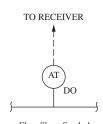
## **Oxygen in Liquids (Dissolved Oxygen)** 8.43

**R. K. KAMINSKI** (1969, 1982)

B. G. LIPTÁK, G. J. RORECH (1995)

M. P. DZIEWATKOSKI (2003)



Flow Sheet Symbol

A. Polarographic Types:

> B. Galvanic C. Coulometric D. Multiple-anode E. Thallium F. Fluorescence

Operating Pressure: Up to 50 PSIG (3.5 barg) or submersion depths of up 25 ft (8.3 m)

Operating Temperature

Range:

Flow Velocity

32 to 122°F (0 to 50°C); special designs up to 175°F (80°C)

at Sensing Membrane: (0.06 m/s)

Materials of Construction: Typical material for sensor housing: PVC or stainless steel; possible electrode mate-

> rials: platinum, gold, silver, zinc, lead, cadmium, and copper; for membrane assembly, ABS plastic or stainless steel mesh-reinforced silicone and/or Teflon® membrane

Preferably in excess of 1 ft/sec (0.3 m/s); some can operate down to 0.2 ft/sec

Speed of Response: 90% in 30 sec; 98% in 60 sec

Common ranges are 0 to 5, 0 to 10, 0 to 15, and 0 to 20 ppm; special units are Ranges:

> available with ranges up to 0 to 150 ppm or down to the 0 to 20 ppb range used on boiler feedwater applications. Systems can also be calibrated in partial pressure units.

Generally,  $\pm 1$  to  $\pm 2\%$  of span; industrial transmitter errors are generally within 0.02 Inaccuracy:

ppm over a 0 to 20 ppm range. Thallium cells are available with a 0 to 10 ppb range

and can read the dissolved oxygen (DO) within an error of 0.5 ppb.

Costs: Portable, battery-operated, 1.5 to 2% FS units that also read temperature cost from

> \$500 to \$2000; replacement probes range from \$250 to \$1000; 1% FS, microprocessorbased portable benchtop units for laboratory or plant service cost from \$1000 to \$2000; industrial-quality (0.02 ppm error limit) DO probe and 4 to 20 mA transmitter

range from \$2000 to \$3500; cleaning assemblies cost from \$500 to \$2000.

Partial List of Suppliers: ABB Inc. Instrumentation (www.abb.com)

ABB TBI Bailey (www.tbi-bailey.com)

Analytical Technology, Inc. (www.analyticaltechnology.com) Automated Aquarium (www.automatedaquariums.com) Broadley-James Corporation (www.broadleyjames. com)

Endress + Hauser Inc. (endress.com) Extech Instruments (www.extech.com) Global Water Instr. Inc. (www.globalw.com) Great Lakes Instruments Inc. (www.gliint.com)

Greenspan Technology Pty Ltd. (www.greenspan.com.au)

Hanna Instruments (www.hannainst.com)

Honeywell Inc. (www.honeywell.com)

Horiba Ltd. (www.horiba.com)

IC Controls Ltd. (www.iccontrols.com)

Innovative Sensors Inc. (www.innovativesensors.com)

Invensys-Foxboro (www.foxboro.com)

Lazar Research Laboratories Inc. (www.lazarlab.com)

Mettler Toledo Ingold Inc. (www.mt.com)
Ocean Optics Inc. (www.oceanoptics.com)

Orbisphere Laboratories (www.orbisphere.com)
Rosemount Analytical, Liquid Division (www.emersonprocess.com)

Royce Technologies (www.royceinst.com)

Sensorex (www.sensorex.com)

Techne Inc. (www.techneusa.com)

Teledyne Analytical Instruments (www.teledyne-ai.com)

Waltron Ltd. (www.waltronltd.com)

Uniprobe Instruments Ltd. (www.uniprobe.co.uk)
Van London Company Inc. (www.vanlondon.com)
Yokogawa Corp. of America (www.yca.com)

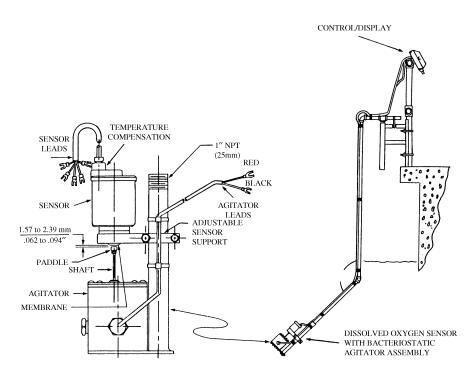
YSI Inc. (www.ysi.com)

