

**HEAT AND MASS TRANSFER  
IN HETEROGENEOUS CATALYSIS. XXXI.\*****DYNAMIC BEHAVIOUR OF A DISCONTINUOUS MIXED REACTOR  
IN CATALYTIC REACTION OF HYDROGEN WITH OXYGEN**

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The effect of heat and mass transfer between the external surface of a catalyst particle and the bulk of reaction mixture on dynamic behaviour of a discontinuous ideally mixed reactor has been studied on a mathematical model for exothermic, first order reaction. A case is being discussed in which under certain given conditions two stable and one unstable steady states exist of a catalyst particle at a single value of partial pressure of the reactant. It has been found that the course of temperature steadying of the catalyst particle and of partial pressure of the reactant in the reactor depend on ratio of the reactor volume to the amount of catalyst. Theoretical conclusions were experimentally verified by a model reaction of hydrogen with oxygen on a platinum catalyst. Measurements were performed in a discontinuous tubular reactor with recycle at 21°C with the concentration range of hydrogen in the air from 0 to 4% vol., with only one catalyst pellet 7.25 mm × 7.05 mm. The measured values are in a very good agreement with theory. Further, it has been found that the regime of reactor steadying is somewhat dependent on the final temperature of the pellet in the preceding experiment, which is obviously a consequence of water adsorption inside the catalyst pellet.

This contribution is related to our previous paper<sup>1,2</sup> where was experimentally studied on a mathematical model the effect of heat and mass transfer between the external surface of a catalyst particle and the bulk of reaction mixture (further on called external heat and mass transfer) on dynamic behaviour of a mixed flow reactor. The aim of this work is to study the effect of external heat and mass transfer on dynamic behaviour of a discontinuous, mixed reactor.

**THEORETICAL**

Mathematical model describing the effect of an imperfect external heat and mass transfer on steady states of the catalyst particle is described in our previous work<sup>3</sup>. It is assumed that the re-

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action rate is a function of concentration of a single reactant and of temperature on the external surface of the particle. Calculation is limited to the first order reaction, for the temperature dependence of the rate constant the Arrhenius equation is used

$$r_R = k_{pHS} \exp [(E/RT_s T) (T_s - T)]. \quad (1)$$

For the transfer rate of the reactant to the external surface of the particle into the bulk of reaction mixture the relation was used

$$r_D = k_{GH} a_m (p_H - p_{Hs}). \quad (2)$$

For the rate of transfer from the external particle surface into the bulk of reaction mixture the relation was used

$$r_h = k_h a_m (T_s - T). \quad (3)$$

The catalyst particle is assumed to be non-porous and having an infinite thermal conductivity. The temperature inside the particle then equals to the temperature on the particle surface. The rate of chemical reaction in steady state equals to the transfer rate of the reactant to the external particle surface and the rate of heat evolved in the chemical reaction equals to the rate of heat transfer from the external surface of the particle into the bulk of reaction mixture

$$r_R = r_D, \quad (4)$$

$$r_h = r_R (-\Delta H). \quad (5)$$

A relation describing the dependence of a dimensionless reaction rate in steady state of a particle on relative partial pressure of the reactant was obtained on combining and modification of Eqs (1) to (5)

$$R\beta = (P_H - R\beta\Phi_m) \exp \left[ \frac{\Theta R\beta\Phi_m \Omega_m}{1 + R\beta\Phi_m \Omega_m} \right]. \quad (6)$$

In Eq. (6) parameters  $\Theta$ ,  $\Phi_m$  and  $\Omega_m$  are defined by relations

$$\Theta = E/(RT), \quad \Phi_m = r_{0m}/(k_{GH} a_m p_{Hm}), \quad \Omega_m = (-\Delta H) k_{GH} p_{Hm}/(k_h T). \quad (6a-c)$$

Values of these parameters are decisive for the effect of external heat and mass transfer and they determine the form of dependence of reaction rate on partial pressure of the reactant. The meaning of parameters is described in detail in our previous paper<sup>3</sup> and is not discussed here. Dependence of reaction rate in steady state of the catalyst particle on partial pressure of the reactant will be hereinafter called "curve  $(R\beta)_e$ ".

