objectifs : Au cours de la vinification, l'oxygène et le dioxyde de carbone sont souvent simultanément présents à l'état dissous dans la phase liquide. Nous proposons ici une approche simple et rationnelle, basée sur les principes usuels du génie chimique et de la thermodynamique. On peut ainsi avoir accès à la compréhension et à des règles pratiques pour maîtriser les effets de ces deux gaz dissous, et en particulier de leur interaction. Cette étude propose ainsi une explication de l'«effet protecteur» contre l'oxydation que l'on constate lorsque le dioxyde de carbone dissous est présent à forte concentration.

Méthodes et résultats : On a pu établir dans cette étude une relation théorique quantitative, appelée «droite d'équilibre de saturation binaire», qui relie la concentration maximale possible pour l'oxygène dissous à la concentration en dioxyde de carbone dissous. Pour notre domaine expérimental, cette relation correspond à $C_{O_{2max}} \cong -0{,}005\ C_{CO_2} + 7{,}9\ mg.L^{-1}$. Des expérimentations spécifiques de saturation d'une phase liquide hydro-alcoolique, où de l'air et du dioxyde de carbone sont simultanément injectés, ont été réalisées et les résultats expérimentaux ont permis de valider cette approche dans le cas du bullage dans un liquide.

Conclusion : Cette étude montre qu'une protection complète du vin contre l'oxygène n'est obtenue que lorsque du dioxyde de carbone est produit in situ par la fermentation des levures et donc dans le cas où celui-ci est à saturation dans la phase liquide. En parallèle, il est intéressant de noter qu'une micro-oxygénation serait totalement inefficace en de telles périodes. Dans le cas où il n'y a aucune production du CO_2 mais où une concentration dissoute initiale élevée en CO_2 est présente, l'effet « protecteur » agit seulement par une réduction du taux de transfert d'oxygène dans le vin.

Signification et impact de l'étude : La compréhension physique de ces phénomènes réside dans le fait que, lorsqu'une phase d'air gazeux ou d'oxygène pur est en contact avec un liquide saturé en dioxyde de carbone dissous, ce dernier, qui n'est pas à l'équilibre avec la phase gazeuse, désorbe dans la phase gazeuse. Cette étude appréhende la complexité de l'équilibre gaz/liquide quand deux gaz dissous sont simultanément présents dans un liquide et met en lumière son implication dans le procédé de vinification.

Mots clés : gaz dissous, micro-oxygénation, dioxyde de carbone, oxygène, vinification

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INTRODUCTION

Carbon dioxide (CO$_2$) and oxygen (O$_2$) are very often present simultaneously, in the form of dissolved gas, in many steps of wine making. The quality and the organoleptic perception of a wine are affected by their presence. Indeed, the sparkling effect of dissolved carbon dioxide is likely to enhance the perception of the fragrance of the wine. As for dissolved oxygen, its presence at high concentration directly governs the oxidation rate of specific components of the wine, leading either to beneficial or detrimental effects on the organoleptic perception (Singleton, 1987; Dubourdieu and Lavigne, 1990; Schneider, 1998; du Toit *et al.*, 2006; Li and Wang, 2008; Lopes *et al.*, 2009).

It is commonly accepted that there is an interrelation between the effects of these two dissolved gases: when high concentrations of carbon dioxide are present, the wine is "protected" from oxygen, and thereby from oxidation phenomena (Ribereau-Gayon *et al.*, 1998; Jackson, 2008). The influence of dissolved carbon dioxide during the process of micro-oxygenation, especially on the kinetics of oxygen dissolution, has also been recently reported (Devatine *et al.*, 2007).

In this work, we have tried to propose a simple rational approach, based on usual chemical engineering and thermodynamic principles, to provide understanding and practical rules for controlling the effects of these two dissolved gases, and especially their inter-relationship.

Indeed, oxygen transfer into the wine can occur in two ways:

1) not desired and results from accidental or uncontrolled contact with air during manipulations, such as transfer in different tanks (Vidal *et al.*, 2001 and 2004; Castellari *et al.*, 2004);

2) desired and results from the controlled addition of oxygen. Oxygen should be introduced into the wine in controlled quantities and at a controlled rate in order to induce the necessary oxidation reactions of the wine (Atanasova *et al.*, 2002; Drinkine *et al.*, 2007). This is, for instance, the case of micro-oxygenation, a commonly implemented treatment, which aims at providing oxygen in a way equivalent to the slow diffusion of oxygen through wood barrel walls, as used for wine ageing (Gomez-Plaza and Cano-Lopez, 2011).

