

Displacement Adsorption in the Non-Steady State Computer Modelling Study

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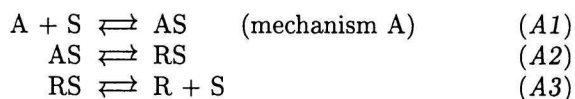
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Nonstationary kinetic behaviour of a simple model mechanism (of an overall reaction $A \rightleftharpoons R$) with displacement adsorption ($A + RS \rightleftharpoons AS + R$, S being the catalyst active site) is analyzed. Examples of transient responses are presented that are typical for the mechanism with a displacement adsorption. However, in many cases mechanisms with direct and displacement adsorption cannot be distinguished by means of the transient response methods. An interesting relation between kinetics and thermodynamics in unsteady flow systems is described.

Kinetics of heterogeneous catalytic reactions is investigated usually under the stationary conditions. Rate equations are developed mainly according to the well-known methodology developed by *Langmuir* [1], *Hinshelwood* [2], *Hougen and Watson* [3]. In this approach, a catalytic reaction is represented by a series of adsorption, surface reaction, and desorption processes. Some authors prefer some type of power law rate equations.

For example, an overall reaction $A \rightleftharpoons R$ may be written as a sequence of the adsorption (A1) of reactant (A) on the catalyst active site (S), surface reaction (A2), and product (R) desorption (A3)



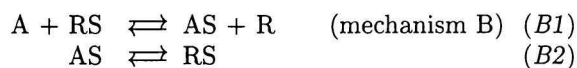
In this mechanism, reactant may bond only to the vacant active site.

In our studies of amine reactions on acid catalysts very strong interaction product—catalyst was observed by *Vavřinec* [4]. During the elimination of secondary amines, $R_2NH \rightarrow RNH_2 + R\text{-alkene}$, formed primary amine is very strongly bonded to the catalyst. The desorption of the amine product is thus very slow, active sites being occupied by the product molecules and the elimination reaction could be inhibited. However, we have observed that the reaction can proceed on by means of the displacement of the product molecules by the reactant (secondary amine) molecules.

As *Morávek* and *Sadovnikov* [5] remarked, this idea of displacement adsorption was suggested by *Ipatieff* in 1913. *Sadovnikov* and *Geftler* [6], *Rozovskii* and co-workers [7, 8], and *Morávek* [9–12] published other

experimental confirmations of this adsorption mechanism. Although displacement adsorption might occur in many reactions still little attention has been paid to this reaction step. One cause may be the difficulty in experimental revealing of the displacement adsorption.

Morávek and *Sadovnikov* [5] discussed kinetic consequences of the displacement adsorption in a simple reaction $A \rightleftharpoons R$ in the steady state. Instead of the classical mechanism A (see above) they considered alternative mechanism (B) consisting of the displacement adsorption (B1) and surface reaction (B2)

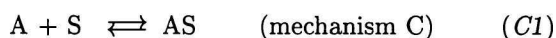


Note, that for this mechanism to proceed, preadsorbed supply of the product (R) molecules is necessary. *Morávek* and *Sadovnikov* showed that mechanisms A and B are indistinguishable in the steady state.

This ambiguity of interpretation of stationary kinetic data is well known [13–15]. Therefore, nonstationary (transient response) methods are more and more applied in the research of catalytic reaction kinetics [16–20]. These methods are believed to give deeper insight into the real nature of kinetics and mechanism. Nonstationary methods consist in imposing some kind of perturbation, usually concentration step change, on the reaction system that is in a steady or initial state. Responses of concentration on this change are recorded.

In this study, nonstationary behaviour of a mechanism containing displacement adsorption is analyzed in general. The model mechanism (C) is, in fact, combination of the mechanisms A and B

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Note two parallel routes for the adsorption of reactant (A) molecules – on the vacant active sites (S), step (C1), and by the displacement of adsorbed product, step (C4). Thus, unlike mechanism B, this mechanism does not invoke any assumption of the product preadsorption. No product preadsorption exists, for example, in the case of amine elimination mentioned above.