Mathematical model for the description of dynamic behaviour of a discontinuous, ideally mixed reactor has been derived under the assumption that accumulation of matter in the catalyst particle is negligible and the thermal conductivity of the particle is so high that the temperature at any point of the particle is the same as it is on its surface. Under the mentioned assumptions, the steadying of the catalyst particle temperature and of the partial pressure of the reactant in a reactor is described by a system of two non-linear differential first-order equations

$$\frac{d\Delta T}{d\tau} = R\beta B - \Delta TB/(\Phi_m \Omega_m) = -\Delta TB/(\Phi_m \Omega_m) + P_H B \left[ \Phi_m + \exp\left(\frac{-\Theta \Delta T}{1 + \Delta T}\right) \right]^{-1}, \quad (7)$$

$$\frac{dP_H}{d\tau} = -R\beta = -P_H \left[ \Phi_m + \exp\left(\frac{-\Theta \Delta T}{1 + \Delta T}\right) \right]^{-1}, \quad (8)$$

with boundary conditions:

for

$$\tau = 0 \text{ is } \Delta T = \Delta T_{in}, P_H = P_{H,in}, \quad (9a)$$

for

$$\tau \rightarrow \infty \text{ is } (d\Delta T/d\tau) = (dP_H/d\tau) = 0, \quad (9b)$$

$$\Delta T = P_H = 0. \quad (9c)$$

In Eqs (4) and (8) the quantities  $\tau$ ,  $P_H$ ,  $\Delta T$  and  $B$  are defined by relations

$$\tau = t \text{ Da}/V, \quad P_H = p_H/p_{Hm}, \quad \Delta T = (T_s - T)/T, \quad (10a-c)$$

$$\text{Da} = W r_{om} R T / p_{Hm}, \quad B = V(-\Delta H) p_{Hm} / (W c_{pk} R T^2). \quad (10d,e)$$

The system of Eqs (7) and (8) has been calculated numerically by the Runge-Kutte method (Merson's modification).

### *Dynamic Behaviour of Reactor*

The reaction rate of exothermic reaction increases above the value in the kinetic region because of an imperfect heat and mass transfer and in some of the cases there correspond to a single partial pressure of the reactant three values of the reaction rate, *i.e.* the catalyst particle has three steady states (Fig. 1). Dependence of the reaction rate on partial pressure of the reactant consists of three branches: kinetic branch, diffusion branch and the branch of unstable steady states of the particle. On the kinetic branch the point ( $P_H = 0, R\beta = 0$ ) is located and corresponds to the kinetic reaction regime. The diffusion branch approaches asymptotically the curve defined by relation

$$(r_D)_{\max} = k_{GH} a_m P_H. \quad (11)$$

Points on this curve determine the greatest possible rates of transfer of reactant to the particle surface under given hydrodynamic conditions. The branch of unstable steady states of the particle is connecting the kinetic and diffusion branches.

The dynamic processes are studied here taking place in a reactor at constant temperature of the bulk of reaction mixture. The course of the dynamic process

is accompanied by changes of temperature of the catalyst particle, of partial pressure of the reactant in the reactor and of the reaction rate. To record the course of changes of the above mentioned quantities it is recommended to use trajectories firstly in a phase plane  $R\beta$  on  $P_H$ , and secondly in  $\Delta T/(\Phi_m \Omega_m)$  on  $P_H$ . In steady state of the particle the relation is valid

$$\Delta T_e = (R\beta)_e \Phi_m \Omega_m \quad (12)$$

The curve  $(R\beta)_e$  is, therefore, identical with the curve  $\Delta T_e/(\Phi_m \Omega_m)$  (Fig. 1). If the above mentioned reaction takes place in a discontinuous ideally mixed reactor, the course of the dynamic process is dependent under constant hydrodynamic conditions only on the ratio of thermal capacity of the catalyst particle to the mass capacity of the reactor volume. All quantities which are related with capacity of the system are included in parameter  $B$  (Eq. (10e)). The parameter  $B$  can be interpreted as a ratio of heat which would be released by reacting of the reactant contained in the reactor at its standard partial pressure to the heat accumulated in the particle at temperature of the bulk of reaction mixture. Its value can be varied by changing the ratio of catalyst amount to the reactor volume.

