ChE-309 TP-5
Oxygenation of water

instructions for use, spring 2025

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1. Statement of the objective

The aquarium de Genève hired you to design an oxygenation column for the water supply of their tropical fish aquarium. As fish require to be supplied with oxygen for their aerobic metabolism, your task is to ensure a sufficient dissolved oxygen concentration (saturation concentration) is present in the supplied water. The concentration of oxygen in water at saturation depends on the temperature and salinity of the water.
You are informed that dissolved oxygen content of 5-7 mg/L in the water is sufficient to support aquatic life. Importantly, the first signs of stress are noticed if the content falls below 4 mg/L, and deaths can be expected when the concentration drops to 2 mg/L. Knowing this, the required oxygen concentration in the water can be considered to be 7 mg/L at a temperature of 20°C. Finally, since there are micro-organisms essential to the ecosystem in the aquarium water that will move through the oxygenation column, the type of column used must not use turbulent flow (which could cause high stresses that could damage the micro-organisms). Therefore, a laminar flow falling film column will be used to re-oxygenate water from the aquarium.

2. Theoretical basis

2.1 Gas-liquid mass transfer

The transfer of material in the form of atoms or molecules which have a mass between a gas and a liquid at their phase boundary is of primary importance in many chemical engineering processes. For example, for bio-processing applications due to the need for oxygen in aerobic respiration. The transfer of a solute molecule such as oxygen from the gas phase to the liquid phase is the physical phenomenon that allows life in water and the metabolism of aerobic cells in bioreactors. In general, we will call this phenomenon "mass transfer" (as opposed to the transfer of heat or momentum). Mass transfer analysis is very important in multi-phase systems where the interfacial boundary layers provide high transfer resistance.

For the simple case when a dilute component is transferring in a system by convection, the mass transfer rate is directly proportional to the driving force and the area available for the process. This can be expressed as follows:

Transfer rate ∝ (transfer surface) * (driving force)

The coefficient of proportionality in this equation is called the mass transfer coefficient, so that:

Transfer rate = (mass transfer coefficient) * (area) * (driving force)

For each fluid on either side of the interface, the driving force can be expressed in terms of the difference in concentration between the "bulk" of the fluid phase and the interfacial concentration. Therefore, the mass transfer rate at an interface is given by the equation:

$$\mathbf{N_A = k_m\, A\, \Delta C_A = k_m\, A\, (C_A - C_{Ai})} \qquad \text{(Eq.1)}$$

Where N_A is the mass (molecular) transfer rate [mol/s] of component "A" (other units are possible but the molar reference is the most convenient here). Remember, this relation is only valid when A can be considered dilute in the system. If A is not dilute, then its transfer will cause an advective effect which will alter the simple linear relationship shown in Eq. 1. An example of gas-liquid mass transfer is shown in Figure 1, which shows the situation at the interface between gas and liquid phases containing component A. Suppose that A is transferred from the gas to the liquid with C_{AL} the concentration of A in the liquid, C_{ALi} the concentration at the liquid-side interface, C_{AG} the concentration in the gas and C_{AGi} the concentration at the gas-side interface.

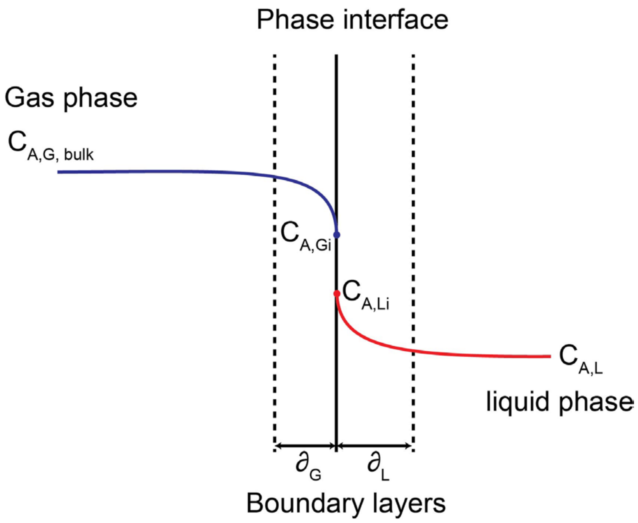


Figure 1. Concentration gradient for gas-liquid mass transfer (for the case of the transfer of "A" from gas to liquid)

