EFFECT OF MASS TRANSFER ON THE SELECTIVITY
OF CONSECUTIVE REACTIONS IN A GAS–LIQUID SYSTEM

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A mathematical model of a gas–liquid discontinuous reactor was analyzed to find the range of conditions in which the selectivity of consecutive competitive reaction can be expected to decrease on account of mass transfer. The prediction obtained from the mathematical model was tested on a model reaction of addition of chlorine to 1,5-cyclooctadiene.

The effect of diffusion on the rate of chemical reaction in a gas–liquid system has been often studied for a number of reaction systems. It has been largely described in terms of absorption accelerated by the chemical reaction, and several theories concerning the mechanism of the process have been set forth[1]. Much less attention has been paid to the effect of mass transfer at the interface on the selectivity of complex reactions. Van de Vusse[2], the first to analyze the effect of diffusion on the selectivity of consecutive reactions, as well as other authors employed the film theory as a basis for the description of the process in question. For a numerical solution of the mathematical model he introduced the pseudo-steady state concept, in which no allowance is made for time changes in the concentrations. Similar simplifications have been made also in other studies[3−6]. The pseudo-steady state concept allows the mathematical model to be simplified to a system of ordinary differential equations. A more rigorous approach to a discontinuous reactor taking time change of concentrations into account, used in the present study, leads to a system of partial differential equations; this model has been used to examine the effect of diffusion on the reaction rate in a gas–liquid system[7].

The mathematical model was analyzed to obtain the conditions ranges within which the selectivity of consecutive reactions can be expected to lower due to mass transfer. It is not easy to test this lowering in selectivity experimentally on a model reaction; in fact, a suitable model reaction must be fast enough as compared with the gas diffusion in the liquid, and not insignificant is also the demand that a sufficiently accurate and precise analytical method be available. Chlorination of n-decane[2] is so slow that selectivity decrease was observed only on chlorination of a 50 mm laminar layer of the liquid, which could be regarded as a physical model of a liquid film. The selectivity of substitution chlorination of toluene in the side chain[4] remained unaffected by diffusion. Of the model reactions so far studied, the most suitable is chlorination of p-cresol[3,5], in which an adverse effect of mass transfer on the selectivity of consecutive reactions in the gas–liquid system could be proved. In the present study, addition of chlorine to 1,5-cyclooctadiene was employed as the

model reaction for verification of the predictions arrived at by analyzing the mathematical model.

THEORETICAL

The mathematical model describing the effect of mass transfer on the chemical reaction in a gas–liquid system is based on the film theory. According to this concept, at the gas–liquid interface is concentrated the resistance to the mass transfer in a laminar liquid film of thickness L, in which transport of all of the components is only due to molecular diffusion. Let us consider a system of consecutive competitive reactions in which the gaseous component A reacts with the liquid component B_0 and consecutively with the product of the previous reaction B_1:

$$A + B_0 \rightarrow B_1 \tag{A}$$

$$A + B_1 \rightarrow B_2 . \tag{B}$$

The corresponding kinetic equations are

$$r_A = -k_1 c_A c_{B_0} - k_2 c_A c_{B_1} \tag{1}$$

$$r_{B_0} = -k_1 c_A c_{B_0} \tag{2}$$

$$r_{B_1} = k_1 c_A c_{B_0} - k_2 c_A c_{B_1} . \tag{3}$$

Fig. 1 portrays two cases of the reaction course. In the case a, the rate of the mass transfer exceeds considerably that of the chemical reaction; no concentration gradients occur within the laminar liquid film and the reaction proceeds in the kinetic region. In the case b, on the contrary, the rate of the chemical reaction is so high that the concentration of the gaseous component in the laminar film drops significantly, the concentrations of the other components in the film varying too. Part of the gas component enters the turbulent liquid bulk, where it reacts further.

