

A general analysis of mass transfer accompanied by multiple equilibrium reactions*

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Received on January 29, 1986.

Abstract

A general analysis of mass transfer accompanied by single/multistep equilibrium reactions has been presented in the specific context of gas treating with chemical solvents. The analysis takes into account the gas film resistance to mass transfer as well as the possibility of more than one species figuring in both gas and liquid phases. In this form the analysis presented here provides a framework for computer simulation of an important class of gas-treating processes with minimum user intervention and can be used routinely for both absorption and desorption accompanied by instantaneous reversible reactions as well as for simultaneous absorption of reactant and desorption of product species. The application of the new computational procedure is illustrated with several commonly encountered reaction schemes.

Key words: Equilibrium reactions, instantaneous reversible reactions, absorption, desorption, gas treating, enhancement factor, computer simulation

1. Introduction

Many gas treating processes involve absorption of one or more gaseous solutes in a liquid solvent, followed by one or more instantaneous reversible reactions or the so-called 'equilibrium reactions' that the solute species undergo with various liquid phase reactants and/or intermediate reaction products (*e.g.* absorption of SO_2 in water with/without additives, absorption of H_2S in amines, absorption of Cl_2 in NaOH , etc.).

The analysis of such a system for predicting the pertinent enhancement factors usually follow the time-honoured treatment due to Olander¹ and Danckwerts². Attempts to extend this approach which worked well with a single absorbing solute undergoing a single equilibrium reaction to multistep equilibrium reactions are in evidence in the literature. For example, Bhattacharya and Ramachandran³ analysed the problem of absorption of a solute undergoing a two-step complex equilibrium reaction which is

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[‡] Presented at the National Symposium on 'Modelling and simulation in chemical engineering,' held at the Department of Chemical Engineering, Indian Institute of Science, Bangalore during August 22–24, 1985. NCL Communication Number 2982.

typical of Cl_2 absorption in NaOH . Chang and Rochelle⁴ had given a similar film theory treatment of absorption of a single gas accompanied by multistep non-interacting/interacting equilibrium reactions. The latter authors were also the first to analyse the problem of gas absorption with a single equilibrium reaction *via* Danckwerts' surface renewal theory. Application of surface renewal theory to the case of multiple equilibrium reactions is very complicated and can be accomplished only through a tedious numerical computation. Chang and Rochelle had approximated the solutions obtainable *via* surface renewal theory by the corresponding film theory solutions by replacing the diffusivities by their square roots and had extensively applied such a theory to SO_2 absorption in $\text{NaOH}/\text{Na}_2\text{SO}_4$ solutions⁵ and SO_2 absorption in organic acid buffer solutions⁶.

Astarita and Savage⁷ had recast the film theory model for single gas absorption followed by a single, generalised equilibrium reaction in a slightly different form and used the model equations to derive some interesting asymptotic behaviour of the system for extremes of driving forces for absorption/desorption. Astarita *et al*⁸ later extended a similar analysis to the case of absorption of H_2S and CO_2 into aqueous amines.

2. Scope of generalisation

The aforesaid Olander-Danckwerts approach offers a scope of generalisation in following three respects:

- (i) Gas-film resistance, often important in practice, especially when the absorbing species is present in low concentrations along with non-reacting inerts, has not been considered so far in the literature.
- (ii) With one notable exception⁸ most other work already referred to had considered only one absorbing species whereas in practice one encounters more than one absorbing species (absorption of CO_2 , H_2S , COS , etc., in amines) or sometimes both absorbing and desorbing species (absorption of Cl_2 in sodium carbonate solution accompanied by desorption of CO_2).
- (iii) A third, more subtle, difficulty is faced in trying to make a computer simulation package for this class of gas-treating process⁹. In a typically sparse system where the number of components are usually much more than the number of reactions the choice of unknown species concentrations to be solved for is by no means obvious and the required user intervention would make the utility of the computer simulation package more restricted than it needs be.

The purpose of the present paper is to provide a fairly general analysis of the process of gas absorption and/or desorption accompanied by equilibrium reactions keeping the above three points in mind and to provide a framework for computer simulation of such systems. In the case of single equilibrium reactions, the method presented will be shown to yield general analytical expressions for enhancement factor that reduce to expressions available in the literature derived under simplified conditions. The utility of the present method has been illustrated for a number of commonly encountered reaction schemes discussed in the literature.

