

# EFFECT OF EXTERNAL HEAT AND MASS TRANSFER ON REGIME OF CATALYST PARTICLES FOR EXOTHERMIC CONSECUTIVE REACTIONS

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An extensive change of the ratio of reaction rates and thus of selectivity of consecutive reactions may take place if an imperfect heat and mass transfer between the external surface of the catalyst particles and the bulk of reaction mixture becomes significant. Heat and mass transfer at the surface of catalyst particles is usually negligible in industrial units but in laboratory reactors such high velocities of reaction mixture around the particle at which the effect of imperfect heat and mass transfer at the surface of catalyst particles is eliminated cannot be arranged for. The determined selectivity can thus considerably differ from that one of the catalyst in an industrial unit. Here, we are trying to estimate the direction and magnitude of changes in the regime of catalyst particles which are taking place due to the imperfect heat and mass transfer at the external surface of the catalyst particles.

This study is related to paper<sup>1</sup> where the effect of heat and mass transfer between the external surface of catalyst particles and the bulk of reaction mixture was studied (further on also the external diffusion) on the selectivity of two consecutive reactions without heat effects.

The model considerations for the non-isothermal case are based on the assumption of two consecutive first order reactions



taking place on a non-porous catalyst particle. The balance equations for the steady state have then the form

$$r_1 = r_{DA} \equiv k_{1s}c_{As} = k_{GA}a_m(c_A - c_{As}), \quad (1)$$

$$r_1 - r_2 = r_{DR} \equiv k_{1s}c_{As} - k_{2s}c_{Rs} = k_{GR}a_m(c_{Rs} - c_R), \quad (2)$$

$$Q = r_1(-\Delta H_1) + r_2(-\Delta H_2). \quad (3)$$

Under assumption that the ratio of mass transfer coefficients A and R (i.e.  $k_{GA}/k_{GR}$ )

equals to one (molecular weights do not differ considerably) the equations can be normalized in the following way:

$$R_1 = C_A / \left[ \Phi_A + \exp \left( - \Theta_1 \frac{\Delta T_1 + \Delta T_2}{1 + \Delta T_1 + \Delta T_2} \right) \right], \quad (4)$$

$$R_2 = (C_R + R_1 \Phi_A) / \left[ \Phi_A + \frac{k_{1n}}{k_{2n}} \exp \left( - \Theta_2 \frac{\Delta T_1 + \Delta T_2}{1 + \Delta T_1 + \Delta T_2} \right) \right], \quad (5)$$

$$R_1 + \alpha R_2 = \Delta T_2 / (\Omega \Phi_A), \quad (6)$$

where  $\Phi_A$ ,  $\Theta_1$ ,  $\Theta_2$ ,  $\Delta T_1$ ,  $\Delta T_2$ ,  $\alpha$  and  $\Omega$  are dimensionless parameters defined by relations

$$\Phi_A = r_{1n} / (k_{GA} a_m c_{Am}), \quad (7)$$

$$\Theta_1 = E_1 / (RT_n), \quad (8)$$

$$\Theta_2 = E_2 / (RT_n), \quad (9)$$

$$\Delta T_1 = (T_0 - T_n) / T_n, \quad (10)$$

$$\Delta T_2 = (T_s - T_0) / T_n, \quad (11)$$

$$\alpha = (-\Delta H_2) / (-\Delta H_1), \quad (12)$$

$$\Omega = (-\Delta H_1) c_{Am} k_{GA} / (k_h T_n). \quad (13)$$

Equations (4) to (6) represent the relation between the reaction rates and the system of parameters in the steady state. Parameter  $\Phi_A$  represents the ratio between the reaction rate of the first reaction at kinetic conditions (*i.e.* not affected by the heat and mass transfer) and the highest possible diffusion rate of the reactant A. If the diffusion rate is considerably greater than the reaction rate its value approaches zero (kinetic region) in the opposite case, infinity (diffusion region – diffusion as the first operation becomes the determining step). Parameter  $\Phi_A$  is thus a suitable coordinate for description of changes of the reaction regime on the catalyst particles at transition from the kinetic region to the diffusive one.

