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Assessment of kinetic modeling procedures of TAP experiments

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Abstract

Transient experiments can provide more information than steady-state experiments and are particularly useful in unraveling complex reaction networks. Modeling of the data allows to obtain quantitative information, e.g., sorption and rate constants as well as diffusion coefficients. To ensure correct estimation of the model parameters operating conditions that aim at eliminating diffusion resistances have to be defined as well as identification of the accessible parameters. Moreover, a statistical analysis of the model and its parameters after regression has to be performed. These issues are discussed here for temporal analysis of products (TAP) experiments as an example of a transient technique.

Keywords: TAP; Temporal analysis of products; Sticking coefficient; Parameter identification; Data correlation; Durbin–Watson statistics

1. Introduction

Catalytic reaction engineering is concerned with catalyst design and development to primarily improve or design new industrial processes. Proper reactor design requires knowledge on transport phenomena and reaction kinetics. Thus already early on the importance of diffusion and reaction in porous catalyst particles has been recognized [1,2] and the use of gradient free reactors [3] has been advocated. Mears [4] emphasizes intrinsic kinetics. Finally the catalytic reaction engineering approach to modeling is further refined and involves experimental design, parameter estimation and model discrimination [5–7].

Transient experiments can provide more information than steady-state experiments and are particularly useful in unraveling complex reaction networks. Wagner and Hauffe [8,9] set the concept of transient response methods forth in the late 1930s. In the 1960s renewed interest was shown in transient methods and the first fundamental transport-kinetics model for a pulse reactor was developed [10,11]. Since then a number of groups have made contributions to the theoretical and experimental developments of transient response methods, summarized in numerous review papers and monographs [12–27].

Temporal Analysis of Products or TAP experiments are performed under vacuum conditions with very small pulsed quantities of reactants. The time resolution of the TAP experiments is on the order of submilliseconds about two orders of magnitude better than flow experiments. Real catalyst samples can be used and this is what it sets apart from traditional surface science experiments. Details on the set-up can be found in Gleaves et al. [28]. Numerous studies deal with the modeling of TAP experiments [29–37].

The current paper discusses good practice of kinetic modeling of transient experiments taking TAP experiments as an example. It starts out with revisiting gas transport through the TAP reactor by Knudsen flow from the point of view of kinetic gas theory. This analysis shows that the TAP reactor is very well suited for kinetic studies as there are no external mass and heat transfer limitations as well as no radial concentration gradients and the catalyst zone is isothermal even in the case of strongly exo- or endothermic reactions. The second part discusses parameter estimation from transient experiments. It stresses two issues related to transient experiments: parameter identifiability and data correlation.

2. Transport and reaction in the TAP reactor

The established approach for steady-state kinetic modeling is to obtain intrinsic data free from heat and mass transfer limitations. This considerably simplifies the mathematical model and thus allows reliable parameter estimation [5,38,39].

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Notation

a_v	specific surface area, $m^2\,m^{-3}$
B_k	permeability, m^2
C_A	concentration of component A, $mol\,m^{-3}$
D	effective Knudsen diffusion coefficient, $m^2\,s^{-1}$
D	Knudsen diffusion coefficient, $m^2\,s^{-1}$
D_{AA}^{K}	effective Knudsen diffusion coefficient, $m^2\,s^{-1}$
D_{AB}	effective molecular diffusion coefficient, $m^2\,s^{-1}$
d_i	diameter of the interstitial voids, m
d_p	particle diameter, m
DW	Durbin–Watson coefficient
e_i	experimental error for experiment i
e_t	residals at time t
F	value of the F-test
F_A	total flux of component A, $mol\,m^{-2}\,s^{-1}$
H	Henry's coefficient
k	Boltzmann constant, $kg\,m^2\,s^{-2}\,K^{-1}$
k_a	adsorption constant, $m^3\,mol^{-1}\,s^{-1}$
k'_a	adsorption constant defined by Eq. (11), s^{-1}
k_j	rate constant of reaction j, $mol\,m^{-3}\,s^{-1}$ or s^{-1}
L	reactor length, m
M	molecular weight, $g\,mol^{-1}$
n_A	concentration of component A, $mol\,m^{-3}$
n_{col}	average number of collisions
p	pressure, Pa
R	ideal gas constant, $J\,mol^{-1}\,K^{-1}$
r_j	rate of reaction j, $mol\,m^{-3}\,s^{-1}$
s^0	initial sticking coefficient
s^2	variance
t	time, s
T	absolute temperature, K
t-value	value of the students t-distribution
v	mean molecular velocity, $m\,s^{-1}$
x	axial reactor coordinate, m
x_i	independent variable for experiment i
X_A	conversion of component A
y_i	i-th observed value of the dependent variable
z	space parameter inside the pores, m
z_w	collision frequency, s^{-1}
Greek symbols	
α	number of adsorption sites
β	model parameter
ε	bed porosity
ρ	autocorrelation coefficient
λ	mean free path, m
μ	gas viscosity, $kg\,m^{-1}\,s^{-1}$
σ	surface site density, $mol\,m^{-2}$
σ_A	collision diameter, m^2
τ	tortuosity
τ_{micro}	characteristic diffusion time in micropores, m
θ_A	surface coverage of component A
ν_{ij}	stoichiometric coefficient
∇	differential operator $\Sigma_i \delta/\delta x_i$
Subscripts	
bl	bed 1
z	microporous

Some guidelines to assess the importance of concentration and temperature gradients are available for non-steady-state experiments [40], but very little experimental support exists. In this section the gas transport through the TAP reactor is analyzed and it is shown that operating the reactor at sufficiently low pressures leads to an "ideal" reactor type where transport does not interfere with kinetics.