3. Analysis

Consider N species denoted as $A_1, A_2, \dots, A_i, \dots, A_N$ participating in K independent instantaneous reversible reactions represented as:

$$\sum_{j=1}^N \nu_{ij} A_j = 0 \quad \text{with } i = 1 \text{ to } K \quad (1)$$

in the liquid phase, where ν_{ij} is the stoichiometric coefficient of the j th species in the i th reaction (which is taken as positive or negative depending on whether the particular species is a reactant or a product, respectively). For generality all the species will be considered as volatile in the model equations. In actual practice some of the species will be non-volatile and this case can easily be treated as a particular case of this general analysis by taking the corresponding gas-film mass transfer coefficients as zero.

Let r_i be the net rate of the i th reaction at a position x in the diffusion film (defined such that $\nu_{ij} r_i$ represent the quantity of j th species consumed per unit time per unit volume by that reaction). Then the mass balance equation for the j th species can be formulated as:

$$D_j \frac{d^2 A_j}{dx^2} = \sum_{i=1}^K \nu_{ij} r_i \quad (2)$$

with $j = 1$ to N .

Diffusivity of each species is assumed to be constant and represented by binary diffusion coefficient of that species in the bulk solvent.

The corresponding equation in dimensionless form is

$$\frac{d^2 a_j}{dy^2} = \sum_{i=1}^K \frac{\nu_{ij}}{s_j} \frac{r_i}{D_{ref} A_{ref}} \delta^2 \quad (3)$$

where A_{ref} is any suitable and chosen concentration used to non-dimensionalise the variable A_j , D_{ref} is the diffusivity of a chosen species to normalise D_j .

The boundary condition at $x = 0$ for the j th species is:

$$H_j k_{rj} (A_j^* - A_{js}) + D_j \left(\frac{dA_j}{dx} \right)_{x=0} = \sum_{i=1}^K \nu_{ij} r_{is} \quad (4)$$

where r_{is} is the net rate of the i th reaction at the gas-liquid interface and A_j^* is the equilibrium solubility corresponding to the gas-phase concentration of j th species A_{jg} ($A_j^* = A_{jg}/H_j$).

Equation (4) can be expressed in dimensionless form as:

$$\gamma_j (a_j^* - a_{js}) + \left(\frac{da_j}{dy} \right)_{y=0} = \sum_{i=1}^K \frac{\nu_{ij} \delta r_{is}}{s_j D_{ref} A_{ref}} \quad (5)$$

where $\gamma_j = H_j k_{rj} \delta / D_j$. (6)

The second boundary condition is that at $y = 1$,

$$a_j = a_{j0}. \quad (7)$$

It may be noted here that as all reactions are instantaneous, various species are at equilibrium in the bulk and only $(N - K)$ bulk concentrations can be fixed independently.

Integrating equation (3) once and using the boundary condition given by equation (5), we have:

$$\frac{da_j}{dy} = \sum_{i=1}^K \frac{\nu_{ij} G_i(y)}{s_j} - \gamma_j (a_j^* - a_{j0}) \quad (8)$$

$j = 1 \text{ to } N$

where

$$G_i(y) = \int_0^y \frac{r_i \delta^2}{D_{ref} A_{ref}} dy + \frac{r_i \delta}{D_{ref} A_{ref}}. \quad (9)$$

Integrating equation (8) between the limits 0 and 1 and using boundary condition (7) we obtain:

$$a_{j0} = \frac{1}{1 + \gamma_j} \left[\gamma_j a_j^* + a_{j0} - \sum_{i=1}^K \frac{\nu_{ij} Q_i}{s_j} \right] \quad (10)$$

with $j = 1 \text{ to } N$ and where,

$$Q_i = \int_0^1 G_i(y) dy. \quad (11)$$

Equation (10) gives the surface concentration of all the species in terms of characteristic parameters Q_1 through Q_K defined by equations (9) and (11). It is to be noted that the species concentrations are thus mapped into the K -dimensional Q parameter space. The additional K relations needed to complete the problem formulation are obtained by applying equilibrium conditions at the gas-liquid interface. Thus,

$$\prod_{j=1}^N a_{j0}^{-\nu_{jl}} = K_l (A_{ref})^{\sum_{j=1}^N \nu_{jl}} = K_l^* \quad (12)$$

with $l = 1 \text{ to } K$.

