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Determination of Transport Coefficients in Microporous Solids

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Abstract. Macroscopic transient methods are reviewed with respect to their applicability to the investigation of molecular transport in microporous sorption systems. Various levels of sophistication of data evaluation for non-equilibrium sorption results obtained by means of batch methods are identified and characterised. Special attention is paid to the characterisation of *Fickian* (intracrystalline) diffusion as well as to the identification and quantification of additional rate mechanisms that, in general, may simultaneously occur in molecular sieve systems. A state-of-art determination of transport coefficients is exemplified for the systems benzene/microporous gallosilicate of MFI-type, n-hexane/silicalite-I and p-ethyltoluene/ZSM-5. Their sorption rate behaviour can be understood either by *Fickian* diffusion or by *Fickian* diffusion and intracrystalline molecular immobilisation/mobilisation and surface barrier penetration, respectively. To analyse complex sorption rate patterns in microporous systems, the method of *total curve fitting with full parameter region consideration* becomes mandatory.

Keywords: measurement method, mathematical model, zeolite, intraparticle diffusion

1 General Remarks

It is important to recognise the complexity of transport behaviour in porous solids for the development, design and optimisation of processes for both sorption separation and purification as well as for heterogeneous catalysis. Microporous solids which combine high intraparticle volume with mostly uniform micropore size and specific molecular interaction sites offer a basis for new selective sorption and catalytic operations. In particular, significant differences in both equilibrium and non-equilibrium sorption characteristics have already been utilised for many practical separation purposes (*cf.* Ruthven [118], Yang [135]). The development of mathematical models to describe, optimise and predict sorption processes and their performance has indicated that the role of 'material constants' such as sorption heats and entropies, capacities and transport parameters has changed from pure sorbent selection criteria to important parameters for process simulation. The more process dynamics dominates performance improvement process simulation itself becomes increasingly the basic approach to process optimisation. To utilise fundamental equilibrium and kinetic parameters for improved process simulation, the methods for their determination become a crucial tool of process development. Especially, kinetic properties rise as performance determining quantities. These quantities are relevant both to equilibrium and non-equilibrium processes. However, for equilibrium processes kinetic phenomena were often neglected. This leads to wasting that part of potential process effectiveness that may be available in the unused region between actual process conditions and their non-equilibrium boundary. Complementarily, sorbent capacity may often be left unused, if an equilibrium process is being performed under kinetic conditions. Therefore, accurate knowledge of kinetic parameters that were system-specific is needed even in particular case of equilibrium processes to define the process bounds. To properly understand the real rate-determining regions, attention must be given to accurate kinetic experiments and data evaluation. This situation is illustrated by Fig. 1, *cf.* outer shell.

On the other hand, those parameters are genuinely connected with both the actual composition and the structure of a solid to be tailored for a particular separation problem. Therefore, high art of sorbent synthesis and modification are challenged to generate appropriate properties of interaction between solid and fluid phase components. The realisation of transport mechanisms that correspond to an *a priori* given ideal microporous structure, *i.e.* the full utilisation of the particular structure-related sorption properties (both

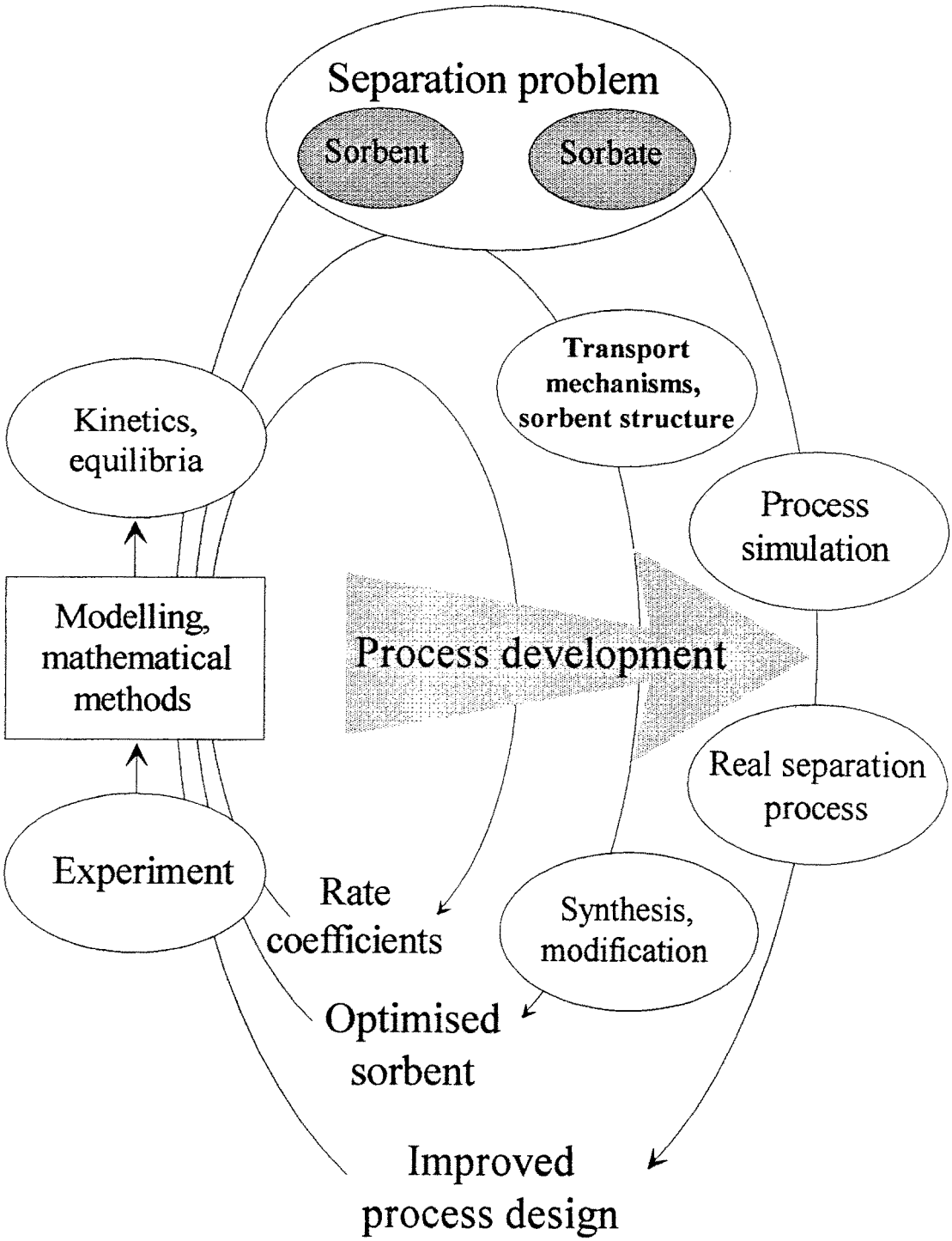


Fig. 1. Shell model of advanced process development.

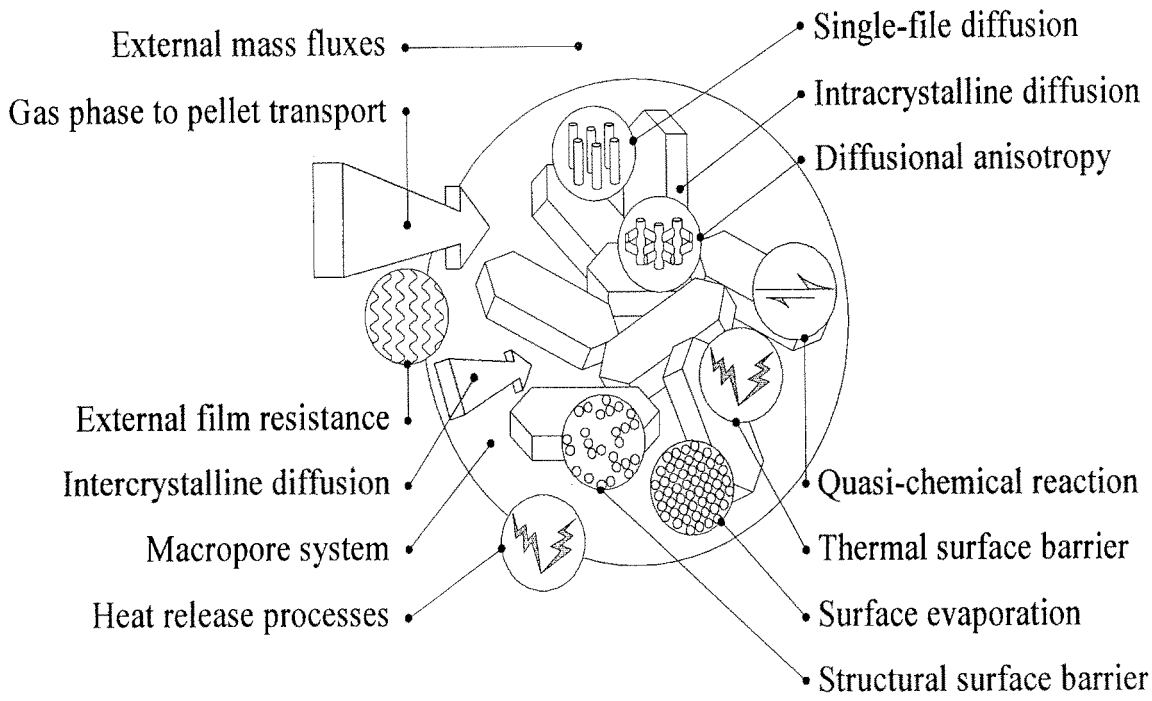


Fig. 2. Rate processes influencing sorption uptake by sorbent particle with biporous structure.

equilibrium and non-equilibrium ones) is most important. In this way, significant progress in recognition of fundamental ways to higher process efficiency can be achieved. In reality, such an approach becomes possible by iterations with respect to improved structure properties, the removal of overlaid disturbances, as well as, with respect to the increase of experimental accuracy and the development of models which are adequate to real processes (*cf.* middle shell in Fig. 1). Although this cycle leads to an optimised sorbent, it does not yet allow for a fully optimised process. The latter can only be achieved *via* determination of correct system-specific rate constants (*cf.* inner shell in Fig. 1).

