

学術情報リポジトリ

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メタデータ	言語: eng
	出版者:
	公開日: 2010-04-06
	キーワード (Ja):
	キーワード (En):
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URL	https://doi.org/10.24729/00008655

Gas Absorption Accompanied by an Irreversible Second-Order Reaction with a Volatile Reactant

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(Received June 15, 1979)

The problem of gas absorption accompanied by an irreversible second-order reaction with a volatile reactant has been considered. An approximate analytical solution for the reaction factor has been derived on the basis of the film theory and has been compared with the numerical solution. It has been shown that the present approximate solution is in good agreement with the numerical solution.

1. Introduction

Gas absorption accompanied by chemical reaction with a volatile reactant in the liquid phase is a process often encountered in the chemical industry. Some typical examples of industrial importance are absorption of carbon dioxide into aqueous ammonia solutions, chlorination of lower olefines, oxidation of lower aldehydes, etc. Recently, Pangarkar¹) has considered this problem and presented an approximate analytical solution for the reaction factor based on the assumption of a linear concentration profile for the volatile reactant in the liquid.

The purpose of this paper is to show that the approximate method employed by Hikita et al.²⁾ to obtain the approximate analytical solution for the simultaneous absorption of two gases which react between themselves in a liquid can be used satisfactorily for the present problem, yielding much more accurate values of the reaction factor than the Pangarkar's approximate solution¹⁾.

2. Approximate Solution

Let us consider the case where a solute gas A dissolves into the liquid and then reacts with a volatile reactant B, which is already present in the liquid phase, according to the following irreversible reaction

$$A + \nu B \rightarrow \text{products.}$$
 (1)

For simplicity, the reaction is assumed to be second order, i.e. (1,1)th order, although the extension to the case of an (m,n)th-order reaction is straightforward. It is also assumed that there is no gas-phase resistance for the mass transfer of the solute gas A,

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but that the gas-phase resistance for the volatile reactant B is not negligible, as assumed by Pangarkar¹⁾. Further, the film theory is used as a mass transfer model to analyze the present problem. Typical concentration profiles of A and B for this case are shown in Fig. 1.



Fig. 1. Concentration profiles for solute gas A and volatile reactant B.

The differential equations describing the diffusion of A and B in the liquid, based on the film theory, are given by

$$D_A \frac{\mathrm{d}^2 A}{\mathrm{d}x^2} = kAB \tag{2}$$

and

$$D_B \frac{\mathrm{d}^2 B}{\mathrm{d}x^2} = \nu k A B . \tag{3}$$

The boundary conditions are

 $x = 0 \quad ; \quad A = A_i, \quad B = B_i, \tag{4a}$

$$D_B(\mathrm{d}B/\mathrm{d}x) = H_B k_{GB}(B_i - B^*), \qquad (4b)$$

$$x = x_f$$
; $A = 0$, $B = B_0$. (5)

The concentration profiles of A and B in the liquid may be obtained by solving Eqs. (2) and (3) under conditions (4) and (5). The reaction factor for A can then be obtained from

$$\beta = -(x_f/A_i) (dA/dx)_{x=0} .$$
 (6)

Eqs. (2) and (3) are nonlinear and cannot be solved analytically. Hence we derive an approximate solution as follows.

Elimination of the kinetic terms from Eqs. (2) and (3) gives

$$D_A \frac{\mathrm{d}^2 A}{\mathrm{d}x^2} = \frac{D_B}{\nu} \frac{\mathrm{d}^2 B}{\mathrm{d}x^2}.$$
 (7)

Integrating this equation twice and using boundary conditions (4a) and (5), we obtain the following relationship between the concentrations of the solute gas A and the volatile reactant B

$$\frac{B}{B_0} = 1 + \frac{1}{rq} \left(\frac{A}{A_i}\right) - \left(1 + \frac{1}{rq} - \frac{B_i}{B_0}\right) \left(1 - \frac{x}{x_f}\right), \tag{8}$$

where

$$r = D_B/D_A , \qquad (9)$$

$$q = B_0 / \nu A_i . \tag{10}$$

Substituting Eq. (8) into the right-hand side of Eq. (2), the following differential equation is obtained

$$D_A \frac{d^2 A}{dx^2} = kAB_0 \left[1 + \frac{1}{rq} \left(\frac{A}{A_i}\right) - \left(1 + \frac{1}{rq} - \frac{B_i}{B_0}\right) \left(1 - \frac{x}{x_f}\right)\right].$$
(11)

Here, it is assumed that the concentration profile of A in the liquid film is linear and can be approximated by

$$A = A_i + (dA/dx)_{x=0}x = A_i - \beta A_i(x/x_f).$$
(12)

This linearized concentration profile has been used successfully in our previous paper²). Rearranging Eq. (12), we obtain

$$x/x_{f} = [1 - (A/A_{i})]/\beta.$$
(13)

Substitution of this expression into Eq. (11) leads to

$$D_A \frac{d^2 A}{dx^2} = k B_0 \left[\left(\frac{a}{A_i} \right) A^2 - \left(a - \frac{B_i}{B_0} \right) A \right], \qquad (14)$$

with

$$a = \frac{1}{rq} - \frac{1}{\beta} \left(1 + \frac{1}{rq} - \frac{B_i}{B_0} \right).$$
(15)

Here we linearize Eq. (14) by making the following approximation

$$A^2 = (2/3)A_i A . (16)$$

This method of approximation was originally suggested by Hikita and Asai³⁾ for the analysis of gas absorption accompanied by an irreversible (m,n)th-order reaction and has been widely used with sufficient accuracy to linearize the nonlinear differential equations in many problems in chemical absorption. Substituting Eq. (16) into Eq. (14), we obtain

$$D_A \frac{d^2 A}{dx^2} = k B_0 \left(\frac{B_i}{B_0} - \frac{a}{3}\right) A .$$
 (17)

