Wine/Enology

Grape Chemistry Group at Va Tech

GASES: CARBON DIOXIDE, ARGON, AND NITROGEN

Learning Outcomes. *The student will understand the practical features and use of the three gases commonly used in the wine industry. Each gas has its own characteristic advantages as a sparging and displacement tool. The student will understand how and when gases should be utilized.*

Chapter Outline

Carbon Dioxide (CO_2)

Nitrogen (N_2)

Argon (Ar)

Use of Gases in Wine Production

Managing Oxygen during Bottling

Section 1.

Depending upon goals, the following gases find application in winemaking: argon, carbon dioxide, nitrogen, air/oxygen, ozone, and sulfur dioxide. Carbon dioxide, nitrogen, and/or argon are used as sparging gases, to pressurize wine tanks, and to blanket wines in an attempt to displace oxygen.

Regardless of what gases are used at the winery, it must be understood that anything that comes in contact with wine must be food-grade quality or higher. Because each of these gases is used also in industrial processes, various low quality grades are available. These low-purity grades should *not* be used in the winery.

The general properties of nitrogen, argon, and carbon dioxide are listed in Table 1.

Table 1. General Properties of Various Gases Used in Winemaking

Properties of Gases	**Nitrogen**	**Argon**	**Carbon Dioxide**	**Air**
Molecular Weight (g/mole)	28.13	39.95	44.01	29
Density (kg/m^3) (15°C, 1 atm)	1.189	1.691	1.875	1.365
Specific Gravity	1.38	1.53	2.264	1.23
Solubility in Water (mL/L at 20°C)	1.54	3.3	87.8	1.85

Carbon Dioxide (CO_2)

Newly fermented wines are saturated with CO_2. As a result of out-gassing and post-fermentation processing (racking, fining, etc.), levels drop to near 1,000 mg/L during the first several months of aging. Depending on intrinsic properties of the wine and cellaring practices, additional decreases of 100 mg/L, or more, may be seen during the first year, possibly with negligible losses thereafter. The factors impacting carbon dioxide solubility include the following:

- temperature
- alcohol
- carbohydrates
- phenols
- proteins

- cellar practices

Because solubility is, in part, temperature dependent, fermentation and storage temperatures contribute to CO_2 retention. For example, in wine of 11% alcohol (at atmospheric pressure), increasing the temperature from 0 to 20°C (32 to 68°F) decreases CO_2 solubility from 2.9 to 1.4 g/L. Protracted fermentations may play a role in establishing relatively-high concentrations of soluble carbon dioxide.

Alcohol levels are also important in retention of CO_2. Because solubility is inversely related to the concentration of alcohol, CO_2 retention at equivalent temperatures is greater in wines of lower, compared with higher, alcohol levels. Other contributing factors include reducing sugar and viscosity arising from carbohydrates and phenols. Polysaccharides originating from the grape, as well as yeast autolysate, have white wine concentration ranges from 170 to 970 mg/L.

Carbon dioxide and protein interactions are partially responsible for maintaining CO_2 in solution. The CO_2-protein interaction is electrostatic. Carbonic acid (CO_2 in solution) is bound to positively-charged protein fractions. Thus, more CO_2 is adsorbed at lower, rather than higher, pH values owing to the increased density of positive charge.

Cellar processing plays an important role in gas retention. Storing wine at low temperatures aids in retention, whereas warming accelerates out-gassing. Racking, fining, and filtration may reduce the amount present, whereas use of CO_2 in purging tanks and lines may lead to increases. Some wineries sparge wines with CO_2 before or during bottling. In the United States, CO_2 additions are permitted in wines, provided that not more than 3.92 g/L is present at the time of sale. By comparison, OIV levels are set at 1.0 g/L.

Sensory Considerations for Carbon Dioxide

Carbon dioxide can provide a tactile sensation, magnify the sense of acidity, and enhance aromatic intensity. As such, white wines designed for early release may be produced using residual CO_2 to elevate fruit character and enliven the palate, or may have carbon dioxide added at bottling.

- Carbon dioxide is perceptible in water at 200 mg/L, and in wine at about 500 mg/L.
- At levels greater than 700 mg/L, CO_2 may be tactilely perceivable, and at greater than 1000 mg/L (depending upon the wine matrix), CO_2 bubbles may be observed.

Measurement of Carbon Dioxide

Carbon dioxide in wine can be measured using a variety of analytical techniques and instruments, including the following:

- Carbodoseur
- titration
- blood gas analyzers
- CO_2-specific electrodes

Among these, the simplest is the Carbodoseur, which is a glass tube that measures the volume of CO_2 out-gassed from a fixed quantity of wine. Using the included calibration chart, one can directly read the concentration of CO_2 (mg/L) in the wine sample. Since the Carbodoseur method doesn't require the sample to be treated to facilitate "release" of CO_2, results may be variable depending upon pH, temperature, etc.

