Fast to Instantaneous Reaction Regime Transition in a Gas-Liquid Vessel

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In gas absorption with chemical reaction, the solution to the diffusion-reaction equation depends on the relative rate of diffusion to reaction. Astarita (1967) and Danckwerts (1970) present expressions for the absorption rate in the various reaction regimes, using both film and penetration theory. For a second-order bimolecular reaction, the criteria used to determine the applicable reaction regime are functions of the reactant concentrations among other parameters. Solutions for the slow and fast reaction regimes have repeatedly been applied in experimental studies to determine the volumetric mass transfer coefficient, k_La, and the interfacial area per unit volume, a, respectively. Ridgway et al. (1989) demonstrated that an instantaneous reaction can be used to measure k_La in a semibatch, agitated gas-liquid reactor. To experimentally determine both k_La and a, the current practice is that the system conditions must be duplicated in separate tests or some physical method of measuring a must be utilized.

By extending the instantaneous reaction method, a semibatch system, which undergoes a transition from the fast regime to the instantaneous regime as the liquid reactant is depleted, can be developed. The advantage of such an experimental technique would be that values for both k_La and a could be calculated from a single, uninterrupted test.

Theory

The general form of the unsteady-state diffusion-reaction equation with second-order reaction has been solved numerically by Brian et al. (1961) and Pearson (1963) for a wide range of variables. van Krevelen and Hoftizer (1948) demonstrated that the solutions are approximated well in the condensed form

$$E=\frac{\sqrt{M\dfrac{E_i-E}{E_i-1}}}{\tanh\sqrt{M\dfrac{E_i-E}{E_i-1}}}$$

where E is the enhancement factor present in the system, E_i is the instantaneous enhancement factor, and $M^{1/2}$ is the Hatta number, the ratio of the reaction rate to the convective mass transfer rate. Equation 1 is presented graphically as the solid lines in Figure 1.

The values of E_i and $M^{1/2}$ determine the applicable reaction regime. Two limiting types of behavior are exhibited in Figure 1. When $M^{1/2} \ll E_i$, the solution lies along the diagonal and $E = M^{1/2}$, indicating the diffusion rate of the liquid-phase reactant is sufficiently large to maintain its bulk concentration to the interface. In this case, the absorption process operates in the fast reaction regime and a value of a can be calculated by fast reaction theory.

When $M^{1/2} \gg E_i$, the solution lies in the region where the curves are horizontal and $E = E_i$. Here, the absorption rate depends on the diffusion of both reactants. Under these conditions, the system operates in the instantaneous reaction regime, and a value for k_La can be determined (Ridgway et al., 1989).

Special attention must be given to the portion of the curves that lie in the lower left corner of the figure. The instantaneous criteria $M^{1/2} \gg E_i$ is applicable to systems that meet the re-

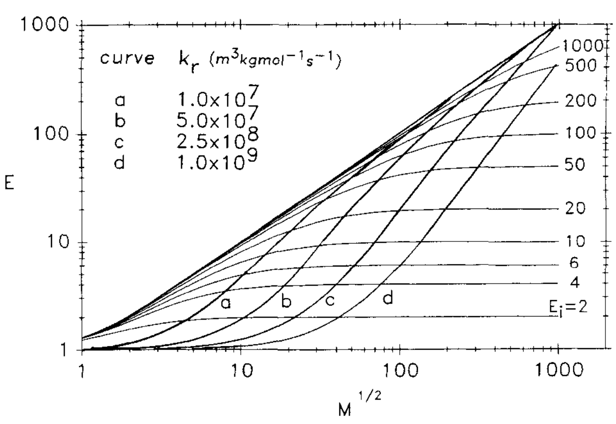

Figure 1. Enhancement factors as predicted by Eq. 1 and simulation tracks demonstrating the regime transition.

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quirement of $B_{\text{bulk}}/A^* \gg 1$, where B indicates the liquid-phase reactant and A the reactant diffusing from the gas. These concentrations lead to large values of E_i. The data in the lower left portion of the figure correspond to the values of $B_{\text{bulk}}/A^* < 1$. For this case, Pearson (1963) presents a different criterion for when instantaneous profiles are applicable.

$$k_r A^* t' \gg \log_{10}\left(\frac{B_{\text{bulk}}}{A^*}\right)^{-1}$$

where t' equals the length of time that diffusion has occurred. For penetration or surface renewal theory, this time represents the age of a surface element.

Simulations of a Transient Absorption Process

Simulations of a semibatch gas absorption were performed. In the system represented, both phases are assumed mixed well. The initial liquid-phase reactant concentration is depleted by continuous gassing at a constant gas-phase concentration. It is assumed that gas-phase resistance is negligible. A system operating at steady state would be represented by a single point on Figure 1. A transient system generates a locus of points which track from the upper right to the lower left. The exact path depends on the value of the second-order rate constant.