Substituting for a_{j0} and rearranging we obtain a set of K non-linear algebraic equations:

$$F_l = \log K_l^* + \sum_{j=1}^N \nu_{jl} \log \left[\frac{\gamma_j a_j^*}{\gamma_j + 1} + \frac{a_{j0}}{\gamma_j + 1} - \sum_{i=1}^K \frac{\nu_{ij} Q_i}{s_j (\gamma_j + 1)} \right] = 0 \quad (13)$$

with $l = 1 \text{ to } K$.

Equation (13) provides K equations for the unknowns Q_1 to Q_K . The dimensionless rate of absorption (or desorption) of the gaseous or volatile species j can be shown to be related to parameters Q_i by the following relation:

$$I_j = \frac{R_j}{k_L \cdot A_{\text{ref}}} = \frac{\gamma_j}{\gamma_j + 1} \left[a_j^* - a_{j0} + \sum_{i=1}^K \frac{\nu_{ij} Q_i}{s_j} \right]. \quad (14)$$

4. Illustrative applications

In the ensuing section the application of the above computational procedure is illustrated for a number of commonly encountered reaction schemes, involving both single and multiple steps.

4.1 Single step reaction schemes

For this case, $K = 1$ and hence there is only one unknown parameter Q_1 to solve for. The general expression for the dimensionless rate of absorption of a species A_j is obtained in terms of this parameter as:

$$I_j = \frac{\gamma_j}{1 + \gamma_j} \left[a_j^* - a_{j0} + \frac{\nu_{j1} Q_1}{s_j} \right]. \quad (15)$$

For a number of representative reaction schemes considered by previous workers^{1,2,4} the explicit analytical expressions for Q_1 can be easily obtained as the meaningful root of a quadratic equation in Q_1 (equation (13)). These are assembled in Table I. Given the equilibrium constant and the stoichiometry for the reaction, bulk gas phase concentrations and the gas film mass transfer coefficients of the respective volatile species, bulk liquid phase concentrations of the $(N - K)$ species, and the diffusivity ratios, it is a simple matter to calculate Q_1 and then I_j for a given scheme. Thus equation (15) (along with Table I) represents the most general analytical expression for the enhancement factor for single gas absorption coupled with a generalised single-step equilibrium reaction.

For each of the schemes in Table I, if the gas film resistances are assumed to be absent, the simplified expressions for the corresponding enhancement factors as tabulated by Danckwerts² or Chang and Rochelle⁴ result, thus validating our new approach.

Scheme 4 represents in a rather simplified manner a case of simultaneous absorption and reaction of a gaseous species A_1 accompanied by desorption of a volatile product A_2 . Also in the case of simultaneous absorption of two gases participating in two equilibrium reactions involving common reactant and product species (e.g. absorption of H_2S and CO_2 in amines¹⁰), a shift reaction of the simplified form such as scheme 4 may sometimes result. An illustrative plot of the influence of desorption of product species (characterised by parameter γ_2) on the rate of absorption of A_1 for this scheme is shown in fig. 1 for a particular case of $a_2^* = 0$, $K_1^* = 1$, $a_{10} = 0$, $\gamma_1 = 100$. The case of $\gamma_2 \rightarrow 0$ denotes a case of no product desorption and reduces to Scheme 1.

