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Use of stirred batch reactors for the assessment of adsorption constants in porous solid catalysts with simultaneous diffusion and reaction. Theoretical analysis

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Abstract

A simple, pseudo-equilibrium model was derived for a catalytic system with a first order chemical reaction and simultaneous diffusive and adsorptive processes, in order to assess the corresponding kinetics and Henry law's-type adsorption parameters. Solutions from this model were compared to exact solutions from a more detailed, general model. It was shown that under most of the experimental conditions used in stirred batch reactors and the usual model considerations, it is only possible to assess apparent adsorption parameters. Also, we observed that a stable relationship between the concentrations in the gas and solid phases is reached. The error produced in assuming that the apparent adsorption constant is the real one was calculated to be very important. The value of the apparent adsorption constant depends on various system properties and experimental conditions, such as the Thiele modulus, the amount of catalyst and the contact time. The ratio between the apparent and real adsorption constants was shown to be the transient effectiveness factor at any moment. This ratio reaches a maximum value for the pseudo-equilibrium state, that is always larger than the steady-state effectiveness factor, becoming closer as long as the system's adsorption capacity decreases. The analysis determines the operative conditions to reduce the parametric correlation. Also a criterion for the applicability of usual approximations in the assessment of kinetics and equilibrium adsorption parameters in porous solid catalysts by means of pulse injection methods is established.
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1. Introduction

The assessment of the diffusion, adsorption and chemical reaction parameters of heterogeneous catalytic systems, under practical reaction conditions, is subjected to serious limitations. Because all the processes occur simultaneously, it is very difficult to characterize them properly and, moreover, according to the system, each step impacts differently on the overall performance observed. Some particular cases, where most of the resistance to the overall rate of change can be ascribed to only one of the steps, are easier to describe, model, and evaluate (Hill, 1977). One of the simplifications used is the quasi-steady-state assumption, where mass balances in the fluid phase of the reactors are assumed transient while the catalytic solid is considered to be in the steady state. The rate of change of the amount of reactant can then be expressed in terms of concentration in the fluid phase and the well-known steady-state effectiveness factor. But in general, and particularly under the conditions prevailing in the chemical process or petroleum refining industries where porous solid catalysts are used, extremely simplified treatments are usually not possible.

Perfectly mixed reactors, where the limitations to transport processes external to the catalyst particles are negligible, can be used in the laboratory to assess diffusion, adsorption and chemical reaction parameters (Schobert and Ma, 1981a,b; Miró et al., 1986). Adsorption, diffusion and rate constants may be estimated in a dynamic experiment by sampling the fluid phase continuously and extracting the constants by fitting a model to the transient fluid phase concentrations. The latter

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method is sensitive to noise and quite often the constants are correlated; consequently, extracting them can be difficult. Often several sets of data are needed. Moreover, adsorption parameters that are assessed in reacting systems frequently do not coincide with those corresponding to pure compounds in non-reacting systems, due to the interaction between reactant and products and the lack of clearly limiting steps (Smith, 1981). To simplify the analysis, it is common to assume that the chemical reaction and the diffusive transport processes do not influence the amount of reactants adsorbed in the solid (e.g. Pruski et al., 1996). Nevertheless, in reacting systems where the molecular size of reactants or products is close to the size of the catalyst pores (for example, when molecular sieves are used), it is to be expected that diffusion plays a key role. This fact has been confirmed by theoretical calculations of intracrystalline diffusivities (Satterfield, 1981; Xiao and Wei, 1992; Masuda et al., 1996) and by experimental evidences of intraparticle diffusion control (Karger and Ruthven, 1992; Masuda et al., 1996).

These considerations are even more important in systems where reactants molecules are very large, like in the catalytic cracking of hydrocarbons (O'Connor and van Houtert, 1986; Biswas and Maxwell, 1990). Besides the need to know the mass transfer and chemical reaction kinetics parameters for process modelling and reactor design purposes, it would be very useful to know the extent of adsorption under process conditions, so as to assist in the design and optimization of the stripping step (Lee et al., 2004).

In this work a simple model is derived in order to optimize determination of simultaneous diffusion, adsorption and chemical reaction parameters in a linear system. The theoretical analysis includes the errors in the values of the kinetics and adsorption constants that are assessed under the usual approaches.

2. Theoretical model

The important assumptions are similar to those of Bidabehere and Sedran (2001):

- Reactor design and operation to ensure complete mixing in the fluid phase.
- Intraparticle diffusion is assumed to be the controlling mechanism for mass transfer in the catalyst particles, and Fick's law applies.
- Adsorption equilibrium is attained at the internal surface of the spherical catalyst particles and the adsorption isotherm is linear ($q = KC$, where K is the Henry's constant).
- The reaction is considered irreversible, first order in reactant concentration. Catalyst deactivation is assumed negligible.

