Mass transfer with instantaneous chemical reaction in finite gas–liquid systems

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Abstract

The moving-boundary problem of gas absorption accompanied by an instantaneous irreversible chemical reaction in a limited gas–liquid system has been analyzed. Analytical solutions have been derived, under the restrictions of equal diffusivities of the two reacting species and stoichiometric factor of unity, for the cases of significant or negligible gas-film and surfactant-film resistances. A numerical scheme has been developed for the general case of unequal diffusivities and/or stoichiometric factor differing from unity. The effects of various parameters like film thickness, gas-bubble volume, stoichiometric factor, initial concentration in the liquid phase, etc., have been illustrated. Furthermore, the importance of the surfactant-film and gas-film resistances has also been demonstrated. The analytical solution has been found to be in agreement with the numerical solution, thus demonstrating the efficacy of the concept of negative concentration in solving such problems. ©2000 Elsevier Science S.A. All rights reserved.

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1. Introduction

Gas absorption accompanied by an instantaneous chemical reaction is important in many industrial applications. A chemical reaction may be considered to be instantaneous whenever its rate is exceedingly large compared to the rate of diffusional process, e.g. an ionic reaction which involves only a proton exchange. Some typical examples of instantaneous reactions are absorption of hydrogen sulphide in solution of sodium hydroxide, absorption of ammonia in sulfuric-acid solution, etc.

In the course of gas absorption with instantaneous reaction, the solute diffuses from the gas phase into the liquid phase and reacts immediately and completely upon contact with the reactant (B) present in the solution. A sharp reaction plane is thus formed in the liquid phase parallel to the gas–liquid interface. This constitutes a moving-boundary problem because the reaction front moves with time owing to the depletion of component B in the liquid. Thus, the problem of mass transfer with instantaneous chemical reaction is analogous to the classical Stefan's problem. Danckwerts [3] as well as Sherwood and Pigford [8] developed a theory of gas absorption with an instantaneous chemical reaction for an infinite body of a gas in contact with a semi-infinite liquid

medium. For gas absorption in thin liquid films surrounded by limited gas pockets, the effect of finite thicknesses of the media would be strongly imposed. The gas phase is actually finite in many applications, and this is not merely a more general feature of analysis.

When a surface-active agent contaminates the gas–liquid interface, the surface resistance plays an important role in determining the actual rate of mass transfer. The gas-phase resistance, although often negligible for slower reactions, is never really zero and particularly affects the overall mass-transfer rate when the gas–liquid reaction is fast. In the limiting case of an instantaneous reaction, the gas-phase resistance may become the controlling one, e.g. in absorption of ammonia in sulfuric-acid solution [2].

This paper presents a theoretical analysis of the gas absorption with an instantaneous chemical reaction of the type

A(gasphase) + Y_A B(liquid phase) → Product(liquid phase) in systems with finite thicknesses of gas and liquid media. An analytical solution has been obtained for the case of equal diffusivities of A and B in the liquid phase, and stoichiometric factor of unity, using the concept of negative concentration proposed by Sada and Ameno [7]. The solution has also been analytically extended to the more general case of significant gas-film and surfactant-film resistances.

de Lind van Wijngaarden et al. [4] and Versteeg [9] pointed out the 'equal diffusivities' condition to be a severe
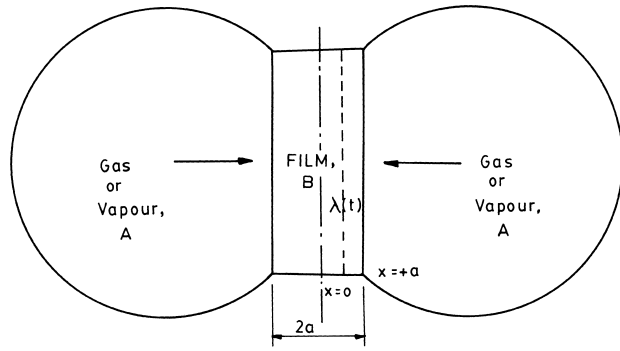
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Fig. 1. A schematic diagram of a finite gas–liquid film system.

limitation. Analytical solution of the diffusion equations for unequal diffusivities was not possible in their work, and hence numerical methods were resorted to. A numerical solution for the general problem has been obtained here using a space transformation (that immobilizes the moving-reaction front) in conjunction with the Crank-Nicolson implicit finite-difference scheme. Computational convergence difficulties often arise in this tricky problem which deceptively appears simple. A double-step iterative method has to be used to accurately obtain the converged position of the reaction front at any marked time. Development of this numerical scheme is one of the modest contributions of the present paper to the solution of moving-boundary problems.

2. Mathematical model

We consider a liquid film surrounded by gas on either side as shown in Fig. 1. Because of symmetry, we only need to analyze one half of the film. The liquid in the film is assumed to be stagnant. Let the position of the reaction front at any moment be given by $x_r(t)$. The pertinent partial differential equations and the initial and boundary conditions describing the process may be stated as follows:

Continuity of species A:

$$\frac{\partial C_A}{\partial t_c} = D_A \frac{\partial^2 C_A}{\partial x^2} \quad \text{for} \quad 0 \leq x < x_r \tag{1}$$

Continuity of species B:

$$\frac{\partial C_B}{\partial t_c} = D_B \frac{\partial^2 C_B}{\partial x^2} \quad \text{for} \quad x_r < x < a \tag{2}$$

Initial conditions:

At $t_c = 0$; $C_A = 0$ for $x = a$;

$C_B = C_{B0}$ for $x < a$ \hfill (i)

Boundary conditions:

At $x = 0$; $\dfrac{\partial C_B}{\partial x} = 0$ for $t_c > 0$ \hfill (ii)

At $x = +a$; $-V_p \dfrac{\partial C_{Ag}}{\partial t_c} = S\, D_A \dfrac{\partial C_A}{\partial x}$ \hfill (iii)

where V_p is volume of the gas pocket; for example, in the context of a foam bubble, $V_p = V_b/12$ for a regular pentagonal dodecahedron, as an idealized structural model of the real polyhedral bubble, and $C_A = K_e\, C_{Ag}$, by the assumption of equilibrium at gas–liquid interface. The volume of gas pocket can be taken as a constant for lean mixtures of component A with an inert gaseous component.

