### Table 14: Concentration in liquids and headspace at concentrations typical in wine at 25°C

<table>
<thead>
<tr>
<th>Compound</th>
<th>Partition coefficient</th>
<th>High = more volatile</th>
<th>Low = less volatile</th>
<th>$C_{in}$ wine [mg/L]</th>
<th>$C_{in}$ gas [mg/L]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nitrogen $^1$</td>
<td>62.05</td>
<td>1.00</td>
<td>1.00</td>
<td>8</td>
<td>496.4</td>
</tr>
<tr>
<td>Oxygen $^2$</td>
<td>32.21</td>
<td>0.52</td>
<td>1.93</td>
<td>4</td>
<td>128.8</td>
</tr>
<tr>
<td>Carbon Dioxide $^3$</td>
<td>1.46</td>
<td>0.02</td>
<td>42.56</td>
<td>700</td>
<td>1020.6</td>
</tr>
<tr>
<td>Hydrogen Sulfide $^1$</td>
<td>0.41</td>
<td>0.01</td>
<td>151.83</td>
<td>0.0015</td>
<td>6.13E-04</td>
</tr>
<tr>
<td>Sulfur Dioxide $^4$</td>
<td>3.405.10$^{-2}$</td>
<td>0.00055</td>
<td>1822.0</td>
<td>100</td>
<td>3.4054</td>
</tr>
<tr>
<td>Ethylhexanoate $^4$</td>
<td>8.85.10$^{-3}$</td>
<td>0.00014</td>
<td>7012.0</td>
<td>1.02</td>
<td>0.009</td>
</tr>
<tr>
<td>Isoamylacetate $^4$</td>
<td>8.21.10$^{-3}$</td>
<td>0.00013</td>
<td>7559.8</td>
<td>4.74</td>
<td>0.039</td>
</tr>
<tr>
<td>Acetaldehyde $^4$</td>
<td>4.09.10$^{-3}$</td>
<td>0.00007</td>
<td>15183.4</td>
<td>0.0420</td>
<td>1.72E-04</td>
</tr>
<tr>
<td>Ethylacetate $^4$</td>
<td>3.73.10$^{-3}$</td>
<td>0.00006</td>
<td>16631.6</td>
<td>208</td>
<td>0.776</td>
</tr>
<tr>
<td>Ethanol $^1$</td>
<td>2.6.10$^{-4}$</td>
<td>0.00000</td>
<td>238857</td>
<td>94700</td>
<td>24.6</td>
</tr>
<tr>
<td>Isoamylalcohol $^4$</td>
<td>7.10$^{-5}$</td>
<td>0.00000</td>
<td>375225</td>
<td>357</td>
<td>0.059</td>
</tr>
<tr>
<td>Water $^1$</td>
<td>3.10$^{-5}$</td>
<td>0.00000</td>
<td>2038054</td>
<td>9.10$^5$</td>
<td>27.4</td>
</tr>
<tr>
<td>Acetic acid $^1$</td>
<td>1.10$^{-5}$</td>
<td>0.00000</td>
<td>8350889</td>
<td>600</td>
<td>0.0044</td>
</tr>
<tr>
<td>Lactic acid $^1$</td>
<td>5.84.10$^{-10}$</td>
<td>9.41E-12</td>
<td>1.06E-11</td>
<td>2000</td>
<td>1.17E-06</td>
</tr>
<tr>
<td>Tartaric acid $^1$</td>
<td>4.09.10$^{-20}$</td>
<td>6.59E-22</td>
<td>1.52E-21</td>
<td>5000</td>
<td>2.04E-16</td>
</tr>
</tbody>
</table>

Values derived from $^1$Sander, 1999 in water, $^2$Huber 2006 in water, $^3$in wine, own calculation $^4$calculated from Diban et al. 2008 in model solution 12%vol

### 1.3 Gas Exchange with Membrane Contactor

A recent developed method for exchanging gases is the use of membrane contactors. “A membrane contactor is a device that achieves gas/liquid or liquid/liquid mass transfer without dispersion of one phase within another.” (Gabelman & Hwang, 1999).

The most frequent design of these contactors is the use of hollow fibers (Figure 9) (Gabelman, Hwang, & Krantz, 2005).