### INTRODUCTION

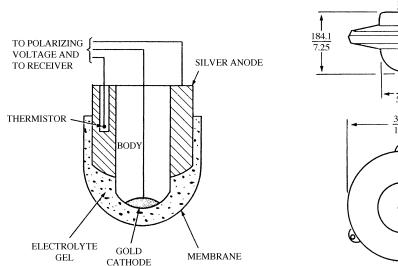
Section 8.42 was devoted to the discussion of oxygen analyzers in gas. This section deals with oxygen analysis in liquids. The distinctions between the analyzers used for these two services are not clear cut. The different electrochemical cell-type sensors (e.g., polarographic, galvanic, coulometric) can be used for both applications, as discussed in the previous section. Therefore, their treatment is somewhat shortened in this section. The most commonly used dissolved oxygen (DO) probe is the polarographic type.

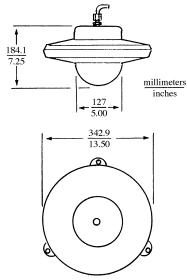
### **Probe Cleaners and Newer Sensors**

Similarly, probe cleaners have already been discussed in Sections 8.1, 8.2, 8.28, 8.33, 8.41 and will also be discussed in Section 8.48 in connection with pH probes. Therefore, their treatment here will also be abbreviated, although Figure 8.43a does describe a vibratory paddle-type probe cleaner. This unit cleans the membrane surface by a backand-forth motion close to the surface. The agitator paddle is coated with a biological growth-inhibiting substance that minimizes the biological growth on the membrane surface.



**FIG. 8.43a**Cleaner assembly for keeping the membrane surface of a dissolved-oxygen probe free of buildup or biological growths.





**FIG. 8.43b**Probe-type polarographic cell oxygen detector and flotation collar in which it can be mounted.

Galvanic and polarographic sensors continue to dominate the dissolved oxygen measurement applications for both on-line and off-line analysis. However, significant advances have been made with the introduction of equilibrium-state voltametric and fluorescence-based probes. These have the advantage of analyte sensitivities, which are relatively independent of membrane coating, and, since they consume little or no analyte as a result of the measurement process, they are able to work in processes where there is little or no flow past the face of the sensor.

All oxygen detectors used for gaseous samples can also measure the oxygen concentration in liquid streams if the oxygen is first removed from the liquid. This approach has the major advantage that only a clean gas mixture will contact the oxygen detector.

### **POLAROGRAPHIC CELL**

The basic polarographic cell is illustrated in Figure 8.43b. It is very similar to the galvanic cell discussed in the next paragraph. However, the polarographic cell has *two* noble-metal electrodes and requires a polarizing voltage to reduce the oxygen.

The dissolved oxygen in the sample diffuses through the membrane into the electrolyte, which usually is an aqueous KCl solution. If there is a constant polarizing voltage (usually 0.8 V) across the electrodes, the oxygen is reduced at the cathode, and the resulting current flow is proportional to the oxygen content of the electrolyte. This current flow is detected as an indication of oxygen content. The oxidation-reduction reactions, in the case of a gold-silver cell and with KCl electrolyte, are as follows:

At the gold cathode,

$$O_2 + 2H_2O + 4 \text{ electrons} \rightarrow 4(OH^-)$$
 8.43(1)

and at the silver anode,

$$4Ag + 4(Cl^{-}) \rightarrow 4AgCl + 4$$
 electrons 8.43(2)

A variety of designs are available to extend the working life of the cell to several months. These include a number of membrane and electrolyte reservoir designs in addition to the use of a larger silver anode. The silver chloride at the anode can be converted back to silver by reversing the polarizing voltage.

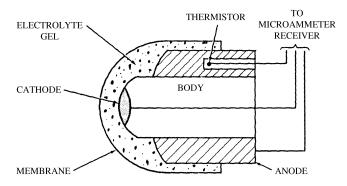
## **Sample Temperature and Flow**

The polarographic cell, like galvanic cells, is affected by temperature. Therefore, it is necessary to either control the sample temperature or to provide temperature compensation to attain high-precision measurements. In case of DO measurement, high precision corresponds to  $\pm 1$  to  $\pm 2\%$  error. If the sample temperature is allowed to vary between 32 and  $110^{\circ}\text{F}$  (0 and  $43^{\circ}\text{C}$ ), the measurement error in some designs will rise to approximately  $\pm 6\%$ .

Both galvanic and polarographic cells require a minimum sample flow velocity. This is necessary to eliminate stagnant layers of sample over the membrane, which otherwise would interfere with the continuous transfer of oxygen into the cell. The higher sample velocities are also beneficial because of their scrubbing action. Some suppliers provide a combination cell that, for maximum cleaning effect, includes a sample pump that directs a 5 ft/sec (1.5 m/s) flow velocity against the membrane.