At $x = x_r(t_c)$; $C_A = 0$; $C_B = 0$ \hfill (iv)

At $x = x_r(t_c)$; $Y_A D_A \dfrac{\partial C_A}{\partial x} = -D_B \dfrac{\partial C_B}{\partial x}$ \hfill (v)

Dependence of the position of the reaction front on time renders the problem nonlinear via conditions (iv) and (v) and Eqs. (1) and (2). Although the apparent form of these equations and conditions is linear, the time-dependent boundary condition makes the moving-boundary problems inherently nonlinear(Cf. [10]).

By perfect differential

$$dC_A = \left(\frac{\partial C_A}{\partial x_r}\right)_{t_c} dx_r + \left(\frac{\partial C_A}{\partial t_c}\right)_{x_r} dt_c \tag{3}$$

and $C_A(x_r) = 0$, we obtain

$$\frac{dx_r}{dt_c} = -\frac{(\partial C_A/\partial t_c)|_{x_r}}{(\partial C_A/\partial x_r)|_{t_c}} \tag{4}$$

Eq. (4) describes the inward drift of the reaction front away from the gas–liquid interface.

2.1. Analytical solutions

2.1.1. Concept of negative concentration

Typical instantaneous concentration profiles of the solute A and liquid-phase reactant B in a quiescent liquid of a finite depth, for absorption accompanied by an instantaneous reaction, are shown in Fig. 2. Inasmuch as the component A is consumed by reaction with reactant B, the concentration of B may be regarded as a fictitious negative concentration of A [7]. Thus , the concentration of B in the spatial domain $x_r < x < a$ is taken as $C_B = -C_A$, and the diffusion coefficient is taken as a step function of the concentration, i.e. $D = D_A$ if $C_A > 0$ and $D = D_B$ if $C_A < 0$. However, if $D_A \neq D_B$ no analytical solution would still be possible. We therefore present here first the analytical results for the restricted case of equal diffusivities and of stoichiometric factor of unity. Under these constraints, the concept of negative concentration transforms the original moving-boundary problem into a linear one.

We define the following dimensionless variables:

$$X = \frac{x}{a}; \quad T = \frac{D_A t_c}{a^2}; \quad C = \frac{C_A}{C_{A0}^*} \quad \text{and} \quad q = \frac{C_{B0}}{C_{A0}^*} \tag{5}$$
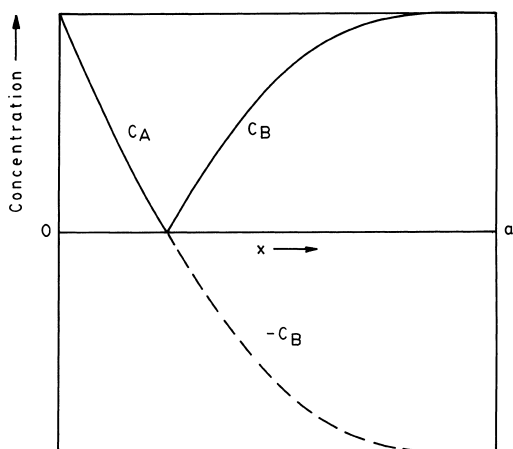
Fig. 2. Typical concentration profiles for gas absorption accompanied by an instantaneous chemical reaction.

If we introduce these dimensionless variables and substitute $C_B = -C_A$, $D_B = D_A$, and $Y_A = 1$, Eqs. (1) and (2) become identical as:

$$\frac{\partial C}{\partial T} = \frac{\partial^2 C}{\partial X^2} \tag{6}$$

The initial and boundary conditions (i)–(iii) transform into the following set:

$$T = 0; \quad C = -q; \quad 0 \le X < 1 \tag{vi}$$

$$X = 0; \quad \frac{\partial C}{\partial X} = 0; \quad T > 0 \tag{vii}$$

$$X = 1; \quad \frac{\partial C}{\partial X} = -\alpha \frac{\partial C}{\partial T}; \quad T > 0 \tag{viii}$$

Now we introduce a new variable, U, defined as

$$U = C + q \tag{7}$$

In terms of U, Eq. (6) and conditions (vi)–(viii) become

$$\frac{\partial U}{\partial T} = \frac{\partial^2 U}{\partial X^2} \tag{8}$$

$$T = 0; \quad U = 0; \quad 0 \le X < 1 \tag{ix}$$

$$X = 0; \quad \frac{\partial U}{\partial X} = 0; \quad T > 0 \tag{x}$$

$$X = 1; \quad \frac{\partial U}{\partial X} = -\alpha \frac{\partial U}{\partial T} \tag{xi}$$

Using Laplace transform technique for the linear problem (Eq. (8) and conditions (ix)–(xi)) and incorporating initial condition at boundary $X = 1$, i.e.

$$U(1, 0) = 1 + q, \tag{xii}$$

we obtain

$$\frac{C(X, T) + q}{1 + q} = \frac{\alpha}{1 + \alpha} + \sum_{n=1}^{\infty} \frac{2\alpha \exp(-P_n^2 T) \cos(P_n X)}{[1 + \alpha + \alpha^2 P_n^2] \cos(P_n)} \tag{9}$$

where P_n's are roots of

$$\tan P_n = -\alpha \, P_n \tag{10}$$

The necessary and sufficient condition, which would elegantly prove the reductionality of the present analytical solution to the asymptotic limits of physical absorption and of semi-infinite media is [1]:

$$\frac{-(\partial C_A/\partial x)|_{x=0,\,\text{Instantaneous reaction}}}{-(\partial C_A/\partial x)|_{x=0,\,\text{Physical absorption}}}\bigg|_{\text{finite system}}$$

$$= 1 + \frac{C_{B0}}{Y_A C_{A0}^*}\bigg|_{\text{Semi-infinite system}}$$

The reaction front is determined by the spatial locus corresponding to change of sign of C.

