

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

Contents

1) Two types of limitations in gas diffusion	1
2) Normal diffusion (capillary-type diffusion).....	2
3) Knudsen diffusion.....	3
4) References.....	4

1) Two types of limitations in gas diffusion

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

There exist two main types of gas diffusion barriers: Capillaries and porous membranes. Depending on the type of barrier and therefore on the mean free path of gas molecules, two limitations of gas diffusion are distinguished:

- Normal diffusion or capillary-type diffusion
- Knudsen diffusion

In the normal diffusion regime, the capillary diameter (d) is much larger than the mean free path (λ) of gas molecules, whereas conversely in the Knudsen diffusion regime the diameter of a pore is much smaller than the mean free path.

As a result, the diffusion of gas molecules through the capillary is dominated in the former case by interactions between the gas molecules themselves and in the latter case by interactions between the gas molecules and the pore wall. Naturally, this affects the flux of gas molecules passing the capillary and hence, the limiting current of the AGS.

For capillary-type AGS, one usually deals with normal diffusion (thus also referred to as capillary-type diffusion), whereas for membrane-type AGS Knudsen diffusion applies.

One has to keep in mind one important assumption when calculating the limiting current of AGS. The diffusion of the active species to the sensing electrode is assumed to be the rate-determining step in the AGS reaction process. I.e. each active gas molecule flowing through the whole capillary 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 diffusion)

Collisions between the 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:

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

where $D(i, M)$ is the normal diffusion coefficient of the active species i (e.g. oxygen molecules) in the inert gas matrix M (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 due to the pressure gradient along the capillary created by the diffusion of active species due to the diffusion gradient.

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):

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

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

where P is the total pressure, R is the gas constant and T is the absolute temperature of the gas sensor. Equations (2.1) and (2.2) are equivalent and solely differ in the notation of the logarithmic part. Both notations will be displayed hereafter.

Applying Faraday's law leads to the limiting current:

$$I_L = zFAJ_i = \frac{-zFD(i, M) AP}{RTl} \ln(1 - X_i) \quad (3.1)$$

$$I_L = zFAJ_i = \frac{zFD(i, M) AP}{RTl} \ln\left(\frac{1}{1 - X_i}\right) \quad (3.2)$$

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

Moreover, it is known that the normal diffusion coefficient generally is given by:

$$D(i, M) = D_s \left(\frac{T}{273}\right)^\alpha \frac{1}{P} \quad (4)$$

where D_s is the standard diffusion coefficient (at 273 K and 1 atm) and α is a constant depending on the kind and the composition of the gas mixture.

Inserting into equations (3.1) and (3.2) gives:

$$I_L = \frac{-zFDsA}{Rl} \left(\frac{T}{273}\right)^\beta \ln(1 - X_i) \quad (5.1)$$

$$I_L = \frac{zFDsA}{Rl} \left(\frac{T}{273}\right)^\beta \ln\left(\frac{1}{1 - X_i}\right) \quad (5.2)$$

Most interestingly, it can be seen that the limiting current is **independent of the total pressure**. It is proportional to T^β (where $\beta = \alpha - 1$) and to $-\ln(1 - X_i)$ and $\ln(1/(1 - X_i))$, 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 an approximation:

$$\ln(1 - x) = -\sum_{n=1}^{\infty} \frac{x^n}{n} = -x - \frac{x^2}{2} - \frac{x^3}{3} - \dots \approx -x \quad \text{if } x \ll 1 \quad (6)$$

Inserting in equation (5.1) yields the well-known **linear relationship** for the signal of an electrochemical sensor in dependence of the target gas concentration:

$$I_L = \frac{zFDsA}{Rl} \left(\frac{T}{273}\right)^\beta X_i \quad \text{if } X_i \ll 1 \quad (7)$$

or further simplified:

$$I_L = a \cdot X_i \quad \text{if } X_i \ll 1 \quad (8)$$

where a is the sensitivity of the electrochemical sensor.

3) Knudsen diffusion

Pores in porous membranes can be seen as very small capillaries. As mentioned before, in the case of Knudsen diffusion, the mean free path of gas molecules is relatively very 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 behavior. Hence, the flux of active species through the capillary is given by:

$$J_i = -D_{Kn}(i, M) \frac{dC_i}{dz} \quad (6)$$

where $D_{Kn}(i, M)$ is the Knudsen diffusion coefficient of the active species i (e.g. oxygen molecules) in the inert gas matrix M (e.g. nitrogen molecules). This equation has no contribution from a flow term like $X_i J_i$ in equation (1) as only collisions between the gas molecules and the capillary play a role. The pressure gradient along the capillary has not to be considered.

Using the same boundary conditions for the differential equation (6) as for equation (1) yields:

$$J_i = \frac{D_{Kn}(i, M) P}{RTl} X_i \quad (7)$$

Applying again Faraday's law gives the limiting current in the Knudsen regime:

$$I_L = \frac{zFD_{Kn}(i, M) AP}{RTl} X_i \quad (8)$$

Contrary to the normal diffusion coefficient, the Knudsen diffusion coefficient is independent of the total pressure:

$$D_{Kn}(i, M) = Kd \left(\frac{T}{M}\right)^{1/2} \quad (9)$$

where K is a constant, d is the diameter of the capillary and M is the molecular weight of the diffusing species. Thus, we obtain the following expression for the limiting current in the Knudsen regime:

$$I_L = \frac{zFKdA}{MRl} P \left(\frac{1}{T}\right)^{1/2} X_i \quad (10)$$

In stark contrast to the normal diffusion regime, the limiting current is proportional to P , to $T^{-1/2}$ and to X_i .

4) References

Important:

- R.B. Evans, G.M. Watson and E.A. Mason, „Gaseous diffusion in porous media at uniform pressure“, Journal of Chemical Physics, 35, 6, 2076-83, 1961
- T. Usui, A. Asada, M. Nakazawa and H. Osanai, „Gas polarographic oxygen sensor using an oxygen/zirconia electrolyte“, Journal of Electrochemical Society, 136, 2, 534-42, 1989

Notable:

- C.S. Tedman Jr., H.S. Spacil and S.P. Mitoff, „Cathode materials and performance in high-temperature zirconia electrolyte fuel cells“, Journal of Electrochemical Society, 116, 9, 1170-5, 1969
- T. Usui, K. Nuri, M. Nakazawa and H. Osanai, „Output characteristics of a gas-polarographic oxygen sensor using a zirconia electrolyte in the knudsen region“, Japanese Journal of Applied Physics, 26, 12, 2061-4, 1987
- L. Qingfeng, X. Gang, H.A. Hjuler, R.W. Berg and N.J. Bjerrum, „Limiting current of oxygen reduction on gas-diffusion electrodes for phosphoric acid fuel cells“, Journal of Electrochemical Society, 141, 11, 3114-9, 1994

MEMBRAPOR AG is continuously improving its products and documentations. This document is subject to change without prior notice. Membrapor AG accepts no liability for any consequential losses, injury or damage resulting from the use of this document or the information contained within it.