226. Chemical Selectivities Disguised by Mass Diffusion
I. A Simple Model of Mixing-Disguised Reactions in Solution

1st Communication on the Selectivity of Chemical Processes

by **Roland J. Ott** and **Paul Rys**

Technisch-Chemisches Laboratorium
Eidgenössische Technische Hochschule, Zürich

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Summary. The influence of mass diffusion on substrate and positional selectivities is discussed. A simple model is developed which allows a description and simulation of the coupling of the mass diffusion with the chemical reaction during the mixing process of two reactant solutions. For competitive, consecutive reactions and competitive, parallel reactions the general behaviour and the dependence of the product selectivity on diffusion effects is demonstrated.

1. Introduction. – Kinetic studies can be used to establish the mechanism of a reaction if, and only if, the results represent the real course of the chemical reaction, namely the bond breaking and bond making step. In the case of fast reactions this condition is not always fulfilled as pre-equilibrium diffusion processes can disguise the kinetics of chemical reactions and hence affect the distribution of the products in competitive reactions (diffusion-*disguised* selectivity). In general there are at least two situations in which diffusion effects may be involved in reactions in solution. The observed kinetics of a reaction can be

a) influenced by the rate of mixing of the reaction solutions¹) (= mixing-*disguised* kinetics) or

b) determined by the rate of formation of the encounter complex (= encounter rate-*determined*²) kinetics).

To avoid a misinterpretation of the kinetic data one has to take into account such diffusion effects.

It is necessary to specify clearly the influence of the diffusion process on various selectivities: Whereas the *positional* selectivity depends on the probability of a successful collision *within* the encounter complex and therefore is not linked directly with diffusion effects, the *substrate* selectivity of fast reactions is, in most cases, disguised by such diffusion effects. The results of various investigations [3] are explicable with the help of this concept of disguised kinetics and selectivity.

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1) For an introduction to the treatment of mixing problems see [1]. For comprehensive papers compare [2].

2) We speak of encounter rate-*determined* kinetics if the kinetics are influenced by two processes namely the formation of the encounter complex and the chemical reaction within the encounter complex. In encounter rate-*limited* (controlled) reactions the kinetics are given only by the rate of formation of the encounter complex.

Furthermore, empirical correlations based on studies of reaction kinetics, such as the linear selectivity relationship of free energies [4] postulated by *H. C. Brown*, will only provide useful information about the actual course of a reaction if diffusion effects are eliminated [5].

2. The Selectivity of Reaction Systems Disguised by Mixing. – In order to carry out a chemical reaction it is necessary to bring together the two reacting species *i.e.* to mix them. If such mixing processes have an influence on the rate of a chemical process they will also influence its selectivity[3]). A knowledge of the effect of mixing is therefore of decisive importance in the control and optimization of the distribution of the products formed. Basically one has to distinguish between steady state and non-steady state reaction systems. Several reports have appeared concerning the influence of diffusion processes on the selectivity of steady state systems in the field of heterogeneous catalysis [6]. In the present paper we concern ourselves with non-steady state systems such as those encountered in reactions carried out batch-wise.

3. The Basic Concept of a Mixing-Reaction Model. – In order to describe the mixing process occurring during the addition of one solution to another by a model it is useful to consider the following processes:

a) addition of one solution to another;
b) eddy diffusion (mechanical transport of the eddies, e.g. by stirring);
c) molecular diffusion (transport processes within the eddy).

If we add a solution of a species **A** to a solution of a species **B** eddies of solution **A** in solution **B** are created. As a first approximation we will consider these eddies as spherical drops with constant mean radius $\bar{R}$. This radius $\bar{R}$ depends on the intensity of the turbulence created by mixing and may be controlled, for example, by mechanical stirring. From the theory of turbulence [7] one can estimate the minimum mean size of such elements of liquid. For the usual solvents *e.g.* water, methyl and ethyl alcohol the mean minimum radius $\bar{R}$ of the eddies in optimal turbulence is approximately 10^{-2} to 10^{-3} cm; this corresponds to an agglomeration of about 10^{12} to 10^{15} molecules. The size of this liquid element increases with increasing viscosity of the solvent. In a mechanically well-stirred solution, the single eddies undergo a fast mutual interchange (a so-called eddy diffusion [8]). Generally this eddy diffusion is much faster than the molecular diffusion within the eddy. Owing to this fact a very important simplifying assumption can be made for our model, namely that the concentration gradient between the interface of the eddies and the solution can be neglected. Consequently the concentrations at the interface of the eddies correspond at any time to those in the surrounding solution. In order to obtain a simple mathematical description of the mixing processes, we consider one of the reactants (*e.g.* species **A**) and the resulting products to be immobile in the eddy into which the mobile molecules of the other substance (*e.g.* species **B**) penetrate by molecular dif-

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[3]) The selectivity of competing processes can be defined as the ratio of their relaxation times. The relaxation time (τ) of a process is the time needed for the system to traverse a fraction $^1/_e$ of its path to equilibrium.

fusion[4]. The moment the chemical reaction occurs the diffusing mobile molecules (species **B**) change their identity and consequently are considered as immobilized in the eddy.

In the present paper we will consider the influence of mixing effects on the selectivity of the two most common competitive reactions, namely the competitive, consecutive and the competitive, parallel reactions.

Competitive, Consecutive Second-Order Reactions:

$$\mathbf{A} + \mathbf{B} \xrightarrow{k_1} \mathbf{R} \quad \text{primary reaction}$$
$$\mathbf{R} + \mathbf{B} \xrightarrow{k_2} \mathbf{S} \quad \text{secondary reaction} \qquad (\textit{Scheme 1})$$

k_1, k_2: real second-order rate constants.

To form one molecule of the secondary product **S** two molecules of **B**, in two consecutive reaction stages, are immobilized. In Fig. 1 the mixing-*determined* reaction course of a competitive, consecutive reaction is schematically sketched: One molecule of **B** can react with a molecule of **A** only if it can move successfully through the peripheral zone of the **R** molecules already formed, *i.e.* if it does not react with the primary product **R** to give the secondary product **S**. The probability that this secondary reaction takes place decreases with an increase in the rate of diffusion. The yield of the product **S** is therefore a measure of the efficiency of the transport processes occurring in the reaction system. In the most extreme case of a mixing-*limited* reaction none of product **R** but only product **S** will be found at the end of the reaction, irrespective of the magnitude of the ratio k_1/k_2.

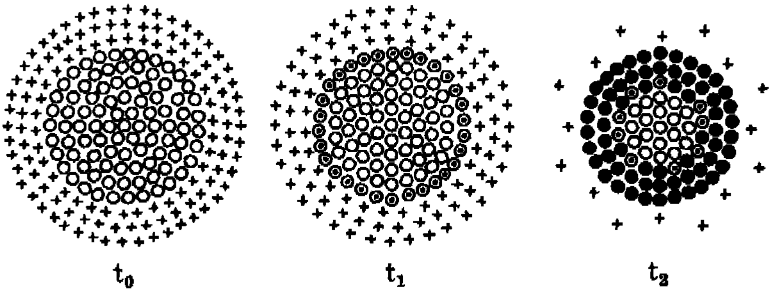

Fig. 1. *Schematic representation of a mixing*-determined *reaction course for competitive, consecutive second-order reactions* (Scheme 1), *assuming constant eddy size.* $t_0 < t_1 < t_2$: reaction times; mobile species: + reagent **B**; immobile species: ○ reagent **A**; ⊙ primary product **R**; ● secondary product **S**

Similarly, one could consider the molecules **B** to be immobile in the eddies into which the mobile molecules **A** could penetrate by molecular diffusion from the surrounding solution. In this case the product **R** has to be considered as a new mobile species which could diffuse to a further molecule of **B** and would be immobilized by reaction. These two approaches should in principle give similar descriptions of the system.

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[4] In reality a diffusing molecule **B** entering into the eddy replaces a solvent molecule. The fact that this is not considered in the present model does not affect the applicability (usefulness) of the model.

Competitive, Parallel Second-Order Reactions:

$$A + B \xrightarrow{k_3} P \qquad (Scheme\ 2)$$
$$C + B \xrightarrow{k_4} Q$$

k_3, k_4: real second-order rate constants.

The species **A** and **C** compete for the same reagent **B**. In Fig. 2 the mixing-*determined* reaction course of competitive, parallel reactions is shown schematically: If the concentrations of the molecules **A** and **C** are equal and if $k_3 \gg k_4$ the reaction zone of product **P** precedes the reaction zone of product **Q**. In order that the reagent **B** can react with **A** to give **P** it has to diffuse first through the already formed zone of product **P** which contains many more unreacted molecules of **C** than of **A**. Component **C** therefore, appears to react faster than would be expected from the ratio k_3/k_4. This leads to a decrease in the selectivity, which tends to the value 1 for the most extreme case of processes *limited* by mixing.