Svoboda [41] analyzed the gas transport through the TAP reactor in terms of the Dusty Gas Model. Mason and coworkers [42,43] developed the Dusty Gas Model to describe gas transport through packed beds. Depending on the pressure in the reactor different means of gas transport apply. Svoboda [41] arrives at the following expression for the flux of a binary mixture A/B:

$$F_A = -\frac{D_{AA}^{K} D_{AB}}{D_{AA}^{K} + D_{AB}} \nabla n_A - \frac{D_{AA}^{K} D_{BB}}{D_{AB}^{K} + D_{AB}} \frac{n_A}{n} \nabla n_A \frac{B_k k T}{\mu} n_A \nabla n \tag{1}$$

The first term represents the diffusive flow due to partial pressure gradients, the second term the diffusive flow due to total pressure gradients and the third term represents viscous flow according to Darcy's law.

For an equimolar mixture of gases having similar molecular weights, Svoboda [41] estimated the different contributions of each of the three terms in the right-hand side of Eq. (1) to the overall flux. At very low pressures the first term dominates and the equation can be simplified to:

$$F_A = D_{AA}^{E} \nabla n_A \tag{2}$$

This regime is referred to as Knudsen flow. Experiments are carried out in this pressure regime to facilitate data interpretation. Knudsen flow implies that the collisions between molecules and the solid particles dominate and that intermolecular collision are negligible. This mode also excludes gas-phase reactions.

The pressure corresponding to Knudsen flow can be calculated using the criterion that the mean free path, λ (m), has to be larger than the diameter of the interstitial voids, d_i (m) [44]:

$$\lambda \gg d_i \tag{3}$$

The diameter of the interstitial voids, d_i, is related to the particle diameter, d_p (m), by the following equation [45]:

$$d_i = \frac{2\varepsilon}{3(1-\varepsilon)} d_p \tag{4}$$

Table 1
Typical TAP-2 reactor configuration

Reactor diameter	4.0 mm
Reactor length	25.4 mm
Catalyst particle size	0.25 mm
Interstitial void space	$0.4\ \mathrm{m_G^3 m_R^{-3}}$
Bed tortuosity	$5.5\ \mathrm{m_G^3 m_R^{-3}}$

Kinetic gas theory gives the following expression for the mean free path as a function of pressure:

$$\lambda = \frac{kT}{\sqrt{2}p\sigma} \tag{5}$$

where k (J/K) is the Boltzmann constant, T (K) the absolute temperature, p (Pa) is the pressure and σ ($\mathrm{m^2}$) the collision diameter. The collision diameter depends on the size and geometry of a molecule. The pressure in the reactor below that a gas flow can be considered as Knudsen flow, depends on the gas that is used. For example, the pressure in the reactor at 298 K has to be kept below 10 Pa to meet the Knudsen flow criterion for the diffusion of argon ($\sigma = 0.36\ \mathrm{nm^2}$) and the reactor configuration given in Table 1.

Fig. 1 shows the calculated temporal pressure profile inside the TAP microreactor as a function of the dimensionless axial coordinate, z/L, and the dimensionless time, $t/(\varepsilon L^2/D_A)$ by introduction of 1 nmol of argon at 298 K. In Fig. 1 a maximum of the pressure at the reactor entrance at time = 0 s is observed that quickly decreases as a function of time and axial coordinate. The pressure at the reactor entrance equals ~100 Pa during a short period of time. For the considered case of the diffusion of argon, for a short period of time and over a short distance the Knudsen criterion (10 Pa) is violated.

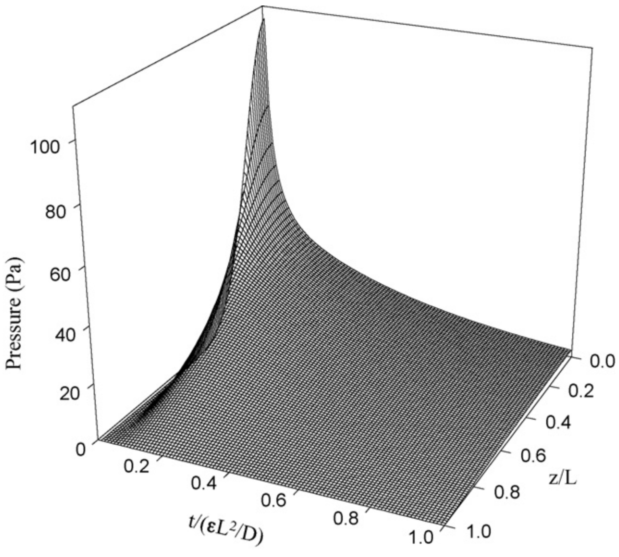

Fig. 1. Calculated temporal pressure profile in the TAP reactor as a function of dimensionless time and dimensionless axial coordinate (a pulse of 1 nmol of argon at 298 K reactor configuration given in Table 1).

The effective Knudsen diffusion coefficient, $D_A(\mathrm{m_g^3\,m_r^{-1}s^{-1}})$, is a direct result of the kinetic theory of gases:

$$D_A = \frac{\varepsilon}{\tau}D = \frac{\varepsilon d_i}{3\tau}\left(\frac{8RT}{\pi M}\right)^{1/2} \tag{6}$$

where M ($\mathrm{kg\,mol^{-1}}$) is the molecular weight of the gas, $\tau(\mathrm{m_g^2 m_r^{-2}})$ is the bed tortuosity.

