

## Pulse experiments over catalyst beds : a windows of measurable reation rate coefficients

**Citation for published version (APA):**

Huinink, J. P., Hoebink, J. H. B. J., & Marin, G. B. M. M. (1996). Pulse experiments over catalyst beds : a windows of measurable reation rate coefficients. *Canadian Journal of Chemical Engineering*, 74(5), 580-586. <https://doi.org/10.1002/cjce.5450740505>

**DOI:**

[10.1002/cjce.5450740505](https://doi.org/10.1002/cjce.5450740505)

**Document status and date:**

Published: 01/01/1996

**Document Version:**

Publisher's PDF, also known as Version of Record (includes final page, issue and volume numbers)

**Please check the document version of this publication:**

- A submitted manuscript is the version of the article upon submission and before peer-review. There can be important differences between the submitted version and the official published version of record. People interested in the research are advised to contact the author for the final version of the publication, or visit the DOI to the publisher's website.
- The final author version and the galley proof are versions of the publication after peer review.
- The final published version features the final layout of the paper including the volume, issue and page numbers.

[Link to publication](#)

**General rights**

Copyright and moral rights for the publications made accessible in the public portal are retained by the authors and/or other copyright owners and it is a condition of accessing publications that users recognise and abide by the legal requirements associated with these rights.

- Users may download and print one copy of any publication from the public portal for the purpose of private study or research.
- You may not further distribute the material or use it for any profit-making activity or commercial gain
- You may freely distribute the URL identifying the publication in the public portal.

If the publication is distributed under the terms of Article 25fa of the Dutch Copyright Act, indicated by the "Taverne" license above, please follow below link for the End User Agreement:

[www.tue.nl/taverne](http://www.tue.nl/taverne)

**Take down policy**

If you believe that this document breaches copyright please contact us at:

[openaccess@tue.nl](mailto:openaccess@tue.nl)

providing details and we will investigate your claim.

# Pulse Experiments over Catalyst Beds: A Window of Measurable Reaction Rate Coefficients

J. P. HUININK<sup>1</sup>, J. H. B. J. HOEBINK\* and G. B. MARIN

Eindhoven University of Technology, Laboratorium voor Chemische technologie,  
P.O. Box 513, 5600 MB Eindhoven, The Netherlands

The elimination of concentration profiles in porous catalyst pellets is not straightforward for transient kinetic experiments since profiles may arise from limited diffusion rates, but also from accumulation in the pellets. For TAP pulse experiments, dominated by Knudsen diffusion on the reactor scale, intrapellet diffusion is typically instantaneous for industrial catalysts. The Knudsen diffusivity for beds of porous pellets can be calculated from its value for non-porous pellets by accounting for the intrapellet porosity. The window of measurable rate coefficients is governed by a Damköhler number of the first type. A criterion is derived for experimental conditions, that allow intrinsic kinetic measurements with porous catalysts. The size of the admitted pulse should be sufficiently large to avoid pulse depletion by adsorption.

L'élimination des profils de concentration dans des pastilles de catalyseur poreux n'est pas simple dans les expériences de cinétique transitoire du fait que les profils peuvent venir de vitesses de diffusion limitées, mais également de l'accumulation dans les pastilles. Pour les expériences d'impulsion TAP, dominées par la diffusion de Knudsen à l'échelle du réacteur, la diffusion à l'intérieur des pastilles est typiquement instantanée avec les catalyseurs industriels. La diffusivité de Knudsen dans les lits de pastilles poreuses peut être calculée à partir de la valeur de diffusivité des pastilles non poreuses en tenant compte de la porosité à l'intérieur des pastilles. La fenêtre des coefficients de vitesse mesurables est fonction du nombre de Damköhler du premier type. Un critère est calculé pour les conditions expérimentales qui permet des mesures cinétiques intrinsèques avec des catalyseurs poreux. La taille de l'impulsion admise devrait être assez grande pour éviter l'atténuation de l'impulsion par adsorption.

Keywords: transient kinetics, intrinsic kinetics, pulse experiments, porous catalysts, TAP.

Pulse experiments with reactants over catalyst beds are performed to explore reaction mechanisms and to gather kinetic rate data. In comparison to steady-state experiments, extra information is obtained due to the time-resolved observations, which allows a better discrimination between alternative kinetic models, as well as estimations of the rate constants of individual elementary steps (Biloen, 1983). Temporal Analysis of Products, TAP, is a set-up with recognised high time resolution (Gleaves et al., 1988; Svoboda, 1993; Zou et al., 1994).

The TAP microreactor is a fixed bed reactor with a typical residence time of 100 ms, which is operated batchwise by submitting pulses of reactants with a width at half height of typically 0.2 ms. A well defined state of the catalyst surface can be maintained upon admission of a pulse, since pulse sizes can be made sufficiently small to cause absolute changes limited to 1% of the surface coverage. Reactor outlet responses, corresponding with the outlet molar flow rates, are obtained via mass spectrometry.

