O_2-Diffusion: Inert Gas and Pressure Dependencies

Scope

Please refer to Application Note AN002 for a basic introduction to the O_2 measurement principle. With this background, this document explains the mechanisms governing O_2 diffusion. Understanding these principles helps clarify why the choice of inert gas can influence calibration, and why the sensor signal remains relatively stable at elevated pressures (>1 bar) while exhibiting an increasingly pronounced pressure dependence as the pressure decreases toward vacuum conditions.

When dealing with complex gas mixtures, please also refer to Application Notes AN006 and AN007.

1 The Diffusion of Gases

Diffusion is a thermodynamical process in gases, where gas molecules migration is induced by thermal motion, trying to equalize concentration gradients. We describe the processes by statistical means instead of the behaviour of individual molecules and thus we must make certain assumptions about the system and limit the description to certain parameter ranges (like temperature and pressure). We can expect other effects not described under these assumptions to become apparent, once we approach the limits of our defined parameter ranges and assumptions about the system.

1.1 The Diffusion Limited Zirconia Sensor Design

Let us review a qualitative cross section view of an active sensor cell in fig. 1. The oxygen concentration all around the cell is assumed to be constant and non-zero, while the zirconia electrode expels oxygen diffusion into the sensor cell.

1.1.1 Measurement Principle and Assumptions

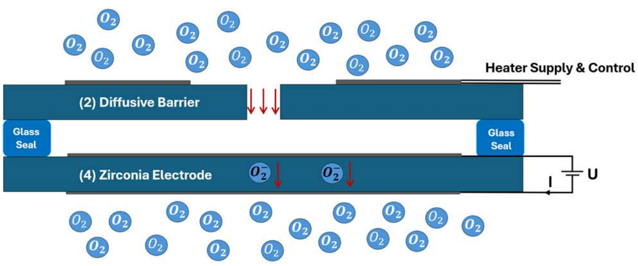

Figure 1: A schematic cross section with a symbolic, qualitative depiction of oxygen concentrations in and around the sensor.

We assume the following to be true:

- When active, the zirconia electrode (4) is capable of a much higher oxygen transportation rate than the diffusion rate through the barrier (2)
    - Thus, the oxygen concentration within the sensor cell chamber is far below the ambient oxygen concentration
- The oxygen concentration on the outside of the cell is constant and non-zero
- The system has reached an equilibrium state

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- No rapid changes in and/or gradients of:
  - Temperature
  - Concentration
  - Flows
  - Pressure
- The gas mixture consists only of oxygen and a background gas, that does not interact with the cell in any way
- Pressure and temperature are such, that the mean free path of gas molecules is far smaller than the diameter of the diffusion opening

If these assumptions are true, we will get a **current signal that is proportional to the influx of oxygen via the diffusion opening**, resulting in the sensor current *Is* to be:

$$Is(O_2) = -k \cdot \ln(1 - \frac{[O_2]}{100\,\%})$$

(at a given volumetric oxygen concentration *[O_2]*, k denoting the sensor specific calibration constant).

1.1.2 Diffusion

The diffusion coefficient of oxygen in other gases varies widely, let us consider the following examples to illustrate this:

Gas mixture	D [$cm^2 s^{-1}$]
O_2-He[1]	3.07
O_2-Ne	1.34
O_2-N_2	0.858
O_2-Ar	0.822

Let us consider the case of O_2-He and imagine O_2-molecules (atomic mass of 16) as large and He-molecules (atomic mass of 2) as small marbles, shown in the figure below. A massive O_2-marble can easily push away small He-marbles and thus "forces" its way through the gas mixture and thus diffuse at a higher rate.

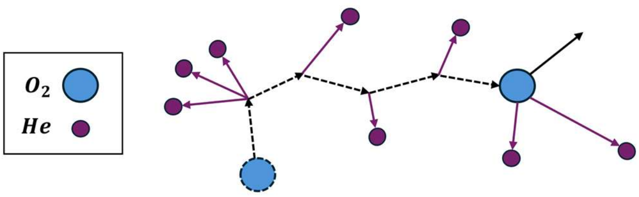

Figure 2: A qualitative illustration of an oxygen molecule diffusing through helium atoms. The mass difference leads to a higher mobility of oxygen in helium.

