VAN LONDON
Est.1961

pHoenix Co.

Education Series
Dissolved Oxygen Guide
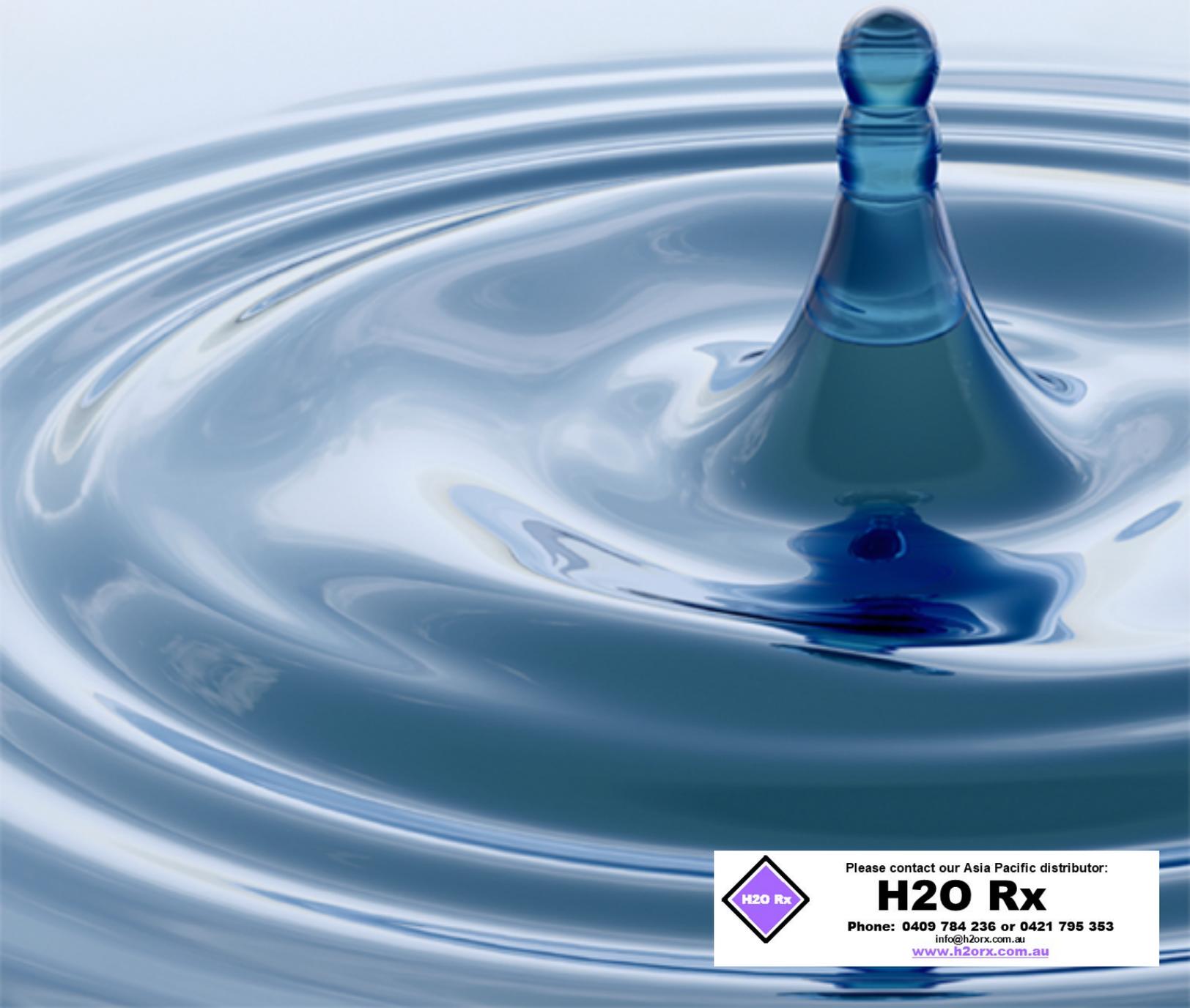
Dissolved Oxygen Guide

Introduction

Dissolved oxygen probes provide a convenient approach to essentially direct measurement of molecular oxygen. The membrane isolates the electrode from the sample, and oxygen is detected as it diffuses across the membrane. The probe can be used to measure any system where oxygen is present. Calibration of the sensor is readily achieved if knowledge of oxygen concentration or solubility at a specific condition is known.