In stationary kinetic studies the effects of transport phenomena inside porous catalyst pellets can often be eliminated by a proper choice of the experimental conditions. Such procedures, however, are not straightforward for transient experiments. Intrapellet profiles of the pulsed reactant may arise not only from a limited diffusion rate, but also from accumulation in the pores. Since the pulsed reactant is usually adsorbed on the catalyst surface, the effects will become even more pronounced when the applied pulse size is small in comparison to the sorption capacity of the catalyst. The latter holds for a typical TAP experiment, since usually a small amount of molecules per pulse is admitted to the reactor.

The present contribution addresses the influence of intrapellet diffusion on the measured pulse responses, as obtained with the TAP technique, and indicates the experimental conditions at which diffusion limitation does not affect the assessment of intrinsic kinetics. First, a situation where chemical reactions are absent is analysed by comparison of responses over beds of non-porous and porous catalysts. Next, simultaneous reaction and diffusion in porous catalysts is considered in order to define a window of rate coefficients that can be measured with the TAP set-up.

## Modelling of TAP responses in beds of porous pellets without chemical reaction

The continuity equations describing the TAP response for a fixed bed of porous solids were presented by Zou et al. (1994), and consist of second order differential equations on the scale of the bed and on the scale of the pellet. The solution of these equations is not straightforward for a general case. Therefore, it is worthwhile for situations of practical concern, to compare the characteristic time of diffusion on the pellet scale with the characteristic time of diffusion on the bed scale. The latter is expressed by the first normalised moment of the inert pulse coming out of the reactor (Huinink, 1995):

$$t_{bed} = \frac{l_b^2 \epsilon_b}{2 D_{eA,b}^K} \dots \dots \dots (1)$$

The characteristic time of diffusion on the pellet scale is (Biloen, 1983; Huinink, 1995):

$$t_{pellet} = \frac{\pi l_p^2 \epsilon_p}{4 D_{eA,p}^K} \dots \dots \dots (2)$$

<sup>1</sup>Present address: Shell Internationale Petroleum Maatschappij B.V., P.O. Box 162, 2501 AN Den Haag, The Netherlands.

\*Author to whom correspondence should be addressed. E-mail TGTCJH2@CHEM.TUE.NL

Three different situations may occur:

1.  $t_{pellet} \gg t_{bed}$   
On the time scale of a pulse experiment, only diffusion in the interstitial voids occurs, and the model solution for the TAP response is equal to the solution for the case of non-porous pellets (Gleaves et al., 1988).
2.  $t_{pellet} \approx t_{bed}$   
This situation corresponds with the continuity equations described by Zou et al. (1994) for porous pellets.
3.  $t_{pellet} \ll t_{bed}$   
During a pulse experiment, the concentration of component A inside any pellet is always equal to the concentration at its external surface. The larger the pores of the pellets, the more easily this situation is met.

In the latter case the continuity equation for component A on the bed scale is given by:

$$[\varepsilon_b + (1 - \varepsilon_b)\varepsilon_p] \frac{\partial C_A}{\partial t} = D_{eA,b}^K \frac{\partial^2 C_A}{\partial x^2} \dots \dots \dots (3)$$

The equation has the following initial and boundary conditions:

$$t = 0 \wedge 0 \leq x \leq l_b: C_A(x) = \delta_x \frac{n_{p,A}}{\varepsilon_b A_s} \dots \dots \dots (4)$$

$$t \geq 0 \wedge x = 0: \frac{\partial C_A}{\partial x} = 0 \dots \dots \dots (5)$$

$$t \geq 0 \wedge x = l_b: C_A = 0 \dots \dots \dots (6)$$

The Dirac delta function expresses that at time zero all A is present at  $x = 0$ , while  $C_A = 0$  holds in the remainder of the bed. Equation (5) reflects the closed inlet valve after admission of the pulse, and Equation (6) corresponds with the vacuum conditions at the reactor outlet.

The initial and boundary conditions are the subject of discussion in the literature. As the initial condition, Zou et al. (1994) assumed an equivalent gas phase concentration in an inlet section of the reactor, which is packed with inert material and is assumed to be ideally mixed if the packing diameter in the inlet section is much larger than the diameter of the pellets of the applied catalyst. Creten (1995) assumed that the flux into the inlet section is expressed by a Dirac function at time  $t_{lag}$ , the latter corresponding to the lag time that is being observed experimentally and ascribed to various delays. His approach satisfies the requirement of a non-zero concentration at the inlet after submission of the pulse. Svoboda (1993) proposed a non-ideal pulse forcing function for the inlet flux, which should be determined experimentally. The present initial condition, Equation (4), has the advantage of recognizing explicitly that the manifold volume can be neglected and that the flow resistance (Zou et al., 1994) of an inlet section, if any, is independent of the pellet diameter. Moreover, it agrees with a non-zero concentration at the reactor inlet at all times. At the outlet of the reactor, Creten (1995) applied a continuity equation over the sieve closing the reactor. Zou et al. (1994) argued that continuity of flux and concentration at the reactor outlet leads to Equation (6), since the mean gas velocity outside the reactor

is typically very large due to molecular flow. The various alternative propositions for the initial and boundary conditions have been tested for their influence on simulated pulse responses in the present work, and their effects appeared to be rather marginal.

