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# Delayed binary and multicomponent gas diffusion in conical tubes

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HIGHLIGHTS

- Mass transport is delayed by the conical geometry of tubes representing pores.
- Delay effect increases with ratio of inlet to outlet tube radius.
- Development and mathematical description of a novel steady-state diffusion cell.
- Comparability to the transient two-bulb-diffusion-cell.

GRAPHICAL ABSTRACT
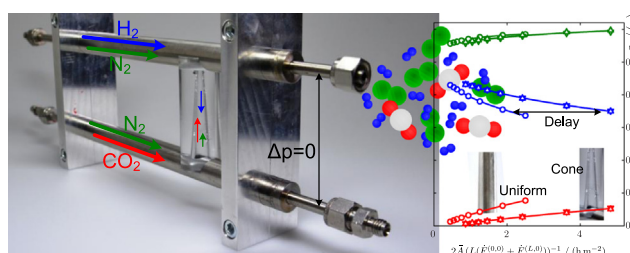
ABSTRACT

Catalyst pores are typically non-uniform along their longitudinal axis, and the transport of gaseous reactants and products takes place in a somehow tapered confinement. In a previous study we observed a diffusion delay in single tapered pores by means of a transient two-bulb-diffusion-cell (Veltzke et al., 2015). Processes in heterogeneous catalysis, however, are typically operated under steady state conditions. Hence also the diffusion processes are non-transient and reactant species are permanently consumed while product species steadily emerge. To mimic steady-state multicomponent diffusion in a cone, we developed a novel two-pipe-diffusion-cell and described the mass transport by an analytical model.

Here we can show that the delay effect, which is caused by volumetric changes in longitudinal direction, also exists for steady-state binary and multicomponent diffusion. It is experimentally confirmed that the diffusion hindrance increases with conicity of the test tube. Also the results are transferable to those of the transient two-bulb-diffusion-cell. The measurement of steady-state experiments, however, is much faster.

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1. Introduction

The relevance of gaseous diffusion from the macroscale in reactors to the microscale in catalyst pores is most substantial for the overall yield and performance in heterogeneous catalysis. Due to the unique properties of microscale pores that arise from their small size and large specific surface area, high reaction rates per unit volume are given (Wang and Coppens, 2008). In terms of mass transport limitation, the transport mechanisms of reactants

to the catalytically active site and those of the products from the active site of the catalyst determine the amount of required catalyst. For this reason, it is the objective in research to improve the mass transport without decreasing the specific surface area.

A crucial parameter for the mass transport is the pore geometry. Some studies about the influence of the geometry on gas diffusion are given in literature (Dogu and Dogu, 1980; Loewenberg, 1994; Dogu, 1998; Graur et al., 2015). Recently, an experimental and analytical study on transient diffusion of an ideal ternary mixture was presented by the authors where it was shown that the mass transport is slower in a conical tube compared to a uniform one with identical average cross section (Veltzke et al., 2015). Diffusion processes in heterogeneous catalysis, however, are

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typically non-transient since reactant species are permanently consumed while product species steadily emerge. Mass transport studies involving the influence of pore geometry obtained on transient considerations cannot be transferred to the more realistic steady-state conditions arbitrarily. The aim of the present paper, hence, is to study ideal binary and ternary diffusion through an idealized single pore under stationary conditions.

To obtain steady-state diffusion we designed an experimental setup consisting of two pipes perfused steadily by different gases (gas mixtures) that are orthogonally connected to a test tube (either uniform or conical). A mathematical description of this novel gas diffusion cell is derived in order to predict the steady-state binary and multicomponent diffusion process. A further aspect of the model is the consideration of the fluid velocity by the Reynolds number which is used as a weighting factor to iteratively determine the concentrations of the outflowing gas mixture streams. The numerical solution of this model allows us the prediction of the concentrations of gases leaving the system. Further, the effect of the conicity of test tubes is investigated experimentally. We can show that the conicity of the test tubes leads to a delay of the transport which confirms the findings in Veltzke et al. (2015).

The first part of this paper is focused on the mathematical description of the considered experiment and the model development. Afterwards, the experimental setup and procedure are described and the experimental results are compared to the theoretical ones. The last chapter concludes the findings.

2. Model development and analysis

Independently of the diffusion process being transient or steady-state, the mathematical description is distinguished by the number of involved gas species. The common approach to describe binary molecular diffusion is Fick's law (Fick, 1855) which defines that the molar flux is proportional to its concentration gradient and directed against it. For a ternary gas mixture, however, multicomponent effects arise that can be explained by the Maxwell-Stefan equations while Fick's law fails (Duncan and Toor, 1962).