Knudsen flow has been experimentally verified in the TAP reactor by several groups [28,29,32,46] and an excellent agreement was found between the experimental data and Eq. (6) in all studies, which included a variation of the temperature, mass of the gas, reactor packing and reactor dimensions.

For multicomponent gas mixtures, the diffusion of each component is described in Eq. (6) and is independent as long as the total pressure meets the Knudsen criterion.

2.1. Sticking coefficient

The sticking coefficient, s^0 (−), is defined as the ratio of the net adsorption frequency and the collision frequency with the surface. The number of collisions depends on the distance traveled by a molecule through the catalyst bed. The kinetic gas theory gives a simple relation for the number of collisions per molecule per second:

$$z_w = \frac{v}{\lambda} \tag{7}$$

where z_w ($\mathrm{s^{-1}}$) is the collision frequency and v ($\mathrm{m\,s^{-1}}$) is the mean molecular velocity. Substitution of the diameter of the interstitial voids for the mean free path and the Knudsen diffusion coefficient gives the number of collisions per second in the reactor:

$$z_w = \frac{v}{d_i} = \frac{3\tau D_A}{\varepsilon d_i^2} \tag{8}$$

Multiplying the collision frequency by the average residence time gives the average number of collisions, n_{col} (−), in the TAP reactor. Substituting the expression for the residence time of an inert gas leads to the following expression:

$$n_{\mathrm{col}} = \frac{3\tau}{2}\frac{L^2}{d_i^2} \tag{9}$$

The average number of collisions depends only on the packing characteristics: the length of the reactor and the diameter of the catalyst particles. Hence, every gas at every temperature undergoes the same number of collisions through a given packing. This result is not surprising since raising the temperature, increases the velocity of the molecules but not the path length through the reactor.

For the reactor configuration given in Table 1, the average number of collisions, n_{col}, is approximately 2×10^5. Metal surfaces have typical site densities of 5×10^{18} sites/$\mathrm{m^2}$, giving for non-porous particles and a completely packed reactor approximately 4×10^{16} adsorption sites. Using a pulse size of 2×10^{14} molecules, every site is hit on the average approximately 1000 times.

The rate coefficient for adsorption in units of $\mathrm{m}^3\ \mathrm{mol}^{-1}\ \mathrm{s}^{-1}$ is expressed as [47]:

$$k_a = \frac{s^0}{\sigma}\sqrt{\frac{RT}{2\pi M}} = \frac{s^0 v}{4\sigma} \tag{10}$$

where a is the surface site density ($\mathrm{mol\ m}^{-2}$).

The adsorption rate coefficient obtained from TAP experiments, k'_a (s^{-1}) is defined as:

$$k'_a = \frac{\sigma a_\mathrm{v}(1-\varepsilon_b)}{\varepsilon_b} k_a \tag{11}$$

where a_v ($\mathrm{m}^2\ \mathrm{m}^{-3}$) is the specific surface area, which is for non-porous spherical particles:

$$a_\mathrm{v} = \frac{6}{d_\mathrm{p}} \tag{12}$$

Substitution of Eqs. (12), (11) and (4) into Eq. (10) leads to the following expression for the sticking coefficient:

$$s^0 = \frac{k'_a}{v/d_i} \tag{13}$$

Since in a TAP experiment the change in the surface coverage is very small during a single pulse (or $1 - \Theta_\mathrm{A} = 1$), the sticking coefficient can be related to the conversion in the case of an irreversible adsorption by stating that the fraction that has not adsorbed ($1 - X_\mathrm{A}$) after each collision is equal to $1 - s^0$. This leads after n_col collisions to:

$$1 - X_\mathrm{A} = (1 - s^0)^{n_\mathrm{col}} \tag{14}$$

This equation is only valid for very small and constant values of values of s^0.

A sticking coefficient of $s^0 = 10^{-4}$ corresponds to a conversion of more than 99%. Hence, in the case of sticking coefficients larger than 10^{-4} no transient response at the reactor exit will be observed. All molecules will be adsorbed. However, it is feasible to reduce the catalyst bed length to 3 mm by packing inert beads around it. Since the average number of collisions is proportional to L^2, the average number of collisions in the bed will be 100 times smaller. Now, in a single pulse experiment a transient response will be obtained as long as $s^0 < 10^{-2}$. Real catalysts are usually not non-porous spherical particles, but instead will have much higher surface areas, and hence the average number of collisions will be much higher. In these cases during a multipulse experiment, the first pulses will be completely adsorbed. Continuing pulses will lead to a surface coverage that is no longer negligible and $s^0(1 - \Theta_\mathrm{A})$ becomes sufficiently small to observe a non-zero transient response at the reactor exit.

Fig. 2 shows a series of oxygen pulses (2×10^{15} O_2 molecules per pulse) over a 1 wt.% Pd/SiO_2 catalyst at 100 °C. Ten milligrams of catalyst was sandwiched in between two layers of quartz particles. The diffusivity of oxygen through quartz has been determined from pulses over a reactor filled with quartz particles only. The diffusivity of oxygen through the catalyst bed has been calculated from the Argon diffusivity using the square root ratio of the molecular weights.