Main aim of the present study is to analyze transient kinetic behaviour of the mechanism C and find whether this mechanism can be distinguished from the mechanism A by the transient response methods and thus help experimenters in their laboratory work. Computer modelling is used for this purpose. Morávek—Sadovnikov's results [5] are thus extended to a more general and reliable, while still simple, mechanism and detailed true kinetic analysis is given. An experimenter may ponder, bearing in mind the results of presented model computations, if some displacement adsorption is not hidden in his data.

First it is shown that mechanisms A and C are indistinguishable in the steady state. Examples of transient responses of the mechanism C are given, which cannot be obtained with the mechanism A. However, these mechanisms are often indistinguishable even by means of transient response methods. Interesting connection between transient kinetics and thermodynamics is noted – it is shown that though a reaction is coming close to the equilibrium, its rate, in a flow system, may be increasing.

MATHEMATICAL MODEL

An isothermal differential flow reactor with constant flow rate is assumed. This type of reactor is used in our laboratory for nonstationary experiments and is often encountered in other published works. Mathematical model of the reactor is as follows

$$dp_i/dt = (u/\epsilon L)(p_i^0 - p_i) + (\rho_c RT/\epsilon)r_i \quad (1)$$

$$d\theta_i/dt = r_i/q \quad (2)$$

where, for instance, for the product formation in the mechanism C, the rate is expressed

$$r_R = k_4 p_A \theta_R - k_{-4} p_R \theta_A + k_3 \theta_R - k_{-3} p_R \theta_v \quad (3)$$

A similar reactor model has been used, for example, by Kobayashi and Kobayashi [16]. Model equations were solved using the well-known Michelsen's method [21].

In all published studies only the responses of the gas-phase or surface concentrations are discussed. It is our experience that these responses do not give the whole information on the behaviour of elementary steps. In our computations we trace also the responses of the rate of each elementary step. Rates are computed from the equations like eqn (3).

RESULTS AND DISCUSSION

Steady State

Before presentation of the results of computer modelling of transient responses we extend Morávek—Sadovnikov's conclusion (see above, [5]) and show that also mechanisms A and C are indistinguishable in the steady state.

Note that mechanism C does not consist of only consecutive steps. Therefore, in contrast to the mechanism A, steady rates of its elementary steps are generally neither identical nor equal to the overall rate. From the stationary form of the reactor balance equations it can be found that following relations are valid for the mechanism C: $r_1^{ss} = r_3^{ss}$, $r_2^{ss} = r_1^{ss} + r_4^{ss} = r_3^{ss} + r_4^{ss}$

Classical Langmuir—Hinshelwood—Hougen—Watson approach is thus not applicable here. Theory of stationary rates by Horiuti [22] and Temkin [23] can be used. According to it, the rate of an overall reaction is equal to the rate of any elementary step multiplied by the stoichiometric number of that step. Expressing the overall reaction rate in mechanism C in this way, the same equation as for mechanisms A and B [5] is obtained

$$r = q_S(ABp_A - CDp_R)/(a + Bp_A + Dp_R)$$

However, parameters in this equation have now different meaning, viz.: $A = 2k_2k_3/b$, $B = bk_1/c$, $C = 2k_{-1}k_{-2}/d$, $D = dk_{-3}/c$, where $a = 1$, $b = k_2 + 2k_3 + k_{-2}$, $c = k_2k_3 + k_{-1}k_{-2} + 2k_{-1}k_3$, $d = k_2 + 2k_{-1} + k_{-2}$.

Non-Steady State

Two types of perturbations are modelled in this study. The first one is the step increase of the reactant inlet partial pressure from 0 to 1400 Pa made onto the fresh catalyst. When the steady state is achieved, reactant feed is shut down and this is the second kind of perturbation.