Starting from (Eq. 1), the mass transfer rate of component A through the gas boundary layer is as follows:

$$\mathbf{N_{AG} = k_G\ A\ (C_{AG} - C_{AGi})} \qquad \text{(Eq. 2)}$$

and the rate of mass transfer of A through the liquid boundary layer is:

$$\mathbf{N_{AL} = k_L\ A\ (C_{ALi} - C_{AL})} \qquad \text{(Eq. 3)}$$

Where k_G is the gas phase mass transfer coefficient k_L is the liquid phase mass transfer coefficient. If we assume that equilibrium exists at the interface (usually a good assumption), C_{AGi} and C_{ALi} can be linked by an equilibrium relationship. For the dilute case, the equilibrium concentration in the gas phase can be approximated by a linear function of the concentration in the liquid. This is called Henry's law. Therefore, according to Henry's law, one can write:

$$C_{AGi} = m\, C_{ALi} \qquad \text{and} \qquad C_{ALi} = C_{AGi} / m$$

where m is the concentration-based Henry's law constant (note that there are many forms of Henry's law constants). These equilibrium relationships can be incorporated into (Eq. 2) and (Eq. 3) in the equilibrium state for the gas phase:

$$\frac{N_A}{A\, k_G} = C_{AG} - mC_{ALi} \qquad \text{(Eq. 4)}$$

or for the liquid phase:

$$\frac{N_A}{A\, k_L} = \frac{C_{AGi}}{m} - C_{AL} \qquad \text{(Eq. 5)}$$

The mass transfer coefficient described above is useful when the flow profile is unknown or turbulent, however, if one of the phases is stagnant or the flow profile is known, the concentration profile at the interface can be resolved directly. This method is very useful when one wishes to calculate the thickness of the boundary layer, the diffusivity or the dimensioning of equipment. Laminar flow on the wetted wall of a column is an important example of a system that meets these criteria, and we will use this to estimate the mass transfer coefficient.

2.2 Mass transfer in a wet-wall column

The falling film principle (in a wet-wall column) is used in many different industrial applications for mass transfer between fluids, e.g. sulfonation of biological products or flue gas cleaning. The mass transfer rate has been extensively studied in wet-wall columns because this type of equipment is of simple design. Furthermore, the falling liquid film is assumed to have a fixed and known interfacial area (without waves or undulations, laminar flow) which can be the case for most columns at laboratory scale. On the contrary, in the case of columns at the pilot or industry-scale level, the film conditions will often show turbulence and undulations. The interfacial area thus becomes unknown and the subsequent analysis is more complex. Only mass transfer data obtained in a column with a simple geometry and flow system can shed light on the mass transfer mechanism.

The wet-wall column is a vertical tube or pipe with a device for the supply and removal of liquid. The gas flows through the column and the liquid flows down as a film on a section of the column. Most experiments reported on a wet-wall column involve the evaporation of pure liquids by introducing air currents or other gases.

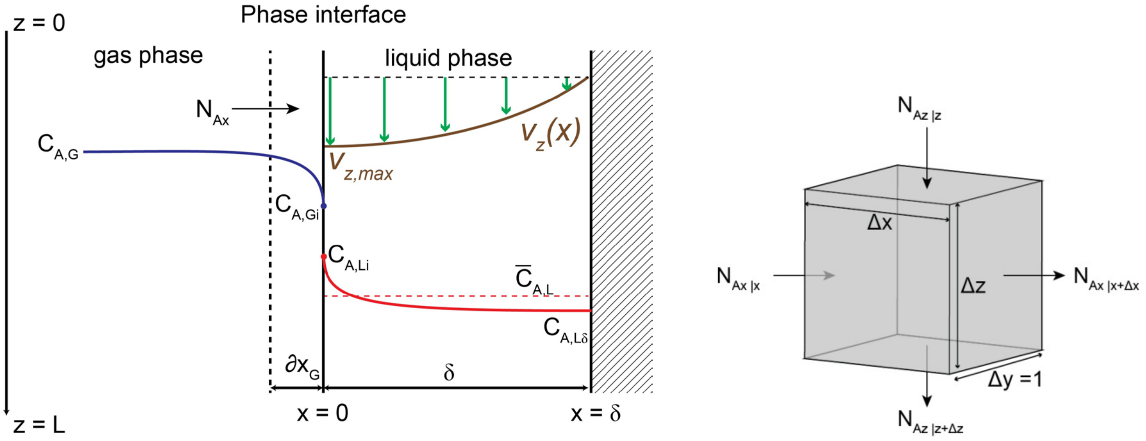


Figure 2. Diffusion of solute A in a descending laminar film: velocity profile (a) and concentration profile, (b) small mass balance element.

