The cork paradox

J.A. Casey

12 Conrad Street
North Ryde, New South Wales 2113

If the corks are steep'd in scalding water a while before you use them, they will comply better with the mouth of the Bottle, than if forc'd in dry: also the moisture of the Cork doth advantage it in detaining the Spirits.

Therefore is laying the Bottles sideways to be commended, not only for preserving the Corks moist, but for that the Air that remains in the Bottle is on the side of the Bottle where it can neither expire, nor can new be admitted, the Liquor being against the Cork, which not so easily passeth through the Cork as the Air.

"Vinetum Brittanicum", by John Worlidge, pp 107-108, 1676 edition.

Introduction

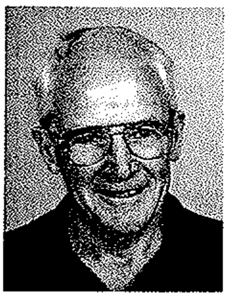
The origins of wine-bottling are obscured by the difficulty of defining what constitutes 'bottling' and 'bottles' in the modern sense of the words. The ancient Romans were reputedly aware of the advantages of anaerobic storage of wine in ceramic vessels sealed with cork, and according to Pliny the Elder, crude sparkling wines were being made at Dea Augusta (now Die) in the first century A.D. by sealing partly fermented wines in pottery containers. References to wine in "bottles" also occur in the Bible, the Chester Plays (*ca.* 1350) and Shakespeare. However, bottling as a serious activity did not emerge until the late 16th, early 17th centuries, when recognisable glass bottles sealed with cork began to become more common, particularly in England.

The two most obvious advantages of a cork-sealed bottle as a domestic container for wine are that it is a portable and that it protects the wine from the depredations of aerobic micro-organisms. In addition, oxidation of the wine is postponed indefinitely, and the character of many wines is enhanced and refined. All these effects are dependent on isolating the wine from contact with oxygen.

Attempts to provide a comprehensive explanation of the role of cork stoppers as closures for wine bottles are made difficult by an apparent contradiction in the behaviour of cork. Pristine corks are manifestly permeable to gases and vapours, yet when used as closures for wine bottles, they are able to provide an adequate barrier to the entry of oxygen. Bottled wines sealed with corks do not become oxidised, but maintain and develop a flavour and bouquet that are dependent on the exclusion of oxygen. They also remain protected from the activity of any film yeasts or acetic acid bacteria present in the wine.

The semi-permeability of some common materials has been recognised for a very long time, (see Worlidge, *above*). These materials were said to "breathe", in that they are impermeable to liquids, but at the same time they allow the passage of water vapour, particularly that from perspiration. Leather in shoes is a good example.

The concept of 'breathing' was applied to corks by many experts in the late 19th century, including Pasteur. They were trying to reconcile the known permeability of cork to gases with its undisputed ability to promote the preservation and development of bottled wine. They theorised that the entry of minute amounts of oxygen through the cork and into the bottle might play some beneficial role in the preservation and refinement of the wine, just as it does in some other wine-making processes. This was because other closure materials, which at the time were thought to be impermeable to gases, failed to prevent the gradual degradation of the wine. At the same time, other experts held that the cork must be an effective oxygen barrier because wine sealed in glass containers by fusing the neck developed the same characteristics as those of wine in bottles sealed with corks. The controversy was resolved by the work of J. Ribéreau-Gayon in the 1930s, (Traité d'Œnologie, 1947). He was able to demonstrate conclusively that the total or near-total exclusion of oxygen was essential for the wine to be conserved and develop 'bottle bouquet'. This gave an indirect confirmation of the then unrivalled superiority of the cork stopper as a barrier to oxygen. Subsequently, it was shown that metal closures fitted with suitable gas impermeable gaskets could equal or even surpass the performance of cork stoppers as closures for wine bottles. The notion that "breathing" corks were essential for the development of bottled red or white wines was discredited and survived only in the hearts and minds of amateur œnophiles.