Moreover, for the particular case of zeolite catalysts, we assume the same model can be used to describe processes where either the configurational diffusion or the conventional diffusion in the zeolite micropores are the mass transfer limiting step. It can be easily shown that in order to use the same equations, simple variable redefinitions have to be made (Bidabehere and Sedran, 2001). This simple model can also be used to describe compound catalysts, like those used for FCC, provided that restrictions to mass transfer, adsorption and reaction in the matrix component are considered negligible in comparison to those in the zeolite component (Pine et al., 1984; Scherzer, 1989). Lee et al. (2004) have shown that adsorption in the matrix of those catalysts is low.

It is convenient to define the following dimensionless variables:

$$\tau = \frac{D}{R^2}\, t, \quad \rho = \frac{r}{R}, \quad \xi = \frac{q(r,t)}{KC_0}, \quad \chi = \frac{C(t)}{C_0} = \frac{C(t)}{N_0/V_g} \quad (1)$$

to write the mass balance for the reactant inside the solid pores:

$$\frac{\partial \xi(\rho,\tau)}{\partial \tau} = \nabla^2 \xi(\rho,\tau) - \phi^2 \xi(\rho,\tau), \tag{2}$$

where

$$\phi = R\sqrt{\frac{k}{D}} \tag{3}$$

is the Thiele modulus. Initial and boundary conditions are

$$\xi(\rho,0) = 0, \quad \left.\frac{\partial \xi}{\partial \rho}\right|_{\rho=0} = 0, \quad \xi(1,\tau) = \chi(\tau). \tag{4}$$

There exist an exact solution to this problem, that can be written in terms of the volume-averaged concentration in the solid as (Kim, 1989)

$$\overline{\xi} = s_1 \chi - s_2 \frac{d\chi}{d\tau} + s_3 \frac{d^2\chi}{d\tau^2} - \cdots + \sum_{n=1}^{\infty}\left(\frac{e^{-\lambda_n \tau}}{\lambda_n}\right)$$
$$\times \left(-\chi(0) + \frac{1}{\lambda_n}\left.\frac{d\chi}{d\tau}\right|_{\tau=0} - \frac{1}{\lambda_n^2}\left.\frac{d^2\chi}{d\tau^2}\right|_{\tau=0} + \cdots\right), \tag{5}$$

where

$$\lambda_n = \phi^2 + n^2\pi^2, \quad s_i = \sum_{n=1}^{\infty}\frac{6}{\lambda_n^i},$$

$$\overline{\xi}(\tau) = 3\int_0^1 \xi(\rho,\tau)\rho^2\, d\rho. \tag{6}$$

In order to know the concentration profile of the reactant inside the solid at any moment, it is necessary to know the changes in concentration in the gas phase, since dynamic balances in both phases are coupled by boundary conditions shown in Eqs. (4). When a chemical reaction proceeds in a stirred batch reactor, the composition of the gas phase $\chi(\tau)$ will vary as a function of time, and indeed this is the information that can be gathered experimentally. The evolution of the composition of the gas phase can be linked to the mass balance inside the pores by means of

$$\frac{d\chi}{d\tau} = -\alpha \left.\frac{d\xi}{d\rho}\right|_{\rho=1} \tag{7}$$

subjected to the initial condition

$$\chi(0) = 1, \tag{8}$$

where the parameter α, that relates solid and gas phase volumes, is defined as follows:

$$\alpha = \frac{V_s}{V_g}\,K = \frac{m_{Cat}}{\rho_{Cat}V_g}\,K. \tag{9}$$

3. Results and discussion

Numerical solutions for the system of Eqs. (2)–(4) and (7)–(9), with given values of the parameter α and Thiele modulus ϕ, were obtained by means of a finite differences method with a Crank–Nicholson scheme (Ames, 1975).

The profiles of the volume-averaged reactant concentration inside the solid can be easily analyzed when an arbitrarily constant concentration in the gas phase is considered. In effect, it can be seen in Eq. (5) that if $\chi(\tau)$ is constant, at long times the volume-averaged concentration in the catalyst $\bar{\bar{\xi}}$ will tend to $s_1\chi$. Since $s_1 \leqslant 1$ and it diminishes with increasing values of the Thiele modulus, it is clear that the effect of a slower diffusion process is to decrease the amount of reactant adsorbed in comparison to the amount determined by the adsorption equilibrium (Kim, 1989). This factor s_1 is thus controlled by the ratio between the rates of chemical reaction and diffusion. Only in systems without chemical reaction or with instantaneous diffusion, where ϕ tends to 0, s_1 tends to 1 and $\bar{\bar{\xi}} = \xi = \chi$, a true equilibrium is reached all over the particles.

