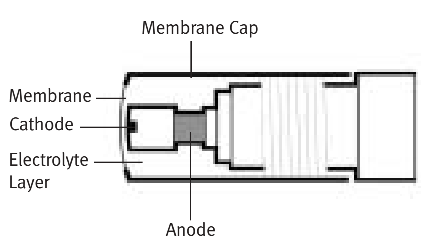
Orion DO Theory

Introduction
Air can be regarded as having a constant percentage (approximately 20.9%) of oxygen. Wherever air comes in contact with water, the oxygen in the air will dissolve in the water. The amount of oxygen that dissolves in the water depends on many factors: whether there is adequate time and adequate mixing to fully saturate the water, the water temperature, the air pressure, the salt content of the water, and whether there are substances in the water which consume the oxygen. Since the oxygen content is important for many biological and chemical processes, measurements of the amount of oxygen actually dissolved in a water sample is of great importance. Membrane oxygen electrodes are the most widely used and accepted method for real-time measurements of oxygen in water.

Basic Definitions
The concentration of oxygen is usually expressed in milligrams of oxygen per liter (mg/L) of water, or parts per million (ppm). Electrodes measure the partial pressure of the oxygen, which is the fraction due to oxygen multiplied by the total pressure (due to oxygen and all the other components of air, such as nitrogen or water vapor). For a given partial pressure of oxygen in the air, the concentration that will be present in saturated pure water is fixed at any one temperature, and has been measured by many scientists over the years. These tables are built into modern oxygen meters, which compensate automatically for temperature. These meters will compare the calculated concentration with the observed, and report a percent saturation. One difficulty with this calculation is that the presence of dissolved salts in the water lowers the amount of oxygen that can dissolve, and the relationship between partial pressure and concentration is different. These relationships have been worked out for natural waters of varying salinity and some meters contain this information, as well. This correction is commonly called salinity correction.

Oxygen Electrodes
These electrodes, known as “Clark-type” after their inventor, Dr. Leland Clark, have a thin organic membrane covering a layer of electrolyte and two metallic electrodes. Oxygen diffuses through the membrane and is electrochemically reduced at the cathode. There is a carefully fixed voltage between the cathode and an anode so that only oxygen is reduced. The greater the oxygen partial pressure, the more oxygen diffuses through the membrane in a given time. This results in a current that is proportional to the oxygen in the sample. Temperature sensors built into the probe on some advanced measurement systems allow compensation for the membrane and sample temperatures, which affect diffusion speed and solubility.



Oxygen Electrodes

The meter uses cathode current, sample temperature, membrane temperature, barometric pressure and salinity information to calculate the dissolved oxygen content of the sample in either concentration (ppm) or percent saturation (% Sat). The voltage for the reduction can either be supplied electronically by the meter (potentiometric oxygen electrode) or dissimilar metals may be used for the two electrodes, chosen so that the correct voltage is generated between them (galvanic electrode).

Practical Considerations
Stirring — Consumption of oxygen by the probe can cause a lowering of the oxygen concentration at the boundary layer between the sample and the probe membrane. For this reason, sample stirring is recommended.

Membranes — Two types are commonly used, loose membranes, and membrane cap assemblies. While loose membranes are less expensive, they are more difficult to install, and will give lower precision in results. The stretch of the membrane determines how thick the electrolyte layer adjacent to the cathode is, which affects the time response of the probe. Precision manufactured membrane cap assemblies give a reproducible electrolyte layer thickness, speed up probe servicing, and eliminate assembly problems.

Electrolyte — The electrolyte in any Clark-type oxygen electrode must be replaced periodically, after its capacity to reduce oxygen is depleted. The time the electrolyte lasts depends on the rate by which oxygen is reduced. Probes with a very small diameter cathode will typically have very low current, resulting in low oxygen consumption by the probe. This results in low stir sensitivity, as well as very long electrolyte life. Commercially available probes require electrolyte replacement in the time period of two weeks to six months, depending on design and use.