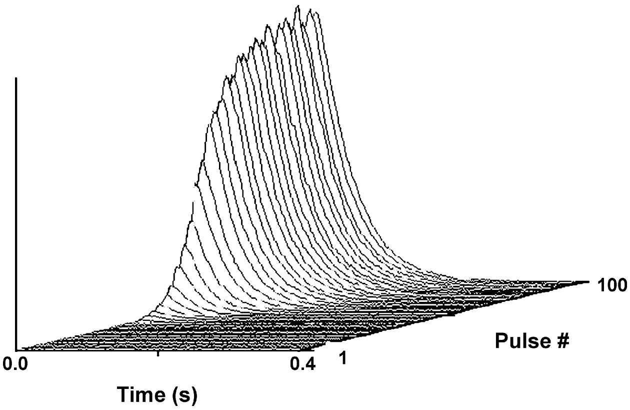

Fig. 2. Oxygen break-through curve showing the oxygen pulse responses when a series of 2×10^{15} O_2 molecules per pulse are introduced over 10 mg 1.0 wt.% Pd/SiO_2 catalyst at $T = 100$ °C.

The first few pulses are completely adsorbed but then a break-through of the oxygen flow can be observed. The transport of oxygen through the TAP reactor has been modeled as Knudsen flow and the resulting differential equations have been solved by a Laplace method (see further in this section). The change in coverage during a single pulse has been neglected but the absolute accumulated coverage has been taken into account during the integration of the complete pulse series. The pulses have been integrated and these values that correspond to $1 - X_{O_2}$ have been modeled by assuming a dissociative oxygen chemisorption requiring a number of palladium surface sites equal to α:

$$s(\theta_\mathrm{o}) = s^0(1 - \theta_\mathrm{o})^\alpha \tag{15}$$

The model fit is shown in Fig. 3. An s^0 of 0.24 was estimated from the data with α equal to 2.5 and the number of adsorption sites N_sites amounted to 3×10^{-5} mol g_cat. These experiments thus give not only the number of adsorption sites and the

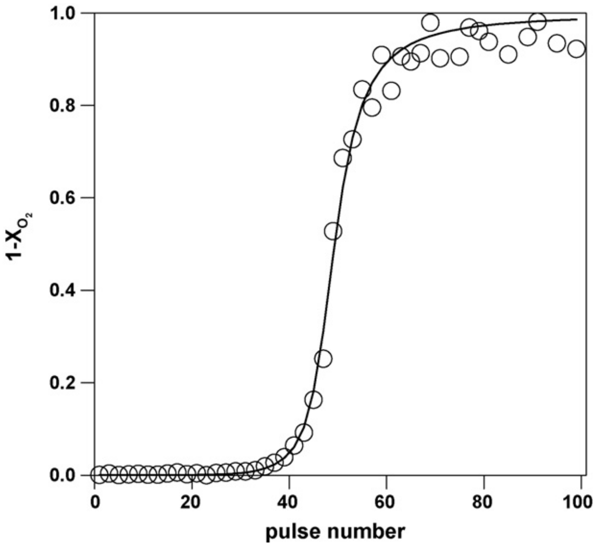

Fig. 3. Oxygen breakthrough curve, i.e., fraction of oxygen released from TAP reactor after each subsequent pulse over a Pd/SiO_2 catalyst (conditions see caption of Fig. 2). Open circles: experimental data, line: model.

sticking coefficient but also the dependence of the sticking coefficient on the surface coverage. The exponent α has been estimated slightly higher than the value of 2 expected for dissociative oxygen chemisorption.

A purely diffusion process implies the absence of all external mass transfer limitations as well as radial concentration gradients. Even for very exothermal reactions the adiabatic temperature rise is very small due to the small quantity of reactants introduced in the reactor (~1 nmol). This allows a good isothermal reactor operation (at least in the center of the reactor). Hence by operating the TAP reactor in the Knudsen flow regime not only a simplified mathematical description is achieved but also the reactor operation has become "ideal" for intrinsic kinetic studies where the transport of heat and matter do not interfere with kinetics.

In the Knudsen flow regime, the continuity equation for a non-reacting species is given by the one-dimensional diffusion equation (Fick's second law):

$$\varepsilon_b \frac{\delta C_A}{\delta t} = D_A \frac{\delta^2 C_A}{\delta x^2} \tag{16}$$

For a discussion on the initial and boundary conditions see Refs. [28,48]. Constales et al. [49] recently analyzed the error caused by non-ideal boundary and initial conditions.

For reacting species a source term is added as well as a mass balance for the solid phase:

$$\varepsilon_b \frac{\delta C_A}{\delta t} = D_A \frac{\delta^2 C_A}{\delta x^2} - (1 - \varepsilon_b)\sigma a_v \sum_{j=1}^{n} v_{ij} r_j \tag{17}$$

$$\frac{\partial \theta_A}{\partial t} = \sum_{j=1}^{n} v_{ij} r_j \tag{18}$$

with

$$r_j = k_j \prod_k c^{n_k} \prod_m \theta^{n_m} \tag{19}$$

For porous samples the situation is more complicated. Concentration profiles inside the pores for transient experiments might arise even in the absence of chemical reaction. As shown by Huinink et al. [50] internal diffusion phenomena have to be taken into account when the inter- and intrapellet characteristic diffusion times (L^2/D) are of the same order of magnitude. For most industrial catalysts the characteristic diffusion times on the pellet scale is much smaller than the characteristic diffusion times on the bed scale thus a uniform profile inside the pellets can be assumed. In that case the catalyst bed porosity needs to be adjusted for the larger available gas volume [50]. In the case of microporous solids (zeolites, active carbons) internal diffusion has to be accounted for explicitly in the model (see example in the next section).