• John Casey

The reasons for the effectiveness of cork stoppers as oxygen barriers are not altogether clear, and the aim of this article is to discuss the likely mechanisms by which corks are able to impede oxidation of the bottled wine. Despite the lack of reliable experimental evidence, a plausible explanation of the paradoxical behaviour of cork stoppers can be surmised from the unique physical properties of cork and the well-established behaviour of gases and vapours.

The structure of cork

Cork is not like other solid materials. Its rigidity, opaqueness and finely textured surface belie its 80 - 85% void volume. The Specific Gravity of the structural material of cork is 1.15[1] (Gibson *et al.*, 1981), but the Specific Gravity of commercial cork ranges from 0.15 to 0.22. A typical cork stopper consists of about 3 grams of solid material and some 17 mL of gas, usually air. It could be described as a pneumatic seal rather than as a plug. The light-weight cellular structure and the largely gaseous nature of cork are also revealed in the micro-photographs of Gibson *et al.*, (1981) and Colagrande (1996), and by the fact that while subjected to hydraulic pressures of 20 atmospheres or more, corks sink in water, (Kelvin, 1890; cited by Gibson *et al.*, 1981). ▶

[1] The S.G. of the noted material in wood is 1.5.

In brief, the chemical reactions are esterifications, the acid hydrolysis of saccharides and glycosides and in the long term, the formation of hydroxy-methyl furfural and possibly Maillard compounds. The formation of esters is not considered to have any significant sensory effects, but recent experimental results of Francis *et al.*, (1996) support the conclusion that a slow, acid-catalysed hydrolysis of non-volatile glycosides is the mechanism of flavour development in wine. When oxygen is excluded, there is also a general lowering of the Redox Potential, a change in state of compounds sensitive to the Redox Potential, and seasonal fluctuations in the Redox Potential. The last phenomenon is presumed to be due directly and indirectly to temperature changes. The Redox Potential is at its lowest in early autumn, and this may account for the long-held belief of some winemakers that bottled wines are at their best at vintage time. Figure 2 is a schematic representation of the interaction of the dual effects of chemical reactions and oxidation state.

Although the cumulative effect of oxygen eventually destroys the essential character of bottled wine, most wines can absorb a certain amount of oxygen without undergoing significant sensory deterioration. In a previous article, (Casey, 1996), it was proposed that while there is adequate Free SO_2 remaining in the wine, the absorption of small amounts of oxygen does not have any adverse sensory effects. Also, that the onset of the symptoms of oxidation appears quite suddenly when the concentration of Free SO_2 drops to a certain critical value, e.g., in the region of 5-15mg/L for white wines and zero or near-zero for red wines. The adverse effects of oxygen are cumulative, and further contact with oxygen results in a gradual intensification of 'oxidised' characters to the point where the wine becomes undrinkable.

In some wines the onset of 'oxidation' is masked by the flavour of the wine, and this applies particularly to wines which have been bottled for some time. Moreover, winetasters are often tolerant of slight oxidation when it occurs in very old or highly esteemed wines. The occasional toleration of slight oxidation can lead to confusion about its significance to the quality of the wine, and sometimes, to its acceptance as "development" [sic]. There should be no equivocation on this point. The onset of incipient oxidation in bottled wines marks

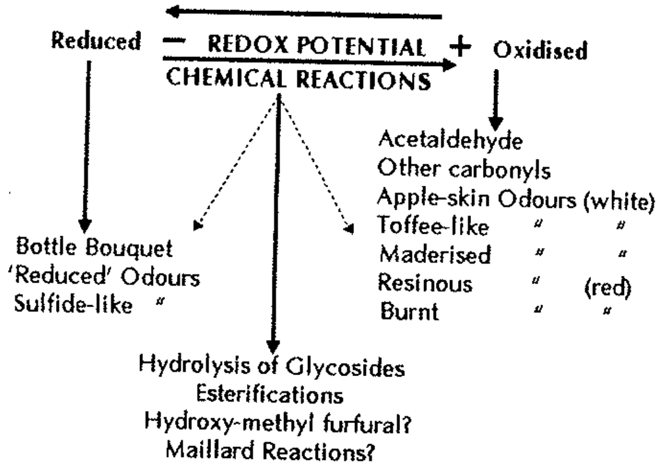


Figure 2. The development of bottled wines depends on both the extent of chemical reactions and the oxidation state.