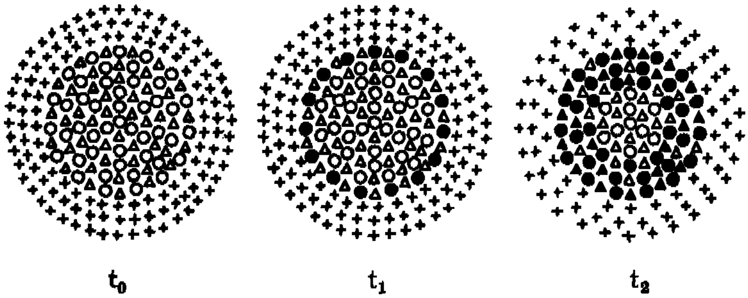

Fig. 2. *Schematic representation of a mixing-*determined *reaction course for competitive, parallel second-order reactions* (Scheme 2), *assuming constant eddy size.* $t_0 < t_1 < t_2$: reaction times; mobile species + reagent **B**; immobile species: ○ reagent **A**; △ reagent **C**; ● product **P**; ▲ product **Q**.

4. Mathematical Description of the Mixing-Reaction-Process[5]

– The molecular diffusion process of the mobile molecules within the eddies can be considered as a 'random walk' and as a non-steady state diffusion process; it can be described by the second *Fickian* equation:

$$D\nabla^2[\mathbf{B}] = \frac{\partial[\mathbf{B}]_{tot}}{\partial t} \tag{1a}$$

For spherical geometry we have to put $(\partial^2/\partial r^2 + 2/r\ \partial/\partial r)$ in place of ∇^2:

$$D\left(\frac{\partial^2[\mathbf{B}]}{\partial r^2} + \frac{2}{r}\frac{\partial[\mathbf{B}]}{\partial r}\right) = \frac{\partial[\mathbf{B}]_{tot}}{\partial t} \tag{1b}$$

$[\mathbf{B}]$	concentration of the mobile molecules **B** [mol/l]
$[\mathbf{B}]_{tot}$	total concentration of the mobile and immobilized molecules **B** [mol/l]
D	diffusion coefficient of the mobile molecules **B** [cm²/s]
r	polar coordinate [cm]
t	time [s]
∇^2	*Laplacian* operator

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[5] For a more detailed derivation of the equations which are used to describe the mixing-reaction system see Appendix. For definition of symbols, see list at end.

The diffusion equation (1) represents the general type of a parabolic partial differential equation for equalization processes (*e.g.* mass, heat flow); it describes the correlation between the local and temporal change of concentration. The left hand side of the equation (1) represents the difference in flux in and out of the two opposite boundaries of a volume element. The right hand side is the amount accumulated in that volume element. The equation formally expresses the fact that these two quantities must be equal. *Fick*'s second equation is not, therefore, a statement of a new mechanistic assumption or proposition. It is merely a necessary condition for the conservation of material. It follows that the left hand side must be concerned with the mobile molecular species subject to the diffusional statistical motion which opposes maintenance of an existing gradient of concentration. The right hand side, however, does not imply anything about the state of the molecules (mobile, immobilized or both) added to the volume element. In any event, this concentration refers to the total number of molecules which have arrived in the volume element but have not departed. It follows that $[\mathbf{B}]_{tot} = [\mathbf{B}]$ only if a pure diffusion process takes place. In the case when an immobilization process takes place at the reactive sites **A** of the substrate – in the present case, a change of chemical identity of the species **B** by chemical conversion – the following equation is generally valid:

$$[\mathbf{B}]_{tot} = [\mathbf{B}] + \Phi([\mathbf{B}], t) \tag{2}$$

$\Phi([\mathbf{B}], t)$ immobilization function

For competitive, consecutive reactions (*Scheme 1*) equation (3) is valid.

$$[\mathbf{B}]_{tot} = [\mathbf{B}] + [\mathbf{R}] + 2\,[\mathbf{S}] \tag{3}$$

$[\mathbf{R}]$ concentration of primary product **R** [mol/l]
$[\mathbf{S}]$ concentration of secondary product **S** [mol/l]

Combining equation (3) with *Fick*'s second equation (1b) we obtain the diffusion-reaction equation (4) for spherical geometry:

$$D\left(\frac{\partial^2[\mathbf{B}]}{\partial r^2} + \frac{2}{r}\,\frac{\partial[\mathbf{B}]}{\partial r}\right) = \frac{\partial[\mathbf{B}]}{\partial t} + \frac{\partial[\mathbf{R}]}{\partial t} + 2\,\frac{\partial[\mathbf{S}]}{\partial t}\,. \tag{4}$$

The local concentration change of the two species **R** and **S** are given by the differential equations (5) and (6).

$$\frac{\partial[\mathbf{R}]}{\partial t} = k_1\,[\mathbf{B}]\,([\mathbf{A}]_0 - [\mathbf{R}] - [\mathbf{S}]) - k_2\,[\mathbf{B}]\,[\mathbf{R}] \tag{5}$$

$$\frac{\partial[\mathbf{S}]}{\partial t} = k_2\,[\mathbf{B}]\,[\mathbf{R}] \tag{6}$$

$[\mathbf{A}]_0$ initial concentration of **A** [mol/l]
k_1, k_2 real second-order rate constants [l/(mol s)]

For competitive, parallel reactions (*Scheme 2*), equation (7) is valid:

$$[\mathbf{B}]_{tot} = [\mathbf{B}] + [\mathbf{P}] + [\mathbf{Q}] \tag{7}$$

$[\mathbf{P}]$ concentration of product **P** [mol/l]
$[\mathbf{Q}]$ concentration of product **Q** [mol/l]

Combining the equation (7) with *Fick*'s second equation (1b) we obtain the diffusion-reaction equation (8) for spherical geometry:

$$D\left(\frac{\partial^2[\mathbf{B}]}{\partial r^2} + \frac{2}{r}\frac{\partial[\mathbf{B}]}{\partial r}\right) = \frac{\partial[\mathbf{B}]}{\partial t} + \frac{\partial[\mathbf{P}]}{\partial t} + \frac{\partial[\mathbf{Q}]}{\partial t} \qquad (8)$$

The local concentration change of the two species **P** and **Q** are given by the differential equations (9) and (10):

$$\frac{\partial[\mathbf{P}]}{\partial t} = k_3\,[\mathbf{B}]\,([\mathbf{A}]_0 - [\mathbf{P}]) \qquad (9)$$

$$\frac{\delta[\mathbf{Q}]}{\delta t} = k_4\,[\mathbf{B}]\,([\mathbf{C}]_0 - [\mathbf{Q}]) \qquad (10)$$

$[\mathbf{C}]_0$	initial concentration of **C** [mol/l]
k_3, k_4	real second-order rate constants [l/(mol s)]

The equations (4) – (6) and (8) – (10) can be normalized by introducing the following dimensionless parameters[6]:

$$\mathbf{X} = \frac{r}{\mathrm{R}};\quad \mathbf{T} = \frac{D}{\mathrm{R}^2}\,t;\quad \mathbf{B}_\mathbf{B} = \frac{[\mathbf{B}]}{[\mathbf{B}]_0};\quad \Omega_{\mathbf{B},1} = \frac{[\mathbf{R}]}{[\mathbf{B}]_0};\quad \Omega_{\mathbf{B},2} = \frac{[\mathbf{S}]}{[\mathbf{B}]_0};$$

$$\Omega_{\mathbf{B},3} = \frac{[\mathbf{P}]}{[\mathbf{B}]_0};\quad \Omega_{\mathbf{B},4} = \frac{[\mathbf{Q}]}{[\mathbf{B}]_0};\quad \mathbf{E} = \frac{[\mathbf{A}]_0}{[\mathbf{B}]_0};\quad \mathbf{M} = \frac{[\mathbf{C}]_0}{[\mathbf{A}]_0};$$

$$\varphi^2_{\mathrm{B},1} = \frac{\mathrm{R}^2 k_1[\mathbf{B}]_0}{D};\quad \varphi^2_{\mathrm{B},2} = \frac{\mathrm{R}^2 k_2[\mathbf{B}]_0}{D};\quad \varphi^2_{\mathrm{B},3} = \frac{\mathrm{R}^2 k_3[\mathbf{B}]_0}{D};\quad \varphi^2_{\mathrm{B},4} = \frac{\mathrm{R}^2 k_4[\mathbf{B}]_0}{D}$$

$[\mathbf{B}]_0$	initial concentration of the mobile molecules **B** [mol/l]
R	mean radius of the eddies [cm]
$\varphi^2_{\mathrm{B},i}$	normalized rate constant of the reaction step i with respect to $[\mathbf{B}]_0$. This expression corresponds to the square of the so-called *Thiele-Modul* which is used to characterize diffusion determined (steady state) heterogeneous reactions [6] [12]. φ^2_{B} is proportional to the ratio of relaxation times of diffusion and chemical reaction [11] [13].