### **GALVANIC CELL**

The operating theory of the dissolved oxygen galvanic cell is the same as that of the galvanic cell used for gaseous samples. With the exception of the considerations related to



**FIG. 8.43c**Probe-type galvanic cell oxygen detector.

the drying-out problem, all the design considerations are identical. The main difference is that most dissolved oxygen sensors are installed in dirty water, so they require special cleaners, agitators, and specialized sample systems.

The ranges of the galvanic cell dissolved oxygen analyzers can be as low as 0 to 20 ppb for applications such as the measurement of dissolved oxygen (DO) content of boiler feedwater.

## **Cell Designs**

All galvanic cells consist of an electrolyte and two electrodes (Figure 8.43c). The oxygen content of the electrolyte is equalized with that of the sample. The reaction is spontaneous; no external voltage is applied. In this reaction, the cathode reduces the oxygen into hydroxide, thus releasing four electrons for each molecule of oxygen [Equation 8.43(3)]. These electrons cause a current flow through the electrolyte. The magnitude of the current flow is in proportion to the oxygen concentration in the electrolyte.

The most common electrode materials are gold, silver, copper, and lead, and the most frequently used electrolyte is potassium hydroxide (KOH). The cathode must be a noble metal (silver or gold) for the cathode potential to reduce molecular oxygen when the cell circuit is closed. A base metal is selected for the anode (lead, cadmium, copper, zinc, or silver) with good stability and without any tendency toward passivation. The electrolyte [KOH, potassium chloride (KCl), or potassium bicarbonate (KHCO<sub>3</sub>)] is selected to minimize its dissolution of the anode when the cell is open.

In the case of a lead anode, the cell reactions can be expressed as follows:

Cathode: 
$$O_2 + 2H_2O + 4$$
 electrons  $\rightarrow 4(OH^-)$  8.43(3)

Anode: 
$$2Pb \rightarrow 2(Pb^{++}) + 4$$
 electrons **8.43**(4)

The galvanic-cell designs are subject to various degrees of contamination by background gases in the process stream. As a very general rule, the following background gases can be considered harmless: argon, butane, carbon monoxide, ethane, ethylene, helium, hydrogen, methane, nitrogen, and

propane. However, the following gases are likely to contaminate the cell: chlorine and other halogens, high concentrations of carbon dioxide, hydrogen sulfide, and sulfur dioxide.

# **Special and Flow-Through Cells**

Special cells have been developed to minimize the effect of the background gases. When an acid gas (such as CO<sub>2</sub>) is present that would neutralize a potassium hydroxide electrolyte in the background, a potassium bicarbonate electrolyte can be considered. Special cells are also available for the measurement of oxygen in acetylene and fuel gases.

In flow-through cell designs, sampling systems are usually required to bring the process stream to the analyzer and to filter it, scrub it with caustic, or treat it in other ways as preparation for the measurement. The probe-type membrane design does not require a sampling system if it can be located in a representative process area where the pressure, temperature, and velocity of the process stream are compatible with the cell's mechanical and chemical design.

## **Probe Design**

In this design (Figure 9.43c), the electrodes are wetted by an electrolytic solution that is retained by a membrane (usually Teflon) that acts as a selective diffusion layer, allowing oxygen to diffuse into the electrolyte solution while keeping foreign matter out. The sensor is usually mounted in a thermostatically controlled housing, and a thermistor is provided to compensate for minor temperature variations.

The ion current established in the electrolyte can be expressed by the following equation:

$$i_x = \frac{nFAPmCs}{L}$$
 8.43(5)

where

 $i_v$  = the ion current

n = the number of electrons involved in the electrode reaction

A = the area of the cathode surface

F = Faraday's constant

Pm = the permeability coefficient of the membrane

L = the thickness of the membrane

Cs = oxygen concentration

Equation 8.43(5) shows the relationship among the cell components. The Nernst equation [Equation 8.43(1)] also applies to the galvanic cell and explains why electrode potentials are a function of the absolute temperature. In addition, the ionic activity also varies with temperature, thus causing additional temperature sensitivity.

The characteristics of the membrane are critical to performance. The ideal membrane would be inert, stable, strong, permeable to oxygen, and impermeable to water molecules or other ions. In most cases, a compromise solution is accepted.

