GAS ABSORPTION ACCOMPANIED BY A TWO-STEP REVERSIBLE AND IRREVERSIBLE CONSECUTIVE REACTION INTO FINITE LIQUID

— VARIATION OF THE ENHANCEMENT FACTOR WITH THE ORDER OF REACTION* —

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The film theory solution is presented for gas absorption with two-step reversible and irreversible consecutive reaction, \(2A \rightarrow A^* + A\) (a) and \(A^* + B \rightarrow P\) (b), when the volume of the main body of the liquid is finite. The enhancement factor depends on the volume of \(a_0 = k_mC_0^{n-1}/k_A C_{m'}^{n-1}\). For a small value of \(\sqrt{M_m} = (\sqrt{k_m C_0^{n-1} D_3(k_3)}\), the variation of the enhancement factor between those accompanied by the \(m\)-th and the \((m-m')\)-th order reaction can be elucidate by varying the value of \(a_0\) from zero to infinity. Further, the enhancement factor for gas absorption accompanied by consecutive reaction (a) and (b) is derived by the van Krevelen approximation. For a small value of \(\sqrt{M_m}\), the enhancement factor also shifts between those accompanied by the \(m\)-th and the \((m-m'-1)\)-th order reaction as the value of \(a_0\) varies from zero to infinity.

Introduction

In the previous papers\(^\text{(2,3)}\) we discussed gas absorption accompanied by a complex reaction in terms of the film theory. The reaction scheme considered was that a gaseous species A being dissolved undergoes reaction with a nonvolatile reactant B in the liquid phase by \(2A \rightarrow A^* + A\), \(R_a = k_mC_0^{n-1} C_A^{n-1}\) (a) and \(A^* + B \rightarrow P\), \(R_b = k_bC_{m'}^{n-1}\) (b). The overall reaction rate of the solute A can be expressed by

\[
R_a = k_mC_0^{n-1} + k_mC_0^{n-1}/k_A C_{m'}^{n-1}
\]

This type of reaction is known as the Michaelis-Menten relationship in the enzyme reaction\(^\text{(4)}\). Thus, it is worthwhile discussing this type of reaction from the standpoint of gas absorption.

In one paper\(^\text{(3)}\), the variation of the enhancement factor with the order of reaction for a single reaction is treated. In the other paper\(^\text{(3)}\), dependence of the enhancement factor on the order of reaction is given for the two-component reaction.

The treatment above has been confined to the case where the chemical reaction is fast enough to maintain the concentration of A near zero in the bulk of the liquid.

\(x^* = u^* x/\nu\)

\(\delta = \text{thickness of the concentration boundary film [cm]}

\(\delta^* = u^* \delta/\nu\)

\(a_1, A_2 \quad \text{dimensionless radius defined by Eq. (4)}\)

\(\nu = \text{kinematic viscosity [cm}^2/\text{sec]}

\(\phi = \text{relative area of an isolated electrode} = (r_e/r^2)\)

Literature Cited

1) Yoshida, T.: Graduation Thesis in Kyoto Univ. (1972)
liquid but slow enough not to affect appreciably the interfacial concentration of A. However, when the volume of the main body of the liquid should be considered finite, as in the case of chemical absorption in a liquid film or in an agitated vessel, the resistance due to chemical reaction in the bulk of the liquid cannot be neglected, and the concentration of A at the outer surface of the film cannot be considered zero. The concentration of A in the bulk of the liquid is kept constant so that the mass of A crossing the outer surface of the film becomes equal to the amount of A being removed by chemical reaction in the bulk of the liquid.

In this paper, we present the film theory solution for gas absorption with the reactions (a) and (b), when the amount in the bulk of the liquid is finite and thus the resistance due to chemical reaction in the bulk of the liquid cannot be disregarded. Variation of the enhancement factor with the order of reaction can be given by considering the gas absorption accompanied by the reactions (a) and (b).