Concerning the lag time, mentioned before, Creten (1995) developed an experimental correlation, which was incorporated into his TAP reactor model. Zou et al. (1994) consider that the lag time may be safely neglected, whenever the time scale of a TAP signal measurement is over 0.1 s. In the present work the lag time was considered as a separate parameter in the regression of experimental TAP data.

The solution of Equations (3)–(6) with respect to the molar flow rate at the reactor outlet is:

$$F_{A|x=l_b} = \frac{D_{eA,b}^K}{[\varepsilon_b + (1 - \varepsilon_b)\varepsilon_p]} \frac{n_{p,A}\pi}{l_b^2} \times \sum_{n=0}^{\infty} (2n+1)(-1)^n \exp\left(-\frac{(2n+1)^2 \pi^2}{4} \frac{D_{eA,b}^K t}{[\varepsilon_b + (1 - \varepsilon_b)\varepsilon_p] l_b^2}\right) \dots \dots \dots (7)$$

Equation (7) can be compared with the situation 1, mentioned before, where pellet diffusion is very slow or even absent. The molar outlet flow rate is in that case analogous to Equation (7) with the capacity term  $\varepsilon_b + (1 - \varepsilon_b)\varepsilon_p$  replaced by the interstitial voidage  $\varepsilon_b$ . From a comparison of both solutions, the relation between effective Knudsen diffusivities in beds of non-porous and porous pellets can be found when the diffusion in the pellets is fast compared to the diffusion in the bed:

$$D_{e\text{porous}}^K = \frac{D_{e\text{non-porous}}^K}{\left(1 + \frac{\varepsilon_p(1 - \varepsilon_b)}{\varepsilon_b}\right)} \dots \dots \dots (8)$$

The effective Knudsen diffusivity in beds of porous catalyst pellets is equal to its value for beds of equal-sized non-porous pellets, but adjusted for the larger available gas volume, provided the pores are not too small. For pellets with an average pellet diameter of 200  $\mu\text{m}$ , the latter occurs typically at a pore diameter of 2 nm, as met in zeolites. In such case, the characteristic times for diffusion on the bed and pellet scale would have the same order of magnitude, meaning that the effective Knudsen diffusivity in the pellet pores has to be taken into account in the interpretation of a single pulse TAP experiment and, as a corollary, could be determined separately from the experimental data.

### Model validation with beds of non-porous and porous pellets

The Knudsen diffusion concept was verified experimentally by determining diffusivities as a function of the pulse size for various inert gases. Effective Knudsen diffusivities were calculated by applying single-response non-linear regression (Marquardt, 1963) to the complete TAP curves. The experimentally observed lag time  $t_{lag}$  was estimated as a separate parameter. Its value was always more than one order of magnitude smaller than the time scale of signal measurement, but could not be neglected as proposed by Zou et al. (1994). A typical example is shown in Figure 1,

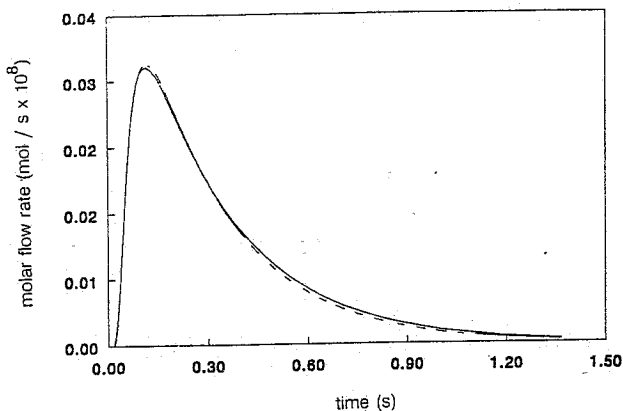


Figure 1 — Experimental (solid curve) and calculated (dotted curve) TAP response. ( $\gamma$ -alumina,  $210 < d_p < 250 \mu\text{m}$ , bed length  $37 \text{ mm}$ ,  $\varepsilon_{bed} = 0.48 \text{ m}_g^3/\text{m}_c^3$ ,  $n_{p,Ar} = 7.56 \times 10^{15}$  molecules,  $D_e = 0.93 \times 10^{-3} \text{ m}_g^3/\text{m}_r\text{s}$ ,  $T = 298 \text{ K}$ ).

and indicates an adequate fit. The dependence of the effective Knudsen diffusivity on temperature, molar mass and pellet size was verified. All results, reported elsewhere (Huinink, 1995), confirmed earlier studies (Gleaves et al., 1988; Zou et al., 1994). The bed tortuosity may be calculated from the measured effective Knudsen diffusivity and the well-known Knudsen relation, once the interstitial voidage has been determined experimentally. A mean value of  $5.5 \text{ m}_g^2/\text{m}_r^2$  was obtained for mean pellet diameters in the range  $0.2\text{--}0.5 \text{ mm}$  (Huinink, 1995).