Parameters  $\Theta_1$ ,  $\Theta_2$  represent the dimensionless activation energies of the first and second reactions,  $\Omega$  the thermal contribution of the first reaction. The temperature difference  $\Delta T_1$  represents the difference between the temperature of the bulk of the reaction mixture and the standard temperature,  $\Delta T_2$  represents the difference between

the surface temperature of catalyst particle and the bulk temperature. Parameter  $\alpha$  is the ratio of reaction enthalpies of the second and first reactions.  $C_A$  and  $C_R$  are dimensionless concentrations defined as the ratio of actual concentrations to standard one -  $c_{Am}$ . Finally  $R_1$  and  $R_2$  are the dimensionless relative reaction rates defined as the ratio of actual reaction rates to the rate of the first reaction at standard temperature  $T_n$ , standard concentration  $c_{Am}$  when the external heat and mass transfer are eliminated.

For selectivities are used variously defined factors. For our study the following definition is used

$$S = (r_1 - r_2)/r_1 = (R_1 - R_2)/R_1 \quad (14)$$

The selectivity factor defined in this way represents the ratio of the rate at which the required intermediate is formed to the rate at which the reactant reacts.

## RESULTS

Apart from mass transfer, also heat transfer between the external surface of catalyst particles and the bulk of reaction mixture may take place with reactions with heat effects. For consecutive first order reactions a general rule can be set: an imperfect mass transfer between the flowing mixture and the catalyst is responsible for deterioration of selectivity. To the catalyst surface less reactant is delivered (its concentration decreases), and the removal of intermediates from the particle surface into the bulk of reaction mixture deteriorates (their concentration increase). Because of these concentration changes the reaction rate of the first reaction decreases and the reaction rate of the second one increases and thus the selectivity decreases. For reactions with a small thermal effect taking place in a liquid phase may be assumed that an imperfect heat transfer is not taking place, while the same assumption cannot be made for reactions with a considerable thermal effect and for reactions in gaseous phase.

The imperfect heat transfer with endothermic reactions will be responsible for undercooling of the particle, with exothermic reactions for its superheating. Therefore with endothermic systems the reaction rate will decrease while with exothermic it will increase. As the temperature dependences of reaction rates of both reactions can differ, the effect of imperfect heat transfer on selectivity may not be uniquely determined. The effect of heat and mass transfer for actual reaction systems cannot be considered separately since the over-all change of the particle regime is always the result of combination of both these factors. Thus it is obvious that, when an imperfect heat transfer takes place, the second reaction affects the reaction rate of the first reaction and *vice versa*. This is because the temperature difference between the bulk of the reaction mixture and the particle surface is the result of summation of thermal contributions of both reactions. Their rates are thus mutually related.

A typical example of reaction rates at transfer from the kinetic to the diffusive region for both the exo- and endothermic consecutive reactions is given in Fig. 1. The maximum on curve 3 results from contradictory effects of imperfect heat and mass transfer as they appear with exothermic reactions. The monotonous decrease of reaction rate of the endothermic reaction corresponding to, in the same direction acting, imperfect heat and mass transfer is illustrated by curve 5.

With exothermic reactions is interesting the problem of existence of several steady states of the particle regime at the same conditions. For example with a simple irreversible first order reaction a region of parameters can be found where the equation describing the particle behaviour has three solutions. Similarly, for a system of consecutive reactions as many as five solutions may be found as is illustrated in Fig. 2. For a simple reaction the region of multiplicity of solutions is characterized by two stable and one unstable steady states. The curve of steady states consists of two branches of stable states – of the kinetic and diffusive branches which are separated by the part of the curve on which unstable states are situated. The particle regime is transferred from the kinetic branch to the diffusive one by a step change in the point of maximum value of parameter  $\Phi_A$  for the region of several states and from the diffusive branch to the kinetic one in the point of minimum value at which several steady states still exist.

