

**POSSIBLE APPLICATION OF APPROXIMATE MODELS
FOR CALCULATION OF SELECTIVITY OF CONSECUTIVE REACTIONS
UNDER THE EFFECT OF MASS TRANSFER**

František KAŠTÁNEK and Marie FIALOVÁ

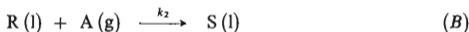
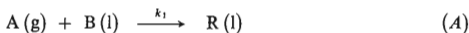
*Institute of Chemical Process Fundamentals,
Czechoslovak Academy of Sciences, 165 02 Prague 6 - Suchbát*

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The possibility of use of approximate models for calculation of selectivity of consecutive reactions is critically analysed. Simple empirical criteria are proposed which enable safer application of approximate analytical relations. A more universal modification has been formulated by use of which the difference of selectivity calculated by the exact numerical method and by the approximate analytical method is at maximum 12%.

Majority of industrially interesting reactions in the two-phase systems (*e.g.* gas-liquid) take place as consecutive reactions. This complication causes that also selectivity of formation of the required product must be taken into consideration in calculation of the reactor. The reached selectivity is the decisive process parameter as concerns the economy of following treatment of reaction products.

In this study the possibilities of mathematical modelling of selectivity of consecutive reactions are critically analysed. On the basis of the film theory of mass transfer, criteria of validity and use of various approximate models are given. The reaction scheme is considered, when the absorbed gas A reacts with the reactant B in the liquid at formation of the intermediate product R, which further reacts with the dissolved gas at the formation of the final product S according to equations



When both reactions (A) and (B) are of the first order with respect to both components it is possible, under assumption of validity of the film theory of mass transfer, to write the system of equations in the normalised form

$$d^2a/d\xi^2 = (h_1^2 r_B q_B) ab + (h_2^2 r_R q_R) ar \quad (1)$$

$$d^2b/d\xi^2 = (h_1^2) ab \quad (2)$$

$$d^2r/d\xi^2 = -[(r_B q_B / r_R q_R) h_1^2] ab + h_2^2 ar \quad (3)$$

with the boundary conditions

$$\xi = 0, \quad a = 1; \quad (4)$$

$$db/d\xi = dr/d\xi = 0; \quad (5)$$

$$\xi = 1, \quad a = \alpha, \quad (6)$$

$$b = r = 1; \quad (7)$$

$$-da/d\xi = \gamma^2 a \delta. \quad (8)$$

The system of Eqs (1)–(8) does not have an exact analytical solution, but it is possible to solve it numerically, as has been done by Van de Vusse¹ (for $\alpha = 0$) and Onda² (for $\alpha = 0, r = 0$) or by Teramoto and coworkers^{3,4} for a more general case ($\alpha \neq 0$) and with the boundary condition (8).

The more general solution (with the boundary condition (8)) for the enhancement factor β^* and thus for the reaction rate N_A gives

$$\beta^* = N_A / k_{L,A} C_{A1} = -(da/d\xi)_{\xi=0}, \quad (9)$$

which is practically identical with the solution for $\alpha = 0$ as can be easily seen from the approximative relations for calculation of selectivity (see further on), but there is a significant difference of both solutions in the case of selectivity.

For expression of the correct selectivity it is thus necessary to solve the model with a more general condition $\alpha \neq 0$. But introduction of this boundary condition into the numerical procedure causes certain complications. The profiles of components a , b , and r in vicinity of the point $\xi = 1^*$ must be correctly numerically modelled.

Numerical solution of the system of Eqs (1)–(8). The method of finite differences⁶ has been used. Second derivations were substituted by the second central difference and for better computation accuracy the first derivatives were approximated for the component A by the back and for the components B and C by forward differences out of 3 points. The systems of algebraic equations were solved by the Thomas method. For the case of continuous operation in the boundary condition for the component A in the point $\xi = 1$ the values α^2 have been linearised by the product $\alpha^{(k)} \cdot \alpha^{(k+1)}$, where $\alpha^{(k)}$ is the value of α from the preceding operation.