the beginning of the end. It is either naive or deceitful to say that these wines are 'developed' if they have been bottled for less than one or two years.

Conclusions

The production and use of cork stoppers to seal wine bottles is an empirical technology with a very long and continuing history of trial and error. Apart from Hooke's revelation of the micro-structure of cork in 1664, and the detection by Tanner *et al.*, of 2,4,6, T.C.A. in 1982, scientific 'breakthroughs' have been rare. Even scientific explanations of the properties and behaviour of cork are often tenuous and lacking in reliable experimental data. The present article is no exception, and the foregoing explanation of the oxygen barrier properties of cork stoppers is largely speculative. Despite all this, the performance of cork stoppers as long-term oxygen barriers has been established by more than a hundred years of practical experience, and their effectiveness when used correctly remains unaffected by the plausibility or otherwise of attempts to account for it.

References

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

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

Caloghiris, M., E. J. Waters, and P. J. Williams. (1997) Australian J. Grape & Wine Research 3, 9 - 17.

Casey, J. A. (1989) Flexible packages for wine. *The Australian Grapegrower & Winemaker* 304, 57 - 63.

Casey, J. A. (1991) The enigmatic properties of cork. *The Australian Grapegrower & Winemaker* 328, 83 - 89.

Casey, J. A. (1992) Sulfur dioxide levels in bottled wine. *The Australian Grapegrower & Winemaker* 348, 37 - 41.

Casey, J. A. (1993) Cork as a closure material for wine. *The Australian Grapegrower & Winemaker* 352, 36 - 41.

Casey, J. A. (1996) Oxidation, serendipity and sulfur dioxide. *The Australian Grapegrower & Winemaker* 388, 42 - 52.

Colagrande, O. Il Tappo di Sughero. Chiriotti Editori, 1996, Pinerolo, Italy.

Francis, I. L., Tate, M. E., and Williams, P. J. (1996) The effect of hydrolysis conditions on the aroma released from Semillon grape glycosides. Australian J. Grape & Wine Research 2, 70 - 76

Gibson, L. J., K. E. Easterling and M. F. Ashby. (1981) The structure and mechanics of cork. Proc. Royal Soc., London. A377, 99 - 117.

Lefebvre, A. (1981) Le bouchage liège des vins. Actualités Œnologiques et Viticoles: 335 - 349; Dunod, Paris.

Traité d'Œnologie:

1947. Transformations et Traitments des Vins. by J. Ribéreau-Gayon. Béranger, Paris.

1966. Vol. II, Compositions, Transformations et Traitments des Vins. by J. Ribéreau-Gayon and E. Peynaud. Béranger, Paris.

1976. Sciences et Techniques des Vins, Vol. III; Vinifications et Transformations des Vins. by J. Ribéreau-Gayon, E. Peynaud, P. Ribéreau-Gayon and P. Sudraud. Dunod, Paris.

atmospheric oxygen depends exclusively on how well the closure system is able to restrict penetration by oxygen.

The ability of any closure to exclude oxygen is handicapped by two practical requirements.

- The sealing and barrier properties need to be maintained throughout the anticipated shelf-life, i.e., one to ten or more years.
- It must be possible for the closure to be opened conveniently at any time during that period.