The contact of wine with oxygen may also occur, willingly or not, when high concentrations of carbon dioxide are present. Here also, two cases must be considered:

1) The carbon dioxide concentration remains constant because of the constant production by growing yeasts, compensating for the possible stripping by contact with a gaseous phase. This is, for instance, the case when micro-oxygenation is performed during the alcoholic fermentation step;

2) There is no in situ production of carbon dioxide and its concentration is likely to decrease by stripping. This case has already been addressed in previous works (Devatine *et al.*, 2007; Devatine and Mietton-Peuchot, 2009) and the main results are recalled here. Indeed, in this case, significantly lower values of the volumetric oxygen transfer coefficient (k$_L$a) were found, indicating a strong decrease of the transfer efficiency, where the oxygen transfer yield drops from 77%, when the wine is initially carbon dioxide free, to 9%, when it is initially carbon dioxide saturated (Devatine *et al.*, 2007). It was hypothesized that massive desorption of dissolved carbon dioxide into rising bubbles would lower the partial pressure of oxygen and thus the driving force for the interphasic mass transfer. Using this hypothesis, mathematical modelling of oxygen transfer around tiny rising bubbles yielded computed values of the transfer yield which were in close agreement with experimental ones, validating the initial proposed hypothesis (Devatine and Mietton-Peuchot, 2009). Note that in this case, because the stripped carbon dioxide was not replaced, its concentration progressively decreased during the course of the experiment, reaching zero, thus leading to slower but complete saturation by oxygen.

These last results suggest that such effects (*i.e.*, lower oxygen partial pressure) may also occur when the concentration of dissolved carbon dioxide is kept constant, and this, in addition to lower kinetics, would yield lower oxygen concentration at equilibrium. This may be described and demonstrated using very conventional thermodynamic principles of gas-liquid equilibrium, as presented below.

THEORETICAL APPROACH

Let us consider a gaseous space in contact with a liquid containing dissolved oxygen and dissolved carbon dioxide, and let us consider that the system has reached equilibrium.

The total pressure is the sum of the partial pressures of air and carbon dioxide:

$$P_T = P_{air} + P_{CO_2} \qquad (1)$$

The presence of nitrogen is implicitly accounted for in the partial pressure of air: it is assumed to be at solubility equilibrium and does not intervene in the equations. At equilibrium, the concentrations of dissolved gas in liquid are given by Henry's law:

$$C_{CO_2} = \frac{P_{CO_2}}{H_{CO_2}} \qquad (2)$$

$$C_{O2} = \frac{P_{O_2}}{H_{CO_2}}$$

with $P_{O_2} = 0{,}2P_T$ in the case of synthetic air   (3)

which gives:

$$C_{O_2} = \frac{0.2P_{air}}{H_{O_2}} = \frac{0.2(P_T - P_{CO_2})}{H_{O_2}} = \frac{0.2P_T}{H_{O_2}} - \frac{0.2P_{CO_2}}{H_{O_2}}$$

$$C_{O_2} = \frac{0.2P_T}{H_{O_2}} - \frac{0.2C_{CO_2}H_{CO_2}}{H_{O_2}} \qquad (4)$$

Therefore, the relationship between equilibrium dissolved oxygen concentration, in respect to conventional air saturation concentration $C^*_{O_2}\big|_{air} = \dfrac{0.2P_T}{H_{O_2}}$ and dissolved carbon dioxide concentration is:

$$C_{O_2} = C^*_{O_2}\big|_{air} - C_{CO_2}\frac{0.2H_{CO_2}}{H_{O_2}} \qquad (5)$$

Equation 5 corresponds to a linear relation, which will be termed "binary gas equilibrium line", with a slope (m_{bin}) given by:

$$\text{then } m_{bin} = -\frac{0.2H_{CO_2}}{H_{O_2}} \qquad (6)$$

Because $P_T = H_{CO_2}C^*_{CO_2}$ and $0.2P_T = H_{O_2}C^*_{O_2}\big|_{air}$

gives $\dfrac{0.2H_{CO_2}}{H_{O_2}} = \dfrac{C^*_{O_2}\big|_{air}}{C^*_{CO_2}}$

where $C^*_{CO_2}$ is the CO_2 saturation concentration with pure CO_2 at 1 atm.

and $C^*_{O_2}\big|_{air}$ is the O_2 saturation concentration with air at 1 atm.

$$\text{then } m_{bin} = -\frac{C^*_{O_2}\big|_{air}}{C^*_{CO_2}} \qquad (7)$$

We provide an experimental validation of this approach. As mentioned earlier conventional saturation experiments are not useful because the carbon dioxide concentration does not remain constant. Therefore, a specific saturation experiment is proposed where dissolved carbon dioxide concentration is maintained constant by continuous injection of gaseous carbon dioxide, simultaneously with injection of gaseous oxygen. In this case, we do not analyze the transient part of the experiment, but only the values of the concentration at steady state, that is, at equilibrium. There is a direct analogy between this situation and the actual situation of an active fermentation must submitted to contact with air, where in situ production of carbon dioxide by yeasts maintains a constant concentration of this gas in the liquid. Indeed, this production results in a carbon dioxide flux leaving the system, and is equivalent to the injection of gaseous carbon dioxide as in the proposed experiment.