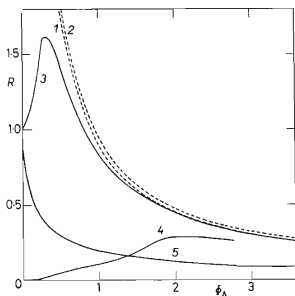


FIG. 1

Dependence of Relative Reaction Rates on Parameter  $\Phi_A$  ( $C_A$  0.9;  $C_R$  0.05;  $k_{1n}/k_{2n} = 100$ ;  $\Delta T_1$  0;  $\alpha$  2;  $\Theta_1 = \Theta_2 = 15$ )

1 Curve of diffusive region for  $R_1$ , 2 curve of diffusive region for  $R_2$ , 3  $R_1$  ( $\Omega$  0.2), 4  $R_2$  ( $\Omega$  0.2), 5  $R_1$  ( $\Omega$  -0.4).

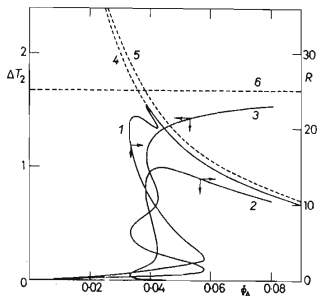


FIG. 2

Dependence of Dimensionless Temperature Difference  $\Delta T_2$  and Relative Reaction Rate on Parameter  $\Phi_A$  ( $C_A$  0.9;  $C_R$  0.05;  $k_{1n}/k_{2n} = 100$ ;  $\Delta T_1$  0;  $\alpha$  2;  $\Theta_1 = \Theta_2 = 15$ ;  $\Omega$  0.6)

1  $R_1$ , 2  $R_2$ , 3  $\Delta T_2$ , 4 diffusive curve for  $R_1$ , 5 diffusive curve for  $R_2$ , 6 diffusive curve for  $\Delta T_2$ .

With consecutive exothermic reactions we may distinguish six basic types of curves with several states as is demonstrated in Fig. 3. The curve of type A has one region in which three steady states of the particle regime correspond to one value of parameter  $\Phi_A$  — its shape is similar to that of single reaction. Two regions of several states exist only with the type B; each of them includes three solutions. The only region of multiplicity for types C, D, E and F may be divided to three parts — one with five and two with three states for one value of parameter  $\Phi_A$ . As is obvious from the given figure, these cases differ by the number of step transitions taking place at a consecutive change of the particle regime from the kinetic to the diffuse region and *vice versa*. In all curves, with the exception of curve A, three stable and two unstable branches may be found. The most interesting shape has the curve D. If the particle regime is changing along the curve of steady states it never reaches the middle stable branch.

The step changes of particle regimes at transfer from the kinetic to the diffusive branch and *vice versa* with systems with several states are accompanied by a corresponding step change of selectivity. Since the problem of selectivity is most interesting for the study of consecutive reactions, solution of the mathematical model was

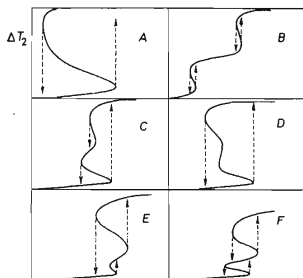


FIG. 3

Schematic Curves for Region of Multiplicity (dependence of  $\Delta T_2$  on  $\Phi_A$ )

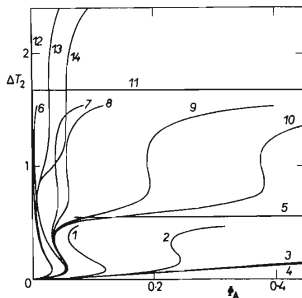


FIG. 4

Dependence of Dimensionless Temperature Difference  $\Delta T_2$  on Parameter  $\Phi_A$  for Various Values of Parameter  $\Omega$  and Ratio  $k_{1n}/k_{2n}$  ( $C_A$  0.9;  $C_R$  0.05;  $\Delta T_1$  0;  $\alpha$  2;  $\theta_1 = \theta_2 = 15$ )