The balance of the component i $(i = A, B_0, B_1)$, expressing the dependence of its concentration on the distance from the interface x and on time t, can be written as

$$D_i . \partial^2 c_i / \partial x^2 = \partial c_i / \partial t - r_i . \tag{4}$$

At any moment of the reaction, the concentration of the gas component at the interface $(x = 0)$ is determined by Henry's law, hence by the solubility of the gas in the liquid:

$$c_A = c_A^i = p_A / H \quad (x = 0, t \geqq 0) . \tag{5}$$

The liquid components are deemed to be absolutely nonvolatile and not to diffuse into the gas phase:

$$\partial c_i / \partial x = 0 \quad (i = B_0, B_1; \; x = 0, \, t \geqq 0). \tag{6}$$

At the film-turbulent liquid bulk interface $(x = L)$ the accumulation of the component in the liquid bulk is assumed to be contributed by the rate of its transport through the interface plus the rate of its formation by the chemical reaction within the liquid bulk:

$$V_L \cdot \partial c_i / \partial t = -F D_i \cdot \partial c_i / \partial x + V_L r_i \quad (i = A, B_0, B_1; \; x = L, \, t > 0). \tag{7}$$

At the beginning the liquid is assumed to be saturated by the gas component:

$$c_A = c_A^i, \quad c_{B_0} = c_{B_0}^0. \quad c_{B_1} = c_{B_2} = 0 \quad (t = 0, \, 0 \leqq x \leqq L). \tag{8}$$

The diffusivities of the liquid components differ so little that we can put $D_{B_0} = D_{B_1} = D_L$; D_A denote as D_G.

Introducing dimensionless variables we can rearrange the system (4) to

$$\partial^2 a / \partial y^2 = [1/(D_G/D_L)] \, (\partial a / \partial \tau) + (Ha)^2 \, ab_0 + (Ha)^2 \, (k_2/k_1) \, ab_1 \tag{9}$$
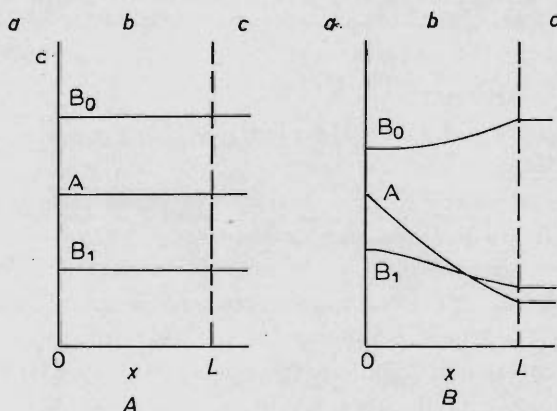

FIG. 1

Concentration profiles in the film for the consecutive gas–liquid reaction. A Kinetic region, B diffusion region. a Gas, b film, c bulk

$$\partial^2 b_0/\partial y^2 = \partial b_0/\partial \tau + (Ha)^2 \, (D_G/D_L) \, (c_A^i/c_{B_0}^0) \, ab_0 \tag{10}$$

$$\partial^2 b_1/\partial y^2 = \partial b_1/\partial \tau - (Ha)^2 \, (D_G/D_L) \, (c_A^i/c_{B_0}^0) \, ab_0 + $$
$$+ (Ha)^2 \, (D_G/D_L) \, (c_A^i/c_{B_0}^0) \, (k_2/k_1) \, ab_1 \tag{11}$$

with the initial conditions

$$a = 1 , \quad b_0 = 1 , \quad b_1 = 0 \quad (\tau = 0, 0 \leqq y \leqq 1) , \tag{12}$$

boundary conditions on the gas–liquid interface

$$a = 1 , \quad \partial b_0/\partial y = \partial b_1/\partial y = 0 \quad (\tau > 0 \; y = 0) , \tag{13}$$

and boundary conditions on the film–liquid bulk interface

$$[1/(D_G D_L)] \, \partial a/\partial \tau = -(V_F/V_L) \, (\partial a/\partial y) - (Ha)^2 \, ab_0 - (Ha)^2 \, (k_2/k_1) \, ab_1 \tag{14}$$

$$\partial b_0/\partial \tau = -(V_F/V_L) \, (\partial b_0/\partial y) - (Ha)^2 \, (c_A^i/c_{B_0}^0) \, (D_G/D_L) \, ab_0 \tag{15}$$

$$\partial b_1/\partial \tau = -(V_F/V_L) \, (\partial b_1/\partial y) + (Ha)^2 \, (c_A^i/c_{B_0}^0) \, (D_G/D_L) \, ab_0 - $$
$$- (Ha)^2 \, (c_A^i/c_{B_0}^0) \, (D_G/D_L) \, (k_2/k_1) \, ab_1 \tag{16}$$

$$(\tau > 0, \, y = 1) .$$

The system of equations $(9)-(11)$ augmented with the boundary conditions $(12)-(16)$ involves a total of five dimensionless parameters, *viz.*