For experimental appraisal of the system it is convenient to discuss the initial conditions in terms of mol ratios ($^*\mathbf{E}$). Therefore, α, the ratio of eddy volume containing **A** or **A** and **C** to solution volume containing **B** is introduced:

$$^*\mathbf{B}_\mathbf{B} = \alpha\,\mathbf{B}_\mathbf{B}\,,\quad ^*\mathbf{E} = \alpha\,\mathbf{E};\quad ^*\Omega_{\mathrm{B},1} = \alpha\,\Omega_{\mathrm{B},1};\quad ^*\varphi^2_{\mathrm{B},1} = \frac{\varphi^2_{\mathrm{B},i}}{\alpha}$$

$i \rightarrow 1, 2, 3, \text{or } 4$

This generalization leads to the equations (11) – (16):

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[6] The normalization was performed using $[\mathbf{B}]_0$. In a similar way $[\mathbf{A}]_0$ could be used in the normalization procedure. This would lead to other dimensionless parameters which would be labelled with the index A, e.g. $\mathbf{B}_\mathbf{A} = [\mathbf{B}]/[\mathbf{A}]_0$.

Competitive, Consecutive Second-Order Reactions (*Scheme 1*):

$$\frac{\partial^2 {}^*B_B}{\partial X^2} + \frac{2}{X}\frac{\partial {}^*B_B}{\partial X} = \frac{\partial {}^*B_B}{\partial T} + \frac{\partial {}^*\Omega_{B,1}}{\partial T} + 2\frac{\partial {}^*\Omega_{B,2}}{\partial T} \tag{11}$$

$$\frac{\partial {}^*\Omega_{B,1}}{\partial T} = {}^*\varphi^2_{B,1}\,{}^*B_B\,({}^*E - {}^*\Omega_{B,1} - {}^*\Omega_{B,2}) - {}^*\varphi^2_{B,2}\,{}^*B_B\,{}^*\Omega_{B,1} \tag{12}$$

$$\frac{\partial {}^*\Omega_{B,2}}{\partial T} = {}^*\varphi^2_{B,2}\,{}^*B_B\,{}^*\Omega_{B,1} \tag{13}$$

Competitive, Parallel Second-Order Reactions (*Scheme 2*):

$$\frac{\partial^2 {}^*B_B}{\partial X^2} + \frac{2}{X}\frac{\partial {}^*B_B}{\partial X} = \frac{\partial {}^*B_B}{\partial T} + \frac{\partial {}^*\Omega_{B,3}}{\partial T} + \frac{\partial {}^*\Omega_{B,4}}{\partial T} \tag{14}$$

$$\frac{\partial {}^*\Omega_{B,3}}{\partial T} = {}^*\varphi^2_{B,3}\,{}^*B_B\,({}^*E - {}^*\Omega_{B,3}) \tag{15}$$

$$\frac{\partial {}^*\Omega_{B,4}}{\partial T} = {}^*\varphi^2_{B,4}\,{}^*B_B\,(M\,{}^*E - {}^*\Omega_{B,4}) \tag{16}$$

5. Procedure for Numerical Solution. – The two systems of equations (11)–(13) and (14)–(16) consist of parabolic partial differential equations (11) and (14) which are coupled with eq. (12), (13) and (15), (16) respectively. Since an analytical solution of such systems does not exist, a numerical approximation must be used. In addition to the stable explicit finite difference method [9], the *Method of Lines* [10] was also used. The detailed procedure has been described elsewhere [11]. The computer programme was written in FORTRAN and the calculations carried out on a CDC 6400/6500 computer.

6. Simulation of Mixing Disguised Competitive, Consecutive Reactions5)**.** – The system of equations (11)–(13) which describes the mechanism of competitive, consecutive second-order reactions coupled with a diffusion process is determined by the three parameters ${}^*E$, ${}^*\varphi^2_{B,1}$, ${}^*\varphi^2_{B,2}$ and the initial and boundary conditions7). For ${}^*E = 1$ and with ${}^*\varphi^2_{B,1}$ constant an increase in the value of ${}^*\varphi^2_{B,2}$ will result in an increase in the relative yield X_S of the secondary product **S**. This is shown in Fig. 3 for 100% conversion (${}^*B_B = 0$). A clearer representation of the influence of diffusion effects on X_S is given in Fig. 4. With an increase of ${}^*\varphi^2_{B,2}$ – *i.e.* an increasing influence of the diffusion process – the relative yield of the product **S** exceeds the value of the reaction controlled process. The smaller the value of ${}^*\varphi^2_{B,2}$ the closer will be the yield of **S** to the reaction controlled value. On the other hand, the extreme

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7) The initial conditions for all calculations are defined in the Appendix (A-22). The boundary conditions are given by equations (A-23) and (A-24).
For given initial conditions and varying boundary conditions (by changing α), calculations for 100% conversion of the species **B** (${}^*B_B = 0$) have shown that X_S and ε_r values are determined solely by the values of ${}^*\varphi^2_{B,1}$, ${}^*\varphi^2_{B,2}$ and ${}^*E$, irrespective of the specific value of α.

case where only the product S is found will be reached when $^{*}\varphi^2_{B,2}$ approaches infinity. The more the process is disguised by diffusion *i.e.* $^{*}\varphi^2_{B,2}$ is large, the less the ratio $^{*}\varphi^2_{B,1}/^{*}\varphi^2_{B,2}$ (respectively k_1/k_2) will effect the relative yield X_S of the product S. In Fig. 5 the effectiveness ε_r of the chemical reaction on the formation of S is shown as a function of $^{*}\varphi^2_{B,2}$ for different ratios of $^{*}\varphi^2_{B,1}/^{*}\varphi^2_{B,2}$ · ε_r represents the factor by which the chemical reactivity influences the selectivity of the total process and is given by the ratio of the reaction controlled and mixing disguised X_S-values [14]: $\varepsilon_r = 1$ means that the selectivity is determined exclusively by the chemical reactivity. The values calculated for the Fig. 3–5 are listed in Table 1.

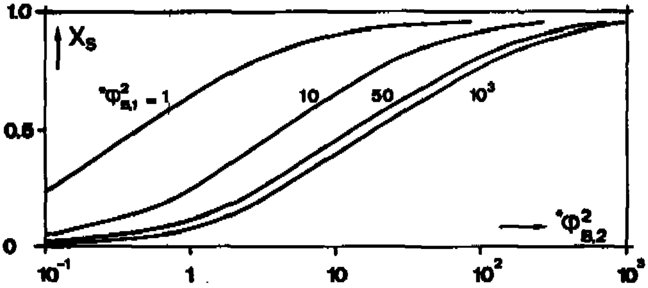

Fig. 3. *Diffusion-Reaction-Model: Calculated relative yields X_S as a function of $^{*}\varphi^2_{B,2}$ for different values of $^{*}\varphi^2_{B,1}$* (spherical geometry) $^{*}E = 1$; $^{*}B_B = 0$

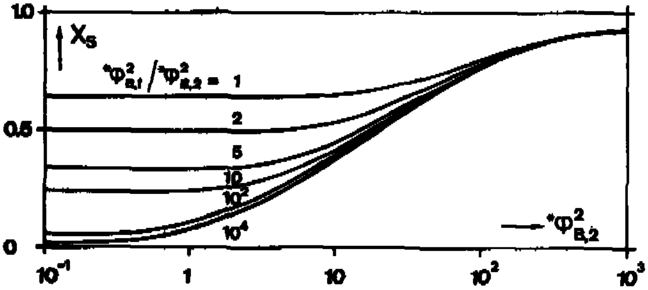

Fig. 4. *Diffusion-Reaction-Model: Calculated relative yields X_S as a function of $^{*}\varphi^2_{B,2}$ for different ratios* $^{*}\varphi^2_{B,1}/^{*}\varphi^2_{B,2}$ (spherical geometry) $^{*}E = 1$; $^{*}B_B = 0$

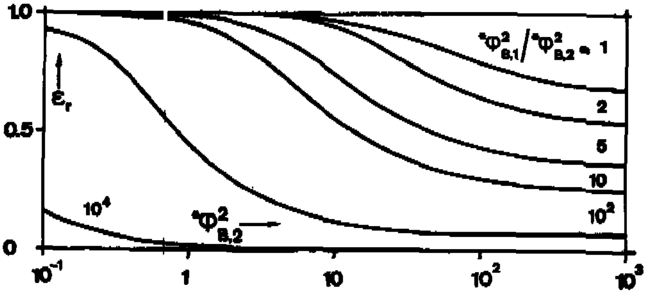

Fig. 5. *Diffusion-Reaction-Model: Calculated effectiveness ε_r as a function of $^{*}\varphi^2_{B,2}$ for different ratios of* $^{*}\varphi^2_{B,1}/^{*}\varphi^2_{B,2}$ (spherical geometry) $^{*}E = 1$; $^{*}B_B = 0$