Sets of the rate constants used for computer simulation are presented in Table 1. Note that the rate constants obey the basic relation [5]

$$K_4 = K_1K_3 = K_A/K_R$$

Responses to the step increase of reactant inlet partial pressure obtained with the set 1 (Table 1) are pre-

Table 1. Sets of the Rate Constants (For numbering of the steps see eqns (C1—C4))

Set	k_1^a	k_{-1}^b	k_2^b	k_{-2}^b	k_3^b	k_{-3}^a	k_4^a	k_{-4}^a
1	10^{-5}	10^{-3}	10^{-1}	10^{-5}	10^{-4}	10^{-2}	10^{-3}	10
2	2×10^{-7}	2×10^{-7}	2×10^{-4}	2×10^{-4}	10^{-4}	10^{-4}	2×10^{-5}	2×10^{-5}
3	5×10^{-4}	5×10^{-6}	25×10^{-6}	5×10^{-5}	25×10^{-5}	25×10^{-7}	5×10^{-2}	5×10^{-6}
4	75×10^{-7}	75×10^{-4}	375×10^{-7}	75×10^{-5}	75×10^{-4}	75×10^{-8}	75×10^{-5}	75×10^{-6}

a) $\text{mol kg}^{-1} \text{s}^{-1} \text{Pa}^{-1}$; b) $\text{mol kg}^{-1} \text{s}^{-1}$.

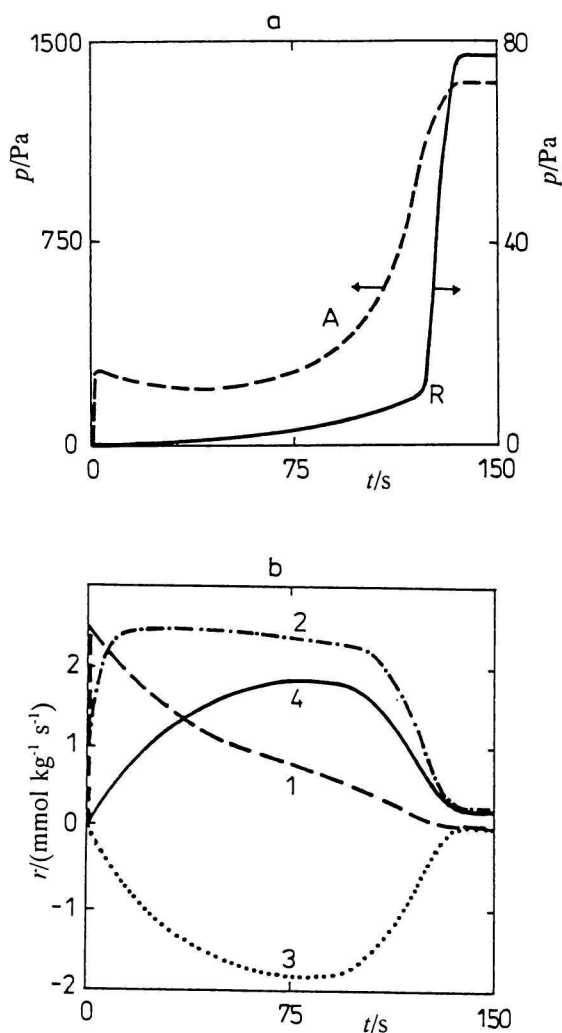


Fig. 1. Responses of the gas-phase concentrations (a) and rates of elementary steps (b) to the start of reactant feed. A – reactant, R – product, for numbering of steps see eqns (C1—C4). Computed with the rate constant set 1 (Table 1).

sented in Fig. 1. The most interesting shape has the curve $p_A(t)$ (Fig. 1a). Kinetic nature of this shape can be deduced from the rate responses (Fig. 1b). The adsorption is potentially not very fast, see the low values of its rate constants (Table 1, set 1). Therefore, outlet reactant pressure (p_A) initially grows steeply (Fig. 1a). Rate of the potentially rapid surface reaction increases very quickly (Fig. 1b) and adsorbed