MATERIALS AND METHODS

1. Tested liquid solutions

The study was done using a model solution of 12% alcohol content (v/v) and 5 g.L^{-1} of tartaric acid, pH = 3.5. This model solution allows the elimination of errors due to possible consumption of oxygen by some compounds present in wine. The solution was transferred into a 3 L glass vessel equipped with specific entry ports for pH and oxygen probes, gas diffusers, and liquid sampling (for measurement of dissolved carbon dioxide).

2. Description of the experimental set-up

The scheme of the set-up is presented in figure 1. Separate tubing was used to inject synthetic air (1) (80% N_2 and 20% O_2) and gaseous carbon dioxide (100% CO_2) (2) from pressurized bottles (Air Liquide, France). Gas flow rates were regulated by a flow meter (sapphire ball, Sho Rate 1353, Brooks Instruments) previously calibrated. Two porous diffusers were used for gas injection: they were dead end tubes (6.4 mm diameter x 46 mm height, Porex Surgical Inc.) made of high density polyethylene. The liquid was stirred at 700 rpm with a magnetic stir bar.

The dissolved oxygen concentration was measured using an optic probe LDO HQ 10 (Hach Lange, USA). Carbon dioxide concentration was measured using a CarboQC system (Anton Paar), where the liquid sample is obtained by pumping with a plunging tube.

3. Experimental procedure

This set-up makes it possible to obtain the kinetics of the oxygen transfer, although we only considered here the final binary gas equilibrium values. The model solution was first degassed by nitrogen bubbling (100% N_2) to eliminate any dissolved oxygen and carbon dioxide. Both gases were then simultaneously injected by two separate similar diffusers at constant flow rates.

Single gas saturation values at the experimental temperature were obtained by measuring the final stabilized value when injecting a single gas.

RESULTS AND DISCUSSION

In a first step, the ability of the system to yield equilibrium values was assessed by measuring the

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saturation concentration of oxygen and carbon dioxide separately. At 20°C, by injection of a single gas in a model solution, we obtained equilibrium concentrations of 7.9 mg.L^{-1} for synthetic air and 1,550 mg.L^{-1} for carbon dioxide, which are close to values for pure water (table 1 and 2 respectively).

The results for simultaneous injection of air and carbon dioxide are presented in figure 2, where six pairs of injection flow rates were tested (a-f). The concentration curves of O_2 and CO_2 were dependent on the different flow rates: the greater the flow rate, the higher the final equilibrium concentration of the gas. For instance, with an air flow rate (Q_{air}) of 0.026 L.min^{-1} and a carbon dioxide flow rate (Q_{CO2}) of 0.27 L.min^{-1}, equilibrium concentrations of 0.6 mg.L^{-1} for oxygen and 1,430 mg.L^{-1} for carbon dioxide were obtained (figure 2a). When we increased Q_{air} to 0.14 L.min^{-1}, the final concentration of oxygen increased (3.6 mg.L^{-1}), whereas that of carbon dioxide decreased (1,050 mg.L^{-1}) (figure 2c).

The interpretation of the values of the final part of the curves, when the O_2 and CO_2 concentrations are no longer varying, is based on two main hypotheses:

1) The system is at steady state, the concentrations are stable and, because there is no consumption, there is no further transfer towards the liquid phase. So, all the injected carbon dioxide and oxygen gas fluxes are found in the output flow, which is then identical to the sum of the two injected flows.

2) The liquid is perfectly mixed and the concentrations of dissolved carbon dioxide and oxygen are at thermodynamic equilibrium with their respective partial pressures in the gaseous output flow.