Moreover, the model predicts that the difference between the amount of reactant adsorbed as given by the adsorption equilibrium and the amount indeed adsorbed, not only depends on kinetics, adsorption and diffusion parameters, but also on the relationship between the volumes of the solid and gas phases and the contact or reaction time involved. In effect, Fig. 1 shows the profiles of dimensionless concentrations of reactant in the gas phase and volume-averaged in the solid, obtained with a value of $\alpha = 1$ and different Thiele moduli. It can be seen that the volume-averaged concentration in the catalyst $\bar{\bar{\xi}}$ is always smaller than the gas phase concentration χ, specially at low reaction times. At longer times, the relative difference between $\bar{\bar{\xi}}$ and $\chi((\chi - \bar{\bar{\xi}})/\chi)$ becomes constant for every value of the Thiele modulus, and it is zero only if the modulus is zero. From these results and the inspection of Eq. (5), it is clear then that the usual assumption (e.g. Pruski et al., 1996; Atias et al., 2003) that $\bar{\bar{\xi}} = \chi$ is only valid when all the time derivatives of χ are equal to zero and $s_1 = 1$. As mentioned, this condition can be obtained only when there is no chemical reaction or when diffusion is extremely fast. However, even in systems with very small Thiele modulus, the $\bar{\bar{\xi}}$ and χ profiles will become very close only after a certain contact time has elapsed, that makes the time derivatives of χ very small. As an example, for $\phi = 1$, τ should be longer than 0.30. For closed systems where an irreversible chemical reaction proceeds, the time derivatives of χ never cancel and the profiles do not coincide, except that at certain "long" dimensionless time, with a value that is a function of the Thiele modulus, total conversion can be reached. It can also be observed that at low dimensionless times the volume-averaged concentration in the catalyst $\bar{\bar{\xi}}$ increases as a consequence of the high initial flux from the gas phase and the low chemical
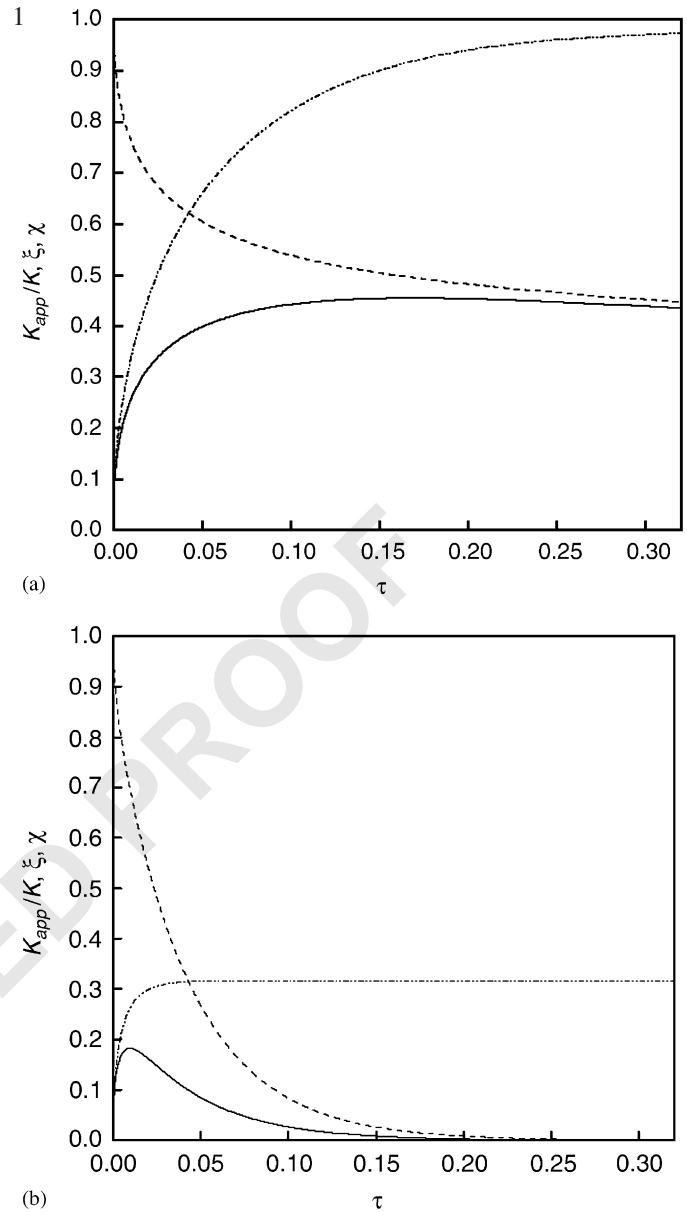

