

TRANSIENT KINETIC AND THERMODYNAMIC BEHAVIOUR OF LANGMUIR ADSORPTION IN A FLOW SYSTEM

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Various kinetic pathways to the adsorption equilibrium in an isothermal differential bed of adsorbent are illustrated on several examples. Discussion is based on the computed transient responses of adsorption rate and distance from adsorption equilibrium to the start of adsorptive feed. It is shown that adsorption behaviour in flow system may not be smooth and very steep changes on the rate responses may appear. Even the simple reaction need not approach equilibrium smoothly but at a jump. The approach assuming "closeness to the equilibrium" should be used very carefully, in this case.

Key words: Adsorption equilibrium; Kinetics of adsorption; Nonstationary kinetics; Transient response method; Heterogeneous catalysis.

This work originated during our computer modelling studies of nonstationary kinetics in heterogeneous catalysis^{1,2}. Nonstationary methods³⁻⁶ were introduced in the kinetic research to overcome some lacks in traditional, stationary approaches. The rates of all consecutive elementary steps are constant and they equal to each other in the steady state. Under nonstationary conditions, each step proceeds according to its own kinetic nature³. It may be expected that nonstationary data reflect this nature and are not, contrary to the stationary responses, some kind of average (or composed) response³. When a nonstationary method is used, the reaction system that is in a steady or initial state is submitted to a certain perturbation; mostly a concentration step change is applied in the inlet stream. Concentration responses to this change are then recorded.

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An inevitable part of any mechanism in heterogeneous catalysis is the adsorption step. Adsorption of a substance is usually studied under the equilibrium conditions with the aim to obtain adsorption isotherms. However, during the transition state in a multistep process, adsorption equilibrium may not be established. Adsorption kinetics is usually investigated by measuring the increase of the adsorbed amount during adsorption. Such experiments are usually done in batch systems. Little effort has been devoted to transient studies of adsorption in flow systems. Kobayashi⁷ studied transient adsorption behaviour of oxygen, ethene, and carbon dioxide on a silver catalyst. Renken *et al.*⁸ performed similar experiments on adsorption of acetic acid and vinyl acetate on a Pd catalyst and SiO₂ support. Lu *et al.*⁹ used the transient method for studying the adsorption of acetylene on a Pt catalyst.

In this study, transient behaviour of only one reaction (one-step reaction), namely adsorption, is analyzed. The purpose of this paper is to show, by means of computer modelling, how interesting nonstationary phenomena may be even in the case of the simple, Langmuir, adsorption.

MODEL

In our model, we assume the Langmuir mechanism of adsorption of an adsorptive, A, on the active site (S), *i.e.*,



Continuous feed, ideal mixing, and constant flow rate are further considered. This model may be used to interpret nonstationary experiments performed in our laboratory. Similar models have been used in other published works. The set of differential equations describing this "reactor" is as follows:

$$dp_A/dt = (u/\varepsilon L)(p_A^0 - p_A) - (\rho_c RT/\varepsilon)r \quad (2)$$

$$d\Theta_A/dt = r/q \quad (3)$$

where the rate of adsorption, r , is:

$$r = k_+ p_A \Theta_v - k_- \Theta_A \quad (4)$$

The same expression was used by Langmuir in his pioneer work¹⁰. Obviously, it holds $\Theta_v + \Theta_A = 1$.

In the equations, p_A means adsorptive partial pressure, t is time, u linear velocity of the gas flow, ε adsorbent void fraction, L length of adsorbent bed, p_A^0 adsorptive inlet partial pressure, ρ_c adsorbent bulk density, R universal gas constant, T absolute temperature, Θ_A adsorptive fractional coverage, q total concentration of active sites, k_+ and k_- are forward and reverse adsorption rate constants, respectively, Θ_v vacant site fraction.

Published studies discuss only responses of the gas-phase or surface concentrations. It is our experience that these responses do not give the whole information on the nonstationary behaviour of the reaction. In our computations, we study all individual steps in detail. In this work, we focus only on the adsorption step.