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

$$y^s_{O_2} = \frac{N^s_{O_2}}{N^s_{air} + N^s_{CO_2}} = \frac{N^e_{O_2}}{N^e_{air} + N^e_{CO_2}} = \frac{\frac{1}{5}N^e_{air}}{N^e_{air} + N^e_{CO_2}} \quad (8)$$

The equilibrium concentrations are then:

$$C^f_{O_2} = \frac{y^s_{O_2} P_T}{H_{O_2}} = (\frac{\frac{1}{5}N^e_{air}}{N^e_{air} + N^e_{CO_2}})\frac{P_T}{H_{O_2}} \quad (9)$$

$$C^f_{O_2} = (\frac{N^e_{air}}{N^e_{air} + N^e_{CO_2}})(\frac{1}{5}\frac{P_T}{H_{O_2}}) = \frac{N^e_{air}}{N^e_{air} + N^e_{CO_2}}C^*_{O_2}\Big|_{air} \quad (10)$$

and similarly
$$C^f_{CO_2} = \frac{y^s_{CO_2} P_T}{H_{CO_2}} = (\frac{N^e_{CO_2}}{N^e_{air} + N^e_{CO_2}})\frac{P_T}{H_{CO_2}} = \frac{N^e_{CO_2}}{N^e_{air} + N^e_{CO_2}}C^*_{CO_2} \quad (11)$$

Figure 3 compares the theoretical and experimental values of dissolved oxygen and carbon dioxide concentrations at steady state.

The relationship between the final equilibrium concentrations of this binary system may be established.
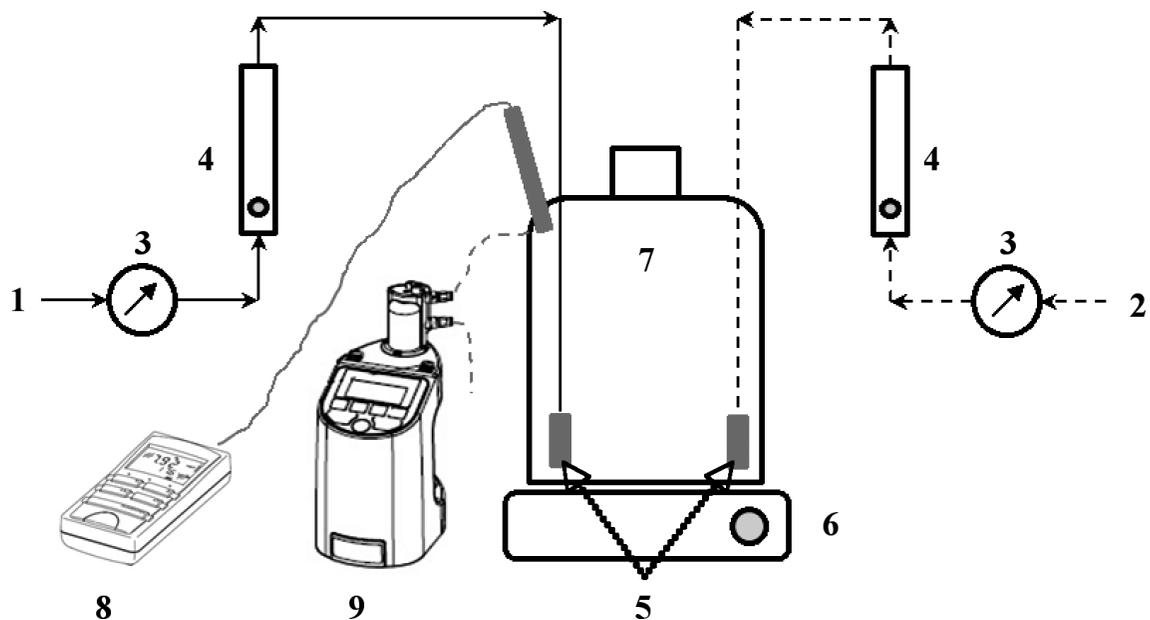
Figure 1 - Scheme of the experimental set-up
1 - synthetic air; 2 - carbon dioxide; 3 - manometers; 4 - flow meters; 5 - gas diffusers; 6 - magnetic stirrer; 7 - glass vessel; 8 - LDO HQ 10 (oxygen probe); 9 - CarboQC (carbon dioxide meter)

Indeed, when considering two experiments A and B, we have established:

for experiment A:

for experiment B:

$$C_{O_2}^{f\,A} = \frac{N_{air}}{N_{air} + N_{CO_2}} C_{O_2}^* \Big|_{air} = y_{air}^A C_{O_2}^* \Big|_{air} \qquad (12)$$

$$C_{O_2}^{f\,B} = \frac{N_{air}}{N_{air} + N_{CO_2}} C_{O_2}^* \Big|_{air} = y_{air}^B C_{O_2}^* \Big|_{air} \qquad (14)$$

$$C_{CO_2}^{f\,A} = \frac{N_{CO_2}}{N_{air} + N_{CO_2}} C_{CO_2}^* = y_{CO_2}^A C_{CO_2}^* \qquad (13)$$