We will consider the mass transfer of solute A in a falling laminar film. The solute A in the gas is absorbed at the interface and is diffused into part of the liquid (component "B") so that it has not penetrated the total distance δ to the wall of the column. At a certain distance z from the inlet, the C_A concentration profile (as a function of x) is shown in Fig. 2a (in blue and red). A mass balance will be performed at this point on the element shown in Fig. 2b.

at the steady state, input flow = output flow.

$$N_{Ax|x}\,(\Delta z) + N_{Az|z}\,(\Delta x) = N_{Ax|x+\Delta x}\,(\Delta z) + N_{Az|z+\Delta z}\,(\Delta x) \qquad \text{(Eq.6)}$$

For a dilute solution, the transport of A in the x-direction in the liquid phase can be considered to occur only by diffusion (there is no advective transport in this direction). Then:

$$n_{Ax} = -\mathcal{D}_{AB}\frac{\partial c_A}{\partial x} \qquad \text{(Eq. 7)}$$

where $\mathcal{D}_{AB}$ is the diffusion coefficient of A in B, and n_{Ax} is the molar flux density [mol s^{-1} m^{-2}] of A in the x-direction. For the z-direction of diffusion is negligible, only advection is considered. This looks like:

$$n_{Az} = 0 + c_A v_z \qquad \text{(Eq. 8)}$$

Where v_z is the velocity of the liquid falling film (keep in mind that $v_z = f(x)$) By dividing (Eq. 6) by ΔxΔz, letting Δx and Δz approach zero and substituting (Eq. 7) and (Eq. 8) in the result, we obtain:

$$v_z\frac{\partial c_A}{\partial z} = D_{AB}\,\frac{\partial^2 c_A}{\partial x^2} \qquad \text{(Eq. 9)}$$

This is a differential equation for c_A and in principle can be solved if v_z and the boundary conditions are known. The velocity profile of the falling film, v_z, qualitatively looks like what is drawn in Figure 2. In the case of laminar flow, it is exactly parabolic and can be accurately determined by performing a momentum balance on the falling film (remember the Navier-Stokes equations). We can use them to show that:

$$v_z(x) = \frac{\rho g \delta^2}{2\mu}\left(1 - \left(\frac{x}{\delta}\right)^2\right) \qquad \text{(Eq. 10)}$$

where ρ and μ are the density and the viscosity of the liquid, g is the gravitational acceleration and δ is the thickness of the falling film. Note that this is not a function of z and we assume that the film is not accelerating as it falls down the column (it is at terminal velocity). Looking at equation 10, we can see that $v_{z,\max} = (\rho g \delta^2) / 2\mu$. By further integrating equation 10, we can find the mean value, $v_{z,\text{avg}} = (\rho g \delta^2)/3\mu = (2/3)\, v_{z,\max}$. The volumetric flow rate, q, can also be related to the velocity profile in a circular column of diameter D (assuming that D is large compared to δ):

$$q = v_{z,\text{avg}}\delta\pi D = \frac{\rho g \delta^3 \pi D}{3\mu} \qquad \text{(Eq. 11)}$$

Solving equation 9 for $c_A = c_A(x, z)$ with the known velocity profile is difficult unless we can simplify the problem. If the solute has penetrated a short distance into the liquid, that is, if the contact time of the fluid is short compared to the diffusion time through the film, then we can make some important simplifications. The validity of this hypothesis can be tested by evaluating the Fourier number for mass diffusion.

