
MATHEMATICAL MODELLING OF ABSORPTION WITH CHEMICAL REACTION IN LIQUID PHASE IN A TRAY COLUMN

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A methodology for the modelling and simulation of tray columns in which gas absorption is accompanied by a chemical reaction is suggested. The presented model is based on the concept of a non-equilibrium stage and the effect of chemical reaction is described by enhancement factors. Pseudo-enhancement factors are introduced for components in liquid phase which take part in the reaction but are not transferred through the gas-liquid interface. A method for calculation of these factors from enhancement factors of components in gas phase and reaction stoichiometry is suggested. The advantages of the so-called global approach to the solution of the system of non-linear algebraic equations forming the column model are shown; this approach enables simply to combine universal equations with specific equations valid for a particular case. An example of CO₂ absorption into aqueous solution of K₂CO₃ and KHCO₃ in a tray column illustrates the usefulness of the approach. The proposed model is compared with simplified models and models in which the concept of pseudo-enhancement factors is not included. The comparison proves the superiority of the presented model.

Gas absorption is frequently accompanied by chemical reaction in the liquid phase. Since the heat capacity of liquid phase is relatively high, most authors assume when modelling the process of absorption with chemical reaction that temperature gradients at the gas-liquid interface can be neglected. Various aspects of the theory of absorption of gases in liquids had been already described in detail in the monographs of Astarita, Savage, Bisio¹ and Danckwerts². Non-isothermal absorption with chemical reaction^{3,4} and the problems concerning multi-component transport through the gas-liquid interface⁵ had been also studied.

Papers paying attention to the problem of absorption with chemical reaction in liquid phase can be classified from various points of view. One of the criterions may be the reaction mechanism: For example, the case of absorption with nonreversible second-order reaction^{6,7,8}, reversible second-order reaction^{9,10}, instantaneous reversible reaction with a general order¹¹, absorption with reversible and irreversible slow first-order reaction^{10,12,13} had been studied. A universal method for the modelling of absorption with one or more simultaneous reactions had been published by Ramachandran¹⁴.

Another classification, taking in account the type of approach used for the modelling of a single separation stage or of a column with continuous contact of phases, can be suggested. One possibility is a detailed description of interfacial phenomena leading to a system of partial differentia

equations. This system is usually solved using finite difference methods^{12,15,16} or it can be converted to a dimensionless form^{8,17} solved by collocation methods^{8,14} or reduced to algebraic equations after introduction of various assumptions, e.g. the linearization of concentration profiles in liquid phase¹⁸. Methods for the calculation of enhancement factors for various types of reaction in liquid phase had been published in many papers^{1,6,7,10,11,19}.

On almost the opposite pole to methods mentioned above, which are based on exact description of the interface and where the simplifications are introduced before the system of partial differential equations is solved, there are methods based on modelling of a general separation stage. They pay attention to bulks of both phases only and the situation at the interface is not taken in account. As a typical example, paper²⁰ could be mentioned in which the chemical reaction is represented by source terms in component balances, or paper²¹ where the achievement of the phase equilibrium between gas and liquid phases is supposed.

As a compromise between both approaches mentioned, there are also methods based on the theory of a non-equilibrium separation stage. Compared with the equilibrium stage concept, the difference is mainly given by the interpretation of the phase equilibrium — while an equilibrium between both phases leaving the stage is supposed for the equilibrium stage concept the presence of phase equilibrium only at the interface is assumed in the second case. General aspects of this theory had been discussed²² and basic equations describing the separation stage had been, presented²³. Applications for packed and stage distillation or absorption columns were published in several papers^{24,25}.

The modelling of the interface or modelling of a single separation stage is a general base for the construction of overall models of various stage separation equipments. Here, not only the choice of model equations but also their ordering and the choice of iteration method used for their solution are important. Principally, two approaches can be distinguished. The common idea used by methods following the first approach is the utilization of some decomposition of calculations, the difference being only in the type and level of the decomposition used^{18,20,21}. The main advantages can be seen in the transparency of these methods and in the reduction of CPU-time and memory requirements, but, unfortunately, most algorithms can be used only for one special case. The second possibility is the utilization of the so-called global approach where all equations describing the separation equipment are solved simultaneously, e.g. by the Newton's method²³⁻²⁶. The most important features of this approach are universality, considerable variability allowed in problem formulation and fast convergence if the initial approximation is not too far from the solution. Increased consumption of CPU-time and higher memory requirements are often mentioned as disadvantages of global methods.

The aim of this paper is to suggest a universally applicable methodology of modelling of absorption accompanied by chemical reaction in the liquid phase. It is apparent that present methods based on the exact description of the interface are usually not sufficiently universal and methods based on the concept of a theoretical stage represent here only a relatively rough approximation. However, the development of a mathematical model of an absorption column with chemical reaction in liquid phase can be based on the idea of a nonequilibrium isothermal stage which was already described and designed for cases without chemical reaction^{23,24}. This approach should be universal enough and, in addition, the description of the situation at the interface is not neglected here.

The real system which served for the verification of the proposed methodology consisted of a gas mixture with CO₂ as the active component and of an aqueous

solution of K_2CO_3 and $KHCO_3$. The appropriate chemical reaction in the liquid phase is reversible and proceeds with a finite reaction rate in the vicinity of the gas-liquid interface. The thermodynamical properties of chemical components considered here are published in literature²⁷ as well as various correlations for mass transfer coefficients, total interfacial area, etc.². Also, reaction-kinetic data had been published in basic monographs^{1,2} and in the paper of Rubio et al.²⁸.

THEORETICAL

UNIVERSAL MODEL OF A NON-EQUILIBRIUM STAGE

The theory of non-equilibrium separation stages was already developed by Krishnamurthy and Taylor²²⁻²⁵. In addition to basic assumptions considered also for older models of equilibrium stages, i.e. ideal mixing in bulks of both phases, steady state and perfect separation of both phases exiting from the stage, it will be supposed that thermodynamic equilibrium takes place at the interface only. The list of equations forming the model starts with component balances formulated separately for each phase:

$$L_{j-1}x_{j-1,i} - (L_j + L_{Sj})x_{j,i} + F_j(1 - \Phi_{Fj})x_{Fj,i}^L - N_{j,i}^L a_j + \sum_{k=1}^m v_{i,k}^L Z_{j,k}^L = 0 \quad i = 1, \dots, n \quad (1)$$

$$V_{j+1}y_{j+1,i} - (V_j + V_{Sj})y_{j,i} + F_j\Phi_{Fj}x_{Fj,i}^V + N_{j,i}^V a_j + \sum_{k=1}^m v_{i,k}^V Z_{j,k}^V = 0 \quad i = 1, \dots, n \quad (2)$$

and with the conditions for steady state at the interface

$$N_{j,i}^L - N_{j,i}^V = 0 \quad i = 1, \dots, n. \quad (3)$$

It should be noticed that Eqs (2) are generally formulated to contain also the source terms for reaction in gas phase. This can be useful for modelling of even more complex absorption columns but here we shall define these terms to be always zero. The significance of most symbols occurring in Eqs (1-3) is obvious from Fig. 1; $Z_{j,k}^L$ and $Z_{j,k}^V$ represent the source terms of k -th chemical reaction on j -th stage in the liquid and vapour phases, respectively, $v_{i,k}^L$ and $v_{i,k}^V$ are the stoichiometric coefficients of i -th component in k -th reaction in the appropriate phase, m is the total number of chemical reactions taking place simultaneously with the absorption, $N_{j,i}^L$ and $N_{j,i}^V$ are the intensities of the flux of i -th component through the interface in the corresponding phase on j -th stage, a_j represents the total interfacial area on stage j .