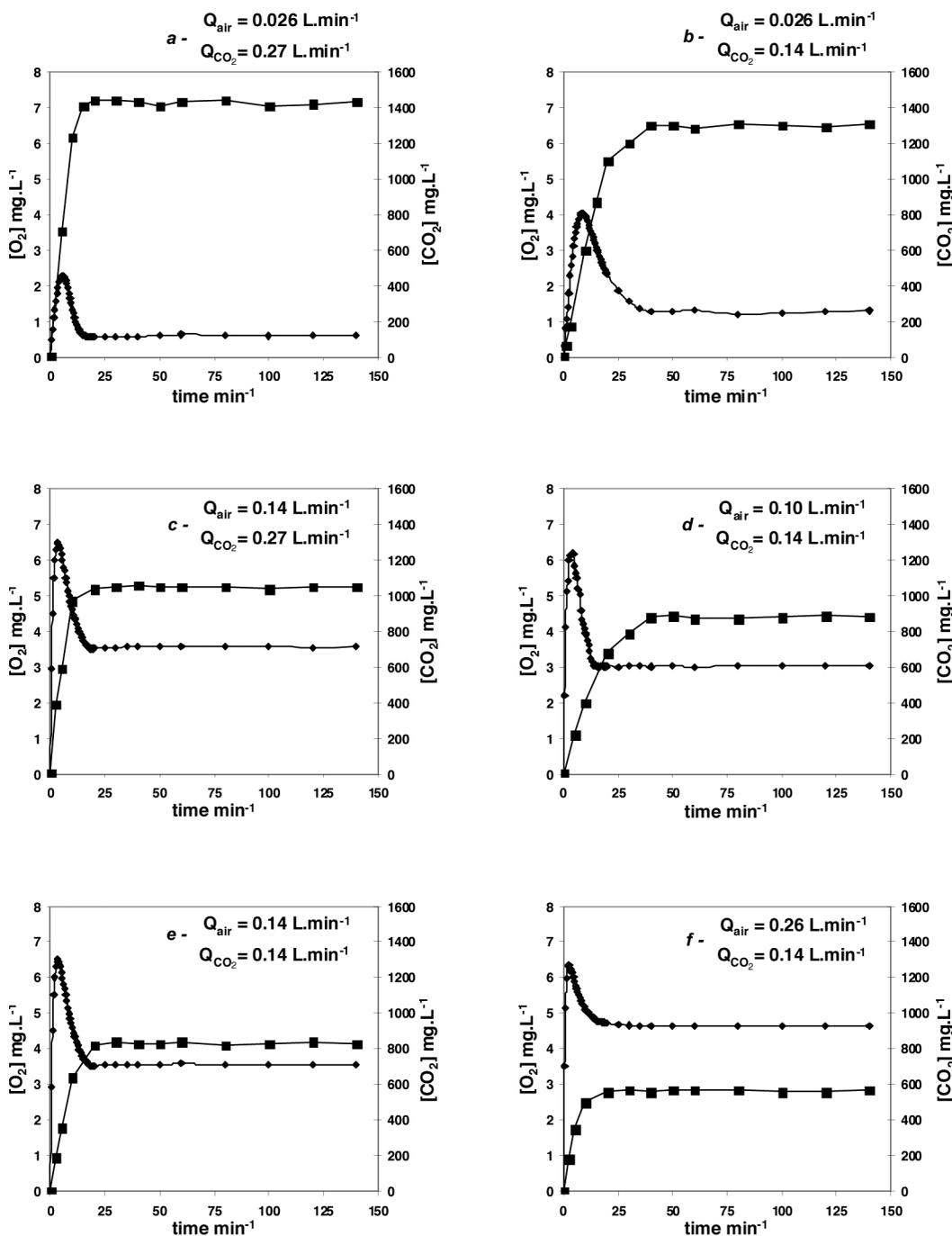$$C_{CO_2}^{f\,B} = \frac{N_{CO_2}}{N_{air} + N_{CO_2}} C_{CO_2}^* = y_{CO_2}^B C_{CO_2}^* \qquad (15)$$

Figure 2 - Output concentrations of dissolved gases (O$_2$ ◆ and CO$_2$ ■) during the injection of synthetic air and carbon dioxide in the model solution. a to f: Influence of the different gas flow rates.

with $y^A_{air} = 1 - y^A_{CO_2}$ and $y^B_{air} = 1 - y^B_{CO_2}$, a linear relation is obtained where the slope is:

$$\frac{C^{fA}_{O_2} - C^{fB}_{O_2}}{C^{fA}_{CO_2} - C^{fB}_{CO_2}} = \frac{y^A_{air} - y^B_{air}}{y^A_{CO_2} - y^B_{CO_2}} \frac{C^*_{O_2}\big|_{air}}{C^*_{CO_2}} \qquad (16)$$

that given :

$$\frac{C^{fA}_{O_2} - C^{fB}_{O_2}}{C^{fA}_{CO_2} - C^{fB}_{CO_2}} = \frac{(1 - y^A_{CO_2}) - (1 - y^B_{CO_2})}{y^A_{CO_2} - y^B_{CO_2}} \frac{C^*_{O_2}\big|_{air}}{C^*_{CO_2}} = -\frac{C^*_{O_2}\big|_{air}}{C^*_{CO_2}} \qquad (17)$$

