

Competitive Diffusion and Adsorption of Gas Mixtures in Vycor Glass Membranes

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Vycor glass membranes have pores in the nano-meter range with a narrow pore size distribution. They strongly adsorb many organic and inorganic gases. Those membranes can be used for gas separation and dosing processes with and without simultaneous reactions. The understanding of mass transfer through the membranes is essential for the successful applications.

In this work the interaction of simultaneous diffusion and adsorption of pure gases and gas mixtures have been studied in a modified Wicke-Kallenbach cell, which has been operated at transient conditions. Fig. 1 shows the function of the cell schematically [1].

A binary sweep gas mixture kept at constant ambient pressure and constant concentrations $c_{1\infty}$ and $c_{2\infty}$ flows with a large flow rate past one side of the membrane, while the other side is capsulated by a closed chamber of volume V . If the two gases cross the membrane at different velocities the pressure within the chamber will either rise and fall or vice versa as a function of time. This time dependent pressure signal is due to combined effects of adsorption, gas phase diffusion and surface diffusion.

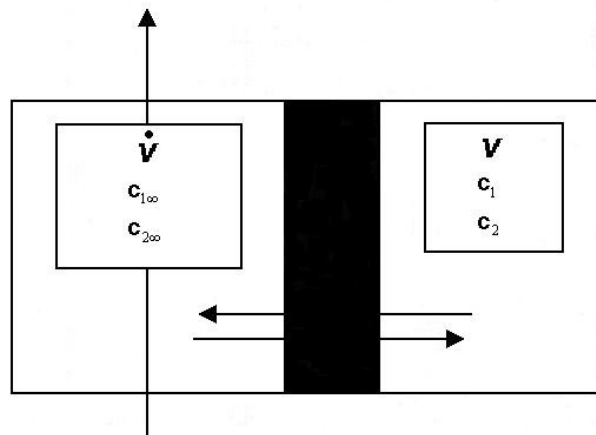


Fig. 1 Diffusion cell (schematically)

At first the membrane permeability was calibrated with the non-adsorbing noble gases He and Ar. The pore diameter of 4 nm was sufficiently smaller than the mean free path of the gas molecules. Therefore, the two gases should pass the membrane with the Maxwell-velocity. It was confirmed experimentally that the permeability of the two gases was exactly proportional to the square root of the molar masses.

The theoretical approach developed leads to the following expression:

$$\frac{\Delta P}{P} = (y_{1,\infty} - y_{1,0}) \left\{ \exp\left(-\frac{t}{t_1}\right) - \exp\left(-\frac{t}{t_2}\right) \right\} \quad (1)$$

with the relaxation times:

$$t_1 = V / (A\beta_1)$$

$$t_2 = V / (A\beta_2)$$

and the mass transfer coefficients:

$$\beta_i = \frac{1 - d_p}{3} w_i \frac{\varepsilon}{L \mu}$$

where the group $\frac{d_p}{L} \frac{\varepsilon}{\mu} = K_0$ has been calibrated with pure He. $y_{1,\infty}$ is the constant mole fraction in the sweep gas, while $y_{1,0}$ is the initial mole fraction in the closed chamber.

Fig. 2 shows the pressure response $\Delta P(t)$ both for He replacing Ar and vice versa. The anticipation of pure Knudsen-type diffusion leads to an almost perfect agreement between the predicted and measured pressure response (the mean errors are between 0.7 % and 2.1 % while the RSQ lie between 0.997 and 0.999).

Experimental results for adsorbable gases like CO₂, C₃H₈ and C₄H₁₀ can also be described by the same two parameter equation as given above for the non-adsorbing gases by taking into account the additional storage capacity of the membrane and the increase of the mobility due to the additional surface diffusion in the membrane. Instead of eqs. 2 and 3 an extended equation for the relaxation times may be written as follows:

$$t_i = \frac{V}{A\beta_i} \frac{1 + f_{Cap,i}(\bar{q}_{sat}, b)}{1 + f_{Dif,i}(\bar{q}_{sat}, b, D_{surface})}$$

where the functions $f_{Dif,i}$ and $f_{Cap,i}$ are derived from the respective sorption isotherms and then set as constant numbers selecting a reasonable average saturation of around 50 % from the maximum saturation.