Calibration — Calibration of this type of probe can be done quickly and conveniently. The first calibration point can be done in water-saturated air, and is frequently done in a special calibration chamber with a water reservoir. Under equilibrium conditions, the partial pressure of oxygen in air-saturated water is equal to that of partial pressure of oxygen in water-saturated air, i.e., air at 100% relative humidity. This means that a probe calibrated in water-saturated air will correctly read the partial pressure of oxygen in a water sample. Since the diffusion rate of oxygen in water and air differs slightly, advanced meters apply a correction factor to the water-saturated air calibration value to obtain the correct air-saturated water value. For most Orion probes, the correction factor is 101.7%. When measuring a low concentration sample (less than 2 ppm), a second calibration point for a zero oxygen standard is often required. At zero oxygen concentration, some probes generate no current, therefore defining the zero point and making a second calibration step unnecessary.

Applications
Applications for dissolved oxygen measurement include processes where the amount of oxygen affects a reaction rate or process efficiency, or indicates an environmental condition. Some important applications include wastewater treatment, wine production, bio-reactions, and environmental water monitoring.

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Henry's Law and Dissolved Oxygen in Water

Henry's Law states that "the partial pressure of a gas in a liquid is equal to the partial pressure of the gas in the vapor above the liquid." Oxygen will dissolve in water so that the level of dissolved oxygen of water will be in equilibrium with the atmosphere, which is approximately 20.9%. Dissolved oxygen levels in the water will vary according to temperature fluctuations, changes in barometric pressure, and salt content.

What is BOD?

BOD (Biochemical Oxygen Demand) is an empirical analysis that is typically performed in municipal or industrial wastewater plants. This analysis determines the amount of oxygen (expressed in mg/L or in ppm) that microorganisms consume from water when they break down organic matter. The results of this analysis are used to calculate the degree of water pollution and to determine the effectiveness of water treatment by wastewater or sewage plants. Untreated wastewater flowing into a treatment facility (influent) will have a high BOD and treated water flowing out of a treatment facility (effluent) should have a greatly reduced BOD value if properly treated.

Why is BOD measurement important?

BOD measurement is important because it is the most fundamental way of determining water pollution levels and of predicting the possible harmful effects of waste discharge. Organic matter that is present in water can be from plants, sugars, proteins or other substances that enter water from natural sources or pollution. This matter is broken down biochemically by organisms such as bacteria, which can multiply as long as organic matter is present as food and oxygen is available for respiration. If high populations of microorganisms or bacteria continually consume dissolved oxygen in the water at an accelerated rate, atmospheric air will not be able to replenish it. This situation could create a lack of dissolved oxygen in the water, threatening or destroying many forms of aquatic life.

How is BOD Determined?

The empirical method that is commonly used in standard laboratory procedures for the determination of BOD is called the "5-Day BOD" or "Dilution" test. This procedure is performed by filling several bottles with specific volumes of either tap or distilled water containing a pH buffer and inorganic nutrients. The dilution water, which is saturated with dissolved oxygen, is then mixed with a known volume of sample, and the initial level of dissolved oxygen is measured*. The bottles are then incubated at a constant temperature of 20˚C and at low light levels for five days. During this time, bacteria is oxidizing the organic matter in the sample and consuming dissolved oxygen in the water. At the conclusion of the test, the dissolved oxygen is again measured* and the BOD can be calculated by taking the difference of the dissolved oxygen values on day one and on day five.

$$\text{BOD (mg/L)} = \frac{(\text{DO value Day 1} - \text{DO value Day 5}) \times \text{Total Volume in Bottle}}{\text{Initial Sample Volume}}$$

* Dissolved oxygen measurement can be made either via electrochemical means such as a Clark-type electrode or by the Winkler Titration. Clark electrode measurements are more reproducible and introduce less error than the Winkler Titration.