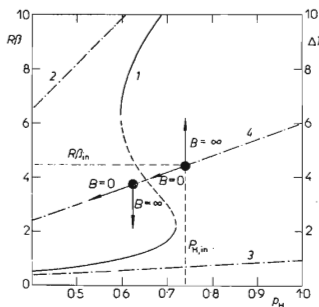


FIG. 1

Example of Dependence of Reaction Rate of Strongly Exothermic Reaction on Partial Pressure of Reactant

$\theta = 20.42$ ,  $\Phi_m = 0.061$ ,  $\Omega_m = 0.5165$ ; dashed line denotes unstable steady states of the catalyst pellet, full points with asterisks denote the direction of motion of the system regime for limiting values of parameter  $B$ . 1 Curve  $(R\beta)_e$ , 2 diffusion region, 3 kinetic region, 4 isotherm in coordinates  $R\beta$  on  $P_H$ .

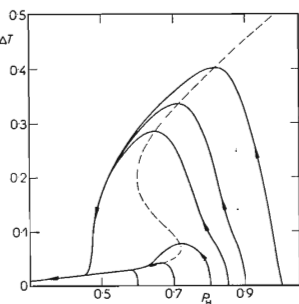


FIG. 2

Dependence of Catalyst Pellet Temperature on Partial Pressure of Reactant for Different Values of Initial Partial Pressure of This Component in the Reactor (case given in Fig. 1) and Value of Parameter  $B = 10$

Dashed line denotes the dependence of catalyst pellet temperature in steady state.

Two limiting cases of dynamic behaviour of the reactor correspond also to limiting values of parameter  $B$ . At the value of parameter  $B = \infty$  the reactor capacity is far greater than the capacity of the catalyst particle. Therefore, at an arbitrary dynamic operation the particle transfers immediately into the steady state without the composition of reaction mixture in the reactor being changed, *i.e.* into a steady state that corresponds to the initial partial pressure of the reactant in the reactor. The changes of partial pressure then take place at steady state of the catalyst particle, *i.e.* the system regime follows the curve  $(R\beta)_e$ . If only a single steady state of the particle situated on the diffusion branch of the curve  $(R\beta)_e$  corresponds to the initial composition of a reaction mixture in the reactor, then the regime of the system is transferred in the dynamic process from diffusion to kinetic branch by a step change. If three steady states correspond to initial composition, then the direction of motion of the system regime depends on the position of the initial state of the particle in respect to the branch of unstable steady states. If the initial state of the particle is on left side from this branch, the regime of the system follows the kinetic branch, and *vice versa*, if it is on right side from this branch, the system regime follows the diffusion branch.

In the second limiting case ( $B = 0$ ) the reactor capacity is far smaller than the capacity of a catalyst particle. The regime of the system therefore follows in the dynamic process the isotherm, that means the initial partial pressure of the reactant in the reactor varies from the value corresponding to the initial pressure to zero without the temperature of the catalyst particle being changed. (Isotherms describe the dependence of reaction rate on partial pressure of the reactant at a constant temperature of the particle. For the first order reaction the isotherms form a family of straight lines passing through the origin and defined by Eq. (6) for the case  $T_s = \text{constant}$ ).

In actual cases, where the value of parameter differs from zero, regime of the system moves in the dynamic process between both limiting cases. Examples of calculated dependence of temperature of the catalyst particle on partial pressure of the reactant in the reactor for a number of values of parameter  $B$  are given in Figs 2 – 4.

## EXPERIMENTAL

### Catalyst

Platinum on alumina was used as a catalyst in a form of pellets 7.25 mm (height)  $\times$  7.05 mm (diameter). The content of platinum was 0.3% weight. The catalyst preparation has been described in detail in our previous publications<sup>2,4</sup>.