The model of non-equilibrium stage further contains the binding conditions for

mole fractions in liquid and vapour bulks:

$$\sum_{i=1}^n x_{j,i} - 1 = 0 \quad (4)$$

$$\sum_{i=1}^n y_{j,i} - 1 = 0, \quad (5)$$

the relations describing the vapour-liquid equilibrium at the interface

$$y_{j,i}^* - K_i^*(\mathbf{x}_j^*, T_j, P_j) x_{j,i}^* = 0 \quad i = 1, \dots, n, \quad (6)$$

equations defining the flowrates in liquid and vapour side-streams

$$L_j - R_j^L L_{Sj} = 0 \quad (7)$$

$$V_j - R_j^V V_{Sj} = 0, \quad (8)$$

and the total enthalpy balance:

$$L_{j-1} h_{j-1}^L + V_{j+1} h_{j+1}^V - (L_j + L_{Sj}) h_j^L - (V_j + V_{Sj}) h_j^V + F_j h_{Fj} + Q_j = 0. \quad (9)$$

If the presence of temperature gradients on the stage is supposed then the last equation should be replaced by separate enthalpy ballances for each phase containing

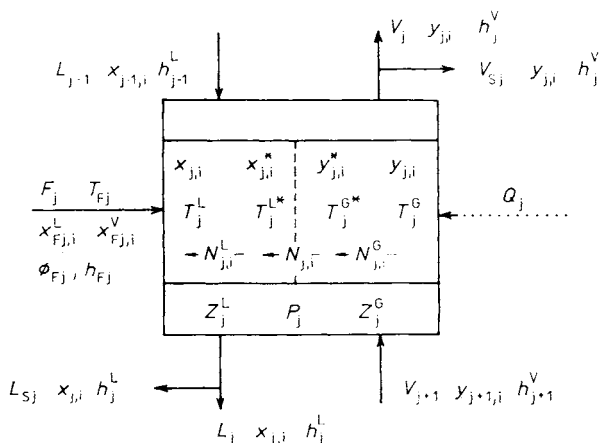


FIG. 1

Universal non-equilibrium separation stage j

a common non-zero term for the heat flux through the interface. In Eq. (9) Q_j represents the heat supplied to stage ($Q_j > 0$) or heat taken away ($Q_j < 0$) by heat exchange.

The system of balance and equilibrium relations (1-9) is joined by transport equations for both phases. The equations describing the multicomponent diffusion had been already derived⁵. If the mass transfer is accompanied by chemical reaction then transport equations must be modified by introduction of enhancement factors^{1,2}. The appropriate relations for liquid and vapour phases can be formulated as follows:

$$N_i^L - \Theta_i^L [k'_{xi}(x_i^* - x_i) + x_i^* \sum_{k=1}^n N_k^L] = 0 \quad i = 1, \dots, n-1 \quad (10)$$

$$N_i^V - \Theta_i^V [k'_{yi}(y_i - y_i^*) + y_i^* \sum_{k=1}^n N_k^V] = 0 \quad i = 1, \dots, n-1. \quad (11)$$

In Eqs (10, 11) the validity of steady state conditions is usually supposed, expressed, for example, by Eq. (3). Instead of considering the intensities of component flux through the interface separately in liquid and vapour phases it is accordingly possible to use a single variable for equal intensities of component flux in both phases ($N_i^L = N_i^V = N_i$). Symbols Θ_i^L and Θ_i^V stand for the enhancement factors for reactions in liquid and vapour phases, resp., while k'_{xi} and k'_{yi} are the mass transport coefficients in liquid and vapour phases corrected for mass transfer velocity (i.e. for convective flux through the interface). Therefore, k'_{xi} and k'_{yi} are dependent on the mass transfer rate. This proves to be advantageous in connection with the description of interfacial phenomena. Disadvantages of the usage of corrected mass transfer coefficients considered above are discussed elsewhere²⁹. The form of correlations need not be necessarily the same for both phases⁵. In liquid phase it is basically possible to use the Lewis-Chang relation

$$k'_{xi} = \sum_k N_k / [\exp(\sum_k N_k / k_{xi,ef}) - 1], \quad (12a)$$

the correction for vapour phase is analogous:

$$k'_{yi} = \sum_k N_k / [1 - \exp(-\sum_k N_k / k_{y,ief})]. \quad (12b)$$

Krishnamurthy and Taylor²³ suggested to calculate the effective mass transfer coefficients from an analogy to the Wilke's relation:

$$k_{i,ef} = (1 - y_i) / \left(\sum_{\substack{k=1 \\ k \neq i}}^n y_k / k_{ik} \right), \quad (13)$$

It is, of course, also possible to use a different relation²⁷:

$$k_{i,ef} = \left(\sum_{\substack{k=1 \\ k \neq i}}^n y_k / k_{ik} \right)^{-1}. \quad (14)$$

Since there are only $n - 1$ independent transport relations (10) and (11) in each phase⁵, the system of equations is supplemented by binding conditions for mole fractions at the interface:

$$\sum_{i=1}^n x_{j,i}^* - 1 = 0 \quad (15)$$

$$\sum_{i=1}^n y_{j,i}^* - 1 = 0. \quad (16)$$

The entire set of relations describing the model of a non-equilibrium separation stage with chemical reaction, i.e. Eqs (1-11), (15) and (16), represents a system of $5n + 5$ equations. The corresponding system of variables associated with this system may include $L_j, V_j, L_{sj}, V_{sj}, T_j, \mathbf{x}_j, \mathbf{x}_j^*, \mathbf{y}_j, \mathbf{y}_j^*, N_j$ - i.e. a total of $5n + 5$ variables.

PSEUDO-ENHANCEMENT FACTORS

Enhancement factors are generally defined only for components transferred through the interface from one to other phase where they enter the chemical reaction. In the phase where chemical reaction is not present the enhancement factors are defined to be unity. Equal to unity are also the enhancement factors of components which do not take part in any chemical reaction in the particular phase. In case of absorption with chemical reaction in liquid phase the enhancement factors of all components in gas phase and of the inerts in liquid phase are considered to be unity.