$$Fo_m = \frac{D_{AB}t}{L_c^2} \qquad \text{(Eq. 12)}$$

where t is the gas-liquid contact time (which is equal to the length of the column, L, divided by $v_{z,\max}$), and L_c is the characteristic diffusion length (in this case, $L_c = \delta$). By combining the known expressions for $v_{z,\max}$ and with a bit of mathematics, we find that:

$$Fo_m = 2D_{AB}L\left(\frac{\pi D}{3q}\right)^{\frac{4}{3}}\left(\frac{\rho g}{\mu}\right)^{\frac{1}{3}} \qquad \text{(Eq. 13)}$$

If $Fo_m \ll 1$ we can assume that the concentration of A when $x = \delta$ is small because the liquid is not present in the column long enough for diffusion to take place throughout the film. This hypothesis allows us to make two very important assumptions: 1) the short contact time of the liquid relative to the diffusion of A into the liquid means that almost all of the A diffusing into the liquid moves down the column at a velocity of $v_{z,\max}$. Applying this assumption, equation 9 can be rewritten as follows:

$$\frac{\partial c_A}{\partial(z/v_{z,\max})} = D_{AB}\,\frac{\partial^2 c_A}{\partial x^2} \qquad \text{(Eq. 14)}$$

2) component A is diffused in a semi-infinite plate (i.e. x extends to ∞). This makes solving the differential equation (eq. 14) much easier. Finally, if the boundary conditions are defined such that $C_A = 0$ at $z = 0$ (for all x), $C_A = C_{ALi}$ at $x = 0$ (for all z), and $C_A = 0$ at $x = \infty$ (for all z) we can solve to obtain:

$$\frac{C_A(x,z)}{C_{ALi}} = \mathbf{erfc}\left(\frac{x}{\sqrt{4D_{AB}\,z/v_{z,max}}}\right) \qquad \text{(Eq. 15)}$$

where erf (y) is the error function of y, and erfc (y) = 1 - erf (y). The erf values are in tabular form or can be found online. This concentration profile can be used in combination with the flow profile to estimate the total amount of "A" transferred to a wet-wall column according to Equation 7 and Equation 8. With some additional development, the total amount of "A" transferred to the wet-wall column can then be used to estimate the gas phase mass transfer coefficient k_G.

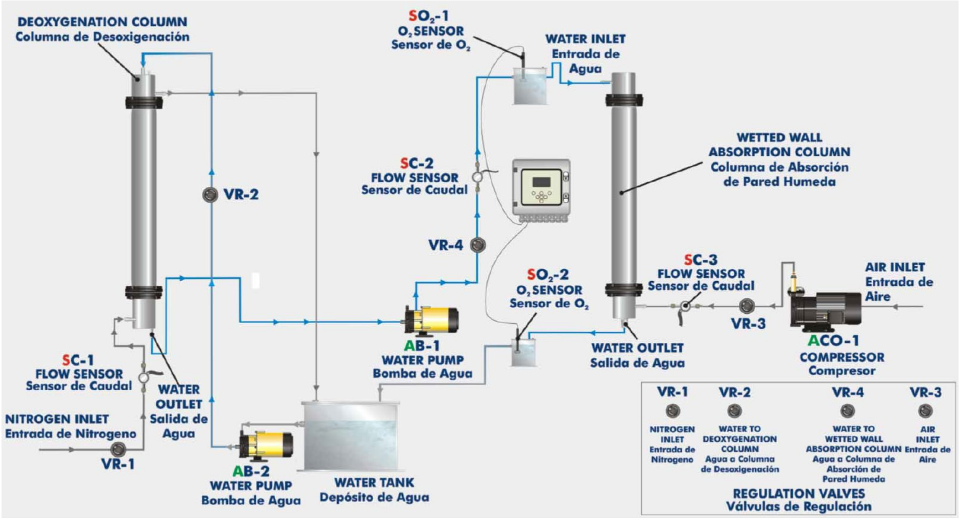
3. Practical Laboratory Exercise

3.1 Objectives

In order to design a water oxygenation column for the Geneva Aquarium, you must obtain a value for the gas phase mass transfer coefficient (k_G). For this purpose, a wet-walled, falling-film gas absorption column has been set up to allow you to investigate the absorption of oxygen in deoxygenated water. To ensure that your calculations are reliable, you must also assess the value of Fo_m. Finally, you must propose a design for the oxygenation column according to the design requirements.