The position of the reaction front (Eq. (4)) is also described by

$$\frac{dX_r}{dT} = -\frac{(\partial C/\partial T)_{X_r}}{(\partial C/\partial X_r)_T} \tag{11}$$

Substituting for C from Eq. (9) into Eq. (11), we obtain

$$\frac{dX_r}{dT}$$
$$= \frac{\sum_{n=1}^{\infty}[2\alpha P_n^2 \exp(-P_n^2 T)\cos(P_n X_r)]/[(1 + \alpha + \alpha^2 P_n^2)\cos(P_n)]}{\sum_{n=1}^{\infty}[2\alpha P_n^2 \exp(-P_n^2 T)\sin(P_n X_r)]/[(1 + \alpha + \alpha^2 P_n^2)\cos(P_n)]} \tag{12}$$

This nonlinear ordinary differential equation is however not amenable to analytical solution and hence it needs to be solved numerically, e.g. by using the fourth-order Runge-Kutta method.

2.1.2. Amounts of gas absorbed, unreacted or reacted

The total amount of gas A absorbed by the half film is

$$M_t = \int_0^{t_c^*} D_A S \left(\frac{\partial C_A}{\partial x}\right)_{x=a} dt_c \tag{13}$$

$$\frac{M_t}{C_{A0}^* a S} = (1 + q)\alpha \left[\sum_{n=1}^{\infty} A_n - \sum_{n=1}^{\infty} A_n \exp(-P_n^2 T^*)\right] \tag{14}$$

This can be evaluated easily from Eq. (14), where

$$A_n = \frac{2\alpha^2}{(1 + \alpha + \alpha^2 P_n^2)}$$

When T^* approaches infinity, Eq. (14) reduces to

$$\frac{M_\infty}{C_{Ao}^* a S} = (1 + q)\alpha \sum_{n=1}^{\infty} A_n \tag{15}$$

Combining Eqs. (14) and (15), we obtain

$$\frac{M_t}{M_\infty} = 1 - \frac{\sum_{n=1}^{\infty} A_n \exp(-P_n^2 T^*)}{\sum_{n=1}^{\infty} A_n} \tag{16}$$

The amount of free solute present in the half film at time t_c^* is

$$M_{\mathrm{fr}} = S \int_{x_r(t_c^*)}^{a} C_A(x, t_c^*)\, \mathrm{d}x \tag{17}$$

This leads to

$$\frac{M_{\mathrm{fr}}}{C_{A0}^* a S} = \left[\frac{\alpha}{1+\alpha} - \frac{q}{1+q}\right](1+q) \sum_{n=1}^{\infty}$$

$$\times \left[\frac{2\alpha(1+q)\exp(-P_n^2 T^*)\sin(P_n X)}{(1+\alpha+\alpha^2 P_n^2)P_n \cos(P_n)}\right]_{X=X_r}^{X=1} \tag{18}$$

The amount of solute A that has reacted in the half film during time t_c^* is

$$M_r = M_t - M_{\mathrm{fr}}$$

2.2. Significant gas-film and surface-film resistances

The surface-film and gas-film resistances cannot be ignored in a number of practical gas–liquid systems. We present now the analysis of this important combined case for the restrictions of equal diffusivities and stoichiometric factor of unity. A diffuses from the bulk of gas to the surface film. The liquid-phase concentration of A at the surfactant-film-gas-interface, C_A^*, is now assumed to be in equilibrium with the interfacial gas-phase concentration C_{Agi}.

The governing differential equation is identical with Eq. (6) while the first of the boundary conditions remains the same as the condition (vii). The second boundary condition, instead of condition (iii), has to be now rewritten in dimensional form as

$$-V_p \frac{\mathrm{d}C_{Ag}}{\mathrm{d}t_c} = K_g S(C_{Ag} - C_{Agi}) = K_s S(C_A^* - C_A)$$

$$= S D_A \frac{\partial C_A}{\partial x}\Big|_{x=a} \tag{19}$$

where

$$C_A^* = K_e C_{Agi} \tag{20}$$

Eq. (20) follows from the assumption of a physical equilibrium at gas-surfactant-film interface. From the last equality in Eq. (19), we have

$$C_A^* = \frac{D_A}{K_s}\frac{\partial C_A}{\partial x}\Big|_{x=a} + C_A \tag{21}$$

while from the second and last term, we obtain

$$C_{Agi} = -\frac{D_A}{K_g}\frac{\partial C_A}{\partial x}\Big|_{x=a} + C_{Ag} \tag{22}$$

From Eqs. (21) and (22), we eliminate C_A^* and C_{Agi} using Eq. (20) and obtain

$$K_e C_{Ag} = \left[\frac{D_A}{K_s} + \frac{D_A K_e}{K_g}\right]\frac{\partial C_A}{\partial x}\Big|_{x=a} + C_A \tag{23}$$

Now, using Eqs. (19) and (23), we obtain the following dimensionless boundary condition at $X = 1$

$$-\alpha\left[\frac{\partial C}{\partial T} + \frac{1}{\beta}\frac{\partial}{\partial T}\frac{\partial C}{\partial X}\right] = \frac{\partial C}{\partial X} \tag{24}$$

where

$$\alpha = \frac{V_p}{K_e S a} \tag{25}$$

and

$$\frac{1}{\beta} = \frac{D_A}{a}\left(\frac{1}{K_s} + \frac{K_e}{K_g}\right) \tag{26}$$

Again introducing the transformation (7), we rewrite condition (24) as

$$-\alpha\left[\frac{\partial U}{\partial T} + \frac{1}{\beta}\frac{\partial}{\partial T}\frac{\partial U}{\partial X}\right] = \frac{\partial U}{\partial X} \quad \text{at } X = 1 \tag{27}$$

Further, the initial condition for the present case is the same as condition (ix).