Since the enhancement factor in liquid phase is not defined for any component taking part in chemical reaction but not crossing the interface, a new term of pseudo-enhancement factors will be introduced here for such components (i.e. active components present in the liquid only). The calculation of pseudo-enhancement factors is based on enhancement factors of gaseous components reacting in the liquid phase, which can be obtained by methods described in literature^{6,11,12}, and on the reaction stoichiometry. Assuming that each of the n^V reacting components from the gas phase takes part in exactly one of the m^L reactions in liquid phase, the pseudo-enhancement factors can be obtained from:

$$\Theta_i^L = \sum_{k=1}^{n^V} \Theta_k^L \sum_{\substack{l=1 \\ v_{k,l} \neq 0}}^{m^L} v_{i,l} / v_{k,l} \cdot \psi_{k,l}, \quad (17)$$

where $\psi_{k,l}$ characterizes the "weight" of l -th chemical reaction. The quantity $\psi_{k,l}$ can be interpreted as e.g. the ratio of the amount of k -th component from gas phase converted by l -th reaction in the liquid phase to the total amount of this component converted by all reactions in the liquid phase in which component k is taking part.

SPECIAL CASES OF THE GENERAL MODEL

In addition to the proposed general model three special models were derived using various restrictions and assumptions. These models represent certain limit cases of the universal model and will be used for comparison. The global calculation method allows easily to develop a number of different models by replacement of some relations in the general model using certain simplifications or special forms of general equations. As a common feature of all models studied here, the assumption of the non-existence of temperature gradients on a tray is postulated.

Model 1

The model is based on the following assumptions:

a) Reaction takes place in the liquid phase in the vicinity of the interface, it is very fast and practically non-reversible (the concentration of dissolved but unreacted component in the liquid bulk is zero by definition).

b) Concentration of components in liquid phase at the interface are practically the same as in the liquid bulk and, therefore, the vapour-liquid equilibrium may be expressed in the form:

$$y_i^* - f_i(\mathbf{x}, T, P) = 0 \quad i = 1, \dots, n. \quad (18)$$

The dimension of the problem is then reduced to $4n + 5$. The explicitness of relations (18) makes possible to eliminate the composition of vapour phase at the interface \mathbf{y}^* from the list of variables and to decrease the problem dimension to $3n + 5$. It is evident that Model 1 can be conveniently used in cases where the solubility of gas is low and the reaction can be considered to be instantaneous and non-reversible. This model is not so convenient for general use.

Model 2

This model is based on the above mentioned concept of non-equilibrium stage. Pseudo-enhancement factors of the components in liquid phase taking part in chemical reaction but not crossing the interface are defined to be unity. For the description of processes at the interface the active components in the liquid phase are treated equally as the remaining inert components. The effect of reaction stoichiometry on the interfacial phenomena is not considered. The universality of this model is again questionable.

Model 3

The proposed concept of pseudo-enhancement factors of reacting compounds in the liquid phase is entirely applied here on contrary to model 2. Owing to the fact that in addition to mass transfer also the effect of reaction stoichiometry is used for the description of the interface, model 3 seems to be well suited for modelling of absorption with chemical reaction in quite a general way.

Model 4

Here, for the modelling of the gas-liquid interface the emphasis is laid on the reaction stoichiometry. General transport equations (10) are for the case of active components in liquid phase substituted by relations based on the stoichiometry conditions in the reaction zone. Therefore, model 4 may be understood as an approximation of the process in a kinetic regime. The process is controlled by chemical reaction while active components in liquid phase are supposed to be present in a sufficient amount. It is evident that this model is also less convenient for general utilization.

GLOBAL APPROACH

The global approach is used here for the solution of the set of equations representing the model of an absorption column in which chemical reaction takes place. That is, the simulation model, which is a square system of nonlinear algebraic equations, is chosen as a subset of the complete system of model equations taking in account the formulation of a particular simulation problem. This system is solved simultaneously. Simulation model can be expressed as follows:

$$\mathbf{F}(\mathbf{X}) = \mathbf{0}, \quad (19)$$

where \mathbf{F} is the system of selected equations forming the model and \mathbf{X} is the corresponding vector of unknowns. The above mentioned necessary condition for system (19) can be expressed as $\dim(\mathbf{F}) = \dim(\mathbf{X})$. The existence of at least one solution of the system is supposed in certain region of feasibility defined by various physical-chemical, technological, and design conditions (for a more detailed discussion concerning the existence and number of solutions see ref.²⁶). This solution can be found e.g. by the Newton's method, where the system of generally non-linear equations (19) is linearized in each iteration. The general iteration scheme of this method applied to system (19) can be written in the form^{23,25}:

$$\mathbf{X}^{k+1} = \mathbf{X}^k - \alpha_k [\mathbf{J}(\mathbf{F}, \mathbf{X}^k)]^{-1} \mathbf{F}(\mathbf{X}^k) \quad k = 0, 1, \dots \quad (20)$$

Evidently, solution of a system of linear algebraic equations is required in each

iteration. In Eq. (20) k is the iteration index, \mathbf{X}^0 is the initial approximation, $\mathbf{J}(\mathbf{F}, \mathbf{X})$ is the Jacobian matrix of mapping \mathbf{F} , i.e.

$$\mathbf{J}(\mathbf{F}, \mathbf{X}^k) = [\partial f_i(\mathbf{X}^k)/\partial x_j]_{i,j=1}^n, \quad (21)$$

α_k is an auxiliary scalar parameter used for the suppression of local divergence. Initially, $\alpha_k = 1$ can be used but if the condition ($\| \cdot \|$ is some vector norm)

$$\|\mathbf{F}(\mathbf{X}^{k+1})\| < \|\mathbf{F}(\mathbf{X}^k)\|, \quad (22)$$

is not fulfilled for some k then smaller values of α_k from the range $(0, 1)$ can be tried, e.g. repeatedly one half of the previous value. If the condition (22) cannot be fulfilled even for several values of α_k then the method is likely to be divergent. In this case it is recommended, for example, to try a different initial approximation.

The existence of all partial derivatives in (21) is a necessary condition for the application of Newton's method. The Jacobian matrix can be evaluated either analytically or numerically using finite difference approximations. Newton's method is a second order method under normal conditions which means in practice that, in case of convergence, a relatively small number of iterations (i.e. 5–10) is required. This should compensate the necessity to evaluate the Jacobian matrix in each iteration. The choice of a good approximation is usually required for this method but for many practical tasks it is often possible to derive reasonable initial estimates based on deeper knowledge of the process or equipment in investigation.