[1] Helium has a high thermal conductivity which can reduce the sensor temperature, if it is not actively monitored and stress the heating element and circuit at high concentrations.

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In practice, this translates to a difference in response – at the same volumetric O_2 concentration in a more O_2 will diffuse in the into the cells chamber in a O_2-He then in a O_2-N_2 mixture and the measured sensor current will reflect this.

1.1.3 Practical Example: Helium Leak Monitoring

Let us imagine an application, where one wants to ensure breathable conditions as there is a risk of a Helium leak from a cryogenic system. When there is no leak, the sensor would be operating in a (mostly) O_2-N_2 gas mixture and reading around 20.9% oxygen. In case of a leak, Helium would be added to the mix and the O_2 and N_2 concentrations would decrease accordingly. In turn, the O_2 diffusion coefficient in the new mixture would increase significantly and thus the oxygen diffusion rate into the chamber of the cell, resulting in an oxygen reading that is too high.

1.2 Pressure

While there is no physical limit, at what pressures the sensor cell can be operated, the specified pressure range is given as 1300-700 mbar(a). At high pressures the sensor signal is independent of pressure while at low pressures, the sensor signal shows a strong pressure dependence.

1.2.1 High Pressure Regime

If all the above-mentioned assumptions are fulfilled and we are solely measuring the oxygen diffusion flux, the sensing cell should not show any pressure dependence. This is due to the following facts:

- The oxygen diffusion constant D is inversely proportional to pressure p: $D \sim \frac{1}{p}$
- The oxygen density ρ (and the sensor current I_s) is proportional to pressure: $\rho \sim p \sim I_s$

Thus, the pressure dependence cancels out as with increasing pressure diffusion gets “harder” while the oxygen density increases by the same amount.

At high pressures the sensor signal is a measure of the volumetric oxygen content and is independent

1.2.2 Low Pressure Regime

Here, the pressure dependence is high, as we enter the Knudsen regime (molecular mean free path ~ diameter of diffusion opening) and the sensor signal becomes a measure of partial oxygen pressure.

It is possible to operate the sensor at low pressures or even in vacuum by employing application specific procedures including an active heater control, pressure compensation and an adapted calibration routine.

1.2.3 Real World Pressure Dependence

As there is not strict cutoff pressure and the theoretical assumptions are in fact approximations, a pressure dependence can be observed. In reality, the inner volume of the cell always has some concentration of oxygen, the diffusion opening cannot be assumed to be a thin aperture and there are temperature gradients within the cell as well as other effects, that are difficult to account for.

The table below lists applications at non-ambient pressure conditions and the expected deviations:

Application	Sensing range	Pressure [bar(a)]	Deviation
Nitrogen generator	1000ppm	5	+1%
Oxygen monitor at 3000m	25%	0.7	-3%
Semiconductor production	1000ppm	0.01	N/A, partial pressure regime

1.2.4 Other pressure related effects

Rapid pressure changes can have other adverse effects on the sensor:

1. Rapid decompression: may momentarily lead to overpressure within the internal sensor chamber and mechanically stress the cell, leading to premature failures, if the glass seal should fail
2. Pressure spikes and rapid pressure changes: the sensor cell must be in a steady state before a measurement is taken. When a pressure change occurs, gas is either migrating out of the censor cell or into it as pressure is equalised, leading to perturbations in the sensor current that do not reflect the oxygen content and are the result of the sensor adjusting to a change in its environment.
3. Sensor temperature changes due to pressure: the difference in gas density also changes thermal equilibrium and the thus sensor temperature. It is recommended to actively monitor the sensor temperature and allow time after significant pressure changes for the system to reach its setpoint.

2 Summary

- Oxygen diffusion rates depend on the background gas and can have a significant impact on the oxygen reading, like in the case of O_2-He
- The current limiting design is mostly insensitive to pressure changes at ambient and above
- Pressure dependence must be accounted for at pressures below the specified minimum of 0.7 bar(a)
- Increased density at elevated pressures may have an impact on the thermals of the system – active heater control is recommended