

MEM4 – Gas Diffusion and Resulting Limiting Current in Amperometric Gas Sensors (AGS)

In this application note the linear relationship between the gas concentration and the limiting current produced by an AGS is discussed. Separate relationships for capillary-type and membrane-type AGS are established, showing different pressure dependencies.

1. Introduction: Capillary- and membrane-type AGS

To obtain a linear relationship between the gas concentration and the current produced by the AGS, the gas diffusion to the sensing (working) electrode must be limited with a barrier so that the gas diffusion is the limiting process of all occurring processes within the detection mechanism.

Two main types of gas diffusion barriers and resulting AGS exist:

- Capillary-type AGS
- Membrane-type AGS

Depending on the type of barrier and the resulting mean free path λ of gas molecules, two gas diffusion regimes are distinguished:

- Normal diffusion
- Knudsen diffusion

Commonly, the Knudsen number Kn is used to characterize these regimes. It depends on the diameter d and the mean free path λ .

$$Kn = \frac{\lambda}{d}$$

In the normal diffusion regime, the diameter is much larger than the mean free path of gas molecules, i.e. the Knudsen number is small. This applies to capillary-type AGS with capillary diameters in the millimetre to centimetre range. As a result, the diffusion of gas molecules through the capillary is dominated by interactions between the gas molecules.

In contrast, in the Knudsen diffusion regime the diameter is much smaller resulting in a large Knudsen number. This applies to membrane-type AGS with pore diameters in the submicron range. Contrary to capillary-type AGS, the diffusion of gas molecules through the capillary is therefore dominated by interactions between the gas

molecules and the pore wall. Naturally, the different diffusion regimes affect the flux of gas molecules passing the barrier and hence, the limiting current of the AGS.

When calculating the limiting current of the capillary-type and membrane-type AGS in the subsequent chapters, the diffusion of the active species to the sensing electrode is assumed to be the rate-determining step in the AGS reaction process. Thus, each active gas molecule flowing through the barrier is immediately consumed at the sensing electrode (by oxidation or reduction). No ad- and desorption effects, nor any saturation effects have an impact.

2. Normal diffusion (capillary-type AGS)

Collisions between gas molecules and the capillary wall can be neglected and, using Fick's first law of diffusion, the flux of active species through the capillary results in:

$$J_i = -D(i, Ma) \frac{dC_i}{dz} + X_i J_i \quad (1)$$

where $D(i, Ma)$ is the normal diffusion coefficient of the active species i (e.g. oxygen molecules) in the inert gas matrix Ma (e.g. nitrogen molecules), C_i and X_i are the molar concentration and fraction of the active species, respectively, and z is the diffusion distance coordinate along the capillary. The positive second term $X_i J_i$ arises from the pressure gradient along the capillary created by the diffusion of active species.

Two boundary conditions are known that help to solve the differential equation (1). On one side, at $z=0$ (outside of sensor), C_i equals the active species concentration to be measured (C_i ambient). On the other side, at $z=l$ (where l is the length of the capillary), C_i is equal to zero based on the assumption that each active species molecule passing through the capillary immediately adsorbs and subsequently, reacts at the sensing electrode. Solving the differential equation yields (Evans *et al.*, 1961):

$$J_i = -\frac{D(i, Ma)p}{RTl} \ln(1 - X_i) \quad (2.1)$$

$$J_i = \frac{D(i, Ma)p}{RTl} \ln\left(\frac{1}{1 - X_i}\right) \quad (2.2)$$

C_i can be expressed in terms of pressure p and temperature T using the ideal gas law. Equations (2.1) and (2.2) are equivalent and solely differ in the notation of the logarithmic part. The following calculations will be performed using the mathematical expression shown in (2.1).

Applying Faraday's law of limiting current I_L results in:

$$I_L = zFAJ_i = -\frac{zFAD(i, Ma)p}{RTl} \ln(1 - X_i) \quad (3)$$

A is the capillary's cross-sectional area; z is the number of electrons transferred in the electrochemical reaction per active species molecule and F is the Faraday constant.

The diffusion coefficient $D(i, Ma)$ of an active species i in an inert gas matrix Ma is calculated using Chapman-Enskog theory.

$$D(i, Ma) = \frac{3}{8} \sqrt{\frac{N_A \mu}{2\pi}} \frac{(k_B T)^{\frac{3}{2}}}{p \sigma(i, Ma)^2 \Omega(i, Ma)} \quad (4)$$

$$D(i, Ma) \propto \frac{T^{\frac{3}{2}}}{p} \quad (5)$$

In equation (4) N_A is the Avogadro constant, μ the reduced mass¹, k_B the Boltzmann constant, $\sigma(i, Ma)$ the average collision diameter and $\Omega(i, Ma)$ the collision integral. An in-depth explanation can be found for example in Atkins *et al.*, 2014.

