The ‘permeability’ of closures

Alan Limmer

There has been a lot of discussion on this important subject of late. It is clear from several closure trials that the performance of the closure as an oxygen barrier has a significant influence on the resulting wine. There has also been much erroneous information printed on the subject of the mechanisms and ability of cork to act as a barrier to oxygen ingress. This includes the unfortunate conclusion by some that corks have a variability of 1000-fold in performance as closures while screw caps are far superior in this respect. It may be useful to look at this subject in more depth.

Mechanisms of gaseous ingress

Gaseous ingress can happen by two mechanisms – diffusion, and permeation. Each is quite distinct, and independent of the other. Diffusion could loosely be considered a passive, random mechanism which is driven by the inherent molecular (kinetic) energy of the gas. This behaviour is defined by Ficks law, which tells us the rate of diffusion of a gas is determined by the concentration gradient of the gas, the length or distance it has to travel over, as well as the diffusion constant (D) of the medium (or it's ability to permit gaseous movement). More on this D value later. The rate of diffusion is directly proportional to each of these parameters. I will not put up the equations here, as that is bound to drop readership by 50% per each equation.

Permeation is a mass transport system which is driven by pressure gradients and is described by Darcy's Law. The variables here are the permeability constant (or roughly speaking, porosity), the pressure gradient, and the distance or length. At this point, it should be obvious that permeation, or permeability has a specific meaning to chemists. So, unless we are specifically referring to the permeability constant for Darcy's Law, it would be better to refer to rates of oxygen ingress as the oxygen transfer rate (OTR). This description covers both means of oxygen ingress.

In the case of the diffusion method, the ingress of oxygen through the closure is driven by the 20% oxygen gradient, given there will be virtually no oxygen in the headspace of wine within days of bottling [1]. Once we reach this post – bottling state, the partial pressure of oxygen in the headspace of the bottle is maintained effectively at zero, irrespective of closure type. This is because wine has a very strong capacity to absorb oxygen – much faster than SO_2 can react with it [1]. The diffusion mechanism also allows for the ingress of oxygen into wines stored under a positive pressure of CO_2 – e.g. Champagne. The oxygen concentration gradient is the same for all wines, whether still or sparkling.

In fact the partial pressure of the oxygen inside the wine headspace will not be quite zero, because another gas law (Henry's) tells us the distribution ratio of oxygen between the liquid and gaseous phase is approximately 1000-fold. So, for the fractions of a part per million of oxygen that may be in the bottled wine at any time, we can expect about 1000 times more to be in the gaseous phase in the headspace, but this will equate to a fraction of a percentile as far as our oxygen concentration gradient is concerned, and will have negligible effect on the diffusion results.

In the case of the permeation mechanism, the ingress of oxygen (and other gases) will be driven by temperature fluctuations, which in turn will produce pressure fluctuations within the bottle. By this method, all gases move at more or less the same rate, and the concentration gradient has no effect on the outcome. Decreasing pressure inside the bottle will cause an influx of gas and increasing pressure an efflux. Effectively, with cycling pressure (temperature) the bottle will be breathing through the closure. With a 3ml headspace, a 5°C temperature change has the effect of changing the internal pressure by about 50%. With constant temperature this mechanism does not exist, and we are back to the diffusive mechanism.

OTR measurements are generally conducted by one of two methodologies. One method is that used to produce the data provided for the Diams by Oeonological Closures Australia (OCA) in the article *"Do corks breathe? or the origin of SLO"* [2]. This method measures a pressure difference across the sample to be tested. This truly is a permeability measurement by the strict definition of the word. As the pressure gradient equalizes the permeability can be calculated. The second method measures the OTR through a closure by sweeping the gas on the other side of the closure through an oxygen sensitive detector. This is more a diffusive method – as long as we maintain constant temperature and pressure. Although somewhat time consuming, this methodology is more widely used and generally known as the MOCON method. This is the methodology used to determine the OTR values in Figure 1. (This data was produced by Southcorp). This data has been cited by some [3,4] as evidence for the 1000-fold variation in the performance of cork as a closure. Similarly it has been used to determine the OTR of other closures. The AWRI exhibited some OTR data derived this way at their presentation to the Screw Cap Symposium (Nov 2004), which is reproduced below in Table 1.