The application of contactors in gas/liquid exchange is called membrane air stripping (MAS); while the use of liquid/liquid exchange is called membrane based solvent extraction (MBSE) (Gascons Viladomat, Souchon, Athès, & Marin, 2006) or osmotic distillation (OD). For wine the hollow fiber membrane contactors have been used for partially de-alcoholisation of wine (Aguera et al., 2010; Diban et al., 2008) and for adjusting dissolved gases (Schmidt et al., 2010). Only gases like O$_2$, N$_2$, CO$_2$ and substances in their gaseous phase can pass through the membranes barrier. The system can be placed in the production area of the winery to adjust the gas concentration of wine before storage in bulk or before the bottling stage (Schmidt et al., 2010). The membrane can be hydrophobic or hydrophilic; for the application in wine and beverages hydrophobic membranes are usually used (Gabelman & Hwang, 1999). The exchange of gases has been shown to be more efficient if the gas is passed through the inside of the hollow fiber (also called tube or lumen side) while the liquid is passed at the outside/shell side (Sengupta, Peterson, Miller, Schneider, &
The main characteristic of the membrane is its hydrophobicity; it allows the liquid to contact the gas without dispersing into it. Only gases or volatile compounds of an average molecule size smaller than 0.05 µm are able to penetrate the pores of the membrane, whereas the liquid remains in the shell side. It can have a gas transfer to either side of the membrane (Schonenberger, Baumann, Jaquerod, & Ducruet, 2014).

Several designs of hollow fiber membrane contactors are possible. First, there is the possibility of a flow parallel to the fibers; second, the flow orthogonal to the fibers and third, there is the use of the baffled membrane contactors which results in a transversal flow. The most efficient design in hollow fiber membrane contactors is the use of baffled contactors (Gabelman & Hwang, 1999). Herein, the liquid enters the contactor through a central tube which is blocked in the middle by a baffle (Figure 10). The liquid has to leave the central tube and has to flow transversal to the fibers. Due to the transversal flow the gas exchange has been shown to be more efficient in baffled contactors than on conventional parallel flow modules. It has been explained by the better contact between the liquid and the fiber surface due to the avoidance of the so called channeling. In the baffled design, the possibilities of flow channels that do not touch the fiber are efficiently reduced (Sengupta et al., 1998). The liquid mass flow characteristics in these baffled modules have been described by Schoner et al. (1998).

**Figure 10: Schematic view of the cross flow hollow fiber module with the direction of flow in the shell side compartment Liqui-Cel® (Membrana)**

The physical mechanism is based on the principle of osmosis. The membrane module is composed of tubular membrane packet. For now, the hollow fiber is in polypropylene with an inside diameter of 0.2 mm and an average pore size of 0.03 µm (Figure 10). The pore size is impermeable for liquid substances, this means only gases or substances in gaseous state can pass through the pores dependent of their volatile rate and the diffusion coefficient.

The small pore size of the membrane and its marked hydrophobicity prevents water to pass through. However this stands as long as the pressure feed does not exceed the breakthrough pressure ($P_B$).
It corresponds to the pressure required to force water to enter the pores, calculated by the following equation:

\[ P_B = \frac{2. \sigma \cos(\theta)}{r} \]  

\( P_B \)  
*Breakthrough pressure [Pa]*

\( \sigma \)  
*Surface tension of the liquid [N.m\(^{-1}\)]*

\( \theta \)  
*Contact angle*

\( r \)  
*Pore radius [m]*

The following formulas are describing the main characteristics important for mass flow and mass flow resistance of the baffled membrane contactor from Liqui-cel, Celgard according to Schoner et al. (1998) and Sengupta et al. (1998). The differences of different membrane sizes can be taken into account using these formulas: the membrane area (\( A \)), the effective membrane area (\( A_{eff} \)), the hydraulic diameter of the liquid flow (\( d_h \)), the mean velocity of the liquid flow (\( v \)), can be calculated according to the following formulas.

