Film and Bulk Reaction for Gas Absorption in “a Single Backmixed Zone”: Modeling of First-Order Reaction (\( A(g) \xrightarrow{k_f} R(l) \))

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Abstract

With only a few exceptions, the extensive literature on gas-liquid absorption and reaction has been devoted to reactions that are considered to be completed entirely in the bulk of liquid or only within the liquid film. This is usually for the sake of simplification of modeling and design. According to Levenspiel [1], Hatta [2] carried out the first significant analysis of this problem; however, today the general rate expressions for this intermediate regime are still unavailable. In this research, a model describing a single backmixed gas-liquid contacting zone has been successfully developed without making any prior assumption about the reaction-diffusive regime within the mass transfer film or imposing any arbitrary boundary conditions. This involves the drawing-up of proper material balances across the film and bulk liquid phases and linking these to the overall material balances on each of the gas and liquid phases. As a result, film and bulk reaction in gas-liquid absorption can be properly calculated. It is shown that significant extents of both film and bulk reaction will exist over three orders of magnitude of the reaction rate constant. Over such a large range of reaction speeds, thus, both film and bulk reaction are definitely significant and this effect should not be neglected. In this case, application of the predictions of the enhancement factor using assumed slow bulk reaction or fast film reaction would be wrong. This is likely to become even more crucially important when calculating the selectivity of multiple gas-liquid reactions.

Keywords: chemical absorption, film and bulk reaction, reactor modeling, enhancement factor.

1. Introduction

The extensive literature on gas-liquid absorption and reaction has, with only a few exceptions, been devoted to reactions that are considered to be completed entirely in the bulk of liquid or only within the liquid film. This is usually for the sake of simplification of modeling and design [3].

This assumption is quite reasonable for instantaneous and fast reactions and for slow and infinitely slow reactions. However, with this assumption, it is quite obviously wrong for an intermediate case where the reaction occurs significantly both within the film and within the main body of the liquid [4].

Moreover, according to Levenspiel [1], Hatta [2] carried out the first significant analysis of this problem; however, today the general rate expressions for this intermediate regime are still unavailable. The derivations and discussions of this case can be found in the texts devoted to this subject, such as Sherwood and Pigford [5] and Danckwerts [6], and also Kramers and Westerterp [7].

The objectives in this research is to properly calculate the precise extent of the film and bulk reaction without making any prior assumption which

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is imposed upon the reaction-diffusive regime within the mass transfer film (fast, slow, etc) in “a single backmixed zone” (see Figure 1).

2. Model Formulation and Method of Solving

Considering a first-order irreversible reaction of the dissolved gas in the liquid, \( \text{A(g)} \xrightarrow{k_{r1}} \text{R(l)} \), which is used to demonstrate the effect of a chemical reaction on the absorption of gas A in water. In this case, the local rate of reaction is [6]:

\[
 r = -\frac{dC_A}{dt} = k_{r1}C_A
\]

\( k_{r1} \) being the first-order reaction-rate constant and \( C_A \) the local concentration of dissolved gas.

The absorption process occurring is thus described by the following steady state equation and boundary conditions:

\[
 D_A \frac{d^2C_A}{dx^2} = k_{r1}C_A, C_A = C_A^*, x = 0
\]

\[
 C_A = C_{Abo}, x = \delta
\]

By routine analytical techniques, this equation is integrated to:

\[
 C_A = \left[ C_{Abo} \sinh \left( \frac{k_{r1}}{D_A} x \right) \right] + \left[ C_A^* \sinh \left( \frac{k_{r1}}{D_A} \delta \right) \right]
\]

\[
 M = \frac{D_A k_{r1}}{k_L k_{r1}}
\]