Table 1. *Diffusion-Reaction-Model*: *The influence of the parameters* $^*\varphi^2_{B,1}$ *and* $^*\varphi^2_{B,2}$ *on competitive, consecutive second-order reactions* (Scheme 1; *spherical geometry*)
$^*E = 1$; $^*B_H = 0$; RC: reaction-controlled ($^*\varphi^2_B \to 0$)

$^*\varphi^2_{B,1}/^*\varphi^2_{B,2}$	$^*\varphi^2_{B,1}$	$^*\varphi^2_{B,2}$	mol % **S**[8])	X_S	ε_r
1	RC	RC	31.8	0.636	1.000
	0.1	0.1	31.9	0.639	0.998
	1	1	32.1	0.642	0.993
	2	2	32.2	0.644	0.988
	10	10	32.6	0.653	0.974
	50	50	36.8	0.736	0.864
	100	100	39.9	0.799	0.796
	250	250	43.8	0.876	0.726
	500	500	45.6	0.912	0.697
	1000	1000	46.5	0.931	0.683
2	RC	RC	24.8	0.497	1.000
	0.2	0.1	24.9	0.498	0.996
	2	1	25.0	0.500	0.992
	20	10	26.4	0.529	0.940
	40	20	29.2	0.585	0.850
	200	100	38.8	0.776	0.640
	400	200	42.5	0.850	0.585
5	RC	RC	16.7	0.334	1.000
	5	1	16.9	0.337	0.991
	12.5	2.5	17.5	0.350	0.954
	50	10	22.6	0.451	0.741
	100	20	27.5	0.549	0.608
	180	36	31.6	0.632	0.528
	300	60	35.1	0.702	0.476
	1000	200	42.3	0.845	0.395
10	RC	RC	11.6	0.232	1.000
	1	0.1	11.7	0.234	0.991
	10	1	12.0	0.241	0.963
	25	2.5	13.6	0.272	0.853
	50	5	16.5	0.329	0.705
	100	10	20.9	0.418	0.555
	250	25	28.0	0.560	0.414
	500	50	33.4	0.668	0.347
	1000	100	38.1	0.761	0.305
	2000	200	41.9	0.839	0.277
10^2	RC	RC	2.6	0.052	1.000
	10	0.1	2.8	0.056	0.929
	50	0.5	4.0	0.080	0.650
	100	1	5.9	0.118	0.441
	500	5	14.5	0.291	0.179
	1000	10	19.9	0.399	0.130
	5000	50	32.8	0.657	0.079
10^4	RC	RC	0.1	0.002	1.000
	1×10^3	0.1	0.6	0.013	0.154
	5×10^3	0.5	2.8	0.056	0.036
	1×10^4	1	4.9	0.097	0.021
	4×10^4	4	12.2	0.243	0.008
	1×10^5	10	19.5	0.389	0.005
	4×10^5	40	30.6	0.612	0.003

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[8]) Mol-% are related to the initial moles of **B**.

Fig. 6 shows the relative yields X_s calculated for the ratio $^*\varphi^2_{B,1}/^*\varphi^2_{B,2} = 1$ (or $k_1/k_2 = 1$, respectively) as a function of the parameter *E. At all values of $^*\varphi^2_{B,2}$, the relative yield X_S decreases as *E increases. The greater the value of $^*\varphi^2_{B,2}$ the smaller is the decrease in the yield of X_S.

Fig. 7 shows the influence of the parameter *E on the effectiveness of the chemical reactivity on the formation of **S**. For a given value of $^*\varphi^2_{B,2}$ the influence of the chemical reactivity on the selectivity of the process decreases with increasing values of *E. The calculated values for the Fig. 6 and 7 are listed in Table 2.

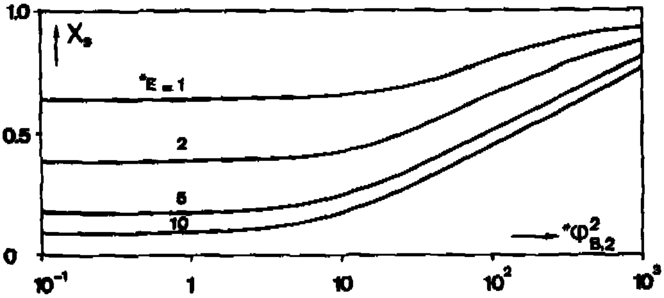

Fig. 6. *Diffusion-Reaction-Model: Calculated relative yields X_S as a function of $^*\varphi^2_{B,2}$ for different values of *E (spherical geometry)* $^*\varphi^2_{B,1}/^*\varphi^2_{B,2} = 1$; $^*B_B = 0$

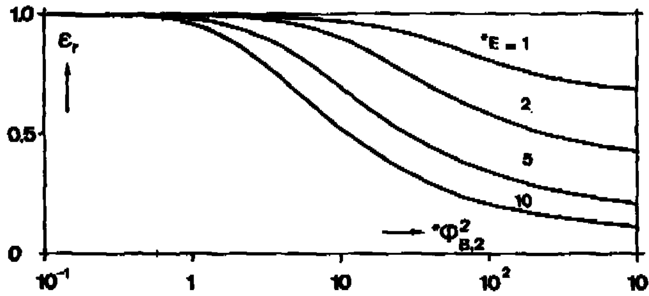

Fig. 7. *Diffusion-Reaction-Model: Calculated effectiveness ε_r as a function of $^*\varphi^2_{B,2}$ for different values of *E (spherical geometry)* $^*\varphi^2_{B,1}/^*\varphi^2_{B,2} = 1$; $^*B_B = 0$

In Fig. 8 the simulated data are plotted in a manner which allows an easy survey of the experimental results. The relative yield X_S is shown as a function of $^*\varphi^2_{B,2}$ for various *E $^*\varphi^2_{B,2}$ and $^*\varphi^2_{B,1}/^*\varphi^2_{B,2}$ (or k_1/k_2, respectively) values. The X_S values which can be obtained, for instance, by varying $[\mathbf{B}]_0$ only and keeping $[\mathbf{A}]_0$ and the mixing conditions constant, all lie on an S-shape curve (selectivity curve) whose position along the $^*\varphi^2_{B,2}$-axis depends only on the value of *E $^*\varphi^2_{B,2}$. As a consequence of this, the relative k_2 values for different substrates can be found from the relative positions of the respective selectivity curves using a particular value of *E as a reference point.

7. Simulation of Mixing Disguised Competitive, Parallel Reactions. – The system of equations (14)–(16) which describes the mechanism of competitive, parallel second-order reactions coupled with a diffusion process is determined by

Table 2. *Diffusion-Reaction-Model: The influence of the parameter* *E *on competitive, consecutive second-order reactions* (Scheme 1; *spherical geometry*)
$^*\varphi^2_{B,1}/^*\varphi^2_{B,2} = 1$; $^*B_B = 0$; RC: reaction-controlled ($^*\varphi^2_B \to 0$)

*E	$^*\varphi^2_{B,2}$	mol % S[8]	X_S	ε_r	*E	$^*\varphi^2_{B,2}$	mol % S[8]	X_S	ε_r
1	RC	31.8	0.636	1.000	5	RC	8.8	0.177	1.000
	1	32.1	0.642	0.993		1	8.9	0.178	0.982
	10	32.6	0.653	0.974		10	12.5	0.251	0.704
	50	36.8	0.736	0.864		50	20.9	0.419	0.421
	100	39.9	0.799	0.796		100	25.4	0.508	0.348
	500	45.6	0.912	0.697		500	35.8	0.717	0.246
	1000	46.5	0.931	0.683		1000	40.2	0.804	0.220
2	RC	19.1	0.382	1.000	10	RC	4.7	0.093	1.000
	1	19.3	0.387	0.987		1	4.8	0.097	0.963
	10	21.1	0.422	0.905		10	9.0	0.179	0.522
	50	28.5	0.571	0.669		50	17.5	0.350	0.267
	100	32.5	0.650	0.588		100	22.2	0.444	0.210
	500	41.4	0.829	0.460		500	33.4	0.668	0.140
	1000	44.1	0.881	0.434		1000	38.1	0.761	0.123

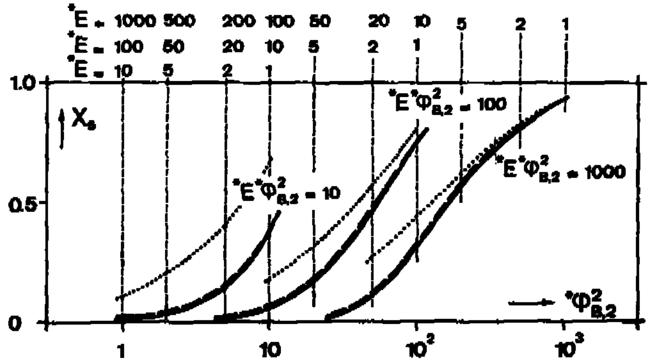

Fig. 8. *Diffusion-Reaction-Model: Calculated relative yields* X_S *as a function of* $^*\varphi^2_{B,2}$ *for different* $^*E$ $^*\varphi^2_{B,2}$ *and* $^*\varphi^2_{B,1}/^*\varphi^2_{B,2}$ *values (spherical geometry)* ...... $^*\varphi^2_{B,1}/^*\varphi^2_{B,2} = 1$; – – – $^*\varphi^2_{B,1}/^*\varphi_{B,2} = 10$; — $^*\varphi^2_{B,1}/^*\varphi^2_{B,2} = 100$; $^*B_B = 0$

the four parameters *E, $^*\varphi^2_{B,3}$, $^*\varphi^2_{B,4}$, M and the initial and boundary conditions[9]). For *E = 1 the relative yield of the product Q, expressed as the mol fraction X_Q, approaches a mixing-limited selectivity-value for each $^*\varphi^2_{B,3}$ value as $^*\varphi^2_{B,4}$ increases. This is shown in Fig. 9 for 100% conversion ($^*B_B = 0$).