Gleaves and coworkers [28,46,51,52] derived for a number of reactor configurations and typical mechanisms, analytical solutions as well as the expressions for the zeroth and first moments. Expressions for the different moments have also been reported in the case of porous catalyst samples [53,54]. This allows a rapid evaluation of the most important kinetic parameters. However, all these moment expressions are derived for reactants only. Lafyatis et al. [55] estimated the surface lifetimes of reaction intermediates based on a moment analysis for the hydrogenation of benzene over a Pt/SiO_2 catalyst.

In the case of a reactor consisting of only catalyst particles, a one-zone configuration, and first order kinetics an analytical solution for the transient responses at the reactor exit can be readily derived. This becomes more complicated for a reactor configuration of three zones where the catalyst is packed between two layers of inert material [52]. A three-zone reactor configuration is used to avoid axial temperature gradients over the catalyst bed. However, when the catalyst zone becomes sufficiently small, easy mathematical expressions for the conversion are available [56]. This reactor configuration presents other advantages notably a very uniform concentration profile over the catalyst zone even at high conversions [57].

For a quantitative description of TAP experiments dealing with complex kinetics, analytical solutions or moment-based analysis are no longer possible or at least not generally applicable. A numerical solution of the governing equations presents a more flexible approach regarding larger reaction networks. Two different approaches have been used. One is based on solving the partial differential equations by a Laplace transformation and then calculating the exit flow by a numerical Fast Fourier Transform algorithm [58,59,29,30]. This approach is only possible for linear equations (first order kinetics and low surface coverages). The other approach uses a numerical integration of the partial differential equations. The diffusion equation is rather straightforward to solve numerically by, for example, the method of lines [60]. In this method only the axial coordinate of the partial differential equation is discretizised and the resulting system of ordinary differential equations is solved by means of an appropriate ODE solver preferably one that can handle stiff ODE's. Van der Linde et al. [61] give more details on the methods of lines applied to transient models.

A number of TAP reactor models have been developed base on either of the two above-mentioned methods [28,41,46,47,61–66]. The models differ from one another by a slightly different description of the different zones that constitute a TAP reactor. These models are usually validated by fitting inert gas curves and/or give simulations results. A number of studies deal with the modeling of the kinetics based on TAP data [29–36] or with the diffusion of molecules in microporous materials such as zeolites or carbons [67–69]. The latter models have been extended to biporous materials including first order reaction within the micropores [70,71]. Froment and Dewaele [72] were able to obtain the width of the distribution curve for the adsorption sites for CO and CO_2 over α-Al_2O_3 by incorporating a continuous function for the heat of adsorption in their model. Even a Monte-Carlo method has been developed [73].

3. Modeling of transient experiments

3.1. Identifiability

Walter and Pronzanto [74] give guidelines concerning the identifiability of the model parameters. This approach also applies to the level of the model itself if there are several rival models to be considered (distinguishability).

A parameter is structural globally identifiable if there exists a unique model response that corresponds with just one specific value of the parameter over the whole parameter space. If this is true for just a part of the parameter space then the parameter is said to be locally identifiable. Walter and Pronzanto [74] give a rigorous mathematical method to prove the identifiability of a parameter. Asprey and Macchietto [75] propose a simpler but approximate method.

3.2. Experimental identifiability

To be able to estimate a parameter from a response curve in a transient experiment the following conditions need to apply:

- The parameter needs to be structural identifiable.
- The sensitivity coefficient of the parameter needs be non-zero over at least a part of the studied time interval.
- The sensitivity coefficient needs to be independent from the sensitivity coefficients of the other parameters.

Often it can be quite difficult to prove the parameter identifiably or even to find out if a parameter can be estimated correctly from the experimental data. Especially in the case of single response regression unidentifiable models can occur, where a continuous set of parameters lead to the same model prediction. Writing the differential equations with dimensionless groups of parameters helps to identify the model structure. Sensitivity analysis is a very powerful tool in parameter identifiability. An indication of the parameter sensitivity during the regression analysis is obtained if a method is used that calculates the derivatives and thus the Jacobian matrix. Note that the parameter sensitivity depends on the experimental conditions. It is therefore necessary to study the influence of the experimental conditions on the parameters by means of simulations or by setting up an experimental design before starting an experimental study.

As an example the sorption and diffusion over zeolite samples in the TAP reactor is discussed. Transient methods give access to characteristic times of physical and chemical phenomena. In the case of diffusion processes, these characteristic times are proportional to L^2/D, where L is the characteristic length of the diffusion process. Other parameters appear usually also in the form of lumped groups of parameters that cannot be estimated independently. The identifiable parameters for the model taking into account sorption and diffusion inside the micropores are listed in Table 2. The first three parameters in Table 2 are the characteristic diffusion times in the three zones of the reactor (quartz zone, catalyst bed and another quartz zone). H′ is the product of the void spaces of the catalyst bed and the catalyst porosity with the Henry coefficient for physisorption. τ_{micro} is the characteristic time for diffusion inside the micropores.