These two considerations place a limit on the magnitude of the contact pressure between the glass and the sealing material. The greater the contact pressure, the more rapid the decline in the resilience of the materials used to make stoppers and gaskets. Prolonged pressure causes loss of gas in disperse solids (cork, expanded polymers) and 'creep' in more solid materials (plastisols). Higher contact pressure also increases the force required to overcome friction between the sealing surfaces when the bottle is opened. The design of a closure system necessarily involves some compromises to balance conflicting criteria, including the short and long-term effectiveness of the oxygen barrier.

How much oxygen enters a sealed bottle?

Assuming that entry of oxygen into the wine eventually results in an equimolar reduction in the concentration of Total SO_2, estimates of the rate of oxygen entry into bottles of wine can be made from the decrease in Total SO_2 during a period of storage. Because of the inevitable drop in SO_2 caused by the incorporation of variable amounts of air at the time of bottling, these estimates can only be made after the wine has been bottled for a certain time; that is, after the initial post-bottling decrease. Table 1 shows some published values for mean SO_2 decrease in bottled white wines at various intervals after bottling.

The trials from which these results are taken were not designed to measure oxygen transmission rates, and the estimates of something less than 1mL of oxygen per year can only be regarded as a first approximation. It seems likely that the rate of oxygen ingress is not constant, and also that it could depend on the composition of the wine. Nevertheless, any indication of the magnitude of expected decreases in SO_2 due to oxygen permeation is useful. When used in combination with reliable estimates of decreases in SO_2 resulting from filling and sealing operations, it would allow a more accurate prediction of Total SO_2 levels required to give a satisfactory shelf-life. A similar approach is recommended for the management of the shelf-life of bag-in-box wines (Casey, 1989).

Table 1. Rate of decrease of Total SO_2 in bottled white wine.

Closure	Period (months after bottling)	Mean Decrease in Total SO_2 (Mg/L)	(mg/closure/year)	Source
38mm Cork	24th - 60th	20	5.0	Bach (1982) (750 mL bottles)
R.O.	"	17	4.3	
44mm Cork	19th - 40th	10	4.3	Casey (1992) (750 mL bottles)
R.O.T.E.	16th - 22nd	3	2.3	Caloghiris *et al.*, (1997) (375 mL bottles)
R.O.T.E. + Cork	"	3.5	2.7	
38mm Cork	"	4	3.0	

The effects of oxygen on bottled wine

Wines ready for bottling are generally considered to be 'stable'. That is, they are unlikely to undergo further significant physical, chemical or microbial changes. However, most bottled wines very slowly undergo changes in sensory properties, and some minute changes in chemical composition. The nature and significance of these changes, and the dependence of some of them on the exclusion of oxygen, are discussed at length in the various editions of Traité d'Œnologie (1947, 1966, 1976).

immobilised, and they accumulate on the internal surfaces. The sorption of water vapour by the cork almost certainly involves some interaction between water molecules and accessible hydroxyl groups. However, because of its finite adsorptive capacity, cork does not become an impenetrable barrier to these molecules. Although the total concentration of an adsorbed substance in the cork becomes greater than in the surrounding atmosphere, its concentration in the vapour phase remains in equilibrium with this atmosphere. Water vapour is the most conspicuous example of this phenomenon, but other volatile materials, including chloro-anisoles, can accumulate on vacant surfaces, particularly when the moisture content of the cork is low.

Corks in bottles

When a cork stopper is inserted in the neck of a bottle, its external volume is reduced by some 45%, and the partial pressures of the individual gases inside the cork cells are approximately doubled. Shortly after corking, minute bubbles can often be seen emanating very slowly from the cork/wine interface, although it is not possible to identify their precise source or their composition. Formation of these bubbles usually occurs only in the twelve hours or so after corking, but it is inevitable that some permeation of gas will continue indefinitely. Gases can also be expected to permeate very slowly out of the cork to the atmosphere. The magnitude of these changes can be estimated from the diminished volume of cork stoppers after they are removed from bottles. Several years after insertion, the unrestrained volume of a 24 x 44mm cork is some 4-6mL less, and its weight is 1-2 grams more than before insertion (Casey, 1993). Because cork is not permeable to liquids, the changes in weight and volume indicate an adsorption of 1-2g of volatile material, and a gas loss of 5-8mL. After a decade or more, the cork becomes saturated with condensed liquid vapour, its volume approaches the volume of the bottle bore, and the total gas loss is some 10 - 12mL.

