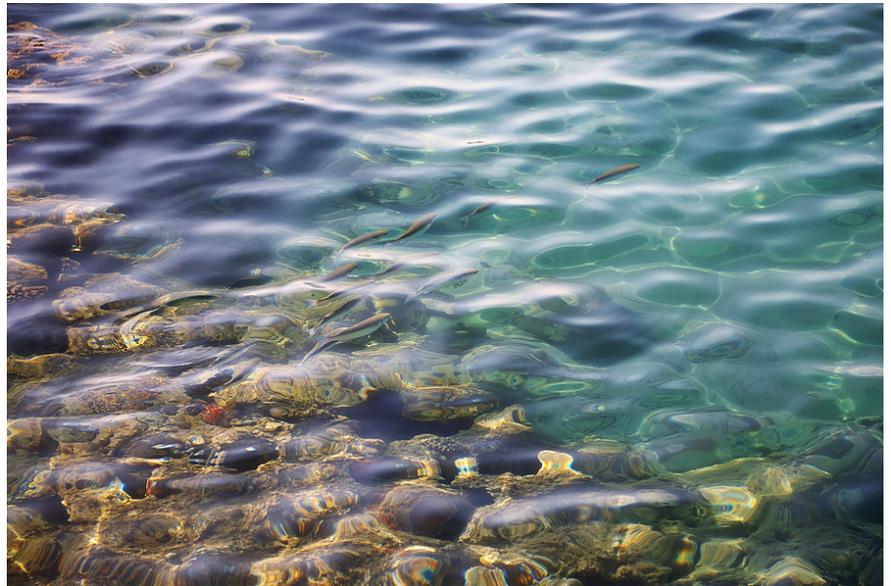


Principles of Optical Dissolved Oxygen Measurements

Optical O₂ Sensors and Henry's Law



Tech Tip

KEYWORDS

- Henry's law
- Dissolved oxygen
- Optical sensors

TECHNIQUES

- Fluorescence
- Oxygen Sensing

APPLICATIONS

- DO in seawater
- Liquids analysis

The behavior of gases dissolved in liquids is an intriguing and extensive area of study, and one which plays a key role in applications from pharmaceutical research to beverage production. In the discipline of chemical engineering, much time is spent during process engineering courses focusing on the laws and relationships that govern the behavior of liquid/gas systems in highly variable environmental conditions. In this technical tip, we discuss how Henry's law relates to the operation of Ocean Insight optical oxygen sensors.

Ocean Insight Optical Oxygen Sensors

NeoFox Oxygen Sensor systems detect the partial pressure of oxygen in the environment, and do so via a fluorescence phase-shift method. A special dye is embedded into a thin film sol-gel matrix and coated onto the tip of an optical fiber probe or self-adhesive patch, and a blue LED is used to excite the dye's fluorescence (**Figure 1**).

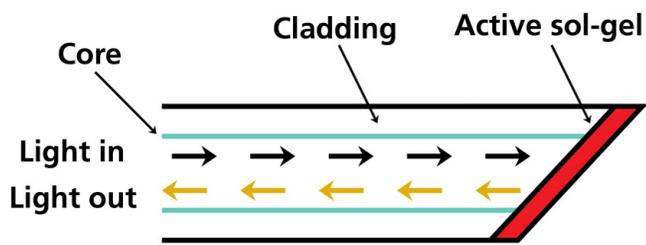


Figure 1. Ocean Insight oxygen sensors use an LED excitation source to transmit light to the sensor material, which is coated onto the tip of a fiber optic probe. Fluorescence is collected through the same probe and routed to an avalanche photodiode for detection.

Aspects of this fluorescence are monitored by the detector, and behave as a function of partial pressure oxygen and temperature. Because the system is solely responding to the partial pressure of oxygen, several parameters must be known about the system when converting to dissolved oxygen units.

William Henry formulated a key law in 1803, which states: "At a constant temperature, the amount of a given gas that dissolves in a given type and volume of liquid is directly proportional to the partial pressure of that gas in equilibrium with that liquid."

Basically, this states that the partial pressure of a gas in a two-phase gas/liquid system will equilibrate to the same level in each phase, which is an intuitive concept. However, dissolved oxygen units are often reported in mg/L (or ppm) – a value that will change based on the type of liquid and its properties such as salinity, despite having the same partial pressure. How can this be? This is not as intuitive, and requires some clever math to make the proper conversion.

Oxygen Sensing Conversion Algorithms

Measuring dissolved oxygen in seawater is a good example to illustrate Henry's law as it is a common application that allows for various dilutions of its salinity. At 20 °C, seawater will equilibrate in air (20.9% oxygen) to 7.2 mg/L, while pure fresh water will equilibrate to a slightly higher 9.1 mg/L; with no salt present there is more potential for gas loading into the liquid phase.

But the two partial pressures are identical, equilibrating to 0.209 atm oxygen (at 1 atm total pressure). Ocean Insight oxygen sensors would not be able to differentiate between these two solutions; accurate reporting of the value in mg/L would require knowledge of each solution's salinity and temperature. We can demonstrate this by looking at various oxygen concentrations bubbled through different dilutions of seawater, and seeing how NeoFox oxygen probes respond.

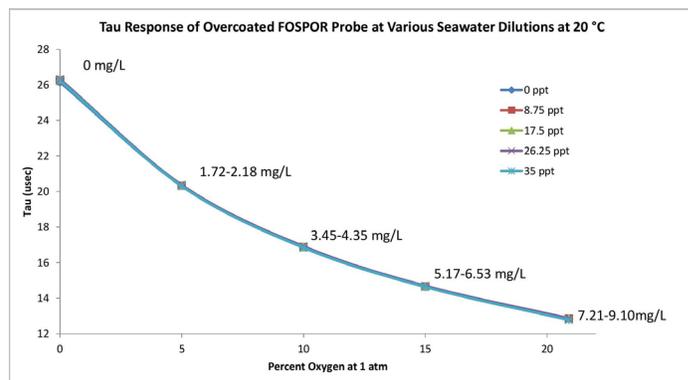


Figure 2. Measurement of oxygen in seawater demonstrates how DO values vary with changes in salinity.