$\Omega$  0.2; 1  $k_{1n}/k_{2n} = 1$ , 2 10, 3 100, 4 500, 5 diffusive curve for  $\Delta T_2$  ( $\Omega$  0.2).  $\Omega$  0.6; 6  $k_{1n}/k_{2n} = 10$ , 7 100, 8 150, 9 500, 10 1000, 11 diffusive curve for  $\Delta T_2$  ( $\Omega$  0.6).  $\Omega_1$ ; 12  $k_{1n}/k_{2n} = 10$ , 13 500, 14 1000.

oriented to consideration of the effect of individual reaction parameters on selectivity in the range covering the possible region of several states. In the plane: reaction variable ( $\Delta T_2$  is chosen) – modulus  $\Phi_A$  are plotted always several isocurves for the given parameter. The advantage of this procedure lies mainly in the clarity of its graphical illustration.

*Heat effects.* In order to fulfill the condition of increased reaction rate above the value in the kinetic region, it is necessary that the effect of imperfect heat transfer prevails over the effect of imperfect mass transfer. This is possible only for strongly exothermic reactions with a considerable temperature dependence. The greater are values of reaction enthalpies the more heat is evolved at the catalyst surface. The imperfect heat transfer due to increased surface temperature contributes to the increase of the reaction rates, and therefore a greater heat effect of the system is the reason of easier transfer of the particle regime into the diffusive region. When approaching the diffusive region, temperature of the particle surface increases to a certain limiting value. Systems with greater values of  $\Omega$  and  $\alpha$  are not characterized only by reaching a greater diffusive temperature of the surface but by the fact as well that increase of the surface temperature corresponding to the heat evolved by the reaction takes place already at lower values of  $\Phi_A$  (Figs 4,5). Variation of selectivity is illustrated in Fig. 6.

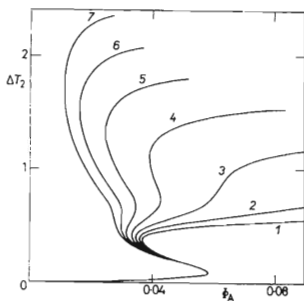


FIG. 5

Dependence of Dimensionless Temperature Difference  $\Delta T_2$  on Parameter  $\Phi_A$  for Various Values of Parameter  $\alpha$  ( $C_A$  0.9;  $C_R$  0.05;  $k_{1n}/k_{2n} = 100$ ;  $\Delta T_1$  0;  $\theta_1 = \theta_2 = 15$ ;  $\Omega$  0.6)

1  $\alpha = 0.5$ ; 2 1.0; 3 1.5; 4 2.0; 5 2.5; 6 3.0;  
7 3.5.

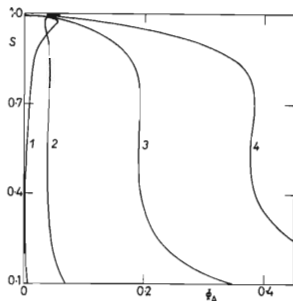


FIG. 6

Dependence of Selectivity Factor on Parameter  $\Phi_A$  for Various Values of Parameter  $\Omega$  ( $C_A$  0.9;  $C_R$  0.05;  $k_{1n}/k_{2n} = 100$ ;  $\Delta T_1$  0;  $\alpha$  2;  $\theta_1 = \theta_2 = 15$ )

1  $\Omega = 0.2$ ; 2 0.4; 3 0.6; 4 0.8.

*Effect of activation energies and ratio of rate constants in kinetic region.* In systems with greater activation energy small change of the surface temperature is causing a considerable change of the reaction rate. Therefore, exothermic reactions with large values of parameter  $\Theta$  appear easily in the diffusive region. The ratio of  $\Theta_1$  and  $\Theta_2$  is for consecutive reactions important.