Without reliable experimental evidence, what happens to this gas must remain a matter for conjecture (Figure 1). In the initial stages, it is probable that the major movement of nitrogen and oxygen is from the cork to the external atmosphere. The net diffusion of gases from the cork surface is driven by the higher partial pressures of gases in the cork and their instant dilution in the infinite volume of the surrounding atmosphere. At the same time, any movement in the direction of the wine is inhibited by contact between the cork face and the wine. After the initial effusion, the more thorough wetting of the cork face by the wine eliminates gas cavities on the surface and inhibits the permeation of gas from the cork directly into the wine. This is because formation of gas cavities in the liquid at microscopic dimensions requires very high gas pressures, and in the absence of pre-existing gas cavities at the interface, a net permeation directly into the liquid is dependent on the rate of diffusion or reaction of the gas in the wine. Diffusion rates are some 10,000 times slower in liquids than in gases.

Using indigo carmine as an indicator, Ribéreau-Gayon in 1931 estimated an entry of several tenths of a mL of oxygen in the first few weeks after bottling, and several hundredths of a mL in the next four months, but offered no evidence of the source or route of this ingress. The results for bottles stored standing were more variable and sometimes as high as several mL per year, (Traité d'Œnologie, 1966, Vol. II, pp 559-560).

The partial pressure of carbon dioxide in most wines is much higher than in the atmosphere and the cork cells. The net movement of carbon dioxide is from the wine, to the cork and then to the atmosphere. In the author's experience, the upright storage of bottles of white wine sealed with cork leads to a detectable loss of carbon dioxide from the wine after a month or so. The same wines stored horizontally retain adequate concentrations of carbon dioxide for a far longer period, although there is a noticeable diminution over a number of years. In round terms, a CO_2 loss of 0.25g/L from a bottled wine would represent the permeation of 140mL of CO_2 gas through the closure. The presence of some carbon dioxide is essential to maintain a degree of 'freshness' in the wine, and it also inhibits the rate of absorption of oxygen.

The effect of storage position on barrier properties

The effect of wine contact on the ingress of oxygen into cork-sealed bottles can be seen in the experimental results of Bach (1982, 1988). In the course of a comprehensive trial of filling methods, closures and storage conditions, a bottled white wine was sealed with 38mm corks and then stored either horizontally or upright at either 11-12°C or 18-22°C for periods up to six years. The bottles stored upright were the first to show signs of oxidation, particularly at the warmer storage temperatures, and all those stored horizontally resisted oxidation for quite a number of years. All the bottles sealed with a hollow, polyethylene closure became oxidised, but not quite as soon as the standing corked bottles. Bottles sealed with a gasketted metal closure were the most resistant to oxidation. Interestingly, although storage position affected the performance of cork stoppers, it had no effect on the rate of oxidation of wines sealed with the polyethylene or metal closures. The explanation for this difference is that cork surfaces have a relatively high affinity for water molecules, and the wine-contact surfaces become thoroughly wetted after a short time, even in the presence of surface coatings. Polyethylene and many other synthetic polymers are hydrophobic and can support microscopic, stable gas cavities in contact with the liquid[2]. The presence of gas cavities facilitates the dispersal of gas permeating through the closure.

The results of Bach offer confirmation of what winemakers have known for centuries. The effectiveness of cork stoppers as closures for bottles of wine is dependent on their maintaining full contact with the wine, and that this effectiveness is enhanced if the bottles remain undisturbed at a relatively low, even temperature.