Table 2
Identifiable model parameters and their physical representation

Accessible parameters	τ_{bl} (s)	τ_{b2} (s)	τ_{b3} (s)	$\mathrm{H}'(-)$	τ_{micro} (s)
Physical constants	$\frac{\varepsilon_{\mathrm{b1}} l_{\mathrm{b1}}^2}{D_{\mathrm{b1}}}$	$\frac{\varepsilon_{\mathrm{b2}} l_{\mathrm{b2}}^2}{D_{\mathrm{b2}}}$	$\frac{\varepsilon_{\mathrm{b3}} l_{\mathrm{b3}}^2}{D_{\mathrm{b3}}}$	$\frac{1-\varepsilon_b}{\varepsilon_b}\varepsilon_z H$	$\frac{\varepsilon_z l_z^2}{D_z}$

Table 2 shows that the model contains four different characteristic diffusion times and one parameter that relate to the ratios of the concentrations between the different ‘‘phases’’ (H′, bed/micropores). Although these five parameters have been identified as accessible in this model it does not mean that all 5 parameters can be estimated simultaneously from the experimental data. Under a given set of experimental conditions, certain parameters may have no influence on the response curve. To facilitate the parameter estimation, the first three parameters in Table 2 can be determined from independent experiments by pulsing the reactants over a reactor filled with quartz particles only or by calculating them from the diffusion experiment with an inert gas using Eq. (6). These parameters then remain constant during the regression analysis of the TAP data, leaving two parameters to be estimated. Keipert and Baerns [67] showed that the micropore diffusion time could be estimated over approximately four orders of magnitude. To study the interaction between the diffusion in the micropores and to determine in which range the respective parameters can accurately be estimated from TAP response curves, simulations were carried out as a function of the characteristic times of diffusion in the micropores for two different values of the Henry coefficient.

The simulations presented in Fig. 4 show that the characteristic time for diffusion inside the micropores, τ_{micro}, can only be estimated over a limited range depending on the value of the Henry coefficient, H'. For $H' = 1$ only the transient response curves with characteristic diffusion times between $10^{-3} < \tau_{\mathrm{micro}} < 1$ s can be differentiated from another. Outside the range the shape of the response curve no longer changes significantly. Using larger samples can extend this range. At higher values of the Henry coefficient this range has become $10^{-2} < \tau_{\mathrm{micro}} \leq 10^{2}$ s. In analogy the two bottom graphs in Fig. 4 show that the range over which H can be measured depends on the characteristic diffusion times. It is even possible to obtain rather similar transient responses for different values of H' and τ_{micro}. However, if the data at various different temperature are obtained, one can estimate the H' and τ_{micro} independently from another due to the different temperature dependence of H' and τ_{micro}. For biporous catalysts a careful evaluation of the physical model is even more important as the number of compartments that are described by an exponential decay increases. Hence model distinguishability reduces. This situation in the case of FCC catalysts has been analyzed in [71].

3.3. Parameter estimation

The estimation of the parameters is based on regression analysis of the experimental data with the appropriate model. In the case of transient experiments this leads always to a nonlinear regression analysis. Non-linear regression analysis with a complex model containing several parameters to be estimated

