

## EFFECT OF EXTERNAL MASS TRANSFER ON THE SELECTIVITY OF INDEPENDENT AND CONCURRENT REACTIONS WITHOUT HEAT EFFECTS\*

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Mathematic model was used in investigations on the influence of mass transfer between the external surface of a catalyst particle and the reaction mixture bulk on the process selectivity in a system of independent reactions and in a system of concurrent reactions without heat effects. A discussion is presented on changes in the process selectivity when the reaction régime passes from the kinetic into the diffusion region and on consequences of the imperfect external mass transfer with respect to the yield of the required product in fundamental types of isothermal reactors. It has been observed that the imperfect external mass transfer favours the reaction of the less reactive substance in the case of systems of independent reactions and suppresses the reaction of a higher order with respect to the common component in the case of systems of concurrent reactions.

The aim of the present work was to investigate on a simplified mathematical model the influence of the mass transfer between the external surface of a catalyst particle and the reaction mixture bulk (designated as external mass transfer in the further text) on the process selectivity in a system of two independent reactions and in a system of two concurrent reactions without heat effects. A detailed investigation concerning the effect of external mass transfer on the selectivity of reactions over a solid catalyst has not been so far reported in the chemical literature. This effect has been usually studied on a system of independent reactions<sup>1,2</sup> and there is most frequently reported the case of a simultaneous influence of the internal and external mass (and heat) transfer; the solution of the mass transfer in the catalyst particle is based on the assumption that the boundary conditions at the external surface of the particle are determined by the effect of the external mass transfer<sup>3-6</sup>. This method is exact but calculations are very difficult and the results cannot be readily interpreted and verified by experiments.

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*Model of a Catalyst Particle*

The calculation was performed for a system of two independent reactions (A) and (B)



and a system of two concurrent reactions (C) and (D)



It is assumed that the reaction rate is a function of the concentration of starting compounds at the external surface of the catalyst particle (1a) to (1d).

$$r_1 = k_1 c_{As}^n, \quad (1a)$$

$$r_2 = k_2 c_{Bs}^m, \quad (1b)$$

$$r_3 = k_3 c_{As}^n, \quad (1c)$$

$$r_4 = k_4 c_{As}^m. \quad (1d)$$

The rate equations (1a) to (1d) must comprise the effect of the mass transfer in the catalyst particle on the reaction rate. The external mass transfer rate was described by equations (2a), (2b).

$$r_{Ad} = k_{gA} a_m (c_A - c_{As}), \quad (2a)$$

$$r_{Bd} = k_{gB} a_m (c_B - c_{Bs}). \quad (2b)$$

In the steady state of the catalyst particle, the rate of the external mass transfer is equal to the reaction rate of the particular compound. Combination of the above relations results in a system of equations describing the dependence of the reaction rate on the concentration of compounds (3a) to (3d).

$$r_1 = k_1 (c_A - r_1 / k_{gA} a_m)^n, \quad (3a)$$

$$r_2 = k_2 (c_B - r_2 / k_{gB} a_m)^m, \quad (3b)$$

$$r_3 = k_3 [c_A - (r_3 + r_4) / k_{gA} a_m]^n, \quad (3c)$$

$$r_4 = k_4 [c_A - (r_3 + r_4) / k_{gA} a_m]^m. \quad (3d)$$

Equations were transformed into the dimensionless form (4a) to (4d).