The behaviour of sorption systems under equilibrium and non-equilibrium conditions became a great research challenge since crystalline microporous materials were first utilised for practical purposes. As far as sorption kinetics on zeolites is concerned, during earlier years it seemed obvious that intracrystalline diffusion, due to very narrow diameters of micropore channels, offers the strongest resistance to molecular transfer in these sorbents. However, the utilisation of zeolites as secondary particles (pellets) with a macropore system led to the conclusion that, in general, interference occurs between micropore and macropore transport mechanisms. This has been well understood and documented (*cf.* Do [41], Dubinin [45], Jordi *et al.* [66], Kocirik *et al.* [78], Lee *et al.* [82], Ruckenstein [114], Ruthven [118], Zolotarev *et al.* [143, 144]). Fast progress in uncovering the multiplicity of phenomena which take place during kinetics of sorption by zeolite crystals (*e.g.* Beschmann *et al.* [14], Bülow *et al.* [20, 22, 24, 25, 27], Dubinin *et al.* [44], Micke *et al.* [94], Rees [110]), was galvanized by the application of self-diffusion methods such as the NMR pulsed field gradient technique (*e.g.* Caro *et al.* [29], Kärger *et al.* [71, 73, 75], Pfeifer [105]) and the quasi-elastic neutron scattering experiment (*e.g.* Caro *et al.* [29], Jobic *et al.* [64, 65]) to zeolitic sorption systems. It was also achieved by a number of sophisticated kinetic methods (*e.g.* Bülow *et al.* [21, 27], Caro *et al.* [29], Do [41], Dubinin *et al.* [44], Eic *et al.* [47], Grenier *et al.* [53], Jordi *et al.* [66], Karge *et al.* [70], Paravar *et al.* [104], Rees *et al.* [109], Riekert [112], Shah *et al.* [120], Yasuda [137]). This work led to a far-reaching reconsideration of the hitherto known experimental and theoretical state of art in this field. Nowadays known rate-limiting processes occurring during sorption by molecular sieves are illustrated in Fig. 2.

Development of experimental procedures was accompanied by extended research on theory for both the direct data evaluation for experiments (*e.g.* Barrer

[3, 7], Do *et al.* [42], Jordi *et al.* [66], Krishna [81], Micke *et al.* [92, 96, 97, 98], Oprescu *et al.* [103], Shen *et al.* [122], Sun *et al.* [124, 125], Yasuda *et al.* [137, 140]) and the understanding of fundamentals of sorbate dynamics, especially by means of mathematical experiments such as molecular dynamics and Monte Carlo methods (*e.g.* Bull *et al.* [19], Catlow *et al.* [32], Cheetham *et al.* [33], Dahlke *et al.* [38], Demontis *et al.* [39], Henson *et al.* [58], June *et al.* [69], Kawano *et al.* [77], Pickett *et al.* [106], Tsykalo *et al.* [129], Yashonath *et al.* [136]). The latter methods, however, will not be dealt with in this paper. Major attention will be paid to the interaction between refinement of experimental methods and complementary development of corresponding theoretical procedures for their data evaluation. During recent years, the accuracy of determination of transport coefficients increased to an extent which allows recognition of the intrinsic physical nature of molecular mobility for a given sorption system. Such optimisation is depicted schematically by the inner shell in Fig. 1.

The unexpectedly high molecular mobility in zeolite crystals proven by self-diffusion techniques was shown under *equilibrium* conditions of molecular motion. However, it was clear from the very beginning that this approach to molecular mobility alone neither allows one to sufficiently depict and predict complex transport behaviour in microporous sorption systems, nor, does it provide information to completely model kinetic sorption separation processes. This is mainly due to the influence of various other *non-equilibrium* processes that may be superimposed upon intracrystalline diffusion (*cf.* Fig. 2) and that can hardly be identified by equilibrium methods, only.

The above mentioned development of non-equilibrium methods to determine transport diffusivities, the knowledge of which is sought for reasons illustrated in Fig. 1, was based on a variety of macroscopic batch techniques which were known for many years since this development took place. They were utilised with data evaluation resorted to explicit solutions of *Fick's* diffusion equation derived for both constant and variable boundary conditions (*cf.* Barrer [5, 8], Crank [36], Kärger *et al.* [73]) at ideal requirements. However, since the theory existed for ideal conditions, the experimental efforts were focused on generating idealised concentration batches. On the other hand, the boundary conditions assumed in theoretical analysis of adsorption or desorption rate curves may not always be those in real experiments. Thus, for a bed of crystals of finite thickness with sorbate entering the bed through one face only, there are transient pressure gradients within the bed normal to that face and, therefore, boundary conditions which vary with depth in the bed and with time. For curved (equilibrium) sorption isotherms this can lead to different rates of adsorption and desorption (*e.g.* Barrer *et al.* [13]). However, apparent diffusivities will not differ in the *Henry's* law range of the sorption isotherm even if boundary conditions used for the analysis are not those used in the experiment, although, the value of the diffusivity may still be erroneous. Figure 2 summarises other factors that may be responsible for non-ideal system behaviour in real experiments.

The interrelationship between experiment, data evaluation and theoretical progress is being directed to steadily increase the accuracy of the determination of transport coefficients to prove evidence for the underlying mechanism and to ascertain intrinsic constants for the process under consideration. In this way, the improvement not only allows one to identify diffusional properties, but also to distinguish those from other inherent phenomena and to verify the obtained results by other independent methods. A major direction of further research on fundamentals of sorbate mobility is the understanding of the relationship between transport diffusivity and self-diffusivity or, in general, the elucidation of the interrelationship between non-equilibrium and equilibrium transport parameters during sorption by microporous crystals.

2 Comparison of Batch Methods

The actual discussion of the interaction between refinement of experimental methods and complementary development of corresponding theoretical procedures is based on physical modelling of mass transfer by Fick [48] and on appropriate mathematical solutions given by Fourier [49]. If the concentration a of a fluid within a porous volume V_s is considered, the transport of fluid species therein obeys

$$\frac{\partial}{\partial t}a = \frac{\partial}{\partial x}\left(D\frac{\partial}{\partial x}a\right), \quad t > 0, \quad x \in V_s, \quad (1)$$

with t and x denoting, respectively, time and coordinates in V_s. The coefficient D is called (intracrystalline) *Fickian* diffusivity which, in general, changes with concentration a and temperature T. Initial analytical treatments did not account for these dependences of D. The transport equation was solved for idealised boundary conditions which neglect external contributions to the diffusion system.

2.1 *Asymptotic and Integral Methods*

The solution of the diffusion Eq. (1) for a batch system with limited volume to investigate real kinetics, was known at least since 1928, *cf.* March *et al.* [85], and was tabulated 1930, *cf.* McKay [90]. Asymptotic data evaluation was utilised as the main method until the seventies (*e.g.* Barrer *et al.* [6, 9, 10], Brandt *et al.* [18], Riekert [112], Timofejev [128]). This was due to the belief that 'side' effects could be neglected, *e.g.* diffusion was the presupposed overall dominant rate process, and due to the absence of appropriate computational tools. Most of the asymptotic methods are based on the analytical solution of *Fick's* diffusion law under ideal conditions (no consideration of external mass fluxes), *e.g.* Carslaw *et al.* [31], Crank [36], Jost [68]. Asymptotic *formulae* which are easy to handle, were derived both as the 'square root of time law' (sqr(t) law) (*e.g.* Barrer *et al.* [9]) and as the specific shape of the explicit solution (*e.g.* Prinz *et al.* [107]) which is represented by an exponential series. The sqr(t) law method ensures higher accuracy of results than the asymptote's method does because the highest concentration gradients (*i.e.* highest mass fluxes) occur at the beginning of uptake (*i.e.* in the small time region). For large uptake times, however, vanishing concentration gradients exist. The *formulae* proposed for the calculation of effective diffusivities utilising the half-uptake periods of the sorption curves (*e.g.* Timofejev [128, p. 104]) combine the utilisation of asymptotic behaviour (specific shape of the exponential series) with an integral value which is characteristic of the overall process (the half-uptake period itself). The theory of statistical moments, which also is an integral method, utilises the equality of the moments for a complete analytical solution of the diffusion law and for a measured uptake curve (*e.g.* Dubinin [45], Zikanova [142]). This method is also easy to handle. All *asymptotic and integral methods* show the following common features:

- *Fickian* diffusion is presupposedly the only transport process inside the sorbing medium, and the transport coefficient calculated is independent of the characteristic shape of the uptake curve.
- The theoretical solution for the complete model for the sorption system must be known explicitly, *i.e.* external rate-limiting processes are either neglected or extremely simplified. Therefore, the experimental conditions are assumed to be ideal (often, this implies the assumption of the linearity of the sorption isotherm as well). This ideal consideration has consequences for data evaluation since the experimental data have to be 'purified' from visible apparatus effects (*e.g.* the uptake curves are often cut for small times; however, here the highest mass fluxes and strongest apparatus effects occur).
- The evaluation procedure (as an explicit calculation of one *single* value, only) becomes very simple. The analytical solution, if needed at all, must only be known in tabulated form.