The analytical solution of Eq. (8), subject to initial condition (ix) and boundary conditions (x) and (27), is obtained by applying the Laplace transform technique. The final form of solution is

$$\frac{C(X, T) + q}{1 + q} = \frac{\alpha}{(1+\alpha)} + \sum_{n=1}^{\infty}$$

$$\times \frac{2\alpha(\beta - \alpha P_n^2)\exp(-P_n^2 T)\cos(P_n X)}{[\beta + \alpha\beta - (2\alpha - \alpha^2 - \alpha^2\beta)P_n^2 + (\alpha^2 P_n^4/\beta)]\cos(P_n)} \tag{28}$$

where P_n's are roots of

$$\tan P_n = -\frac{\alpha\beta P_n}{[\alpha P_n^2 - \beta]} \tag{29}$$

The position of reaction front is obtained from Eq. (11) and the following expressions:

$$\frac{\partial C}{\partial T} = (1+q)\sum_{n=1}^{\infty}$$

$$\times \frac{2\alpha(\beta - \alpha P_n^2)(-P_n^2)\exp(-P_n^2 T)\cos(P_n X)}{[\beta + \alpha\beta - (2\alpha - \alpha^2 - \alpha^2\beta)P_n^2 + (\alpha^2 P_n^4/\beta)]\cos(P_n)} \tag{30}$$

$$\frac{\partial C}{\partial X_r} = (1+q)\sum_{n=1}^{\infty}$$

$$\times \frac{(-2\alpha)(\beta - \alpha P_n^2)P_n \exp(-P_n^2 T)\sin(P_n X)}{[\beta + \alpha\beta - (2\alpha - \alpha^2 - \alpha^2\beta)P_n^2 + (\alpha^2 P_n^4/\beta)]\cos(P_n)} \tag{31}$$

The analytical solution of Eq. (11) incorporating expressions (30) and (31) is however not possible, and hence the

fourth-order Runge-Kutta method has been used to evaluate the position of the reaction front. The total amount of gas absorbed by the half film and that unreacted at time T^* are easily evaluated from Eqs. (13) and (17), respectively, together with Eq. (28).

3. Numerical solution of the general problem ($D_A \neq D_B$; $Y_A \neq 1$)

The general problem of mass transfer with instantaneous chemical reaction, not being amenable to any analytical solution, has been solved numerically using the front-fixing method. The resulting nonlinear differential equations for the two regions are solved separately using the Crank–Nicolson implicit finite-difference scheme. The solutions for the two regions (i.e. concentration profiles of A and B) are coupled through the boundary conditions at the location of the reaction front. Thomas algorithm has been used to solve the tridiagonal system of finite-difference equations. The numerical procedure is iterative, marking the time, in order to obtain the convergent values of X_r and $\dot{X}_r$.

Region Containing A ($x_r(t) < x \leq a$)

The moving boundary is fixed by means of the following coordinate transformation:

$$\xi = \frac{a - x}{a - x_r(t)} \quad \text{such that } 0 < \xi \leq 1 \tag{32}$$

and the moving boundary is fixed at $\xi = 1$. With this transformation, the species continuity equation for A becomes

$$\frac{\partial C_A}{\partial t_c} = \frac{D_A(\partial^2 C_A/\partial \xi^2)}{(a - x_r(t))^2} - \frac{\xi \dot{x}_r(t)(\partial C_A/\partial \xi)}{a - x_r(t)}$$
$$\text{for } 0 < \xi \leq 1 \tag{33}$$

Region Containing B ($0 \leq x < x_r$)

The moving boundary is fixed in this region by the Landau transformation

$$\xi = \frac{x}{x_r(t)} \tag{34}$$

such that $0 \leq \xi < 1$. The species continuity equation for B becomes

$$\frac{\partial C_B}{\partial t_c} = \frac{D_B}{(x_r(t))^2} \frac{\partial^2 C_B}{\partial \xi^2} + \frac{\xi \dot{x}_r(t)}{x_r(t)} \frac{\partial C_B}{\partial \xi} \quad \text{for} \quad 0 \leq \xi < 1 \tag{35}$$

In terms of dimensionless time T, Eqs. (33) and (35) become

$$\frac{\partial C_A}{\partial T} = \frac{1}{(1 - X_r(T))^2} \frac{\partial^2 C_A}{\partial \xi^2} - \frac{\xi \dot{X}_r(T)}{(1 - X_r(T))} \frac{\partial C_A}{\partial \xi} \tag{36}$$

and

$$\frac{\partial C_B}{\partial T} = \frac{p}{(X_r(T))^2} \frac{\partial^2 C_B}{\partial \xi^2} + \frac{\xi \dot{X}_r(T)}{X_r(T)} \frac{\partial C_B}{\partial \xi} \tag{37}$$

where

$$p = \frac{D_B}{D_A}; \quad X_r = \frac{x_r}{a}; \quad \text{and} \quad \dot{X}_r(T) = \frac{dX_r(T)}{dT}$$

