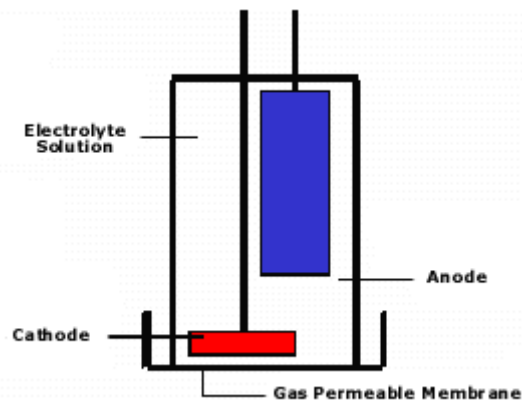


# Introduction to Dissolved Oxygen

## Introduction

Many gases mix with water like nitrogen and oxygen without chemically reacting with it. Some gases chemically react with water e.g. ammonia, CO<sub>2</sub>, and HCl. Oxygen does not react with water. Dissolved Oxygen (DO) is really a physical distribution of oxygen molecules in water. There are two main sources of DO in water: atmosphere and photosynthesis. Waves and tumbling water mix air into water where oxygen readily dissolves until saturation occurs. Oxygen is also produced by aquatic plants and algae as a by-product of photosynthesis.

## Basic Principle in DO measurement (OR What is Being Measured?)



The electrochemical method of measuring DO requires a cathode, anode, electrolyte solution and a gas permeable membrane. The material of the membrane is specially selected to permit oxygen to pass through. Oxygen is consumed by the cathode which will create a partial pressure across the membrane. Oxygen will then diffuse into the electrolyte solution.

Thus, a DO meter actually measures the pressure of oxygen in water. It can be used to measure DO in any medium.

## Polarographic or Clark Cell Method

Dr. Clark first discovered the cell to measure oxygen in 1956. This is basically an amperometric (polarographic) cell that is polarized around 800 mV. This cell, named after Dr. Clark, is built around the popular Ag/AgCl half-cell and a noble metal such as gold, platinum or palladium. Reduction of oxygen is achieved between 400 to 1200 mV, hence a need for a voltage of around 800 mV. This is provided externally by a battery source.

Electrolyte used: KCl or KBr

Cell	Reaction
Anode	$2\text{Ag} + 2\text{Cl}^- \rightarrow 2\text{AgCl} + 2\text{e}^-$
Cathode (Platinum, gold or palladium)	$2\text{e}^- + \frac{1}{2} \text{O}_2 + \text{H}_2\text{O} \rightarrow 2 \text{OH}^-$
Total Reaction	$2\text{e}^- + \frac{1}{2} \text{O}_2 + \text{H}_2\text{O} + 2\text{Ag} + 2\text{Cl}^- \rightarrow 2 \text{OH}^- + 2\text{AgCl} + 2\text{e}^-$

From the above reaction, every time oxygen is reduced at the cathode, 4 electrons or current is generated directly proportional to the oxygen consumed (reduced) at the cathode.

There are four major problems associated with this type of DO measurement: .

Problem	Description
Isolation of Anode	Since the net result of the chemical reaction is AgCl, over time, a build up of AgCl will coat the anode. Once the whole anode is covered, reaction stops and the oxygen probe stops working. The probe can be reactivated by cleaning the anode to remove the AgCl deposit which can be a time-consuming procedure.
Zero shift	The result of the above reaction produced more OH <sup>-</sup> ions which will move the pH value of the electrolyte. The electrolyte, which is around neutral pH value, will moves into the alkaline range. This causes a zero shift, and over time, the electrolyte will need to be changed.
Depletion of Chloride	The net reaction also consumes Cl <sup>-</sup> ions. Over time, the chloride ions will be consumed and the electrolyte needs to be replaced.
Warm-up Time	The major disadvantage is the need for an external power source of approximately 800 mV to be applied to the electrode. As soon as the probe is disconnected, power supply is cut off. On connecting the probe again, the user must wait for the probe to be polarized, that is, for the current loop to be stabilized. This warm-up time is approximately 10 minutes. Any measurement taken before this warm-up time period will be normally a higher value and will result in wrong readings.

### Galvanic Cell Method

The galvanic probe principle was introduced by Macreth in 1964 and has gone through a few changes.

The main advantage of a galvanic probe is that it does not need an external power supply to provide polarization as required by the Clark Cell. This is achieved by using two dissimilar metals. In the presence of an electrolyte, there is an electromotive voltage produced between the two metals. At approximately 800 mV, this is large enough to reduce the oxygen at the cathode. If lead and gold or lead and silver is used, the differential voltage is approximately 800 mV.

Hence, a galvanic probe is really a self-polarizing amperometric cell. The single biggest advantage is the fact that the cell is now always ready and there is no warm up time.

Electrolyte used: KCl or KBr

Cell	Reaction
Anode (Zinc or Lead)	$Zn \rightarrow Zn^{2+} + 2e^{-}$
Cathode	$2e^{-} + \frac{1}{2} O_2 + H_2O \rightarrow 2OH^{-}$
Total Reaction	$Zn + 2e^{-} + \frac{1}{2} O_2 + H_2O \rightarrow Zn^{2+} + 2e^{-} + 2OH^{-}$ $Zn + \frac{1}{2} O_2 + H_2O \rightarrow Zn(OH)_2$ $\rightarrow ZnO \text{ (white precipitate) } + H_2O \text{ or:}$ $Zn + \frac{1}{2} O_2 \rightarrow ZnO$

Hence one molecule of oxygen produces 4 electrons and there is a direct relationship between the oxygen consumed at the cathode and the current produced by the cell.

The net result of the chemical reaction is simply ZnO which is reasonably stable and does not coat the anode. Water is recreated and the electrolyte is not consumed. Theoretically, the electrolyte will go on forever without replenishment.

Hence, because of the advantages galvanic probe has, Eutech Instruments has chosen this superior technology to make it easier for users.

## DO Measurement Considerations

The amount of DO that can be held by water depends on 3 factors: water temperature, salinity, and atmospheric pressure; Amount of DO increases with decreasing temperature (colder water holds more oxygen). Amount of DO increases with decreasing salinity (freshwater holds more oxygen than saltwater does). Amount of DO decreases with decreasing atmospheric pressure (amount of DO absorbed in water decreases as altitude increases).

The chart below shows the solubility of DO in mg/l in water at various temperature.