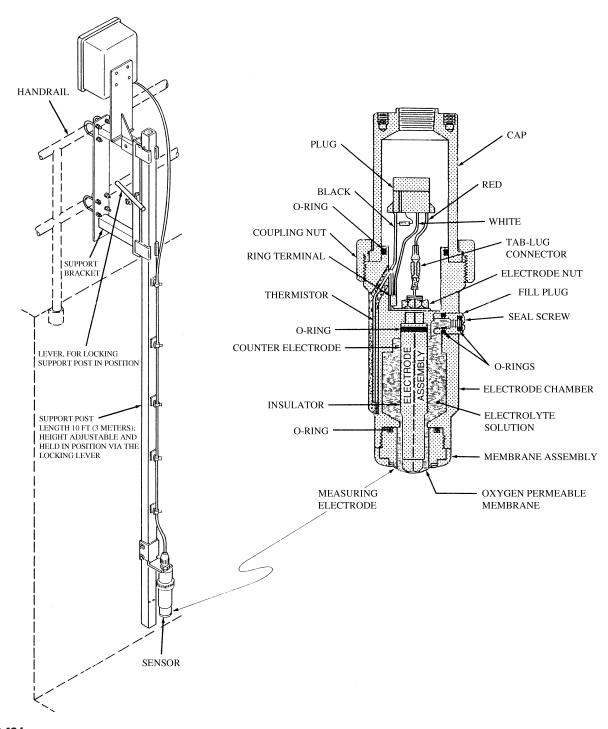


FIG. 8.43d
The design of a galvanic DO cell and its rail mounting installation. (Courtesy of ABB Inc., formerly Fisher & Porter Co.)

**Installation** The design of a galvanic (amperometric) cell with gold-copper electrodes designed for rail mounting is shown in Figure 8.43d. The maintenance requirements of this design have been reduced by providing an electrolyte supply that lasts for two to three years and by making the membrane assembly easily replaceable. These analyzer systems are available in weatherproof housing,

with 1% of span inaccuracy and with 4 to 20 mA transmitter output.

# **Flow-Through Design**

In the flow-through cells, the process sample stream is bubbled through the electrolyte. The oxygen concentration of the electrolyte is therefore in equilibrium with the sample's

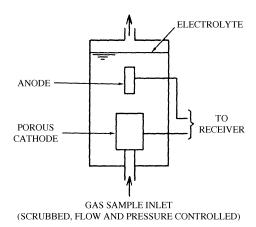


FIG. 8.43e

Flow-through trace oxygen analyzer cell.

oxygen content, and the resulting ion current between the electrodes is representative of this concentration.

In some trace analyzer designs, the cathode is made out of a porous metal, and the sample gas passes through this electrode, immersed in the electrolyte. Oxygen reduction tends to be complete within the pores of this electrode (Figure 8.43e).

These types of cells are usually provided with sampling consisting of (but not limited to) filtering and scrubbing components and flow, pressure, and temperature regulators.

### **COULOMETRIC SENSOR**

In the coulometric sensor, the sample gas diffuses through a diffusion barrier to the cathode of the electrochemical cell, where it is reduced to hydroxyl ions. Due to the conductivity of the potassium hydroxide electrolyte, the ions migrate to the anode, where they are oxidized back to oxygen. An external voltage drives this reaction, which results in a cell current that is proportional to the oxygen concentration in the gas sample.

A main advantage of this design is its nondepleting nature, as neither electrode undergoes a chemical change during measurement. Also, there is no need for periodic sensor replacement, and the unit is not subject to *oxygen shock*. This sensor is suited for ppb, ppm, and percentage measurements up to 25%. The areas of application of the coulometric analyzer are similar to those of the galvanic sensor.

## **MULTIPLE-ANODE DETECTOR**

The multiple-anode detector (Figure 8.43f) has three electrodes. Two are interspaced (noted by + and - in the figure) and covered with electrolyte. Oxygen is consumed at many cathodes but is generated at many anodes.

$$2H_2O \rightarrow O_2 + 4H^+ + 4e^-$$
 8.43(6)

Because a balance exists in this cell, there is no net generation of products. A number of advantages are claimed

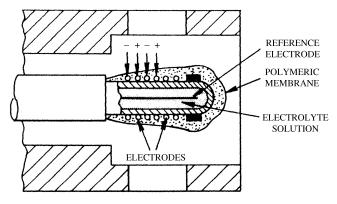


FIG. 8.43f

Multiple-anode oxygen detector.

for this technique. These include that fouling affects only the response time, there is no deterioration of electrodes, and membrane replacement is not required.