To follow the approach to the adsorption equilibrium, we have introduced a quantity called the relative distance from equilibrium, D . It is a fraction, the numerator of which consists of the expression formally identical with the expression for equilibrium constant (adsorption coefficient), but containing actual values of concentrations of the species taking part in the adsorption. The denominator is equal to the value of the adsorption coefficient. Thus, the relative distance from the adsorption equilibrium, D , is given:

$$D = (\Theta_A / p_A \Theta_v) / K_A, \quad (5)$$

where $K_A = k_+ / k_-$. Obviously, in the adsorption equilibrium, D is equal to unity. From the surface mass balance (Eq. (3)) it follows that in the steady state, where $d\Theta_A/dt = 0$, adsorption rate, r , always equals to zero. This means that the adsorption is always in equilibrium when the steady state is established.

Model ordinary differential equations were solved by the Michelsen's method¹¹ suitable for stiff systems.

RESULTS AND DISCUSSION

Responses to the start of the adsorptive, A, feed were modelled. Adsorptive was supposed to be injected into the continuous feed of an inert gas. Three different sets of rate constants were used in the computer simulations (Table I). The selected values represent significantly different adsorption rates and equilibrium states.

Responses computed with the rate constant set 1 (Table I) for various adsorptive inlet pressures are presented in Fig. 1. The obtained responses are easily understandable. The rate of adsorption decreases continuously with increasing surface coverage, while the adsorptive output pressure rises gradually. Adsorption continues smoothly approaching the equilibrium. The stationary (or equilibrium) surface coverage and the time of establishing the steady state depend on the inlet pressure of the adsorptive. The shapes of corresponding responses are only slightly different.

Rather unusual responses were obtained with set 2 (Table I) – see Fig. 2. Particularly, the responses of the rate and of the distance from equilibrium