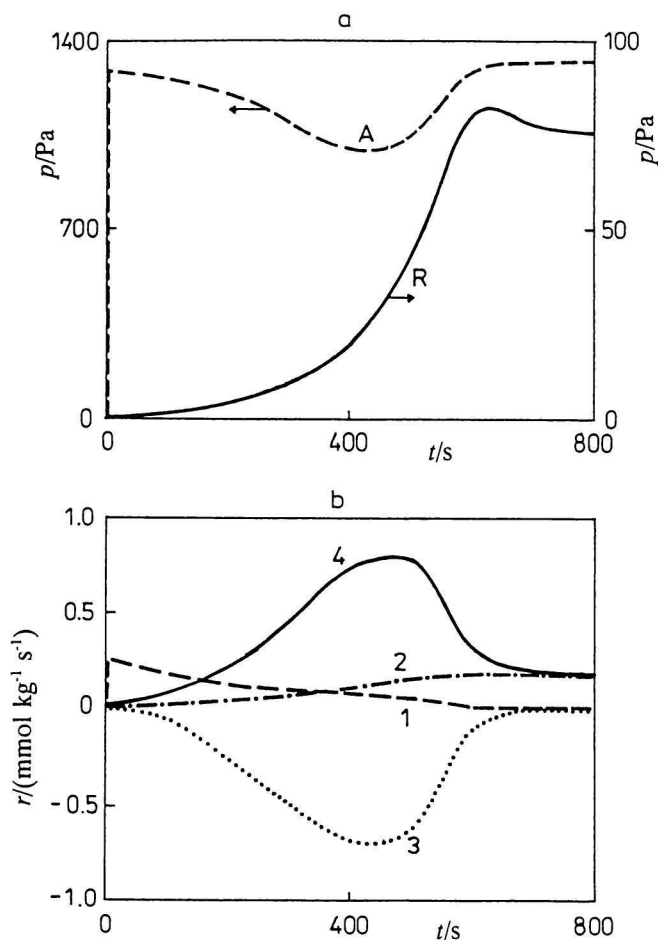


Fig. 2. Responses of the gas-phase concentrations (a) and rates of elementary steps (b) to the start of reactant feed. A – reactant, R – product, for numbering of steps see eqns (C1—C4). Computed with the rate constant set 2 (Table 1).

reactant molecules are fast transformed to the adsorbed product molecules. Product molecules can be displaced and the rate of displacement adsorption really increases (Fig. 1b). Rapid displacement adsorption supplies the reactant (species AS) for the surface reaction, therefore, surface reaction rate changes only slowly for a long time.

Fast displacement adsorption followed by the fast surface reaction cause large consumption of the reactant molecules from the gas phase. Consequently, long delay with minimum on the curve $p_A(t)$ (Fig. 1a) re-

sults. It was also found that decreasing the values of $k_{\pm 4}$, with no change in K_4 , resulted in disappearing of the delay and in a monotonous increase of the reactant partial pressure up to the stationary value.

This shape of the reactant transient response (Fig. 1a) thus may be considered as specific for the mechanism C.

Step 3 – product desorption – goes on in the backward direction during the whole transition state (see Fig. 1b). This is because the equilibrium of step 3 is shifted to the left (*cf.* the ratio of its rate constants, Table 1, set 1). Product readsorption promotes the displacement adsorption by supplying the reactant (species RS) for it. It also means that the product is released to the gas phase only by the displacement adsorption.

Only product gas-phase concentration is easily measurable in a differential reactor. Its transient response has no specific shape, see Fig. 1a. Similar shapes were often observed also in our modelling studies of the mechanism A.

Second example, computed with the set 2 (Ta-

ble 1), gave similar results (Fig. 2) with respect to the reactant. The adsorption is potentially slow, therefore, reactant output pressure instantaneously attains nearly the input value (Fig. 2a). Slow adsorption decelerates surface reaction as can be speculated from its low rate (Fig. 2b). However, the high concentration of reactant molecules in the gas phase speeds up the displacement adsorption. Transformation of the reactant A to the product R then goes on more quickly and temporal decrease of the reactant partial pressure occurs (Fig. 2a).