Hatta number:

$$Ha = L(k_1 c_{B_0}^0/D_G)^{1/2} \tag{17}$$

expressing the chemical reaction rate-to-mass transfer rate ratio. Previous calculations have indicated that with Hatta number below 0·2 the gas–liquid reaction should proceed in the kinetic region, the rate as well as the selectivity being unaffected by the mass transfer[2]. For an evaluation of this characteristics, the gas diffusivity D_G, film thickness L and the kinetic parameters of the reaction have to be determined. It follows from the correlation equations for assessment of the laminar layer thickness[8] that for most liquids the thickness lies in the range $10-200 \, \mu m$. The diffusivity of gases in liquids usually falls within the region $5 \cdot 10^{-5} - 5 \cdot 10^{-6} \, cm^2/s$. The pseudo-first order rate constant $(k_1 c_{B_0}^0)$ is the most variable of the quantities involved in Hatta number.

The *diffusivity ratio* D_G/D_L, estimated from Wilke's equation[1], approaches 2 for most real systems. This value has been therefore employed in all calculations.

The ratio of the volume of the liquid in the film to that of the liquid bulk

$$V_F/V_L = LF/[(1 - \varepsilon) - LF]. \tag{18}$$

The specific area of the interface F in common arrangements attains values[9] in the range $1 - 50 \text{ cm}^2/\text{cm}^3$, the relative residence of the gas[10] ε is usually 0·1 to 0·4. Thus the posible ratios of the volume of the liquid in the film to that of the liquid bulk in real reactors should be $V_F/V_L > 0·001$.

The rate constant ratio k_2/k_1 is determined by the reaction kinetics and can attain values within a wide region.

The gas-to-liquid component concentration ratio $c_A^i/c_{B_0}^0$ can be varied by changing the partial pressure of the gas and the concentration of the liquid component in the starting mixture. In real systems the ratio is usually $c_A^i/c_{B_0}^0 < 1$.
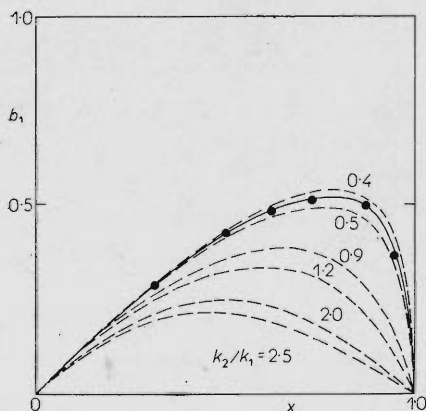

FIG. 2

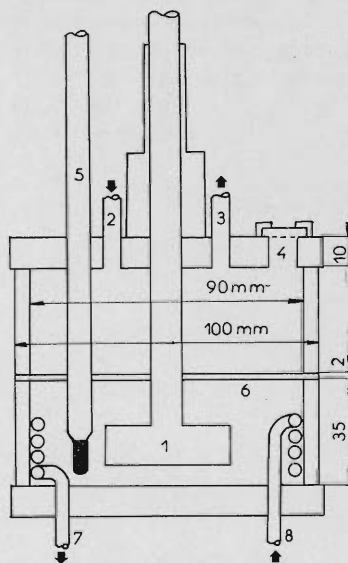Determination of the rate constant ratio k_2/k_1

FIG. 3

Apparatus for measurements in the gas–liquid system. 1 Stirrer, 2 chlorine inlet, 3 chlorine outlet, 4 sampling, 5 thermometer, 6 membrane, 7 cooling water outlet, 8 cooling water inlet

EXPERIMENTAL

Reaction kinetics. In analogy with similar processes[11] we assumed that the reaction of 1,5-cyclo-octadiene with chlorine was first order with respect to chlorine, cyclooctadiene, and dichlorocyclooctene. For estimation of the rate constant an adiabatic batch reactor was used, in which solutions of cyclooctadiene and chlorine in tetrachloromethane were mixed, and the dependence of temperature on time was measured. The results were corrected for the measuring apparatus lag, determined by measuring the dependence of temperature on time on mixing two volumes of tetrachloromethane with different temperatures. The half-life for the reaction of 50 ml of chlorine solution, concentration 0·1 mol/l, with 1 ml of pure cyclooctadiene at initial temperature —13°C was below 0·05 s, the corresponding rate constant thus was $k_1 > 100$ l/mol s. The effect of the mass transfer on the reaction selectivity was studied in the temperature region 20—40°C, where the rate constant $k_1 > 1000$ l/mol s. The rate constant ratio k_2/k_1 was determined based on the dependences of the dichlorocyclooctene content on the degree of conversion of cyclooctadiene, obtained at 20°C in a discontinuous reactor in which chlorine solution in tetrachloromethane (0·32 mol/l) was added to cyclooctadiene solution in the same solvent (1 mol/l) with stirring. The experimental dependence is plotted in Fig. 2 together with curves calculated for several k_2/k_1 rate constant ratios. It can be seen that the rate constant ratio approaches $k_2/k_1 = 0·5$.