$\Theta_1 = \Theta_2$ . Both the temperature dependences of reaction rates are similar, the transition from kinetic to diffusion regime is dependent on the relation of  $k_{1n}$  to  $k_{2n}$ . For  $k_{1n} > k_{2n}$  with increasing value of parameter  $\Phi_A$  the first and the second reaction are consecutively transferred to the diffusive regime. For  $k_{1n} = k_{2n}$  the imperfect heat transfer has the same effect on both reactions. The case when  $k_{1n} < k_{2n}$  has no practical significance and therefore it is not considered here. In Fig. 7 is demonstrated the change of selectivity for different values of ratio  $k_{1n}/k_{2n}$  which represents the kinetic selectivity and which is characteristic for the given catalyst.

$\Theta_1 < \Theta_2$ . The effect of imperfect mass transfer toward the diffusive region for  $k_{1n} > k_{2n}$  is the same as that of imperfect heat transfer, it decreases the selectivity. This is because increase of the surface temperature of the particle is preferring the second reaction. This is necessary to bear in mind when the catalyst properties are measured in the laboratory when both heat and mass transfer processes may become significant. The first reaction can by its heating of the surface significantly increase the reaction rate of the still slow second reaction having a considerable temperature

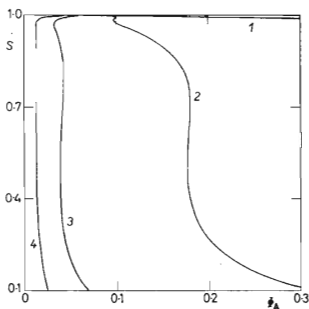


FIG. 7

Dependence of Selectivity Factor on Parameter  $\Phi_A$  for Various Values of Ratio  $k_{1n}/k_{2n}$  ( $C_A$  0.9;  $C_R$  0.05;  $\Delta T_1$  0;  $\alpha$  2;  $\Theta_1 = \Theta_2 = 15$ ;  $\Omega$  0.6)

1  $k_{1n}/k_{2n} = 10$ , 2 100, 3 500, 4 1000.

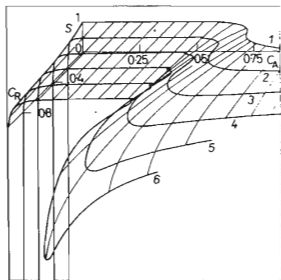


FIG. 8

Area of Steady States of Catalyst Particles in Region  $S$ ,  $C_A$ ,  $C_R$  ( $\Phi_A$  0.1;  $k_{1n}/k_{2n} = 100$ ;  $\Delta T_1$  0;  $\alpha$  2;  $\Theta_1 = \Theta_2 = 15$ ;  $\Omega$  0.6)

1  $C_R = 0$ ; 2 0.2; 3 0.4; 4 0.6; 5 0.8; 6 1.0.

dependence. The experimentally determined selectivity will then considerably differ from the kinetic one which might be the reason for rejecting a good catalyst.

$\theta_1 > \theta_2$ . This case appears to be the most interesting one. If the imperfect mass transfer always acts in the direction of deteriorating the selectivity, the imperfect heat transfer in this case improves selectivity. Because of these two contradictory effects it is possible to expect with a certain probability that a region of such reaction conditions exist in which the selectivity will improve at transfer of the particle from the kinetic to the diffusive regime. This interval of reaction parameters will obviously be very narrow.

*Effect of concentration around the particle catalyst.* Increase of concentration of the reactant A or intermediate R contributes to the increase of reactions rates. This simultaneously increases for exothermic reactions the effect of evolved heat, temperature of the catalyst surface increases and reaction rates of both reactions increase so that they become comparable with the diffusion rate.