Equation (5) shows the important temperature and pressure dependencies of the diffusion coefficient.

For practical reasons, one can often find the standard diffusion coefficient $D_s(i, Ma)$ at $T = 273$ K and $p = 1013.25$ hPa in literature. Expressing $D(i, Ma)$ with $D_s(i, Ma)$ gives:

$$D(i, Ma) = D_s(i, Ma) \left(\frac{T}{(273\text{ K})} \right)^{\frac{3}{2}} \left(\frac{(1013.25\text{ hPa})}{p} \right) \quad (6)$$

Inserting (6) into (3) yields:

$$I_L = zFAJ_i = -(1013.25\text{ hPa}) \frac{zFAD_s(i, Ma)}{RTl} \left(\frac{T}{(273\text{ K})} \right)^{\frac{3}{2}} \ln(1 - X_i) \quad (7)$$

The crucial statement of (7) is that the limiting current I_L is **independent of the total pressure**. Because diffusion changes with temperature, the limiting current I_L does too, resulting in a temperature-dependence of baseline current and sensitivity.

¹ The reduced mass μ is calculated from the molar masses of active and target species, respectively.

When measuring gas concentrations in the **ppm-range** the values of X_i are very small and one can use the Taylor series for the logarithmic term:

$$\ln(1 - x) = - \sum_{n=1}^{\infty} \frac{x^n}{n} = -x - \frac{x^2}{2} - \frac{x^3}{3} \dots \approx -x, \text{ if } x \ll 1 \quad (8)$$

Inserting this expression into (7) yields the well-known **linear relationship** for the signal of an electrochemical sensor in dependence of the target gas concentration:

$$I_L = zFAJ_i = (1013.25 \text{ hPa}) \frac{zFAD_S(i, Ma)}{RTl} \left(\frac{T}{(273 \text{ K})} \right)^{\frac{3}{2}} X_i, \text{ if } X_i \ll 1 \quad (9)$$

This equation can be further simplified into,

$$I_L = aX_i, \text{ if } X_i \ll 1 \quad (10)$$

where a is the sensor's sensitivity.

Remark comment: The series expansion depicted in equation (8) is valid for small values of X_i . Most MEMBRAPOR sensors are designed to operate in this range, i.e. between a few ppm to a few thousands of ppm. Sensors designed for nominal ranges larger than 40'000 ppm start to deviate from condition (8). This results in deviations of a few percent between the linear approach and the exact values. Hence, applications requiring exact concentration values, should use the logarithmic expression shown in equation (7). Further information on the exact calculations are given in application note [MEM2](#) or directly from MEMPRAPOR's technical support team.

3. Knudsen diffusion (membrane-type AGS)

Pores in porous membranes can be considered as very small capillaries. As mentioned before, in the case of Knudsen diffusion, the Knudsen number is large, so that interactions between the gas molecules themselves can be neglected and the interaction between the gas molecules and the capillary wall (pore wall) determines the diffusion behaviour. Hence, the flux of active species through the capillary is given by:

$$J_i = -D_{Kn}(i, Ma) \frac{dC_i}{dt} \quad (11)$$

where $D_{Kn}(i, Ma)$ is the Knudsen diffusion coefficient of the active species i (e.g. oxygen molecules) in the inert gas matrix Ma (e.g. nitrogen molecules). This equation has no contribution from a flow term like (1) as only collisions between gas molecules and the capillary play a role and therefore the pressure gradient along the capillary is negligible. Using the same boundary conditions for the differential equation (11) as for equation (1) and the same expression for C_i , the result is

$$J_i = D_{Kn}(i, M) \frac{p}{RTl} X_i \quad (12)$$

The limiting current I_L in the Knudsen regime can also be calculated by applying Faraday's law:

$$I_L = zFAJ_i = \frac{D_{Kn}(i, M)pzFA}{RTl} X_i \quad (13)$$

Contrary to normal diffusion, in the Knudsen regime the Chapman-Enskog formalism cannot be used because the capillary size is larger than the mean free path of molecules. This results in a weak interaction between molecules and a pressure-independent diffusion coefficient.

$$D_{Kn}(i, Ma) = \frac{d}{3} \sqrt{\frac{8RT}{\pi M_i}} \quad (14)$$

In (14) d is the pore diameter and M_i the diffusing gas' molar mass. Applying (14) to (13) results in a pressure-dependent limiting current.

$$I_L = zFAJ_i = \left(\frac{d}{3} \frac{zFA}{Rl} \sqrt{\frac{8R}{\pi M_i}} \right) \frac{p}{\sqrt{T}} X_i \quad (15)$$

(15) shows that the limiting current is pressure dependent in the case of Knudsen diffusion.

4. References

Important:

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