The corresponding boundary conditions are as follows:

$$C_A(\xi, 0) = 0; \quad C_B(\xi, 0) = C_{B0} \quad \text{for } T = 0 \tag{38}$$

$$\alpha \frac{\partial C_A}{\partial T} = \frac{1}{(1 - X_r(T))} \frac{\partial C_A}{\partial \xi} \quad \text{for } \xi = 0 \text{ and } T \geq 0 \tag{39}$$

$$C_A = 0; \quad C_B = 0 \quad \text{at } \xi = 1 \text{ and for } T \geq 0 \tag{40}$$

$$\frac{Y_A}{(1 - X_r(T))} \frac{\partial C_A}{\partial \xi} = \frac{p}{X_r(T)} \frac{\partial C_B}{\partial \xi} \quad \text{at } \xi = 1 \text{ and for } T \geq 0 \tag{41}$$

$$\frac{\partial C_B}{\partial \xi} = 0 \quad \text{at } \xi = 0 \text{ and for } T \geq 0 \tag{42}$$

Further, the equation for the position of reaction front can be rewritten as

$$\frac{dX_r}{dT} = -(1 - X_r) \frac{(\partial C_A/\partial T)|_{X_r}}{(\partial C_A/\partial X_r)|_T} \tag{43}$$

Using Crank–Nicolson implicit finite difference scheme, the Eqs. (36) and (37) are discretized into the following pair:

$$-rC_{A_{i+1}}^{j+1} + [2r + 2(1 - X_r^j)^2]C_{A_i}^{j+1} - rC_{A_{i-1}}^{j+1}$$
$$= (r - A_j)C_{A_{i+1}}^j + [2(1 - X_r^j)^2 - 2r]C_{A_i}^j$$
$$+ (r + A_j)C_{A_{i-1}}^j \tag{44}$$

where

$$A_j = \frac{\xi_i \dot{X}_r^j (1 - X_r^j)\delta T}{\delta \xi}$$

and

$$r = \frac{\delta T}{(\delta \xi)^2}$$

and

$$-prC_{B_{i+1}}^{j+1} + [2pr + 2(X_r^j)^2]C_{B_i}^{j+1} - prC_{B_{i-1}}^{j+1}$$
$$= [pr + A_j]C_{B_{i+1}}^j + [2(X_r^j)^2 - 2pr]C_{B_i}^j$$
$$+ (pr - A_j)C_{B_{i-1}}^j \tag{45}$$

where

$$A_j = \frac{\xi_i X_r^j \dot{X}_r^j \delta T}{\delta \xi}$$

The boundary conditions become

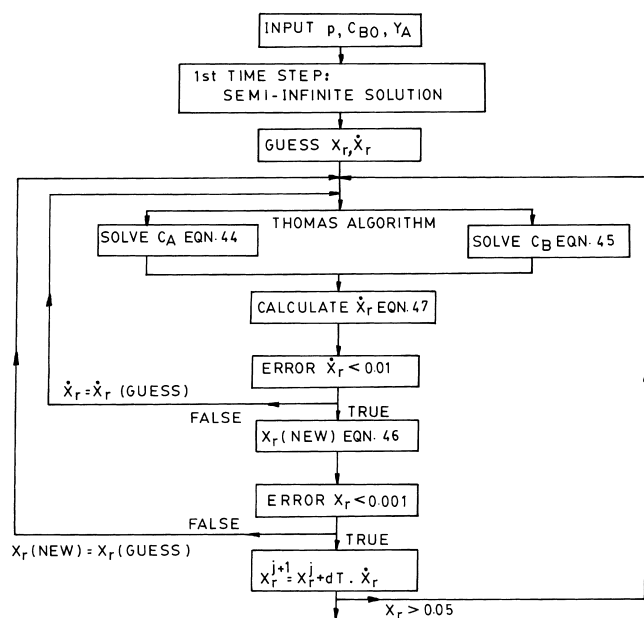$$\frac{1}{X_r^j} = 1 + \frac{Y_A(C_{AMD}^j - C_{AMD-1}^j)}{(C_{BMD}^j - C_{BMD-1}^j)} \tag{46}$$

Fig. 3. Flow-chart of the algorithm used in the numerical solution of the moving-boundary problem.
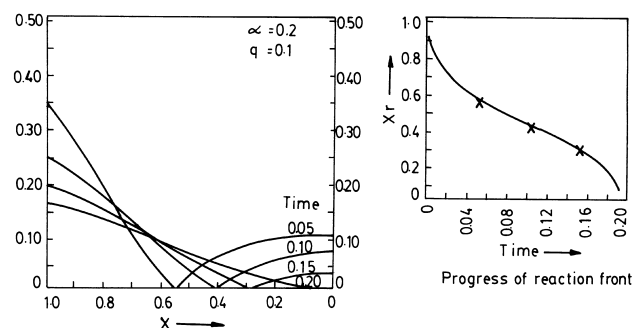

Fig. 4. Evolution of the reaction front and the concentration profiles of A and B within the liquid film with time.

At each time, the concentration profiles are computed iteratively until converged values of X_r and $\dot{X}_r$ are obtained.