* This is a reason of smaller inaccuracies in numerical data in the paper by Teramoto³, see Table I of the original study.

Approximate solution of the system of equations (1) to (8). For chemical engineering purposes the analytical solution, though approximate seems to be more attractive than the numerical. The results of these approximate models are usually sufficiently accurate for engineering purposes.

In the approximate solution of the model (1)–(3), in principle is applied the classical Van Krevelen–Hoftijzer procedure, originally performed for solution of Eq. (A) alone. Eqs (1) to (3) are linearized by substitution of values of components b and r in the reaction terms by constant values, equal to concentrations of these components on the interface^{3,4}

$$b = b_i; \quad r = r_i. \quad (10)$$

The same procedure has been chosen recently by Pangarkar and Sharma⁵. The detailed derivation of relations for selectivity ϕ of the intermediate product R, defined here*

$$\phi = \frac{dC_{R1}}{-dC_{B1}} = \frac{dY}{dX_B} = \frac{N_{Rf} + N_{R1}}{N_{Bf} + N_{B1}}, \quad (11)$$

where

$$Y = C_{R1}/C_{B0} \quad (12)$$

$$X_B = 1 - C_{B1}/C_{B0} \quad (13)$$

are given in the original literature³.

It is obvious that the made approximation represents simplification of reality which might have an unfavorable effect especially in calculation of selectivity at some combinations of parameters of the model. Disagreement with the exact solution can be expected especially when the concentration of the component B in the film decreases or when the concentration of component R on the interface is small. On the contrary it is possible to expect that the agreement between the numerical and approximate model value β^* would be satisfactory with regard to definition of the enhancement factor (Eq. (9)) and to the fact that the concentration profile of component A in the film is not too sensitive to the approximation (10).

In original studies where the derivations of the approximate model are presented, the ranges of variables for which the agreement of approximate and numerical solutions is acceptable are not given. The model has been presented as universal^{3,4} with regard to the fact that the error in calculation of selectivities is lower than 8%

* Pangarkar⁵ considers the so-called selectivity index

$$\phi' = (N_{Rf} + N_{R1})/(N_{Sf} + N_{S1})$$

and is always on the safe side of the calculation (approximate values are smaller than the numerical ones). This information can cause in unconditional application of the model serious problems as is obvious from our results. From the already published studies has also not resulted the effect of the ratio of reaction rate constants (k_1/k_2) on applicability of the approximate model.

The applicability of the approximate mathematical model (I)–(8) has been verified on numerous computation material in a wide range of variable parameters of the model ($h_1 = 0.5-60$, $s = 1-1\ 000$, $M_B^{1/2} = 0.2-42$) with the limitation (10) and with these conclusions:

1) Model by Teramoto and coworkers^{3,4} is suitable for calculation of the enhancement factor β^* and the absorption rate with the consecutive chemical reaction. The approximate values were not always smaller than the numerical ones, but the error did not exceed 3% relative. Positive deviations were found for some values $s \geq 100$ and were in average smaller than 1% rel. The largest negative deviations, higher than 2% rel. were found for $h_1 \leq 10$. This results are in agreement with the conclusions for a simple reaction (A).

2) Application of the approximation by Teramoto and coworkers^{3,4} for calculation of selectivity is limited and the model does not hold universally. The error in determination of selectivity depends significantly on the value h_1 or factor $M_B^{1/2}$ and the value $s = h_1^2/h_2^2$. At values $h_1 > 10$ the error can reach even several hundredths of percent, while the deviation can be both negative and positive (largest deviations were found just on the dangerous side). The comparison of approximate and numerical values for some selected cases is given in Table I. The greatest errors are always for low values of s . The minimum errors are met in cases, when the parameter $h_1 < 5$. Nearly absolute agreement can be reached in the case when it is possible to consider the equation (A) to be of the first order. Maximum errors have been reached in cases when the reaction (A) can be considered, in the sense of the Danckwerts criteria almost instantaneous. But under these conditions it is possible to obtain an acceptable error, when the value s is suitable. Similarly, with the general case of the irreversible 2nd order reaction (reaction (A)), according to the combination of parameters h_1 and s different errors are obtained. The most unfavourable situation is met when the ratio of reaction constants tends to one.