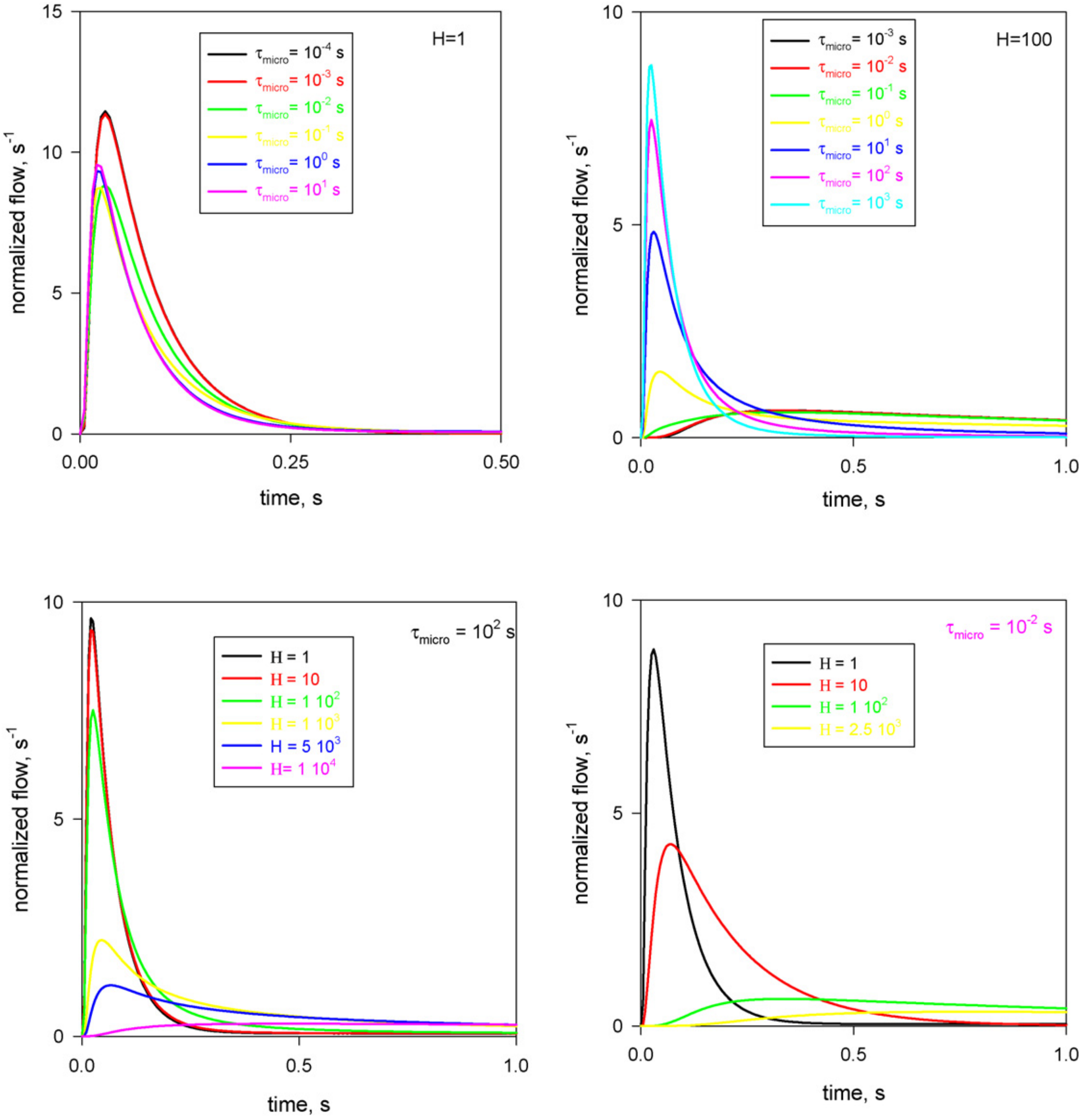

Fig. 4. Simulated TAP response curves for a microporous sample for different values of the characteristic micropore diffusion time and Henry coefficient.

can be a formidable task. Froment and Hosten [9] give a good review on the subject of parameter estimation for steady-state kinetics. A case study for parameter estimation from differential/algebraic equations that shows well the problems involved is described by Biegler et al. [76]. Some more practical issues and available software for parameter estimation can be found in Van der Linde et al. [61].

Non-linear regression is based on iterative optimization techniques such as the Levenberg–Marquardt algorithm that often uses numerical derivatives. Calculating the numerical derivatives can be a very costly computational step in the case of a complex non-steady-state model. If the derivatives are calculated by a finite difference approximation, an optimum perturbation size should be determined. Preferably one should calculate the parameter sensitivity coefficients during the integration step [77]. Moreover, the algorithm needs good initial values of the parameter to converge to the global minimum. Wrong initial values can cause the algorithm to converge to a local minimum (thus wrong parameter estimates) or prevent it from converging at all. In certain cases for transient experiments initial values for the parameter estimates can be obtained from moment analysis. In any case several different initial values need to be checked to ensure that the global minimum has been reached.

Consider the general non-linear model:

$$y_i = f(x_i; \beta) + \varepsilon_i \tag{20}$$

where y are the n dependent variables, subject to experimental error, x are the independent variables, accurately set at each desired level and known exactly, β are the p model parameters and ε are the n experimental (unobservable) errors. The corresponding least square criterion reads:

$$S(\beta) = \sum_{i=1}^{n} [y_i - f(x_i, \beta)]^2 \xrightarrow{\beta} \text{Min} \tag{21}$$

Often a lag time is observed due to uncertainties in timing and dead volumes. This lag time should be handled as a separate parameter to be estimated. The alternative procedure, described by Soick et al. [36] by defining ‘‘the shortest difference’’, resembles to orthogonal regression and thus assumes an experimental (random) error in the time coordinate. The timing error is a systematic error but the measurement of the time itself is very precise compared to the error of the mass spectrometer response.

The least square criterion assumes the following error model:

- the experimental errors are normally distributed,
- with zero mean,
- constant variance σ^2,
- and is independently distributed.

In this case for single response regression the least squares criterion and the maximum likelihood criterion are identical.

Once the regression analysis has been accomplished, a reliability analysis has to be performed. This involves a proper F-test, the evaluation of the individual confidence limits and the joint confidence regions [7]. Note that a high correlation between two parameters invalidates the individual confidence limits. Furthermore, residual plots have to be examined carefully to find out if there are trends that are not well explained by the model.

The last above cited property of the error model is often not met in the case of transient experiments where time-dependent data are collected that can be strongly correlated. A check on the validity of the independence of the observations has to be carried out (for example, by a Durbin–Watson test, see Ref. [78]). In this case the correlation has to be diminished by increasing the sampling time or the least squares procedure has to be replaced by a weighted least squares with the proper error variance as weights.

To illustrate the importance of independent observations for the estimation of parameters from TAP experiments, argon diffusion response curves over 250 μm quartz particles at 62 °C have been modeled at different sampling times for single pulses and for a series of pulses that have been averaged to improve the signal to noise ratio. The diffusion curve is characterized by one single parameter, the Knudsen diffusion coefficient [28]. Fig. 5 shows the model fit in case of a single (no averaging) pulse. The model describes the data quite satisfactorily showing no systematic deviations. Table 3 lists the estimated parameters, the Knudsen diffusivity with the corresponding residual sum of squares, the F-value, the t-value and the Durbin–Watson coefficient, DW, for the different pulse experiments. The Durbin–Watson test has been developed to detect serial correlation of the residuals [79,80]. Such a correlation arises from either the lack of fit or from a correlation within the data. Assuming an exact model, a low value of the Durbin–Watson coefficient will be observed for positively correlated data whereas for non-correlated data a value of around 2 is typical [78]. From Table 3 a trend can be observed of the F-value and the t-value with the sampling time. These values are rather large at small sampling times but the low DW value indicates a correlation between the observations. Positively correlated data lead to smaller confidence intervals. Moreover, from Table 3 it is also clear that averaging the pulse responses leads to less noise and better fits (lower residual sum of squares, higher F-value and t-value) but to stronger data correlation. Another way to illustrate the correlations of the data is by plotting the residuals at time t versus the residuals at time $t-1$ expressed by the following equation that defines the auto-correlation coefficient ρ [78]:

$$e_t = \rho e_{t-1} \tag{22}$$

The auto-correlation coefficient can be calculated by plotting the residuals between the experimental data and the model predictions at each time, $e(t)$, versus the residuals,