(a)

(b)

Fig. 1. Dimensionless reactant concentration profiles in the gas (- - - - -) and solid (——) phases and relationship K_{app}/K (—··—) as a function of dimensionless time for various values of the Thiele modulus. Parameter $\alpha = 1$. (a) $\phi = 1$; (b) $\phi = 10$.

reaction rate due to the low values of $\bar{\bar{\xi}}$. Later, the concentration of reactant in the gas phase decreases, thus diminishing the flux of reactant into the catalyst, and the chemical reaction rate increases due to the higher values of $\bar{\bar{\xi}}$, with the result that a maximum in the volume-averaged concentration in the catalyst develops (see Fig. 1).

A better comprehension of the meaning of these results can be obtained in terms of real time, considering some typical data from fluidized bed batch reactors (Pruski et al., 1996). For zeolite Y, for example, the values of diffusivity of various paraffinic and aromatic hydrocarbons can be considered to fluctuate between 10^{-15} and $10^{-14}\,\mathrm{m^2/s}$ at temperatures about $500\,^\circ\mathrm{C}$ (Masuda et al., 1996; Bidabehere and Sedran, 2001). Zeolite

Table 1
Relative errors ($e=((K-K_{app})/K)100$) in the assessment of K_{app} at different dimensionless times for various values of the Thiele modulus and $\alpha = 1$

Dimensionless time τ	Thiele modulus ϕ			
	$\phi = 0$	$\phi = 1$	$\phi = 5$	$\phi = 10$
0.01	65.7	65.9	68.0	73.5
0.10	16.0	18.0	43.8	68.3
0.20	3.29	5.93	42.5	68.3
0.30	0.0	2.9	42.5	68.3
0.50	0.0	2.0	42.5	68.3

crystals usually range from 0.3 to 1.0 μm, and reaction times of 2–10 s could be considered representative (Pruski et al., 1996; Bidabehere and Sedran, 2001; Al-Khattaf and de Lasa, 2002). Under these conditions, maximum experimental dimensionless times of 0.1 are expected for systems with fast diffusion, and of 0.01 for systems with slower diffusion. Values of α from 1 to 10 represent the conditions used in, e.g., Pruski et al. (1996) or Bidabehere and Sedran (2001), which are about 1 g of catalyst and a gas phase volume of approximately 45 cm³. Then, typical experimental conditions are represented properly by the values of the parameters selected for this analysis.

The values of the adsorption constants obtained by assuming that the relation between the amount of adsorbed reactant and its concentration in the gas phase is not influenced by the simultaneous diffusion and chemical reaction processes, are indeed "apparent", and, as it will be shown, they also depend on reaction time. They should be defined as $K_{app} = \overline{q}/C$ or, in terms of dimensionless variables (refer to Eqs. (1)),

$$K_{app} = \frac{\overline{\xi}}{\chi} K. \tag{10}$$

The variation of the relationship between K_{app} and K along the reaction time is depicted in Fig. 1, where the very strong influence of the Thiele modulus on the maximum value that can be reached in the relationship can be seen. A pseudo-equilibrium state is attained where K_{app}/K remains constant, that is, both $\overline{\xi}$ and χ do change, but their relationship becomes constant, as previously described. This defines a pseudo-equilibrium state, and the value of K_{app} at that point, that depends on α and ϕ, will be named then K_{app}^{pE}. Moreover, the larger the Thiele modulus, the shorter the dimensionless time at which this particular state is reached. The adsorption constants K_{app}^{pE} and K are the same only when the Thiele modulus is zero. The relative errors e derived from the assumption that $K = K_{app}$,

$$e = \frac{K - K_{app}}{K} \tag{11}$$

are shown in Table 1. It can be seen that even in systems with a relatively small Thiele modulus, say, one or smaller, the relative error is lower than about 10% dimensionless time is longer than about 0.2 for $\alpha = 1$.

It can also be concluded that at any time the ratio K_{app}/K also represents the value of the effectiveness factor. In effect,
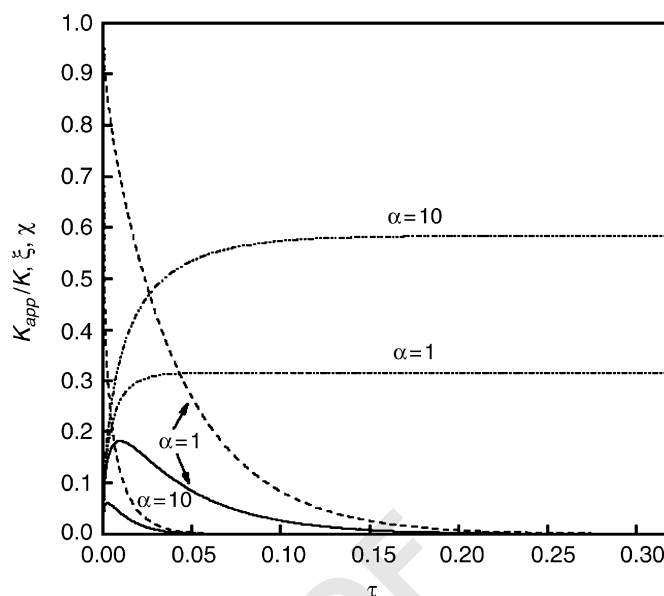