**Hydraulic diameter**

\[ d_h = \frac{4 \text{ volume of voids filled with fluid}}{\text{wetted surface area of the bed}} = \frac{4V_m}{A_{eff}} = \frac{d_o^2 - d_i^2 - nd_{hf}^2}{nd_{hf}^2} \]  

\( d_o \)  
*Outer diameter of the contactor [m]*

\( d_i \)  
*Inner diameter of the contactor [m]*

\( d_{hf} \)  
*Outer diameter of the hollow fibers [m]*

\( n \)  
*Number of hollow fibers in the contactor*

The geometric void fraction (\( \varepsilon_{th} \)) means the fraction of the contactor that is free to flow for liquid, the void fraction is describing the relative area available for liquid flow, meaning the total volume of the membrane subtracting the area that is filled by the fibers. It is defined in equation (60).

\[ \varepsilon_{th} = 1 - \frac{nd_{hf}^2}{d_o^2 - d_i^2} \]  

The mean superficial velocity (\( v \)) can be calculated dividing the volumetric flow rate (\( Q \)) by the area available for flow (equation (61)).

\[ v = \frac{2Q}{\pi L} \times \frac{\ln(d_o/d_i)}{d_o - d_i}/\varepsilon_{th} \]  

\( Q \)  
*Volumetric flow rate [m.s\(^{-1}\)]*

\( L \)  
*Effective length of the fibers [m]*
Figure 11 is showing the mean superficial velocity calculated for a Liqui-cell 4x28x50 membrane contactor. The velocities are in the order of 0.01 – 0.05 m.s\(^{-1}\) during the passage into the membrane using the recommended minimum and maximum flow rates; this is showing the very slow average flow through the membrane, which is mainly caused by the effect, that the flow is in radial direction and not parallel.

![Figure 11: Mean superficial velocity in shell side dependent on volume liquid flow rate at Liqui-cell Extra Flow 4x28 membrane contactor (own calculation)](image)

The total transfer area (A) of the membrane can be calculated based on the total area of the outside of the fibers. Therefore, the area of a single fiber has to be calculated and then be multiplied by the total number of the fibers (equation (62)). The effective area (A\(_{eff}\)) is the area that is covered by pores. Thus; with a higher porosity the effective membrane area is bigger and therefore the membrane can be more efficient. The real transfer area is the area covered by pores (equation (63)).

\[
A = n \cdot \pi \cdot d_{hf} \quad \quad (62)
\]

\[
A_{eff} = n \cdot \pi \cdot d_{hf} \cdot \varepsilon \quad \quad (63)
\]

\(\varepsilon\) Porosity (dimensionless)

### 1.3.1 Overall Mass Transfer in Hollow Fiber Membrane Contactors

The mass transfer in membrane contactor is said to be purely diffusion driven. Thus, the concepts of mass transfer according to FICK’s law can be applied to describe the process. The overall mass transfer coefficient \(k_L\) can be determined experimentally by applying a mass balance and the logarithmic mean concentration difference as the driving force for the transfer. This is done very similar than in the modeling of countercurrent heat exchangers. The main difference is that the driving force is a concentration or partial pressure gradient in gas exchange and not a temperature gradient as in heat exchangers. As diffusion in liquids is several orders of magnitude slower in gases, conventionally the corresponding liquid phase concentrations are used for the calculations of the transfer coefficients in membrane...
contacters. Therefore, the partial pressures of the gas phase have to be transferred to the corresponding liquid concentrations using the Henry’s law constants (equation (7)) (Gabelman & Hwang, 1999).

The flow through membrane \((F_L)\) is defined as the difference of the outlet and inlet concentration multiplied by the liquid mass flow \((Q_{\text{Liquid}})\) divided by the membrane area (Equation (64)).

\[
F_L = \frac{(C_{\text{liquid, in}} - C_{\text{liquid, out}}) \times Q_{\text{Liquid}}}{A}
\]  

\(F_L\) Flux through membrane \([\text{mol.s}^{-1}.\text{m}^2]\)
\(C_{\text{liquid, in}}\) Concentration of liquid at the inlet of the membrane contactor \([\text{mol.m}^{-3}]\)
\(C_{\text{liquid, out}}\) Concentration of liquid at the outlet of the membrane contactor \([\text{mol.m}^{-3}]\)
\(Q_{\text{Liquid}}\) Flow of Liquid \([\text{m}^3.\text{s}^{-1}]\)

The average concentration difference as the driving force for diffusive equilibrium adjustments is conventionally expressed as the logarithmic mean difference \((\Delta C_{LM})\) at the inlet and the outlet of the membrane contactor. As the flow in the membrane is countercurrent the position 0 is the inlet of the liquid (liquid in) and the outlet of the gas (gas out); so is the position 1 the outlet of the liquid (liquid out) and the inlet of the gas (gas in) (equation (65)).