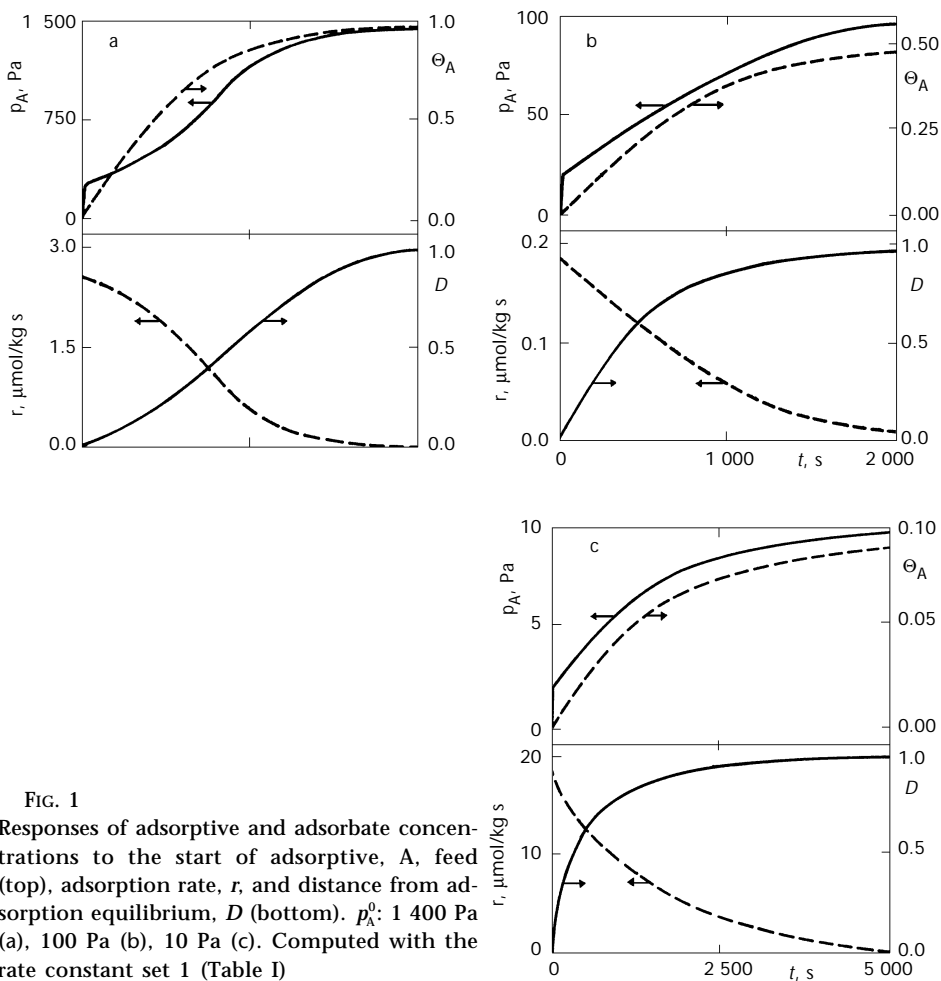


FIG. 1

Responses of adsorptive and adsorbate concentrations to the start of adsorptive, A, feed (top), adsorption rate, r , and distance from adsorption equilibrium, D (bottom). p_A^0 : 1 400 Pa (a), 100 Pa (b), 10 Pa (c). Computed with the rate constant set 1 (Table I)

are surprising. Regardless of the inlet pressure of the adsorptive, the rate of adsorption is relatively high and constant immediately after the start of feed. It decreases steeply just before the steady state is attained. The surface coverage grows up monotonously until the surface is practically totally covered. The time and way of establishing the equilibrium, but not the equilibrium surface coverage, are influenced by the adsorptive inlet pressure. The system seems to settle steadily far from the equilibrium but just before the steady state, it instantaneously jumps to the equilibrium. This behaviour can be observed, in particular, for relatively high values of the adsorptive inlet pressure.

Compared with the previous example, the values of the rate constants and adsorption coefficient are relatively high (Table I). The rate of adsorption is thus more determined by the values of the rate constants than by the values of concentrations (within the framework of the mass-action law). Because of the high values of rate constants, the rate is high even under the low inlet pressure of the adsorptive; responses are not qualitatively different when increasing the pressure. The rate is still high even when the surface coverage is high and the concentration of vacant active sites is thus low. Only when their concentration falls below a certain critical, very low, value, adsorption rate drops.

A fairly large nonstationary distance from equilibrium under a relatively high inlet pressure of the adsorptive in Fig. 2 is caused by the conditions in the gas phase. An increase in the partial pressure of the adsorptive shifts the adsorption more away from the equilibrium (*cf.* the value of adsorption coefficient in Table I). The reverse reaction rate, which is not directly affected by the adsorptive, does not change very much until the steady state is reached. However, the forward reaction rate, which is directly affected by the adsorptive, falls down very fast just before reaching the steady state (due to the minimum concentration of vacant active sites) and becomes

TABLE I
Rate and equilibrium constants of adsorption

Set	k_+	k_-	K_A
1	10^{-5}	10^{-3}	10^{-2}
2	$2 \cdot 10^{-2}$	$2 \cdot 10^{-4}$	10^2
3	10^{-1}	10	10^{-2}

equal to the reverse reaction rate. A steady state in which the adsorption is in equilibrium thus results.

The first example (Fig. 1) shows typical responses of weak (*i.e.*, with a low value of adsorption coefficient) and slow adsorption while the second one (Fig. 2) represents a strong (*i.e.*, with a high value of adsorption coefficient) and rapid adsorption.

It could be expected, that after increasing the values of the rate constants in set 1, and with no change in K_A , responses similar to set 2 should be obtained. Such example, computed with set 3 (Table I) is shown in Fig. 3. The shift in direction from Fig. 1 to Fig. 2 is evident although the rate, equilib-