The asymptotic and integral methods have been proven to be insufficient because they presupposedly reduce the transport mechanism to *Fickian* diffusion alone, whereat external influences on sorption runs was completely ignored. Many of discrepancies in molecular mobility characteristics reported in the past seem ascribable to violations of those strong presumptions. Often deviations from pure *Fickian* diffusion were discussed in accord with this argument (Barrer [8], Bülow *et al.* [22], Kärger *et al.* [74], Riekert [112]) and additional evidence was introduced, *e.g.* variation of crystal size as well as of shape and height of particle layer, introduction of heat sinks, *etc.* These additional effects require complete repetitions of whole experimental series varying certain parameters (with respect to which the transport properties have to be invariant). These procedures must be considered as a compulsory expenditure of those evaluation methods.

2.2 *Total Curve Fitting Methods*

Many solutions of *Fick's* second law were developed to quantitatively describe superimposed transport mechanisms such as surface barriers, simultaneous heat transfer or reversible and irreversible (chemical) reactions as well as long-range diffusion (*e.g.* Barrer [8], Carslaw *et al.* [31], Crank [36], Do [41], Dubinin [45], Jordi *et al.* [66, 67], Kärger *et al.* [73], Kocirik *et al.* [80], Lee *et al.* [83], Micke *et al.* [91], Ruckenstein *et al.* [114], Zolotarev *et al.* [144]). For a more realistic description of the complex behaviour in microporous solids, superimposed rate mechanisms have to be considered. This, however, is connected with an increased number of transport coefficients sought, which, in principle, cannot be found by either asymptotic or integral methods. As far as the integral methods are concerned, the number of transport coefficients is coupled with an increase in their order (*e.g.* Tunickij *et al.* [130]). If the specifics of intrinsic kinetic processes are extractably contained in their time dependences, the *shape* of the kinetic curves must comprise the relevant information.

It cannot be extracted, however, from particular instants of a kinetic behaviour, *e.g. Fickian* diffusion and surface barrier penetration may lead to identical values of the first statistical moment of uptake curves without indicating different transport mechanisms. Thus, a complete fit of a theoretical rate curve to the measured uptake data becomes unavoidable, but, in this way, the validity of the underlying mechanisms can be checked rather straightforwardly. The latter ensures a feedback from the calculated results to measured data. This interaction represents an entirely new quality of data evaluation compared with that of asymptotic and integral methods. *Total curve fitting* exhibits the following advantages and disadvantages:

- *Fickian* diffusional transport can be distinguished from additional overlaid rate processes that, in particular, can be identified both qualitatively and quantitatively. The experimental conditions are still assumed as being ideal that leads, in this respect, to similar restrictions as described above.
- For curve fitting purposes, the simulated curve needs not be given explicitly. This theoretical curve has to be calculable at any instant. In general, idealisations mentioned in the previous paragraph are still applied so that the solution becomes explicitly calculable and computational work is drastically reduced (this refers also to implementation of corresponding algorithms).
- Inevitably the method requires the utilisation of computers for evaluation of rate constants. Thus, it needs much more effort than the asymptotic and integral methods do.

2.3 *Total Curve Fitting Method with Consideration of Apparatus Effects*

A disadvantage of the method of *total curve fitting* becomes obvious during the data evaluation procedure, because no *real* apparatus is available for the generation of an *ideal* concentration jump. Just at the moment when highest mass fluxes occur, the apparatus exhibits its strongest deviation from ideal behaviour (this is, in fact, one of the biggest error sources for the sqr(t) derivative approach, widely used as quick evaluation method). Model equations that extend the external mass balance by additional apparatus effects (*cf.* mass balance equations ($\Leftrightarrow$) in Table 1 and the 'Real' items of Table 2), such as finite mass fluxes through valves (which also have a finite response and opening time as well as an own, sometimes variable, dead space, *etc.*), volume changes within finite times, concentration changes within finite periods and others, are known for many years (*e.g.* Syrkin *et al.* [127]). However, to simulate the kinetic process, their introduction into a complete rate model complicates the equation system to a large extent. In general, this results in a system of non-linearly coupled, partial differential equations. Its solution requires sophisticated numerical methods. Such models also have additional advantages, *e.g.* restrictions such as the linearity of the isotherm, the uniform size of the particles, *etc.*, must not be maintained any longer. The *total curve fitting approach including consideration of apparatus effects* shows the following characteristic features:

- Particular rate processes can be fitted over the complete time region of the experiment (that is, without cutting the small-time part of the uptake curve). Especially, *Fickian* diffusional processes can be quantified with high accuracy. It becomes possible to distinguish between both transport processes that were superimposed on *Fickian* diffusion and influences of the apparatus dynamics on the uptake rate.
- Those experimental conditions that are not ideal (*i.e.* that are *real*, indeed) can be treated without additional systematic error in determining transport coefficients. This type of errors might have been generated by apparatus effects, especially, at the beginning of the experiment. Not only is the apparatus effect removed as a disturbance, but the evaluation in the region where the influence of the intrinsic sorption process on the uptake curve is the highest, is also included into data evaluation. Furthermore, one can recognise whether or not an apparatus effect dominates the uptake curve and, thus, the determination of the transport coefficients becomes either impossible or too inaccurate.
- The theoretical curve has again to be calculated at any instant of the experimental period. No case is yet known (to the authors' knowledge), for which the solution of such a model system would have been obtained explicitly as a closed *formula*. However, the computational effort increases tremendously compared to the case without consideration of disturbances caused by apparatus. This has to be paid for removing such disturbances and for higher accuracy.
- The introduction of non-linear isotherms into the complete model of the sorption system requires careful fitting of equilibrium data that has to be done over the complete concentration region to be investigated.
- In addition to the intrinsic uptake curve fitting, the parameters that describe the apparatus (*e.g.* delay

times, finite valve capacity, *etc.*) have to be determined from data of blank experiments, in general. With respect to a certain fluid, this is needed only once for a given apparatus and for a given type of sorbing species over the considered pressure and temperature domains.

2.4 *Total Curve Fitting Method with Full Parameter Region Consideration*

The advantage to recognise an additional transport process superimposed on *Fickian* diffusion is connected with an increase of the number of parameters that have to be determined. In the case of a complex sorption rate process for a single fluid component, the number of parameters is always higher than the number of measured uptake curves. This increased number does not allow determination of the transport coefficients from the data yielded from only one experimental run without additional information that is necessary to complete the model equations to a fully determined system. Such additional information is either given *a priori* (*e.g.* by previous experimental runs under similar conditions or by complementary experiments) or it may stem from additional equations that should be valid for the same experimental run. To exemplify the latter, in the case of heat transfer that occurs simultaneously with mass transport, the (sorbent particle) temperature *vs.* time dependence can be measured and, for the general fitting procedure, the heat balance should be accounted for to fit the temperature *vs.* time curve. Independent information may also stem from additional equations that must be valid over the concentration domain considered (*e.g.* for certain sorption systems, the *Barrer* constant-jump-length model that leads to an affine linear dependence of diffusivity on concentration). Total curve fitting in this full parameter region has the advantage that one can recognise certain microphysical peculiarities of molecular transport (*e.g.* Micke *et al.* [95]). Such analysis leads to inverse mathematical problems, the solution of which requires considerable computational effort. Using manual procedures of curve-by-curve fitting imposes manifold complete calculation runs over the entire region of parameter, *e.g.* concentration, until a decision can be taken on whether or not the additional equations assumed were valid. The *full parameter region total curve fitting* shows the following characteristic features in addition to the ones described above for the total curve fitting:

- Particular rate processes can be fitted both over the complete time domain of the experiment and over the entire concentration region or over a certain temperature region. This fitting method should be considered as an indivisible procedure (in contrast to the consideration of *single* experiments, only) which requires additional physical information to explain the underlying process. Especially, for pure *Fickian* diffusion, this procedure reduces to the proof of a particular underlying microphysical mechanism (*Barrer* constant-jump-length model [8, p. 302], the free volume theory modified for zeolites, Kärger *et al.* [76], the modified *Eyring* transition-state theory, Kärger *et al.* [75] or other microphysical rate models).
- Physically plausible concentration and temperature dependences of rate constants for superimposed mechanisms, which were extracted from the overall uptake process observed macroscopically, become available (*e.g.* Micke *et al.* [95, 96]). The relevance of these dependences becomes comparable with that of the information on equilibrium states. Those are comprehensive with respect to a single experimental uptake run.
- Not only does the computational effort compared with that for total curve fitting increase, but the data evaluation process itself becomes investigative. The particular steps of this fitting procedure require highly sophisticated numerical algorithms.