Product concentration response in Fig. 2 is completely different from that in Fig. 1. Particularly, the maximum on the product concentration response (Fig. 2a) is very interesting. It is caused by the decrease of the rates of product readsorption (Fig. 2b, curve 3) and displacement adsorption (Fig. 2b, curve 4). Moreover, the former rate decreased probably due to the increase of the surface reaction rate (Fig. 2b, curve 2). It is really remarkable that these three rate effects are composed in this manner that the maximum appears. Nevertheless, this shape of product

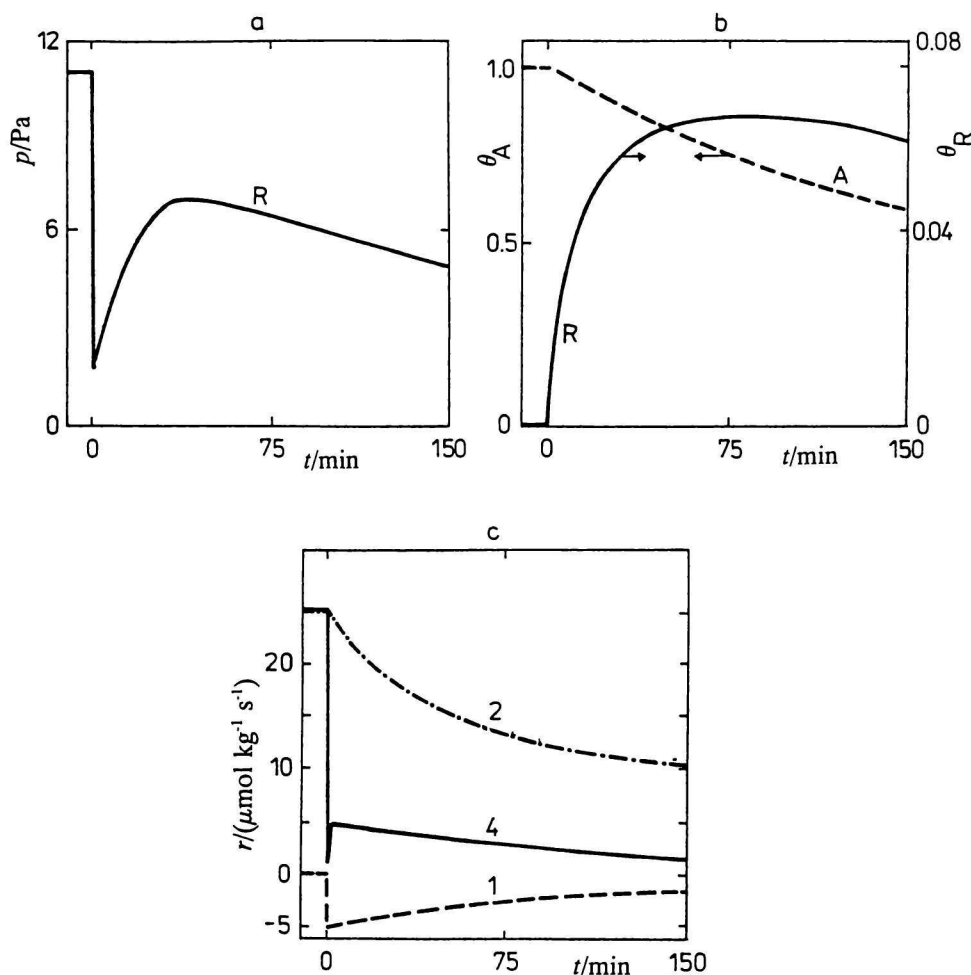


Fig. 3. Responses of the gas-phase (a) and surface (b) concentrations and rates of elementary steps (c) to the cutting off reactant feed. A – reactant, R – product, for numbering of steps see eqns (C1–C4). Computed with the rate constant set 3 (Table 1).

response is not specific for the mechanism C. Similar maxima were observed also in our studies of the mechanism A when adsorption and desorption were potentially very rapid and surface reaction was slow.