For the verification of Equation (8), four different types of packing were applied in single pulse TAP experiments: quartz (Merck) and  $\alpha\text{-Al}_2\text{O}_3$  (AKZO), which both were non-porous, as well as  $\gamma\text{-Al}_2\text{O}_3$  (Degussa) and Li/Sn/MgO, both being porous. The Li/Sn/MgO catalyst was prepared as described by Korf et al. (1987, 1989). All tested materials had the same pellet diameter range of  $210\text{--}250 \mu\text{m}$ . Single pulse experiments were performed with argon (Hoekloos, 99.9999%) at  $298 \text{ K}$  in the non-porous beds of quartz and  $\alpha\text{-Al}_2\text{O}_3$  with a length,  $l_b$ , of  $0.037 \text{ m}_r$ . Effective Knudsen diffusivities on the bed scale,  $D_{e,b}^K$ , were estimated by non-linear regression of the complete outlet TAP curves with the equivalent of Equation (7) for non-porous pellets, and appeared to yield the same value of  $1.68 \times 10^{-3} \text{ m}_g^3/\text{m}_r\text{s}$ ; see Table 1.

Next, single pulse TAP experiments were performed with argon at  $298 \text{ K}$  over beds of the porous materials, Li/Sn/MgO and  $\gamma\text{-Al}_2\text{O}_3$ , with a length of  $0.037 \text{ m}$ . Estimations of the effective Knudsen diffusivities,  $D_{e,b}^K$ , obtained again through non-linear regression of the complete outlet TAP curves with the equivalent of Equation (7) for non-porous pellets, are also listed in Table 1. They are considerably smaller than the values which were measured with beds of non-porous pellets, as could be expected from Equation (8). The pellet porosity,  $\varepsilon_p$ , calculated with Equation (8), is also shown in Table 1 and compared with values obtained from mercury porosimetry and BET measurements. The agreement is satisfactory, confirming the validity of Equation (8) and, hence, also the hypothesis that pellet scale diffusion is instantaneous compared to bed scale diffusion.

It was verified that the characteristic time for diffusion in pellets was much smaller than in the bed. From the bed scale diffusivities for the non-porous pellets, Knudsen diffusivities inside the porous pellets were calculated, using the Knudsen relation, the hydraulic diameter concept and the

TABLE 1

Pellet Porosities, as Determined from Pulse Experiments with Argon at  $T = 298 \text{ K}$ ,  $d_p = 210\text{--}250 \mu\text{m}$  and  $\varepsilon_b = 0.48 \text{ m}_g^3/\text{m}_r^3$ , and from Independent Porosity Measurements

Packing	$D_e^K$ ( $\text{m}_g^3/\text{m}_r\text{s}$ ) $\times 10^{-3}$	$\varepsilon_p$ $\text{m}_g^3/\text{m}_c^3$	$\varepsilon_{BET}$ $\text{m}_g^3/\text{m}_c^3$	$\varepsilon_{merc.}$ $\text{m}_g^3/\text{m}_c^3$
quartz	1.67	0	—	—
$\alpha\text{-Al}_2\text{O}_3$	1.68	0	—	—
Li/Sn/MgO	1.43	0.15 <sup>1</sup>	0.23	—
$\gamma\text{-Al}_2\text{O}_3$	0.93	0.73 <sup>1</sup>	0.66	0.61

<sup>1</sup>calculated with Equation (8),  $D_e^K \text{ non-porous} = 1.67 \times 10^{-3} \text{ m}_g^3/\text{m}_r\text{s}$  and  $\varepsilon_b = 0.48 \text{ m}_g^3/\text{m}_r^3$ .

mean intraparticle pore diameters of Li/Sn/MgO and  $\gamma\text{-Al}_2\text{O}_3$ , which were  $500$  and  $8 \text{ nm}$ , respectively, as obtained directly from BET measurements. The characteristic time of diffusion on the pellet scale was  $0.001 \text{ s}$  for Li/Sn/MgO, which is very short compared to  $0.2 \text{ s}$  on the bed scale. Hence, it can be assumed that the concentration in the pores equals the concentration at the external surface of the pellets. For  $\gamma\text{-Al}_2\text{O}_3$  pellets, the characteristic time for pellet diffusion is  $0.07 \text{ s}$ . Due to smaller pore diameters the difference with the bed scale is less pronounced, but probably large enough to assure a uniform pellet profile.

#### Modelling of TAP responses with chemical reaction

An estimation of rate coefficients of chemical reactions can only be obtained from pulse experiments, if these rate coefficients have values within a certain range. If the value is too high, the response signal of a reactant can no longer be distinguished from noise because of nearly complete conversion. In the case of a too low a value, the injected pulse has left the reactor before significant reaction has occurred, meaning that the response will hardly differ from the response resulting from diffusion only. In both situations quantitative estimation of rate coefficients is impossible.

