TECHNICAL NOTE 1.2:

Equilibrium Dynamics of Semi-Permeable Membranes

Introduction

The equilibrium of dissolved gas sensors with surrounding water requires diffusion of molecules from a liquid across a semi-permeable membrane to a gaseous headspace. Once in the gas phase, detectors are used to measure a concentration in gaseous form. Several factors affect the time it takes to equilibrate a gas head-space with a surrounding water parcel through a semi-permeable membrane. The main factors are described below.

When treating equilibrium with need for a high level of accuracy, fugacity instead of partial pressure should be used. However, the error for CO_2 in our measure at atmospheric pressure and temperature range of natural waters is less than about 1 uatm.

The equilibration dynamics can be described using the Laws of Diffusion, whereby the diffusion coefficient of the semi-permeable membrane is a function of the gas solubility coefficient of the membrane material, and the permeability of that gas through the membrane. The thickness of the membrane, its area, and the dead volume being equilibrated play crucial roles in the time of equilibration.

Equilibration Rate

The equilibration rate of membrane equilibrators is often measured in terms of a time constant, t63. This represents the time it takes to reach ~63% of equilibrium. The flux of gases across a membrane is a function of the gradient in concentrations across the membrane. For example, the flux of a gas across a membrane will be rapid when the difference in concentration between the surrounding water and the gas headspace is large. As gas molecules move across the membrane, either into or out of the gas headspace, the concentration gradient decreases, and as a result, the gas flux across the membrane slows.

Gas transfer across a membrane is described by the material permeability, where permeability is the transport flux of the gas of interest through the membrane per unit driving force per unit membrane thickness.

The instantaneous rate of equilibration is directly proportional to the magnitude of the gradient, meaning the equilibration will be described by an exponential function. The time constant for equilibration, where the water side boundary concentration is not changing, is then 63% of the complete response. Each successive time constant then describes 63% of the remaining equilibration. Normally equilibrium is considered to occur in about 5 time constants.

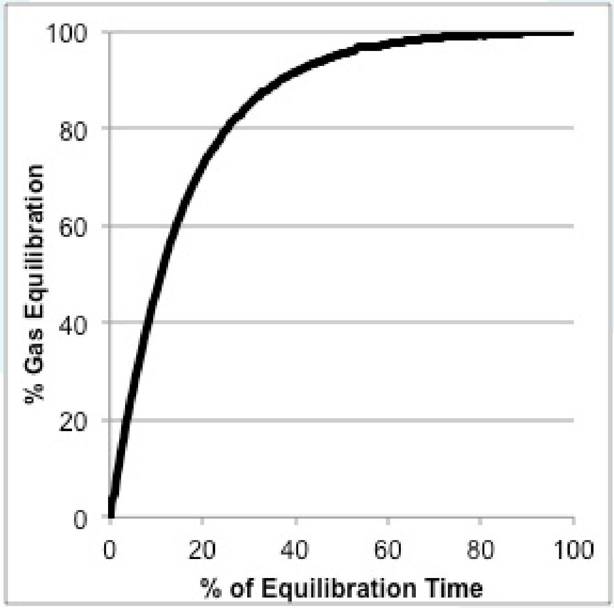

Figure 1. Equilibration of gases across a membrane barrier.

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Effect of the Water Boundary Layer

The water side boundary layer also provides resistance to the gas mass transfer. Advection of dissolved gases to near the membrane surface is a rapid process, but must give way to a layer where diffusion dominates because of the non-slip condition at the solid interface. passage through this diffusion layer is the rate limiting factor in the transfer from the water to the outer surface of the semi-permeable membrane. Temperature once again has an effect on the diffusion rate. In all cases, warmer temperatures improve the response time of membrane equilibration.

The thickness of the water boundary layer can vary and is determined by the hydrodynamics next to the membrane surface. The thicker the boundary later, the longer it takes for gas to diffuse through it. Stagnant water will produce the thickest boundary layer, resulting in the slowest response time. Maximizing the water shear across the membrane surface will reduce the boundary layer thickness to a minimum. Adding a Pro-Oceanus pumped head assembly to your sensor is recommended to increase water shear and therefore reduce response time. The effect of high shear also reduces the potential for biofouling of the instrument.

Effect of Membrane Geometry

The rate at which gases can diffuse through a semi-permeable membrane is inversely proportional to the thickness of the membrane. Membranes that are less than 10 microns in thickness can be manufactured and used in submersible dissolved gas sensors, improving response time substantially. The drawback of these exceptionally thin membranes is the reduction in durability with the greater potential for failure at large hydrostatic pressures.

The membrane area directly affects response time, and a larger surface area will improve the equilibration rate. As with the reduction in thickness, increasing the membrane area can create more potential for failure under some conditions.

Figure 1. Pro-Oceanus CO_2- Pro CV with flat membrane technology

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