In this context, note the near-symmetry to the time axis of the responses of the rates of product desorption (remember that it goes in backward direction) and displacement adsorption in Figs. 1b and 2b. It means that the product is readsorbed by nearly the same rate as it is released to the gas phase by the displacement.

Surprisingly, the displacement adsorption may manifest itself even after the reactant feed is shut down (after the steady state has been achieved). It could be expected that cutting off reactant feed should substantially limit the displacement adsorption. However, Fig. 3 demonstrates something different. There is very high concentration of the reactant molecules on the catalyst surface in the steady state (*cf.* Fig. 3b). When the reactant feed is stopped, reactant gas-phase concentration decreases instantaneously and the reactant starts to desorb (see the negative rate of its adsorption, Fig. 3c). Desorbed reactant molecules quickly re-adsorb by the potentially rapid displacement adsorption as is seen from the consecutive increase of its rate in Fig. 3c. Product surface concentration thus increases (Fig. 3b) and the rate of surface reaction decreases only slowly (Fig. 3c). All these phenomena result in delayed temporary increase of the product output partial pressure (Fig. 3a) which cannot be expected in the mechanism A.

Computations with other sets of the rate constants were performed on the mechanism C and compared with analogical simulations of the mechanism A. No other shapes of measurable responses were found for the mechanism C that could not be obtained for the mechanism A. So, in most cases it would not be possible to distinguish between mechanisms A and C even by means of the transient response methods.

On the Relation between Equilibrium and Kinetics in Flow Systems

Interesting relation between kinetics and equilibrium was observed simulating the mechanism C.

To follow the pathway of an elementary step to equilibrium we have introduced a quantity called the relative distance from equilibrium. It is a fraction, the numerator of which consists of an expression formally identical with the expression for the equilibrium constant but containing the actual values of the concentrations of the species taking part in the particular step. The denominator is equal to the value of the equilibrium constant of the particular step. For instance, the relative distance from equilibrium of displacement adsorption – step 4 in the mechanism C – is given by $D_4 = (p_R \theta_A / p_A \theta_R) / K_4$. Obviously, in the equilibrium of the i -th step D_i is equal to one.

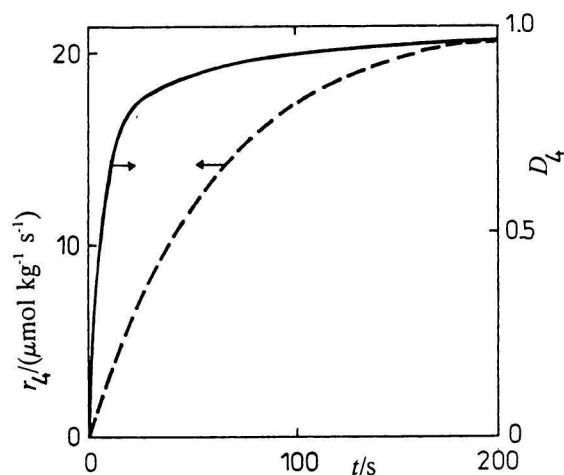


Fig. 4. Responses of the rate (r_4) and distance from equilibrium (D_4) of the displacement adsorption to the start of reactant feed. Computed with the rate constant set 4 (Table 1).

It is commonly believed that the rate of a reversible reaction diminishes when moving to equilibrium. It can be seen in Fig. 4, however, that the rate of displacement adsorption does not decrease when coming close to equilibrium. On the contrary, the rate even increases and near to the equilibrium has a maximum value, which remains then constant.

This is because the overall reaction occurs in a flow reactor. Its actual rate, actual rate of its elementary steps, and all the actual distances from equilibrium are dependent on the concentrations of the reacting species. Concentrations of reactants and products of a particular elementary step are affected not only by the elementary steps themselves but also by continuous feeding and removing of the components. Forcing a reaction step by the continuous feed, and also by the other steps, can result in such phenomena as Fig. 4 presents.

