Mass-transfer enhancement factors for reversible gas–liquid reactions: comparison of DeCoursey’s and Onda’s methods

(Received 17 October 1984)

INTRODUCTION

For the calculation of mass-transfer enhancement factors for reversible gas–liquid reactions, DeCoursey recently published an approximate analytical method on the basis of Danckwerts’ surface renewal theory (DeCoursey, 1982). The model was satisfactorily tested analytically under some asymptotic conditions. In other conditions, testing was not completely satisfactory. Using numerical results from Secor and Beutler (1967), available for a low product loading only, relatively large differences were found at an equilibrium constant $K = 1$. Also, at a higher product loading, relatively large differences were found with solutions obtained from a so-called pragmatic method of Danckwerts. In order to resolve the discrepancies, DeCoursey recommended further testing of his model with a numerical method. We have done this using our numerical method for the calculation of enhancement factors for CO$_2$ absorption kinetics on the basis of Higbie’s penetration model (Cornelisse et al., 1980). Our results are presented below.

Apart from DeCoursey’s recently published approximate solution, there also exists a second, older, approximated theory covering the same mass transfer with reaction system but starting from the film theory (Onda et al., 1970). In his paper, DeCoursey suggested Onda’s theory to be unsatisfactory because:

(a) the boundary conditions assumed for the concentration profiles of the reactants in the reverse direction (E and F) are not identical;
(b) the net rate of the reaction does not reduce to zero in the bulk of the liquid, although here equilibrium is supposed to exist; and
(c) Onda’s enhancement factors and other dimensionless parameters are defined in an unconventional way.

Therefore DeCoursey did not compare his results with Onda’s model. However, we showed earlier that Onda’s method can be successfully used to calculate the enhancement factors for the reversible absorption of CO$_2$ in aqueous solutions of diisopropanolamine (DIPA) (Cornelisse et al., 1980). We therefore decided to include Onda’s approximation in our present evaluation.

TYPES OF KINETICS INVESTIGATED

Two different kinds of kinetics were investigated, viz.:

(i) a normal, $1,1$ order equilibrium reaction

\[ A + B = E + F \]  \\
with

\[ K = c_E c_F / (c_A c_B) \]

(ii) a CO$_2$/diisopropanolamine (DIPA) type of equilibrium reaction which can be visualized as a $1,1,1$ order
reaction but with a particular stoichiometry and a corresponding equilibrium constant:

\[ A + 2B = E + F \]  

with

\[ K'' = \frac{c_E c_F}{c_A c_B}. \]  

**COMPARISON OF DE COURSEY’S AND ONDA’S MODEL**

Using equal diffusion coefficients, a condition which was found to be imperative for the application of DeCoursey’s model (because only then can his main mass balance differential equation be solved analytically), both Onda’s and DeCoursey’s models were set up for the two kinetic schemes. Care was taken to introduce the same input parameters, viz. \( QB \), \( QE \) and \( QF \), the Hatta number and, further, for the kinetics according to eq. (1), \( K \) as defined above, and for the \( CO_2/DIPA \) type of kinetics the dimensionless parameter:

\[ K = K'' c_{Bo}. \]  

For Onda’s model, the \( QB \), \( QE \) and \( QF \) parameters and also the output parameter \( E(A) \) should be redefined in view of Onda’s different normalization. This was done by multiplying them by \( 1/(1 + QA) \), e.g. for the enhancement factor:

\[ E(A, \text{Onda}) = E(A, \text{DeCoursey}) \times \frac{1}{1 + QA} \]  

in which \( QA \) can be found from the equilibrium equation

\[ QA = \frac{QE \cdot QF}{(KQB)} \]  

with \( K \) the equilibrium constant according to either eq. (2) or eq. (5), depending on the kinetics considered.

**Table 1. Input parameters and values screened for the comparison of the approximate analytical methods of Onda and DeCoursey for the calculation of the mass-transfer enhancement factor for normal and \( CO_2/aqueous \) diisopropanolamine type 1,1,1 order equilibrium reactions**

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Values</th>
</tr>
</thead>
<tbody>
<tr>
<td>( K )</td>
<td>0.01, 1, 100, 10,000, 1,000,000, 100,000,000</td>
</tr>
<tr>
<td>( QB )</td>
<td>0.1, 1, 10, 100, 1000</td>
</tr>
<tr>
<td>( QE/QB ) and ( QF/QB )</td>
<td>0.0 and 0.0, 0.1 and 0.1, 1.0 and 1.0, 0.1 and 1.0, 1.0 and 0.1</td>
</tr>
<tr>
<td>( Ha )</td>
<td>0.1, 1, 10, 30, 100, 300, 1000, 10,000, 100,000</td>
</tr>
<tr>
<td>ab/desorption</td>
<td>( QB ) positive, resp. ( QB ) negative and (-1 &lt; QA &lt; 0)</td>
</tr>
</tbody>
</table>

By programming both Onda’s and DeCoursey’s methods the enhancement factors could be calculated for a large number of conditions, both for absorption and for desorption. All combinations of the parameter values shown in Table 1 were screened. Thus all typical types of reaction regimes were covered, viz. slow reaction, instantaneous reaction, pseudo-first-order reaction, both reversible and quasi-reversible (high \( K \)). For desorption, the parameters were screened, by setting \( QB \) negative, while meeting the condition of \( QA < -1 \), imperative for a physically meaningful result.

From this comparative work we could conclude that both methods yield substantially the same results (Table 2). The largest differences were found:

(a) at low values of \( K \) (with differences up to 14% for absorption and up to 25% for desorption), for which we have no explanation, and
(b) at \( Ha = 1 \) (differences generally between -21 and 3%, neglecting a few calculational artefacts of 31%) with the highest results usually obtained for the method of DeCoursey. These differences can be explained qualitatively from the different underlying mass-transfer models, as at \( Ha = 1 \) the penetration theory normally gives a somewhat higher result than the film theory (Westerterp et al., 1984).