Fig. 10 shows for *E = 1 and M = 1 that for every $^*\varphi^2_{B,3}/^*\varphi^2_{B,4}$ ratio the relative yield X_Q approaches the same mixing-limited value of 0.5. This limiting selectivity value depends on the parameters *E and M as demonstrated in Fig. 11 and Fig. 12, respectively. The calculated values for the Fig. 9–12 are listed in the Tables 3–5.

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[9]) The initial conditions for all calculations are the same as those used in the calculations of the competitive, consecutive reaction system (Appendix, (A-22)), except that [R] = [S] = 0 is replaced by [P] = [Q] = 0.
X_Q values for 100% conversion of the species B are determined solely by the values of $^*\varphi^2_{B,3}$, $^*\varphi^2_{B,4}$, M and *E (compare footnote [7]).

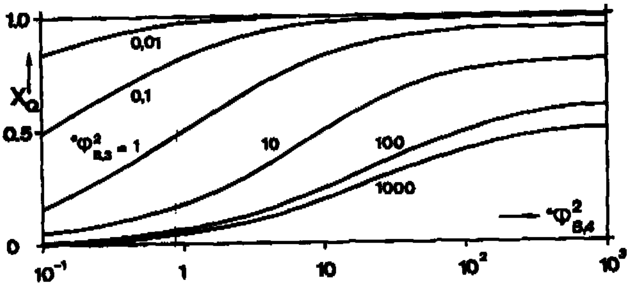

Fig. 9. *Diffusion-Reaction-Model: Calculated relative yields* X_Q *as a function of* $^*\varphi^2_{B,4}$ *for different values of* $^*\varphi^2_{B,3}$ *(spherical geometry)* $^*E = 1$; $M = 1$; $^*B_B = 0$

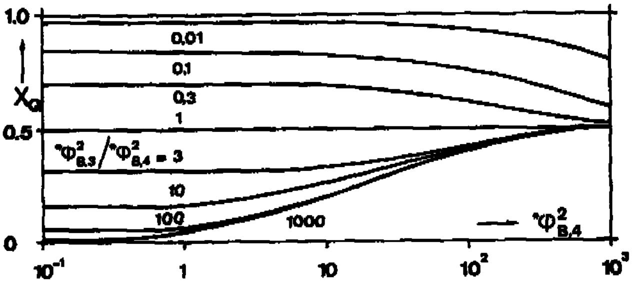

Fig. 10. *Diffusion-Reaction-Model: Calculated relative yields* X_Q *as a function of* $^*\varphi^2_{B,4}$ *for different ratios* $^*\varphi^2_{B,3}/^*\varphi^2_{B,4}$ *(spherical geometry)* $^*E = 1$; $M = 1$; $^*B_B = 0$

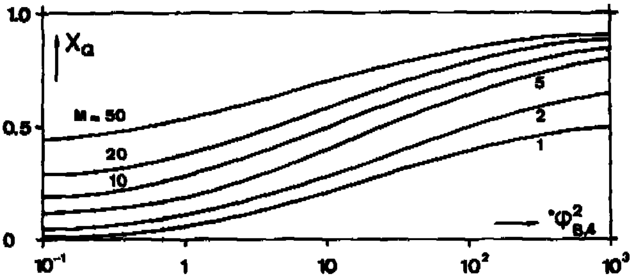

Fig. 11. *Diffusion-Reaction-Model: Calculated relative yields* X_Q *as a function of* $^*\varphi^2_{B,4}$ *for different values of* M *(spherical geometry)* $^*\varphi^2_{B,3}/^*\varphi^2_{B,4} = 100$; $^*E = 1$; $^*B_B = 0$

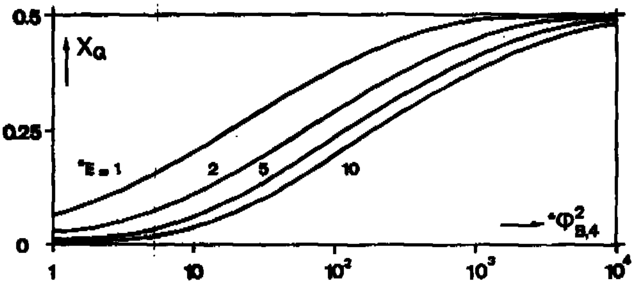

Fig. 12. *Diffusion-Reaction-Model: Calculated relative yields* X_Q *as a function of* $^*\varphi^2_{B,4}$ *for different values of* $^*E$ *(spherical geometry)* $^*\varphi^2_{B,3}/^*\varphi^2_{B,4} = 100$; $M = 1$; $^*B_B = 0$

Table 3. *Diffusion-Reaction-Model: The influence of the parameters* $^*\varphi^2_{B,3}$ *and* $^*\varphi^2_{B,4}$ *on competitive parallel second-order reactions* (Scheme 2; *spherical geometry*)
$^*E = 1$; $M = 1$; $^*B_B = 0$
RC: reaction-controlled ($^*\varphi^2_B \rightarrow 0$)

$^*\varphi^2_{B,3}/^*\varphi^2_{B,4}$	$^*\varphi^2_{B,3}$	$^*\varphi^2_{B,4}$	X_Q	$^*\varphi^2_{B,3}/^*\varphi^2_{B,4}$	$^*\varphi^2_{B,3}$	$^*\varphi^2_{B,4}$	X_Q
10^{-2}	RC	RC	0.966	10	1	10^{-1}	0.160
	10^{-3}	10^{-1}	0.966		10	1	0.170
	10^{-2}	1	0.966		10^2	10	0.247
	10^{-1}	10	0.965		10^3	10^2	0.404
	3×10^{-1}	30	0.961		10^4	10^3	0.489
	1	10^2	0.936				
	3	3×10^2	0.887	10^2	RC	RC	0.033
	10	10^3	0.804		1	10^{-2}	0.035
					10	10^{-1}	0.045
10^{-1}	RC	RC	0.835		10^2	1	0.075
	10^{-2}	10^{-1}	0.835		10^3	10	0.200
	10^{-1}	1	0.830		5×10^3	50	0.340
	1	10	0.825		10^4	10^2	0.396
	3	30	0.817		10^5	10^3	0.488
	10	10^2	0.757				
	10^2	10^3	0.593	10^3	RC	RC	0.005
					10^2	10^{-1}	0.010
1	RC	RC	0.500		10^3	1	0.049
	10^{-2}	10^{-2}	0.500		3×10^3	3	0.100
	10^3	10^3	0.500		10^4	10	0.200
					5×10^4	50	0.340
10	RC	RC	0.160		10^5	10^2	0.400
	10^{-1}	10^{-2}	0.160		10^6	10^3	0.488

Table 4. *Diffusion-Reaction-Model: The influence of the parameter* M *on competitive, parallel second-order reactions* (Scheme 2; *spherical geometry*)
$^*\varphi^2_{B,3}/^*\varphi^2_{B,4} = 100$; $^*E = 1$; $^*B_B = 0$
RC: reaction-controlled ($^*\varphi^2_B \rightarrow 0$)

M	$^*\varphi^2_{B,4}$	X_Q	M	$^*\varphi^2_{B,4}$	X_Q
1	RC	0.033	10	RC	0.174
	10^{-1}	0.045		10^{-1}	0.180
	1	0.075		1	0.270
	10	0.200		10	0.500
	10^2	0.396		10^2	0.710
	10^3	0.488		10^3	0.860
2	RC	0.057	20	RC	0.264
	10^{-1}	0.060		10^{-1}	0.275
	1	0.105		1	0.370
	10	0.270		10	0.580
	10^2	0.495		10^2	0.785
	10^3	0.690		10^3	0.880
5	RC	0.109	50	RC	0.425
	10^{-1}	0.110		10^{-1}	0.435
	1	0.180		1	0.530
	10	0.400		10	0.710
	10^2	0.635		10^2	0.850
	10^3	0.835		10^3	0.890