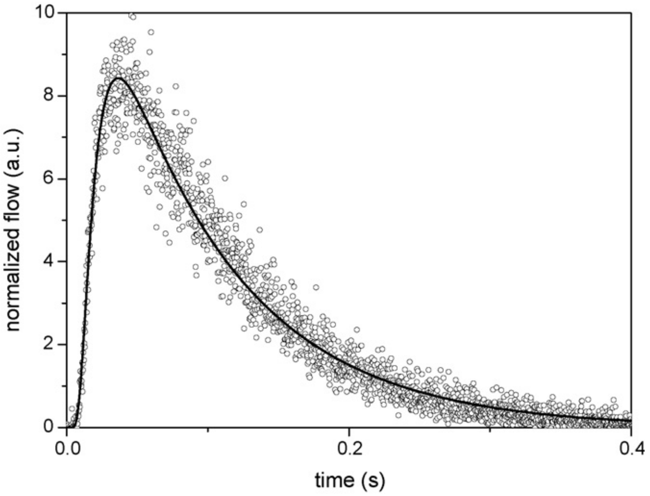

Fig. 5. Experimental data (symbols) and model calculation (line) for a pulse of argon (−0.2 nmol) over a bed of quartz particles (d_p = 250 μm) at 62 °C.

Table 3
Various statistical tests for the parameter estimation of the diffusivity from a TAP response curve at different sampling times and with different number of pulses averaged

Sampling time (ms)	Number of pulses averaged	Parameter estimate	$\sum(y_{exp} - y_{calc})^2$	F	t-value	DW
0.2	1	11.73	440	2.8×10^5	523	1.71
1	1	11.85	65	7.6×10^4	272	1.94
2	1	11.86	49	2.5×10^4	156	2.00
0.2	16	11.79	58	2.1×10^6	1442	0.84
1	16	11.91	7	7.4×10^5	850	1.28
2	16	11.94	3	4.3×10^5	653	1.18
0.2	121	11.75	29	4.2×10^6	2000	0.19

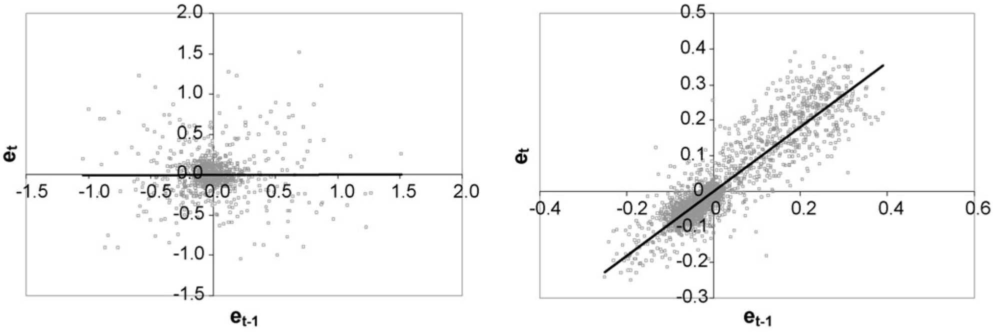

Fig. 6. Examples of the correlation of the residuals $e(t)$ vs. the residuals $e(t-1)$ of the argon diffusion curves for the case of a single curve with a sampling time of 1 ms (left) and 121 averaged curves with 0.2 ms sampling time (right). The solid lines are linear regression equations with as slope the auto-correlation coefficient p.

$e(t-1)$, set back one time interval. This is illustrated in Fig. 6 for the data of the third and last row of Table 3. From this figure it is clear that the autocorrelation coefficient for the single pulse data at 2 ms sampling time is zero, as the data are distributed randomly. On the other hand, for the data corresponding to 121 averaged pulses a strong linear correlation can be observed with a slope equal to 0.9.

4. Concluding remarks

Kinetic modeling of transient TAP experiments has been discussed in the framework of the modeling approach established for steady-state experiments. A similar approach can be adapted but some issues that are specific for the transient mode need to be taken into consideration.

The gas transport through the TAP reactor can be a very complex phenomenon including Knudsen diffusion, molecular diffusion and viscous flow, due to the transient behavior of the experiment. However, the pressure can be chosen such that only Knudsen diffusion prevails. This experimental condition allows for a mathematical description of the experiment. This is analogous approach in modeling of steady-state kinetics where kinetic studies are performed in reactors with well-known hydrodynamic behavior, e.g., CSTR's and plug flow reactors. Moreover, operating the TAP reactor in the Knudsen flow regime assures the absence of external mass and heat transfer limitations. However the existence of internal diffusion limitations needs to be verified carefully as concentration profiles inside the pores for transient experiments might arise even in the absence of chemical reaction. For most mesoporous samples, a uniform profile inside the pellets can be assumed. In the case of microporous solids internal mass transport has to be accounted for explicitly.

A careful inspection of the model equations in dimensionless form is necessary to reveal the identifiable parameters. Parameters can only be properly estimated over limited range of experimental conditions that can depend on other parameters. As transient response curves are sums of exponential decay curves the data can be fitted well by an incorrect physical model. However often, the different temperature behavior of the phenomena involved (sorption, diffusion) helps to distinguish between them.

A reliability analysis based on statistics is required for a correct evaluation of the model and its parameter estimates but in the case of transient experiments complications arise due to the a positive correlation of the time dependent data. Neglecting the correlation of the data will not result in different parameter estimates but will lead to too narrow confidence intervals on the parameters.

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