Fig. 2. Influence of the value of the parameter α on the dimensionless reactant concentration profiles in the gas (- - - -) and solid (——) phases and relationship K_{app}/K (– · · –) as a function of dimensionless time. Thiele modulus $\phi = 10$.

for a first order reaction, the effectiveness factor is defined as

$$\eta = \frac{\int_0^R 4\pi k q(r) r^2 \, \mathrm{d}r}{\frac{4}{3}\pi R^3 k q(R)} = \frac{\overline{q}}{KC} = \frac{K_{app}}{K}. \tag{12}$$

The evolutions of the effectiveness factors as a function of the dimensionless time, for various Thiele moduli, then, can be observed in Fig. 1.

The effect of the amount of catalyst on the relationship between K_{app} and K can be studied by varying the value of α while the Thiele modulus is constant. Fig. 2 shows the results obtained for $\phi = 10$. If α increases, both the gas and solid phase concentration profiles develop faster, and the value for the relationship K_{app}^{pE}/K increases, thus diminishing the error originated in the assumption of no interaction between adsorption, chemical reaction and diffusion processes. The same trends were observed for different values of the Thiele modulus, but when $\alpha < 1$, the increase in K_{app}^{pE}/K with α is lower. In those cases, the overall capacity of the solid is small as compared to that of the gas phase. Then, gas phase concentration changes slowly, keeping values close to the initial ones. The volume-averaged concentration in the solid will tend to the value $s_1\chi$, that is, $\overline{\xi}/\chi$ will tend to s_1, which does not depend on α.

The impact of the temperature can be analyzed if the chemical reaction and the diffusion rates change with temperature following Arrhenius' law, and that the energy of activation of the chemical reaction is higher than that of the diffusive process. If the temperature is increased in additional experiments, the Thiele modulus will increase. Moreover, the higher the temperature, the lower the adsorption constants, as predicted by the Van't Hoff equation, and the parameter α will decrease. The consequences will be that K_{app} will decrease more than K. This causes an error on the heat of adsorption if it is measured by temperature variations.

1   The following equation shows how the reactant mass balance in the gas phase is linked to changes in the volume-averaged
3   concentration in the catalyst $\overline{\xi}$ (Bidabehere and Sedran, 2001):

$$\frac{\mathrm{d}\chi}{\mathrm{d}\tau} = -\alpha\left(\frac{\mathrm{d}\overline{\xi}}{\mathrm{d}\tau} + \phi^2\overline{\xi}\right). \tag{13}$$

5   An expression for $\overline{\xi}$ in the pseudo-equilibrium state can be obtained from Eq. (10) and introduced into Eq. (13) to give

$$\frac{\mathrm{d}\chi}{\chi} = -\frac{\alpha\phi^2}{(1 + \alpha(K_{\mathrm{app}}^{pE}/K))}\frac{K_{\mathrm{app}}^{pE}}{K}\,\mathrm{d}\tau. \tag{14}$$

7

The transient responses of the reactant gas phase concentrations
9   given by the best fits of

$$\chi(t) = \chi^*(0)\exp(-p\tau) \tag{15}$$

11   to the exact solutions of Eqs. (2)–(4) and (7)–(9) were analyzed in order to define the initial condition $\chi^*(0)$, that is necessary
13   to integrate Eq. (14).

Results showed that the exponential factor p is

$$p = \frac{\alpha\phi^2}{(1 + \alpha(K_{\mathrm{app}}^{pE}/K))}\frac{K_{\mathrm{app}}^{pE}}{K} \tag{16}$$

15

provided that the final time employed in the calculations is
17   large enough for K_{app} to reach the steady value K_{app}^{pE}. Fig. 3 shows the evolutions of the dimensionless reactant gas phase
19   concentrations predicted by both the exact (Eqs. (2)–(4) and (7)–(9)) and the pseudo-equilibrium models (Eq. (14)) for $\alpha = 1$
21   and $\phi = 5$, 10. It can be seen that, except for short dimensionless times, the solution of the pseudo-equilibrium state equation
23   matches the exact one.