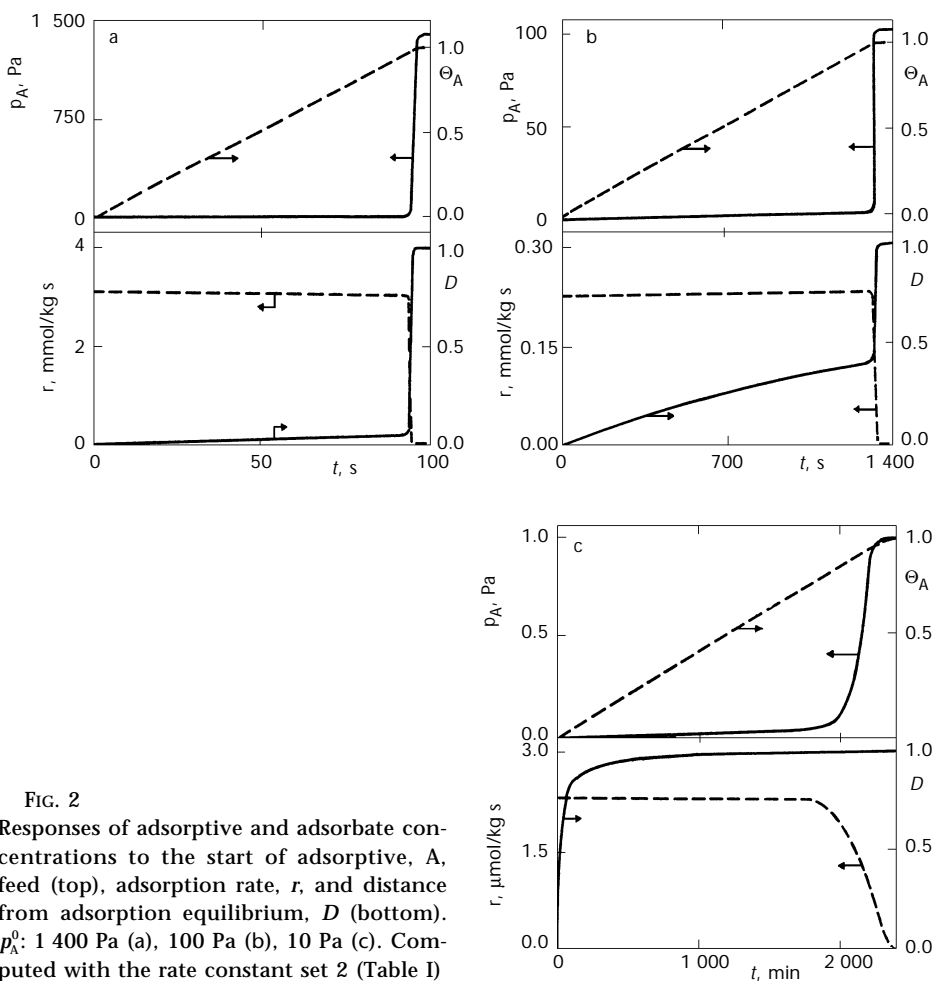


FIG. 2 Responses of adsorptive and adsorbate concentrations to the start of adsorptive, A, feed (top), adsorption rate, r , and distance from adsorption equilibrium, D (bottom). p_A^0 : 1400 Pa (a), 100 Pa (b), 10 Pa (c). Computed with the rate constant set 2 (Table I)

rium, and partial pressure responses do not show such steep changes. In this case, adsorption is very fast near the equilibrium and during the whole rest of the transient period remains very close to the equilibrium.

It is seen from Figs 1 to 3 that the $p_A(t)$ response contains most of the information that are accessible experimentally. Responses to the amount adsorbed are very similar and difficult to distinguish experimentally, in spite of principal differences in the underlying rate and equilibrium responses.

Some comments on the relation of computed curves to the adsorption isotherm should be added. As has been shown above, the discussed adsorption model corresponds to the ideas of Langmuir adsorption isotherm. All adsorptive inlet pressures used for simulations with set 2 correspond to nearly constant part of Langmuir isotherm, *i.e.*, that part where the adsorbed amount is practically independent of adsorptive pressure and close to the total coverage. This may be one of the reasons for nearly the same shapes of concentration and rate responses obtained for all adsorptive pressures used in simulations with set 2. On the other hand, adsorptive inlet pressures for set 1 correspond to the initial, steeply ascending part of the isotherm. The inlet pressure used for set 3 is in the region where the ascending part strats to level off. Because of the same value of adsorption coefficient, sets 1 and 3 have the same Langmuir isotherm. Corresponding steady-state concentrations were really the same for the same value of adsorptive pressure, *cf.* Figs 1 and 3. However, each of these sets gave a differ-