### Apparatus and Analytical Method

The measurements were carried out in a discontinuous tubular reactor with recycle at atmospheric pressure at temperature 21°C, within the range of concentration of hydrogen in air 0 to 4% vol. The schematic view of the apparatus is given in Fig. 5. The system of charging and purification

of hydrogen and air is identical with that indicated in our previous papers<sup>2,4</sup>. In the circulation circle was situated the tubular reactor of diameter 40 mm and 200 mm high, the dryer with potassium hydroxide, rotameter and thermal conductivity cell. A rotary pump with an output of 1500 l/h was used for circulation. The volume of the circulation loop could be changed by connection of additional volumes. The measurement was always made on a single catalyst pellet which was freely suspended in the reactor tube ( $W = 0.393$  g,  $a_m = 0.588$  m<sup>2</sup>/kg). The composition of reaction mixture in the circulation loop (further on called only the reactor) was measured during the experiment as well as temperature difference between the pellet centre and the bulk of reaction mixture. The reaction course was followed by measurement of the hydrogen concentration in the reaction mixture in the reactor. The hydrogen concentration was determined from the change of thermal conductivity of the mixture. The thermal conductive cell was used (PN M 39, 68, Diopta Turnov) linked to a linear recorder EZ 4. Constant flow rate of 3 l/h of the reaction mixture through the cell was kept during the measurement. The described analytical method enables to determine the hydrogen concentration in the air with the  $\pm 0.5\%$  rel. accuracy.

#### Measurements of Temperature of the Catalyst Pellet

The temperature in centre of the catalyst pellet and temperature in the bulk of reaction mixture was measured simultaneously with the hydrogen concentration in the reaction mixture. Results of previous model experiments<sup>4</sup>, in which were measured both the temperature in the centre and on the external surface of the pellet during the reaction of hydrogen with oxygen on a platinum catalyst, have shown that the temperature difference between the surface and the centre of a pellet is by far smaller than the temperature difference between the pellet surface and the flowing gas. For evaluation of experiments the actual temperature difference between the pellet surface and the flowing gas was, therefore, substituted by the experimentally determined temperature difference

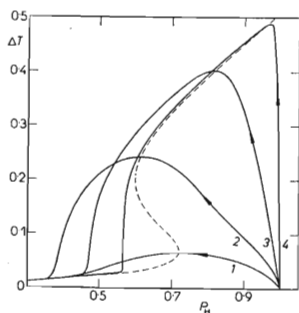


FIG. 3

Dependence of Catalyst Pellet Temperature on Partial Pressure of Reactant in Reactor for Different Values of Parameter  $B$

Other symbols used are the same as in Fig. 2. 1  $B = 1$ , 2  $B = 3$ , 3  $B = 10$ , 4  $B = 100$ .

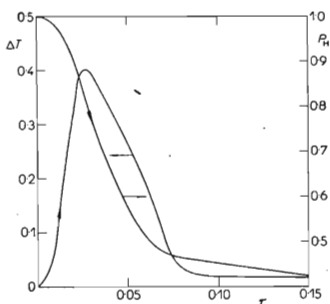


FIG. 4

Dependence of Catalyst Pellet Temperature and Partial Pressure of Reactant in Reactor on Time for Value of Parameter  $B = 10$

between the pellet centre and the flowing gas. Temperature was measured by thermocouples of the type copperconstantan (varnished conductor of 0.1 mm diameter, constantan conductor of 0.08 mm diameter with teflon insulation of 0.01 mm). Electromotive force of the thermocouple for determination of temperature of the bulk of reaction mixture being in a probe situated in the axial axis of the reactor, was measured by technical compensator QTK; of the thermocouple for measuring of the temperature in the pellet centre by a linear recorder EZ 4. Accuracy of measurements of temperature difference between the pellet centre and the bulk of the reaction mixture was estimated to be  $\pm 0.5^\circ\text{C}$ . The details of experimental arrangements are given in previous papers<sup>2,4</sup>.