1. Basic Equation for Gas Absorption with a Reaction

The problem to be considered is a process of gas absorption accompanied by reactions (a) and (b). The mass balance equations for the component A and B in the film can be given in the following dimensionless form:

\[
\frac{d^2 Y_A}{dx^2} = \nu_B \frac{d^2 Y_B}{dx^2} = M_w Y_A^{m-1} \left( \frac{v}{z_L} - 1 \right) \tag{1}
\]

with the boundary conditions

1. \[x = 0; \quad Y_A = 1, \quad \frac{dY_A}{dx} = 0\]
2. \[x = 1; \quad Y_A = Y_{A0}, \quad Y_B = Y_{B0}\]

\[
\frac{dY_A}{dx} = M_w Y_A^{m-1} + \alpha_0 Y_{A0}^{m-1} Y_A^{w-1} \left( \frac{v}{z_L} - 1 \right) \tag{3}
\]

Eq. (1) corresponds to the interpolation formula which can give the shift of the enhancement factor between those accompanied by the \((m, 0)-th\) and \((m-1, n)-th\) order reactions.

The last equation, Eq. (3), is obtained by equating the mass of A crossing the outer surface of the film with the amount of A being removed by chemical reaction in the bulk of the liquid.

The enhancement factor, \(\phi\), is defined by

\[
\phi = -\left( \frac{dY_A}{dx} \right)_{x=0} \tag{4}
\]

When the nonvolatile reactant B in the liquid phase exists sufficiently in excess, the mass balance equation of the component A in the film is

\[
\frac{d^2 Y_A}{dx^2} = M_w Y_A^{m-1} \left( \frac{v}{z_L} - 1 \right) \tag{5}
\]

with the boundary conditions

1. \[x = 0; \quad Y_A = 1\]
2. \[x = 1; \quad Y_A = Y_{A0}\]

2. Solution of Basic Equations

2.1 Numerical solution for the case of nonvolatile reactant in excess

For \(m = 1\) and \(m' = 2\) (case I), Eq. (5) reduces to

\[
\frac{d^2 Y_A}{dx^2} = M_w \frac{Y_A^{m-1}}{1 + \alpha_0 Y_A^{w-1}} \left( \frac{v}{z_L} - 1 \right) \tag{6}
\]

From Eq. (8-1), subject to the boundary conditions (6) and (7), the enhancement factor is given as follows:

\[
\phi = \left( \frac{2M_w}{\alpha_0} \left( \frac{1-Y_{A0} - \frac{1}{\alpha_0} \ln \frac{1+\alpha_0}{1+\alpha_0 Y_{A0}}}{1+\alpha_0 Y_{A0}} + \frac{M_w^2 Y_{A0}^{m-1}}{1+\alpha_0 Y_{A0}^{w-1}} \left( \frac{v}{z_L} - 1 \right) \right) \right)^{1/2} \tag{9-1}
\]

Here the value of \(Y_{A0}\) can be determined numerically by

\[
\int_{Y_{A0}}^{1} dY_A \left[ \frac{2M_w}{\alpha_0} \left( \frac{1-Y_{A0} - \frac{1}{\alpha_0} \ln \frac{1+\alpha_0}{1+\alpha_0 Y_{A0}}}{1+\alpha_0 Y_{A0}} + \frac{M_w^2 Y_{A0}^{m-1}}{1+\alpha_0 Y_{A0}^{w-1}} \left( \frac{v}{z_L} - 1 \right) \right) \right] = 1. \tag{10-1}
\]

For \(m = 2, m' = 2\) (Case II) and \(m = 2, m' = 3\) (Case III), the corresponding relationships to Eqs. (8-1), (9-1) and (10-1) are shown in Table 1.

2.2 The van Krevelen approximation

By assuming that the reactant B in the liquid phase is kept at constant concentration equal to the interfacial concentration, \(C_{B_i}\), the basic differential equation for the gas absorption is

\[
\frac{d^2 Y_A}{dx^2} = \nu_B \frac{d^2 Y_B}{dx^2} = M_w \frac{Y_A^{m-1}}{1 + \alpha_0 Y_A^{w-1}} \left( \frac{v}{z_L} - 1 \right) \tag{11}
\]

Eliminating the interfacial concentration of B, \(C_{B_i}\), in the same way as van Krevelen's, one gets

\[
\alpha = \alpha_0 \left( 1 - \frac{1}{\alpha_0} \frac{Y_{A0}}{\nu_B Y_{B0}} - \hat{\phi} \right)^{1-n} \tag{12}
\]

If one uses \(\alpha\) defined by Eq. (12) in place of \(\alpha_0\) in Table 1, every relation derived is valid without any correction.