It is worthwhile to mention, that the additional storage and mobility effects (both due to adsorption) partly compensate each other. If both extension functions were equal, the pressure responses were the same as for pure Knudsen diffusion.

In Figs. 3 and 4 selected experimentally determined pressure responses are shown in order to demonstrate the power of the extended prediction method.

Fig. 3 demonstrates that in exchanging different mixtures of the two adsorbable gases C₃H₈ and CO₂ there is an influence of the gas compositions on the shape of the response curves.

Fig. 4 shows that temperature has an effect on the course of the transients in case of exchanging pure C₃H₈ by pure CO₂ and vice versa. The results confirm that at higher temperatures the pressure responses for these gases approach the Knudsen type behaviour. This means that the pressure responses vanish at sufficiently high temperatures, since the molecular masses of both gases are the same.

A good quantitative agreement between the observed complex transient behaviour and the predictions was found for a broad range of experimental conditions.

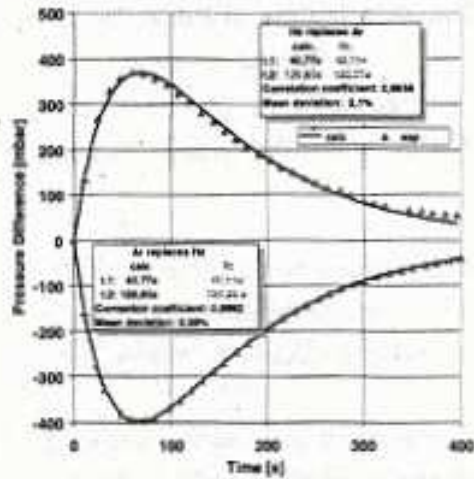


Fig 2. Predicted and measured pressure responses for He replacing Ar and vice versa.

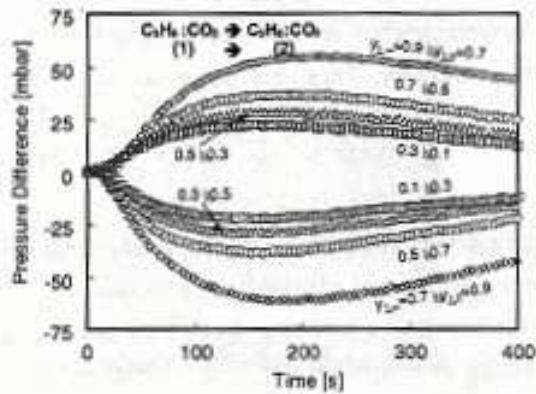


Fig 3. Observed transients for exchanging C_3H_8/CO_2 mixtures with varying compositions.

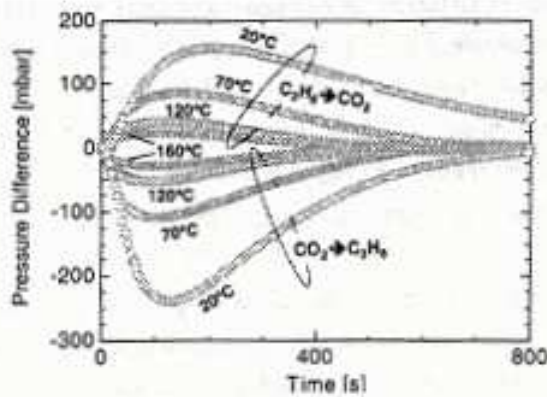


Fig 4. Observed transients for exchanging C_3H_8 and CO_2 at different temperatures.

Reference

[1] A. Tuchlenski, P. Uchtyl, A. Seidel-Morgenstern, „An experimental study of combined gas phase and surface diffusion in porous glass“ Journal of Membrane Science 140, 1998, 165-184