Table 1. Oxygen transfer rates.

	$cc O_2$/day	
	Mean	Range
ROTE	0.0005	0.0002 - 0.0008
Cork	0.0179	0.0001- 0.122

Based on the MOCON measurements in Fig 1 and Table 1, we see a 1000 fold variation for cork, the synthetics in a tight band around 0.01cc/day and the screw cap at between 0.0002 and 0.0008cc/day. This puts the screw caps at the low end of the spectrum, and generally quoted as being far more consistent than cork.

Interpreting the data

However, things are not always as simple as they may appear. Common sense should tell us there is something wrong with the ▸

1000-fold conclusion. While the MOCON data in Fig 1 shows the bulk of corks above the synthetic OTR, in practice, the OTR of corks is markedly less than the synthetics – which are known to be' highly permeable'. The wines under synthetics in the AWRI closure trial expired within the first two to three years. Further, the SO_2 data for the AWRI closure trial has always exhibited a high degree of predictability, irrespective of closure type, with only relatively small variations between closures.

The SO_2 results for the 63-month period are produced in Table 2.

Table 2. 63 months data from AWRI closure study (n=8)

	Free SO_2 (mg/L)		Total SO_2 (mg/L)		OD420	
	mean	std dev	mean	std dev	mean	std dev
Altec	12	1.0	75	1.6	0.17	0.004
One + One	8	1.6	68	3.2	0.20	0.006
REF 2	7	2.3	65	6.7	0.20	0.014
REF 3	3	1.7	52	9.1	0.23	0.013
ROTE	14	1.9	80	3.5	0.17	0.005

The SO_2 data, although useful is problematic in two ways. The Free SO_2 is complicated by the equilibria mechanisms where the dissociation constants (K) of the various sulfite components are trying to maintain constant values in the situation where the components are constantly changing with the loss of SO_2. That is why they are called constants. This trend can be seen by comparing the Standard Deviations (SD) for Free SO_2. The SD is a statistical measure of confidence, or variability for the set of results being measured. The smaller the number, the closer (less variable) the data set. The SD of the Ref 3 Free SO_2 data would have us believe it is more consistent than ROTE. This is not the case. A look at the Total SO_2 SD data tells a different story

The total SO_2 levels provide a slightly better picture, where we see the Ref 3 cork about 2.5 times as variable as ROTE, and the Ref 2 about twice as variable. Once again though, the total SO_2 is not a very precise indicator of oxygen ingress (oxidation), although this measurement has been postulated as such. To be so, we would have to believe that all oxygen entering the system was eventually going to oxidise SO_2 through to sulfate (SO4=). The literature (1) tells us this is not the case. Typically assays come up well short in terms of finding enough sulfate for the total SO_2 lost. Further, the oxidation reaction of SO_2 is associated with a complex array of oxy radicals (rather than simple oxygen) with some largely unknown components. Consequently the precise ratio of SO_2 lost for O2 ingress is undetermined and likely to vary with different wines. The rates of SO_2 lost for different wines is also different (5). What all this means is there is a significant background loss of total SO_2 that has nothing to do with contemporary oxygen ingress. This is clearly demonstrated when the SO_2 results for the AWRI ampoule experiment are compared to closures with demonstrable OTRs. The results are as follows in Table 3.

So, we can see that the anaerobic ampoule has lost almost as much SO_2 as the closures enduring oxygen ingress. Which means that the bulk of the SO_2 we have lost has had little to do with oxygen ingress through the closure. Comparative results within a single wine still have some merit. While problematic in interpretation, the SO_2 results are still indicative of the point at which oxidative symptoms will occur in individual wines, and hence variability in sensory aspects. But we cannot use them to quantify oxygen ingress.