3. Computed Results and Discussion

3.1 Enhancement factor from numerical solution

Figure 1 shows typical examples of the relation between \(\phi\) and \(\sqrt{M_w/z_L}\) as a parameter of \(\sqrt{M_w/z_L}\), which is calculated by Eq. (9-1). Broken lines show the same relationships when the amount of the reactant liquid is infinite. It is apparent from this figure that the effect of \(\sqrt{M_w/z_L}\), that is, the amount of liquid is exaggerated in the region where \(\sqrt{M_w}\) is small. As \(\sqrt{M_w}\) increases, the effect of \(\sqrt{M_w/z_L}\) becomes smaller and the enhancement factor approaches that for the gas absorption as the amount of liquid becomes infinite. A similar relationship also is given
Table 1 Enhancement factor for the cases II and III

<table>
<thead>
<tr>
<th>Case m m'</th>
<th>Basic differential equation</th>
<th>Enhancement factor</th>
<th>Deciding equation of Yₐ₀</th>
</tr>
</thead>
<tbody>
<tr>
<td>II 2 2</td>
<td>( \frac{d^2Y_A}{dx^2} = M₂ \frac{Y_A^3}{1 + \alpha_0 Y_A} ) (8-2)</td>
<td>( \left{ \begin{array}{l} 2M₂ \left( 1 - \frac{1 - Yₐ₀}{1 - \alpha_0} \right) + \frac{1}{\alpha_0^2} \ln \left( \frac{1 + \alpha_0 Yₐ₀}{1 + \alpha_0 Yₐ₀} \right) \ - M₂^2 Yₐ₀ \left( \frac{v}{z_L} - 1 \right)^{1/2} \end{array} \right} )</td>
<td>( \left{ \begin{array}{l} \frac{2M₂}{\alpha_0^2} \left( Y_A - Yₐ₀ \right) - \frac{Y_A - Yₐ₀}{\alpha_0} \ + \frac{1}{\alpha_0^2} \ln \left( \frac{1 + \alpha_0 Yₐ₀}{1 + \alpha_0 Yₐ₀} \right) \ + \frac{M₂^2 Yₐ₀}{(1 + \alpha_0 Yₐ₀)^2} \left( \frac{v}{z_L} - 1 \right)^{1/2} \end{array} \right} = 1 )</td>
</tr>
<tr>
<td>III 2 3</td>
<td>( \frac{d^2Y_A}{dx^2} = M₂ \frac{Yₐ₀^3}{1 + \alpha_0 Yₐ₀} ) (8-3)</td>
<td>( \left{ \begin{array}{l} 2M₂ \left( 1 - \frac{1 - Yₐ₀}{1 - \alpha_0} \right) - \tan^{-1} \left( 1 + \alpha_0 Yₐ₀ \right) \ - \tan^{-1} \left( 1 + \alpha_0 Yₐ₀ \right) \end{array} \right} )</td>
<td>( \left{ \begin{array}{l} \frac{2M₂}{\alpha_0^2} \left( Y_A - Yₐ₀ \right) - \frac{Y_A - Yₐ₀}{\alpha_0} \ - \frac{1}{\alpha_0^2} \left( \tan^{-1} \left( \sqrt{\alpha_0 Yₐ₀} \right) - \tan^{-1} \left( \sqrt{\alpha_0 Yₐ₀} \right) \right) \ + \frac{M₂^2 Yₐ₀}{(1 + \alpha_0 Yₐ₀)^2} \left( \frac{v}{z_L} - 1 \right)^{1/2} \end{array} \right} = 1 )</td>
</tr>
</tbody>
</table>

Fig. 1 Relation of \( \phi \) vs. \( \sqrt{M_i} \) as a parameter of \( \sqrt{M_i/\sqrt{z_L}} \) for the case I

Fig. 2 Relation of \( \phi \) vs. \( \sqrt{M_i/(1 + \alpha_0)} \) as a parameter of \( \alpha_0 \) for the case I

For case II and III.