The equation now reduces to a form which can be solved analytically. The solution of

Eq. (17) under conditions (4a) and (5) gives the following expression for the reaction factor for A

$$\beta = \frac{\gamma \eta}{\tanh \gamma \eta} , \qquad (18)$$

where γ and η are the dimensionless parameters and are defined as

$$\gamma = \sqrt{kB_0/D_A} x_f = \sqrt{kB_0D_A}/k_L , \qquad (19)$$

$$\eta = \sqrt{\frac{B_i}{B_0} - \frac{1}{3} \left[\frac{1}{rq} - \frac{1}{\beta} \left(1 - \frac{B_i}{B_0} + \frac{1}{rq} \right) \right]} .$$
 (20)

In order to predict the reaction factor, it is necessary to know the interfacial concentration B_i of the reactant B. This value is given by the following expression¹⁾

$$\frac{B_i}{B_0} = \frac{\left[(1+rq-\beta)/rq\right] + (H_B k_{GB}/k_{LB}) (B^*/B_0)}{1+(H_B k_{GB}/k_{LB})}, \qquad (21)$$

which can be obtained by integrating Eq. (7) twice under conditions (4b) and (5). This equation and the above Eqs. (18) to (20) constitute the approximate solution of the reaction factor in the case where the gas-phase resistance for B is present.

When the value of $H_B k_{GB}/k_{LB}$ is very large, practically no gas-phase resistance exists and B_i is nearly equal to B^* as seen from Eq. (21). On the other hand, when the value of $H_B k_{GB}/k_{LB}$ is very small, the reactant B can be regarded as being nonvolatile and Eq. (21) reduces to the well-known expression obtained by van Krevelen and Hoftijzer⁴⁾ for absorption of a single solute gas A accompanied by an irreversible secondorder reaction with a nonvolatile reactant B.

3. Comparison with Numerical Solution

Figures 2 and 3 show the comparison between the approximate and numerical solutions for the reaction factor obtained by the present authors for the cases of rq = 19 and various values of $H_B k_{GB}/k_{LB}$ and B^*/B_0 . The numerical solution was obtained by the Runge-Kutta method. The approximate analytical solution obtained by Pangarkar¹) by assuming a linear concentration profile in the liquid film for the volatile reactant B is also shown in Figs. 2 and 3. As shown in Fig. 3, the comparison for the case of $B^* \neq 0$ is limited to the region where the concentration gradient of B at the gas-liquid interface is positive and the absorption of B in the gas phase into the liquid phase does not take place. As can be seen in these two figures, the present approximate solution is in good agreement with the numerical solution. The maximum deviation from the numerical solution occurs when $H_B k_{GB}/k_{LB} \rightarrow \infty$ and $B^*/B_0 = 0$ and is only about 7.0%. The accuracy of the present approximate solution increases with increasing B^*/B_0 and decreasing $H_B k_{GB}/k_{LB}$. Pangarkar's approximate solution¹ is also close



Fig. 2. Effect of $H_B k_{GB} / k_{LB}$ on reaction factor: rq = 19, $B^* / B_0 = 0$.



Fig. 3. Effect of B^*/B_0 on reaction factor: rq = 19, $H_B k_{GB}/k_{LB} \rightarrow \infty$.

to the numerical solution. However, Pangarkar's solution contains the modified Bessel functions of fractional order and is troublesome to use. Further, when $H_B k_{GB}/k_{LB} \rightarrow \infty$ and $B^*/B_0 = 0$, Pangarkar's solution does not lead to the correct asymptotic reaction factor for the limiting case of $\gamma \rightarrow \infty$, i.e. the reaction factor for absorption accompanied by an irreversible instantaneous reaction, which is given by

$$\beta_{\infty} = 1 + rq \,. \tag{22}$$

From the results described above, it may be concluded that the present approximate solution is superior in the ease of use to Pangarkar's approximate solution and can be used with satisfactory accuracy for engineering calculations.

Notation

A_i	: interfacial concentration of solute gas A, g-mol/cm ³
B _i	: interfacial concentration of reactant B, g-mol/cm ³
B ₀	: liquid bulk concentration of reactant B, g-mol/cm ³
<i>B</i> *	: concentration of reactant B in equilibrium with bulk gas, p_B/H_B , g-mol/ cm ³
D _A , D _B	: liquid-phase diffusivities of solute gas A and reactant B, cm ² /sec
H _B	: Henry's law constant for reactant B, atm cm ³ /g-mol sec
k	: second-order reaction rate constant, cm ³ /g-mol sec
k _{GB}	: gas-phase mass transfer coefficient for reactant B, g-mol/cm ² sec atm
k _L	: liquid-phase mass transfer coefficient for solute gas A, D_A/x_f , cm/sec
k _{LB}	: liquid-phase mass transfer coefficient for reactant B, D_B/x_f , cm/sec
p _B , p _{Bi}	: partial pressures of reactant B in bulk gas and at gas-liquid interface, atm
q	: concentration ratio, $B_0/\nu A_i$
r	: diffusivity ratio, D_B/D_A
x	: distance from interface into liquid, cm
x _f	: liquid film thickness, cm
Greek lett	ers

β : reaction factor for solute gas A
 β_∞ : reaction factor for absorption with an irreversible instantaneous reaction
 γ : dimensionless parameter defined by Eq. (19)
 η : dimensionless parameter defined by Eq. (20)
 ν : stoichiometric coefficient for reaction (1)

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