Figure 4 shows the experimental values from figure 3 plotted against this straight line. For zero dissolved carbon dioxide concentration, the equilibrium oxygen value corresponds to saturation value in respect to air. Therefore, the complete equation is:

$$C_{O_2} = -\frac{C^*_{O_2}\big|_{air}}{C^*_{CO_2}} C_{CO_2} + C^*_{O_2}\big|_{air} \qquad (18)$$

Using the values of $C^*_{O_2}\big|_{air}$ and $C^*_{CO_2}$ obtained from our experiments with single gas injection, we obtain:

$$C_{O_2} = -\frac{7,9\,\text{mg.L}^{-1}}{1550\,\text{mg.L}^{-1}} C_{CO_2} + 7,9\,\text{mg.L}^{-1} \cong -0,005\,C_{CO_2} + 7,9\,\text{mg.L}^{-1} \qquad (19)$$

The very good agreement between experiments and theory validates the approach and its hypotheses. Therefore, for a liquid in contact with air, the relation between the maximum possible dissolved oxygen concentration, in respect to a given dissolved carbon dioxide concentration, has been established, both theoretically and experimentally.

The values of Henry's constant are crucial to demonstrate the relationship. Indeed, the solubility of a gas decreases when temperature increases and this is quantified by the values of Henry's constant H_{O_2} given in table 1 for a gas phase containing oxygen in contact with water (adapted from Perry, 1997). The value of Henry's constant depends on the gas used (table 1: oxygen (H_{O_2}) and table 2: carbon dioxide (H_{CO_2})), on the composition of the liquid phase, and on the liquid temperature. From them, we can easily compute, in water, the saturation concentrations for oxygen $C^*_{O_2}\big|_{air}$ (table 1) and for carbon dioxide $C^*_{CO_2}$ (table 2).

The slight differences with our experimental single gas saturation values originate from different properties of the model solution compared to water and from the
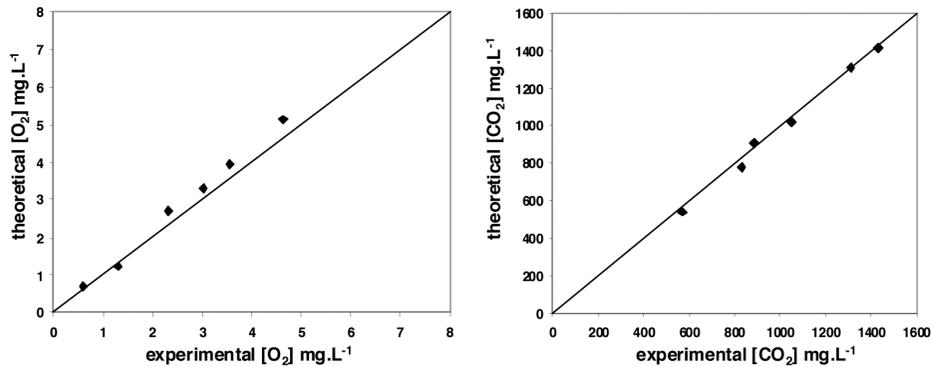

Figure 3 - Comparison of theoretical and experimental values of dissolved oxygen and carbon dioxide concentrations at steady state.

Table 1 - Henry's constant of oxygen H_{O_2} versus temperature (from Perry, 1997; liquid phase = water) and its saturation concentration $C^*_{O_2}\big|_{air}$ for a gas phase = air ambient (oxygen = 20.95 %).

T (°C)	H_{O_2} (Pa.m³.kg⁻¹)	$C^*_{O_2}\big|_{air}$ (mg.L⁻¹)	T (°C)	H_{O_2} (Pa.m³.kg⁻¹)	$C^*_{O_2}\big|_{air}$ (mg.L⁻¹)
0	1.45×10^6	14.6	25	2.49×10^6	8.5
5	1.66×10^6	12.8	30	2.71×10^6	7.8
10	1.86×10^6	11.4	35	2.89×10^6	7.4
15	2.07×10^6	10.2	50	3.35×10^6	6.3
20	2.28×10^6	9.3	100	3.99×10^6	5.3

fact that, for oxygen, the reference gas is ambient air at 20.95% of SO_2. Note that gas solubility in wine is very similar to that of the model solution: for instance, at 19°C, for the same synthetic solution, the experimental value of Henry's constant is $H = 2.47 \times 10^6$ Pa.m³.kg⁻¹ and for wine it is $H = 2.72 \times 10^6$ Pa.m³.kg⁻¹ (Devatine *et al.*, 2007).