Solubilization of Oxygen from the atmosphere into water

The solubility of oxygen in water is achieved by physical solution which does not involve chemical interaction between the compounds. The solubility equilibrium is a function of the following factors:

- the concentration of oxygen in the gas phase at the water-atmosphere interface
- the attractive molecular forces between water molecules and oxygen molecules
- the kinetic energy of the water and oxygen molecules

Physical changes in temperature and pressure have a pronounced effect on the solubility factors.

Effect of Pressure Changes

The percent concentration of oxygen molecules in air is essentially constant in the atmosphere close to earth (approximately 21% by volume and 23% by weight). The actual number of oxygen molecules per unit volume of air depends upon the temperature and pressure of the air. Air is compressible, and, at a constant temperature, a specific weight of gas will change in volume in a reverse ratio to pressure. The practical effect is that the amount of oxygen at an interface of air and water decreases as the pressure of air is decreased, or since the percentage concentration of oxygen in the air remains constant, the actual concentration of oxygen at the air-water interface is directly proportional to atmospheric pressure (Henry's Law). At Denver, Colorado, (elevation approximately 5000') the concentration of oxygen at the interface is about 84% of that which would exist at sea level.

Effect of Temperature Changes

At a constant pressure, the volume of a specific weight of air changes in direct ratio to the absolute temperature (Kelvin Scale = Degrees Centigrade + 273; or Rankin Scale = Degrees Fahrenheit + 460). As air cools from 100°F to 0°F the volume decreases by 17.9%, and at 0°F the concentration of oxygen per unit volume is 21.8% greater than it is at 100°F. Thus, the concentration of oxygen at the air-water interface increased by a decrease in the air temperature.

The temperature of the water is also important because of two other factors:

- The amount of water vapor in the air at the air-water interface increases as the temperature of water increases, which results in a decrease in oxygen concentration at the interface. The decrease is about 6% as the temperature of water changes from $32^{o}F$ to $100^{o}F$.
- After oxygen is dissolved in water, it is the same temperature as the water. Both the kinetic energies of the water molecules and the O_2 molecules are directly proportional to absolute temperature. Higher kinetic energies tend to overcome the attractive molecular forces between the water and oxygen molecules and contribute to decreased solubility of oxygen at higher water temperatures.

Effect of Dissolved Materials

The presence of dissolved materials in water potentially can reduce the solubility of oxygen if the dissolved materials interact with water to decrease the attractive molecular forces between water and oxygen. For example, dissolved inorganic salts, such as sodium chloride, potassium chloride, or sodium sulfate, reduce the solubility of oxygen in water.

Theory

A polarographic molecular oxygen probe consists of two metals of different nobility which serve as electrodes. The more noble metal is the cathode. If a potential of about 0.5 volts is applied to the two electrodes (negatively to the cathode) and the electrodes are immersed in an electrolyte, molecules of oxygen dissolved in the electrolyte will diffuse to the surface of the cathode and pick up electrons which, in combination with water, will produce hydroxyl ions. At essentially the same time, hydroxyl ions will give up electrons at the anode and form an oxide. The resulting transfer of electrons establishes a current flow through an external circuit and may be displayed on a millivolt or microampere meter.