Closures as gas barriers

Molecules of gas are extremely pervasive, and the total exclusion of oxygen from a bottle of wine sealed with a conventional closure is just not practicable. Glass bottles are not permeable to oxygen, and the protection of bottled wine from

[2] cf. the sudden appearance of bubbles on the inner surfaces of PET bottles of soft drinks when the cap is loosened.

In addition to the 'honey-comb' construction, the walls of the individual cork cells are traversed by a number of minute channels, plasmodesma. It is thought that these channels, which are too small for the passage of liquids as such, allow the permeation of gases and vapours, (Lefebvre, 1981), and therefore, molecules of gas can diffuse throughout the cellular structure. That is, the process of permeation of gases is purely physical and does not require dissolution in or chemical reaction with the matrix.

How permeable is cork?

The ease with which cork absorbs water vapour from its surroundings is the simplest demonstration of its permeability to gases and vapours. The equilibrium moisture content of corks fluctuates with the Relative Humidity of the air, even when their external surfaces are coated with paraffins and silicones. When stored over water in a sealed container, cork stoppers absorb several hundred milligrams of water vapour from the moist atmosphere in a matter of days or weeks. The initial rate of moisture pick-up by a dry cork is of the order of 50mg per day. However, as more of the hygroscopic internal surfaces become hydrated, the rate of pick-up slows and eventually stops when the adsorbing surfaces become saturated. The same corks will then lose most of that moisture after several days' storage in a dry environment, or after several hours in a 102°C oven.

If dry corks are inserted into 45 x 18mm stainless steel tubes with only their end faces exposed, they increase in weight by 1-2mg per day when stored in moisture-saturated air, (Casey, 1991). Cork stoppers used to seal wine bottles for several years increase in weight by 1-2g.

Although the oxygen molecule is larger than the water molecule, the permeation rate of oxygen could reasonably be expected to be at least of the same order of magnitude as that of water vapour. Volatile substances with much larger molecules are absorbed quite quickly by cork. Cork stoppers exposed to the vapour of phenol had initial pick-up rates of 50mg per day, and those exposed to chloroform vapour increased in weight by a gram or more over several days (Casey, 1991).

There are no published values for Oxygen Transmission Rates through cork, but it is doubtful if any such figures could be used directly to estimate the rate of oxygen permeation into a cork-sealed bottle of wine. When a cork is compressed in the neck of a wine bottle, permeation of oxygen from the atmosphere is impeded by the elevated pressure of the gases inside the cells and by the wine covering the inner face of the cork. While the cork remains in the bottle, liquid vapour condenses on the cell walls, and it seems likely that this too would increasingly impede the permeation of gases. Despite the permeability of cork, the process of oxygen permeation into a bottle of wine along the length of a 44mm cork stopper is not as straightforward as permeation through 25-100µm plastic films.

The behaviour of gases

A gas is not a continuous fluid, but a swarm of highly energetic particles. The motive force for diffusion or permeation is the kinetic energy of the individual gas or vapour molecules. The individual molecules do not obey the Ideal Gas Laws, but respond only to the constant buffeting from other molecules, and collisions with boundary surfaces in a largely directionless and formless void. Their motion has neither purpose nor sustained direction, and becomes even more frenzied as the temperature increases. The impetus for the gradual diffusion of a gas in any particular direction is brought about by the probability that there are more molecules with a net movement from, rather than towards regions of high concentration. That is, although the individual molecules career about aimlessly, the net movement of a certain proportion is towards regions containing fewer molecules of that gas. Thus the net movement of oxygen in or out of the cork, towards the wine or towards the atmosphere, is driven exclusively by the magnitude of its concentration gradient in that direction. The presence of other gases may retard, but does not prevent this diffusion.