Manipulations during wine making, where contact with air may occur, are done at different temperatures, as for example tartaric stabilisation which is done at low temperature. So, it was interesting to quantify the influence of temperature on the binary gas saturation curve. We have:

$$C_{O_2} = -\frac{C_{O_2}^* \big|_{air}^{in\,wine}}{C_{CO_2}^* \big|_{air}^{in\,wine}} C_{CO_2} + C_{O_2}^* \big|_{air}^{in\,wine} \qquad (20)$$

with $\quad C_{O_2}^* \big|_{air}^{in\,wine} = \dfrac{0.2095 \times 1.013 \times 10^5}{H_{O_2} \big|^{in\,wine}}$

When extrapolating the same approach to micro-oxygenation of real wine with pure oxygen, we obtain:

$$C_{O_2} = -\frac{C_{O_2}^* \big|_{pure\,O_2}^{in\,wine}}{C_{CO_2}^* \big|_{pure\,O_2}^{in\,wine}} C_{CO_2} + C_{O_2}^* \big|_{pure\,O_2}^{in\,wine} \qquad (21)$$

with $\quad C_{O_2}^* \big|_{pure\,O_2}^{in\,wine} = \dfrac{1.013 \times 10^5}{H_{O_2} \big|^{in\,wine}}$

Figure 4 - Equilibrium concentrations for oxygen and carbon dioxide present simultaneously in solution (T = 20°C) – experimental and theoretical (eq. 17) points.

$C_{O_2}^* \big|^{in\,wine}$ can be approximated by $C_{CO_2}^* \big|^{in\,synthetic\,solution}$ (1,550 mg.L⁻¹ at 20 °C from this work) and, for both gases, the influence of temperature was derived proportionally to the temperature variations of their Henry's constants in respect to water. The obtained numerical values are given in table 3.

The equations 18 and 19 are drawn in figure 5 for different temperatures.

Table 2 - Henry's constant of carbon dioxide H_{CO_2} versus temperature (from Perry, 1997; liquid phase = water) and its saturation concentration $C^*_{CO_2}$ for a gas phase = pure carbon dioxide.

T (°C)	H_{CO_2} (Pa.m³.kg⁻¹)	$C^*_{CO_2}$ (mg.L⁻¹)	T (°C)	H_{CO_2} (Pa.m³.kg⁻¹)	$C^*_{CO_2}$ (mg.L⁻¹)
0	3.09×10^4	3275.9	15	4.99×10^4	2031.8
5	3.58×10^4	2829.7	20	5.80×10^4	1745.6
10	4.25×10^4	2385.5	25	6.70×10^4	1511.5

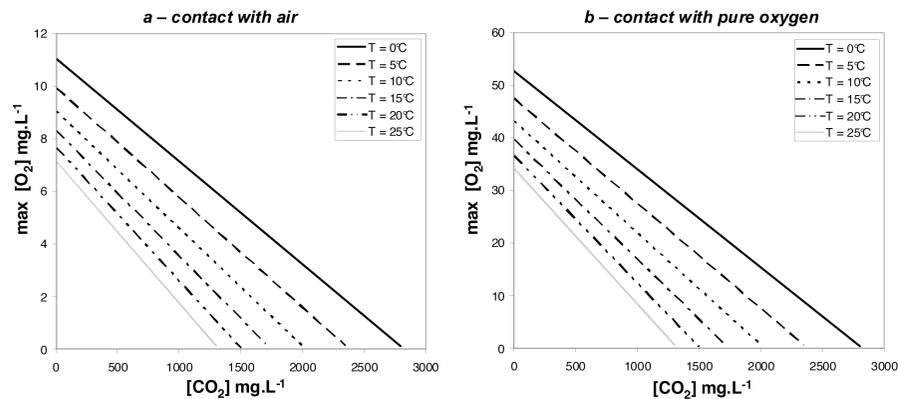**Table 3 - Numerical values of coefficients in eq. 18 and 19 as a function of temperature.**

T (°C)	$C_{O_2}^* \big|_{air}^{in\,wine}$ (mg.L⁻¹)	$C_{O_2}^* \big|_{pure\,O_2}^{in\,wine}$ (mg.L⁻¹)	$C_{CO_2}^* \big|^{in\,wine}$ (mg.L⁻¹)
0	11.0	52.6	2908.8
5	9.9	47.5	2512.6
10	9.1	43.2	2116.4
15	8.3	39.7	1804.1
20	7.7	36.7	1550.0
25	7.2	34.1	1342.1

Figure 5 - Graph of the maximum possible dissolved oxygen concentration in wine as a function of dissolved carbon dioxide concentration. a) contact with air. b) contact with pure oxygen.