#### Determination of the Reactor Volume

The volume of the reactor was determined indirectly from the rate of change of hydrogen concentration in the reactor at the change of hydrogen concentration at the inlet without chemical reaction. Reactor in the flow arrangement was filled by a mixture of hydrogen and air with partial pressure of hydrogen 0.0325 atm and at the beginning of the measurements the hydrogen inlet into the reactor was closed. The reactor volume was determined from the time in which the hydrogen concentration in the reactor decreased to one half of the initial value

$$V = Ft_{0.5}/\ln 2. \quad (13)$$

#### Measurement Procedure

The catalyst was at the beginning of a series of measurements activated with hydrogen. After disconnecting the reactor from the circulation loop by use of the by-pass (Fig. 5), the required

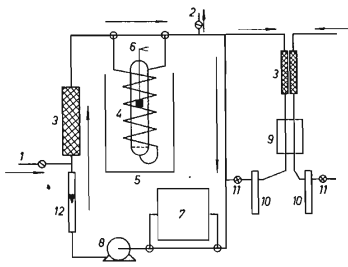


FIG. 5

#### Schematic View of the Apparature

1 Inlet of reaction mixture, 2 outlet of reaction mixture, 3 dryer, 4 reactor, 5 thermostat, 6 thermocouple, 7 additional volume, 8 circulation pump, 9 thermal conductivity cell, 10 flow meter, 11 control valve, 12 rotameter.

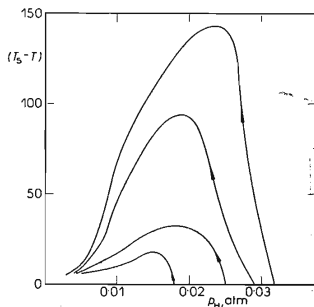


FIG. 6

Experimental Dependence of Catalyst Pellet Temperature on Partial Pressure of Hydrogen in the Reactor of 2.1 l Volume

value of initial hydrogen concentration was set for each experiment, the inlet and outlet of reaction mixture were closed and at the same time the reactor was again connected into the circulation loop. After finishing the experiment, the reactor was flushed by air. Under given reaction conditions the dependence of hydrogen concentration in the reactor and of the temperature of the catalyst pellet on the time of experiment was determined. The measurements were made at different reactor volumes and they were stopped when the pellet temperature was close to the temperature of the reactor bath or when the pellet temperature reached the maximum.

## RESULTS AND DISCUSSION

In our previous work<sup>4</sup>, it was proved experimentally that on a given catalyst at the temperature 21°C there exist in a certain interval of partial pressures of hydrogen for one partial pressure three steady states of the catalyst particle, two of them being stable and one unstable. For verification of results obtained by the study on a mathematical model, a series of experiments was carried out at various initial values of partial pressure of hydrogen in the reactor. Initial values of the temperature of a catalyst pellet were in all experiments identical with the temperature of the bulk of reaction mixture resp. of the reactor bath. The measured dependences for various values of the reactor volume (parameter  $B$ ) are given in Figs 6 to 10. Results of measurements are in a good qualitative agreement with the estimated effect of the reactor volume on its dynamic behaviour. In our study it has been found that the

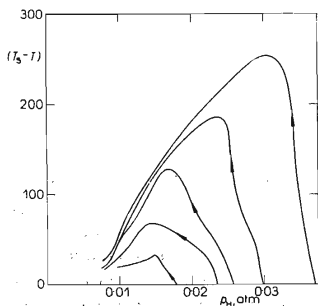


FIG. 7

Experimental Dependence of Catalyst Pellet Temperature on Partial Pressure of Hydrogen in the Reactor of 7.2 l Volume

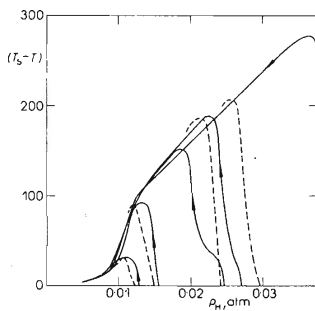


FIG. 8

Experimental Dependence of Catalyst Pellet Temperature on Partial Pressure of Hydrogen in the Reactor of 23.2 l Volume

Dashed line denotes dependence in the case the experiment was stopped in the moment of reaching the maximum pellet temperature.