2.5 *Total Curve Fitting Method for Mixture Kinetics*

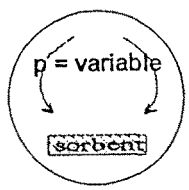
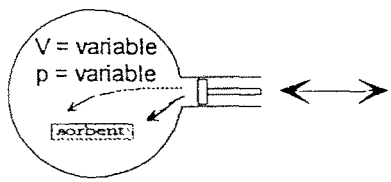
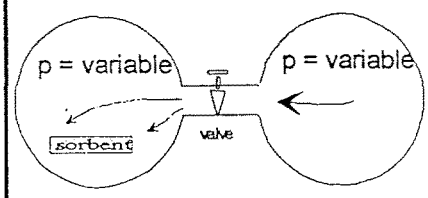
In the case of a single kinetic mechanism for a mixture, the number of parameters is always higher than the number of measured uptake curves of one experimental run, even if pure *Fickian* diffusion of the mixture occurs. The *Fick's* second law obtains the following shape:

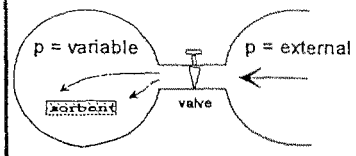
$$\frac{\partial}{\partial t}a_i = \sum_{j=1}^{N}\frac{\partial}{\partial x}\left(D_{ij}\frac{\partial}{\partial x}a_j\right),\ i = 1(1)N,$$

$$i.e.\ \ \frac{\partial}{\partial t}a = \frac{\partial}{\partial x}\mathcal{D}\frac{\partial}{\partial x}a,\ t > 0,\quad x \in V_s, \qquad (2)$$

where $\mathcal{D} = \{D_{ij}\}_{i,j=1}^{N}$ denotes the matrix of diffusion coefficients (*cf.* Kärger *et al.* [72], Marutovsky *et al.* [89], Micke *et al.* [92], Qureshi *et al.* [108]) and $a = \{a_i\}_{i=1}^{N}$ stands for the vector of partial concentrations. Already for pure *Fickian* diffusion of a binary mixture ($N = 2$), the inherent four diffusivity parameters (if the complete model with non-vanishing cross-coefficients

Table 1: Batch methods, their (symbolic) gas phase mass balances in sorption cell (⇔), principal advantages (⬀) and disadvantages (⬂) and applicability to ***Fickian*** diffusion of mixtures (⇳)

 Ideal closed arrangement	⬀: - Closed mass balance - No apparatus effects - Explicit solutions available (***Henry*** isotherm) ⬂: - Not practicable ⇳: - General solution available ⇔: $\frac{V_v}{R\,T}\frac{d}{d\,t}p + V_s\frac{d}{d\,t}\bar{a} = 0$
 Frequency response method (FRM) Single step method (piezometric)	⬀: - Closed mass balance - Full repeatability of adsorption and desorption runs - Deviations from pure ***Fickian*** diffusion directly detectable - Differential measurements near to equilibrium ⬂: - Limited to sufficiently low concentration ⇳: - Predestined for co-diffusion; counter-diffusion not practicable - No access to partial concentrations (FRM) ⇔: $\frac{d}{d\,t}\left(V_v\,p\right) + R\,T\,V_s\frac{d}{d\,t}\bar{a} = 0$
 Constant volume / variable pressure method (piezometric)	⬀: - Closed mass balance - Applicable to broad concentration ranges - Differential concentration mode can easily be adapted to isotherm shape ⬂: - Valve influences (dead volume, finite capacity and time delay) cannot be neglected ⇳: - Co-diffusion and counter-diffusion without restriction practicable ⇔: $\frac{V_v}{R\,T}\frac{d}{d\,t}p + V_s\frac{d}{d\,t}\bar{a} = J_{valve}\left(t\,,\,p(\,t\,)\right)$



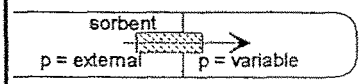
Constant pressure method (gravimetric)

- Open mass balance compensated by direct measurement of sorbed amount
- Predestined for long-time observations
- Differential concentration mode can easily be adapted to isotherm shape

- Mechanical weighing required (oscillations)
- Not suitable for fast processes

- No access to partial concentrations

$$\Leftrightarrow: \frac{V_v}{R\,T}\frac{d}{d\,t}p + V_s\frac{d}{d\,t}\bar{a} = J_{valve}\left(t, p(t)\right)$$



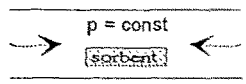
Monocrystal permeation method*

- Direct measurement of mass flux through the crystal
- Apparatus effects almost excluded

- Sorbent deployment reduces the applicability to sufficiently large monocrystals
- Open mass balance
- Information refers to one (single) crystal
- Superimposed transport mechanisms hardly be identified

- Counter-diffusion experiments hardly be carried out

$$\Leftrightarrow: \frac{V_v}{R\,T}\frac{d}{d\,t}p = J_{sorbent}\left(t, p(t)\right)$$



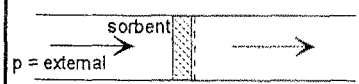
Ideal open arrangement

- No apparatus effects
- Explicit solutions available for many transport mechanisms
- Kinetic process completely independent of isotherm

- Not practicable

- Explicit solutions available

$$\Leftrightarrow: \frac{d}{d\,t}p = 0$$



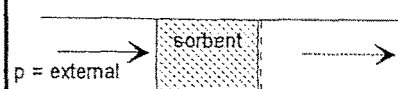
'Zero' length column method (ZLC)
IRFT method

- Heat influences can be excluded
- Open mass balance is compensated by direct measurement of sorbed amount (IRFT)
- direct quantitative concentration measurement (IRFT)
- direct observation of immobilisation processes (IRFT)

- Open mass balance
- Maintenance of constant partial pressures
- Transport coefficient only for 'zero' loading (ZLC)
- Limited to *Henry* region (ZLC)
- Application to desorption processes (ZLC)
- Limited to sufficiently high concentration of IR sensitive components (IRFT)

- No additional restrictions

$$\Leftrightarrow: V_v\frac{d}{d\,t}c + V_s\frac{d}{d\,t}\bar{a} = \beta\,(c_0 - c)$$



Finite column length method

- Measurement under practice-relevant conditions

- Overlaid transport mechanisms not recognisable
- Determination of overall transport parameters
- Column parameters difficult to estimate (e.g. dispersion, convection, long-range diffusion)
- Maintenance of constant partial pressures
- Linear isotherm region required

- No further restrictions

$$\Leftrightarrow: V_v\frac{d}{d\,t}c + u\frac{d}{d\,x}c - E\frac{d^2}{d^2x}c + V_s\frac{d}{d\,t}\bar{a} = 0$$

Disadvantages ( ) hold for mixtures ( ) anyway, but advantages ( ) may become restricted.

*For further permeability and membrane measurements, *cf.* Kärger *et al.* [73].

Table 2. Batch methods and model approaches to transport coefficients (fundamentals (Theory); evaluation with ideal conditions (Ideal); evaluation with real apparatus effects (Real)).

Experimental method	References
Ideal closed arrangement	Theory: 31_T, 36_T, 68_T, 85_T
Frequency response method Single step method (piezometric)	Theory: 15_T, 16_A, 67_I, 98_T, 99_I, 137_I^M, 138_I Ideal: 30_A, 67_I, 131_I, 139_I Real: 109_I, 124_I, 137_I
Constant volume/variable pressure method (piezometric)	Theory: 12_T, 22_I, 92_T^M, 95_T, 96_T, 123_I Ideal: 9_I, 22_I, 23_I, 52_I, 55_T, 132_I, 141_I Real: 20_I, 27_I, 29_I, 95_T, 96_T
Constant pressure method (gravimetric)	Theory: 8_I, 36_I, 43_I, 73_I, 88_I^M, 118_I Ideal: 8_I, 46_A, 52_A, 107_A, 118_I, 141_I Real: 120_I.
Permeation method	Theory: 1_A, 3_A^M, 4_A, 7_A, 11_A Real: 1_A, 11_A, 104_A, 119_A, 133_A
Ideal open arrangement	Theory: 51_A, 86_A^M, 89_I^M, 144_I
'Zero' length column method (ZLC) IRFT method	Theory 47_A, 73_A, 94_T, 97_T Ideal: 63_A, 70_A^M, 100_A^M, 101_A^M, 102_A, 115_A, 117_A, 121_A Real: 94_T, 97_T, 100_T^M
Finite column length method Pulse chromatographic	Theory: 17_I^F, 40_I, 56_I, 60_I^M, 72_I^M, 89_I^M, 118_I, 126_I Ideal: 28_I^M, 50_I, 54_I, 69_A^M, 72_I^M, 84_A, 86_I^M, 89_I^M, 113_I, 116_I^M, 126_I Real: 34_I^M, 35_I, 61_I^M