It is interesting to observe that the initial values $\chi^*(0)$ for
25   the pseudo-equilibrium model are less than one. While in the exact model the initial dimensionless concentration is $\chi(0) =$
27     $C(0)/C_0 = 1$ the parameter $\chi^*(0)$ of the pseudo-equilibrium model has physical meaning only for the case of instantaneous
29   diffusion. In that case, the mole balance at the initial instant can be written

31     $$N_0 = V_s q(0) + V_g C(0) \tag{17}$$

leading to

33     $$C(0) = \frac{N_0}{V_g}\frac{1}{(1 + (V_s/V_g)K)} = C_0\frac{1}{(1 + \alpha)}, \tag{18}$$

$$\chi^*(0) = \frac{1}{(1 + \alpha)}. \tag{19}$$

35   The initial values of the pseudo-equilibrium model $\chi^*(0)$ tend to the value given by Eq. (19) for any α when $\phi \to 0$. However,
37   as the diffusive resistance is increased, it becomes increasingly larger (see Fig. 3) and it is close to one if $\phi \to \infty$. This
39   variation of the initial value $\chi^*(0)$ with α and ϕ is complex.

The experimental change of reactant gas phase concentration
41   as a function of time obtained by pulse injection of reactant in a batch stirred reactor is well approximated by an exponential
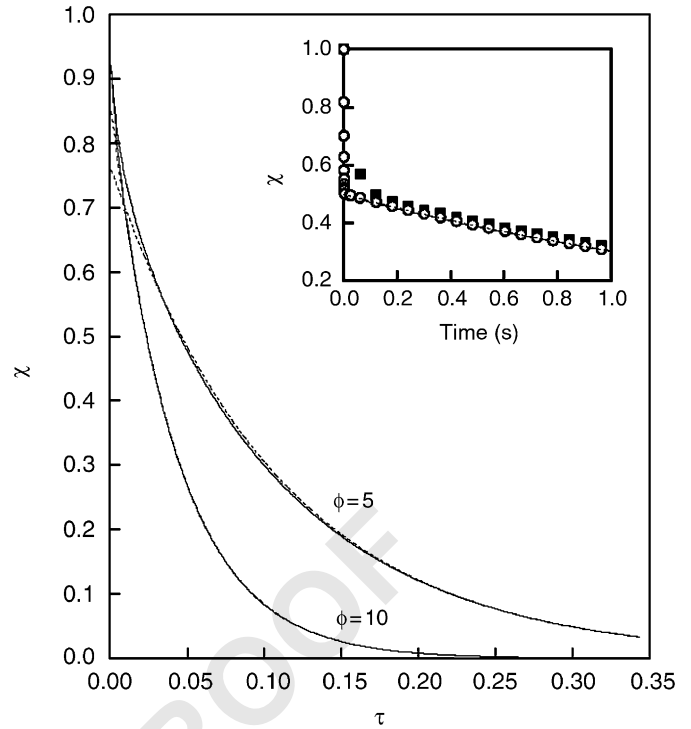43

Fig. 3. Evolution of the dimensionless reactant concentration in the gas phase as a function of dimensionless time. Solutions from the pseudo-equilibrium model (Eq. (14)) (- - - -) and from the system of Eqs. (2)–(4) and (7)–(9) (exact solution, ——). Inner figure, solutions from the pseudo-equilibrium model (—— $\phi = 1$, - - - . $\phi = 0.1$) and exact solutions (■ $\phi = 1$, ○ $\phi = 0.1$). For all the cases, parameter $\alpha = 1$.

equation. Further analysis on the expression for p shows that for systems with high capacity for adsorption, that is $\alpha(K_{\mathrm{app}}^{pE}/K) \gg$ 45
1, p tends to ϕ^2 and the kinetics constant k can be assessed from the experimental data, since χ becomes proportional to 47
$\exp(-\phi^2\tau)$. In this case, no information can be obtained about the adsorption parameter. On the contrary, when the amount of 49
catalyst and/or the adsorption constant are small ($\alpha \ll 1$), p tends to $\alpha\phi^2(K_{\mathrm{app}}^{pE}/K)$, and then χ becomes proportional to 51
an exponential function $\exp(-(V_s/V_g)K_{\mathrm{app}}^{pE}kt)$. It can be seen that the rate of change of $\ln(\chi)$ against time depends on the 53
product of kinetics and adsorption parameters, and infinite pairs of these parameters are possible. Thus, the conventional pulse 55
techniques in gradientless reactors, leading to transient curves of concentrations at a given temperature (e.g. Ma and Roux, 57
1973; Furusawa et al., 1976; Kelly and Fuller, 1980; Oberoi et al., 1980; Frost, 1981; Schobert and Ma, 1981a,b; Miró et 59
al., 1986), would be adequate for the estimation of adsorption and reaction parameters only when it is possible to change α 61
over a wide range of values. In cases where the design of the reactor or the system's capacity of adsorption imposes $\alpha \ll 1$ 63
or $\alpha(K_{\mathrm{app}}^{pE}/K) \gg 1$, alternative strategies and techniques need to be developed. 65