Differentiation of equation (3) and multiplying by \(-D_A V\bar{a}\) gives:

\[
 N_A \bigg|_0 = D_A \left( \frac{dC_A}{dx} \right) V\bar{a} \left[ k_L V a(C_A^* \cosh \sqrt{M}) - C_{Abo} \cosh \sqrt{M} \right] E_A
\]

\[
 = \frac{\bar{r}}{R}
\]

\[
 N_A \bigg|_x = D_A \left( \frac{dC_A}{dx} \right) V\bar{a} k_L V a(C_A^* \cosh \sqrt{M} C_{Abo} \cosh \sqrt{M}) E_A
\]

where \( E_A = \sqrt{M \tanh \sqrt{M}} \)

\[
 N_A \bigg|_\delta + QC_{Abo} = k_{r1} C_{Abo} V + QC_{Abo}
\]

\[
 C_A^* = \frac{N_A \bigg|_{x=0} + k_1}{k_2}
\]

**Figure 1** Mass balance (on A) over a single backmixed zone (element).

Note:  
(a) classical chemical reactor  
(b) simple schematic of backmixed zone

where \( Q \) is the volumetric liquid flow rate through the zone.

Substituting equation (5) into equation (6) gives:

\[
 C_{Abo} = \frac{V a k_L E_A C_A^* + QC_{Abo} \cosh \sqrt{M}}{(V a k_L E_A + k_{r1} + QC_{Abo} \cosh \sqrt{M}) \cosh \sqrt{M}}
\]

Eliminating \( C_{Abo} \) by substituting equation (7) into equation (4) and rearranging for \( C_A^* \) gives:

\[
 C_A^* = \frac{N_A \bigg|_{x=0} + k_1}{k_2}
\]
Considering a single backmixed zone (Figure 1), the material balance on component A over the “bulk” of the zone liquid at the steady state is written:

\[
\text{Molar flow rate of reactant A from the film-bulk} + \text{rate of reactant A entering the bulk} = \text{reaction rate of reactant A in the bulk of liquid} + \text{rate of component A leaving from the bulk of liquid}
\]

Assuming the gas and liquid phases are perfectly back-mixed and that a single gas A is absorbed and then consumed by first-order reaction \((\text{A}(	ext{g}) \rightarrow \text{R}(	ext{l}))\), the rate of absorption at the interface (see Figure 1) is given by:

\[
\text{rate of reactant A entering the gas phase} = \text{rate of reactant A leaving from the gas phase} + \text{Molar flow rate of reactant A from the gas phase into the film-bulk interface}
\]

where \(k_2 = \frac{V_k L a(1 - \frac{1}{k_1 \cosh \sqrt{M}})}{E_A}\),

\(k_1 = \frac{1}{[1 + \frac{k_1}{k_1 a E_A} + \frac{Q}{V k L a E_A}] \cosh \sqrt{M}}\),

\(k_3 = \frac{QC_{A(b)i}}{k_1}\)

According to Henry’s law \((p_A = H_A C_A^* = y_{A0} P)\), \(C_A^*\) in equation (8) is eliminated, then:

\[
N_A\bigg|_{t=0} = \frac{y_{A0} P k_2}{H_A} - k_3
\]

\[
G_i y_{Ai} = G_o y_{Ao} + N_A\bigg|_{t=0}
\]

\[
G_i y_{Ai} - G_o y_{Ao} = N_A\bigg|_{t=0}
\]

where \(G_i, G_o\) are inlet and outlet gas molar flow rates, respectively.

Because there is no net change in the throughput of the inert gases,

\[
G_i (1 - y_{Ai}) = G_o (1 - y_{Ao})
\]

Eliminating \(G_o\) by rearranging equation (11) and substituting into equation (10) gives:

\[
N_A\bigg|_{t=0} = G_i \frac{(y_{Ai} - y_{Ao})}{(1 - y_{Ao})}
\]

Equating equation (12) with equation (9) and rearranging gives a quadratic equation:

\[
\frac{(k_2 P)^2}{H_A} y_{A0}^2 - (k_2 P + k_3) y_{A0} + (k_3 + G_i y_{Ai}) = 0
\]

This quadratic equation can be solved for the outlet gas composition if the inlet parameters (Table 1) are given. In order to calculate other parameters, it can be then back substituted into the previous equations. The overall results can be used to show how the relative