$$R_1 = (C_A - \Phi_{A1} R_1)^n, \quad (4a)$$

$$R_2 = K_1 (C_B - \Phi_{A1} K_2 R_2)^m, \quad (4b)$$

$$R_3 = (C_A - \Phi_{A2}R)^n/K_3, \quad (4c)$$

$$R_4 = (C_A - \Phi_{A2}R)^m/K_4, \quad (4d)$$

wherein

$$C_A = C_A/c_{A0}; \quad C_B = c_B/c_{B0}, \quad (5a,b)$$

$$R_1 = r_1/r_{10m}; \quad R_2 = r_2/r_{10m}, \quad (6a,b)$$

$$R_3 = r_3/(r_{30m} + r_{40m}), \quad (6c)$$

$$R_4 = r_4/(r_{30m} + r_{40m}), \quad (6d)$$

$$R = (r_3 + r_4)/(r_{30m} + r_{40m}), \quad (6e)$$

$$K_1 = k_2/k_1 c_{Am}^{-m}; \quad K_2 = k_{gA}/k_{gB}, \quad (7a,b)$$

$$K_3 = 1/(1 + c_{Am}^{m-n} k_4/k_3), \quad (7c)$$

$$K_4 = 1/(1 + c_{Am}^{n-m} k_3/k_4), \quad (7d)$$

$$\Phi_{A1} = r_{10m}/k_{gA} a_m c_{Am}, \quad (8a)$$

$$\Phi_{A2} = (r_{30m} + r_{40m})/k_{gA} a_m c_{Am}. \quad (8b)$$

Calculation of an isothermal discontinuous reactor was performed on the basis of equations (9a) to (9e)

$$dx_A/d\tau_1 = R_1, \quad (9a)$$

$$(c_{B0}/c_{A0})(dx_B/d\tau_1) = R_2, \quad (9b)$$

$$dx_R/d\tau_2 = R_3, \quad (9c)$$

$$dx_S/d\tau_2 = R_4, \quad (9d)$$

$$d(x_R + x_S)/d\tau_2 = dx/d\tau_2 = R, \quad (9e)$$

and calculation of an isothermal continuous stirred tank reactor was effected on the basis of relations (10a) to (10e)

$$x_A = R_1 \vartheta_1, \quad (10a)$$

$$x_B = (c_{A0}/c_{B0}) R_2 \vartheta_1, \quad (10b)$$

$$x_R = R_3 \vartheta_2, \quad (10c)$$

$$x_S = R_4 \vartheta_2, \quad (10d)$$

$$x = (R_3 + R_4) \vartheta_2, \quad (10e)$$

wherein the dimensionless reaction time is defined by relations (11a,b)

$$\tau_1 = r_{10m} t W / V c_{A0}, \quad (11a)$$

$$\tau_2 = (r_{30m} + r_{40m}) t W / V c_{A0}, \quad (11b)$$

and the dimensionless mean residence time is defined by relations (12a,b)

$$\vartheta_1 = r_{10m}W/Fc_{A0}, \quad (12a)$$

$$\vartheta_2 = (r_{30m} + r_{40m})W/Fc_{A0}, \quad (12b)$$

(the standard concentration of compound A is in this case equal to the initial concentration of compound A in a discontinuous batch reactor or to the concentration of compound A in the feed of a continuous stirred tank reactor).

## RESULTS AND DISCUSSION

### *Independent Reactions*

The calculations were performed for a system of reactions in which there reacts a single starting compound in each reaction. The results may also be applied to reactions of several reactants when some compounds are used in a great stoichiometric excess. As shown by an earlier analysis<sup>7</sup> concerning these compounds in a great stoichiometric excess, it is possible to neglect their concentration gradient at the external surface of the catalyst particle and to assume that the concentration at the external surface area is equal to the concentration in the bulk of the mixture. A simple scheme of independent reactions (A), (B) may thus also illustrate for example an oxidation or hydrogenation of a mixture of two substances with a great excess of oxygen and hydrogen, respectively.

The rate ratio of both reactions in the kinetic region is determined by properties of the catalyst and the proceeding reactions (13)

$$R_1/R_2 = k_1c_A^n/k_2c_B^m. \quad (13)$$

In the region of a strong influence of the external mass transfer, this transfer is the rate determining step. The rate ratio of both reactions is then exclusively determined by properties of the mass transfer (14)

$$R_1/R_2 = k_{gA}c_A/k_{gB}c_B. \quad (14)$$

Since the mass transfer coefficients of the individual substances are approximately equal<sup>8</sup> it may be assumed that a system of two independent reactions behaves in the external mass transfer region as a system of first-order reactions with an approximately equal rate constant value. The passage from the kinetic into the diffusion region is thus accompanied by an apparent equalisation of reactivities of the individual substances (Fig. 1). The ratio of reaction rates is then determined by the ratio of concentrations of the starting compounds in the particular reactions when used in the lowest stoichiometric amount (Fig. 2).