The case of an empty reactor, as well as a packed bed reactor, will be considered with Knudsen diffusion as the main transport mechanism. Realisation of this mechanism may require that the size of submitted pulses should be smaller for the empty reactor than for a packed bed reactor. For a packed bed of non-porous pellets, the continuity equation for reactant  $A$  is:

$$\frac{\partial C_A}{\partial \tau} = \frac{\partial^2 C_A}{\partial z^2} + Da_1 C_A \dots \dots \dots (9)$$

with  $z = x/l_b$ , the dimensionless reactor coordinate, and the dimensionless time defined as:

$$\tau = \frac{D_{eA,b}^K t}{\varepsilon_b l_b^2} \dots \dots \dots (10)$$

The Damköhler number, defined as the ratio of the time scale of diffusion to the time scale of reaction, is given by:

$$Da_1 = \frac{-R_{vA} l_b^2}{C_A D_{eA,b}^K} \dots \dots \dots (11)$$

This Damköhler number should be considered as a Damköhler number of the first type (Janssen and Warmoeskerken, 1987), as the time scale of the residence in the reactor in the absence of reaction coincides in a TAP experiment with the time scale of diffusion. For a packing of porous pellets and a small time scale of diffusion inside the pellets in comparison with the time scale of diffusion in the bed, Equations (9)–(11) still hold, with the minor modification that  $\varepsilon_b$  should be replaced by  $\varepsilon_b + (1 - \varepsilon_b) \varepsilon_p$ , as outlined before.

The initial and boundary conditions, given by Equations (4)–(6), are also valid in this case when adapted to the new independent variables. Obviously, Equation (9) corresponds to an empty reactor if  $\varepsilon_b = 1$ . The solution of Equation (9) can be derived via Laplace transformation. The molar flow rate at the outlet of the reactor as function of  $\tau$  is obtained from the concentration profile:

$$F_{A|z=1} = \frac{D_{eA,b} n_{p,A} \pi}{\varepsilon_b l_b^2} \exp(-Da_1 \tau) \sum_{n=0}^{\infty} (2n+1)(-1)^n \exp\left(-\frac{(2n+1)^2 \pi^2 \tau}{4}\right) \dots \dots \dots (12)$$

In the situation of diffusion only,  $Da_1 = 0$  and Equation (12) reduces to the equivalent of Equation (7).

The outlet molar flow rates of reactant *A*, calculated from Equation (12) and relative to the outlet flow rate at the same time, but in the absence of reaction, are shown in Figure 2 for different values of the  $Da_1$  number. Curve *A* presents the case  $Da_1 = 0$ , corresponding with diffusion only. The figure illustrates that a smaller signal will be observed if  $Da_1$  increases. One could assume that a reactant's response signal can still be distinguished from zero if its area is about 1% of the area when diffusion only occurs. That situation corresponds with  $Da_1 = 25$ , curve *E*, and determines the upper limit of detectable Damköhler numbers. When assuming that an approximately 10% decrease of the peak width at half height can be distinguished from the case that diffusion only occurs, the lower limit  $Da_1 = 0.25$ , curve *B*, is found. An elaborate analysis, leading to similar results, was presented by Weerts (1995). Therefore, in principle, the limits for the minimum and maximum rate coefficients that can be measured, are set by the requirement:

$$0.25 < Da_1 < 25$$

#### HOMOGENEOUS GAS PHASE REACTIONS

For a single, homogeneous, first order reaction:



the Damköhler number becomes:

$$Da_1 = \frac{\varepsilon_b k_1 l_b^2}{D_{eA,b}^K} \dots \dots \dots (15)$$

In order to find the corresponding delimitations for the rate coefficient  $k_1$ , the various factors in the Damköhler number, Equation (15), have to be taken into account. The effective Knudsen diffusivity can be obtained from the well-

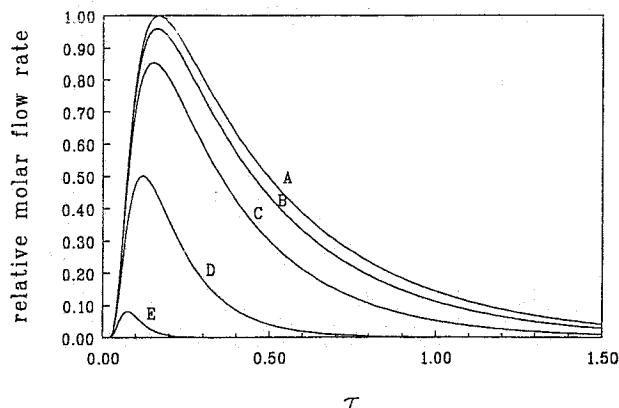


Figure 2 — Molar flow rates of reactant *A* at the outlet of the TAP microreactor, calculated with Equation (12) and relative to the situation where  $Da_1 = 0$ , for different values of the Damköhler I number: A) 0, B) 0.25, C) 2.5, D) 5.0 and E) 25.

known Knudsen relation, which is applicable for an empty reactor, and for a packed bed. In the latter case, the hydraulic diameter concept (Huizenga and Smith, 1986) is needed as well.