4. Results and discussion

4.1. Analytical solution

As the reactive gas A comes in contact with the liquid-phase reactant B at the interface, the two species react quickly and completely. For some short but finite time the reaction front would remain at the interface. If the supply of A is sufficiently high, we would see the reaction front moving towards the center of the film. Fig. 4 illustrates this situation and shows how the two concentration profiles and the advancing front position evolve with time of contact between the gas and liquid film. Once the reaction front reaches the center of the film, all of B would be consumed and the problem would then reduce to one of pure diffusion of A, if B is the limiting component. The component A would finally attain the equilibrium value of concentration. The positions of the reaction front calculated from the numerical solution of Eq. (12) are in perfect agreement with those calculated from the sign change of the concentration profile, as shown on the right hand side in Fig. 4. Here, the crosses represent front positions determined from sign changes of the concentration profile. Thus, the present method accurately predicts the position of the reaction front and also the concentration profile in the film. When either A or B gets completely consumed, the solution reduces to that for the pure diffusion problem. The total amount of gas A absorbed by the film, the amount of A reacted, and that which remained unreacted in the film have also been computed along with their variations with time.

$$\dot{X}_r^j = -(1 - X_r^j)\frac{[C_{\mathrm{AMD}}^j - C_{\mathrm{AU}}^{j-1}]}{[C_{\mathrm{AMD}}^j - C_{\mathrm{AMD}-1}^j]}\frac{\delta\xi}{\delta T} \tag{47}$$

where

$$U = \frac{1 - X_r^{j-1}}{1 - X_r^j}$$

and

$$\alpha\frac{[C_{\mathrm{A}i}^{j+1} - C_{\mathrm{A}i}^j]}{\delta T} = \frac{1}{(1 - X_r^j)}\frac{[C_{\mathrm{A}i+1}^j - C_{\mathrm{A}i-1}^j]}{\delta\xi} \tag{48}$$

$C_{\mathrm{A}-1}^j$ is a fictitious quantity which is eliminated using Eqs. (44) and (48). This leads to

$$C_{\mathrm{A}0}^{j+1} = C_{\mathrm{A}0}^j - \frac{2\delta T[C_{\mathrm{A}0}^j - C_{\mathrm{A}1}^j]}{\delta\xi(1 - X_r^j)[(1 - X_r^j)\delta\xi + 2\alpha]} \tag{49}$$

3.1. Algorithm

The flow-chart of the algorithm is shown in Fig. 3. For the first time step, the semi-infinite solution is used. For the subsequent times, at each step there are $(N+1)$ nodal points at which concentrations have to be determined in each of the two regions, i.e. of A and B, respectively. $(N-1)$ equations for A are given by Eq. (44) and additional two equations are obtained from the left and right hand boundary conditions. Similarly, for B, Eq. (45) and the two boundary conditions furnish the required number of equations. For A, these boundary conditions are Eq. (49) for L.H.B.C. and $C_{\mathrm{A}}^j = 0$ for R.H.B.C. whereas for B the L.H.B.C. is $C_{\mathrm{B}0}^j = C_{\mathrm{B}1}^j$ and R.H.B.C. is $C_{\mathrm{B}}^j = 0$.

4.1.1. Effect of initial solute concentration, $C_{\mathrm{B}0}$, on the movement of reaction front

For large $C_{\mathrm{B}0}$, the reaction front moves backward towards the surface of the film after first having advanced towards the center of the film. Initially the rate of diffusion of A is large owing to the steep concentration gradients. This
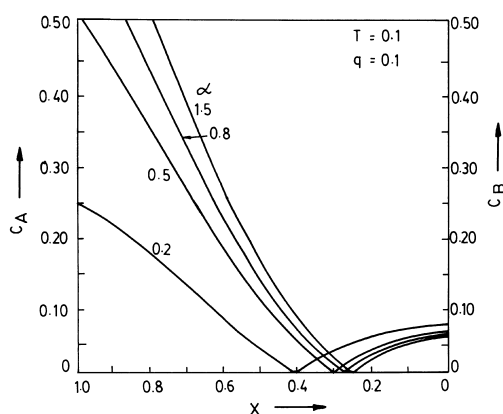
Fig. 5. Effect of film thickness, gas-pocket volume, and equilibrium distribution factor on the evolution of concentration profiles and the reaction front with time.

causes the reaction front to move initially towards the center. This movement is however halted and even reversed as the component A in the gas gets depleted and as the supply of A to the liquid gets diminished. Concentration of B being still large in the central region of the liquid film, the species B diffuses towards the region containing unreacted A and gradually depletes that region of free A in the process. This, in effect, pushes the reaction front back towards the gas–liquid interface. If A is the limiting component, the reaction front would eventually return right back to the gas–liquid interface when all of A has been exhausted. For still larger C_{B0} ($q > 0.4$), the entire amount of A will be reacted at the reaction front which itself would remain stationary at the gas–liquid interface owing to the overwhelming excess of the species B in the liquid film.

4.1.2. Effect of film thickness, gas-pocket volume and equilibrium-distribution factor

In the present dimensionless formulation, the film thickness, a, gas pocket volume, V_p, and the equilibrium distribution factor, K_e, are combined into a single parameter, α. Fig. 5 shows the concentration profile in the half film for a range of α values typical of practical gas–liquid systems. At time $T = 0.1$, an increase in α value from 0.2 to 0.8 results in a change in position of reaction front from 0.4 to 0.26 indicating the increase in the extent of B consumed, and hence in the extent of absorption of component A. The enhancement in the rate of absorption of component A with an increase in α follows an asymptotic behaviour, i.e. an increase in α from 0.2 to 0.5 changes X_r from 0.4 to 0.3 whereas a further increase in α from 0.5 to 0.8 shows a change in X_r from 0.30 to 0.26 only. Thus, it shows a limiting influence of this parameter on the gas absorption rate in the liquid film.