A generally valid simple criterion, has been determined on basis of an analysis of a number of model data in the above given range of parameters, which enables to evaluate the safe application of the approximate model for calculation of selectivity. The error in determination of selectivities of the intermediate product R is always smaller than 12% relative, when

$$h_1/s < 0.4 \quad \text{for} \quad h_1 \leq 50. \quad (14)$$

TABLE I
Comparison of approximate and numerical selectivities for selected situations, $\delta = 99$

h_1	$r_{B \rightarrow B}$	$r_{R \rightarrow R}$	s	β^* , approx. this study	β^* , num.	ϕ , approx. this study	ϕ , approx. ref. ³	ϕ , num.	Error in ϕ , %	
									ref. ³	this study
0.5 ^a	0.3243	0.4436	4	0.952	0.953	0.656	0.656	0.656	0	0
1 ^a	0.8076	0.1773	4	1.210	1.218	0.927	0.923	0.927	0.4	0
2 ^a	0.8008	0.1637	4	1.553	1.592	0.843	0.823	0.841	2.1	0.2
5 ^a	0.8008	0.1031	4	2.126	2.241	0.584	0.516	0.559	7.7	4.5
10	0.1	0.1	4	1.312	1.286	0.407	0.484	0.415	16.6	1.9
20	0.1	0.1	4	1.412	1.299	0.215	0.452	0.215	110.2	0
20	0.1	0.1	10	1.360	1.295	0.489	0.623	0.484	28.7	1.0

^a Reference³.

When $h_1 < 10$ and for $h_1/s < 1.25$ the error is smaller than 8%. For $h_1 = 0.5 - 60$ and for $h_1/s < 0.3$ the error is smaller than 13%.

With regard to the limited validity of this model an attempt has been made for formulation of its more universal modification, which would be applicable also in the region beyond the criteria (14). The system of relations (1) to (3) with the boundary conditions (4) to (8) has been linearised so that the concentration of components in the reaction terms of right hand sides of Eqs (1)–(3) has been substituted by relations

$$a \equiv 1; \quad b \equiv b_i; \quad r \equiv r_k \quad (15)-(17)$$

Concentration of component b has been, as in the case of the original trivial model, substituted by the concentration in the phase interface and the final concentration of component r has been substituted by the value r_k which depends on the dimensionless parameter ξ . By integration of Eqs (1) and (3) with the corresponding boundary conditions and with regard to definitions (15) to (17) the relations are obtained

$$b_i = 1/\{1 - [1 - \beta^* - \alpha] h_1^2/\gamma'^2\} \quad (18)$$

$$r_k = \frac{1 - (h_1^2 b_i/\gamma'^2) (r_B q_B / r_R q_R) [1 + \beta^*(\xi - 1) - \alpha]}{1 - (h_1^2/\gamma'^2 s) [1 + \beta^*(\xi - 1) - \alpha]} \quad (19)$$

Then

$$d^2 a / d\xi^2 = \gamma'^2 a, \quad (I')$$

where

$$\gamma'^2 = h_1^2 r_B q_B b_i + h_2^2 r_R q_R r_k.$$

Solution of Eq. (I') can be obtained by some of the known methods, *e.g.* by collocation.