In this passage, the changes of the reaction rate ratio are illustrated by dependence on the  $\Phi_{A1}$  parameter which determines the position of the catalyst particle regime between the kinetic and diffusion region (this parameter is zero in the kinetic region and grows to infinity in the diffusion region). When the reaction regime passes from the kinetic into the diffusion region, the rate values of both reactions always monotonously decrease (with reactions of zero heat of reaction) but the reaction rate ratio may monotonously decrease or increase. The dependence of the reaction rate ratio on the  $\Phi_{A1}$  parameter may also exhibit an extremum but only in those cases when concentrations of starting compounds in both reactions are approximately equal, when their reactivity is approximately identical but when the reactions are of a different order. The extremum may be ascribed to a higher sensibility of the higher-order reaction to the drop of concentration at the particle surface and the passage into the diffusion region occurs at lower  $\phi_{A1}$  parameter values than with reactions of a lower order. As shown by results of calculations however, the extremum dependence could be hardly utilized on a practical scale, *e.g.*, to increase the process selectivity in an industrial reactor.

Since the rate constants considerably increase with increasing temperature while

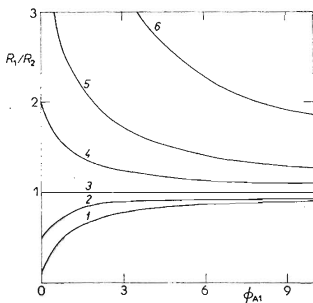


FIG. 1

Selectivity Change in a System of Independent Reactions due to the Reaction Region Change from the Kinetical Region to the Diffusion Region Under the Identical Concentration of Starting Compounds

$c_A = c_B = 1 \text{ mol/m}^3, n = m = 1. 1 k_2/k_1 = 10; 2 k_2/k_1 = 2; 3 k_2/k_1 = 1; 4 k_2/k_1 = 0.5; 5 k_2/k_1 = 0.25; 6 k_2/k_1 = 0.1.$

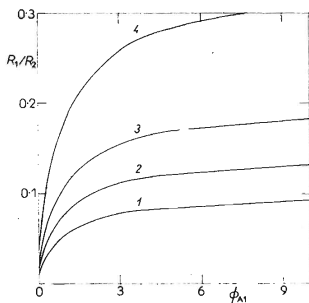


FIG. 2

Selectivity Change in a System of Independent Reactions due to the Reaction Regime Change from the Kinetical Region to the Diffusion Region in the Case of an Identical Rate Constant Ratio

$k_2/k_1 = 10. 1 c_A/c_B = 0.1; 2 c_A/c_B = 0.143; 3 c_A/c_B = 0.2; 4 c_A/c_B = 0.333.$

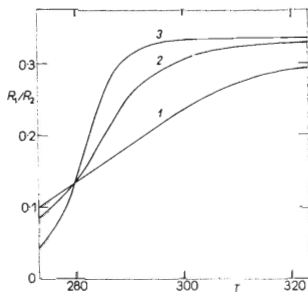


FIG. 3

Effect of the External Mass Transfer on the Temperature Dependence of the Selectivity in a System of First Order Independent Reactions

$k_2/k_1 = 10$ . 1  $E_1 = E_2 = 5$  kcal/mol; 2 10 kcal/mol; 3 20 kcal/mol.

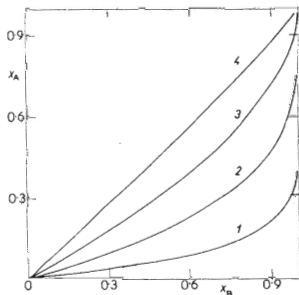


FIG. 4

Effect of the External Mass Transfer on the Selectivity of Independent Reactions in an Isothermal Discontinuous or Tubular Reactor

$k_2/k_1 = 10$ ,  $c_A = c_B \cdot \phi_{A1}$  values: 1 0; 2 0.25; 3 1; 4 10.

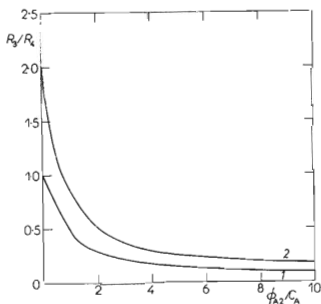


FIG. 5

Selectivity Change in a System of Independent Reactions Accompanying the Passage of the Reaction Regime from the Kinetic into the Diffusion Region

$n = 2$ ,  $m = 1$ .  $K_3 C_A / K_4$  value: 1 1; 2 2.