The maximum reaction rate coefficient is to be measured in an empty reactor because the Knudsen diffusivity is then maximal. For a TAP microreactor with a diameter of 5.6 mm the effective Knudsen diffusivity, calculated from the Knudsen relation for a molar mass of 28 kg/kmol amounts to  $1.15 \text{ m}_g^3/\text{m}_r \cdot \text{s}$  at 500 K. From  $Da_1 = 25$  it follows that a maximum reaction rate coefficient of  $1.6 \times 10^4 \text{ s}^{-1}$  can be measured.

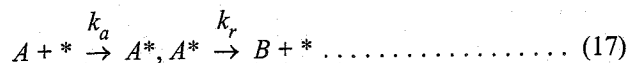
Packing reduces the mean free path of the molecules in the reactor, causing a lower Knudsen diffusivity. The resulting lower effective diffusivity means that the measurable reaction rate coefficients decrease as well. The minimum reaction rate coefficient is measured in a packed bed with the hydraulic diameter of the interstitial voids as small as possible. In the TAP microreactor, the smallest pellets which can be used have a diameter of 200  $\mu\text{m}$ . For argon at 500 K the effective Knudsen diffusivity in such a bed is  $2.2 \times 10^{-3} \text{ m}_g^3/\text{m}_r \cdot \text{s}$ , assuming a porosity of 0.48  $\text{m}_g^3/\text{m}_r^3$  and a tortuosity of 5.5  $\text{m}_g^2/\text{m}_r^2$ . The value of the minimum measurable reaction rate coefficient therefore is 0.64  $\text{s}^{-1}$ , as follows from  $Da_1 = 0.25$ .

Summarising, first order reaction rate coefficients of homogeneous reactions can be determined in the range:

$$1 \leq k_1 \leq 1 \times 10^4 \text{ s}^{-1} \dots \dots \dots (16)$$

#### CATALYTIC REACTIONS

For a reaction involving adsorption of reactant *A* with a rate coefficient  $k_a$  and a surface reaction with a rate coefficient  $k_r$ , followed by instantaneous desorption to product *B*:



the continuity Equation (9) for *A* still holds, but the Damköhler number is now given by:

$$Da_1 = \frac{(1 - \varepsilon_b) k_a a_v L_t \theta_* l_b^2}{D_{eA,b}^K} \dots \dots \dots (18)$$

if the catalyst pellets are non-porous, or by:

$$Da_1 = \frac{k_a a_i L_i \theta_* l_b^2}{D_{eA,b}^K} \dots \dots \dots (19)$$

in case of porous pellets, but in the absence of internal concentration gradients.

Equations (9) and (18) and (19) show that the response of reactant *A* depends only on the Damköhler number, e.g. on the ratio of the time scales of bed diffusion and adsorption. As the fraction of empty sites,  $\theta_*$ , is involved in the latter, Equation (9) should be combined with the continuity equation for the adsorbed species, which accounts for the changes in the catalyst surface coverage, following upon the admission of a pulse of reactant *A*. However, as a first approximation,  $\theta_*$  may be considered as a constant in a typical TAP experiment, since the inlet pulse size is usually much smaller than the number of active sites on the catalyst. In fact, the actual value of  $\theta_*$  may even be preset by admitting a chosen number of pulses before performing the single pulse experiment aimed at obtaining the kinetic data. Such a procedure provides an extra means to manipulate beforehand the time scale of adsorption and accordingly, the value of the Damköhler number, which can also be influenced by a proper choice of other experimental conditions like surface area and total number of active sites.

Analogous to the situation of homogeneous gas phase reactions, Equation (14), the accessible window for rate coefficients of the catalytic sequence described by Equation (17), is also governed by the range  $0.25 \leq Da_1 \leq 25$ , now expressed by Equations (18) or (19). Adsorption does not occur on the time scale of a TAP single pulse experiment if  $Da_1 < 0.25$ , meaning that kinetic data cannot be obtained, since the pulse distortion of *A* is due to diffusion only. If  $Da_1 > 25$ , the response of *A* also does not give any information. Indeed, if the surface is not completely precovered with *A*, the pulse of *A* will be adsorbed totally, and otherwise the pulse distortion of *A* is due to diffusion only. In the intermediate region  $0.25 < Da_1 < 25$  the adsorption rate coefficient may be estimated from the pulse response of *A*.

The influence of the surface reaction rate coefficient  $k_r$  is mainly reflected in the response of the product *B*, for which component a continuity equation, analogous to Equation (9), should be taken into account (Huinink, 1995). An accessible window for estimation of  $k_r$  is obtained along similar lines as followed here for  $k_a$ .