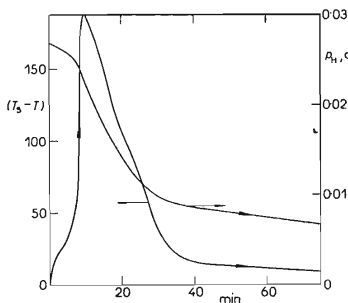


Fig. 9

Experimental Dependence of Catalyst Pellet Temperature and Partial Pressure of Hydrogen in the Reactor of 23.2 l Volume

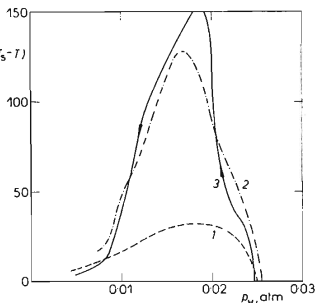


FIG. 10

Effect of Reactor Volume on Dependence of Catalyst Pellet Temperature on Partial Pressure of Hydrogen in the Reactor

1  $V = 2.1$  l, 2  $V = 7.2$  l, 3  $V = 23.2$  l.

dynamic behaviour of the reactor is also somewhat dependent on the final state of the catalyst pellet, at which was the preceding experiment stopped. If it was stopped at a high degree of hydrogen conversion *i.e.* in the state when the pellet temperature was low, there appeared at the beginning of experiment a plateau and the pellet temperature was increasing more slowly than in a case when the preceding experiment had been finished at a lower degree of conversion, *i.e.* at a high temperature of the pellet and the pellet was cooled in the flowing air. We suppose that the mentioned phenomenon is the result of water adsorption in the catalyst pellet which occurs in case when at a low temperature the mixture containing hydrogen passes over the catalyst. Water adsorption also affects the shape of the curve  $(R\beta)_e$  (Fig. 8). In case the water adsorption was not eliminated by terminating the experiments at a high temperature of the pellet the interval of partial pressure of hydrogen in which there exist more steady states, is greater than in case when the experiment was terminated at a high temperature of the pellet. The water adsorption in this way increases the apparent activation energy of the reaction at low temperatures. As the consequence of the mentioned phenomenon and for reasons mentioned in preceding papers<sup>2,4</sup> the quantitative agreement could not be obtained between dependences determined by the experimental study of dynamic behaviour of a discontinuous reactor and dependences calculated from the mathematical model of the first order reaction with an activation energy independent on temperature.

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## LIST OF SYMBOLS

$a_m$	external surface of a mass unit of the catalyst
$B$	parameter defined by Eq. (10e)
$c_{pk}$	specific heat of the catalyst
$Da$	Damköhler number (Eq. (10d))
$E$	activation energy of reaction
$F$	volumetric feed rate of the reaction mixture into the reactor
$k$	rate constant of reaction at temperature $T$
$k_{GH}$	mass transfer coefficient
$k_b$	heat transfer coefficient
$p_H$	partial pressure in the bulk of reaction mixture
$p_{Hm}$	standard partial pressure in the bulk of reaction mixture
$p_{Hs}$	partial pressure at the external surface of catalyst particles
$P_H$	relative partial pressure in the bulk of reaction mixture (Eq. (10b))
$r_D$	mass transfer rate
$r_h$	heat transfer rate
$r_0$	reaction rate at temperature $T$ and partial pressure $p_H$ at conditions when the effect of external mass and heat transfer is eliminated
$r_{0m}$	reaction rate $r_0$ at temperature $T$ and partial pressure $p_{Hm}$
$r_R$	reaction rate
$R = r_R/r_0$	effectiveness factor of external mass and heat transfer
$R$	gas constant
$R\beta = r_R/r_{0m}$	dimensionless reaction rate (Eq. (6))
$t$	time
$t_{0.5}$	half-time of flushing of the reactor
$T$	temperature of the bulk of reaction mixture
$T_s$	temperature of the external surface of catalyst particle
$V$	volume of reactor
$W$	weight of catalyst
$\beta = r_0/r_{0m}$	dimensionless parameter
$\Delta H$	heat of reaction
$\Delta T$	dimensionless temperature difference (Eq. (10c))
$\Theta$	parameter defined by Eq. (6a)
$\tau$	dimensionless time (Eq. (10a))
$\Phi_m$	parameter defined by Eq. (6b)
$\Omega_m$	parameter defined by Eq. (6c)

## Subscripts

e	value of quantity in steady state
H	reactant, respectively hydrogen
in	value of quantity at the beginning of dynamic operation

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