The total membrane resistance \((R_{\text{Total}})\) can then be calculated by dividing the mean driving force \((\Delta C_{LM})\) by the flow through the membrane \((F_L)\) (equation (66)). The overall transfer coefficient \((k_L)\) is the inverse of the membrane resistance (equation (67)) flow divided by concentration difference.

\[
\Delta C_{LM} = \frac{(C_{\text{liquid, in}} - c_{\text{gas, out}}) - (C_{\text{liquid, out}} - c_{\text{gas, in}})}{\ln \left( \frac{(C_{\text{liquid, in}} - c_{\text{gas, out}}) / (C_{\text{liquid, out}} - c_{\text{gas, in}})}{C_{\text{liquid, out}} - C_{\text{liquid, in}}} \right)}
\]  

\(R_{\text{Total}} = \frac{\Delta C_{LM}}{F_L} = \frac{\Delta C_{LM} \times A}{(C_{\text{liquid, in}} - C_{\text{liquid, out}}) \times Q_{\text{Liquid}}}
\]  

\(k_L = \frac{F_L}{\Delta C_{LM}} = \frac{(C_{\text{liquid, in}} - C_{\text{liquid, out}}) \times Q_{\text{Liquid}}}{\Delta C_{LM} \times A}
\]  

\(k_L\) Overall transfer coefficient \(\left[\text{m.s}^{-1}\right]\)
\(\Delta C_{LM}\) Logarithmic mean concentration difference \(\left[\text{mol.m}^{-3}\right]\)
\(c_{\text{gas, in}}\) Concentration of gas at the inlet of the membrane contactor expressed in liquid equivalent \(\left[\text{mol.m}^{-3}\right]\)
\(c_{\text{gas, out}}\) Concentration of gas at the outlet of the membrane contactor expressed in liquid equivalent \(\left[\text{mol.m}^{-3}\right]\)
\(F_L\) Liquid flow \(\left[\text{mol.m}^{-2}.\text{s}^{-1}\right]\)
\(A\) Total membrane surface area \(\left[\text{m}^2\right]\)
In some cases if only liquid concentrations are known a useful simplification of this process is necessary; in this case the concentrations on the gas phase are considered to be negligible (Wiesler & Sodaro, 1996) equation (68), or the concentration does not change and stays constant $C^*$ during the process.

$$k_L = \ln \left( \frac{C_{\text{liquid, in}}}{C_{\text{liquid, out}}} \right) \times \frac{Q_{\text{Liquid}}}{A} = \frac{F_L}{\Delta C_{LM} - C^*} \tag{68}$$

$k_L$ \hspace{1cm} Overall transfer coefficient [m.s$^{-1}$]

$\Delta C_{LM, \text{Liquid}}$ \hspace{1cm} Logarithmic mean concentration of liquid side [mol.m$^{-3}$]

$C^*$ \hspace{1cm} Initial gas concentration expressed in liquid equivalent [mol.m$^{-3}$]

This experimentally-based general view of the overall mass transfer coefficient of the system can be modeled and separated in a transfer in series. The molecules have to pass the liquid boundary layer, later the membrane and in a third step the gas phase boundary layer. The transfer is diffusion driven in all three cases as there is no selectivity of the membrane reported. Hence, the mass transfer in hollow fiber membrane contactors can be estimated to be controlled by three main resistances (Gabelman & Hwang, 1999).

- Resistance of liquid phase boundary layer $R_l$
- Membrane resistance $R_m$
- Resistance of the gas boundary layer $R_g$

It is commonly explained and modeled as three resistances in series; in many publications the use of transfer coefficients $k = \frac{1}{R}$ instead of resistances $R$ is used. The total resistance ($R_{\text{Total}}$) is mathematically described as follows in equation (69), in Figure 12 the concentration gradient in a cross section of a microporous membrane for gas liquid separation can be seen (Mavroudi et al., 2006). The following subchapters are describing the single resistances in more detail.

$$R_{\text{Total}} = \frac{1}{k_L} = \frac{1}{kl} + \frac{H}{km} + \frac{H}{kg} = R_l + R_m + R_g \tag{69}$$

$k_L$ \hspace{1cm} Overall mass transfer coefficient [m.s$^{-1}$]