3.2 Experimental set-up

The plant consists of a packed desorption (stripping) column where nitrogen is bubbled into a flow of water to remove most of the oxygen. The deoxygenated water then passes through an oxygen sensor, then through the wet-wall column (where air flows in the opposite direction), and finally past another oxygen sensor to detect the amount of oxygen that has been transferred to the water. **Ask the instructor about the dimensions of the column.**



3.3 Experimental procedure

1. Start the control program.
2. Partially open the water valve for the packed deoxygenation column (VR-2) and start pump no. 2 (AB-2). Open the nitrogen valve (VR-1) to begin a modest flow rate of N_2.
3. Start AB-1 at a value of 50% of water and the valve (VR-4) of the wet-wall column.
4. Set the flow rate to 10 L/h and check if the water is forming a homogeneous film on the wall. Change the flow rate of water to examine the range of flow rates where the film appears laminar.
5. Readjust the nitrogen and water flows through the deoxygenation column (VR-2) so that the nitrogen bubbles no longer move to the AB-1 pump. Ideally, the water flow rate should be the same as the water flowing through the wet-wall column and the nitrogen flow rate should be sufficient to remove as much oxygen as possible.
6. When the SO2-1 oxygen sensor is stable at a sufficiently low value (preferably 0%), start the airflow (ACO-1 compressor) in the wet-wall column and using the manual valve set it to 1.5 L/min.
7. Once the oxygen concentration in the water leaving the wet-wall column has stabilized, change the water flow rate to another value. *How do you think the mass transfer will change with the flow of water?*
8. Change the air flow rate to and record the change in dissolved oxygen concentration in the water. *How do you think the mass transfer coefficient varies with airflow?*

4. Report

1) Calculate the Reynolds number for air and water flow and evaluate the flow regime in all situations tested: for the film we define $\mathbf{Re} = \frac{4\boldsymbol{\Gamma}}{\boldsymbol{\mu}}$ where $\boldsymbol{\Gamma} = \boldsymbol{\rho\delta v_{z,avg}}$ is the mass flow rate per unit circumference. Laminar flow occurs for Re<1200. Laminar flow with undulations occurs for 25<Re<1200 (ok for this experiment).

2) Using the equation described below, convert the dissolved oxygen saturation [%], to units of mg/L and to µmol/L in water.

The calculation of the dissolved oxygen concentration is performed by the equation below, where temperature is represented by T [°C], O_P is the dissolved oxygen saturation [%], O_M [mg/l] and O_U [μmol/l] represent dissolved oxygen concentrations.

$$
\begin{aligned}
O_M &= \frac{O_P}{100} \times O_2* \times 1.42903 \\
O_U &= \frac{O_P}{100} \times O_2* \times 44.660 \\
T_S &= 273.15 + T \\
\ln O_2* &= A_1 + A_2 \times \frac{100}{T_S} + A_3 \ln\left(\frac{T_S}{100}\right) + A_4 \times \frac{T_S}{100} + S\left\{B_1 + B_2 \times \frac{T_S}{100} + B_3 \times \left(\frac{T_S}{100}\right)^2\right\}
\end{aligned}
$$

$$
\begin{array}{llll}
A_1 = -173.4292 & A_2 = 249.6339 & A_3 = 143.3483 & A_4 = -21.8492 \\
B_1 = -0.033096 & B_2 = 0.014259 & B_3 = -0.0017 &
\end{array}
$$

The equation above is valid when temperature (T) is between 2 and 40 [°C], and salinity is between 0 and 40.

3) From your data, calculate the average k_G (gas phase mass transfer coefficient, i.e., from the gas to the liquid surface) for the conditions analyzed. *How can you do this using the above theory? What assumptions must you make?* Hint: find values for $D_{O2,H2O}$ and *m* on the web and check the Fo_m value.

4) Explain qualitatively how the mass transfer coefficient should vary with increasing water flow (at constant gas flow rate) and gas flow (at constant water flow rate) and compare your rationale with your results.

5) The Geneva Aquarium needs to oxygenate a water flow (1000 L/min) that leaves the aquarium at 5 mg/L of O_2 and should return to the tank at 8 mg/L. You will use a falling film column with many tubes such as the one shown below.

What size columns do you choose and how many are needed? How can the contact surface be changed without affecting the height of the column?