### **THALLIUM CELLS**

Thallium cells are somewhat unique in their operating principle and cannot be classified into the category of either galvanic or polarographic cells. At the same time, they are of the electrochemical type. One thallium-electrode cell design is somewhat similar in appearance to the unit illustrated on Figure 8.43b except that it has no membrane or electrolyte. This cell has a thallium outer-ring electrode and an inner reference electrode. When oxygen contacts the thallium, the following reaction takes place:

$$4\text{TI} + \text{O}_2 + 2\text{H}_2\text{O} \rightarrow 4\text{TI}(\text{OH}) \rightarrow 4(\text{TI}^+) + 4(\text{OH}^-)$$
  
8.43(7)

The potential developed by the cell is a function of the thallous ion concentration at the face of the electrode, and the ion concentration is in proportion to the concentration of dissolved oxygen.

# **Thallium Differential Conductivity Analyzer**

Another cell involving the reaction between thallium and oxygen is the thallium differential conductivity analyzer. This sensor detects the amount of thallous hydroxide formed by the measurement of conductivity. The sample conductivity is sensed both before and after the reaction, and the difference in conductivities is detected as a measure of dissolved oxygen content.

To eliminate temperature gradient problems, the actual instrument has both a sample and a reference flow stream. They are maintained at the same rate, and they flow through a similar flow path. Due to the high sensitivity of this measurement, accuracies of  $\pm 0.5$  ppb are obtained over the minimum range of 0 to 10 ppb. The response speed of this sensor is relatively slow; 95% of the response can be expected in about three minutes.

### **FLUORESCENCE-BASED SENSORS**

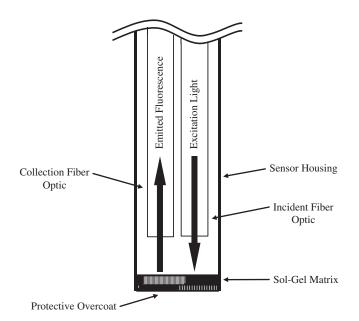
A new class of dissolved oxygen sensors operates on the principle of fluorescence quenching. Some chemical compounds have the ability to absorb light of a particular wavelength and then to re-emit light at a different (longer) wavelength. The intensity of the emitted light can be diminished when another chemical compound interacts with the compound responsible for the fluorescence. Because its intensity is lower than expected, the emitted fluorescence intensity is said to be *quenched*. This phenomenon can be used for the measurement of oxygen.

## **Sensor Design and Operation**

In this case, a compound containing ruthenium is immobilized in a gas-permeable matrix called a *sol-gel*. Sol-gels are very low-density, silica-based matrices suitable for immobilizing chemical compounds such as the ruthenium compound used in this measurement technique. Effectively, the sol-gel is equivalent to the membrane in a conventional DO sensor.

Using fiber optics, light from a light-emitting diode is transferred to the backside of the sol-gel coating. The emitted fluorescence is collected from the backside of the sol-gel with another optical fiber and its intensity is detected by a photodiode. A simplified sensor design is shown in Figure 8.43g. If no oxygen is present, the intensity of the emitted light will be at its maximum value. If oxygen is present, the fluorescence will be quenched, and the emitted intensity will decrease.

The ratio of the emitted intensity when no oxygen is present (Io) to the emitted intensity in the presence of oxygen (I) can be related to the oxygen partial pressure (which can



**FIG. 8.43g**Simplified diagram of a fluorescence-based dissolved oxygen sensor.

be converted to concentration) through the Stern-Volmer equation below:

$$\frac{I_{O}}{I} = 1 + K(P_{O2})$$
 8.43(8)

where

K = a temperature dependent constant

 $P_{O2}$  = the partial pressure of oxygen

This equation shows that, in the absence of oxygen, the ratio  $I_{\rm O}/I$  will be 1.0 and that it will increase linearly as the oxygen concentration increases.

To determine the oxygen content of a solution, it is first necessary to determine  $I_{\rm O}$  when the oxygen concentration is zero. Hence, calibration consists of a minimum of two points; one measurement is made in a zero-oxygen environment, and the other is at near normal oxygen concentrations where measurements are to be made.

The dynamic range for this sensor type is from single-digit ppb through 40 ppm. Response times are approximately 30 sec, and inaccuracy is typically 1% of the measurement range. The sensing element can be damaged by solutions having pH values greater than 10 and by solutions containing high levels of aggressive solvents such as aromatic compounds and ketones. The sol-gel membranes are available with a coating (such as silicone) to provide protection against abrasion.

### **OTHER DETECTION METHODS**

Another method of dissolved oxygen detection involves wetchemistry analyzers. These devices operate intermittently by taking a small sample and adding reagents to it. The reagents develop a color in the sample if a certain component is present. This technique can be applied to dissolved oxygen detection (in addition to many other applications) by colorimetrically determining the concentration of the unknown component.