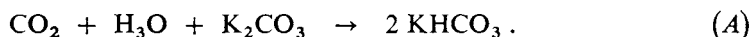
The main advantage of the global approach can be seen in its considerable flexibility and uniformity of the solution procedure for different models and/or simulation problems. Also the possibility to include implicit relations in the simulation model which would otherwise cause serious problems if decomposed methods were used (inner iteration loops etc.) is very important here. Each run of the global method is of course performed for fixed splitting of the overall vector of model variables to subvectors of specified/unknown variables. This cannot be changed during the performance of the solution algorithm. When using the global approach there is no difference between "design" and "simulation" type of calculations in the usual sense²⁶. Higher memory and CPU time requirements are the disadvantages of the method together with the need to supply a relatively good initial approximation.

Certain additional disadvantage can be seen in the fact that some of the Newton iterations could fall into physically and/or technologically unfeasible region where the validity of certain model equations is not guaranteed. However, if the final solution is feasible and from the pure mathematical or computational point of view all equations are well defined even for unfeasible values of model variables then any objections are irrelevant.

EXAMPLE OF APPLICATION

Model of a Separation Tray for a Selected System

The real system investigated here is the absorption of CO_2 into aqueous solutions of alkalines. The gas phase is supposed to contain some inert gas component (e.g. H_2 , N_2 or others) in mixture with CO_2 . The liquid phase is an aqueous solution of K_2CO_3 , KHCO_3 , and inert liquid component (KCl , KNO_3 etc.). The numbering of individual components which is used in model equations below is given in Table I. The chemical reaction taking place in the liquid phase can be considered as reversible and proceeding with a finite reaction rate in the vicinity of the gas-liquid interface^{1,2}:



The modelled column is a plate absorption column with a simple configuration shown in Fig. 2. Several reasonable assumptions can be made for this problem: The temperature gradients are zero at the interface and inerts in both phases as well as K_2CO_3 and KHCO_3 should not be present at or transferred through the interface.

The component balances used here in the model of an absorption stage have the following form:

$$L_{j-1}x_{j-1,i} - L_{j,i} + V_{j+1}y_{j+1,i} - V_jy_{j,i} + F_jx_{Fj,i}^V + v_iZ_j^L = 0 \quad i = 1, \dots, 6. \quad (23)$$

This was obtained by substituting $N_{j,i}^L$ and $N_{j,i}^V$ from Eqs (1) and (2), respectively, into Eq. (3). Stoichiometric coefficients for all components are given in Table I. Source terms Z_j^L occurring in Eq. (23) are usually calculated on the basis of reaction

TABLE I

List of chemical components, stoichiometric coefficients, parameters in the polynomial expression for molar heat capacity $c_p^v = \alpha + \beta T + \gamma T^2 + \delta T^3$ ($\text{J mol}^{-1} \text{K}^{-1}$) and mass transfer coefficients

Component	Number	ν	α	$\beta \cdot 10^{-3}$	$\gamma \cdot 10^{-5}$	$\delta \cdot 10^{-8}$	k_y	k_x
CO_2	1	-1	19.795	73.44	-5.602	1.715	16.2	110.1
Inert in vapour phase	2	0	27.143	9.274	-1.381	0.765	—	—
KHCO_3	3	2	—	—	—	—	—	77.85
K_2CO_3	4	-1	—	—	—	—	—	77.85
H_2O	5	-1	32.243	1.924	1.056	-0.36	15.5	—
Inert in liquid phase	6	0	—	—	—	—	—	60.0

kinetic data. In this system, however, CO_2 is supposed to be the key component and source terms can be calculated from CO_2 balance in liquid phase:

$$Z_j^L = N_{j,1}a_j + L_{j-1}x_{j-1,1} - L_jx_{j,1}. \quad (24)$$

System of equations describing the absorption stage further contains the balance of H_2O in gas phase:

$$V_{j+1}y_{j+1,5} + F_jx_{Fj,5}^V - N_{j,5}a_j - V_jy_{j,5} = 0. \quad (25)$$

A separate equation can be formulated for the calculation of mole fraction of CO_2 in the liquid bulk. It is based on the assumption that the chemical reaction reaches an equilibrium in the liquid bulk. The concentration of dissolved CO_2 can be obtained from the ratio of first and second dissociation constants of carbonic acid:

$$x_{\text{CO}_2} = (K_2/K_1)(x_{\text{HCO}_3^-}/x_{\text{CO}_3^{2-}}). \quad (26)$$

The dependence of K_1 and K_2 on the temperature and on the ionic strength of solution had been published previously².

Next two equations to be included in the model are the binding conditions (4) and (5). The phase equilibrium equations (6) are meaningful only for CO_2 and H_2O as each of the remaining components is present just in one phase. Relations describing the phase equilibrium are semiempirical¹. The total enthalpy balance is also utilized in this case. Molar enthalpies in the vapour phase are calculated on the basis of standard empirical polynomial expressions for c_p ; the appropriate coefficients are presented in Table I. The calculation of molar enthalpies in liquid phase requires to evaluate not only the molar heat capacity but also the terms for heats of reaction,

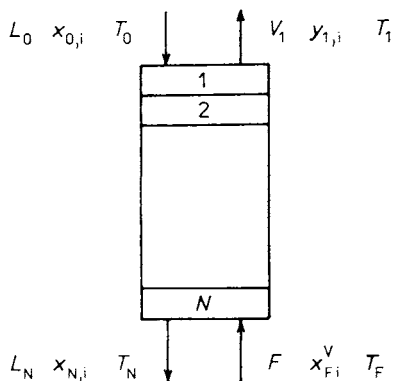


FIG. 2
Scheme of the simulated absorption column

solution and dilution. Two transport relations can be formulated for the vapour phase:

$$N_1 - k'_{y1}(y_1 - y_1^*) - y_1^*(N_1 + N_5) = 0 \quad (27)$$

$$N_5 - k'_{y5}(y_5 - y_5^*) - y_5^*(N_1 + N_5) = 0 \quad (28)$$

and another four for liquid phase

$$N_1 - \Theta_1^L [k'_{x1}(x_1^* - x_1) + x_1^*(N_1 + N_5)] = 0 \quad (29)$$

$$\Theta_3^L [k'_{x3}(x_3^* - x_3) + x_3^*(N_1 + N_5)] = 0 \quad (30)$$

$$\Theta_4^L [k'_{x4}(x_4^* - x_4) + x_4^*(N_1 + N_5)] = 0 \quad (31)$$

$$k'_{x6}(x_6^* - x_6) + x_6^*(N_1 + N_5) = 0. \quad (32)$$

The subset of model equations describing particularly the situation at the interface is completed by inclusion of binding conditions (15) and (16). Mass transfer coefficients are corrected here according to (12a) and (12b) where regression relations for k'_{x1} and k'_{y1} were directly used instead of calculating the effective values. A number of authors, for example see refs^{1,2,9,10,17,19}, had studied various calculation methods for the evaluation of enhancement factor of CO₂, i.e. for the calculation of Θ_1^L . Since the selection of a particular method has no influence on the structure of the solution procedure, Danckwerts method² was utilized in the presented example. The use of implicit relation for Θ_1^L brings no difficulties with the global approach as this relation simply becomes one of the equations in the simulation model. Some other methods for the calculation of enhancement factor were also tested.