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Values</th>
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<tbody>
<tr>
<td>(D_A)</td>
<td>(2.0 \times 10^{-5} \text{ m}^2 \text{ s}^{-1})</td>
</tr>
<tr>
<td>(a)</td>
<td>(70 \text{ m}^2 \text{ m}^{-3})</td>
</tr>
<tr>
<td>(k_L)</td>
<td>(2.14 \times 10^{-5} \text{ m} \text{ s}^{-1})</td>
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<tr>
<td>(H_A)</td>
<td>(7.6 \times 10^6 \text{ N kmol}^{-1} \text{ m}^{-5})</td>
</tr>
<tr>
<td>(P)</td>
<td>(1.01 \times 10^5 \text{ N m}^{-2})</td>
</tr>
<tr>
<td>(V)</td>
<td>(1 \text{ m}^3)</td>
</tr>
<tr>
<td>(y_{Ai})</td>
<td>(0.1)</td>
</tr>
<tr>
<td>(G_i)</td>
<td>(5.0 \times 10^{-6} \text{ kmol s}^{-1})</td>
</tr>
<tr>
<td>(C_{A(b)i})</td>
<td>(0 \text{ kmol m}^{-3})</td>
</tr>
<tr>
<td>(Q)</td>
<td>(5.0 \times 10^{-7} \text{ m}^3 \text{ s}^{-1})</td>
</tr>
<tr>
<td>(k_{1r})</td>
<td>(1.0 \times 10^{-6} \text{ to } 1.0 \times 10^{-3} \text{ s}^{-1})</td>
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Source: Perry and Green [8]
amounts of film and bulk reaction vary depending on how fast the reaction is. In the following illustrative example, an ozone absorption and reaction system is studied. Ozone gas which is a sparingly soluble gas (like carbon monoxide, oxygen, hydrogen, methane, ethane, nitric oxide and nitrogen) is represented by $A$ for an irreversible unimolecular-type reaction $\text{A(g)} \rightarrow \text{R(l)}$: the first-order ozone decomposition reaction. The ozone kinetics data from the literature are shown in Table 1.

3. Results and Discussion

Having already obtained values of the input parameters in Table 1, the graph in Figure 2 was constructed by solving equation (13) over a range of values of the reaction rate constant. It shows how the amount of reaction taking place in the zone (both in the film and bulk of liquid) varies depending on how fast the reaction is. When the reaction rate increases, the mole fraction of component A decreases very quickly.

With the same values of parameters used in Figure 2, the enhancement factor is plotted as a function of Hatta number (Ha) in Figure 3. The curve of $E_A$ vs. Ha shows that for low values of Ha the absorption takes place in the slow reaction regime, and therefore is $E_A$ nearly equal to 1, while for the higher values of Ha the transition to the fast regime takes places, for which $E_A$ is proportional to Ha.

The concentration profile of component A in the liquid film is plotted in Figure 4 for different values of Ha. In this figure the dimensionless concentration profile of component A is plotted for Ha between 0.0021 and 66. Such curves were obtained by means of equation (11).

Compared to the research of Ramachandran [9]...
which shows the results for a pseudo-first order reaction, the trend of the concentration profile of component A in the liquid film is not different. The enhancement factor and Hatta number calculated for his case was 9.85 which was within 0.5% of the exact value.

However, Prisciandaro and Pepe [10] reported that it can be observed that in the condition considered of zero-order reaction, since there is no limiting reactant, the transition to the instantaneous reaction regime cannot be observed and enhancement factor boundlessly grows with Hatta number. Landau [11] further reported that the distinct feature of a zero-order reaction is that the reaction is not influenced by its concentration.

Shown in Figure 5 is the behavior when the reaction rate constant varies over 9 orders of magnitude between $1.0 \times 10^{-6}$ and $1.0 \times 10^{+3}$ s$^{-1}$. The percentage saturation decreases whilst the percentage of film reaction increases. When reaction rate constant is equal to 0.39 s$^{-1}$, the percentage film reaction is exactly fifty. This means that the reaction is taking place exactly half in the liquid film and half in the bulk of liquid. At the highest reaction rate constant, e.g. $k_r=1.0 \times 10^{+3}$ s$^{-1}$, the reaction is virtually completed within the liquid film. On the other hand, when reaction rate constant is very low, e.g. $k_r=1.0 \times 10^{-6}$ s$^{-1}$, there is almost no reaction in the liquid film. All the reactant then reacts in the bulk of liquid phase.