### **OPERATIONAL CONSIDERATIONS FOR ALL SENSORS**

For the purposes of the discussion that follows, it is assumed that oxygen is dissolved in ordinary water. For most applications, the sensors are actually inserted into more complex solutions. However, the major component is usually water and thus, for the sake of the discussion that follows, the physical and chemical properties of such a solution usually can be treated as pure water.

Dissolved oxygen sensors can also be used for measurements in solutions consisting primarily of organic solvents. In this case, one must be aware that the solubility characteristics of oxygen in such a solution can be very different from that in a solution consisting primarily of water. Therefore, the oxygen solubility algorithms preprogrammed into the transmitter for water may not accurately reflect the true oxygen concentration in a solvent.

### **Calibration Methods**

Many dissolved oxygen systems are designed to operate over a very wide concentration range—for example, from 0 to 100 mg/l or up to 500% saturation. Calibration can be based on either one or two points. Additionally, calibration can be performed in air- or oxygen-saturated media or in air (or oxygen) that is saturated with water vapor. The method of calibration will have an influence on accuracy and is often dictated by the desired measurement range.

Given this, manufacturers may suggest different calibration schemes based on the level at which the determination is to be made. For example, if all measurements are to be made at concentrations greater than 0.5 mg/l, then a one-point calibration will usually suffice. (This is not true for fluorescence-based sensors, as was discussed earlier.) In this case, the intercept of the calibration plot is set to equal zero current at zero concentration. This assumption is often valid, given that the background current for most sensors is usually very small in comparison to the values being measured.

On the other hand, if measurements are to be made at levels below 0.5 mg/l, then one will want to set the low

calibration point (the zero signal) in an oxygen-free medium and then set the second calibration point in a medium of higher (and known) oxygen content. This procedure will ensure greater accuracy at lower concentrations.

Special care must be observed when calibrating membranecovered sensors that consume oxygen (e.g., polarographic or galvanic) in a zero-oxygen environment. For this case, the sensor must be exposed to the oxygen-free medium (and polarized) for approximately 1 hr prior to calibrating the zero point. Otherwise, residual oxygen in the electrolyte within the sensor will cause an erroneously high current measurement.

### **Temperature Compensation**

Temperature is an important factor in dissolved oxygen measurements for two reasons. First, the solubility of oxygen in a liquid is temperature dependent and, second, the rate at which oxygen moves across the permeable membrane is also temperature dependent. The change in solubility is inversely proportional to solution temperature, as shown in Figure 8.43h(I). If the user is interested in oxygen concentration values, then a solution temperature change must reflect a

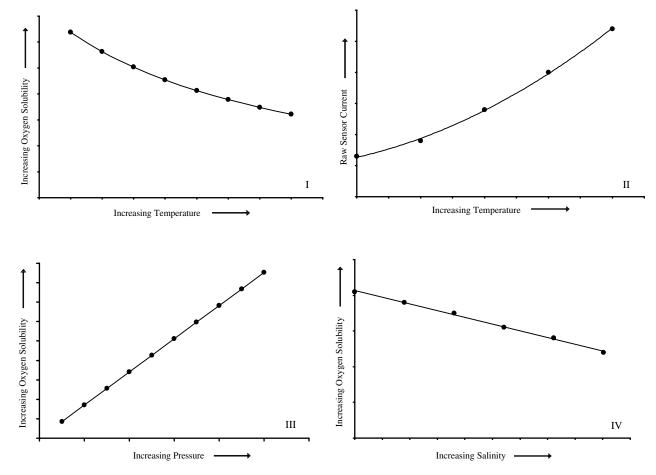


FIG 8.43h

Variation of (I) dissolved oxygen concentration with liquid temperature, (II) sensor current with temperature, (III) dissolved oxygen concentration with pressure (total pressure or oxygen partial pressure), and (IV) dissolved oxygen concentration with salinity. (Graphs generated from data tabulated in Hitchman, M. L., Measurement of Dissolved Oxygen, John Wiley & Sons, New York, 1978.)

change in oxygen concentration on the transmitter display. Practically all dissolved oxygen meters/transmitters employ an algorithm to determine oxygen concentration based on a solution temperature measurement.

Dissolved oxygen sensors are designed to operate under steady-state oxygen transport across the membrane. Ideally, the membrane permeability should never change after calibration. However, membrane permeability increases with increasing temperature. Hence, the sensor signal will increase with temperature, as shown in figure 8.43h(II). For an uncompensated sensor, the change in signal with temperature can be 1 to 6% per degree Celsius.