The titrametric method using carbonic anhydrase is described in Zoecklein et al. (1999). Carbon dioxide-specific electrodes are available for use with an ion-specific pH meter.

Carbon Dioxide and Winery Safety

Oxygen (O_2) and carbon dioxide levels in air are 20.9% and 0.03%, respectively. OSHA minimum levels for O_2 are 19.5%. If CO_2 (or other inert gas) exceeds 10% of the volume of air, unconsciousness will occur.

- Fermenting 1 L of 20% (w/v) grape juice releases more than 60 L of CO_2 . CO_2 displaces oxygen in air to produce levels that are unsafe for breathing. As such, dangerously-high levels of CO_2 can be produced in the winery where it, likely, represents the single most-common cause of death among winery workers. Such incidents are generally associated with entry into "confined space" without, or prior to, adequate ventilation and monitoring.

Thus, carbon dioxide monitors should be used in the cellar, and in fermentation vessels, prior to entry. Inexpensive LED-based carbon dioxide and oxygen monitors are available.

Society is becoming increasingly concerned with so-called greenhouse gas emissions. As such, the wine industry is taking steps to monitor, and then control, emission of carbon dioxide. It is highly likely that in the future the industry will be required to have carbon dioxide and ethanol scrubbers on all fermentation vessels of a certain size.

For information on the amount of carbon dioxide produced in normal winery operations, see Table 2 (also available as a Microsoft Excel worksheet).

Table 2. Annual Winery Carbon Dioxide Emissions

1	Red Wine Fermentation	E1 =	Q_{RWF} x 0.0062				
		Q_{RWF} =	Volume of red wine fermented, gallons per year				
		Q_{RWF} = ____ gal/yr	*input your volume here*				
		E1 = 0 gal/yr	x	0.0062	=	0	lbs/year
2	White Wine Fermentation	E2 =	Q_{WWF} x 0.0025				
		Q_{WWF} =	Volume of white wine fermented, gallons per year				
		Q_{WWF} = ____ gal/yr	*input your volume here*				
		E2 = 0 gal/yr	x	0.0025	=	0	lbs/year
3	Red Wine Storage/Aging	E3 =	Q_{RWS} x 0.02783				
		QW_{RWS} =	Volume of red wine stored/aged, gallons per year				
		Q_{RWS} = ____ gal/yr	*only input volume stored/aged in oak barrels*				
		E3 = 0 gal/yr	x	0.02783	=	0	lbs/year
4	White Wine Storage/Aging	E4 =	Q_{WWS} x 0.02583				
		QW_{WWS} =	Volume of white wine stored/aged, gallons per year				
		Q_{WWS} = ____ gal/yr	*only input volume stored/aged in oak barrels*				
		E3 = 0 gal/yr	x	0.02583	=	0	lbs/year
5	Total Annual Emissions						
			Sum of Lines Items 1, 2, 3 and 4 ===>		=	0	lbs/year
			Divide Above lbs/year by 2000 lb/ton		=	**0.00**	**tons/year**

Nitrogen (N_2)

Nitrogen finds several applications in the winery: as a sparging gas, for removal (displacement) of CO_2 and H_2S (hydrogen sulfide), and to pressurize wine transfers. Nitrogen serves as an effective tool in lowering levels of CO_2.

Compared with CO_2, which has solubility in wine (at atmospheric pressure) of 1,500 mg/L, N_2 is relatively insoluble, at approximately 14 mg/L. Because of this insolubility, N_2 (in low concentrations) can be effectively used to strip other more-soluble volatiles (including CO_2) from wines. The mechanism of action involves the equilibrium between the gaseous form of CO_2 and dissolved carbonic acid:

$$CO_{2\ (gas)} \Leftrightarrow CO_2 \cdot H_2O_{\ (dissolved)}$$

During sparging, N_2 molecules collide with and sweep some of the CO_2 (gas) molecules to the surface, resulting in more $CO_2 \bullet H_2O$ (carbonic acid) shifting to the free gaseous form and, subsequently, out of the system.

Nitrogen is often used as a blanketing gas. While nitrogen's specific gravity is similar to that of air, significant volumes of the gas are needed to displace air in the headspace above a wine or from receiving tanks prior to transfer. As such, it is not as effective as argon in fulfilling this goal.

Argon (Ar)

Argon also occurs naturally in the atmosphere, where it makes up 1% (v/v) of the total. Argon's specific gravity (1.53) is near that of CO_2 (2.264), but it has the advantage of being only 38% as soluble in wine as CO_2. Based upon overall sensory impact, argon may be the best gas to use either alone or in a mixture of gases. The volume of argon needed to displace other headspace gases is usually two to three times the volume of the headspace.

Argon is considerably more expensive than either nitrogen or carbon dioxide. Because of the versatility of these last two gases, it is recommended by most have both carbon dioxide and nitrogen on hand.