Table 3.

	Free SO_2 (mg/l)	Total SO_2 (mg/l)
Initial Ampoule results	27	64
48 month results		
cork	3	32
screw cap	5	37
ampoule	5	39

Relative rates of oxidation

The OD420 results measure the oxidative change in colour and may be more useful as an oxidative index, although plainly, all these results are to some degree interlinked. The SO_2 simply acts to mitigate the oxidative effects of oxygen ingress, and does so by preventing (binding) browning, as well as aldehydic notes. AWRI found the Free SO2 results a useful predictor of the OD420 results 12 months out from the SO_2 measurement [6]. The OD420 results are probably the most overt symptoms a wine consumer would relate to in assessing the state of the wine – for white wines at least. Hence the behaviour of this parameter is of some practical interest.

We can see from the OD420 data in Table 4 that the Ref 2 and 3 corks are about 2.5 times as variable as the ROTE, while the Altec and 1+1 are pretty similar to ROTE. Furthermore, if we look at the change in OD over 63 months, we can get an approximate idea of what relative rates of oxidation have occurred. The synthetic's oxidation parameters were not measured after 36 months, due to extreme oxidation by that time for all samples. The fastest developing of the synthetics was the Betacorque. Using the last recorded Betacorque OD420 data at 36 months, and the 63-month data for the other closures, we can calculate a reasonable estimate for the relative rates of oxidation for each closure. The SD420 data gives an indication of variability in this oxidation parameter.

This approach is however, again slightly problematic, as it has been noted that the OD420 continues to increase even under anaerobic conditions [7]. After 46 months the anaerobic ampoule exhibited about 60% of the increase in OD420 as the ROTE. The oxidative effects from the wine making process may continue for much longer than has generally been assumed. It is likely this is more the case for white wine than red as white wines seem to have less ability to terminate the chain reaction of oxy radicals formed at contact with oxygen [8]. Some of the complex oxy radicals are capable of regenerating themselves via their oxidative reactions. It would be erroneous to attribute the degree of browning in a cellared wine solely to oxygen ingress via the closure. Previous studies [5] have also shown this reaction to be very temperature sensitive, with the rate increasing between 10 and 20° C by a factor of 2.9. Some of the variability frequently noted under cork may have its origins back in the winemaking, and most particularly the bottling process, and the storage conditions.

Notwithstanding the earlier caveat on these results, they clearly spell out for us that the variation in performance of these cork closures is a long way from the 1000 fold MOCON ▸

Table 4.

	Rate of OD420 increase compared to ROTE	Variability compared to ROTE (SD420)
Betacorque	3.3	*
Ref 3 (38 mm)	2.0	2.6
Ref 2 (44 mm)	1.5	2.8
1 + 1	1.5	1.2
Altec	1.0	0.8
Ampoule	0.6	

*36 month OD 420 SD data not available.

estimation. Although further analysis will show us these results are connected.

If we allow for the 'anaerobic oxidation' seen in the ampoule we can guesstimate the relative rates of oxidation due to oxygen ingress as per Table 5.

Table 5.

	Relative rate of oxidation per closure type
Betacorque	2.7
Ref 3	1.4
Ref 2	0.9
1+1	0.9
Altec	0.4
Rote	0.4

The wine under the lowest grade cork (Ref 3) in the trial is developing at about three times the rate as ROTE and is about 2.5 times as variable as ROTE (Table 4). The Ref 2 and 1+1 are developing at about twice the rate of ROTE while the Altec is comparable. The Betacorque is developing at about 6-7 times that of ROTE.

We can also see that the manufacture process introduces a degree of control over not only the OTR in corks (Altec, 1+1), but also their variability. Each of these closures displays two to three times less variability than natural cork (Table 4). Paradoxically perhaps, the cork based Altec is the most consistent (least variable) of all the closures tested.