$kl$ \hspace{1cm} Liquid mass transfer coefficient [m.s$^{-1}$]

$km$ \hspace{1cm} Membrane mass transfer coefficient [m.s$^{-1}$]

$kg$ \hspace{1cm} Gas mass transfer coefficient [m.s$^{-1}$]

$R_l$ \hspace{1cm} Liquid mass transfer resistance [s.m$^{-1}$]

$R_m$ \hspace{1cm} Membrane mass transfer resistance [s.m$^{-1}$]

$R_g$ \hspace{1cm} Gas mass transfer resistance [s.m$^{-1}$]
It is known that the gas-liquid transfer coefficient can be affected by parameters, such as temperature, pressure, dissolved or colloidal compositions of the liquid. However, the transfer coefficient is not only controlled by the quality of the liquid, but also by various parameters which fix the hydrodynamics of the contactor such as the geometry, the specific power dissipated, the gas flow, etc.

The $K_{L_a}$ is the volumetric transfer coefficient ($s^{-1}$) (equation (70)). It is the product of the “a” coefficient, the specific exchange area by the liquid phase volume ($m^2/m^3$) and the overall transfer coefficient.

It permits to quantify the capacity of the transfer in a given context.

$$k_{L_a} = k_L \cdot \frac{A}{V}$$  \hspace{1cm} (70)

$k_{L_a}$ Liquid or gaseous volumetric transfer coefficient [$s^{-1}$]
$k_L$ Overall transfer coefficient [$m.s^{-1}$]
$A$ Membrane surface [$m^2$]
$V$ Shellside or lumenside volume [$m^3$]

This $k_{L,a}$ coefficient can be calculated using equation (67) or (68).

### 1.3.1.1 Liquid Phase Boundary Layer Transfer Coefficient

The main transfer resistance in a membrane contactor is the resistance due to the liquid phase boundary layer (Gabelman & Hwang, 1999). The mass transfer on the liquid side is governed by the liquid properties and the flow characteristics of the liquid. As the flow is nearly laminar in the membrane module there is a boundary layer formed close to the membrane. In this boundary layer film, concentration gradients are formed due to the transport of molecules through the membrane (Baker 2004, Figure 13).
With the equations of the membrane properties and the liquid properties like viscosity, and density the Reynolds (Re), Schmidt (Sc) and Sherwood (Sh) numbers can be calculated. These are numbers to characterize the liquid flow and hereby the boundary layer resistance. Increasing turbulence for example is reducing the laminar layer thickness and hereby reducing the resistance of the liquid phase. These numbers are useful values for the estimation of the liquid membrane transfer coefficient in membrane contactors. With the estimated Sherwood number it might be possible to predict the liquid membrane transfer coefficient at adequate precision (Schoner et al., 1998).

The Schmidt number (Sc) is a dimensionless number describing the ratio of viscosity to mass diffusivity and is used to characterize the fluid flow (Schoner et al., 1998) equation (71)

\[ Sc = \frac{\eta}{\rho \cdot D} \]  

\[ \rho \quad \text{Density [kg.m}^{-3}] \]
\[ \eta \quad \text{Dynamic viscosity [Pa s]} \]
\[ D \quad \text{Diffusion coefficient [m}^2\cdot\text{s}^{-1}] \]

The Reynolds number (Re) is also a dimensionless number given by equation (72):

\[ Re = \frac{\rho \cdot v \cdot d}{\eta} \]  

\[ v \quad \text{Velocity of the fluid [m.s}^{-1}] \]
\[ d \quad \text{Diameter [m]} \]
\[ \rho \quad \text{Volumetric mass of the fluid [kg.m}^{-3}] \]
\[ \eta \quad \text{Dynamic viscosity of the fluid [kg.m}^{-1}\cdot\text{s}^{-1}] \]

In Figure 14, the calculated Reynolds number for a Liqui-cel 4x28 X50 Extra Flow can be seen, it can be concluded that the Reynolds number are small (<15) and therefore laminar flow can be estimated in the module under the operation conditions recommended by the manufacturer. Reason for this low Reynolds number is the very slow flow of the liquid as the flow is tangential.
Sherwood number \( Sh \) is a dimensionless number used in mass transfer operations. It represents the ratio between convective to diffusive mass transports. The number can be correlated to Schmidt and Reynolds number according to the following equation (73) (Schoner et al., 1998) an extensive syntheses for determining the coefficients a, b and c can be found in the review of Gabelman and Hwang (1999):

\[
Sh = a \cdot Re^b \cdot Sc^c \tag{73}
\]