Calculation of the Enhancement Factor of CO₂ for Reaction (A)

The enhancement factor generally depends on the reaction mechanism, kinetics and type of reaction. In case of CO₂ absorption in aqueous solutions of K₂CO₃ and KHCO₃ the reaction is reversible and proceeding with a finite rate. Therefore, this is not the case of a limit regime represented either by an instantaneous or by a very slow reaction. Danckwerts² suggests a general methodology for calculations of the enhancement factor for the regime considered here which can be adopted if the concentration of reaction products in liquid bulk is non-zero. This methodology is based on the observation that the dependence of enhancement factor on the Hatta number and the enhancement factor of instantaneous reaction (Θ_1) is for fast reversible reaction almost identical with the same dependency but for a non-reversible second-order reaction:



According to the film model, the absorption of component A from the gas phase and its reaction with component B in the solution is described by a system of two ordinary differential equations. Using the assumption that the concentration of component A in liquid bulk is zero, the solution of these equations can be approximated by certain implicit nonlinear algebraic equation from which the enhancement factor can be calculated²:

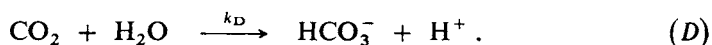
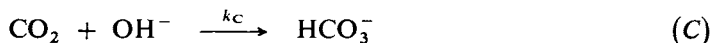
$$\Theta = [M(\Theta_1 - \Theta)/(\Theta_1 - 1)]^{0.5} / \operatorname{tgh} \{ [M(\Theta_1 - \Theta)/(\Theta_1 - 1)]^{0.5} \}, \quad (33)$$

where

$$M = D_A k_2 c_{B,b} / k_{1A}^2 \quad (34)$$

$$\Theta_1 = 1 + D_B c_{B,b} / (b D_A c_A^*) \quad (35)$$

Particularly, absorption of CO₂ into aqueous alkaline solutions can be accompanied by following two reactions:



While slow reaction (D) can be neglected², reaction (C) in this real case corresponds to reaction type (B). Particular forms of relations (34) and (35) can be then formulated:

$$M = D_{\text{CO}_2} k_C c_{\text{OH}^-,b} / k_{1,\text{CO}_2}^2 \quad (36)$$

$$\Theta_1 = 1 + (D_{\text{OH}^-} / D_{\text{CO}_2}) c_{\text{OH}^-,b} / (c_{\text{CO}_2}^* - c_{\text{CO}_2,b}) \quad (37)$$

Calculation of the diffusivity of CO₂ both in the gas phase and in the solution is published elsewhere². The dependence of reaction rate for reaction (C) on the temperature and ionic strength¹ is given by

$$\log k_C = 10.635 - 2.895/T + 0.08I \quad (38)$$

$$I = 1/(2Q_0) \sum_i c_i z_i^2 = x_3 + 3x_4 + x_6 \quad (39)$$

The concentration of OH⁻ ions may be expressed on the basis of a ionic product of water and the second dissociation constant of carbonic acid

$$c_{\text{OH}^-,b} = (K_w / K_2) (c_{\text{CO}_3^{2-}} / c_{\text{HCO}_3^-}), \quad (40)$$

where

$$K_w = c_{\text{H}^+} c_{\text{OH}^-} \quad (41)$$

$$K_2 = c_{\text{H}^+} c_{\text{CO}_3^{2-}} / c_{\text{HCO}_3^-} \quad (42)$$

The dependence of K_w/K_2 ratio on temperature was published by Rubio et al.²⁸. In this calculations, the dependence of molar density on temperature and composition is taken in account. For the ratio of diffusivities of CO_2 and OH^- Danckwerts² observed that its values fall in the following range:

$$D_{\text{OH}^-} / D_{\text{CO}_2} = 1.7 \sim 2.1 \quad (43)$$

Calculation of Mass Transfer Coefficients

If a column with bubble cup trays is considered then Andrew's correlation² can be chosen for the calculation of mass transfer coefficients and interfacial area:

$$k_g = 2.24(V/S)^{0.25} (D^V/\varphi)^{0.5} \quad (44)$$

$$k_{1,A} = 34.8(V/S)^{0.25} (D_A/\varphi)^{0.5} \quad (45)$$

$$a = 1.5 \cdot 10^{-3} (V/S)^{0.5} \varphi^{5/6} S, \quad (46)$$

where V is the gas flowrate, S is the tray cross-section area and φ represents the liquid hold-up on the tray per unit of cross-sectional area. From Eqs (44–46) only the mass transfer coefficients of CO_2 can be calculated while for k_{13} and k_{14} it can be assumed¹ that

$$D_3 = D_4 = D_1/2 \quad (47)$$

Therefore, if other conditions are preserved then

$$k_{13} = k_{14} = k_{11}/\sqrt{2} \quad (48)$$

Formulation of Particular Simulation Models

The four types of models proposed in the theoretical section can be formulated for the presented example using the appropriate general assumptions.

Model 1: Assumption *a*) takes here simply the following form:

$$x_{1,b} = 0 \quad (49)$$

$$x_i^* - x_i = 0 \quad i = 3, 4, 5, 6 \quad (50)$$

Concentrations of gaseous components at the interface can be eliminated from the list of unknowns in this model if we utilize the explicit form of Eq. (18) and substitute

the appropriate fractions into transport equations (27–28). The resulting model contains equations (23), (24), (4), (5), (9), (27), and (28), that is a total of 12 equations per stage for 12 unknowns $L, V, T, x_3, x_4, x_5, x_6, y_1, y_2, y_5, N_1, N_5$.

Model 2: This model consists of equations (23–32), (4), (5), (9), and (15). Using the same substitution as in model 1 the dimension can be also reduced. The enhancement factor of CO_2 is calculated using the procedure described above. For K_2CO_3 and KHCO_3 the enhancement factors are equal to one by definition. Therefore, 19 equations for the same number of unknowns, i.e. $L, V, T, x_1, x_3, x_4, x_5, x_6, x_1^*, x_3^*, x_4^*, x_5^*, x_6^*, y_1, y_2, y_5, N_1, N_5, \Theta_1^L$, form the model of each stage.

Model 3: The selection of equations and variables can be preserved from model 2. The pseudo-enhancement factors Θ_3^L and Θ_4^L are calculated on the basis of relation (17), thus

$$\Theta_3^L = -2\Theta_1^L \quad (51)$$

$$\Theta_4^L = \Theta_1^L. \quad (52)$$

According to the explicitness of Eqs (51–52), it is not necessary to include Θ_3^L nor Θ_4^L in the system of model variables and the dimension of the model can be left unchanged.