The plot in **Figure 2** shows the range of low to high mg/L oxygen values that are possible across this dilution range; as concentration increases the relationship becomes more noticeable. The conversion from gas phase partial pressure oxygen to liq-

uid phase mg/L (ppm) is calculated in the NeoFox firmware via this relationship:

PPM =

$$e^{A1+A2 \cdot T1+A3 \cdot \ln(T2)+A4 \cdot T2+SC \cdot (B1+B2 \cdot T2+B3 \cdot T2 \cdot T2)}$$

• C • PO₂/D, where:

- A1, A2, A3, A4, B1, B2, B3, C and D are constants, hardcoded in the firmware.
- T1 is 100 divided by the temperature (K).
- T2 is the temperature (K) divided by 100.
- SC is the "salinity correction factor," which can be set in software:

- o A1 -173.9894
- o A2 +255.5907
- o A3 +146.4813
- o A4 -22.204
- o B1 -0.037362
- o B2 +0.016504
- o B3 -0.0020564
- o C +0.032
- o D 20.9

- PO₂ is the "percent oxygen," as described above.

The coefficients listed here are specific to aqueous systems at non-extreme conditions. Other coefficients would need to be known for the proper conversion in systems with liquids such as hydrocarbons.

However, this equation does not account for total pressure of the system, which also can influence the ultimate oxygen level the system equilibrates to. Similar relationships have been proposed that do consider this parameter, including this equation by Weiss (1970, *Deep-Sea Research* 17:721-735):

$$\ln DO = A1 + A2 \cdot 100/T + A3 \ln T/100 + A4 T/100 +$$

$$S [B1 + B2 T/100 + B3 (T/100)^2]$$

... where:

- A1 = -173.4292
- A2 = +249.6339
- A3 = +143.3483
- A4 = -21.8492
- B1 = -0.033096
- B2 = +0.014259
- B3 = +0.001700

T = temperature degrees K

S = salinity in g/kg (o/oo)

The DO solubility is calculated in milliliters per liter (ml/L), which must be multiplied by the constant 1.4276 to convert to milligrams per liter (mg/L).

The total barometric pressure correction is calculated by the equation:

$$DO' = D0! (P-u/760-u)$$

... where DO' is the saturation DO at barometric pressure P, D0! is saturation DO at barometric pressure 760 mm Hg, and u is the vapor pressure of water calculated from an empirical equation derived from the *Handbook of Chemistry and Physics* (Chemical Rubber Company, Cleveland, Ohio, 1964)

$$\log u = 8.10765 - (1750.286 / (235+t))$$

...where t is temperature in degrees C.

Open vs. Closed Systems

The NeoFox oxygen sensor system uses a multi-point calibration matrix across a range of oxygen partial pressures and temperatures. The system



uses this matrix to correct for temperature fluctuations in the system.

In the gas phase this is valid and even necessary for correct measurements; if the temperature increases by 10 °C and the oxygen partial pressure stays the same, the system will experience a drop in tau value (fluorescence lifetime) but will also detect the temperature delta and still output the same oxygen partial pressure value.

If the multi-point calibration matrix is used in the liquid phase in an open system, one which is free to equilibrate with the gas-phase environment around it, this also will be valid since the partial pressure conversion will be done as it was in the gas phase. Also, the subsequent dissolved oxygen unit conversion will adjust based on temperature since mg/L oxygen is free to change with the gas phase above it.

However, in a closed system, things are not so straightforward. If you had a perfectly sealed 1 L vessel of water with some oxygen level not near saturation (let's say, 2 mg/L), and with no gas in the vessel at all, a temperature change would cause a false change in reported dissolved oxygen units. In our open system, when temperature changed the liquid was free to exchange oxygen with the environment, and the conversion math accounted for this change in mg/L. However, in our closed system -- which cannot interact with the environment -- a change in temperature also would trigger the conversion math to report a change in mg/L, even though we know we still have our 2 mg of oxygen in our 1 L vessel.

The easiest fix in this scenario is to not allow the secondary conversion (partial pressure to mg/L) to take the temperature change into account, and instead only allow the first conversion (tau to partial pressure) to compensate for temperature. This approach, though, assumes the user knows

the true value of oxygen in the closed system at some initial temperature; going into this type of closed-system conversion without the proper initial points makes it very difficult if not impossible to calculate.

Closed System Example of False Change in DO Units		
Vessel	1 L, sealed, no gas	1 L, sealed, no gas
Oxygen level < saturation:	2 mg/L	2 mg/L
Temperature:	20 °C	30 °C
NeoFox output:	2 mg/L	1.67 mg/L

Despite constant oxygen, false reports of changes in mg/L due to temperature change can occur in closed systems.

Conclusions

Ocean Insight is continually improving how our oxygen sensors process and report data to the user, so that values are as valid and accurate as possible.

Useful Resources

- U.S. Geological Survey Dissolved Oxygen Solubility Tables (<https://water.usgs.gov/software/DOTABLES/>)
- U.S. Geological Survey Tables of Dissolved Oxygen Saturation Values (<https://water.usgs.gov/admin/memo/QW/qw81.11.html>)



www.oceaninsight.com

info@oceaninsight.com • **US** +1 727-733-2447

EUROPE +31 26-3190500 • **ASIA** +86 21-6295-6600