At \( K = 1 \), the differences between DeCoursey’s and Onda’s solution are smaller than those between DeCoursey’s solution and the numerical result of Secor and Beutler, and this may suggest a lower accuracy for the latter method in this region.

For desorption at low \( K \) values Onda’s model sometimes gave obviously wrong results for as yet unknown reasons.

**COMPARISON WITH OUR NUMERICAL PROCEDURE**

Both Onda’s and DeCoursey’s method were examined using our numerical method as well. Only the \( CO_2/DIPA \) type of kinetics according to eq. (3) were investigated as our numerical method was not yet available for the normal 1,1,1 order kinetics. In general, the differences found between our numerical method, on the one hand, and either of the two approximate analytical methods, on the other hand, were again small. At \( Ha = 1 \), our numerical method confirmed the values from DeCoursey rather than from Onda. This is in agreement with the above hypothesis because both our method and DeCoursey’s are based on the penetration theory, while Onda et al. start from the film theory. Thus, DeCoursey’s method of time averaging all mass balances, concentrations, enhancement factors and boundary conditions does not reduce his model to a quasi-film model, which at first sight might have been concluded. Unfortunately the discrepancies at the two lowest \( K \) values could not be sorted out because our numerical model is not stable in this region, but in practice this type of equilibrium reaction is not of much practical importance.

**Table 2. Deviation of the enhancement factor in comparison with DeCoursey’s method (% of DeCoursey’s enhancement factor)**

<table>
<thead>
<tr>
<th>Onda (absorption)</th>
<th>Onda (desorption)</th>
<th>Numerical method</th>
</tr>
</thead>
<tbody>
<tr>
<td>( K )</td>
<td>( Ha )</td>
<td>Low product loading</td>
</tr>
<tr>
<td>0.01</td>
<td>all†</td>
<td>-7 to 7</td>
</tr>
<tr>
<td>1</td>
<td>all†</td>
<td>-10 to 10</td>
</tr>
<tr>
<td>( \geq 1 )</td>
<td>1</td>
<td>-11 to 31</td>
</tr>
<tr>
<td>( \geq 1 )</td>
<td>( \geq 1 )</td>
<td>-2 to 7</td>
</tr>
</tbody>
</table>

†When both \( QE/QB = 1 \) and \( QF/QB = 1 \).
‡That is, the whole range of Table 1.
CONCLUSIONS

For non-instantaneous equilibrium reactions the approximate analytical methods of Onda and DeCoursey give sufficiently accurate results both with and without product loading. For desorption at low K values Onda’s model is less reliable, however. DeCoursey’s model seems somewhat less useful in practice, because his model can be solved only by assuming equal diffusion coefficients.

G. DE LIND VAN WIJNGAARDEN†
G. F. VERSTEEG
A. A. C. M. BEENACKERS‡

Laboratory for Chemical Reactions Engineering
Department of Chemical Engineering
Twente University of Technology, P.O. Box 217
7500 AE Enschede The Netherlands

NOTATION

A volatile component
B, E, F non-volatile reactant species
$c_J$ molar liquid-phase concentration of component J, mol m$^{-3}$
$\delta$ film thickness, m
$D$ diffusion coefficient of A, m$^2$ s$^{-1}$
$E(A)$ enhancement factor

$Ha$ Hatta number; $Ha = \frac{\delta \sqrt{k c_B}}{D}$ for 1,1-1,1 order reaction
$K$ equilibrium constant [eq. (2)] or dimensionless equilibrium parameter [eq. (5)]
$K^*$ equilibrium constant for CO$_2$/DIPA type kinetics [eq. (4)], m$^3$ mol$^{-1}$
$k$ reaction rate constant, m$^3$ mol$^{-1}$ s$^{-1}$
$QA, QB, QE, QF$ dimensionless bulk concentrations normalized on $c_{AI} - c_{AO}$

$^\dagger$Permanent address: Koninklijke/Shell-Laboratorium, Amsterdam (Shell Research BV), P.O. Box 3003, 1003 AA Amsterdam, The Netherlands.
$^\ddagger$Present address: State University of Groningen, Technical Chemistry Department, Nijenborgh 16, 9747 AG Groningen, The Netherlands. Author to whom correspondence should be addressed.

REFERENCES


A model for the devolatilization of large coal particles

(Received 12 March 1986)

INTRODUCTION

Recently there has been a considerable interest in modeling the devolatilization process in large coal particles. To accomplish this goal, it is necessary to distinguish between nonplastic and plastic coals. In plastic coals, the volatiles are transported by gas filled bubbles, whereas in nonplastic coals, diffusion and hydrodynamic flow prevails (Gavalas, 1982). Essenhigh (1962) and LaNauze (1982) have assumed instantaneous pyrolysis reactions and the devolatilization process to be mass transfer controlled. Agarwal et al. (1984) have developed a nonisothermal kinetically controlled model which is applicable only in the case of negligible mass transfer resistance. An important feature of this model (Agarwal et al., 1984), is the incorporation of the multireaction kinetics of Anthony et al. (1975) to account for the activation energy distribution of the pyrolysis reactions. These models do not adequately describe the mechanism of coal devolatilization and in this communication we present a comprehensive model for nonplastic coal particles considering heat and mass transfer resistances as well as the kinetics of the pyrolysis reactions.

THE MODEL

The following assumptions are made in the development of the model:

1. The pyrolysis reactions are represented by a first order process having a global activation energy

$$\frac{dV}{dt} = k(V^*-V)$$  

where

$$k = A \exp(-E/RT).$$