Model 4: The difference between Model 4 and Model 2 can be found in the replacement of transport equations (30–31) by certain “balance-stoichiometric” equations

$$L^*x_1^* - Z_1 - \tilde{L}x_1 = 0 \quad (53)$$

$$L^*x_3^* - 2Z_1 - \tilde{L}x_3 = 0 \quad (54)$$

$$L^*x_4^* + Z_1 - \tilde{L}x_4 = 0 \quad (55)$$

$$L^*x_5^* + Z_1 - \tilde{L}x_5 = 0, \quad (56)$$

where L^* is a fictive flux from the interface to the reaction zone and, similarly, \tilde{L} is a fictive molar flux from the reaction zone to the liquid bulk. Using algebraic manipulations and substitutions, the subset of equations (53–56) containing five unknowns $L^*, \tilde{L}, x_3^*, x_4^*, Z_1$ can be reduced to two equations for unknown x_3^* and x_4^* :

$$(x_1 + x_5)(x_3^* - 2x_1^*) - (x_3 - 2x_1)(x_1^* + x_5^*) = 0 \quad (57)$$

$$(x_1 + x_5)(x_1^* + x_4^*) - (x_1 + x_4)(x_1^* + x_5^*) = 0, \quad (58)$$

Accordingly, the overall system of unknowns is the same as in Model 2.

Example of calculations. For comparison, each of the four models described above was used for simulation of the absorption column depicted in Fig. 2 with the following set of specifications: Total number of stages: 20;

Overhead liquid feed: Flowrate $L_0 = 4\,869.0 \text{ mol s}^{-1}$, temperature $T_0 = 358.15 \text{ K}$, composition $x_{0,1,v} = 0.0$; $x_{0,2} = 0.0$; $x_{0,3} = 0.0442$; $x_{0,4} = 0.0308$; $x_{0,5} = 0.9150$; $x_{0,6} = 0.01$.

Rich gas (bottom feed): Flowrate $F = 586.14 \text{ mol s}^{-1}$, temperature $T_F = 393.15 \text{ K}$, composition $y_{F,1} = 0.1938$; $y_{F,2} = 0.7113$; $y_{F,3} = 0.0$; $y_{F,4} = 0.0$; $y_{F,5} = 0.0949$; $y_{F,6} = 0.0$.

Parameters of the tray: $S = 0.35 \text{ m}^2$, $a = 32.33 \text{ m}^2$, $\phi = 0.035 \text{ m}^2$.

Pressure in the column: $P_0 = 1.981 \text{ MPa}$, $\Delta P = 2.942 \text{ kPa}$ per tray (linear pressure profile is assumed along the column).

The results of calculations represented by the profiles of L , θ_1^L , and by mole fractions of CO_2 , KHCO_3 , K_2CO_3 , and H_2O both in the liquid bulk and at the interface are presented in Tables II–VI and in Figs 3–6 for all models.

TABLE II

Results for the illustrative example: L (mol s^{-1}) and θ_1^L profiles

Tray	Model 1		Model 2		Model 3		Model 4	
	L	θ_1^L	L	θ_1^L	L	θ_1^L	L	θ_1^L
1	4 869.0	—	4 869.1	1.4462	4 869.1	1.4462	4 869.1	1.4460
2	4 869.0	—	4 869.1	1.4461	4 869.1	1.4461	4 869.1	1.4458
3	4 869.0	—	4 869.0	1.4460	4 869.0	1.4460	4 869.0	1.4453
4	4 868.9	—	4 869.0	1.4458	4 869.0	1.4458	4 869.0	1.4445
5	4 868.9	—	4 869.0	1.4455	4 869.0	1.4455	4 869.0	1.4429
6	4 868.9	—	4 869.0	1.4449	4 869.0	1.4448	4 869.0	1.4396
7	4 868.9	—	4 869.0	1.4436	4 869.0	1.4435	4 869.0	1.4331
8	4 868.9	—	4 869.0	1.4409	4 869.0	1.4407	4 868.9	1.4206
9	4 868.9	—	4 868.9	1.4355	4 868.9	1.4351	4 868.9	1.3967
10	4 868.9	—	4 868.9	1.4246	4 868.9	1.4238	4 868.8	1.3542
11	4 868.8	—	4 868.9	1.4029	4 868.9	1.4014	4 868.7	1.2868
12	4 868.8	—	4 868.9	1.3624	4 868.9	1.3598	4 868.6	1.2010
13	4 868.8	—	4 869.0	1.2948	4 868.9	1.2910	4 868.4	1.1203
14	4 868.8	—	4 869.0	1.2046	4 869.0	1.2004	4 868.4	1.0987
15	4 868.8	—	4 869.4	1.1183	4 869.4	1.1151	4 868.7	1.0379
16	4 869.0	—	4 870.4	1.0871	4 870.4	1.0835	4 869.9	1.0136
17	4 870.0	—	4 872.9	1.0257	4 872.9	1.0298	4 873.2	1.0061
18	4 874.3	—	4 878.7	1.0107	4 878.7	1.0094	4 880.1	1.0034
19	4 887.3	—	4 891.6	1.0033	4 891.6	1.0032	4 893.2	1.0028
20	4 915.1	—	4 916.4	1.0012	4 916.4	1.0013	4 916.4	1.0039

TABLE III

Results for the illustrative example: Profiles of CO₂ content in liquid bulk and at the interface

Tray	Model 2		Model 3		Model 4	
	x_1^a	x_1^{*a}	x_1^a	x_1^{*a}	x_1^a	x_1^{*a}
1	0.00002	0.00002	0.00002	0.00002	0.00002	0.00002
.
.
7	0.00002	0.00002	0.00002	0.00002	0.00002	0.00002
8	0.00002	0.00002	0.00002	0.00002	0.00002	0.00003
9	0.00002	0.00002	0.00002	0.00002	0.00002	0.00005
10	0.00002	0.00003	0.00002	0.00003	0.00002	0.00008
11	0.00002	0.00004	0.00002	0.00004	0.00002	0.00015
12	0.00002	0.00007	0.00002	0.00007	0.00002	0.00029
13	0.00002	0.00014	0.00002	0.00014	0.00002	0.00059
14	0.00002	0.00028	0.00002	0.00029	0.00002	0.00115
15	0.00002	0.00061	0.00002	0.00063	0.00003	0.00227
16	0.00002	0.00127	0.00002	0.00131	0.00004	0.00407
17	0.00003	0.00270	0.00003	0.00275	0.00006	0.00615
18	0.00004	0.00530	0.00004	0.00540	0.00010	0.00687
19	0.00009	0.00935	0.00009	0.00939	0.00017	0.00568
20	0.00025	0.01125	0.00025	0.01097	0.00025	0.00391

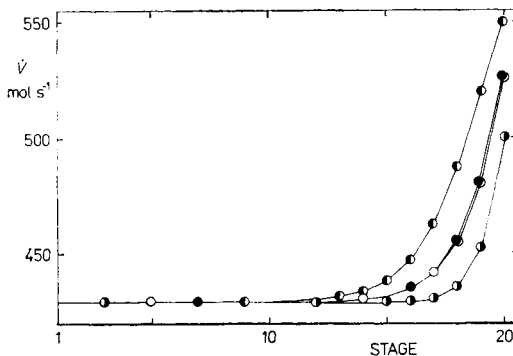
^a Values x_1 and x_1^* are defined to be zero in model 1.