The membraned Oxygen electrode offers the following advantages:

1. The membrane encloses the two electrodes in a captured volume of electrolyte, ensuring constant electrolyte strength and purity so that ions which might otherwise "poison" the probe are not present.
2. The membrane excludes materials that do not diffuse through it. As a result, most materials in the sample that might "poison" the cathode, or might cause an erroneous output from the electrode system are excluded. Potential interferences are limited to reactive gases which diffuse through the membrane, such as chlorine.

Probe Materials and Design

The cathode for a polarographic style probe is typically platinum, the anode is commonly silver, with the electrodes immersed in a potassium chloride electrolyte solution. For convenient application of the probe, the electrode system is enclosed in a housing with the cathode and membrane positioned for exposure to the sample. Only the area of membrane in contact with the cathode need be exposed to the sample.

Membrane Orientation

In order to optimize the performance of the membraned probe, the cathode is located adjacent to the membrane. The cathode is given a convex surface so that the membrane can be drawn closely over the cathode. The platinum surface is roughened to permit the necessary access of electrolyte to the cathode surface. Key features in orientation of the membrane and cathode are that the membrane must be close to the cathode and the orientation must not change during operation of the probe.

Anode Area

As indicated under theory, silver at the surface of the anode is converted to silver oxide as the determination of oxygen proceeds. When silver is not available at the surface of the anode because it has become coated with silver oxide or other reaction products, sensitivity of the probe decreases. Therefore, in order to give the probe an extended performance life, the area of silver relative to the cathode should be as large as is practical.

Membrane Thickness and Cathode Area

Molecular oxygen reaches the cathode by diffusion through a Teflon membrane. For a given thickness of membrane, at a given temperature, the number of molecules of oxygen which pass through the membrane per unit of time is directly proportional to the number of molecules which are present per unit area of water-to-Teflon interface (sometimes referred to as partial pressure) or:

$$N_t = f\,(O_2)$$

where:

- N_t is the number of oxygen molecules arriving at the cathode per second per sq. cm of cathode area at Temperature t.
- O_2 is the concentration of oxygen molecules at the water-to-Teflon interface.

Teflon offers resistance to oxygen diffusion. Thus, at a given temperature and a fixed concentration of oxygen at the water-to-Teflon interface, the number of oxygen molecules arriving at the cathode per unit of time is inversely proportional to membrane thickness, D.

$$N_t = f\,[O_2 \times (1/D)]$$

From these relationships, it is evident that in order to have maximum sensitivity for the probe it is necessary to make the cathode area as large as is practical and to make the Teflon membrane as thin as is practical. The practical consideration for cathode size is its relationship to overall probe size, which usually is determined by where the probe must be placed. Membrane thickness must recognize desired response rate and rugged performance. Thin membranes provide quick response in addition to sensitivity because diffusion equilibrium is reached more wuickly, but thicker membranes are tougher and will provide longer service.

Membranes typically come in 1/2 mil, 1 mil, and 2 mil thicknesses. Response upscale proceeds at approximately a first-order rate. Increased thickness of membrane decreases the rate at which oxygen molecules reach the cathode. As a result, 99% completion of the upscale response is achieved in about 15, 30, and 75 seconds for 1/2, 1 and 2 mil membranes respectively.

Downscale response is significantly different from upscale response. The response rate is essentially second order. The nature of the response indicates that an internal reaction of the probe as well as diffusion through the membrane is involved. For a 1 mil membrane, the time for a 99% response downscale is a function of the starting exposure to oxygen. From 10 mg/L 99% response is obtained in approximately 1 minute. From 100 µg/L, 99% response is obtained in about 70 seconds, and from 10 µg/L, 99% response is obtained in about 50 seconds. These results illustrate that excellent response is obtained in applications such as measurement of oxygen in boiler feed water. The probe may be calibrated at mg/L levels of oxygen and with a 1 mil membrane will require about 1 hour to reach the µg/L operating level. A 1/2 mil membrane will respond from the mg/L to the µg/L level in approximately 30 minutes.