Fig. 6 shows how the nondimensionalized flux of A varies with time and the effect of the parameter α on its temporal variation.
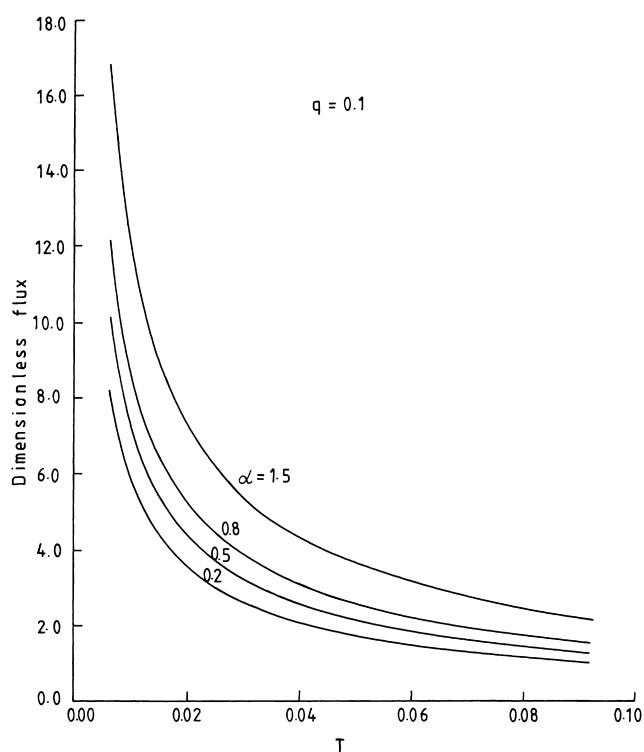

Fig. 6. Effect of film thickness, gas-pocket volume, and equilibrium distribution factor on the variation of nondimensionalized flux of A with time.
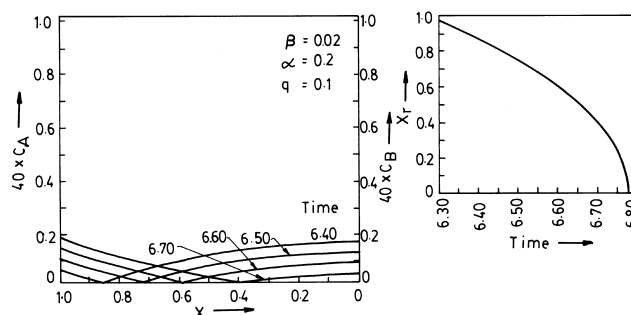

Fig. 7. Effect of gas-phase and surfactant-film mass transfer resistances on the concentration profiles.

4.1.3. Effect of surfactant and gas-film resistances

The surfactant-film resistance and the gas-film resistance show a marked effect on the rate of gas absorption. The gas film mass transfer coefficient, K_g, was estimated from the asymptotic value of Sherwood number of 6.58. The values of surfactant-film mass transfer coefficient for different surfactants such as Teepol, Triton X-100, sodium lauryl sulphate, etc. were taken from the literature [5,6]. The concentration profiles within the film for various values of β have been shown in Figs. 7–9. Obviously, the time for the same amount of A to be absorbed decreases as β is increased. Fig. 10 shows how the time for complete consumption of B depends on β. It is evident from this figure that for $\beta > 10$, the concentration profiles would be identical with those obtained
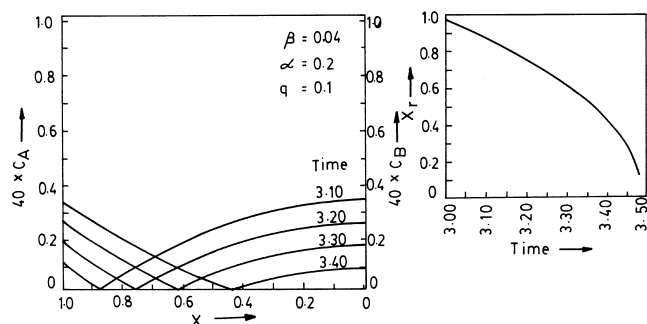
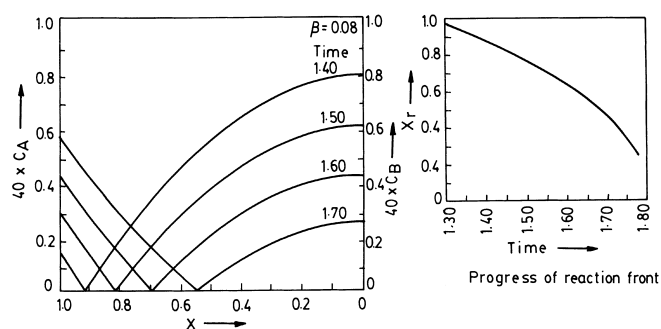Fig. 8. Effect of gas-phase and surfactant-film mass transfer resistances on the concentration profiles.

Fig. 11. Comparison of the numerical simulation with the analytical solution for the special case of equal diffusivities and unit stoichiometric factor.

Fig. 9. Effect of gas-phase and surfactant-film mass transfer resistances on the concentration profiles.