Table I
Expressions for Q_1 in single step equilibrium reactions

Sl. no.	Scheme	$Q_1(x=1)$
1.	$A_1(g) \rightleftharpoons A_2(l)$	$K_1^* \gamma_1 (1 - a_{10}) [K_1^* + 1 + \gamma_1]$
2.	$A_2(g) \rightleftharpoons 2A_1(l)$	$\frac{1}{8(1 + \gamma_1)} \left[\left\{ K_1^* + 4\sqrt{K_1^* a_{10}(1 + \gamma_1)} \right\} \right. \\ \left. + \sqrt{\left\{ K_1^* + 4\sqrt{K_1^* a_{10}(1 + \gamma_1)} \right\}^2 - 16(1 + \gamma_1) \times} \right. \\ \left. \times \left\{ K_1^* a_{10}(1 + \gamma_1) - K_1^*(\gamma_1 + a_{10}) \right\} \right]$
3.	$A_1(l) \rightleftharpoons A_2(g)$	$\frac{\gamma_1(a_{10} - a_2^2)}{1 + K_1^*(1 + \gamma_1)}$
4.	$A_1(g) \rightleftharpoons A_2(g)$	$\frac{K_1^*(1 + \gamma_1)(\gamma_1 + a_{10}) - (1 + \gamma_1)(\gamma_1 a_2^2 + K_1^* a_{10})}{1 + \gamma_1 + K_1^*(1 + \gamma_1)}$
5.	$A_1(g) \rightleftharpoons A_2(l) + A_3(l)$	$\frac{1}{2} \left[\left(a_{30} + a_{20} + \frac{K_1^*}{1 + \gamma_1} \right) \right. \\ \left. + \left\{ \left(a_{20} + a_{30} + \frac{K_1^*}{1 + \gamma_1} \right)^2 - 4K_1^* a_{10} \right. \right. \\ \left. \left. + \frac{4K_1^*}{1 + \gamma_1} (\gamma_1 + a_{10}) \right\}^{1/2} \right]$
6.	$A_1(g) + A_2(l) \rightleftharpoons A_3(l) + A_4(l)$	$\frac{1}{2 \left[\frac{K_1^*}{1 + \gamma_1} - 1 \right]} \left[\frac{K_1^*}{1 + \gamma_1} (\gamma_1 + a_{10} + a_{30}) + (a_{30} + a_{40}) \right. \\ \left. - \sqrt{\left\{ \frac{K_1^*}{1 + \gamma_1} (\gamma_1 + a_{10} + a_{30}) + (a_{30} + a_{40}) \right\}^2 - 4 \left[\frac{K_1^*}{1 + \gamma_1} - 1 \right] \times} \right. \\ \left. \times \left\{ \frac{K_1^*}{1 + \gamma_1} (a_{30}(\gamma_1 + a_{10}) - a_{30} a_{40}) \right\} \right]$

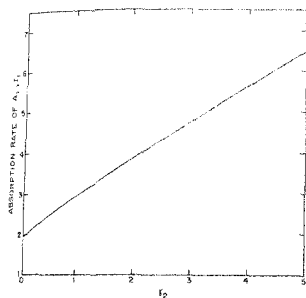


FIG. 1. The absorption rate for Scheme 4: $A_1(g) \rightleftharpoons A_2(g)$.

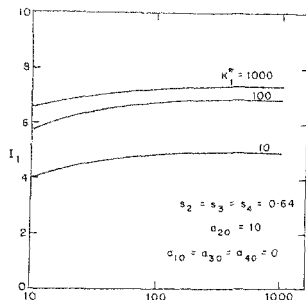


FIG. 2. Absorption rate vs γ_1 plots for Scheme 6. $A_1(g) + A_2(l) \rightleftharpoons A_3(l) + A_4(l)$

For Scheme 6 (illustrative of H_2S absorption in amines), fig. 2 shows rate of absorption of A_1 as a function of the parameter γ_1 . It is seen that for $\gamma_1 > 100$, the gas film resistance can be disregarded and the computed values of I_1 agree with the results of previous workers^{1,2}.

4.2 Multiple step reaction schemes

Gas absorption is often accompanied by a multistep equilibrium reaction such as absorption of chlorine in NaOH solution¹¹ or when multiple equilibrium reactions involve multiple absorbing/desorbing species as may happen under some conditions for simultaneous absorption of H_2S and CO_2 in amines^{10,12}. In such cases there would be K parameters Q_i ($i = 1, K$) to solve for from equation (13) written for K independent reactions. The solution of the K non-linear algebraic equations can be accomplished by any one of several computational methods available. In this work, we had used Marquardt method. The solution procedure is further aided by having recourse to the following feasibility criteria

$$\sum_{i=1}^K \frac{\nu_{ij} Q_i}{S_j} < \gamma_j a_j^0 + a_{j0} \quad (j = 1, N) \quad (16)$$

which is based on the fact that concentration of all species should be non-negative. Illustrative computations have been performed for two particular cases.

Scheme 7

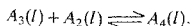
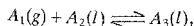


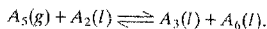
Table II
Feasibility criteria for two step equilibrium reaction Scheme 7

	Stoichiometric matrix, v_{ij}			
	A_1	A_2	A_3	A_4
Q_1, S_1	1	1	1	0
Q_2, S_2	0	1	1	1
LHS of equation (1a)	Q_1	Q_2	Q_3	Q_4
	$\gamma_1 a_{10}$	$\gamma_2 a_{20}$	$\gamma_3 a_{30}$	$\gamma_4 a_{40}$
RHS of equation (1a)	$\gamma_1 a_{10} + a_{a1}$	a_{a2}	a_{a3}	a_{a4}

This scheme, in essence, represents the case of absorption of chlorine in NaOH solutions^{3,11}. In this case, $N = 4$ and $K = 2$ so that two parameters Q_1 and Q_2 are to be solved for. Table II presents the stoichiometric matrix v_{ij} and other quantities required to evaluate the feasibility criteria and these establish a well defined region of search for the parameter values.