Probe Response and Circuit Resistance

The electrical circuit for electron flow from the anode to the cathode is completed by the readout circuitry. If readout is through a galvanometer-type microampere meter, the resistance is that which is present in the winding of the meter and any resistors in series. A meter used for this service may characteristically have an internal resistance of about 2,000 ohms. If a potentiometric readout is provided, the input to the potentiometric circuitry is the voltage drop across a selected closing resistance between the cathode and anode of the probe. In either case, resistance is present in the electrical circuit between the anode and cathode.

The response rate for the probe, when exposed to a change in dissolved oxygen concentration, is influenced by the magnitude of the closing resistance. The response rates presented previously are based on a closing resistance of 2,000 ohms. If the closing resistance is decreased to 100 ohms, the downscale response for the probe using a 1/2 mil membrane will be about 99% complete in 10 seconds. If, for the same probe, the closing resistance is increased to 25,000 ohms, the downscale response will be about 99% complete in 120 seconds.

The upscale response rates of the probe is influenced to a much smaller degree by the closing resistance.

Temperature Effects on Probe Output Current

There are two factors related to temperature which must be recognized in order to correlate the output of the dissolved oxygen probe with concentration of molecular oxygen in the sample.

1. As the temperature of water decreases, kinetic energy of water and oxygen molecules decreases and molecular attraction increases. As a result, the concentration of oxygen which must be present in the water to establish a particular concentration of oxygen at the water-to-Teflon interface increases, and
2. the resistance to oxygen diffusion through the Teflon membrane increases as temperature decreases.

Both of the temperature factors serve to decrease the rate at which oxygen molecules reach the surface of the cathode as temperature decreases. Therefor, if the readout from the Dissolved Oxygen Analyzer is to display the correct reading of oxygen concentration for all samples which have the same concentration of oxygen but are at different temperatures, compensation for the overall temperature effect must be accomplished.

Temperature compensation is accomplished by the use of a suitably designed thermistor as a temperature sensor. The resistance of the thermistor is used to achieve a precise multiplication factor by the analyzer. The resulting display of dissolved oxygen concentration is corrected to within +/- 2% of the actual concentration when the samples are in the temperature range of $0^{o}C$ to $50^{o}C$. Over sample ranges of +/- $10^{o}C$ from the calibration temperature, the D.O. reading is within +/- 1% of the actual concentration.

Effects of Dissolved Solids on Probe Output Current

If a salt is added to and permitted to dissolve in a water sample which contains a specific concentration of dissolved oxygen (but is not saturated), the current output from the probe will increase. As a result, the display meter of the analyzer will incorrectly indicate that the dissolved oxygen concentration in the sample has increased. The reason for the increased output by the probe is that the presence of the dissolved salt decreases the molecular attraction of water and oxygen molecules in the sample. This increases the concentrationof oxygen molecules at the water-to-Teflon interface. The concentration of oxygen in the sample has not changed.

Useful Data

Table 1 presents changes in oxygen solubility from the atmosphere into water at different elevations above sea level. The data are based on a barometric pressure of 760 mm Hg at sea level. The barometric pressure (and oxygen concentration at the atmosphere-water interface) decreases at higher elevation, and, as a result, the equilibrium concentration of oxygen in water decreases. The barometric pressure versus altitude data employed are:

Elevation (Feet Above Sea Level)	Barometric Pressure (mm Hg)
0	760
1,000	747
2,000	709
3,000	684
4,000	661
5,000	638
6,000	616

The data in Table 1 must be utilized with recognition of the basis that barometric pressure is variable as high and low pressure areas move through. A more optimum approach to the correction of oxygen solubility data is to utilize the actual barometric pressure at the location and time of interest. Correct the data for oxygen solubility at sea level by a ratio of actual barometric pressure to 760 mm Hg.

