A critical comparison of approximate solutions for enhancement factor for irreversible second-order reaction

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HIGHLIGHTS

- Numerical solution for enhancement factor for second-order reaction is presented.
- Available approximate solutions are compared with exact numerical solution.
- Maximum relative deviations of all approximate solutions do not exceed 10%.
- Own modifications of the existing approximate solutions are proposed.
- The modified solution exhibits the best accuracy that has ever been achieved.

ARTICLE INFO

ABSTRACT

In this paper, the exact numerical solution for the enhancement factor for mass transfer accompanied by an irreversible second-order reaction based on the film theory is presented. The accuracy of the numerical solution is enhanced by using non-uniform discretization steps and Richardson extrapolation. Approximate analytical solutions available in the literature for the enhancement factor for an irreversible second-order reaction were compared with presented numerical solution. All approximate solutions are able to predict the values of the enhancement factor with the relative deviations within 10% compared to the exact numerical solution for the film theory. However, the applicability of the model and some approximate solutions is limited to the fast reaction regime. The approximate solution of DeCoursey (1974), originally developed for the surface renewal theory, was adapted to the film theory by using a correction factor. The maximum relative deviation of the modified approximate solution is as low as 2.2% for entire range of parameters Ha and E_i (Hatta number and enhancement factor for instantaneous reaction), which is the best accuracy that has ever been reported for an explicit expression for the enhancement factor for an irreversible second-order reaction.

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1. Introduction

Mass transfer in gas-liquid systems accompanied by a chemical reaction has been the subject of scientific evaluation for many decades. Many industrial processes involve reactive absorption in which mass transfer of absorbed component through the gas-liquid interface is followed by a chemical reaction in the liquid phase. The chemical reaction can significantly enhance the rate of absorption and increase the capacity of absorbent compared to physical absorption. Typical industrial applications include removal of H_2S and CO_2 from sour gas streams by means of aqueous solutions of alkanolamines or alkalis and absorption of nitrogen and sulfur oxides into aqueous solutions in gas cleaning or in the production of nitric and sulfuric acid, respectively (Yildirim et al., 2012).

The effect of a chemical reaction on the mass transfer rate has been traditionally expressed in terms of the so-called enhancement factor, which is defined as the ratio of mass transfer rate in the presence of a chemical reaction to that in the absence of a chemical reaction under otherwise identical conditions. Three traditional mass transfer theories have been widely employed to describe the mass transfer accompanied by a chemical reaction, namely the film, penetration and surface renewal theories (Glasscock and Rochelle, 1989). The film theory represents a steady-state model described by ordinary differential equations. This model assumes well-mixed bulk fluids and molecular diffusion through the stagnant films of the finite thickness adjacent to the fluid interface. The penetration and surface renewal theories represent non-steady-state models described by partial differential

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Nomenclature

[A]	relative concentration of component A, dimensionless
[B]	relative concentration of component B, dimensionless
c	molar concentration, kmol m^{-3}
D	diffusion coefficient, m^2 s^{-1}
E	enhancement factor for irreversible second-order reaction, dimensionless
E_i	enhancement factor corresponding to instantaneous reaction, dimensionless
E_1	enhancement factor corresponding to (pseudo-)first-order reaction, dimensionless
F	correction factor defined by Eq. (28), dimensionless
h	integration step, dimensionless
Ha	Hatta number, dimensionless
k_2	second-order reaction rate constant, m^3 kmol^{-1} s^{-1}
n	adjustable parameter, dimensionless
N	number of integration steps, dimensionless
RD	relative deviation, %
x	spatial coordinate, m
X	dimensionless spatial coordinate, dimensionless
X^*	location of reaction plane in case of instantaneous reaction, dimensionless

y	relative concentration in Eqs. (19)–(22), dimensionless

Greek letters

α	auxiliary parameter, dimensionless
γ	auxiliary parameter, dimensionless
δ	liquid film thickness, m
v	stoichiometric coefficient, dimensionless

Subscripts

A	component A
B	component B
P	component P (product)

Superscripts

b	liquid bulk
film	related to film theory
i	gas-liquid interface
pen	related to penetration theory
s-r	related to surface renewal theory

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equations. The penetration theory assumes that liquid elements exist at the gas-liquid interface. Each element stays in the contact with gas for the same time period during which non-steady-state mass transfer takes place between the element and gas. After that, elements are replaced with fresh ones from the liquid bulk. The surface renewal theory is a modification of the penetration theory. Here, it is assumed that liquid elements are randomly swapped by fresh elements from the liquid bulk. At any time, each element at the surface has the same probability to be replaced with another. Some authors promote the use of more advanced models (i.e., penetration and surface renewal theories) for description of mass transfer accompanied by a chemical reaction because they seem to be more realistic and accurate, while others continue to prefer the well-established film theory due to its essential simplicity and claim that the results of both approaches are comparable (Froment et al., 2010; Levenspiel, 1999).

An analytical solution for mass transfer accompanied by a chemical reaction is available only for a limited number of cases, e.g., for first-order or instantaneous reactions. Therefore, an effort has been made to derive approximate expressions for the enhancement factor for other reaction schemes in order to avoid the necessity of a numerical solution of differential equations. The first approximate solution for the enhancement factor for an irreversible second-order reaction was published as early as in 1948 by van Krevelen and Hoftijzer (1948). However, this approximate solution was implicit, which made easy evaluation of the enhancement factor relatively difficult. Later, a number of explicit approximate solutions were developed that allow for direct evaluation of the enhancement factor for an irreversible second-order reaction. The overview of models of mass transfer in gas-liquid systems accompanied by chemical reactions for various reaction schemes was provided by van Swaaij and Versteeg (1992).

Early attempts at a numerical solution for mass transfer accompanied by an irreversible second-order reaction were published by Perry and Pigford (1953), Brian et al. (1961) and Pearson (1963). De Santiago and Farina (1970) presented a numerical solution for mass transfer accompanied by an irreversible second-order reaction based on the film theory. In their work, values of the enhancement factor were calculated for 54 combinations of the Hatta number, Ha, and the enhancement factor for instantaneous

reaction, E_i, out of which 23 combinations fall into the regions governed by limiting cases, i.e., instantaneous and pseudo-first-order reactions for $Ha > 10 \times E_i$ and $Ha < 0.1 \times E_i$, respectively (though, the exact boundaries for limiting cases may vary across different authors). Therefore, only a relatively small number of valuable data points were presented for reliable evaluation of the accuracy of the available approximate solutions. Wellek et al. (1978) used the results of the numerical solution for the film theory previously published by de Santiago and Farina (1970) for critical comparison of eight approximate solutions available at that time. Furthermore, they provided their own approximate solution based on the limiting cases of a general irreversible second-order reaction.

This work is motivated by the relative sparsity of published results of the numerical solution for the enhancement factor of an irreversible second-order reaction for the film theory and emergence of new approximate solutions that have not been thoroughly tested yet. The approximate solutions available in the literature for the enhancement factor for an irreversible second-order reaction are compared with the exact numerical solution for more than 10 000 combinations of Ha and E_i over a wide range of both parameters.

2. Theory

2.1. Governing equations

For mass transfer in gas–liquid systems accompanied by a general irreversible second-order reaction (first order in both reacting components A and B)

$$A + v_B B \rightarrow v_P P \tag{1}$$

the differential mass balance based on the film theory in the steady-state can be written as follows:

$$D_A \frac{d^2 c_A}{dx^2} - k_2 c_A c_B = 0 \tag{2}$$

$$D_B \frac{d^2 c_B}{dx^2} - v_B k_2 c_A c_B = 0 \tag{3}$$