Erroneous results will be obtained if we do not account for this. Therefore, all dissolved oxygen sensors employ specific algorithms to correct for this effect. Algorithms are usually manufacturer specific, because membrane materials play an important role in determining the final mathematical form.

Both solubility and membrane permeability factors are accounted for by temperature compensation employed by the measurement loop. Dissolved oxygen sensors have built-in or adjacent temperature measuring devices that are actively monitored by the transmitter.

## **Pressure Effects**

Dissolved oxygen sensors respond to the amount of oxygen that is present in a liquid. Because oxygen is a gas under normal conditions, the amount of oxygen in a liquid is usually expressed as the partial pressure of oxygen  $(P_{O2})$  or the mole fraction of oxygen  $(X_{O2})$ , equal to 0.209 for air). The two quantities are related through the total gas pressure  $(P_T)$  of the system as follows:

$$P_{O2} = X_{O2}P_{T}$$
 8.43(9)

Furthermore, the solubility (concentration) of oxygen dissolved in a liquid at a given temperature and pressure follows a relatively simple relationship known as Henry's law,

$$S_{O2} = K_H P_{O2} = K_H X_{O2} P_T$$
 8.43(10)

where  $K_H$  is a constant that depends on both temperature and liquid composition. This equation shows that solubility varies linearly with partial pressure and total pressure [Figure 8.43h(III)].

This is an important relationship, because dissolved oxygen transmitters require the input of a pressure value (barometric or system pressure) during calibration and operation. Some will even provide real-time pressure corrections using input from an external pressure sensor.

Some dissolved oxygen analyzers are suitable for measurements in both gas and liquid-phase applications. Additionally, calibration can be performed in either the gas or the liquid phase. In this case, the contribution of water vapor pressure to the total gas pressure (and hence the oxygen

partial pressure) must be accounted for so as to achieve the highest possible accuracy. Therefore, some dissolved oxygen transmitters are designed so that the influence of water vapor can be entered as a relative humidity value during calibration and operation.

For example, oxygen sensors can be calibrated in water saturated with air, in air saturated with water vapor (in each case, the relative humidity being essentially 100%), or in ordinary air (in which case, the relative humidity is less than 100%). In each case, the appropriate water vapor (relative humidity) correction factor can be entered into the software.

# **Salinity Effects**

The salinity (i.e., the amount of a salt dissolved in water) is usually expressed in terms of mass of salt per mass of solution or mass of salt per volume of solution (gr/1000 gr,  $^{\circ}/_{oo}$ ). In more general terms, this quantity can be expressed as the mass of chloride per volume of solution (gr/l). A salinity value is directly obtainable from conductivity measurements.

The solubility of oxygen in water decreases nonlinearly with increasing salinity, as shown in Figure 8.43h(IV). The effect is most noticeable for salinity values greater than 2 gr/1000 gr. For comparison purposes, saltwater has a salinity of approximately 35 gr/1000 gr. At 20°C and 1 atm of pressure, the solubility of oxygen in salt water is approximately 7.3 mg/l. The solubility of oxygen in pure water at the same temperature and pressure is 9.1 mg/l. Therefore, if salinity compensation were ignored, an error of almost 20% would result.

### **Application Considerations**

The applications in which dissolved oxygen sensors are used include biopharmaceutical, water and wastewater, food and beverage, and chemical processing. Each application category dictates slightly different requirements for the sensor and transmitter. Biopharmaceutical applications require that the sensor body be of a hygienic design to allow for cleanability and to resist clean-in-place and sterilize-in-place conditions. Therefore, the sensor bodies are usually polished stainless steel and have no exposed grooves or crevices where matter can accumulate.

Additionally, membranes usually have an outer layer of Teflon to resist the buildup of coating. In contrast, in wastewater applications, the specifications are less stringent, so sensors are usually constructed from polymer materials, have lower temperature and pressure ratings, and are less resistant chemically.

Similar to biopharmaceutical applications, food and beverage usage usually requires that the sensor be of a hygienic design. However, it does not necessarily need to withstand sterilization conditions. Often, in food and beverage applications, the sensor is exposed only to temperatures that are high enough to pasteurize the process liquid.

Chemical process applications require sensor characteristics similar to those for biopharmaceutical and food and beverage applications. In these applications, too, the materials used must withstand higher temperatures and pressures than polymer materials can provide and must have good chemical resistance characteristics. For hazardous area applications, an intrinsically safe sensor must be considered, and manufacturers are usually able to supply intrinsic-safety-related information.