The effect of mass transfer on the selectivity of the gas–liquid reactions was measured on an apparatus[12] depicted in Fig. 3. This apparatus enabled us to apply different interface areas, variable according to the number of holes in the Teflon membrane, at different temperatures and cyclooctadiene concentrations. All experiments were performed with solutions in tetrachloromethane in contact with pure chlorine whose pressure was 100 kPa. The mixture was analyzed gas chromatographically[13].
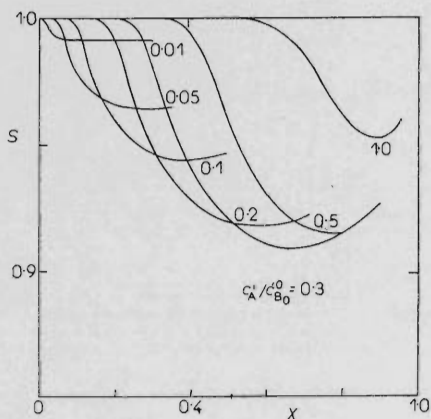

FIG. 4

Dependence of the relative selectivity S on the degree of conversion of the starting substance for various $c_A^i/c_{B_0}^0$ values. $Ha = 2$, $V_F/V_L = 0·1$, $D_G/D_L = 2$, $k_2/k_1 = 1$
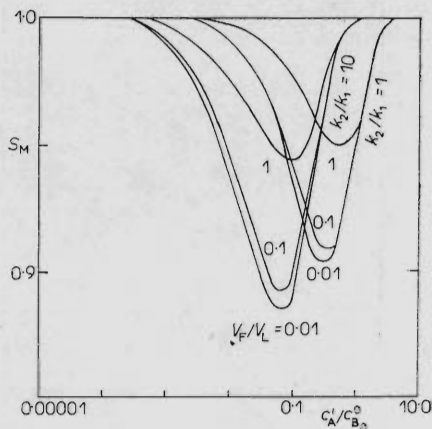
FIG. 5

Dependence of the minimum relative selectivity S_M on the $c_A^i/c_{B_0}^0$ ratio. $Ha = 2$, $D_G/D_L = 2$

RESULTS AND DISCUSSION

Analysis of the mathematical model. There are some difficulties in the numerical solution of the mathematical model, as multi-point implicit schemes are not stable and tend to oscillate, while for simpler schemes short steps have to be chosen and the computations are thus time-consuming. A good compromise was the six-point implicit Crank–Nicholson scheme; it was therefore employed for the solution of the system of equations $(9)-(16)$, performed for a number of chosen parameters. In this manner, the dependences of the concentrations of the components on time and on the film coordinate were obtained. The overall composition of the liquid phase $\bar{c}_i$ was calculated from the mass balance of the film and the liquid bulk:

$$\bar{c}_i(V_F + V_L) = F \int_0^L c_i \, dx + V_L c_i(L) \quad (i = B_0, B_1) . \tag{19}$$

The dependences of the concentrations on the degree of conversion of the starting substance were processed to obtain the dependence of the relative selectivity on the degree of conversion, defined as the ratio of the concentration of the intermediate B_1 in the system in which the mass transfer operates to that concentration in a system occurring in the kinetic region, for the same degree of conversion of the starting substance:

$$S = \bar{c}_{B_1} \text{ (diffusion region)}/\bar{c}_{B_1} \text{ (kinetic region)} . \tag{20}$$

An example of the calculation results is shown in Fig. 4. The selectivity in dependence on the degree of conversion of the starting substance passes an extremum; the value of this minimum selectivity S_M can serve as a convenient simple characteristics
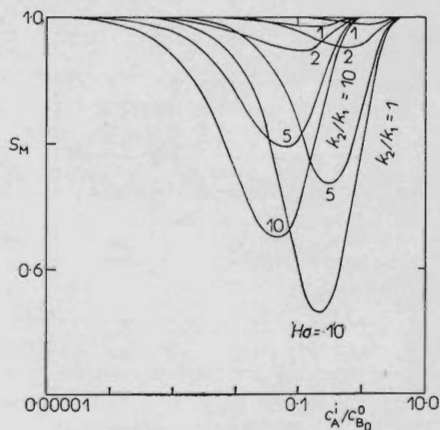

FIG. 6

Dependence of the minimum relative selectivity S_M on the $c_A^i/c_{B_0}^0$ ratio. $V_F/V_L = 1$, $D_G/D_L = 2$

of the system in question. The effect of the various factors on the lowering of the selectivity is processed in Figs 5 and 6 based on these selectivity minima.