Relations for the enhancement factor β^* and selectivity ϕ can be then derived by the familiar procedure. The formally identical system of equations is obtained with that of Teramoto and coworkers³ which must be solved simultaneously with relations (18) and (19).

$$\alpha = \gamma' / [\gamma' \cosh \gamma' + \gamma^2 \delta \sinh \gamma'] \quad (20)$$

$$\beta^* = (\gamma' / \tanh \gamma') (1 - \alpha / \cosh \gamma') \quad (21)$$

$$\beta_i^* = (\gamma' / \tanh \gamma') (1 + \alpha) (1 - 1 / \cosh \gamma') \quad (22)$$

$$\phi = \frac{dY}{dX_B} = \frac{-(\beta_i^* r_R q_R \Gamma_R / \Gamma_A) + (h_1^2 r_B q_B - h_2^2 r_R q_R) \alpha \delta}{\beta_i^* r_B q_B / \Gamma_A + h_1^2 r_B q_B \alpha \delta} \quad (23)$$

$$\Gamma_A = \gamma'^2/h_1^2 b_i \quad (24)$$

$$\Gamma_R = (r_k/sb_i) - (r_B q_B/r_R q_R) \quad (25)$$

$$\gamma^2 = h_1^2 r_B q_B + h_2^2 r_R q_R \quad (26)$$

$$s = h_1^2/h_2^2 \quad (27)$$

$$\delta = (v - x_i)/x_i, \quad (28)$$

where v is the liquid volume related to the unit of interfacial area and x_i the thickness of the film.

The given system of relations for selected ξ_{col} can be solved by a simple iteration, which converges very fast even for a very inaccurate first shot γ' .

In general the values q_B and q_R are not known in advance, but it is possible to determine them from equations

$$q_B = q_{B0}(1 - X_B), \quad (29)$$

$$q_R = q_{B0}Y. \quad (30)$$

The value Y for the given X_B is obtained by numerical integration of relation (23). For the given X_B , Y and ξ_{col} the values of b_i and r_k are estimated and the relation (23) is checked. This procedure also leads surprisingly fast to the required result, but of course some of the familiar optimisation methods can be used.

Correlation of the collocation point is empirical. It is obvious that for $\xi_{\text{col}} = 0$ this model gives the original solution for $a = 1$, $b = b_i$, $r = r_i$ while the maximum value $\xi_{\text{col,max}} = 1$.

The optimum value ξ_{col} is a complex function of h_1 , s , $r_B q_B$ and $r_R q_R$ and has been determined empirically.

For the region $h_1 \leq 10$ and $s \geq 4$ the relation holds

$$\xi_{\text{col}} = \left(\frac{4}{s}\right)^{(1.6r_B q_B)} \left(\frac{r_B q_B}{10.552r_B q_B + 9.755}\right) h_1. \quad (31)$$

For $s > 30$ is into Eq. (31) substituted the value $s = 30$. For the region $h_1 > 10$ the relation holds (again for $s \geq 4$)

$$\xi_{\text{col}} = 2.554 \cdot 10^{-3} (h_1 - 0.5s)^{1.322} + \frac{0.01}{h_1} \left(\frac{r_B q_B}{r_R q_R}\right)^{3.341} + \frac{(h_1 - 0.5s) \cdot 2.91 \cdot 10^{-3}}{(r_B q_B/r_R q_R)^3}. \quad (32)$$

For $(h_1 - 0.5s) < 0$ is the value of the first and second term equal to zero.

Application of Eq. (32) is limited by the value of criterion $\psi \geq 0.1$ for the region $10 < h_1 \leq 20$.

Criterion ψ for values $r_B q_B$ and $r_R q_R \geq 0.1$ is given by relation

$$\psi = \frac{0.4665}{r_B q_B^{0.127}} \frac{(4.38/h_1^{0.718}) - 1.5 r_R q_R}{(4.38/h_1^{0.718}) - 0.15} \left(\frac{10}{h_1}\right)^{0.8} + \frac{[s/(s+6)] - 0.625}{A} \quad (33)$$

where $A = 1.2$ for $s < 10$ and $A = (1 - s \cdot 10^{-3})$ for $s \geq 10$.