### Assessment of intrinsic kinetics from pulse experiments over porous catalysts

Under isothermal conditions, intrinsic kinetics will be observed experimentally if care has been taken to avoid mass transport limitations. External limitation is unlikely when Knudsen diffusion is the main transport mechanism. To assure a uniform concentration within a catalyst pellet, it is imperative, as in steady state experiments, that the time scale of reactant consumption in the pellet is much larger than the time scale of diffusion in the pellet. Moreover, a transient pulse experiment requires that rates are not limited by a short supply of reactant, e.g. internal concentration profiles due to depletion of the pulse should be neglectable. It means that the time scale of all phenomena should be small with respect to the time scale of pulse depletion. The latter can be approximated by the ratio:

$$\frac{n_{p,A}}{-R_{vA} V_r} = \frac{n_{p,A}}{k_a a_i L_i C_A \theta_* V_r} = \frac{\varepsilon_b}{k_a a_i L_i \theta_*} \dots \dots \dots (20)$$

which relates the size of the submitted pulse to the rate of adsorption of *A* by the catalyst bed. The concentration  $C_A$  is based upon the pulse size and the gas volume of the bed. The requirement of a large time scale for pulse depletion might conflict with the wish to apply small pulse sizes for maintaining the Knudsen transport regime or an almost constant surface coverage, and might be achieved by adapting the number of active sites or the empty fraction of them.

The concept of the effectiveness factor is useful when considering internal transport limitation, which might be assumed irrelevant if the observed rate exceeds 95% of the intrinsic rate. Hence, for reaction of Equation (17), the diffusion rate across the outer pellet surface should be larger than 95% of the adsorption rate inside the pellet, when the latter is assumed uniform at the external concentration:

$$-D_{eA,p}^K \frac{dC_A}{dr} \Big|_{r=R_p} \pi d_p^2 \geq 0.95 k_a a_i L_i C_A \Big|_{r=R_p} \theta_* \frac{\pi}{6} d_p^3 \dots \dots (21)$$

The gradient at the outer pellet surface is approximated as  $\Delta C_A / \delta$ . The concentration difference  $\Delta C_A$  will spread upmost over the distance  $\delta = d_p / 2$ . Because of the 95% criterion,  $\Delta C_A \approx 0.05 C_A$ . It leads to:

$$\frac{k_a a_i L_i \theta_* d_p^2}{D_{eA,p}} \leq \frac{12}{19} \dots \dots \dots (22)$$

The inequality of Equation (22) is independent of the bulk gas concentration, and therefore holds at any time and reactor position, relevant for a TAP experiment, provided that pulse depletion is not involved. Combining Equation (19) with the inequality of Equation (22) results in a criterion to be fulfilled by the Damköhler number:

$$Da_1 \leq \frac{12 D_{eA,p} l_b^2}{19 D_{eA,b} d_p^2} \dots \dots \dots (23)$$

If the criterion of Equation (23) is met, and pulse depletion does not occur, internal transport limitations can be neglected. From the Knudsen relation and the hydraulic diameter concept (Huizenga and Smith, 1986), the ratio of Knudsen diffusivities in the pores of the pellets and in the bed can be determined:

$$\frac{D_{eA,p}}{D_{eA,b}} = \frac{3}{2} (1 - \varepsilon_b) \varepsilon_p \frac{\tau_b' d_{pore}}{\tau_p d_p} \dots \dots \dots (24)$$

The criterion of Equation (23) for the Damköhler number thus can be expressed as:

$$Da_1 \leq 0.95 (1 - \varepsilon_b) \varepsilon_p \frac{\tau_b' d_{pore} l_b^2}{\tau_p d_p^3} \dots \dots \dots (25)$$

In a typical TAP experiment with a catalyst bed, the pellet size is  $2 \times 10^{-4}$  m and the bed length is 0.04 m. Pore diameters will be around  $10^{-8}$  m. When assuming for both

the pellet and the bed a tortuosity of 5.5 and a porosity of 0.5, Equation (25) leads to  $Da_1 \leq 0.48$ , which falls in the observable window  $0.25 < Da_1 < 25$ . It means that a range of physically achievable experimental conditions exists that allow measurement of a rate coefficient, not disguised by diffusion limitation in the catalyst pellet. Hence, an experiment would yield intrinsic kinetic information if the experimental conditions are properly chosen as to obey both inequalities of Equations (13) and (25).

## Conclusions

In case of instantaneous diffusion in the pellet pores, the Knudsen diffusivity for porous particles is related to that for non-porous particles via a capacity term that accounts for the intraparticle porosity. The validity of instantaneous diffusion may be tested by comparing the characteristic times of diffusion on the bed and the pellet scale. This assumption will hold for many industrially applied cases, provided the internal pore diameter of the pellets is not too small.

The window of rate coefficients that can be measured with the TAP apparatus is governed by a Damköhler number of the first type. An additional criterion in terms of the Damköhler number allows to estimate the requirements for intrinsic kinetic measurements when the time scale of pulse depletion by adsorption is sufficiently large. Provided the latter holds, there exists for industrial catalysts a range of physically reasonable values for the bed length and the pellet diameter within which internal diffusion can be neglected and kinetic information can be obtained.