Illustrative computational results for a range of K_1^+ and K_2^+ values are shown in fig. 3 for $a_{10} = 0$. For the case of no gas film resistance ($\gamma_1 = 2000$), these results agree well with the analytical solutions derived by Bhattacharya and Ramachandran³ which again validates the alternative computational procedure developed in this paper.

Scheme 8



This scheme is representative of simultaneous absorption of H_2S and CO_2 in amines. Normally, H_2S absorption in amines precedes an instantaneous reversible reaction while the CO_2 absorption is accompanied by a fast, but finite rate reversible reaction¹⁰. However, Ramachandran and Sharma¹² had pointed out that under some conditions CO_2 absorption may also go into the instantaneous regime. Because of the typical interaction of the two equilibrium reactions by means of common reactants and products, suppression of the absorption of one species due to the absorption of other species depending upon the relative magnitude of the equilibrium constants takes place and has already been pointed out by Cornelisse *et al*¹⁰. Using the computational procedure presented herein similar qualitative effect of absorption of species A_1 on the absorption rate of species A_5 is shown in figs 4 and 5 through variation of gas film resistance for species A_1 and equilibrium constant of the first reaction.

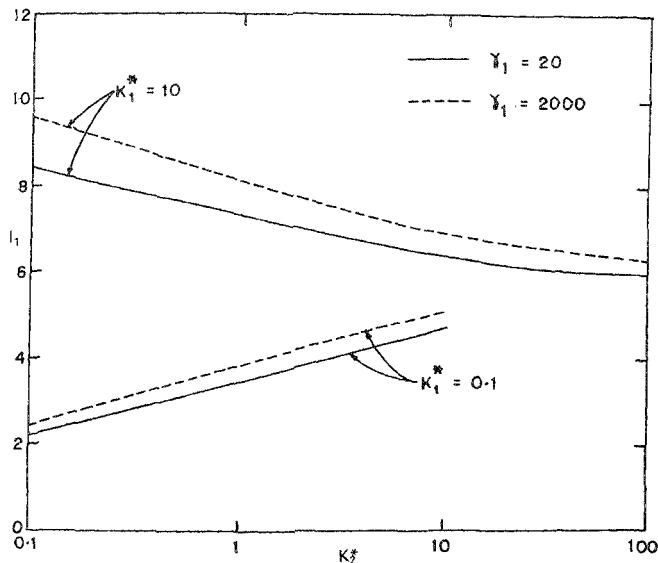


FIG. 3. Rate of absorption of A_1 vs K_2^* for Scheme 7. $A_1(g) + A_2(l) \rightleftharpoons A_3(l)$; $A_2(l) + A_3(l) \rightleftharpoons A_4(l)$

5. Conclusions

On the basis of two-film theory, a general analysis of gas absorption and/or desorption accompanied by single/multiple equilibrium reactions, which accounts for more than one volatile species and gas film resistance, has been given in this paper. The point of departure of our analysis from the classical Olander-Danckwerts treatment is the recognition of the fact that a transformation for the local concentrations of dissolved species in terms of K unique parameters characteristic of K independent reactions exists. These parameters are defined as the dimensionless double space integral of net rates of specific reactions and are expected to have finite values.

The use of this transformation allows one to develop, in a systematic manner, a simple computational procedure for predicting the 'point' rate of mass transfer at any part of the column where bulk gas and liquid phase compositions are specified. Given a matrix consisting of the stoichiometric coefficients for the given reaction scheme, diffusivity ratios, it is now possible to routinely compute the rates of absorption and/or desorption

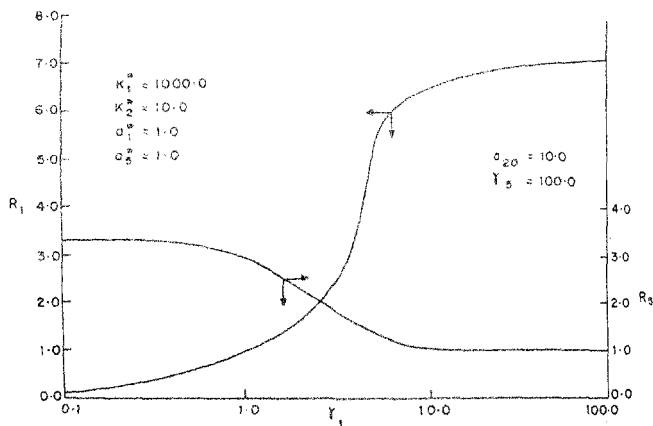
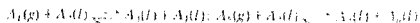


FIG. 4. Effect of absorption of species A_1 on the absorption rate of species A_2 in the Scheme



of various species of interest, with minimum user intervention. Thus the present analysis provides a framework for computer simulation of an important class of gas-treating process.