\( a, b, c \quad \text{Coefficients to be determined experimentally or taken from literature} \)

Or determined experimentally using the liquid mass transfer coefficient (equation (68)).

\[
Sh = \frac{k_l d_h}{D} \tag{74}
\]

\( k_l \quad \text{Liquid phase transfer coefficient \([m.s^{-1}]\)} \)

\( D \quad \text{Diffusion coefficient \([m^2.s^{-1}]\)} \)

With

\[
k_l = \frac{a \left( \frac{v d_h D}{\eta} \right)^b \left( \frac{\eta}{\rho D} \right)^c D}{d_h} \tag{75}
\]

Applying these equations it can be seen that the mass transfer resistance in the liquid phase is dependent of the overall membrane contactor characteristics (hydraulic diameter, flow rate), the liquid characteristics (viscosity, density) and the gas/liquid interactions (diffusivity). As the liquid flow rate is having a great influence on the Reynolds number the influence of this flow rate on the mass transfer is very important. The Reynolds number in the shell side under the recommended operation conditions is always under 100, so the flow can be considered to be always under laminar flow conditions. Hence, for a given contactor design the liquid phase transfer can be adequately predicted if the flow rate and the viscosity of the liquid and the diffusivity of the gas therein are known (Mavroudi et al., 2006).
A problem in the case of wine is that these values differ from wine to wine and are not well described in the literature.

As a conclusion for the liquid side mass transfer, it can be said that this transfer is regulated by the flow properties of the liquid and the diffusion of the gas therein. Although the Reynolds numbers are very small for the conditions used (<100) and laminar conditions are estimated for regular conditions, a more turbulent flow is leading to a smaller boundary layer and a better mass transfer. A higher diffusion of a compound in the liquid should also lead to a better overall mass transfer.

1.3.1.2 Transfer Coefficient within the Membrane

There are three modes of operation for hydrophobic membrane contactors. The properties of the liquid are determining this mode of operation. Depending on these liquid properties the pores of the hydrophobic membrane can be filled with air or with liquid (Mavroudi et al., 2006). As diffusion in gas is approximately 1000 times faster than in liquid (Cussler, 1997), the resistance in dry mode is significantly smaller than in wetted mode. Three different modes are described (Mavroudi et al., 2006).

- **Dry mode**: No liquid is present in the pores; the pores are gas filled; i.e. if water is used in combination with hydrophobic membranes.
- **Wetted mode**: The pores are completely filled with the liquid, i.e. if pure methanol is used with hydrophobic membranes.
- **Partially wetted mode**: The pores are partially filled with liquid, i.e. if a hydrophobic membrane is used for a long time with water at high pressure differences; water vapor condenses in the membrane and partially wets these membranes (Figure 15).

![Figure 15: Partial membrane pore wetting (Mavroudi et al. 2006)](image)

Due to the hydrophobic character of the membrane used here, pure water is prevented from entering the pores in its liquid form except using a high pressure. It is shown that water/ethanol mixtures at around 12 %vol ethanol do not enter the hydrophobic polypropylene (PP) membrane at pressure differences below 2 bars (Castellari, Simonato, Tornielli, Spinelli, & Ferrarini, 2004); the long term effect on membrane wetting has not been determined in wine.
The membrane resistance therefore depends on the mode of operation as described above, the diffusivity of the gas in the gas phase (equation (76)) respectively the diffusivity in the liquid phase in wetted mode (equation (77)) and the membrane properties (Mavroudi et al., 2006). This shows the importance of a thorough drying of the membrane after usage to minimize water content in the membrane pores to keep the transfer at a good rate.

\[
k_{mg} = \frac{D_{g,eff} \varepsilon}{H \tau L}
\]

\[
k_{ml} = \frac{D_l \varepsilon}{\tau L}
\]

\(k_{mg}\) Coefficient transfer in gas [m.s\(^{-1}\)]
\(k_{ml}\) Coefficient transfer in liquid [m.s\(^{-1}\)]
\(H\) Henry constant
\(\tau\) Tortuosity
\(\varepsilon\) Porosity
\(D_{g,eff}\) Effective diffusion coefficient in gas [m\(^2\).s\(^{-1}\)]
\(D_l\) Diffusion coefficient in liquid [m\(^2\).s\(^{-1}\)]

The effective diffusion coefficient can be calculated according to Mavroudi et al. 2006, taking into account a combination of molecular self-diffusion plus Knudsen diffusion in gas filled pores. Analyzing these formulas, it can be see that membrane transfer coefficient is dependent of the membrane properties, the operating mode as well as the gas properties Henry constant and effective diffusion coefficients.