FIG. 3

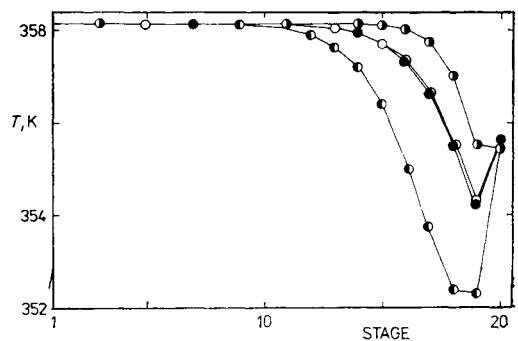
Vapour flow rates. ● Model 1, ○ model 2,
● model 3, ○ model 4

FIG. 4

Temperature profiles, denotation as in Fig. 3

TABLE IV
Results for the illustrative example: Profiles of KHCO_3 content in liquid bulk and at the interface

Tray	Model 1		Model 2		Model 3		Model 4	
	x_3	x_3^*	x_3	x_3^*	x_3	x_3^*	x_3	x_3^*
1	0.0442	—	0.0442	0.0442	0.0442	0.0442	0.0442	0.0442
.	.	—
8	0.0442	—	0.0442	0.0442	0.0442	0.0442	0.0442	0.0442
9	0.0442	—	0.0442	0.0442	0.0442	0.0442	0.0443	0.0443
10	0.0442	—	0.0442	0.0442	0.0442	0.0442	0.0444	0.0445
11	0.0442	—	0.0443	0.0443	0.0443	0.0443	0.0446	0.0449
12	0.0442	—	0.0444	0.0444	0.0444	0.0444	0.0451	0.0456
13	0.0442	—	0.0446	0.0446	0.0446	0.0446	0.0461	0.0472
14	0.0442	—	0.0451	0.0450	0.0451	0.0451	0.0479	0.0501
15	0.0444	—	0.0460	0.0460	0.0461	0.0461	0.0513	0.0556
16	0.0448	—	0.0480	0.0479	0.0481	0.0482	0.0572	0.0651
17	0.0465	—	0.0520	0.0517	0.0527	0.0523	0.0661	0.0779
18	0.0518	—	0.0596	0.0591	0.0600	0.0603	0.0759	0.0889
19	0.0654	—	0.0730	0.0717	0.0734	0.0741	0.0836	0.0942
20	0.0889	—	0.0884	0.0862	0.0884	0.0895	0.0884	0.0954

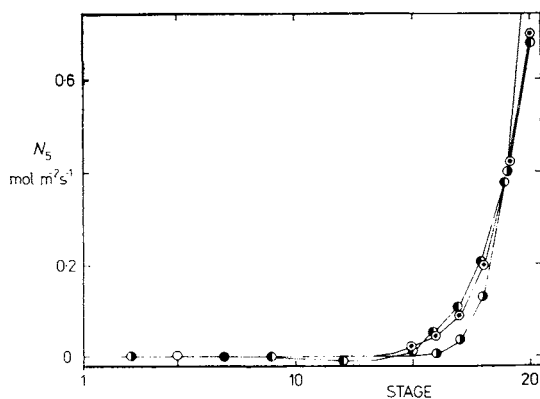


FIG. 5
Profiles of interfacial molar flux of CO_2 , denotation as in Fig. 3

RESULTS AND DISCUSSION

The practical test example presented above represents an important industrial process but, unfortunately, no measured data were available for comparison. Therefore, this

TABLE V

Results for the illustrative example: Profiles of K_2CO_3 content in liquid bulk and at the interface

Tray	Model 1		Model 2		Model 3		Model 4	
	x_4	x_4^*	x_4	x_4^*	x_4	x_4^*	x_4	x_4^*
1	0.0308	—	0.0308	0.0308	0.0308	0.0308	0.0308	0.0308
.	.	—
8	0.0308	—	0.0308	0.0308	0.0308	0.0308	0.0308	0.0308
9	0.0308	—	0.0308	0.0308	0.0308	0.0308	0.0308	0.0307
10	0.0308	—	0.0308	0.0308	0.0308	0.0308	0.0307	0.0306
11	0.0308	—	0.0308	0.0308	0.0308	0.0308	0.0306	0.0305
12	0.0308	—	0.0307	0.0307	0.0307	0.0307	0.0304	0.0301
13	0.0308	—	0.0306	0.0306	0.0306	0.0306	0.0299	0.0293
14	0.0308	—	0.0304	0.0304	0.0304	0.0304	0.0290	0.0278
15	0.0307	—	0.0299	0.0299	0.0299	0.0298	0.0273	0.0250
16	0.0305	—	0.0289	0.0288	0.0288	0.0288	0.0243	0.0202
17	0.0297	—	0.0269	0.0268	0.0268	0.0266	0.0198	0.0136
18	0.0269	—	0.0230	0.0228	0.0228	0.0226	0.0148	0.0080
19	0.0200	—	0.0162	0.0159	0.0160	0.0157	0.0108	0.0053
20	0.0079	—	0.0082	0.0080	0.0082	0.0080	0.0082	0.0045

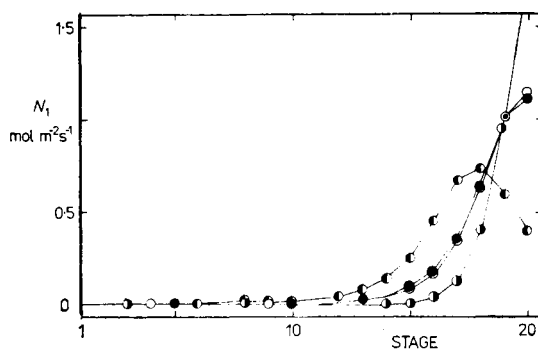


FIG. 6

Profiles of interfacial molar flux of H_2O , denotation as in Fig. 3

example served for testing of the suitability of individual models formulated in the theoretical part. It can be inferred that with increasing numbering of models the reaction stoichiometry is more and more taken in account. Consequently, the calculated interfacial concentrations of KHCO_3 increase from Model 1 to Model 4 and, accordingly, interfacial concentrations of K_2CO_3 , H_2O , and of the liquid inert are decreasing. Concentrations of KHCO_3 and K_2CO_3 have very strong influence on the equilibrium composition of the gas phase and on the molar enthalpy of liquid phase. This is the reason for deviations observed in the calculated profiles of most parameters along the column using different models. Particularly, the differences in temperatures in the column are due to the endothermic character of reaction (A) and also to the increasing concentration of KHCO_3 .