The ease with which gas film resistances can be incorporated in the new procedure compares very favourably with the cumbersome and tedious but straight-forward extension of the classical treatment of Olander-Danckwerts^{3,9}. Thus the new procedure can be used routinely for absorption or desorption accompanied by equilibrium reaction with more than one species figuring in both gas and liquid phases as well as for simultaneous absorption of reactant and desorption of product species.

Finally, it may be noted that although the mathematical treatment given in this paper is via a film theory model for interphase mass transfer, the results that would have been obtained by the theoretically more sound surface renewal theory, can be well approximated by the same film theory solutions with the diffusivity ratios replaced by their square roots.

Nomenclature

- a_i dimensionless concentration of species A_i at any point in liquid film, $A_i/A_{i,ret}$.
 a_i^* dimensionless liquid phase concentration of species A_i in equilibrium with the bulk gas.

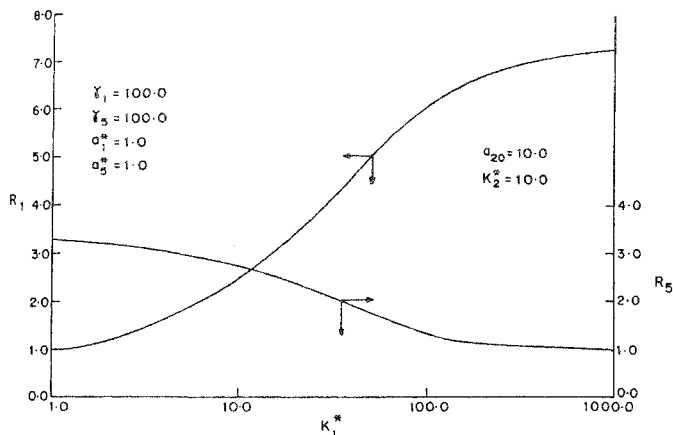
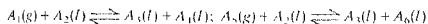


FIG. 5. Effect of equilibrium constant K_1^* on the rates of absorption of species A_1 and A_3 for the Scheme.



- $a_{j\delta}$ dimensionless concentration of A_j at interface.
 a_{j0} dimensionless concentration of A_j in the bulk liquid.
 A_j species A_j or its concentration.
 A_j^* liquid phase concentration of species A_j in equilibrium with bulk gas.
 A_{jg} concentration of A_j in bulk gas.
 $A_{j\delta}, A_{j0}$ concentration of A_j at interface and in the bulk liquid respectively.
 A_{ref} a chosen reference concentration used for normalisation.
 D_j liquid phase diffusivity for species j .
 D_{ref} a chosen diffusivity used for normalisation.
 F_l functional relationship for parameters Q_1 to Q_k (equation 13).
 $G_j(y)$ function defined by equation 9.
 H_j Henry's law constant for species j defined as A_{jg}/A_j^* .
 I_j dimensionless rate of absorption for j th species (equation 14).
 k_L liquid phase mass transfer coefficient of reference species (A_{ref}).
 k_{gl} gas film mass transfer coefficient of species j based on concentration driving force.
 K_l equilibrium constant for the l th reaction.
 K_l^* dimensionless equilibrium constant for the l th reaction (equation 12).
 K number of independent reactions.
 N total number of species taking part in all the reactions.
 Q_i parameter defined by equation 11.
 r_i local rate of i th reaction per unit volume.

r_{i0}	rate of i th reaction at the interface per unit interfacial area.
R_j	rate of absorption of j th species per unit interfacial area.
S_j	diffusivity ratio, $D_{ij}/D_{i,vt}$.
x	distance into the liquid film measured from interface.
y	dimensionless distance variable, x/δ .

Greek

γ_j	dimensionless group $H_j k_{Rj} \delta / D_{i,vt}$.
δ	film thickness.
ν_{ij}	stoichiometric coefficient of the j th species in the i th reaction.

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