Tabelle 5. *Diffusion-Reaction-Model: The influence of the parameter *E on competitive, parallel second-order reactions* (Scheme 2; *spherical geometry*)
$^*\varphi^2_{B,3}/^*\varphi^2_{B,4} = 100$; $M = 1$; $^*B_B = 0$
RC: reaction-controlled ($^*\varphi^2_B \to 0$)

$^*E$	$^*\varphi^2_{B,4}$	X_Q	$^*E$	$^*\varphi^2_{B,4}$	X_Q
1	RC	0.033	5	RC	0.011
	10^{-1}	0.060		10^{-1}	0.012
	1	0.064		1	0.018
	10	0.202		10	0.045
	10^2	0.396		10^2	0.230
	10^3	0.490		10^3	0.405
	10^4	0.495		10^4	0.485
2	RC	0.013	10	RC	0.010
	10^{-1}	0.014		10^{-1}	0.011
	1	0.025		1	0.015
	10	0.105		10	0.024
	10^2	0.295		10^2	0.190
	10^3	0.455		10^3	0.378
	10^4	0.493		10^4	0.477

8. Conclusion. – Coupling of mass diffusion with chemical reactions during the mixing process of two reactant solutions has been simulated with the help of a simple model. The general behaviour of a competitive, consecutive and a competitive, parallel second-order reaction can be adequately described by three or four parameters, respectively. These parameters, which can be varied experimentally in a well defined manner, determine to what extent the product selectivity is disguised by mass diffusion effects. As long as the mixing modulus $^*\varphi^2_B$ of the faster of the competing reactions is smaller than *ca.* 0.1, diffusion effects on product selectivity can be ignored. However, mixing-disguised selectivities are highly probable when $^*\varphi^2_B$ is greater than 10.

Appendix

Derivation of the Diffusion-Reaction Equations (4)–(6) [15]. – After applying the law of conservation of mass of species i to a differential volume element fixed in space in a diffusion-reaction system and allowing the size of the volume element to decrease to zero, one obtains:

$$\frac{\partial c_i}{\partial t} = -\left(\frac{\partial N_{ix}}{\partial x} + \frac{\partial N_{iy}}{\partial y} + \frac{\partial N_{iz}}{\partial z}\right) + r_i \qquad \text{(A-1a)}$$

N_{ix}, N_{iy}, N_{iz}	rectangular components of the molar flux vector $\vec{N}_i$ [mol/(cm² s)]
c_i	molar concentration of species i [mol/cm³]
r_i	molar rate of production by chemical reaction of species i [mol/(cm³ s)]
t	time [s]
x, y, z	rectangular coordinates [cm]

This is the equation of continuity which describes the change of molar concentration of the component i with respect to time at a fixed point in space. This change results from the motion of species i and its chemical reaction.

$$\frac{\partial c_i}{\partial t} = -(\nabla \cdot \vec{N}_i) + r_i \qquad \text{(A-1b)}$$

$\vec{N}_i$	molar flux of species i with respect to stationary coordinates [mol/(cm² s)]
∇	'del' or 'nabla' operator

The vector differential operator ∇ is defined in rectangular coordinates as

$$\nabla = \vec{\delta}_x \frac{\partial}{\partial_x} + \vec{\delta}_y \frac{\partial}{\partial_y} + \vec{\delta}_z \frac{\partial}{\partial_z} \tag{A-2}$$

$\vec{\delta}_x, \vec{\delta}_y, \vec{\delta}_z$	unit vectors associated with the x, y, z-coordinates

In order to obtain the equation which is generally used to describe diffusion the molar flux $\vec{N}_i$ is replaced by the appropriate expression (A-7) which includes the concentration gradient.

$$\vec{N}_i = c_i \vec{v}_i = x_i \sum_{j=1}^{n} \vec{N}_j + \vec{J}_i \tag{A-3}$$

$$x_i = \frac{c_i}{\sum_{j=1}^{n} c_j} = \frac{c_i}{c} \tag{A-4}$$

$$x_i \sum_{j=1}^{n} \vec{N}_j = c_i \frac{\sum_{j=1}^{n} c_j \vec{v}_j}{\sum_{j=1}^{n} c_j} = c_i \vec{v} \tag{A-5}$$

$$\vec{J}_i = -c\, D_i \nabla x_i \tag{A-6}$$

$$\vec{N}_i = c_i \vec{v} - c\, D_i \nabla x_i \tag{A-7}$$

D_i	diffusion coefficient of species i [cm²/s]
$\vec{J}_i$	molar flux of species i relative to the molar average velocity [mol/(cm² s)]
c	total molar concentration [mol/cm³]
$\vec{v}_i$	velocity of species i [cm/s]
$\vec{v}$	molar average velocity [cm/s]
x_i	mol fraction of species i [–]

Equation (A-3) shows that the diffusion flux $\vec{N}_i$ relative to stationary coordinates is the resultant of two vectors, namely the vector given by equation (A-5) which is the molar flux of i resulting from the bulk motion of the fluid and the vector[10]) given by equation (A-6) which, in turn, is the molar flux of i resulting from the diffusion superimposed on the bulk flow.

When equation (A-7) is substituted into equation (A-1b) we get the following diffusion equation:

$$\frac{\partial c_i}{\partial t} = -(\nabla \cdot c_i \vec{v}) + (\nabla \cdot c\, D_i \nabla x_i) + r_i \tag{A-8}$$

Equation (A-8) describes the concentration profiles of the species i in a diffusing system. The only restriction is the absence of thermal, pressure and forced diffusion.

Assumption of Constant c and D_i. – If c and D_i are assumed to be constant[11]) equation (A-8) becomes:

$$\frac{\partial c_i}{\partial t} = -c_i (\nabla \cdot \vec{v}) - (\vec{v} \cdot \nabla c_i) + D_i \nabla^2 c_i + r_i \tag{A-9}$$

Assumption of Zero Molar Velocity. – Considering a single eddy of the substrate we assume that the molar velocity within the eddy is zero. For dilute solutions, this assumption is

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[10]) $\vec{J}_i = -c\, D_i \nabla x_i$ is *Fick*'s first equation of diffusion written in terms of the molar diffusion flux $\vec{J}_i$.

[11]) Usually the experimental work is carried out with dilute solutions, thus the concentration of the solvent is much greater than that of the solutes and remains constant for an incompressible fluid. The sum of all concentrations, *i.e.* c, may be taken as constant.

valid and equation (A-9) becomes:

$$\frac{\partial c_i}{\partial t} = D_i \nabla^2 c_i + r_i \tag{A-10}$$

∇^2 Laplacian operator

The Laplacian operator ∇^2 is defined in rectangular coordinates as

$$\nabla^2 = \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2} \tag{A-11}$$

If, in addition there are no chemical changes occurring, one obtains

$$\frac{\partial c_i}{\partial t} = D_i \nabla^2 c_i \tag{A-12}$$

which is called *Fick*'s second equation of diffusion.

Assumption of Spherical Eddy with Constant Mean Radius. – If we consider a sphere in which diffusion occurs from the surface to the centre, the diffusion-reaction equation (A-10) for a constant diffusion coefficient takes the form

$$\frac{\partial c_i}{\partial t} = D_i \left(\frac{\partial^2 c_i}{\partial r^2} + \frac{2}{r} \frac{\partial c_i}{\partial r} \right) + r_i \tag{A-13a}$$

r = polar coordinate [cm]

Setting $1000\, c_i = [\mathbf{B}]$; $D_i = D$; $r_i = r_B$ we obtain

$$D \left(\frac{\partial^2 [\mathbf{B}]}{\partial r^2} + \frac{2}{r} \frac{\partial [\mathbf{B}]}{\partial r} \right) = \frac{\partial [\mathbf{B}]}{\partial t} - 1000\, r_B \tag{A-13b}$$

Assumption of Zero Diffusion of the Substrate A, the Primary Product R and the Secondary Product S[12]. – As a first approximation to simulate the diffusion-reaction system described in Chap. 4 we assume a stationary (fixed) substrate **A**, primary product **R** and secondary product **S**, *i.e.* the molecules **A**, **R** and **S** are supposed to be fixed within the eddy into which the species **B** diffuses and reacts with **A** or **R**. Although this is a drastic simplification which in reality is certainly not true, it leads to a simple mathematical model that enables one to describe qualitatively the real system.