Solubility of O$_{2 \text{ at conditions}}$ = Solubility$_{760 \text{ mm Hg}}$ x [Barometric Pressure, mm Hg / 760]

The data in Table 2 show the effect of salinity (expressed as chlorinity) in brackish or sea water. The dissolved solids (sodium chloride primarily) react with water molecules and decrease the molecular attraction between oxygen molecules and water molecules. As a result, the solubility of oxygen decreases as the salinity increases.

The data in Table 2 are for a barometric pressure of 760 mm Hg. If the barometric pressure is other than 760 mm Hg, correction to the actual barometric pressure is necessary.

Table 1
Solubility of Oxygen (mg/L) at Various Temperatures and Elevations
(Based on Sea Level Barometric Pressure of 760 mm Hg)

Temperature	Elevation, Feet Above Sea Level						
°C	0	1000	2000	3000	4000	5000	6000
0	14.6	14.1	13.6	13.2	12.7	12.3	11.8
2	13.8	13.3	12.9	12.4	12.0	11.6	11.2
4	13.1	12.7	12.2	11.9	11.4	11.0	10.6
6	12.4	12.0	11.6	11.2	10.8	10.4	10.1
8	11.8	11.4	11.0	10.6	10.3	9.9	9.6
10	11.3	10.9	10.5	10.2	9.8	9.5	9.2
12	10.8	10.4	10.1	9.7	9.4	9.1	8.8
14	10.3	9.9	9.6	9.3	9.0	8.7	8.3
16	9.9	9.7	9.2	8.9	8.6	8.3	8.0
18	9.5	9.2	8.7	8.6	8.3	8.0	7.7
20	9.1	8.8	8.5	8.2	7.9	7.7	7.4
22	8.7	8.4	8.1	7.8	7.7	7.3	7.1
24	8.4	8.1	7.8	7.6	7.3	7.1	6.8
26	8.1	7.8	7.6	7.3	7.0	6.8	6.6
28	7.8	7.5	7.3	7.0	6.8	6.6	6.3
30	7.5	7.2	7.0	6.8	6.5	6.3	6.1
32	7.3	7.1	6.8	6.6	6.4	6.1	5.9
34	7.1	6.9	6.6	6.4	6.2	6.0	5.8
36	6.8	6.6	6.3	6.1	5.9	5.7	5.5
38	6.6	6.4	6.2	5.9	5.7	5.6	5.4
40	6.4	6.2	6.0	5.8	5.6	5.4	5.2

Table 2
Solubility of Oxygen (mg/L) at Various Temperatures and Chlorinity
(Based on a Barometric Pressure of 760 mm Hg)

Temperature	Chlorinity, %					
°C	0	4.0	8.0	12.0	16.0	20.0
0	14.6	13.9	13.2	12.5	11.9	11.9
2	13.8	13.2	12.5	11.9	11.4	10.8
4	13.1	12.5	11.9	11.3	10.8	10.3
6	12.4	11.8	11.3	10.8	10.3	9.8
8	11.8	11.3	10.8	10.3	9.8	9.4
10	11.3	10.8	10.3	9.8	9.4	9.0
12	10.8	10.3	9.8	9.4	9.0	8.6
14	10.3	9.9	9.4	9.0	8.6	8.3
16	9.9	9.4	9.0	8.6	8.3	8.0
18	9.5	9.1	8.7	8.3	8.0	7.6
20	9.1	8.7	8.3	8.0	7.7	7.4
22	8.7	8.4	8.0	7.7	7.4	7.1
24	8.4	8.1	7.7	7.4	7.1	6.9
26	8.1	7.8	7.5	7.2	6.9	6.6
28	7.8	7.5	7.2	6.9	6.6	6.4
30	7.5	7.2	7.0	6.7	6.4	6.2
32	7.3	7.0	6.7	6.5	6.2	6.0
34	7.1	6.8	6.5	6.3	6.0	5.8
36	6.8	6.6	6.3	6.1	5.8	5.6
38	6.6	6.4	6.1	5.9	5.6	5.4
40	6.4	6.2	5.9	5.7	5.4	5.2