If reaction (A) takes place at the interface then components CO_2 , K_2CO_3 , and H_2O are disappearing and simultaneously KHCO_3 is produced. Consequently, the total number of moles in the liquid phase should be decreasing and the mole fractions of CO_2 and KHCO_3 should be higher at the interface than in the liquid bulk while exactly the opposite could be expected for concentrations of H_2O and K_2CO_3 . This is valid entirely only for Models 3 and 4 in which the effect of reaction stoichiometry is considered under interfacial conditions. For Model 2 which is based on pure

TABLE VI

Results for the illustrative example: Profiles of H_2O content in liquid phase and at the interface

Tray	Model 1		Model 2		Model 3		Model 4	
	x_5	x_5^*	x_5	x_5^*	x_5	x_5^*	x_5	x_5^*
1	0.9150	—	0.9150	0.9150	0.9150	0.9150	0.9150	0.9150
.	.	—
8	0.9150	—	0.9150	0.9150	0.9150	0.9150	0.9150	0.9150
9	0.9150	—	0.9150	0.9150	0.9150	0.9150	0.9150	0.9149
10	0.9150	—	0.9150	0.9150	0.9150	0.9150	0.9149	0.9148
11	0.9150	—	0.9150	0.9149	0.9150	0.9149	0.9148	0.9145
12	0.9150	—	0.9149	0.9149	0.9149	0.9148	0.9145	0.9140
13	0.9150	—	0.9148	0.9147	0.9148	0.9147	0.9141	0.9130
14	0.9150	—	0.9146	0.9143	0.9145	0.9143	0.9131	0.9110
15	0.9149	—	0.9141	0.9136	0.9141	0.9135	0.9114	0.9072
16	0.9147	—	0.9131	0.9121	0.9130	0.9118	0.9085	0.9008
17	0.9139	—	0.9111	0.9089	0.9110	0.9084	0.9040	0.8925
18	0.9113	—	0.9074	0.9030	0.9072	0.9019	0.8992	0.8864
19	0.9047	—	0.9008	0.8934	0.9006	0.8911	0.8954	0.8851
20	0.8932	—	0.8933	0.8850	0.8933	0.8819	0.8933	0.8865

“transport” equations, the concentrations of KHCO_3 do not satisfy the expected condition; the calculated values at the interface are generally lower than in the liquid bulk.

The comparison of results obtained by different models leads to the conclusion that Models 2 and 4 give limit values for all model variables while Model 3, which is based on the concept of pseudo-enhancement factors, seems to be suited best for our purpose, i.e. for the simulation of plate absorption columns with simultaneous chemical reaction(-s). On the other hand, it is usually not possible to use complex detailed models directly for simulation of real industrial columns because the dimension of such models is much higher and there are still limitations given by the capacity of computing machinery. Therefore, any simplifying assumptions, if reasonable, are very valuable and the resulting simpler model can be used for initial simulation of separation columns; even those with large number of stages and chemical components. The results can serve later as very reasonable initial values for more advanced models.

To conclude this contribution, it should be emphasized that the main advantage of the presented methodology is its flexibility and universality given by adoption of the global solution method which is independent of the particular simulation model used. The basic assumption for global methods, i.e. representation of the model by a set of simultaneous nonlinear algebraic equations, disables in certain cases to use more exact models especially for the description of interfacial phenomena where a number of simplifying assumptions must be used (film model, approximation of a bubble by a plane etc.). Also the inexact evaluation of certain important parameters of the model (enhancement factors, mass transfer coefficients, etc.) can lead to more or less serious deviations in the simulation results. This point seems to be crucial for wider application of the methodology. For a real system it can be supposed that there are possibilities to find reasonable relations for calculation of enhancement factors and mass transfer coefficients based on experimental data. This can be done either by regression methods or by selection of different existing equations or methods. Anyway, the presented methodology allows to find the model best suited for the given system without any deeper changes in the overall solution method.

LIST OF SYMBOLS

a	total interfacial area on the tray, m^2
c	molar concentration, mol m^{-3}
c_p	molar heat capacity, $\text{J mol}^{-1} \text{K}^{-1}$
D	diffusivity, $\text{m}^2 \text{s}^{-1}$
F	feed flux, mol s^{-1}
F	simulation model
h	molar enthalpy, J mol^{-1}
I	ionic strength
J	Jacobian matrix of mapping F

k_x, k_y	mass transfer coefficients in liquid and vapour phases, resp., $\text{mol m}^{-2} \text{s}^{-1}$
k_f, k_g	mass transfer coefficients in liquid and vapour phases resp., m s^{-1}
k_2	second order reaction rate constant, $\text{m}^3 \text{mol}^{-1} \text{s}^{-1}$
K_1, K_2	the first and the second dissociation constant of carbonic acid, mol m^{-3}
K_w	ionic product of water
L	liquid phase flowrate, mol s^{-1}
n	number of chemical components
N	intensity of molar flux through the vapour-liquid interface, $\text{mol m}^{-2} \text{s}^{-1}$
P	pressure, Pa
Q	heat flux, J s^{-1}
R	reflux ratio
S	column cross-sectional area, m^2
T	temperature, K
V	vapour (gas) phase flowrate, mol s^{-1}
x	mole fraction in liquid phase
\mathbf{x}	vector of molar composition in liquid phase
\mathbf{X}	vector of unknowns in simulation model
y	mole fraction in vapour phase
\mathbf{y}	vector of molar composition in vapour phase
z	ion valence
Z	source term, mol s^{-1}
$\alpha, \beta, \gamma, \delta$	coefficients in the polynomial expression for dependence of gas phase molar heat capacity on temperature
Θ	enhancement factor
ν	stoichiometric coefficient
ρ	molar density, mol m^{-3}
φ	liquid hold-up on a tray per unit of cross-sectional area, $\text{m}^3 \text{m}^{-2}$
Φ	vapour fraction
ψ	weight factor of a chemical reaction

Subscripts

A	component A in reaction (B)
b	bulk
B	component B in reaction (B)
ef.	effective
F	feed
i	component index
i	row index in Jacobian matrix
I	instantaneous (reaction)
j	stage index
j	column index in Jacobian matrix
k	component index
k	iteration index in Newton's method
l	reaction number
S	side-stream

Superscripts

L	liquid phase
V	vapour phase

' corrected
* interfacial

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