**Mounting Considerations** The specific application will determine whether a housing or other mounting structure is required. Dissolved oxygen sensors other than portable-unit types are usually mounted in a support structure that offers a secure mounting point or protection from the process environment.

The mountings used for dissolved oxygen sensors are essentially the same as the ones used for pH sensors (Section 8.48). For simple wastewater applications, the sensors are usually mounted in plastic pipe such that the electrical connections are protected from moisture and debris. In more demanding applications, sensors are mounted in a sturdier (usually stainless steel) housing that is resistant to high temperature, high pressure, and aggressive chemical environments. In these cases, the sensor/housing combinations are most often mounted in a weld-in socket on the process vessel or pipe.

Dissolved oxygen sensors can also be mounted in retractable housings; however, this is usually done only for applications in which the sensor can be cleaned, calibrated, and perhaps sterilized within the housing after being retracted from the process.

## **Bibliography**

- Bond, A. and Anterford, C. D., Comparative study of a wide variety of polarographic techniques with multifunctional instruments, *Anal. Chem.*, 44, 721, 1972.
- Buonauito, R. P., Oxygen analyzers, Meas. Control, February 1990.
- Cali, G. V., Improvements in pH Control & Dissolved Oxygen Instrumentation For Industrial & Municipal Waste Treatment, Proc. Conf. on Application of U.S. Pollution Control Technology in Korea, Seoul, Korea, March 22, 1989.

- Cardis, T. M., Managing data from continuous analyzers, Proc. 1992 ISA Conference, Houston, October 1992.
- D888–92 Standard test methods for dissolved oxygen in water, ASTM International, West Conshohocken, PA, 1996.
- D5462–02 Standard test method for on-line measurement of low-level dissolved oxygen in water, ASTM International, West Conshohocken, PA, 1997.
- DuCross, M. J. F., Automated methods for assessing water quality come of age, Env. Sci. Technol., October 1975.
- Fatt, I., The Polarographic Oxygen Sensor: Its Theory of Operation and Its Application in Biology, Medicine and Technology, CRC Press, Boca Raton, FL, 1976.
- Filer, S. and Hebert, B., PPB dissolved oxygen measurement—calibration and sampling techniques, *Ultrapure Water*, 15, 37, 1998.
- Flato, J., The renaissance in polarographic and voltametric analysis, *Anal. Chem.*, 44, 75A, 1972.
- Gallagher, J. P., Oxygen analyzers, Meas. Data, May-June 1975.
- Guide to the Selection of Oxygen Analyzers, Delta F Corp., Woburn, MA. Heinzle, F., Bucher, B., Dunn, J., Griot, M., Moes, J., and Sandmeiser, F., Measurement and control of dissolved oxygen below 100 ppb, Annals of the New York Academy of Sciences, May 1986, 469, 178–189.
- Hitchman, M. L., Measurement of Dissolved Oxygen, John Wiley & Sons, New York, 1978.
- Höffner, E., The on-line measurement of low level dissolved oxygen, *PowerPlant Chem.*, 3, 406, 2001.
- Linek, V., Sinkule, J., and Vacek, V., Dissolved Oxygen Probes, Institute of Chemical Technology, Prague, Czech Republic, and Pergamon Press, Oxford, U.K., and New York, 1985.
- McLennan, F. and Kowalski, B. R., Process Analytical Chemistry, Blackie Academic & Professional, London, 1995.
- Molvar, A. E., Instrumentation and automation experiences in wastewater-treatment facilities, EPA Document 600/2–76–198, October 1976.
- Neuberger, E. D., Reliable oxygen measurement reduces process costs, Westinghouse Eng., January 1975.
- Razaq, M., A new sensor and a microprocessor-based analyzer for monitoring low parts-per-billion oxygen contamination in high purity process gases, ISA Preprint 91–0535.
- Shinskey, F. G., pH and pION Control in Process and Waste Stream, John Wiley & Sons, New York, 1973.
- Smith, G. R., Oxygen Dynamics, University of Maryland, Baltimore, MD, 1992.
- Wang, H. Y., Transient measurement of dissolved oxygen using membrane electrodes, *Biosensors*, 1989, 4(5), 273–285.
- Wattenberg, H., Atlas of the Dissolved Oxygen Control, Ashgate Publishing, Aldershot, U.K., 1995.
- White, A. F., Peterson, M. J., and Solbay, B. D., Measurement and interpretation of low levels of dissolved oxygen in ground water, *Ground Water*, 28(4), 584–590.
- Wolfbeis, O. S., Fiber-optic sensor and biosensors, Anal. Chem., 74, 2663, 2002.