The critical cork/wine interaction

It would appear there is an interaction between the cork and wine, which does not apply to quite the same extent for the synthetic based closures, or ROTE. The ROTE is quoted as having a MOCON OTR in the range of 0.0002-0.0008 cc/day, while the synthetics have been measured at 0.01cc/day [3]. But, as we have seen from the explanation above, the corks have an actual ingress rate between ROTE and the synthetics, in spite of their widely variable and apparently excessive MOCON OTR's.

As mentioned earlier, there are two modes of gas transport, diffusion, and permeation. The diffusion process follows Ficks' law and is governed by the length of the diffusive pathway, the Diffusion coefficient D and the concentration gradient. Given that the path-length (closure barrier) and concentration gradients (20%) are going to be constant for any given situation, we can see that diffusion of gases is a highly predictable affair. The only variable in our case is the diffusion coefficient D – or the behaviour of the closure regarding its ability to facilitate the diffusion of oxygen.

It is clear that corks are capable of operating with far less variation than the diffusive model of the MOCON results would suggest. Under the MOCON conditions, we could conclude that the D coefficient of the corks is quite variable (1000-fold). Something, in real life (Wine Bottle) has altered this variable to provide a dramatic improvement in the otherwise expected performance of the closure. The diffusion of gas through a liquid is about 10,000 times slower than in gaseous medium. The highest MOCON cork results were in the order of 1cc/day, whereas the ROTE results are broadly around 0.0005cc/day, i.e. 2000 times less. It is reasonable to assume (Table 4) that the OTR of corks in reality is in the order of 1000 times less than their highest MOCON results. It would appear the liquid plug formed in the end of the cork in wine may in fact be providing a highly influential effect on the overall performance of cork as a closure. It is known that corks gain weight from the moment of insertion in the bottle, eventually increasing by 1-2gm [9]. This would equate to the uptake of at least a ml of liquid and may go a long way to explaining the disparity of the MOCON results for corks. The hydrophobic synthetics do not display this tendency to absorb liquid [10].

The other mode of gaseous ingress is the permeation effect described earlier. Once we move out of a temperature (pressure) controlled environment we can expect the permeation effect to influence the performance of the closure. Corks are particularly vulnerable to this situation because of the relatively small headspace traditionally employed. If we increased the headspace values to those comparable to ROTE, this effect would be reduced about three-fold, and the variability of performance under permeation conditions (typical cellars) would improve accordingly. The permeation effect will also be considerably mitigated by the liquid plug in the cork as the viscosity of liquids is approximately 100 times greater than gas. In other words it is about 100 times harder to push a liquid through a porous medium as it is a gas. So, the liquid plug at the cork/wine interface also mitigates this effect. Henry's law can also be expected to play a role at the liquid plug/air interface in the cork, by reducing the amount of oxygen in this plug by about 1000 fold.

The AWRI closure trial investigated the effects of orientation of the samples, with some bottles stored upright and some inverted. The results were the same irrespective of storage orientation [6]. This could be expected, at least where the diffusive model is predominant i.e. constant temperature, with minimal pressure fluctuations. The gas cares not which way up the vessel is before diffusing into the closure. The liquid plug will be formed irrespective of orientation as the relative humidity (RH) inside the bottle is maintained at 100% and corks have been shown to absorb considerable quantities of moisture under these conditions [9].

Perhaps not surprisingly the MOCON results for cork are strongly influenced by the RH they are carried out at (J Peck, pers comm.) – in effect demonstrating the proposition described. It is not possible to conduct MOCON tests at 100% RH. However, one would expect those corks exhibiting the highest MOCON values to be the ones exhibiting the first signs of oxidation, and variability under less than ideal conditions. In other words, they would be the ones most susceptible to the deterioration in the integrity of the all important liquid plug. In these circumstances, some correlation between the MOCON results and the cork performance can be expected. This is demonstrated by comparison of the SO_2 and OD420 results for natural cork and 1+1 in Tables 2 and 4, with the MOCON data for these two closure types (Table 6). From Tables 2 and 4 the 1+1 is seen to exhibit equivalent or lower rates of oxidation than natural cork and provide a lower degree of variability. Similarly, Lopes *et al.* (10), using an in-situ method for determining oxygen ingress found the 1+1 to offer lower and less variable results than natural cork. MOCON data for these two closures demonstrates the same trend.