2.1. Problem statement

To obtain stationary conditions of concentrations on each side of a long test tube with alongside variable cross section, two pipes creepingly perfused with different gas mixtures with n species i are orthogonally connected to each end of the tube. The pipes can be interpreted as infinitely large gas reservoirs. The setup is deduced from the experimental approaches in literature (Taylor and Krishna, 1993; Wicke and Kallenbach, 1941; Soukup et al., 2008) and illustrated in Fig. 1 as an abstraction of an idealized catalyst pore where the concentrations at each end of the tube are constant. This means the consideration of stationary conditions from the reactant-rich end (mix 1) to the product-rich end (mix 2) of the pore.

The first longitudinal coordinate z is defined as that one within the tube with its origin in the system of mix 1 at $z = 0$. According to Fig. 1, the length of the tube is L_{tube} and the varying cross section is $A_{tube}(z)$. Correspondingly, the upper system of mix 1 at $z = 0$ is indicated by the first superscript (0) and the lower system of mix 2 at $z = L_{tube}$ by the first superscript (L). Consequently, the diameter of the tube at the mix 1 system is $d_{tube}^{(0)}$ whereas $d_{tube}^{(L)}$ is that one of the mix 2 system. The second longitudinal coordinate is defined as the flow direction within the pipes with the origin at the inlet into the system of mix 1 at $y_0=0$ and with that one of mix 2 at $y_L=0$. Corresponding to the z-direction, the inlet of a mix system is indicated by the second superscript (0) and the outlet by the second superscript $d^{(0)}$ and $d^{(L)}$, respectively. The diameters of both pipes are identical.

In the following, we derive the species balance in the pipes in the first part, followed by a species balance in the tube. In the last section, we bring both parts together to obtain the model solution.

2.2. Species balance in the pipes

The integral species balance over the mixing zone of pipe A at $z = 0$ (indicated by superscript index 0) in Fig. 1b writes

$$\frac{dN_i^{(0)}}{dt}=n_i^{(0,0)}A_{pipe}-n_i^{\left(0,d^{(0)}\right)}A_{pipe}-J_i^{(0)}A_{tube}^{(0)} \tag{1}$$

and in pipe B at $z = L_{tube}$ (indicated by superscript index L)

$$\frac{dN_i^{(L)}}{dt}=n_i^{(L,0)}A_{pipe}-n_i^{\left(L,d^{(L)}\right)}A_{pipe}+J_i^{(L)}A_{tube}^{(L)}, \tag{2}$$

where dN_i/dt is the temporal change of the amount of species i, n_i is the convective flux in the pipes and J_i is the diffusive flux of species i in the tube counted positive in positive z-direction.
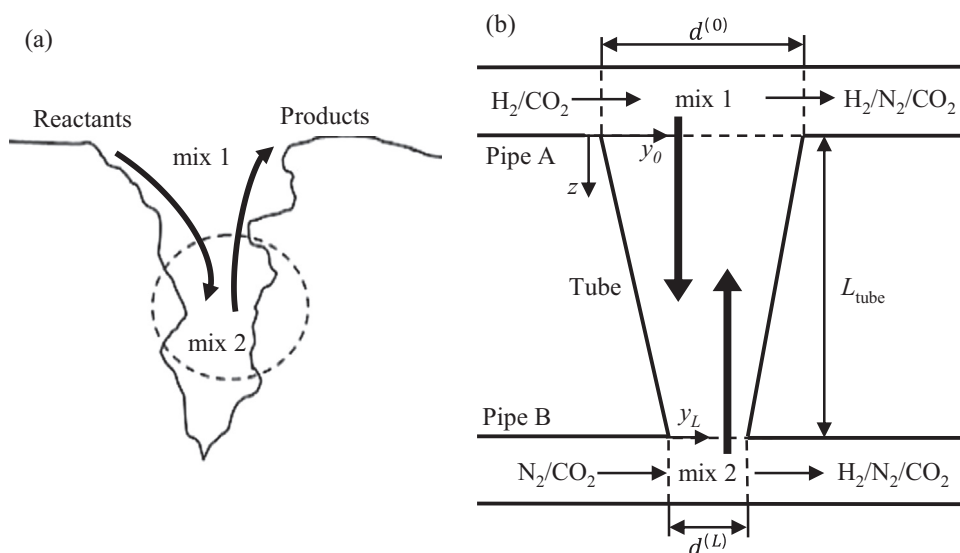

Fig. 1. Abstraction of an idealized catalyst pore to the stationary two-pipe-diffusion experiment. (a) Reactants permanently enter the pore and react to products that steadily leave the pore (Fick, 1855). (b) The abstracted model leads to the stationary diffusion experiment with a conical tube under constant concentration conditions at its ends.