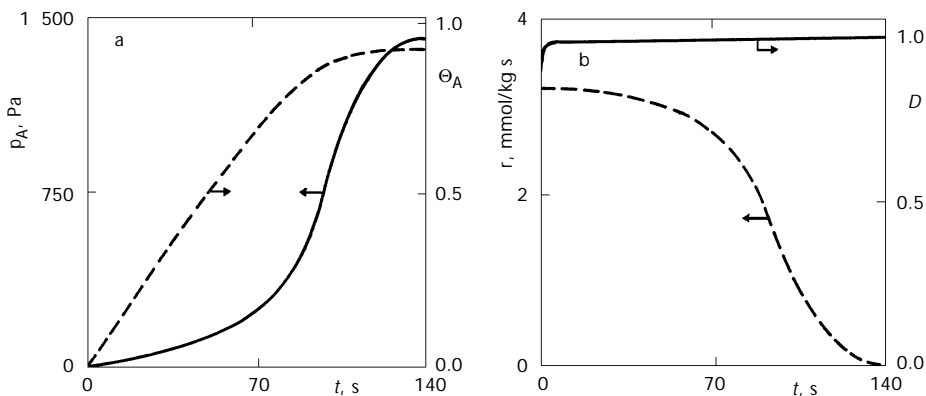


FIG. 3

Responses of adsorptive and adsorbate concentrations to the start of adsorptive, A, feed (a), adsorption rate, r , and distance from adsorption equilibrium, D (b). $p_A^0 = 1\ 400$ Pa. Computed with the rate constant set 3 (Table I)

ent pathway to this common equilibrium adsorption state (see the same figures).

Our computations have another interesting consequence. It is a frequent practice in thermodynamics to assume that involved variables change sufficiently smoothly in the proximity of the equilibrium. The transient behaviour shown in Fig. 2 reveal that this may not be true even in simple case at one elementary reaction step. The system may get to the equilibrium suddenly, at a jump. In our opinion, such behaviour could be expected in flow systems and probably not in the batch arrangement which is free of external forcing.

Let us briefly compare transient responses of the gas-phase concentration of adsorptive, published in the studies mentioned in the introduction, with the results of our computations. Responses similar to those in Figs 1 and 3 were observed by Renken *et al.*⁸ and Lu *et al.*⁹. Step responses like in Fig. 2 were measured by Kobayashi⁷.

CONCLUSIONS

In the kinetic research, conclusions on the rates of elementary steps are often based only on the measurements of the concentration-to-inlet responses. Our analysis reveals that even in the very simple case of one reaction step, transient response of the rate of an elementary step may be more complex than it can be expected from the concentration responses. Concentration responses may disguise unexpected kinetic and equilibrium behaviour.

Kinetic interpretation of concentration responses should be made very carefully, using concentrations of as many species as possible.

In flow systems, it should be remembered that reactions may not approach equilibrium sufficiently smoothly.

SYMBOLS

List of symbols includes the fixed values used in calculations.

D	relative distance from the equilibrium of adsorption
k_f	forward adsorption rate constant, mol/kg s Pa
k_r	reverse adsorption rate constant, mol/kg s
K_A	adsorption coefficient of adsorptive A, Pa
L	length of adsorbent bed, 0.01 m
p_A	(outlet) partial pressure of adsorptive A, Pa
q	total concentration of active sites, 0.3 mol/kg
r	rate of adsorption, mol/kg s
R	universal gas constant, 8.314 J/mol K

t	time, s
T	temperature, 456 K
u	linear velocity of gas flow, 0.05 m/s
ε	adsorbent void fraction, 0.5
ρ_x	adsorbent bulk density, 580 kg/m ³
Θ_A	fractional coverage by adsorptive A

Indexes

0	inlet value
v	vacant active site

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