Further evidence for this effect was determined by comparing the MOCON data of actual corks from bottles which exhibited premature oxidative symptoms. These results are depicted in Fig 2. (courtesy of Richard Gibson, Scorpex)

Table 6.

	OTR (MOCON) cc O2/day. n=24 *	
	45mm Nat	1+1
mean	0.080	0.004
SD	0.3	0.004
CoV %	377	94
min	0.006	0.002
max	1.4	0.005

* These corks were assessed after 6 months upright storage in bottles of wine (courtesy J Peck, G-3Enterprise, Closure division).

While the RH is still 100% in vertically stored bottles, it could be expected the integrity of the liquid plug will be more readily compromised without a liquid seal at the cork interface under adverse conditions. Similarly, corks at the extreme upper end of the MOCON OTRs can be expected to provide some variance, particularly when stored upright. A recent publication [7] which considered this proposition reported some inconclusive results in this regard, although there was a tendency towards the predicted results in some cases. Other reports also suggest this to be the case [11,12].

These same mechanisms can be expected to apply to oxygen ingress via ROTE closures. However, the much larger recommended headspace helps mitigate against the permeation effect, which is particularly important for a pressure sensitive seal. The MOCON data can be expected to be closer to the real life performance for the ROTE because the interaction with the wine will be minimal in terms of providing enhanced performance as a closure. There will be a small contribution however by maintaining the 100% RH at the foil/air interface, just as there is for synthetics. The synthetics have MOCON OTR's of the order of 200-times greater than screw cap. But their comparative rate of oxidation is far less than this (Table 4). We could also expect an increased integrity regarding extreme permeation effects, for both closures by storing the bottle horizontal. But we should not expect the actual ingress results to be of the order of a 1000-times lower than the recorded MOCON results, as for cork. The hydrophobic synthetics appear to have an ingress rate of the order of 20-40-times less than their MOCON results.

With a combination of the above described beneficial interaction between the cork and wine, and manufacture technology, it should be possible to produce a range of cork-based 'technical' closures exhibiting a fine degree of control over the OTR values in-situ. Even very wide variations in the natural OTR of cork (1000 fold) lead to relatively small variations where it counts – in the bottle. In one recent report, even under adverse conditions (non –temperature controlled, vertical storage) the variation of the SD420 was no more than 5% for all closures, including Rote and natural cork [7]. We have to remember though, the OD420 is really a mirror image of the SO_2 behaviour and as such is not a completely precise indicator of the situation. However, the visual browning of the wine is one of the first indicators of oxidation the observant consumer will relate to. This degree of control over the OTR at the narrow range of useful oxygen ingress may prove difficult to achieve by means other than cork. The Diam range would appear to exemplify this possibility. While the P10 has a measured OTR 10 times higher than the P1, there will not be a ten fold higher ingress rate for the P10 under wine conditions. It will perform much closer to the P1. Which means small increments in the actual OTR of a cork closure should be able to be tightly controlled by this means. We should be mindful however that increasing the OTR by this means will also increase the variability of the closure's performance. But we can still expect a high degree of control over the end result, and an improvement on the natural cork data.

Scalping

While discussing the subject of OTR of closures, it is relevant to consider the topic of scalping. There have been several reports regarding the scalping of various aroma/flavour components from wine by closures. Interestingly these results also tend to strongly align themselves with the respective OTR's of the closures under study. The synthetics tend to be attributed with the highest scalping rates, with the ROTE lowest, and cork intermediate [e.g. 13,14]. This trend exists in spite of the wide disparity in the composition of the various closures. Generally scalping studies have focused on the disappearance of the analytes from the wine, rather than the accumulation in the closure. While scalping is a known phenomenon in food packaging, we should not be surprised if in many instances this correlation is more closely connected to the OTR of the closure rather than any absorption attributes.