In considering concentration effects brief mention should be made of the basic types of reactors in which reaction is realized. For example, the catalyst particle in continuous stirred tank reactor is surrounded by reaction mixture with constant composition. Because of low driving force, the transfer of the intermediate from the surface to the bulk of mixture is slowed down. If the effect of external mass and heat

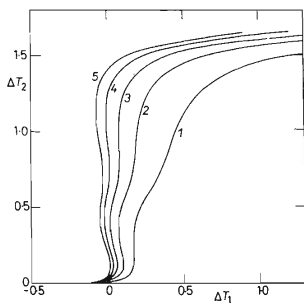


FIG. 9

Dependence of Temperature Difference  $\Delta T_2$  on Difference  $\Delta T_1$  ( $C_A$  0.9;  $C_R$  0.05;  $k_{1n}/k_{2n} = 100$ ;  $\alpha$  2;  $\theta_1 = \theta_2 = 15$ ;  $\Omega$  0.6)

1  $\Phi_A = 0.01$ ; 2 0.02; 3 0.03; 4 0.04; 5 0.05.

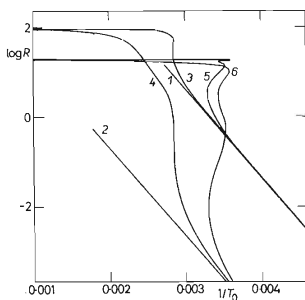


FIG. 10

Dependence of Logarithm of Reaction Rates on Reciprocal Temperature of Bulk Phase ( $C_A$  0.9;  $C_R$  0.05;  $k_{1n}/k_{2n} = 100$ ;  $T_n$  300 K;  $\alpha$  2;  $\theta_1 = \theta_2 = 15$ ;  $\Omega$  0.6)

1 Kinetic curve for  $\log R_1$ ; 2 kinetic curve for  $\log R_2$ ; 3  $\Phi_A$  0.01;  $\log R_1$ ; 4  $\Phi_A$  0.01;  $\log R_2$ ; 5  $\Phi_A$  0.05;  $\log R_1$ ; 6  $\Phi_A$  0.05;  $\log R_2$ .



transfer in this reactor is not eliminated, the selectivity of catalyst is different from that in the kinetic region. Since selectivity is decreased by both imperfect mass and heat transfer (except in the case when  $\Theta_1 > \Theta_2$ ), the reactor yield is lower than if external diffusion is eliminated.

A reactor with piston flow is characterized by the temperature and concentration profiles along the pipe. Let us consider again that the reactor is not operated in the purely kinetic region. Then the concentration of reactant A on the surface of the catalyst particles will always be lower than in the bulk of the reaction mixture, concentration of the intermediate R greater before and lower after reaching the maximum of the product concentration. Temperature of the catalyst surface will always be greater than the temperature of the bulk of the reaction mixture but its profile along the pipe will obviously have a maximum. The yield in the reactor with piston flow will thus be due to the effect of external diffusion also distorted. The dependence of selectivity on dimensionless concentrations of substances A and R is illustrated in Fig. 8.

*Effect of temperature of the reaction mixture.* Increase of temperature generally results in increasing the reaction rate. In this way the ratio is decreased between the rates of diffusion and reaction so that the operating regime of the catalyst moves toward the diffusive region. Fig. 9 demonstrates the dependence of  $\Delta T_2$  on  $\Delta T_1$  for different values of parameters  $\Phi_A$ . Due to external diffusion, the temperature dependence of the reaction rate change, as well. If the dependence of logarithm of reaction rate on reciprocal bulk temperature is straight with a slope determined by activation energies of reaction then in the diffusion region  $\log R$  is practically constant and independent on temperature of the mixture. This is because diffusion is the determining step and its activation energy is approximately 1 kcal/mol. An example of the temperature dependence of relative reaction rates at transfer from the kinetic to the diffusive region is demonstrated in Fig. 10.