Another approach for batch stirred reactors includes the injection of a pulse of reactant and the consideration of com- 67
plete evacuation after reaction (e.g. Pruski et al., 1996; Atias et
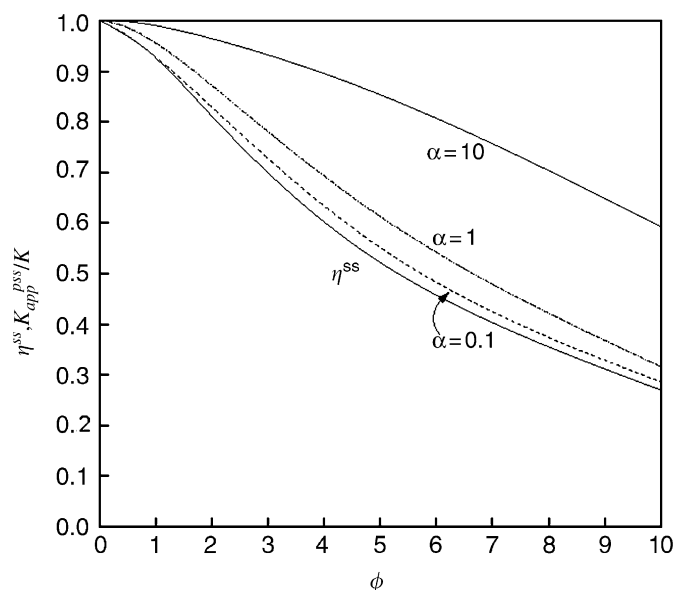
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Fig. 4. Effectiveness factor at the steady state for catalyst particles and relationship K_{app}^{pE}/K as a function of the Thiele modulus for various values of the parameter α.

al., 2003). Using overall system compositions and simulation models that ignore the interaction of diffusion and adsorption, allows only the assessment of K_{app} under some particular conditions.

Analysis of Eq. (14) suggests that it is possible to represent a heterogeneous model where diffusive resistance to mass transport is important, by means of a much simpler expression, which is analogous to a heterogeneous system where the solid catalyst is assumed to follow a steady-state behavior, while the concentration in the gas phase changes. Indeed, this is a well-established hypothesis in the theoretical treatment of heterogeneous catalytic reactors (Aris, 1975),

$$\frac{d\chi}{d\tau} = -\alpha\phi^2\eta^{SS}\chi, \tag{20}$$

where η^{SS} is the effectiveness factor for the particle at the steady state.

Comparisons between the solutions obtained with Eqs. (14) and (20) were made for different values of the parameters α and ϕ. Results confirmed that the time evolutions of the reactant concentration in the gas phase were coincident if α tended to very small values, say $\alpha < 0.1$. In that case $\alpha(K_{app}^{pE}/K) \ll 1$, and Eq. (14) can be reduced to

$$\frac{d\chi}{\chi} = -\alpha\phi^2\frac{K_{app}^{pE}}{K}d\tau \tag{21}$$

and that means that the accumulation term described in the right-hand side of Eq. (13) becomes zero. Under these limiting conditions, the comparison of Eqs. (20) and (21) means that the ratio K_{app}^{pE}/K would equal the steady-state effectiveness factor η^{SS}. Fig. 4 shows values of K_{app}^{pE}/K for reactive systems of different adsorption capacity α as a function of the Thiele

modulus. It can be seen that the smaller the value of α, the closer the ratio K_{app}^{pE}/K is to the steady-state effectiveness factor. However, it can be seen that for any value of ϕ, K_{app}^{pE}/K, equivalent to the pseudo-equilibrium state effectiveness factor, is always larger than η^{SS}.

The dynamics of a system when the accumulation term in the mass balance for the solid is disregarded will be different from the one resulting from Eq. (14). The factor $(1 + \alpha(K_{app}^{pE}/K))^{-1}$ in Eq. (14), that is assumed unity in approximate models (Al-Khattaf et al., 2002), can certainly be very far from that, depending on the experimental conditions and on the values of certain properties of the system. For moderate or high adsorption capacities ($\alpha \geqslant 1$), it tends to unity only for extremely large values of the Thiele modulus.