These phenomena are consistent with thermodynamics. As it is well known [24] the inequality $Ar \geq 0$ holds. Expanding in Taylor series gives

$$(Ar)|_{t+\Delta t} = (Ar)|_t + (d(Ar)/dt)\Delta t$$

Considering that in the equilibrium $Ar = 0$ and out of equilibrium $Ar > 0$, it follows that function (Ar) should decrease when a reaction is coming to the equilibrium. Therefore $(Ar)|_{t+\Delta t} < (Ar)|_t$ and $(d(Ar)/dt)\Delta t < 0$. Because $\Delta t > 0$, inequality $d(Ar)/dt < 0$ follows and from it

$$A dr/dt + r dA/dt < 0$$

If both the rate and affinity are positive, the rate of reaction may increase when the reaction moves to the equilibrium, providing the rate is sufficiently high

and affinity decreases sufficiently rapidly at the same time.

CONCLUSION

Profound kinetic conclusions are very often made in practice on the basis of only (of course, solely measurable) concentration data. Analyzed simple mechanisms show that the relations between concentration and rate may not be so straightforward as could be expected. Measured kinetic data should be used primarily to describe concentration behaviour and assertions on the rates should be made very cautiously.

Mechanisms A, B, and C are indistinguishable in the steady state. Furthermore, the displacement adsorption can occur without noting specific shapes of the measurable transient responses. On the other hand, transient responses, typical for the displacement adsorption and not obtainable with the direct adsorption, can be observed in some cases. Mechanistical interpretation of concentration responses, based on the responses of the rates of elementary steps, was given. Displacement adsorption may be hidden in real kinetic data. Usually, to reveal the displacement adsorption more sophisticated experiments (or perturbations) should be employed.

In a differential reactor negligible influence of the reaction products is supposed due to the low conversion. Whereas this may be valid in the steady state, under nonstationary conditions products can take part in reactions (*cf.*, for instance, product readsorption in Fig. 1).

It is a common practice in kinetic research to operate with reaction equilibrium, closeness to or distance from it, and so on without precisely stating what such notions do really mean. For instance, we have shown that in a flow system, rate of reaction may increase although the reaction gets still closer to the equilibrium. Attempts to discard the nearly equilibrated steps from kinetic considerations in the transient state (for instance [25]), because they are not "rate-determining", are thus questionable.

SYMBOLS

A	reactant
A	affinity
D_i	relative distance from equilibrium of i -th step
k_i	forward rate constant of i -th step, $\text{mol kg}^{-1} \text{s}^{-1}$ or $\text{mol kg}^{-1} \text{s}^{-1} \text{Pa}^{-1}$
k_{-i}	backward rate constant of i -th step, $\text{mol kg}^{-1} \text{s}^{-1}$ or $\text{mol kg}^{-1} \text{s}^{-1} \text{Pa}^{-1}$
K_i	equilibrium constant of i -th step
K_i	adsorption coefficient of i -th component
L	length of catalyst bed, 0.01 m
p_i	(outlet) partial pressure of i -th component, Pa
q	total amount of active sites, 0.3 mol kg^{-1}
q_s	concentration of vacant active sites, mol kg^{-1}

r	reaction rate, $\text{mol kg}^{-1} \text{s}^{-1}$
r_i	rate of i -th step, $\text{mol kg}^{-1} \text{s}^{-1}$
η_i	rate of formation of i -th component, $\text{mol kg}^{-1} \text{s}^{-1}$
R	product
R	gas constant, $8.314 \text{ J mol}^{-1} \text{K}^{-1}$
S	active site
T	temperature, 456 K
u	linear velocity of the gas flow, 0.05 m s^{-1}

Greek letters

ϵ	void fraction, 0.5
ρ_c	catalyst bulk density, 580 kg m^{-3}
θ_i	fractional coverage of i -th component

Indices

o	inlet value
ss	steady state value
v	vacant active site

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