APPLICATION NOTE – DISSOLVED OXYGEN

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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.

Solubilisation 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).

Effect of temperature changes

At a constant pressure, the volume of a specific weight of air changes in direct ratio to the absolute temperature (K). The concentration of oxygen at the air-water interface increases by a decrease in the air temperature. The temperature of the water is also important because of two other factors:

- *The amount of water vapour 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.*
- *After oxygen is dissolved in water, it has the same temperature as the water. Both the kinetic energies of the water molecules and the oxygen 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 sulphate, reduce the solubility of oxygen in water.

Theory

A galvanic oxygen probe consists of two metals of different nobility which serve as electrodes. The more noble metal is the cathode (Silver), the other (lead) is the anode. In the presence of an electrolyte, a voltage around 800 mV is produced between the two metals. 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 internal resistance which is measured as a voltage by the oxygen meter.

The membraned oxygen electrode offers the following advantages:

- *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.*
- *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 galvanic style probe is typically silver, the anode is commonly lead, with the electrodes immersed in an alkaline 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 optimise 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. 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.

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 cm^2 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).

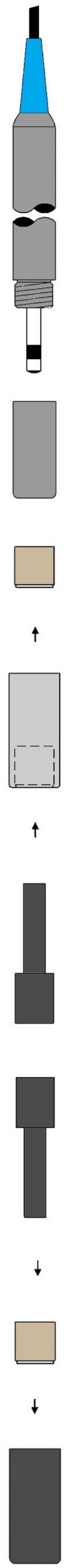
$$N_t = f\ [O_2 \times (1/D)]$$

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 recognise desired response rate and rugged performance. Thin membranes provide quick response in addition to sensitivity because diffusion equilibrium is reached more quickly, 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.

Temperature effects on the probe output



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

- *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.*
- *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. Therefore, if the read-out from the dissolved oxygen meter 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 analyser. 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°C to 50°C.**Effects of dissolved solids on the probe output**

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 output from the probe will increase. As a result, the meter 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 concentration of oxygen molecules at the water-to-Teflon interface. The concentration of oxygen in the sample has not changed.

Maintenance

1. Carefully screw off the measuring head.

2. Cautiously remove the precipitated deposits with the aid of filter paper. **Do not use grinding paper or a glass fibre!**

3. Rinse several times with distilled water and shake carefully off the water drops.

4. Take the measuring head, fill it with new electrolyte solution and very slowly screw it onto the electrode while holding it vertically. **Take care that no air bubbles are present in the measuring head!**

5. Let the electrode rest for a few hours! The electrode is now ready for use.

- *Replace the membrane and O-ring only when damaged, not when calibration is no longer possible!*