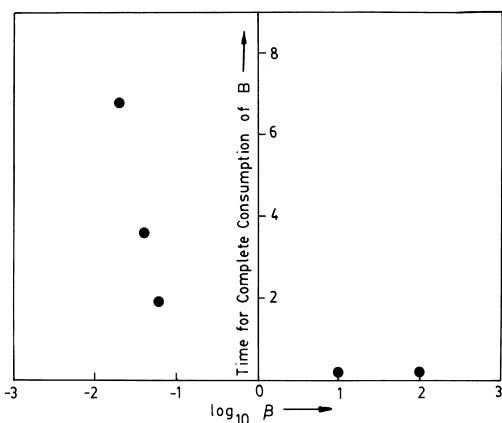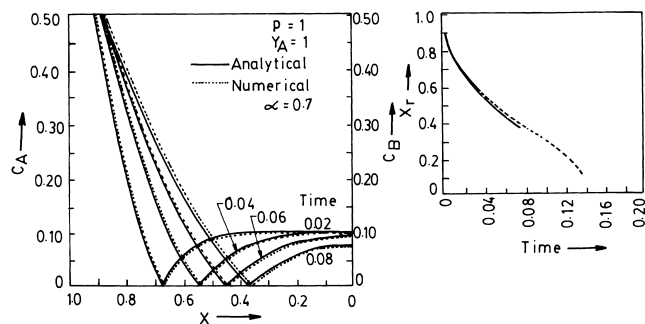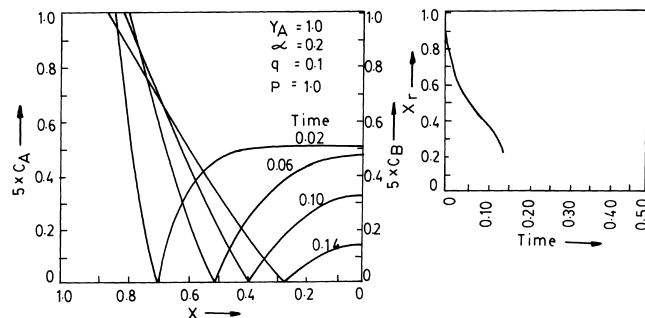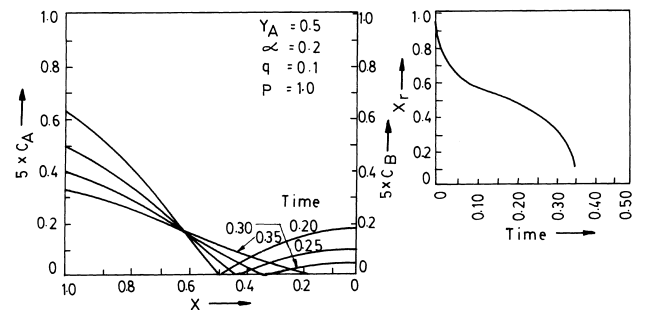Fig. 12. Effect of stoichiometric factor on the evolution of the concentration profiles and locus of reaction front.

Fig. 10. Dependence of the time of complete consumption of B on gas-film and surfactant-film resistances.

4.2. Numerical simulation

The accuracy of the numerical simulation procedure proposed in this paper has been assessed in Fig. 11. The numerical solution of the absorption problem involving instantaneous reaction, with equal diffusivities for species A and B and stoichiometric factor of unity, is in a close agreement with the analytical solution as shown in these figures. This agreement between the two solutions may be regarded as an endorsement on the authenticity and accuracy of each of these solutions.

4.2.1. Effect of stoichiometric factor Y_A

Fig. 12 shows the concentration profiles as well as the evolution of reaction front over time for $Y_A = 0.5$ and 1.0. The reaction front versus time profiles in the two cases are

for no gas-film and surface-film resistances, absorption rates becoming independent of β for greater values of the latter. Under these conditions, the liquid-phase resistance would be the sole significant resistance influencing the gas absorption. It is found from our calculations that the major contribution to the overall resistance comes from the gas-film resistance in the range of β values from 0.02 to 0.1. For $0.1 < \beta < 10$, all the three resistances would be contributory.

similar in nature, but the time gradients of the reaction front position are very steep for $Y_A = 1.0$. The nondimensional time taken by the reaction front to reach the center of the liquid film is 0.36 for $Y_A = 0.5$ against only 0.2 for $Y_A = 1.0$. This may be rationalized as follows: Twice the number of moles of A will have to diffuse for complete consumption of B in case of $Y_A = 0.5$ against that for $Y_A = 1.0$. Thus, for $Y_A = 0.5$, the time for the reaction front to reach the center is expected to be approximately twice as large as that for $Y_A = 1.0$. This rationale is clearly borne out by the above results.

5. Conclusions

An exhaustive analysis of the problem of gas absorption accompanied by an instantaneous chemical reaction in finite gas–liquid systems has been performed using analytical and numerical approaches. The new analytical solutions for the special case of equal diffusivities and unit stoichiometric factor have also been demonstrated to illustrate the behavior of finite systems involving moving reaction fronts. Typical applications of these theoretical advances would be in the analyses of foam-bed reactors and other chemical-engineering or materials-science systems involving stagnant liquid or solid films exposed to finite immiscible liquid or gas pockets.

6. Notation

a	half-film thickness, m
A	component diffusing from the gas phase, or functions defined in Eqs. (44) and (45)
B	component in liquid phase
C	concentration, k mol m^{-3}, or dimensionless concentration
D	diffusion coefficient, $\text{m}^2 \text{ s}^{-1}$
i	index (equals 0,1,2,.....)
j	index (equals 0,1,2,....)
K_e	distribution factor, dimensionless
K	mass-transfer coefficient, m s^{-1}
M	amount of A in a half film, k mol
n	index for roots (equals 1,2,...)
p	ratio of diffusivities (equals D_B/D_A), dimensionless
P	nonzero root of transcendental Eq. (10) or Eq. (29), s^{-1}
q	ratio of initial concentration of B to initial saturation concentration of A in liquid, dimensionless
r	diffusion number, defined in Eq. (44), dimensionless
S	surface area of the liquid film, m^2
t	time, s
T	nondimensionalized time
U	parameter defined in Eq. (47), dimensionless
V	volume, m^3
x	Cartesian coordinate, or position, m
X	nondimensionalized Cartesian coordinate or position, dimensionless
Y_A	moles of liquid-phase reactant B which react per mole of A, dimensionless

6.1. Greek letters

α	dimensionless parameter (equals V_p/K_e S a)
β	dimensionless parameter defined in equation (26)
ξ	space transformation defined in Eqs. (32) and (34), dimensionless

6.2. Subscripts

A	of gas-phase reactant
b	of bubble
B	of liquid-phase reactant
c	of contact
e	equilibrium
fr	free at $t_c = t_c*$
g	in gas phase
i	i th
j	j th
n	n th
r	reacted at $t_c = t_c*$
0	initial
∞	at infinite time of contact

6.3. Superscripts

i	at interface
j	j th
*	saturation or total rate of change with time
$\bullet$	rate of change with time

6.4. Prefix

δ	step size

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