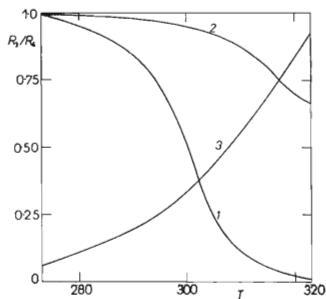


FIG. 6

Effect of the External Mass Transfer on the Temperature Dependence of the Selectivity in a System of Independent Reactions

$n = 2$ ,  $m = 1$ ,  $\Phi_{A2} = 0.001$ .  $E_1(E_2)$  value in kcal/mol: 1 20 (20); 2 10 (10); 3 20 (10).

the mass transfer coefficients are almost independent on the temperature, the increase of temperature results in a shift of the reaction regime on the particle towards the diffusion region. The imperfect external mass transfer may provoke a "secondary" effect of temperature on the selectivity. The "primary" temperature effect is due to difference in activation energies of reactions. When the external mass transfer effect is not excluded, then the increase in temperature results in an apparent equalisation of reactivities of the individual substances (Fig. 3).

The imperfect external mass transfer may considerably affect the reaction course in a reactor. In the case of independent reactions, the consequences are usually unfavourable. Fig. 4 exemplifies the influence of the external mass transfer on the reaction course in an isothermal discontinuous or tubular reactor. In the case of reactions with zero reaction heat, the increase of external mass transfer effect is accompanied by decrease of reaction rates (and thus a decreased reactor effectiveness) as well as by a decreased selectivity of the whole process. In the case of a strong external mass transfer effect it is impossible to achieve a high conversion without interference of slower reactions. Such an unfavourable situation may be observed in refinement reactions aiming to remove a small amount of the reactive contaminant.

In the earlier work<sup>7</sup>, the theoretical considerations were confirmed by hydrolysis of acetals and ketals in water under catalysis of an ion exchange resin membrane.

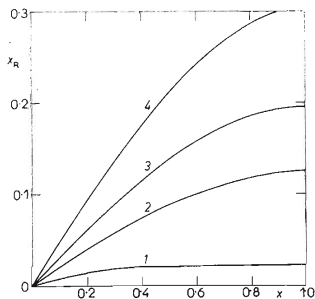


FIG. 7

Effect of the External Mass Transfer on the Selectivity of Concurrent Reactions in an Isothermal Discontinuous Reactor

$n = 2, m = 1, K_3 C_A / K_4 = 1. \Phi_{A_2}$  value: 1 10; 2 2; 3 0.5; 4 kinetic region.

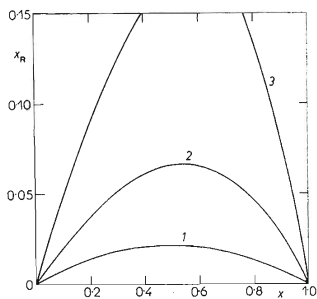


FIG. 8

Effect of the External Mass Transfer on the Selectivity of Concurrent Reactions in an Isothermal Continuous Tank Stirred Reactor

$n = 2, m = 1, K_3 C_A / K_4 = 1. \Phi_{A_2}$  value: 1 10; 2 2; 3 kinetic region.

This membrane consists of a mass which prevents the reactants from diffusion; the internal mass transfer cannot consequently assert itself.

### Concurrent Reactions

As stated above with reactions involving several starting compounds, the imperfect external mass transfer affects mainly that compound which is present in the lowest stoichiometric amount. The conclusions inferred for simple reaction schemes (C), (D) may be therefore extended for the case of more complex reaction systems when the other reactants are present in a great excess. Thus *e.g.*, the above simple scheme may be used for catalytic hydrogenations and oxidations in the liquid phase since the concentration of hydrogen or oxygen is usually much lower than that of other reactants. With respect to the external mass transfer, the reaction thus appears as two concurrent reactions of hydrogen or oxygen.

Similar to independent reactions, the change of the rate ratio of the two reactions in the passage of the catalyst particle régime from the kinetic into the diffusion region is expressed by dependence of this ratio on the  $\Phi_{A_2}$  parameter. As it may be inferred from calculations (Fig. 5), the reaction of a higher order may be entirely suppressed from the theoretical point of view when the reaction is transferred into the diffusion region. The external mass transfer effect increases with increasing difference between the orders of the two reactions.