For a small value of \( \sqrt{M_m} \), Eqs. (9-1), (9-2) and (9-3) reduce to

\[
\phi = \sqrt{M_m} \left( \frac{v}{z_L} - 1 \right) = \sqrt{M_m} \left( \sqrt{M_m} v - \sqrt{M_m} \right)
\]

and then the enhancement factor changes linearly with \( \sqrt{M_m} \). From Eq. (13), the diffusion flux of
component A is given by

\[ N_A = k_L C_A \phi = k_m C_A \left( \frac{e - z_L}{\alpha} \right) \]  

which corresponds to the fact that the resistance to chemical reaction in the bulk of the liquid is controlling.

Figures 2, 3 and 4 show the relations of \( \phi \) vs. \( \sqrt{M_m/(1+\alpha_0)} \) as a parameter of \( \alpha_0 \). The abscissa, \( \sqrt{M_m/(1+\alpha_0)} \), was chosen in view of the fact that for a small value of \( \sqrt{M_m} \) the enhancement factor can be expressed by Eq. (13). For the purpose of comparison, the relationships between enhancement factor and modulus \( \sqrt{M} \) for gas absorption with the zeroth, the first and the second order reaction are illustrated as a dotted line. The enhancement factors for gas absorption with the zeroth and the first order reaction were calculated by the following equations.

\[ \phi = \frac{M_0 e}{z_L} \left( \sqrt{M_m} \leq \sqrt{M_0 e/z_L} - \sqrt{M_0 e/z_L^2 - 2} \right) \]  

for a zeroth order reaction (15)

\[ \phi = \sqrt{M_1} \tan \frac{\sqrt{M_1}}{1 - 1 / \cosh \sqrt{M_1}} + \sqrt{M_1} (\cosh - 1) \sinh \sqrt{M_1} \cosh \sqrt{M_1} \]  

for a first order reaction (16)

The enhancement factor for the second order reaction was evaluated numerically by the same procedure as in Section 2.1. Dotted lines agree with the relationships between enhancement factor and modulus \( \sqrt{M} \) for gas absorption with the zeroth and the first order reaction. For a small value of \( \sqrt{M_m} \), the enhancement factor approximates that for gas absorption with the third order reaction. Thus, when \( \sqrt{M_m} \) is small, the shift of the enhancement factor between those accompanied by the simple reactions with the zeroth, the first and the second orders can be given by varying the value of \( \alpha_0 \) from zero to infinity.

In order to make it clear, plots of the enhancement factor vs. \( \alpha_0 \) are illustrated in Fig. 5.

**3. 2 Enhancement factor from the van Krevelen approximation**

The development in this section is confined to case I, because a similar development can be carried out for case II and III.

Figure 6 shows some examples of the relations between \( \phi \) and \( \sqrt{M_1/(1+\alpha_0)} \), calculated by Eqs. (11) and (12). That is, solid lines are built from Fig. 2 by considering Eq. (12) as described in Section 2.2. For the purpose of comparison, the enhancement factor for the infinite amount of reactant liquid is shown as a broken line. The enhancement factors for the (0, 0)-th and the (1, 0)-th order reaction are also shown as a dotted line.

In the region where \( \sqrt{M_1} \) is small, that is, when the resistance to chemical reaction in the bulk of the liquid is dominant, the concentration of B in the liquid film is almost constant and equal to \( C_{B0} \). Therefore, in this region of \( \sqrt{M_1} \), the value of enhancement factor is in agreement with that shown in Fig. 2. In the previous paper, we clarified that the relationship of \( \phi \) vs. \( \sqrt{M_1/(1+\alpha_0)} \) approaches that for the (1, 0)-th order reaction as \( \alpha_0 \) decreases and that for the (0, 1)-th order reaction as \( \alpha_0 \) increases, when the amount of the liquid is infinite. It is apparent from this figure that the relationship of \( \phi \) vs. \( \sqrt{M_1/(1+\alpha_0)} \) approaches that for gas absorption accompanied by the (1, 0)-th order reaction as \( \alpha_0 \) decreases and that by the (0, 0)-th order reaction as \( \alpha_0 \) increases because a chemical reaction in the bulk of the liquid is a rate-determining step.