For this assumption r_B in equation (A-13b) can be replaced in a competitive, consecutive second-order reaction system by the expression (A-16):

$$\mathbf{A} + \mathbf{B} \xrightarrow{k_1} \mathbf{R}$$

$$\mathbf{R} + \mathbf{B} \xrightarrow{k_2} \mathbf{S}$$

$$\frac{\partial [\mathbf{R}]}{\partial t} = k_1 [\mathbf{A}][\mathbf{B}] - k_2 [\mathbf{R}][\mathbf{B}] \tag{A-14}$$

$$\frac{\partial [\mathbf{S}]}{\partial t} = k_2 [\mathbf{R}][\mathbf{B}] \tag{A-15}$$

$$1000\, r_B = -\frac{\partial [\mathbf{R}]}{\partial t} - 2 \frac{\partial [\mathbf{S}]}{\partial t} \tag{A-16}$$

$$D \left(\frac{\partial^2 [\mathbf{B}]}{\partial r^2} + \frac{2}{r} \frac{\partial [\mathbf{B}]}{\partial r} \right) = \frac{\partial [\mathbf{B}]}{\partial t} + \frac{\partial [\mathbf{R}]}{\partial t} + 2 \frac{\partial [\mathbf{S}]}{\partial t} \tag{A-17}$$

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[12] The competitive, parallel case can be treated in a manner analogous to the competitive, consecutive case; this leads to equations (8), (9) and (10).

Since the concentration of species **A** is changed only by chemical reaction the appropiate equation for this species reduces to

$$\frac{\partial[\mathbf{A}]}{\partial t} = -k_1\,[\mathbf{A}]\,[\mathbf{B}] \tag{A-18}$$

This is similar to equations (A-14) and (A-15) for species **R** and **S**. The right hand side of equation (A-18) can be replaced by equation (A-14) and (A-15):

$$\frac{\partial[\mathbf{A}]}{\partial t} = -\frac{\partial[\mathbf{R}]}{\partial t} - \frac{\partial[\mathbf{S}]}{\partial t} \tag{A-19a}$$

$$\frac{\partial[\mathbf{A}]}{\partial t} + \frac{\partial[\mathbf{R}]}{\partial t} + \frac{\partial[\mathbf{S}]}{\partial t} = 0 \tag{A-19b}$$

The sum of the differentials of the concentrations of **A**, **R** and **S** is zero, hence the sum of the concentrations themselves must be constant and equal to $[\mathbf{A}]_0$

$$[\mathbf{A}] + [\mathbf{R}] + [\mathbf{S}] = [\mathbf{A}]_0 \tag{A-20}$$

When equation (A-20) is substituted into equation (A-14) we obtain the following equations which describe the diffusion-reaction system of spherical geometry assuming a competitive, consecutive chemical reaction:

$$\mathrm{D}\left(\frac{\partial^2[\mathbf{B}]}{\partial r^2} + \frac{2}{r}\,\frac{\partial[\mathbf{B}]}{\partial r}\right) = \frac{\partial[\mathbf{B}]}{\partial t} + \frac{\partial[\mathbf{R}]}{\partial t} + 2\,\frac{\partial[\mathbf{S}]}{\partial t} \tag{A-21a}$$

$$\frac{\partial[\mathbf{R}]}{\partial t} = k_1\,[\mathbf{B}]\,([\mathbf{A}]_0 - [\mathbf{R}] - [\mathbf{S}]) - k_2\,[\mathbf{B}]\,[\mathbf{R}] \tag{A-21b}$$

$$\frac{\partial[\mathbf{S}]}{\partial t} = k_2\,[\mathbf{B}]\,[\mathbf{R}] \tag{A-21c}$$

Assumption of Diffusion from a well stirred Solution of limited Volume. – The solution of the differential equation system (A-21) has to satisfy certain specified initial and boundary conditions. Let us assume that the spherical eddy occupies the space $r < \overline{R}$, while the volume of the bath solution containing the diffusing species **B** (excluding the space occupied by the eddy) is V_s. The concentration of solute **B** in the solution is always uniform and is initially $[\mathbf{B}]_0$. The sphere containing the substrate **A** is initially free from solute **B**:

Initial conditions:

$$\begin{array}{lll} [\mathbf{B}] = 0 & r < \overline{R} & t = 0 \\ [\mathbf{B}] = [\mathbf{B}]_0 & r \geqslant \overline{R} & t = 0 \\ [\mathbf{R}] = [\mathbf{S}] = 0 & r \leqslant \overline{R} & t = 0 \\ [\mathbf{A}] = [\mathbf{A}]_0 & r \leqslant \overline{R} & t = 0 \end{array} \tag{A-22}$$

Boundary conditions: The general solution of a second-order partial differential equation should contain two arbitrary functions. These two arbitrary functions in the mathematical solution must be chosen to satisfy the boundary conditions dictated by the assumption of diffusion into a sphere from a well stirred limited solution.

The arbitrary functions (A-23) and (A-24) result from both the symmetry of the sphere and the law of conservation of mass of the diffusing species **B**. Owing to the symmetry of the sphere, there is no flux of **B** through the origin of the sphere *i.e.* the concentration gradient is zero.

$$\left(\frac{\partial[\mathbf{B}]}{\partial r}\right)_{r=0} = 0;\quad t > 0 \tag{A-23}$$

Applying the law of conservation of mass to the volume of solution V_s for the species **B** we obtain:

$$V_s\left(\frac{\partial[\mathbf{B}]}{\partial t}\right)_{r=\overline{R}} = S_e\left[-\,\mathrm{D}\left(\frac{\partial[\mathbf{B}]}{\partial r}\right)_{r=\overline{R}}\right];\quad t \geqslant 0 \tag{A-24}$$

$$S_e = 4\pi \bar{R}^2 = \frac{3}{\bar{R}} V_e \tag{A-25}$$

$$V_e = \frac{4}{3} \pi \bar{R}^3 \tag{A-26}$$

S_e	surface of the spherical eddy [cm²]
V_e	volume of the spherical eddy [cm³]
V_s	volume of solution [cm³]

When equation (A-25) and (A-26) are substituted into equation (A-24) the following expression is obtained:

$$\left(\frac{\partial[\mathbf{B}]}{\partial t}\right)_{r=\bar{R}} = -3\,\frac{V_e}{V_s}\,\frac{D}{\bar{R}}\left(\frac{\partial[\mathbf{B}]}{\partial r}\right)_{r=\bar{R}};\quad t \geqslant 0$$

$$= -3\alpha\,\frac{D}{\bar{R}}\left(\frac{\partial[\mathbf{B}]}{\partial r}\right)_{r=\bar{R}};\quad t \geqslant 0 \tag{A-27}$$

$\alpha = V_e/V_s$: ratio of eddy volume to solution volume [–]

List of Symbols

$[\mathbf{A}], [\mathbf{B}], [\mathbf{C}]$	concentration of **A**, **B** and **C** respectively [mol/l]
$[\mathbf{A}]_0, [\mathbf{B}]_0, [\mathbf{C}]_0$	initial concentration of **A**, **B** and **C**, respectively [mol/l]
$[\mathbf{B}]_{tot}$	total concentration of the mobile and immobilized molecules **B** [mol/l]
D_i	diffusion coefficient of species i [cm²/s]
$D = D_B$	diffusion coefficient of **B** [cm²/s]
$\vec{J}_i$	molar flux of species i relative to the molar average velocity [mol/(cm² s)]
MD	mixing-disguised
$\vec{N}_i$	molar flux of species i with respect to stationary coordinates [mol/(cm² s)]
N_{ix}	rectangular component x of the molar flux vector $\vec{N}_i$ [mol/(cm² s)]
$[\mathbf{P}], [\mathbf{Q}], [\mathbf{R}], [\mathbf{S}]$	concentration of product **P**, **Q**, **R** and **S**, respectively [mol/l]
$\bar{R}$	mean radius of the eddies [cm]
RC	reaction-controlled (${}^{*}\varphi_B^2 \to 0$)
S_e	surface of spherical eddy [cm²]
V_e	volume of spherical eddy [cm³]
V_s	volume of solution [cm³]
$X_S = \frac{2[\mathbf{S}]}{[\mathbf{R}] + 2[\mathbf{S}]}$	normalized fraction of **B** which reacted to give **S** [–] $X_S = 1$: every **B** molecule has reacted to give **S** (no **R** is found)
$X_Q = \frac{[\mathbf{Q}]}{[\mathbf{P}] + [\mathbf{Q}]}$	normalized fraction of **B** which reacted to give **Q** [–]
c_i	molar concentration of species i [mol/cm³]
c	total molar concentration [mol/cm³]
k_1, k_2, k_3, k_4	intrinsic (real) second-order rate constants [l/(mol s)]
r_i	molar rate of production by chemical reaction of species i [mol/(cm³ s)]
r	polar coordinate [cm]
t	time [s]
$\vec{v}_i$	velocity of species i [cm/s]
$\vec{v}$	molar average velocity [cm/s]
x_i	mol fraction of species i [–]
x, y, z	rectangular coordinates [cm]
${}^{*}\mathbf{B}_B = \alpha\,\mathbf{B}_B = \alpha\,\frac{[\mathbf{B}]}{[\mathbf{B}]_0}$	$\mathbf{B}_B$ is the normalized concentration of **B** with respect to $[\mathbf{B}]_0$ [–] $\mathbf{B}_B = 1$: 0% conversion of **B** $\mathbf{B}_B = 0$: 100% conversion of **B**