$\cdots_A$ Asymptotic data evaluation (*e.g.* sqr(t) derivative fitting) $\cdots^M$ Mixture kinetics treatment
$\cdots_I$ Integral data evaluation (*e.g.* statistical moment fitting) $\cdots^F$ Data evaluation in the frequency domain
$\cdots_T$ Total curve fitting

†Quotations serve as examples without intention for completeness.

is considered) have to be determined from even four measured uptake curves, *i.e.* from two experimental runs which deliver independent, complementary uptake curves (*e.g.* two counter-diffusion runs). The case of mixture kinetics leads to an analogous situation as mentioned in the previous paragraph but with different parameters. Since the influences of the apparatus on the rate curves have to be carefully analysed already for single component kinetics, it becomes understandable, that for mixtures a full control of those effects represents an unalterable prerequisite. Furthermore, a sufficiently correct determination of mixture equilibrium data themselves is quite a strong challenge. *Total curve fitting for mixture kinetics* shows the following characteristic feature:

- The iterative fitting process which was considered as an indivisible procedure for single component uptake process analysis for a full parameter region dependence has now to be applied to the determination of only one single matrix of diffusion coefficients.

This demands to carry out N independent sorption kinetic runs for a mixture with N components (to fit N^2 free parameters) Cussler [37], Marutovsky *et al.* [87], Micke *et al.* [92] if only *Fickian* diffusion is the rate-governing mechanism.

Many questions should be answered before the analysis of complex kinetic mechanisms as done for single component kinetics on molecular sieves may be posed. To these belong the following:

- How should particular kinetic runs be chosen (concentration batches) to ensure the resulting uptake data being independent of each other so that the determination of the matrix $\mathcal{D}$ becomes possible (*e.g.* Hu *et al.* [61], Karge *et al.* [70, 100, 101]);
  Is there an optimum experiment design to achieve a maximum of information;
- Are the straight coefficients D_{ii}, i = 1(1)N, identical with the corresponding single component diffusion coefficients; and does, therefore, the underlying *Fickian* transport model correctly explain mix-

Table 3. Comparison of diffusivities for the system benzene/gallosilicate at 323 K and at 0.350 mmol/cm^3 calculated by means of various evaluation methods.

Method	Diffusivity
Asymptotic, large times[a]	0.8 10^{-14} m^2/s
Asymptotic, small times[a,b]	2.3 10^{-14} m^2/s[b]
Statistical moments method[a]	1.9 10^{-14} m^2/s
Curve fitting without account for apparatus effect[a,b]	2.6 10^{-14} m^2/s
Curve fitting with account for apparatus effect[c]	3.5 10^{-14} m^2/s

[a]Use of the idealised solution for variable boundary conditions in a closed volume and for spherical particle shape
[b]Values depend on arbitrarily chosen cutting bounds
[c]Utilisation of the *Volterra* integral equation technique (software package ZEUS [26])

ture kinetics (*cf.* Krishna [81], Marutovsky *et al.* [87], Yang [134]);

- Are the cross-coefficients D_{ij}, i, j = 1(1)N, i $\neq$ j, always positive, are they symmetric and, moreover, are they invariant with respect to the number N of components?

3 Exemplification of the Approach

In the light of the foregoing, macroscopic sorption uptake rate data will now be analysed. An advanced determination of transport coefficients will be illustrated for the following systems:

* Benzene/MFI-type gallosilicate (twinned epipedonal crystals sized 15 μm $\times$ 6 μm $\times$ 6 μm; both measured data and evaluation described in Micke *et al.* [93]).
* p-Ethyltoluene/Na,H-ZSM-5 zeolite (twinned epipedonal crystals sized 14 μm $\times$ 6.5 μm $\times$ 4.5 μm; measured data and their evaluation given in Bülow *et al.* [95]).
* n-Hexane/silicalite-I (rod-like monocrystals with an average thickness of 41 μm; for details, *cf.* Micke *et al.* [96]).

All uptake data were obtained piezometrically (at constant-volume/variable-pressure conditions, *cf.* Table 1). Pressure *vs.* time dependences were monitored in the doser volume of the experimental arrangement.

For purposes of this paper, emphasis will be placed on data evaluation, *i.e.* their results will neither be interpreted nor discussed deeper than intrinsic evaluation procedures do require. As far as an explanation of different mechanisms involved in the diffusion of the three sorbates in MFI-type molecular sieves is concerned, the study of the original papers cited is recommended.

3.1 System Benzene/MFI-type Gallosilicate

Assuming the validity of *Fick's* second law with constant diffusivity, *i.e.* Eq. (1) becomes reduced to

$$\frac{\partial}{\partial t}a = D\frac{\partial^2}{\partial^2 x}a, \quad t > 0, \quad x \in V_s, \tag{3}$$

and neglecting in a first instance the influence of the apparatus dynamics on sorption uptake rate, the measured data could be evaluated by means of the solution for Eq. (3) under variable boundary conditions (finite sorption volume).

Figures 3 and 4 illustrate a particular, typical experimental uptake pattern obtained for this system, both as a semilogarithmic plot and with linear scaling of pressure, respectively. For comparison, data evaluation as mentioned is indicated in those figures. It takes place by means of asymptotic procedures for either large (Fig. 3) or small times (Fig. 4; sqr(t) approach). However, the evaluation method to be utilised, allows one to distinguish between the intrinsic sorption process and the apparatus dynamics.

Table 3 demonstrates that in the case of pure *Fickian* diffusion, identical diffusivity values become available by all methods considered. The *total curve fitting method* allows one to check for the adequacy of the model.

As follows from data analysis by *full concentration region total curve fitting,* a diffusional mechanism is characteristic of the sorption uptake over the entire concentration (and temperature) region. This mechanism agrees with the *Barrer* constant-jump-length

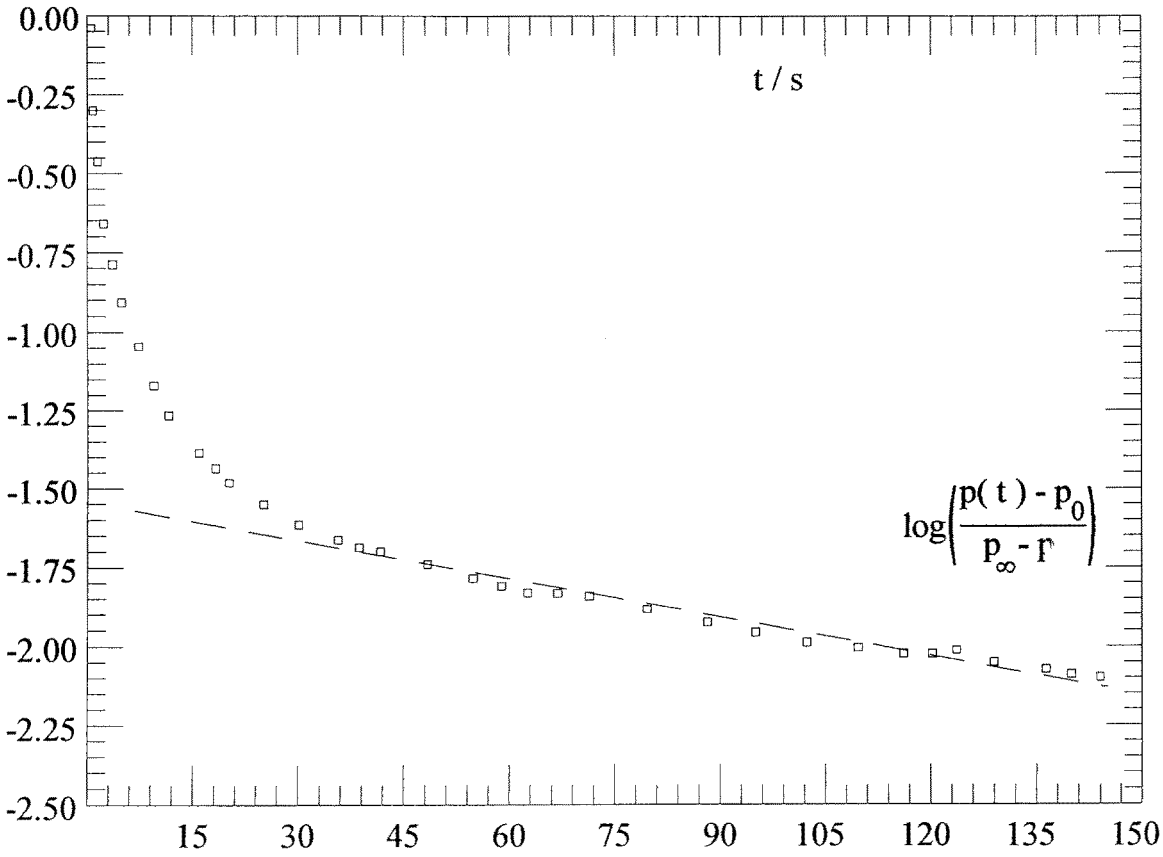


Fig. 3. Semilogarithmic plot of normalised experimental uptake rate data (□) for the system benzene/gallosilicate at 323 K and comparison with the result of asymptotic evaluation (fitted straight line for $a = 0.350$ mmol/cm^3).

model,

$$D_0 = D^* e^{-\frac{E}{RT}}(1-\theta), \quad \theta = \frac{a}{a_\infty}, \tag{4}$$

for which $D^* \approx 2.6 \times 10^{-10}$ m^2/s and $E \approx 26$ kJ/mol were found (*cf.* Fig. 5). Equation (4) is also fulfilled with respect to the temperature dependence (*cf.* Bülow *et al.* [93]). The verification by the method of *full concentration region total curve fitting* leads to the proof of evidence for the underlying rate mechanism.