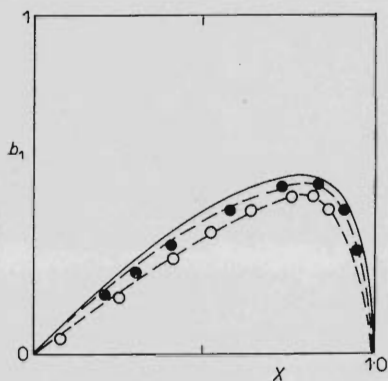The effect of Hatta number is apparent from Fig. 6: the reaction departs from the

FIG. 7

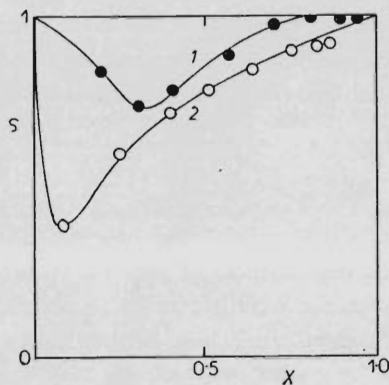Effect of temperature on the selectivity. $c_A^i/c_{B_0}^0 = 0.35$, $V_F/V_L = 6 . 10^{-5}$; ● 30°C, ○ 37°C

FIG. 8

Effect of temperature on the selectivity S. $c_A^i/c_{B_0}^0 = 0.35$, $V_F/V_L = 6 . 10^{-5}$; 1 30°C. 2 37°C

FIG. 9

Effect of the $c_A^i/c_{B_0}^0$ concentration ratio on the selectivity. Temperature 40°C, $V_F/V_L = 8 . 10^{-4}$; $c_A^i/c_{B_0}^0$: 1 0.55, 2 5.5
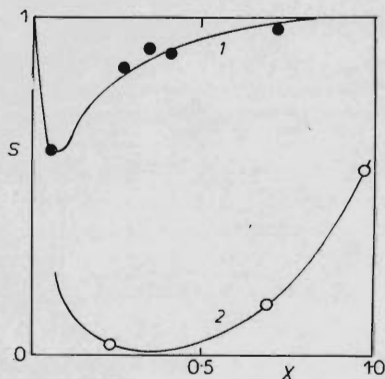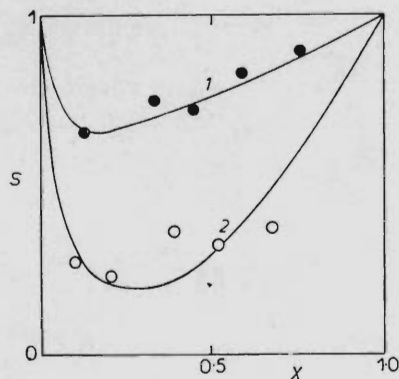

FIG. 10

Effect of the $c_A^i/c_{B_0}^0$ concentration ratio on the selectivity. Temperature 30°C, $V_F/V_L = 1 . 10^{-5}$; $c_A^i/c_{B_0}^0$: 1 0.8, 2 8.0

kinetics regime as Ha increases. Decreasing interface area, in Fig. 5 represented by the V_F/V_L ratio, is accompanied by decreasing selectivity of the reaction. As Figs 5 and 6 demonstrate, the k_2/k_1 rate constant ratio only slightly influences the selectivity decrease due to diffusion. Markedly is the selectivity affected by the concentration ratio of the gas and liquid components; if the difference in the concentrations of the two components is high, the selectivity is not significantly lowered even in the case of high Hatta number values.