${}^{*}\mathbf{E} = \alpha\,\mathbf{E} = \alpha\,\frac{[\mathbf{A}]_0}{[\mathbf{B}]_0}$	initial mol ratio of **A** and **B** [–]
$\mathbf{M} = \frac{[\mathbf{C}]_0}{[\mathbf{A}]_0}$	ratio of initial concentrations of **C** and **A** [–]
$\mathbf{T} = \frac{D}{\overline{R}^2}\,t$	normalized time [–]
$\Phi\,([\mathbf{B}], t)$	immobilization function describing the chemical conversion of **B**
$\mathbf{X} \quad \frac{r}{\overline{R}}$	normalized polar coordinate [–]
${}^{*}\Omega_{B,i} = \alpha\,\Omega_{B,i} = \alpha\,\frac{[\mathbf{i}]}{[\mathbf{B}]_0}$	$\Omega_{B,i}$ is the normalized concentration of the reaction product **i** with respect to $[\mathbf{B}]_0$ [–]
$\alpha = \frac{V_e}{V_s}$	ratio of eddy volume to solution volume [–]
$\vec{\delta}_x$	unit vector associated with the x-coordinate
$\varepsilon_r = \frac{X_S(RC)}{X_S(MD)}$	effectiveness factor of the chemical reaction as a part of the whole process. ε_r is defined as the ratio of the reaction-*controlled* (= RC) and the mixing-*disguised* (= MD) X_S values [–] $\varepsilon_r = 1$: the chemical process is reaction-*controlled*; $\varepsilon_r < 1$: the chemical process is mixing-*disguised*
τ	relaxation time [s]
τ_D	relaxation time of diffusion [s]
$\tau_{R,i}$	relaxation time of the reaction step i [s]
${}^{*}\varphi^2_{B,i} = \frac{1}{\alpha}\,\varphi^2_{B,i} = \frac{1}{\alpha}\,\frac{\overline{R}^2 k_i [\mathbf{B}]_0}{D}$	$\varphi^2_{B,i}$ is *the normalized rate constant of the reaction step* i with respect to $[\mathbf{B}]_0$. It is proportional to the ratio of relaxation times of diffusion and chemical reaction step i. $(= \tau_D/\tau_{R,i})$ [–]
$\varphi^2_B \ll 1$	the chemical process is reaction-*controlled* (limited)
$\varphi^2_B \gg 1$	the chemical process is diffusion-*determined* (disguised by diffusion)
∇	'del' or 'nabla' operator (see Appendix)
∇^2	Laplacian operator (see Appendix)

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REFERENCES

[1] *O. Levenspiel*, 'Chemical Reaction Engineering', J. Wiley, New York 1972, Chap. 10; *Z. Sterbacek & P. Tausk*, Mixing in the Chemical Industry; Vol. 5 (1965); *V. W. Uhl & J. B. Gray*, Mixing, Academic Press, New York 1965.

[2] *K. B. Bischoff* in: Applied Kinetics, Amer. chem. Soc. Publications, Wash. D.C. 1967, p. 2.

[3] *W. S. Tolgyesi*, Canad. J. Chemistry *43*, 343 (1965); *G. A. Olah & N. A. Overchuk*, ibid. *43*, 3279 (1965); *R. G. Coombes, R. B. Moodie & K. Schofield*, J. chem. Soc. B *1968*, 800; *J. G. Hoggett, R. B. Moodie & K. Schofield*, ibid. B *1969*, 1; Chem. Commun. *1969*, 605; *P. F. Christy, J. H. Ridd & N. D. Stears*, J. chem. Soc. B *1970*, 797; *J. H. Ridd*, Accounts chem. Res. *4*, 248 (1971); *R. Fittig & P. Jannasch*, Z. Chem. *1870*, 162; *S. B. Hanna, E. Hunziker, T. Saito & H. Zollinger*, Helv. *52*, 1537 (1969); *E. Hunziker, J. R. Penton & H. Zollinger*, ibid. *54*, 2043 (1971); *P. Rys, A. Schmitz & H. Zollinger*, ibid. *54*, 163 (1971); *E. L. Paul & R. E. Treybal*, A.I.Ch. E. J. *17*, 718 (1971).

[4] *L. M. Stock & H. C. Brown*, Adv. phys. org. Chemistry *1*, 35 (1963); compare also: *R. O. C. Norman & R. Taylor*, Electrophilic Substitution in Benzenoid Compounds, Elsevier, Amsterdam 1965, Chap. 11.

[5] *P. Rys, P. Skrabal & H. Zollinger*, Angew. Chem. *84*, 921 (1972); Angew. Chem. internat. Edit. *11*, 874 (1972).

[6] *A. Wheeler*, Adv. Catalysis *3*, 258 (1958); Catalysis *2*, 153 (1955); *J. Wei & C. D. Prater*, Adv. Catalysis *13*, 203 (1962); *J. Carberry*, J. chem. eng. Sci. *17*, 675 (1962); *C. N. Satterfield*

& *T. K. Sherwood*, 'The Role of Diffusion in Catalysis', Addison-Wesley Publ. Co., 1963; *J. M. Thomas & S. J. Thomas*, 'Introduction to Heterogeneous Catalysis', Academic Press, New York 1967; *A. Clark*, 'The Theory of Adsorption and Catalysis', Academic Press, New York 1970, Kap. 12.

[7] *A. N. Kolmogoroff*, Compt. Rend. Acad. Sci. USSR, *30*, 301 (1941); *J. O. Hinze*, 'Turbulence', McGraw-Hill, New York 1959; *J. T. Davies*, 'Turbulence Phenomena', Academic Press, London 1972.

[8] *P. V. Danckwerts*, 'Diffusion Processes', Gordon and Breach Science Publ., London 1971, Bd 2.

[9] *H. W. Reddick & F. H. Miller*, 'Advanced Mathematics for Engineers', J. Wiley, New York 1948; *G. E. Forsythe & W. R. Wasow*, 'Finite-Difference Methods for Partial Differential Equations', J. Wiley, New York 1960.

[10] *J. S. Hicks & J. Wei*, J. Assoc. Computing Mach. *14*, 549 (1967).

[11] *R. J. Ott & P. Rys*, J. chem. Soc. Faraday I *69*, 1694 (1973); *R. J. Ott*, PhD. Thesis ETH, Zürich 1972.

[12] *G. Emig*, Fortschr. chem. Forsch., Bd. *13*, 451 (1969/70).

[13] *P. Rys*, Text. Res. J. *43*, 24 (1973); *P. Rys*, 'Über die Selektivität chemischer Prozesse', Inaugural Thesis ETH, Zürich 1971.

[14] *F. Pfister*, PhD. Thesis ETH, Zürich 1973.

[15] *R. B. Bird, W. E. Stewart & E. N. Lightfoot*, 'Transport Phenomena', J. Wiley, London 1960; *W. Strieder & R. Aris*, 'Variational Methods Applied to Problems of Diffusion and Reaction', Springer, Berlin 1973; *G. Astarita*, 'Mass Transfer with Chemical Reaction', Elsevier Publ. Comp., Amsterdam 1967; *J. Crank*, 'The Mathematics of Diffusion', Oxford Univ. Press, London 1975.

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227. Chemical Selectivities Disguised by Mass Diffusion. II. Mixing-Disguised Nitrations of Aromatic Compounds with Nitronium Salts[1,2]

2nd Communication on the Selectivity of Chemical Processes[1])

by **Friedrich Pfister, Paul Rys** and **Heinrich Zollinger**

Technisch-Chemisches Laboratorium
Eidgenössische Technische Hochschule, Zürich

(16. XI. 73)

Summary. The results of this study show that three parameters are sufficient to describe the selectivity behaviour of nitrations influenced by mixing as long as a fast combination of the reactant solutions takes place and fast agitation is employed. This is in full agreement with the prediction of the mixing-reaction model developed previously [1]. Furthermore, the results show clearly that in nitromethane the formation rate of nitronium ions from nitric acid is slower than the mixing rate and the rate of the electrophilic substitution proper. From the mixing-disguised selectivity curves for the nitrations of durene and prehnitene with nitronium hexafluorophosphate in nitromethane the ratio of the rate constants k_2 for the second nitrations can be estimated to be 1:2. For the two aromatic compounds the k_1/k_2 ratios are $\gg 10^4$. Finally it could also be shown that small impurities in the solvent (*e.g.* water) can influence strongly the selectivity curves, depending on the method used for mixing.

1. Introduction. – In the Part I of this series [1] a simple mixing-reaction model was developed which allowed a description and simulation of the coupling of

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[1] Part I and 1st Communication *cf.* [1].

[2] Results taken from the PhD. thesis of *F. Pfister* [2].