3.2 *System p-Ethyltoluene/Na,H-ZSM-5*

As it follows from Table 4, *asymptotic and integral methods* do neither lead to correct diffusivity data nor do they recognise the non-equilibrium surface barrier penetration as transport mechanism additional to intracrystalline diffusion.

In this case, the application of the method of *full concentration region total curve fitting* is based on the affine linear dependence of the barrier coefficient α on equilibrium pressure,

$$\alpha = k_a p + k_d. \tag{5}$$

The evidence for the underlying rate mechanism, *i.e. Fickian* diffusion superimposed by non-equilibrium surface barrier, is proven by the validity of Eq. (5) as shown in Fig. 6.

This example demonstrates that in cases where mechanisms more complex than *Fickian* diffusion, occur, *asymptotic and integral methods* fail because of lack of appropriate feedback.

3.3 *System n-Hexane/Silicalite-I*

Considering the occurrence of a complex rate mechanism comprising *Fickian* diffusion superimposed by intracrystalline molecular immobilisation/mobilisation processes, described by

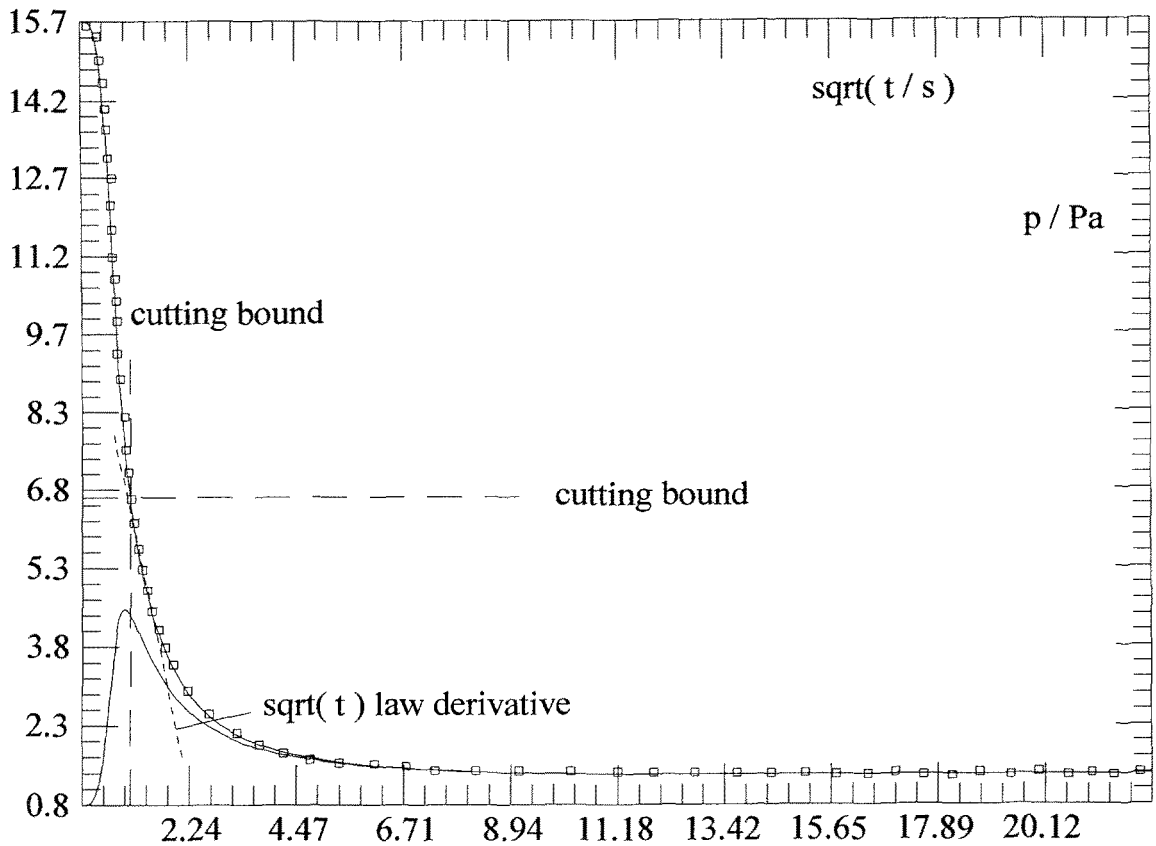


Fig. 4. Experimental uptake rate data (□) for the system benzene/gallosilicate at 323 K (*cf.* Fig. 3), the sqr(t) law fit(..) with cutting bounds (— —) and the result of complete modelling (*Fickian* diffusion and apparatus dynamics).

$$\begin{aligned} \frac{\partial}{\partial t}a &= D\frac{\partial^2}{\partial^2 x}a - \frac{\partial}{\partial t}u, \\ \frac{\partial}{\partial t}u &= k_{au}(u_\infty - u)a \qquad t > 0,\ x \in V_s, \quad (6) \\ &\quad - k_{ua}(a_\infty - a)u, \end{aligned}$$

and accounting for the apparatus dynamics as well, a high-quality fit of the experimental uptake rate curves of the system n-hexane/silicalite-I becomes possible (*cf.* Micke *et al.* [96]). In Eqs. (6), a and u stand for the respective fractions of "mobile" and "immobile" sorbate molecules within the molecular sieve structure, a_∞ and u_∞ designate their corresponding concentrations at sorbent saturation for the temperature given, and k_{au} and k_{ua} denote, respectively, the rate constants for immobilisation and mobilisation in the bulk of molecular sieve crystals. The constancy of the diffusivity D follows from the underlying lattice model (*cf.* Kocirik *et al.* [79]).

The following equations are valid for the rates of immobilisation and mobilisation, respectively,

$$\lambda(\theta_{a+u}) = \frac{k_{au}u_\infty}{1-\frac{1}{2\sigma}\left\{(1-\mathcal{K})(\theta_{a+u}+\sigma)+\mathcal{K}-\sqrt{((1-\mathcal{K})(\theta_{a+u}+\sigma)+\mathcal{K})^2-4\sigma(1-\mathcal{K})\theta_{a+u}}\right\}} \quad (7)$$

for the immobilisation rate and

$$\mu(\theta_{a+u}) = k_{ua}a_\infty\left[1-\frac{1}{2\sigma}\left\{(1-\mathcal{K})(\theta_{a+u}+\sigma)+\mathcal{K} - \sqrt{((1-\mathcal{K})(\theta_{a+u}+\sigma)+\mathcal{K})^2-4\sigma(1-\mathcal{K})\theta_{a+u}}\right\}\right] \quad (8)$$

for the mobilisation rate, where

$$\mathcal{K} = \frac{k_{au}}{k_{ua}}, \quad \sigma = \frac{a_\infty}{a_\infty + u_\infty} \text{ and } \theta_{a+u} = \frac{a^* + u^*}{a_\infty + u_\infty}. \quad (9)$$