The above considerations will be useful in the kinetics analysis of catalytic reactions, when the pseudo-homogeneous assumption is invoked. For example, for a first order reaction,

$$V_g\frac{dC}{dt} = -V_s k_{app}C, \quad C(0) = C_0 \tag{22}$$

whose solution is

$$\frac{C}{C_0} = \exp\left(-\frac{V_s}{V_g}k_{app}t\right). \tag{23}$$

On the other hand, the solution for Eq. (14) is

$$\frac{C}{C_0} = \exp\left(-\frac{(V_s/V_g)K_{app}^{pE}}{1 + (V_s/V_g)K_{app}^{pE}}kt\right). \tag{24}$$

It can be concluded from Eqs. (23) and (24) that

$$k_{app} = \frac{K_{app}^{pE}}{1 + (V_s/V_g)K_{app}^{pE}}k. \tag{25}$$

Provided that K_{app}^{pE} is known together with some system's parameters, Eq. (25) allows determination of the intrinsic kinetics constant, starting from the observed kinetics constant k_{app}, that can usually be estimated from the experimental information without major problems. Particularly, if $(V_s/V_g)K \ll 1$, then

$$k_{app} = K_{app}^{pE}k. \tag{26}$$

The error from assuming $K = K_{app}^{pE}$ in the kinetics analysis of a given first order reaction can be very large, particularly if ϕ is higher than 1, as shown in Fig. 5. For example, when $\alpha = 1$, $K_{app}^{pE} < 0.57K$ if $\phi = 5$, and $K_{app}^{pE} < 0.32K$ if $\phi = 10$. Larger values of α make the error smaller, but Eq. (26) can no longer be applied, because $(V_s/V_g)K_{app}^{pE} > 1$. It can also be seen in Eq. (25) that if $(V_s/V_g)K \ll 1$, then $k_{app} = (V_g/V_s)k$, and it is possible to determine k directly, which in that case is not affected by adsorption nor diffusion.

4. Conclusions

The adsorption constants that are determined by usual methods in stirred reactors are apparent and, even though they are linked to Henry's constants, they also depend on the resistance

1 to diffusion in the catalyst, the amount of solid in the reactor and the time on stream in the experiment. The simple pseudo-
3 equilibrium model developed, that considers the interactions between diffusion, adsorption and reaction, represents properly
5 the evolutions of catalytic systems where a first order chemical reaction occurs. The pseudo-equilibrium state is reached when
7 the ratios between apparent and true adsorption constants, or dimensionless solid and gas phase reactant concentrations, be-
9 come constant. The error generated by the quasi-steady-state assumption is very important, and impacts on the assessment of
11 kinetics constants. The ratio between apparent and true adsorption constants equals the dynamic effectiveness factor and, at
13 the pseudo-equilibrium state, the smaller the adsorption capacity of the system, the closer this factor to the steady-state effec-
15 tiveness factor. Limitations of the models that consider that the solid catalyst follows a steady-state behavior, while the concen-
17 tration in the gas phase changes, were established. The quasi-steady state is applicable for any value of ϕ only if $\alpha < 0.1$.
19 A new analysis proposed for batch stirred reactors allows determination of kinetics and adsorption constants for linear sys-
21 tems by simple algebraic expressions. The pseudo-equilibrium model is a more general approximation than the quasi-steady-
23 state model, since its use is not restricted to systems with low adsorption capacity.

25 **Notation**

Symbols

C	concentration in the gas phase, gmol/m^3
D	diffusivity, m^2/s
e	error defined in Eq. (11)
k	kinetic constant, s^{-1}
K	Henry's constant, dimensionless
m	mass, g
MW	molecular weight, g/gmol
N	number of moles
p	exponential factor defined in Eq. (16), dimensionless
P	pressure, atm
q	concentration in the solid phase, adsorbed compounds, mol/g
r	radial distance, m
R	catalyst particle radius (m) or universal gas constant
s	coefficient of expansion in Eq. (5), defined in Eq. (6)
t	time, s
T	temperature, K
V	volume, m^3
w	mass percentage composition, dimensionless

Greek letters

α	relationship between gas and solid phase volumes, dimensionless
η	effectiveness factor, dimensionless
λ	parameter defined in Eq. (6)
ξ	dimensionless concentration in solid phase
ρ	dimensionless radial distance in the solid, or density, g/cm^3
τ	dimensionless time
ϕ	Thiele modulus, dimensionless
χ	dimensionless concentration in the gas phase

Superscripts

pE	pseudo-equilibrium
SS	steady state
—	volume averaged variable

Subscripts

app	apparent
Cat	catalyst
g	gas phase
HC, 0	hydrocarbons injected
i	system component i
s	solid phase
0	initial

5. Uncited references

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