## Nomenclature

$a_i$	= internal catalyst surface area per unit reactor volume	$m_c^2/m_r^3$
$a_v$	= external catalyst surface area per unit catalyst volume	$m_c^2/m_c^3$
$A_s$	= reactor's cross-sectional area	$m_r^2$
$C$	= concentration	$mol/m_g^3$
$d_i$	= diameter of interstitial voids	$m$
$d_p$	= pellet diameter	$m$
$D_e$	= effective diffusivity	$m_g^3/m_r^3 \cdot s$
$Da_1$	= Damköhler I number	—
$F$	= molar flow rate	$mol/s$
$k_a$	= adsorption rate coefficient	$m_g^3/mol \cdot s$
$k_1$	= first order reaction rate coefficient	$s^{-1}$
$l_b$	= bed length	$m_r$
$L_t$	= maximum molar concentration per unit catalyst surface	$mol/m_c^2$
$n$	= summation integer	—
$n_{p,A}$	= amount of component A in inlet pulse	$mol$
$\dot{R}_{vA}$	= volumetric net production rate of component A	$mol/m_r^3 \cdot s$
$t$	= time	$s$
$t_{bed}$	= time scale for diffusion on the bed scale	$s$
$t_{lag}$	= lag time in TAP response	$s$
$t_{pellet}$	= time scale for diffusion on the pellet scale	$s$
$x$	= axial coordinate in reactor	$m_r$
$z$	= dimensionless axial coordinate	—

## Greek letters

$\delta_x$	= delta function with respect to axial coordinate = $\delta(x=0)$	$m_r^{-1}$
$\epsilon_b$	= bed porosity	$m_g^3/m_r^3$
$\epsilon_p$	= pellet porosity	$m_g^3/m_c^3$
$\theta$	= fractional surface coverage	—
$\tau$	= normalised time	—
$\tau'$	= tortuosity	—

## Superscripts and subscripts

*	= empty sites
A	= with respect to A
b	= bed; interstitial voids
d	= diffusivity
e	= effective
K	= Knudsen
p	= pellet; intraparticle pores
r	= reaction

## References

- Biloen, P., "Transient Kinetic Methods", *J. Mol. Catal.* **21**, 17–24 (1983).
- Creten, G., "TAP-studie: Reactiemechanismen en Transiënte Kinetiek van Katalytische Oxidatiereacties", Ph.D. thesis, Universiteit Gent, Gent, Belgium (1995).
- Gleaves, J. T., J. R. Ebner and T. C. Kuechler, "Temporal Analysis of Products (TAP)-A Unique Catalyst Evaluation System with Submillisecond Time Resolution", *Catal. Rev. -Sci. Eng.* **30**(1), 49–116 (1988).
- Huinink, J. H., "A Quantitative Analysis of Transient Kinetic Experiments: The Oxidation of CO by O<sub>2</sub>/NO on Pt", Ph.D. thesis, Eindhoven University of Technology, Eindhoven, The Netherlands (1995).
- Huizenga, D. G. and D. M. Smith, "Knudsen Diffusion in Random Assemblages of Uniform Spheres", *AIChE J.* **32**, 1–6 (1986).
- Janssen, L. P. B. M. and M. M. C. G. Warmoeskerken, "Transport Phenomena Data Companion", Edward Arnold, London (1987).
- Korf, S. J., J. A. Roos, N. A. de Bruijn, J. G. van Ommen and J. R. H. Ross, "Influence of CO<sub>2</sub> on the Oxidative Coupling of Methane over a Lithium Promoted Magnesium Oxide Catalyst", *J. Chem. Soc. Chem. Commun.*, 1433 (1987).
- Korf, S. J., J. A. Roos, L. J. Veltman, J. G. van Ommen and J. R. H. Ross, "Effect of Additives on Lithium Doped Magnesium Oxide Catalysts Used in the Oxidative Coupling of Methane", *Appl. Catal.* **56**, 119 (1989).
- Marquardt, D. W., "An Algorithm for Least-Squares Estimation of Nonlinear Parameters", *J. Soc. Indust. Appl. Math.* **11**(2), 431–441 (1963).
- Satterfield, C. N., "Mass Transfer in Heterogeneous Catalysis", MIT Press, Cambridge, MA (1970).
- Svoboda, G. D., "Fundamental Transport-Kinetics Models for Interpretation of TAP Reactor Transient Response Data with Application to Reactive Systems", Ph.D. thesis, Washington University, St. Louis, MO (1993).
- Weerts, W. L. M., "Low Pressure CVD of Polycrystalline Silicon: Reaction Kinetics and Reactor Modelling", Ph.D. thesis, Eindhoven University of Technology, Eindhoven, The Netherlands (1995).
- Zou, B. S., M. P. Duducović and P. L. Mills, "Modelling of Pulsed Gas Transport Effects in the TAP Reactor System", *J. Catal.* **148**, 683–696 (1994).

Manuscript received January 19, 1996; revised manuscript received June 19, 1996; accepted for publication July 9, 1996.