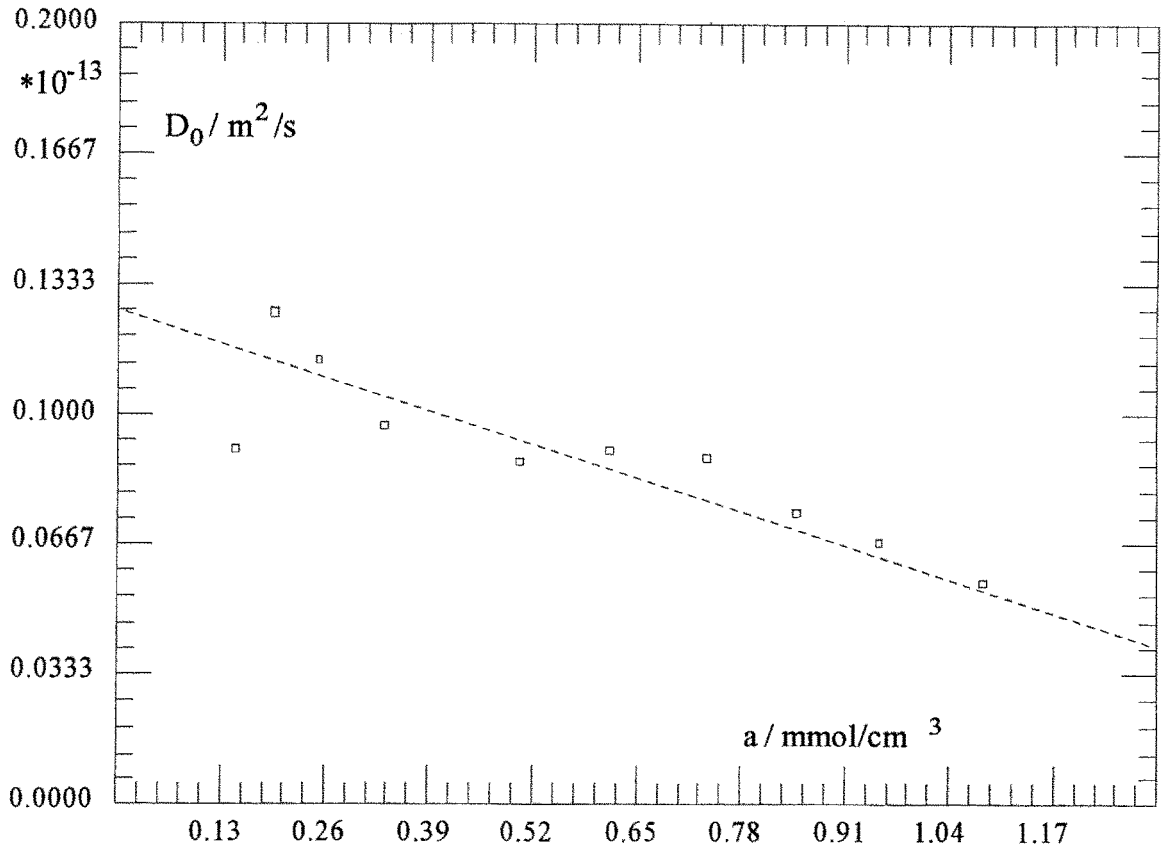


Fig. 5. Linear plot of D_0 *vs.* equilibrium concentration a of the system benzene/MFI-type gallosilicate at 323 K.

Table 4. Comparison of transport coefficients for the system *p*-ethyltoluene/Na,H-ZSM-5 at 343 K and at $a = 0.380$ mmol/cm^3 calculated by means of various evaluation methods.

Method	Diffusivity	Barrier coefficient α (cf. Fig. 6)
Asymptotic, large times[a]	0.9 10^{-13} m^2/s	not recognisable
Asymptotic, small times[a,c]	0.1 10^{-13} m^2/s	not recognisable
Statistical moments method[a]	0.3 10^{-13} m^2/s	not recognizable
Curve fitting without account for apparatus effect[a,c]	0.9 10^{-13} m^2/s	1.9 m/s
Curve fitting with account for apparatus effect[b]	1.3 10^{-13} m^2/s	2.1 m/s

[a]Use of the idealised solution for variable boundary conditions in a closed volume and for spherical particle shape
[b]Utilisation of the *Volterra* integral equation technique (software package ZEUS [26])
[c]Values depend on arbitrarily chosen cutting bounds

To describe the uptake behaviour of the system under consideration at a given temperature, besides the constancy of the *Fickian* diffusivity D over the full region of sorbate concentration, the product $\lambda\mu$ of the rates of immobilisation and mobilisation has also to be invariant with respect to concentration. The dependences given in Eqs. (7) and (8) are obeyed, as shown in Fig. 7. Over the entire concentration region, the *Fickian* diffusivity for n-hexane in silicalite-I at 323 K is independent of concentration and amounts to $D = 5.0 \times 10^{-10}$ m^2/s.

The quantitative data obtained are compared in Table 5. Data evaluation by *asymptotic and integral methods* breaks down. They yield apparent rate constants that are remarkably discrepant to the state-

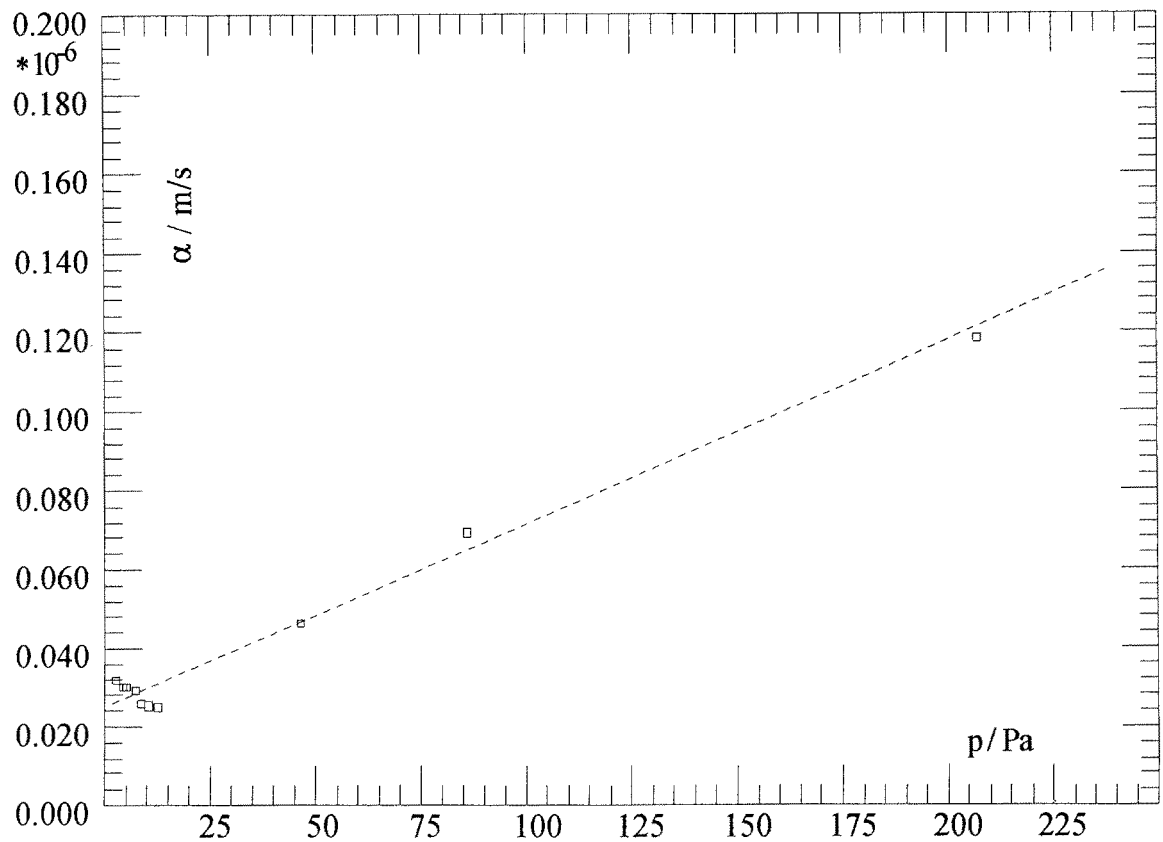


Fig. 6. Barrier coefficient α *vs.* equilibrium pressure p_∞ of the system p-ethyltoluene on Na,H-ZSM-5 at 343 K.

Table 5. Comparison of transport coefficients for the system *n*-hexane/silicalite-I at 323 K and at $a = 1.00$ mmol/cm^3 calculated by means of various evaluation methods.

Method	Diffusivity	Immobilisation
Asymptotic, large times[a]	$4.0\ 10^{-13}$ m^2/s	not recognisable
Asymptotic, small times[a,e]	$4.0\ 10^{-11}$ m^2/s[b]	not recognisable
Statistical moments method[a]	$3.2\ 10^{-12}$ m^2/s	not recognisable
Curve fitting with account for apparatus effect[a,f]	$2.0\ 10^{-12}$ m^2/s	neglected
Curve fitting without account for apparatus effect[a,e]	$1.5\ 10^{-10}$ m^2/s	$\lambda = 1.2$ l/s[c] $\mu = 0.04$ l/s[c]
Curve fitting without account for apparatus effect[d]	$5.0\ 10^{-10}$ m^2/s	$\lambda = 0.9$ l/s $\mu = 0.025$ l/s

[a]Use of the idealised solution for variable boundary conditions in a closed volume and for spherical particle shape

[b]In good accordance with the diffusivity for the full fit due to a small influence of the process of immobilisation at the beginning of the experiment

[c]Due to an increase of the inaccuracy of measurement for small times, a curve fitting like that as given in Fig. 3 (*cf.* eqs. (4) and (5)) was impossible

[d]Utilisation of the *Volterra* integral equation technique (software package ZEUS [26])

[e]Values depend on quite arbitrarily chosen cutting bounds

[f]Additional process becomes visible, but poor data fitting due to missing quantification