## DISCUSSION

Imperfect mass and heat transfer between the external surface of catalyst particle and the bulk of the reaction mixture in a system of consecutive exothermic reactions can substantially affect the actual activity and selectivity of the catalyst. Thus the necessary condition in a laboratory research of catalysts is to consider the effect of heat and mass transfer.

The operating regime of the particle can transfer from the kinetic to the diffusive region if a great reactant concentration in the feed is used, if velocity of the reaction mixture is low, if particles are large and if the bulk temperature is high. This is because each of these described changes is moving the ratio of the diffusion and reaction rates toward lesser values and thus into the region where diffusion affects

the over-all reaction rate. From this is obvious that *e.g.* the more active catalyst can appear as a less selective one. With exothermic reactions, the more expressive the transition of the particle regime and the greater the rate, the greater is the heat effect of the system ( $\Omega$  and  $\alpha$ ), activation energies ( $\theta_1$  and  $\theta_2$ ) and the lower is the kinetic selectivity (the thermal effect of the second reaction is more profound at transfer of the first reaction to the diffusive region).

The effect of external diffusion is negatively affecting the selectivity with the only exception when imperfect heat transfer in the case  $\theta_1 > \theta_2$  acts in the direction of its improvement. As selectivity is together with the catalyst activity its most important property, at testing of new catalysts the effect of external diffusion must be eliminated.

## LIST OF SYMBOLS

$a_m$	external surface of catalyst particles per unit weight [ $\text{m}^2/\text{g}_{\text{cat}}$ ]
$c_A, c_R$	concentrations of substances A and R in unit volume [ $\text{mol}/\text{m}^3$ ]
$C_A, C_R$	dimensionless concentrations of A and R, defined by $C_i = c_i/c_{A_m}$
$c_{A_m}$	standard concentration [ $\text{mol}/\text{m}^3$ ]
$c_{A_s}, c_{R_s}$	concentrations of A and R on the catalyst surface [ $\text{mol}/\text{m}^3$ ]
$E_1, E_2$	activation energies of first and second reactions [cal/mol]
$\Delta H_1, \Delta H_2$	reaction enthalpies of first and second reactions [kcal/mol]
$k_{GA}, k_{GR}$	mass transfer coefficients of A and R [m/h]
$k_h$	heat transfer coefficient [kcal/deg $\text{m}^2$ h]
$k_{1n}, k_{2n}$	rate constants of first and second reactions at standard temperature $T_n$ [ $\text{m}^3/\text{h g}_{\text{cat}}$ ]
$k_{1s}, k_{2s}$	rate constants of first and second reactions at surface temperature of the catalyst particle $T_s$ [ $\text{m}^3/\text{h g}_{\text{cat}}$ ]
$Q$	heat transferred from external surface of the catalyst particle to the bulk of reaction mixture [kcal/h $\text{g}_{\text{cat}}$ ]
$R$	gas constant [cal/deg mol]
$r_1, r_2$	rates of first and second reactions [mol/h $\text{g}_{\text{cat}}$ ]
$r_{DA}, r_{DR}$	transfer rates of substances A and R [mol/h $\text{g}_{\text{cat}}$ ]
$R_1, R_2$	dimensionless relative reaction rates defined by $R_i = r_i/r_{1n}$
$r_{1n}$	reaction rate of first reaction at standard temperature $T_n$ , standard concentration $c_{A_m}$ when the effect of external diffusion is eliminated [mol/h $\text{g}_{\text{cat}}$ ]
$S$	selectivity factor defined by relation (14)
$T_n$	standard temperature [deg]
$T_0$	bulk temperature of reaction mixture [deg]
$T_s$	surface temperature of catalyst particles [deg]
$\Delta T_1, \Delta T_2$	dimensionless temperature differences (Eqs (10) and (11))
$\alpha, \Omega, \theta_1, \theta_2, \Phi_A$	dimensionless reaction parameters (Eqs (12), (13), (8), (9) and (7))

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Translated by M. Rylek.