At the value of $k_r=0.015$ s$^{-1}$, there is 5% film reaction while at the value of $k_r=9.50$ s$^{-1}$, there is 95% film reaction. It can be seen that the reaction rate constants vary by nearly three orders of magnitude. This was previously established theoretically by Mann [12]. Thus, in this large range of reaction speeds both film and bulk reaction are definitely significant which should not be neglected. Over this wide range, application of the predictions of $E_A$ (the enhancement factor) using slow bulk reaction or fast film reaction would be wrong. This is likely to become crucially important when calculating the selectivity of multiple gas-liquid reactions. It is clear that the use of a priori assumptions is not recommended.

4. Conclusion

A model describing a single backmixed gas-liquid contacting zone has been successfully developed without making any prior assumption about the reaction-diffusive regime within the mass transfer film or imposing any arbitrary boundary conditions. This involves the drawing-up of proper material balances across the film and bulk liquid phases and linking these to the overall material balances on each of the gas and liquid phases. As a consequence of applying this proper material balance over each of the film and bulk portions of liquid, the exact extent of film and bulk reaction is calculated naturally without making any a-priori assumptions.

Moreover, it can be concluded that there is significant reaction in both film and bulk over a wide range of reaction rate constants for the 1st-order absorption. Particularly, in the range from 10% to 90% film reaction, the reaction rate constants vary by three orders of magnitude. Over such a large range of reaction speeds, thus, both film and bulk reaction are definitely significant and this effect should not be neglected. Over this wide range, application of the predictions of the enhancement factor using assumed slow bulk reaction or fast film reaction would be
wrong. This is likely to become even more crucially important when the selectivity of multiple gas-liquid reactions is calculated.

**Nomenclature**

- \( a \) Interfacial area \( \text{m}^2 \text{m}^{-3} \)
- \( A \) Reactant A
- \( C_A \) Concentration of reactant A \( \text{kmol m}^{-3} \)
- \( C_A^* \) Concentration of A at gas-liquid interface \( \text{kmol m}^{-3} \)
- \( C_{A_{\text{ab}}} \) Initial concentration of reactant A \( \text{kmol m}^{-3} \)
- \( C_{A_{\text{bo}}} \) Liquid bulk concentration of reactant A \( \text{kmol m}^{-3} \)
- \( D_A \) Diffusivity of reactant A \( \text{m}^2 \text{s}^{-1} \)
- \( E_A \) Enhancement factor, reaction factor
- \( G_i \) Total gas molar flow rate (inlet) \( \text{kmol s}^{-1} \)
- \( G_o \) Total gas molar flow rate (outlet) \( \text{kmol s}^{-1} \)
- \( H_a \) Hatta number
- \( H_A \) Henry constant \( \text{N kmol}^{-1} \text{m}^{-5} \)
- \( k_1, k_2, k_3 \) Constant
- \( k_{r1} \) Reaction rate constant for 1st order reaction \( \text{s}^{-1} \)
- \( k_L \) Liquid side mass transfer coefficient \( \text{m s}^{-1} \)
- \( M \) Film conversion parameter
- \( N_A \big|_{x=0} \) Molar flow rate of A at gas-liquid interface \( \text{kmol s}^{-1} \)
- \( N_A \big|_{x=\delta} \) Molar flow rate of A at outer-liquid film interface \( \text{kmol s}^{-1} \)
- \( P \) Total pressure of the system \( \text{N m}^{-2} \)
- \( p_A \) Partial pressure \( \text{N m}^{-2} \)
- \( Q \) Liquid volumetric flow rate \( \text{m}^3 \text{s}^{-1} \)
- \( r \) Local rate of reaction (1st order) \( \text{kmol m}^{-3} \text{s}^{-1} \)
- \( \bar{R} \) Absorption rate \( \text{kmol s}^{-1} \)
- \( V \) Liquid volume \( \text{m}^3 \)
- \( y_{A_i} \) Mole fraction of reactant A (inlet)
- \( y_{A_o} \) Mole fraction of reactant A (outlet)

**References**