The membrane transfer coefficient can be determined experimentally using the so called Wilson Plot of \(1/k_0\) vs. \(1/v_0^a\). \(a\) is selected to give the best straight line through the data points. The membrane transfer coefficient is given by the intercept of the Wilson Plot (Gabelman & Hwang, 1999). Basis for this determination is that the gas phase transfer coefficient is considered negligible and the liquid phase boundary layer resistance is reduced the higher the liquid velocity. Choosing infinite velocity \(1/v_0 \rightarrow 0\) is reducing this resistance towards zero. Therefore the intercept is giving the residual resistance, the membrane resistance (Figure 16).

![Figure 16: Experimental determination of membrane resistance with Wilson plot (own data)](image-url)
1.3.1.3 **Transfer Coefficient in the Gas Phase**

The gas phase transfer coefficient is often considered negligible, as diffusion in gases is very fast and no significant boundary layer is formed, thus leading to a uniform distribution of the compounds in the gas phase and creating no resistance for transfer of molecules (Gabelman & Hwang, 1999; Keshavarz, Fathikalajahi, & Ayatollahi, 2008; Mavroudi et al., 2006; Shirazian, Moghadassi, & Moradi, 2009). In the two-dimensional model of Shirazian et al. 2009, this assumption is visualized, as there is no concentration gradient in the radial direction in the gas phase (Figure 17). Tarafder, Medermott and Schuth (2007) showed in their experiments that this might be not true and there is a significant influence of the gas phase resistance on the total resistance. Also Mahmud et al. 2002 found their mathematical models not fitting to experimental results at low gas flow rates; the group applied further experiments for precising this effect. They held the liquid velocity constant and changed only the gas velocity which should under previous modeling attempts not change the overall mass transfer coefficients. So in a following attempt they adjusted their equation by a factor considering the gas phase velocity. Gas phase resistance can only be neglected if very high strip gas flow rates or very low vacuum pressures are applied (Mahmud et al. 2002).

The problem in most of the cases is that only liquid or gas phase concentrations are measured, the other concentration change was estimated to be negligible which is not the case especially at low gas flow rates where the limiting factor is the uptake on the gas phase and not the mass transfer.

1.3.2 **Mass Transfer of Pure Water**

Mahmud et al. (2002) showed that the vapor phase water concentration is always very close to the saturated water vapor pressure. They trapped the water with liquid nitrogen and measured the quantity at different flow rates, using a Liqui-cel Extra Flow 2.5x8 Module. They changed air speed from $1.75 \times 10^{-5}$ to $5.10^{-5}$ m$^3$.s$^{-1}$ and always found a water saturated air. They concluded that due to the high concentration of water there is no boundary layer resistance and the water vapor is transferred very efficiently. From these trials, it seems that the equilibrium between gas phase water partial pressure and theoretical saturated vapor pressure of water is reached very fast and can be estimated to be saturated in all cases.
1.3.3 Efficiency of gas exchange

Removal efficiency of O₂

\[ \eta_{O₂} = \frac{[O₂]^{in} - [O₂]^{out}}{[O₂]^{in}} \]  
(78)

With

\([O₂]\) in mg/L or KPa

Efficiency of CO₂

\[ \eta_{CO₂} = \frac{CO₂ \text{ inserted in wine}}{CO₂ \text{ used}} = \frac{[CO₂]^{out} - [CO₂]^{in}}{Q_G / Q_L} \]  
(79)

With

\(Q_G\) Gaz flow rate mg/h
\(Q_L\) Liquid flow rate L/h

Removal efficiency of N₂

\[ \eta_{N₂} = \frac{[N₂]^{in} - [N₂]^{out}}{[N₂]^{in}} \]  
(80)

With

\([N₂]\) in mg/L or KPa