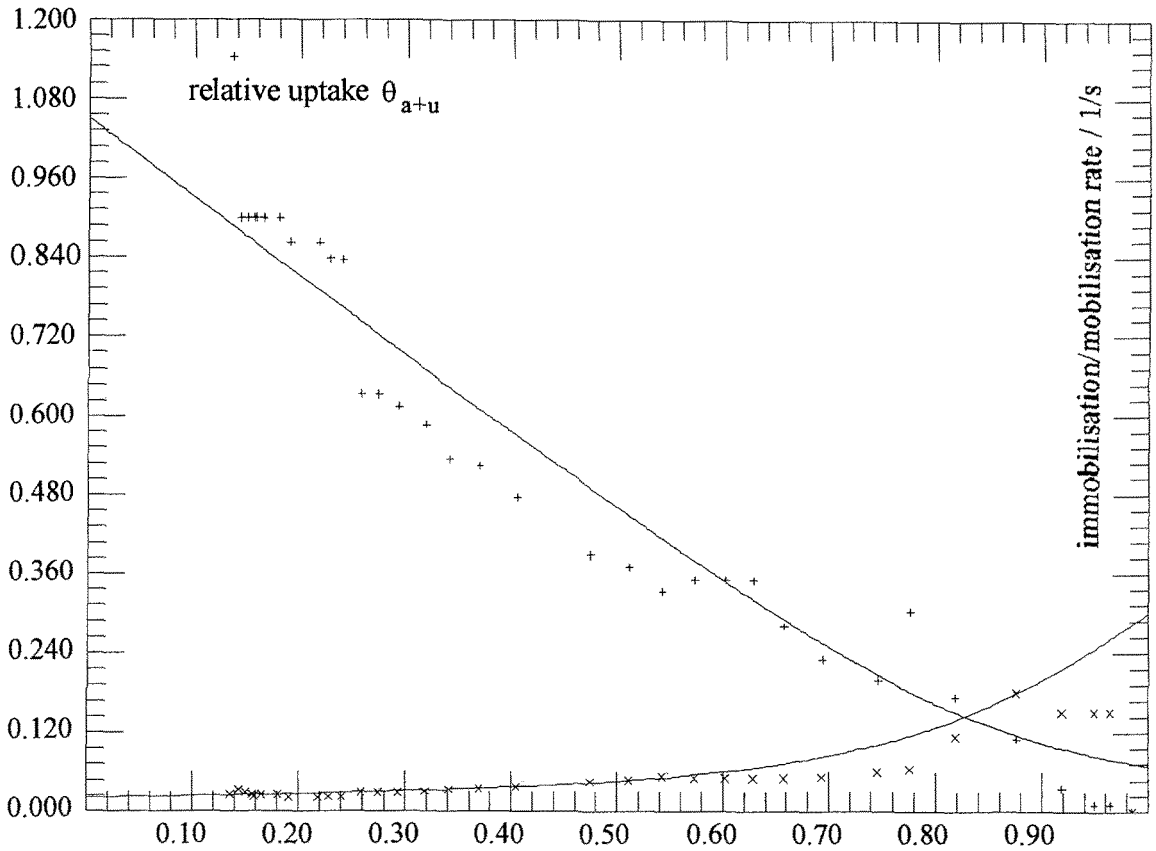


Fig. 7. Concentration dependences of rates of immobilisation (+) and mobilisation (×) for the system n-hexane /silicate-I at 323 K and the fit (−) of these functions by Eq. (7) with $K = 15$; $\sigma = 0.2$; $\lambda(0) = k_{au}u_\infty = 1.05$ 1/s and $\mu(0) = k_{ua}a_\infty = 0.02$ 1/s.

of-art diffusivity values ($D = 5.0 \times 10^{-10}$ m^2/s). The discrepancy in diffusivity values amounts to up to three orders of magnitude, *i.e.* tremendous errors which result from the utilisation of simplified models become obvious. Moreover, there is no way to recognise the constituents of complex rate mechanisms by such models, *e.g. Fickian* diffusion coupled with intracrystalline molecular immobilisation/ mobilisation.

4 Conclusions

Various levels of sophistication of data evaluation for non-equilibrium sorption results obtained by means of batch methods are possible. As long as one is dealing with pure *Fickian* (intracrystalline) diffusion in microporous sorption systems under ideal experimental conditions only, all the necessary information on the molecular mobility is available straightforwardly from segments (*asymptotic methods*), or from low-order statistical moments (*integral methods*) of sorption rate, *e.g.* uptake curves.

However, for evaluation of sorption kinetic data as experimentally obtained by macroscopic transient techniques, the state-of-art procedure *full curve fitting* over the complete time axis of the experiment and over the *full concentration region* is preferred. This method requires not only exact knowledge of both the apparatus dynamics, but also the availability of sophisticated, physically based mathematical models that take into account the complexity of the rate processes occurring simultaneously on the primary sorbent particle level. In contrast to the evaluation of *single experiments* only, which, unfortunately, is still the most frequent approach to sorption kinetics, additional physical information to explain the inherent *Fickian* diffusional process becomes necessary. Otherwise, modelling and quantitative characterisation of superimposed rate mechanisms will hardly be satisfactory. Information to explain the intracrystalline diffusional process may often be available from other experiments such as self-

diffusion measurements that give reliable information on intracrystalline mobility for many systems of practical interest.

Physically plausible concentration and temperature dependences of the rate constants for superimposed mechanisms, which were extracted from the overall uptake process observed macroscopically, become available. Most of these phenomena that cannot be observed yet by either modern self-diffusion methods or mathematical experiments, due to both their physical nature and time constants, are, of significant cognitive value. On the other hand, the *full concentration region total uptake curve fitting* asks for highly sophisticated numerical algorithms. The computational expenses compared with those for single total concentration curve fitting procedures increase considerably. For both cases, particular information on all external disturbances, *e.g.* apparatus dynamics, which may be rate-influencing is needed. Research in this field may indicate unforeseen ways to practical utilisation of composite rate processes that take place in microporous solids.

A state-of-art determination of the transport coefficients is possible by means of advanced experimental techniques together with the modern tools of data evaluation. The concept of *full concentration region total uptake curve fitting* is exemplified for various systems. Their uptake rate behaviour can comprehensively be understood only in conformity with more general theories. For example, the rate behaviour of the system *n*-hexane/silicalite-I can be explained as a superposition of *Fickian* diffusion and intracrystalline molecular immobilisation/mobilisation processes. The intracrystalline diffusion coefficient derived from this confirms spectroscopic self-diffusivity data in contrast to methods that neglect such additional transport process. Probably, many other microporous systems show similar complex sorption rate patterns for the quantitative description of which the above considerations become mandatory.

Although much work has already been done in case of mixture kinetics, the interplay between experimental research, theory and data evaluation in this field is still in its early stages and no conclusions similar to those for single component systems can be drawn as yet.

5 Nomenclature

a	Sorbate concentration	$\langle mol/m^3 \rangle$
a_∞	Sorbate concentration at equilibrium state	$\langle mol/m^3 \rangle$
$\bar{a}$	Average sorbate concentration	$\langle mol/m^3 \rangle$
a_∞	Sorbate saturation concentration	$\langle mol/m^3 \rangle$
c	Gas phases concentration	$\langle mol/m^3 \rangle$
c_0	Initial gas phase concentration	$\langle mol/m^3 \rangle$
D	Transport diffusivity	$\langle m^2/s \rangle$
D_0	diffusivity corrected by the *Darken* equation	$\langle m^2/s \rangle$
D^*	Proportional factor of the Barrer constant-jump-length model	$\langle m^2/s \rangle$
E	Dispersion in the column	$\langle m^2/s \rangle$
E	Activation energy	$\langle J/mol \rangle$
J_{valve}	Mass flux through the valve	$\langle mol/s \rangle$
$J_{sorbent}$	Mass flux through the sorbent membrane	$\langle mol/s \rangle$
k_{au}, k_{ua}	Rate constants for immobilisation ($a \rightarrow u$) and mobilisation ($u \rightarrow a$)	$\langle m^3/mol\ s \rangle$
$\mathcal{K}$	Ratio of rate constants for immobilisation and mobilisation	$\langle\rangle$
p	Pressure	$\langle Pa \rangle$
p_∞	Equilibrium pressure	$\langle Pa \rangle$
R	Universal gas constant, ≈ 8.31431	$\langle J/mol\ K \rangle$
t	Time	$\langle s \rangle$
T	Temperature	$\langle K \rangle$
u	Concentration of immobilised sorbate	$\langle mol/m^3 \rangle$
u_∞	Equilibrium concentration of immobilised sorbate	$\langle mol/m^3 \rangle$
$\bar{u}$	Average concentration of immobilised sorbate	$\langle mol/m^3 \rangle$
u_∞	Saturation concentration of immobilised sorbate	$\langle mol/m^3 \rangle$
u	Convection in the column	$\langle m/s \rangle$
V_s	Sorbent volume	$\langle m^3 \rangle$
V_v	Volume of the sorption zone	$\langle m^3 \rangle$
x	Space co-ordinate	$\langle m \rangle$
α	Surface barrier penetration coefficient	$\langle m/s \rangle$
λ	Linearised rate constant of sorbate immobilisation process	$\langle 1/s \rangle$
μ	Linearised rate constant of sorbate immobilisation process	$\langle 1/s \rangle$
θ	Normalised concentration given as index	$\langle\rangle$
σ	Relative immobilisation rate at saturation state	$\langle\rangle$

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