In summary it may be conceptually helpful if we consider the sealing (OTR) properties of a cork to be due not so much to the physical properties of cork persé, but to its ability as a medium to facilitate a liquid seal. In other words, the cork provides a useful medium or support structure for the liquid seal to interact with the atmosphere according to the gas laws described by Fick, Darcy and Henry. The performance of a cork to provide a near airtight seal while exhibiting a wide variation in its physical properties has more to do with the laws of gas behaviour than the sealing properties of the cork. While these same laws apply to other closures, none benefit to quite the same extent as the cork from these helpful properties.

This leaves the hydrophobic synthetics with a higher rate of OTR than may be useful in many cases, and the ROTE providing a high integrity seal dependant on precise technology, and largely without the assistance of the described gas laws.

References

1) Poulton, J.R.S 1970. Chemical protection of wine against oxidation. Die Wynboer 466:July:22-23.

2) Limmer A.Do corks breathe?, or the origin of SLO. *Australian & New Zealand Grapegrower and Winemaker.* June 2005

3) The role of oxygen in the ageing of bottled wine. Allen Hart, Andrew Kleinig.*The Australian & New Zealand Grapegrower & Winemaker* 2005 No.497a pp 79- 88.

4) Stelzer, T., Taming the screw: a manual for winemaking with screw caps. Winepress, 2005.

5) Ough, C. S. (1985). Some effects of temperature and SO_2 on wine during simulated transport or storage. Am. J. Enol. Vitic. 36:18-22.

6) Closures – Results from the AWRI three years post-bottling. P Godden, L Francis, J. Field, M. Gishen, A.Coulter, P. Valente, K. Lattey, P. Høj, and E. Robinson. Proceedings 2002 Romeo Bragato Conference

7) The impact of closure types and storage conditions on the composition, colour and flavour properties of a Riesling and a wooded Chardonnay wine during five years storage. G.K. Skouroumounis, M.J. Kwiatkowski, I.L. Francis, H. Oakey, D.C.Capone, B. Duncan, M.A. Sefton and E.J.Waters. Australian Journal of Grape and Wine Research. 11, 378-384, 2005.

8) A Radical view of oxidative reactions in wine. R Boulton. IX Congreso Latinamericano de Viticultura y Enolgia CHILE 2003

9) The cork paradox; Casey. Australian Grapegrower & Winemaker. Annual Technical issue 1998 p15-20

10) Nondestructive Colorimetric Method To Determine the Oxygen Diffusion Rate through Closures Used in Winemaking. P Lopes, C. Saucier, and Y. Glories . Journal of Agricultural and Food Chemistry. 2005,53, 6967-6973

11) Bach, H.P (1982) Der Einflu verschiedener Verschlüsse auf den Wein während der Lagerung in Abhängigkeit vom Füllverfahren und der Lagermethode - 1. Mitteilung: Der Einflu auf die Analytic. - Die Wein-Wissenschaft 37, 400-429

12) Bach, H.P. (1988)) Der Einflu verschiedener Verschlüsse auf den Wein während der Lagerung in Abhängigkeit vom Füllverfahren und der Lagermethode – 2. Mitteilung: Der Einflu auf die Sensorik. Die Wein-Wissenschaft 43, 199-213.

13) Flavour 'scalping' by wine bottle closures. D. Capone, M. Sefton.AWRI Technical Review #144 June 2003.

14)Flavour 'scalping' by wine bottle closures. Australian & New Zealand Wine Industry Journal 18 (5), 16-20. (2003) Capone, D.L., Sefton, M.A., Pretorius, I.S. and Høj, P.B.

Alan Limmer has more than 20 years in winemaking, holds a PhD in Chemistry, is a former director NZ Winegrowers, and was awarded Officer NZ Order of Merit (ONZM) 2004 for Services to winemaking. Contact details: stonecroft@xtra.co.nz