CONCLUSION

In this work, we have proposed understanding and quantification by simple equations of the "protective" effect of dissolved carbon dioxide against oxygen. In this case, the term "protective" corresponds to a negative aspect of the presence of dissolved oxygen in the liquid. This dissolved oxygen may result from uncontrolled manipulations and contacts with surrounding air and may induce undesired oxidation reactions. Note that this "protective" effect can be detrimental and may lead to inadequate processing when dissolved oxygen is needed to induce desired oxidation reactions, as in the case of micro-oxygenation.

During the wine making steps in which the production of CO_2 is high, the saturation concentration of CO_2 is reached and unwanted contact with air results in low kinetics of oxygen transfer together with low values of the equilibrium oxygen concentration. In fact, the equilibrium value is dependent on the ratio of the CO_2 production rate and the air flow rate in contact with the liquid, similarly to what was shown in our experiments with injection of the two gases. Similarly, the greater the CO_2 production by yeasts, the greater the "protective" effect against oxygen from air contact. The equation giving the maximum dissolved oxygen concentration in respect to dissolved carbon dioxide concentration was derived and appeared to be a very simple linear relationship (equation 16), termed the "binary gas equilibrium line".

In the case where there is no production of CO_2 but where a high initial dissolved carbon dioxide concentration is present, the "protective" effect acts only by reducing the rate of oxygen transfer. For instance, in the case of an initially carbon dioxide saturated wine, our previous work has shown a 10-fold decrease of the observed $k_L a$ values, corresponding to correlatively strong reduction of the oxygen transfer fluxes (Devatine *et al.*, 2007). For a contact with a gas at a given $k_L a$ value, 95% saturation is obtained at a time equal to $5/k_L a$. So, these lower $k_L a$ values result

in an important time delay in reaching oxygen saturation in initially carbon dioxide saturated solutions. Indeed, for short accidental contacts with air, the protective effect is efficient.

A complete protection is only obtained when carbon dioxide is produced. An interesting parallel conclusion is that micro-oxygenation is totally inefficient in such periods.

The physical understanding of this phenomenon can be found in the fact that as soon as a gaseous air or pure oxygen phase is in contact with a carbon dioxide saturated liquid, the dissolved carbon dioxide, which is not at equilibrium with the gaseous phase, tends to escape into this gaseous phase, thereby diluting the gaseous oxygen. This results in lowering the driving force for the transfer as well as decreasing the oxygen equilibrium concentration. Note that this protective effect is very efficient when the gaseous contact occurs through bubbles, where dilution up to thermodynamic equilibrium is rapidly achieved. This might not be as efficient when contact occurs through the open interface of a relatively large and renewed head space.

This work has shown that two gases cannot be treated independently when simultaneously present in a liquid. This work, developed here for dissolved oxygen and carbon dioxide in aqueous solutions, can be extrapolated to any system of several gases dissolved in a liquid.

Notations

C   dissolved gas concentration in the liquid phase ($mg.L^{-1}$)

$C^*_{CO_2}$ carbon dioxide saturation concentration for a gas phase = pure CO_2 ($mg.L^{-1}$)

$C^*_{O_2}\big|^{in\ wine}$ oxygen saturation concentration in wine for a gas phase = air ($mg.L^{-1}$)

$C_{O_2}^*\big|_{pure\,O_2}^{in\,wine}$ oxygen saturation concentration in wine for a gas phase = pure O_2 (mg.L^{-1})

$C_{O_{2max}}$ maximum possible concentration of dissolved oxygen (mg.L^{-1})

H — Henry's constant (Pa.m^3.kg^{-1})

$k_L a$ volumetric transfer coefficient (s^{-1})

m_{bin} slope of the "binary gas equilibrium line"

N — partial molar flow rate of gas (mol.s^{-1})

P_{air} partial pressure of air (Pa)

P_T total pressure (Pa) = $P_{air} + P_{CO_2}$

P_{O_2} partial pressure of oxygen in gaseous phase (Pa)

P_{CO_2} partial pressure of carbon dioxide in gaseous phase (Pa)

Q — volumetric flow rate of gas (m^3.s^{-1})

$y^s_{O_2}$ mole fraction of oxygen in the output gas flow (-)

Subscripts / Superscripts

*   saturation

A   experiment A

B   experiment B

CO_2 carbon dioxide

e   in the input gas flow

f   final

O_2 oxygen

s   in the output gas flow

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