The external mass transfer effect may also influence the temperature dependence of the process selectivity. Increase of the temperature disfavours the reaction of a lower activation energy and of a higher order (Fig. 6). The influence of temperature on the selectivity of a particular process thus depends on the difference between the reaction orders and on the difference between the activation energies of reactions.

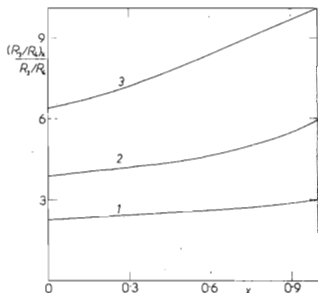


FIG. 9

Dependence of the Selectivity Ratio of Concurrent Reactions in the Kinetic Region and the Region Affected by the External Mass Transfer on the Overall Conversion

$n = 2$ ,  $m = 1$ ,  $K_3 C_A / K_4 = 1$ .  $\Phi_{A_2}$  value:  
1 2; 2 5; 3 10.



In chemical reactors, the external mass transfer effect brings about decreased yields of products which are formed by reactions of higher order (Figs 7 and 8). The change of the overall conversion degree results in a change of the reaction rate ratio because of the changed concentration of the starting compound in the reaction mixture which is then accompanied by the shift of the reaction regime towards the kinetical or diffusion region. The shift of the particle regime during the reaction towards the kinetical or diffusion region depends on the "predominating" order of the reaction. The external mass transfer is of order one with respect to the starting compound; when both reactions are of a higher order than one, then the increasing conversion degree of the starting compound brings about shift towards the kinetic region and *vice versa* when both reactions are of a lower order than one. When the order of one reaction is higher than one and that of the other reaction lower than one, the increasing conversion degree may be accompanied by either increase or decrease of the external mass transfer effect, depending on the predominance of the influence of one or the other reaction. Fig. 9 exemplifies the dependence between the external mass transfer and the conversion degree.

## LIST OF SYMBOLS

$a_m$	the external surface area of particles in a weight unit of the catalyst [m <sup>2</sup> /g]
$c_A, c_B$	concentration of compounds A and B in the reaction mixture bulk [mol/m <sup>3</sup> ]
$c_{Am}, c_{Bm}$	standard concentration of compounds [mol/m <sup>3</sup> ]
$c_{A0}, c_{B0}$	concentration of compounds in the feed of the reactor [mol/m <sup>3</sup> ]
$c_{As}, c_{Bs}$	concentration of compounds at the external surface of the particle [mol/m <sup>3</sup> ]
$C_A, C_B$	dimensionless concentrations of compounds defined by relations (5a,b)
$E$	activation energy of the reaction [kcal/mol]
$F$	rate of the reactor feed [m <sup>3</sup> /h]
$k_1, k_2, k_3, k_4$	rate constants of reactions in schemes (Y) to (D)
$k_{gA}, k_{gB}$	coefficients of the external transfer of compounds A and B [m/h]
$K_1, K_2, K_3, K_4$	dimensionless constants defined by relations (7a) to (7d)
$r_1, r_2, r_3, r_4$	reaction rates in schemes (A) to (D) [mol/g <sub>kat</sub> h]
$r_{Ad}, r_{Bd}$	external transfer rate of compounds A and B [mol/g <sub>kat</sub> h]
$r_{10m}, r_{20m}, r_{30m}, r_{40m}$	standard reaction rates at the standard concentration of compounds and under conditions which exclude the external mass transfer effect [mol/g <sub>kat</sub> h]
$R_1, R_2, R_3, R_4$	dimensionless reaction rates defined by relations (6a) to (6d)
$R$	dimensionless overall rate in the system of side reactions defined by the relation (6e)
$t$	reaction time [h]
$T$	temperature [K]

$V$	reactor volume [ $\text{m}^3$ ]
$W$	weight of the catalyst [g]
$x$	the overall conversion [—]
$x_A, x_B, x_R, x_S$	conversion of compounds A, B, R, and S
$\Phi_{A1}, \Phi_{A2}$	dimensionless parameter defined by relations (8a,b)
$\tau_1, \tau_2$	dimensionless reaction time in a discontinuous batch reactor defined by relations (11a,b)
$\vartheta_1, \vartheta_2$	dimensionless mean residence time in a continuous stirred tank reactor defined by relations (12a,b)

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