PRO OCEANUS
Stability in a sea of change.

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.

There is a finite time that is required for the shift between the dissolved and gas phases of a substance due to the kinetics of solubility. The rate is dependent on temperature and salinity, and to a much lesser degree, pressure.

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 in the membrane, and the permeability of that gas through the membrane. The thickness of the membrane also plays a crucial role in the time for equilibration. Temperature and salinity can dramatically affect the diffusion through a membrane.

EQUILIBRATION RATE

The equilibration rate of membrane equilibrators is often measured in terms of a time constant, t_{63}. This represents the time it takes reach ~63% of equilibrium. The flux of gases across a membrane is a function of the gradient of difference between the concentrations on either side of the membrane. For example, the flux of a gas across a membrane will be rapid when the difference in concentration in 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 rate of gas flux across the membranes slows.

Facility of gas transfer through a membrane is described as permeability, where permeability is the product of the gas diffusivity and gas solubility in the membrane material Temeprature affects the rate of equilibration through changing the solubility of gases in the membrane, such that cooler waters result in increased solubility, thereby slowing the equilbiration process.
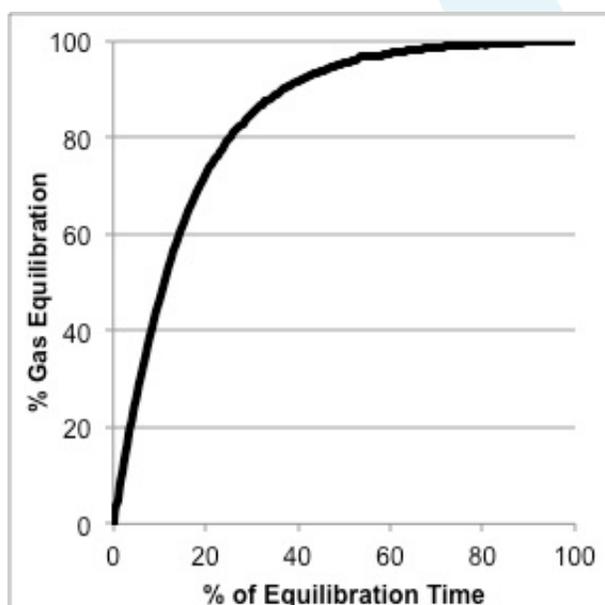
The instantaneous rate of equilibration is directly proportional to the magnitude of the gradient and this means that the equilibration will be described by an exponential function. The time constant for equilibration, where the water side boundary concentration is not changing, is then about 63% of the complete response. Each successive time constant then describes about 63% of the remaining equilibration

t_{63} is taken as one fifth of the total time to equilibrate, t_{90} is approximately half the time to equilibrate, and t_{95} is roughly 60% of the time to equilibrate. t_{99} is taken as t_{eq}.

Figure 1. Equilibration of gases across a membrane barrier.

Effect of the Water Boundary Layer

There is also the effect of the water-side boundary layer. Advection transfers the dissolved gas to near the membrane surface is a rapid process, but diffusion of gas through the water boundary 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 a major effect on the diffusion rate. In all cases, warmer temperatures improve the response time of the instruments, while cooler waters will slow the process.

The thickness of the water boundary layer can vary (and as a result, so too does the time to diffuse through the boundary layer) is determined by the hydrodynamics next to the membrane surface. 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 and is recommended using a Pro-Oceanus pumped head assembly. 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 membrane is inversly proportional to the thickness of the semi-permeable membrane. Membranes that are less than 10 microns in thickness can be manufactured and used in submersible dissolved gas sensors, improving response time substaintially. The drawback of these exceptionally thin membranes is the reduction in durability and greater potential for failure at large hydrostatic pressures.

The membrane area directly affects response time, and 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.