This approximate model has at calculation of selectivity in average smaller deviations from the numerical solution and up to the value $h_1 = 20$ has a more general validity than the model by Teramoto and coworkers^{3,4}. The error is not exceeding 12% rel. Some selected results are given in Table I.

LIST OF SYMBOLS

- $a = C_A/C_{Ai}$
 a_i interfacial area of the gas-liquid system per unit of liquid volume (cm^2/cm^3)
 A_r total interfacial area of 1-g contact (cm^2)
 $b = C_B/C_{Bi}$
 $b_i = C_{Bi}/C_{Bi}$
 C concentration (mol/l)
 D diffusivity (cm^2/s)
 $h_1 = x_1 \sqrt{(k_1 C_{Ai}/D_B)} = (D_A/k_{L,A}) \sqrt{(k_1 C_{Ai}/D_B)}$
 $h_2 = x_1 \sqrt{(k_2 C_{Ai}/D_R)} = (D_A/k_{L,A}) \sqrt{(k_2 C_{Ai}/D_R)}$
 k reaction rate constant (mol/l s)
 $k_{L,A}$ mass transfer coefficient of component A in liquid (cm/s)
 N reaction rate per unit of interfacial area (mol/cm² s)
 $q_B = C_{Bi}/C_{Ai}$
 $q_{B0} = C_{B0}/C_{Ai}$
 $q_R = C_{Ri}/C_{Ai}$
 $r = C_R/C_{Ri}$
 $r_B = D_B/D_A$
 $r_i = C_{Ri}/C_{Ri}$
 r_k value of r dependent on dimensionless collocation parameter
 $r_R = D_R/D_A$
 $s = k_1 D_R/k_2 D_B (= h_1^2/h_2^2)$
 v liquid volume per unit of interfacial area (cm^3/cm^2)
 $X_B = 1 - C_{Bi}/C_{B0}$ conversion of component B
 x_1 liquid film thickness (cm)
 $Y = C_{Ri}/C_{B0}$ total yield of intermediate product R
 $\alpha = C_{Ai}/C_{Ai}$
 β^* modified enhancement factor
 $\beta_f^* = \beta^* - [-(da/d\xi)_{\xi=1}]$
 $\gamma^2 = h_1^2 r_B q_B + h_2^2 r_R q_R$

$$\gamma'^2 = h_1^2 r_B q_B b_i + h_2^2 r_R q_R r_k$$

$$\Gamma_A = \gamma'^2 / h_1^2 b_i$$

$$\Gamma_R = r_i / s b_i - r_B q_B / r_R q_R$$

$$M_B = k_{C_{B0}} D_A / k_{L,A}^2$$

$$\delta = (v - x_1) / x_1$$

$$\xi = x / x_1 \quad \text{dimensionless distance}$$

ϕ momentary selectivity of intermediate product R

ϕ' selectivity index

ψ criterion

Subscripts

A	component A
B	component B
col	collocation value
f	liquid film
i	gas-liquid interface
l	bulk liquid
R	component R
0	feed
1	first reaction represented by Eq. (1)
2	second reaction represented by Eq. (2)

REFERENCES

1. Van de Vusse J. G.: Chem. Eng. Sci. 21, 631 (1966).
2. Onda K., Sada T., Kobayashi T., Fujine M.: Chem. Eng. Sci. 25, 761 (1970).
3. Teramoto M., Nagayasu T., Matsui T., Hashimoto K., Nagata S.: J. Chem. Eng. Jap. 2, 186 (1969).
4. Teramoto M., Hashimoto K., Nagata S.: J. Chem. Eng. Jap. 6, 522 (1973).
5. Pangarkar V. G., Sharma M. M.: Chem. Eng. Sci. 29, 561 (1974).
6. Fialová M.: Thesis. Czechoslovak Academy of Sciences, Prague 1982.

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