Movement of gases in cork stoppers

Because there is no absolute barrier to the movement of gases, the concentrations of gases and vapours in the cork cells of a pristine cork stopper inevitably approach equilibrium with the composition of the surrounding atmosphere, Figure 1(0). If the structural material of the cork has any affinity for particular gases or vapours, then some of these molecules become

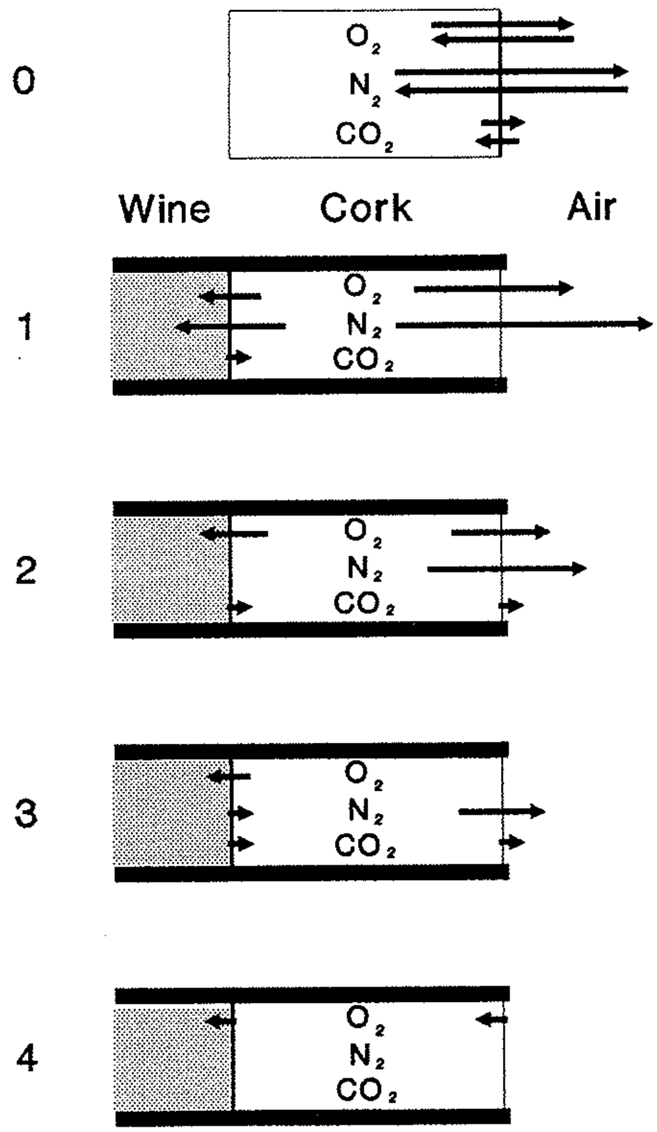


Fig. 1. Hypothetical exchange of gases in cork-sealed wine between wine, cork and atmosphere.

Legend for Figure 1.

(0) Uncompressed cork is permeable to volatile materials, and the gas content of its cells reflect the composition of the storage atmosphere. Some volatile materials have a tendency to be adsorbed on the cell walls, and the concentration of these materials in the cork becomes higher than in the surrounding atmosphere.

(1) When the cork is inserted in the neck of a bottle, the pressure of the gases in the cork is nearly doubled. Gases permeate out of the cork, some to atmosphere and some into the wine. The partial pressure of carbon dioxide in wine is higher than it is in the atmosphere, and the carbon dioxide permeates into the cork.

(2&3) Oxygen reacts chemically with constituents of the wine and continues to permeate slowly into the wine. Nitrogen is chemically inert to wine, and its permeation into the wine stops when the partial pressures are equalised. While the partial pressures of the gases in the cork are higher than they are in the atmosphere, they continue to permeate into the atmosphere. The decrease in gas pressure in the cork cells causes a decrease in the resilience of the cork.

(4) After the partial pressure of the oxygen in the cork reaches its partial pressure in the atmosphere, it is maintained at this level by permeation from the atmosphere while the wine continues to absorb and react very slowly with oxygen diffusing from the face of the cork.