Effect of the ratio of the reaction rate to the rate of diffusion on the selectivity. This ratio is involved in Hatta number. The diffusivity of chlorine in tetrachloromethane, as obtained from Wilke's equation[1], is $D_G = 3 \cdot 7 \cdot 10^{-5}$ cm^2/s at $20-40°C$; the thickness of the laminar film, as estimated by using van Krevelen–Hoftijzer equation[14], is $L = 28$ μm. The measurements were carried out for initial concentrations of cyclooctadiene in the region $c_{Bo}^0 = 0 \cdot 23 - 5 \cdot 0$ mol/l. Hatta number over the entire region of measurements was $Ha > 5$. The chemical reaction was thus faster than the diffusion to such an extent that the selectivity could be expected to decrease. Although it was not possible to assign particular Ha values to the individual experiments because the rate constant value was not known accurately enough, the effect of Hatta number on the selectivity could be tested qualitatively. The only quantity involved in Hatta number that varies appreciably with temperature is the rate constant. Hatta number thus increases with rising temperature, and in accordance with the results of calculation, the selectivity of reaction can be expected to decrease. Fig. 7 shows the dependences of concentration of the intermediate on the degree of conversion of the starting material determined at two different temperatures; in Fig. 8 these results are converted to the dependence of the relative selectivity S on the degree of conversion of the starting substance.

Effect of the concentration ratio of the gaseous and liquid components on the selectivity. As follows from the solution of the mathematical model[15], the selectivity can only be expected to lower in a definite region of the concentration ratio of the gaseous and liquid components, *viz.* for c_A^i/c_{Bo}^0 ranging from 10^{-2} to 10^2. Assuming that the solubility of chlorine in the reaction mixutre is not affected by the composition of the latter and can be identified with that in tetrachloromethane, the c_A^i values at a constant pressure of chlorine in contact with the liquid, 100 kPa, is a function of temperature solely; the values for tetrachlormethane are $2 \cdot 32$, $1 \cdot 83$, and $1 \cdot 44$ mol/l at 20, 30, and $40°C$, respectively.

Figs 9 and 10 present the results of measurements, where the only variable was the initial concentration of cyclooctadiene. In all cases the selectivity decreased with increasing c_A^i/c_{Bo}^0 concentration ratio. As follows from a comparison with Figs 5 and 6, additional drop of cyclooctadiene concentration should bring about increasing selectivity; unfortunately, the analytical method employed did not enable measurements to be carried out in this region.

Effect of the interface area on the selectivity. The apparatus used made possible measurements in the region $V_F/V_L < 8 . 10^{-4}$; the ratios $8 . 10^{-4}$, $6 . 10^{-5}$, and $1 . 10^{-5}$ were actually used. In this region the decrease in selectivity was independent of the interface area. This is consistent with the solution of the mathematical model, according to which departures from selectivity at $V_F/V_L < 0.01$ should vary but little with decreasing interface area (Fig. 5). The calculation also predicted a small effect of diffusion on the selectivity at high interface area values. Measurements of addition of chlorine to cyclooctadiene in the gas–liquid system, carried out in a vigorously stirred reactor in which the chlorine was fed below the liquid level $\left(c_{B_0}^0 = 0.23 \text{ mol/l}\right)$, gave a dependence of the concentration of the intermediate on the degree of conversion which was identical with the dependence obtained in the kinetic region.

LIST OF SYMBOLS

$a \; = c_A/c_A^i$,   dimensionsless concentration of the gaseous component
$b_j = c_{B_j}/c_{B_0}^0$,   dimensionless concentration of the component j
    $(j = B_0, B_1)$
c_j concentration of the component j (k mol/m^3)
c_j^0 initial concentration of the component j (k mol/m^3)
c_A^i concentration of the gaseous component in the liquid phase at the interface   (k mol/m^3)
D_j diffusivity of the component j (m^2/s)
D_+ diffusivity of the gaseous component in the liquid phase   (m^2/s)
D_L diffusivity of the liquid components in the liquid phase   (m^2/s)
F specific interface area   (m^2/m^3)
H Henry's constant   (Pa m^3/k mol)
Ha Hatta number (Eq. (*17*))
k rate constant   (m^3/k mol)
L thickness of the laminar film   (m)
p_A partial pressure of the component A   (Pa)
r reaction rate   (k mol/m^3)
S relative selectivity (Eq. (*20*))
S_M minimum relative selectivity in dependence in the degree of conversion
t time   (s)
V_F specific volume of the liquid in the laminar film   (m^3/m^3)
V_L specific volume of the liquid in the turbulent bulk   (m^3/m^3)
x film coordinate   (m)
$X = (c_{B_0}^0 - c_{B_0})/c_{B_0}^0$, degree of conversion
$y \; = x/L$,   dimensionless coordinate of the film
ε relative residence of the gas   (m^3/m^3)
$\tau \; = tD_L/L^2$,   dimensionless time

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