ZIRCONIA OXYGEN ANALYSIS

The zirconia oxygen analyzer is an analyser for the measurement of ppm to % levels of oxygen in a gas or mixture of gases. The zirconia cell is an electrochemical galvanic cell employing a high temperature ceramic sensor containing stabilized zirconium oxide.

Within an instrument the zirconia cell is mounted in a temperature controlled furnace with the necessary electronics to process the signal from the detection cell. Measurements are displayed directly via a digital display as oxygen concentration over the range 0.01ppm to 100%.

Theory

The zirconia cell is a high temperature ceramic sensor. It is an electrochemical galvanic cell comprising of two electrically conducting, chemically inert, electrodes attached to either side of a solid electrolyte tube. This is shown schematically in Figure 1.

The tube is completely gas tight and made of a ceramic (stabilized zirconium oxide) which, at the temperature of operation, conducts electricity by means of oxygen ions. The potential difference across the cell is given by the Nernst equation.

\[
E = \frac{RT}{4F} \log \frac{P_1}{P_2}
\]

where:

- \( E \) is the potential difference (volts)
- \( R \) is the gas constant (8.314 J mol\(^{-1}\) K\(^{-1}\))
- \( T \) is the absolute temperature (K)
- \( F \) is the Faraday constant (96484 coulomb mol\(^{-1}\))
- \( P_1 \) & \( P_2 \) are the partial pressures of the oxygen on either side of the zirconia tube

Note

The partial pressure of the gas is equal to the molar concentration of the component in a gas mixture times the total pressure of the gas mixture.

\[
pO_2 = cO_2 \ p_2
\]

where:

- \( pO_2 \) = Oxygen partial pressure
- \( cO_2 \) = Molar concentration of oxygen
- \( p_2 \) = Total pressure

E.g. For atmospheric air, \( cO_2 = 20.9\% \)

\[
pO_2 = \frac{0.209 \times 1}{100}
\]

\[
pO_2 = 0.209 \text{ atmospheres}
\]
Theory (cont)

The Nernst equation can therefore be reduced to

$$E = 0.0496T \log_{10} \frac{P_1}{P_2}$$

Thus, if the oxygen partial pressure at one of the electrodes is known and the temperature of the sensor is controlled, then measurement of the potential difference between the two electrodes enables the unknown partial pressure to be calculated.

Note
In sensors of this type, the temperature has to be above 450 °C before they become active as a conducting electrolyte.

Principle of Operation

The zirconia cell used by Systech Illinois, is made of zirconium oxide stabilized with yttrium oxide as the ceramic with porous platinum electrodes. This cell is shown in Figure 1.

Molecular oxygen is ionized at the porous platinum electrodes.

$$\text{PtO} \rightarrow \text{Pt} + \frac{1}{2} \text{O}_2$$
$$\frac{1}{2} \text{O}_2 + 2e^- \rightarrow \text{O}^2-$$

The platinum electrodes on each side of the cell provide a catalytic surface for the change in oxygen molecules, $\text{O}_2$, to oxygen ions, and oxygen ions to oxygen molecules. Oxygen molecules on the high concentration reference gas side of the cell gain electrons to become ions which enter the electrolyte. Simultaneously, at the other electrode, oxygen ions lose electrons and are released from the surface of the electrode as oxygen molecules.

The oxygen content of these gases, and therefore the oxygen partial pressures, is different. Therefore, the rate at which oxygen ions are produced and enter the zirconium oxide electrolyte at each electrode differs. As the zirconium oxide permits mobility of oxygen ions, the number of ions moving in each direction across the electrolyte will depend on the rate at which oxygen is ionized and enters the electrolyte at each electrode.
Principle of Operation (cont)

The mechanism of this ion transfer is complex, but it is known to involve vacancies in the zirconia oxide lattice by doping with yttrium oxide.

The result of migration of oxygen ions across the electrolyte is a net flow of ions in one direction depending upon the partial pressures of oxygen at the two electrodes. For example, in the Nernst equation:

\[
E = 0.0496T \log_{10} \frac{P_1}{P_2}
\]

If \(P_1 > P_2\), ion flow will be from \(P_1\) to \(P_2\), i.e. a positive E.M.F.
If \(P_1 < P_2\), ion flow will be from \(P_2\) to \(P_1\), i.e. a negative E.M.F.
If \(P_1 = P_2\), there will be no net ion flow, i.e. a zero E.M.F.

In the zirconia analyzer, the Nernst equation is written

\[
E = 0.0496T \log_{10} \frac{PO_{2sample}}{PO_{2reference}}
\]

The analyser uses air as a reference, a constant oxygen concentration of 20.9%, and the zirconia cell is mounted inside a furnace whose temperature is controlled to 650°C (923 K).

Thus, our Nernst equation further reduces to:

\[
E = 45.78 \log_{10} \frac{PO_{2sample}}{0.209}
\]

The analyzer electronically calculates the oxygen partial pressure, and therefore oxygen concentration, of a sample gas with unknown oxygen concentration. This is accomplished by measuring the potential, \(E\), produced across the zirconium cell electrodes, substituting for \(E\) in the Nernst equation and anti-logging to obtain \(PO_2\). The cell potential output is shown in Figure 2

By anti-logging the equation, the output signal can be displayed directly on a digital readout meter as oxygen concentration in ppm or %.
**Calibration**

As the zirconia instrument uses an absolute measurement principle once built and factory calibrated, *it does not require* any further factory calibration.

Factory calibration consists of calibration of the electronics to accept the millivolt input signal from the detection cell and checking that the instrument then reads correctly on air, 20.9%. The instrument is then further checked for correct reading on ppm oxygen content in nitrogen.

**Applications**

The zirconia analyzers may be used for measurement of oxygen at any level between 0-100% in gases or gas mixtures.

The only restriction on the instrument’s usage is that the gas to be measured *must not* contain combustible gases or any material that will poison the zirconium oxide detection cell.

Any combustible gas, e.g. CO, H2, hydrocarbons such as methane, in the sample gas entering the instrument will combine with any oxygen in the sample gas in the furnace due to the high temperature at which the furnace is kept. This will actually reduce the amount of oxygen in the sample gas and cause the instrument to give an incorrect low reading.

Materials that will poison the detection cell are:

- Halogens e.g. Chlorine
- Halogenated Hydrocarbons e.g. Methylchloride
- Sulphur containing compounds e.g. Hydrogen Sulfide
- Lead containing compounds e.g. Lead Sulfide

Gases or gas mixtures containing any of the above are not suitable for oxygen determination with a zirconia type oxygen analyzer.

The applications for the ZR800 are industrial gas producers, industrial gas users and for safety monitoring.

- **Gas Producers** - for ensuring product quality either by measuring for an oxygen impurity or for monitoring for oxygen purity.
- **Gas Users** - to ensure reliability of inert gas blankets
  - to ensure quality of gases used as production materials in the chemical industry.
- **Safety Monitoring** - to ensure sufficient oxygen is present in a working atmosphere where the atmosphere can become oxygen deficient.