For a small value of \( \sqrt{M_m} \), the enhancement factor shifts between those accompanied by the \( m \)-th and the \((m-1)-th \) order reaction even when the amount of the reactant liquid is finite.

**Conclusion**

The film theory solution for gas absorption with two-step reversible and irreversible consecutive reactions (a) and (b) was presented, when the main body of the liquid is finite. By the aid of the van Krevelen approximattion, the enhancement factor for the two-component reaction was also derived. By considering gas absorption accompanied by the reactions
(a) and (b), that is, by varying the value of $\alpha_0$ from zero to infinity, the shift of the enhancement factor between those accompanied by the simple reaction was given.

Nomenclature

- $C = \text{concentration in liquid phase [mol/cm}^3\text{]}$
- $D = \text{diffusivity in liquid phase [cm}^2\text{/sec]}$
- $k_m = m$-th order reaction rate constant $[(cm^3/mol)_w - Vsec^{-1}]$
- $k_{IL} = \text{liquid-phase mass transfer coefficient for component A [cm/sec]}$
- $M_m = k_mC^DAlk$ [$-$]
- $m, m', n = \text{order of reaction} [-]$
- $v = \text{liquid volume per unit interfacial area [cm}^3\text{ / cm}^2\text{]}$
- $x = z/z_L$ $[-]$
- $Y = C/C_A$ $[-]$
- $z = \text{distance into liquid phase from interface [cm]}$
- $z_L = \text{thickness of liquid film [cm]}$

\[\alpha = k_mC_{A_{\infty}}^{m-1}/k_{b0}C_{B_{\infty}}^{m-1} \quad [-]\]

\[\alpha_0 = k_mC_{A_{\infty}}^{m-1}/k_{b0}C_{B_{\infty}}^{m-1} \quad [-]\]

\[\phi = \text{enhancement factor defined by Eq. (4)} \quad [-]\]

\[\nu_B = D_B/D_A \quad [-]\]

\[\langle \text{Subscripts} \rangle\]

- $A = \text{solute gas}$
- $B = \text{reactant in liquid phase}$
- $i = \text{gas-liquid interface}$
- $m, m', n = \text{order of reaction}$
- $0 = \text{in the bulk of the liquid}$

**REATIONS OF IODINE IN AQUEOUS SOLUTIONS CONTAINING SODIUM HYDROXIDE**

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Reactions of iodine in aqueous phase were studied by a concentration relaxation method. From the result of the present investigation, the mechanism of the absorption of iodine in air by aqueous sodium hydroxide solution is as follows:

(Step 1) Molecular iodine in air dissolves into the aqueous phase through the gas-liquid interface according to Henry's law.

(Step 2) Instantaneous reversible reactions take place in the aqueous phase and HIO, I$^-$, and I$_2$ form.

(Step 3) HIO formed by the above reaction is consumed gradually and IO$_2^-$ forms, while the instantaneous reversible reactions of step 2 are in equilibrium at any instant.

Overall consumption rate of HIO can be approximated by the rate equation of the second-order reaction with respect to HIO.

**Introduction**

One of the important aims of the containment spray during a maximum accident in a boiling- or pressurized-water reactor is to restrain the leakage of the radioactive iodine vapor from reactor fuel to the atmosphere. Usually, sodium hydroxide solution is used as a containment spray liquor.

Authors have reported the dependency of partition equilibrium of iodine between air and aqueous sodium hydroxide solution upon both temperature and concentration$^{1-3}$). In these previous reports, it was concluded that iodine dissolved into aqueous phase undergoes many complex reactions and that the final main chemical species in the solution at equilibrium are I$_2$, I$^-$, I$_3^-$, and IO$_2^-$. By following the concentration change of these species with time in the previously reported experiments$^4$), where air containing constant concentration of iodine vapor was passed through a sodium hydroxide solution until the equilibrium was reached, it was noted that both rapid and slow chemical reactions participated in the overall reaction of iodine in the aqueous phase. In order to estimate the overall rate