Four simulations are represented on the figure. The following parameter values were utilized for the simulations. These values are representative of the case of the absorption of slightly soluble gases,

where

$D_A = D_B = 3 \times 10^{-9}\ \text{m}^2 \cdot \text{s}^{-1}$
$A^* = 1 \times 10^{-4}\ \text{kmol} \cdot \text{m}^{-3}$
$k_L = 4 \times 10^{-4}\ \text{m} \cdot \text{s}^{-1}$
$k_r = 1 \times 10^7,\ 5 \times 10^7,\ 2.5 \times 10^8,\ 1 \times 10^9\ \text{m}^3 \cdot \text{kmol}^{-1} \cdot \text{s}^{-1}$
B_{bulk} = decreasing from 2 $\text{kmol} \cdot \text{m}^3$ to $5 \times 10^{-8}\ \text{kmol} \cdot \text{m}^{-3}$

Discussion

Examining the four simulations, the desired regime transition occurs for a rate constant between 3×10^7 and 5×10^7 $\text{m}^3 \cdot \text{kmol}^{-1} \cdot \text{s}^{-1}$. For higher values of k_r, the system never tracks along the diagonal for feasible liquid-reactant concentrations, indicating that it does not operate in the fast reaction regime. Conversely, for a rate constant of $1 \times 10^7\ \text{m}^3 \cdot \text{kmol}^{-1} \cdot \text{s}^{-1}$, no portion of the path tracks into the horizontal region of the figure. This indicates that the system never enters the instantaneous reaction regime.

Interestingly, the semibatch system operates in the fast reaction regime before the instantaneous regime, due to the relative rates of mass transfer and reaction. In the fast regime, the rates of reaction and mass transfer are of comparable magnitude. As the liquid-phase reactant is consumed, both reaction and diffusion rates decrease, with the diffusion rate decreasing more rapidly due to the different functionalities of the two with respect to B_{bulk}. In the instantaneous regime, the absolute reaction rate is smaller than in the fast regime, but relative to the diffusion rate it is greater. The ability to measure liquid-phase concentrations of less than $10^{-6}\ \text{kmol} \cdot \text{m}^{-3}$ is required to collect data in the instantaneous regime.

The simulations were made using a constant value of A^*. An unsteady-state, gas-phase mass balance shows that as the absorption rate decreases (due to a decrease in the enhancement factor) the gas concentration must increase. Ridgway et al. (1989) found this to be the case, using a reaction between ozone and indigo disulfonate. This decrease in the value of A^* results in a decrease in E_i while leaving the value of $M^{1/2}$ unchanged. This effect would result in the transition from fast to instantaneous operation occurring more quickly in an actual system than is demonstrated by the simulations.

Particular attention must be given to the portion of the transient paths located in the lower left corner of the figure. As an example, in this region consider a system with $k_r = 3 \times 10^7\ \text{m}^3 \cdot \text{kmol}^{-1} \cdot \text{s}^{-1}$ at the point where $B_{\text{bulk}}/A^* = 0.1$. Utilizing Pearson's criterion, the instantaneous profile is shown to apply for $t' > 3 \times 10^{-4}$ s. Since the average lifetime of a surface element in a well-agitated tank is on the order of 10^{-3} to 10^{-2} s (Astarita, 1967) the assumption that the instantaneous profile applies is valid, even though the condition $M^{1/2} \gg E_i$ is not satisfied. Ridgway et al. (1989) demonstrated that data could be collected in the region where $B_{\text{bulk}}/A^* < 1$.

The ozone-indigo system displayed indications of the desired regime transition, but the full transition could not be realized. The reaction rate was too large, $k_r > 2 \times 10^8\ \text{m}^3 \cdot \text{kmol}^{-1} \cdot \text{s}^{-1}$, to allow the system to start in the fast regime. The early points fall in the transition region between the two regimes. Despite the fact that the fast reaction criteria were not satisfied, the early portions of the indigo response curves presented in Ridgway et al. (1989) were utilized to calculate an order of magnitude estimate for a to test the feasibility of the method. An algorithm identical to that presented was utilized, except that the fast reaction regime rate expression was used. The failure to meet the given criteria and the lack of a precise value of the rate constant for the ozone-indigo reaction prohibit an exact calculation. The calculated values of a are in the range 20–70 m^{-1} for the well-agitated system. On an order of magnitude basis, they are in agreement with the published values of a (Bhakuri et al., 1987; Mehta and Sharma, 1971).

Notation

a = interfacial area per unit volume liquid, m^{-1}
A^*, A_{bulk} = liquid-phase concentration of the gaseous reactant at the interface and in the bulk liquid, respectively, $\text{kmol} \cdot \text{m}^{-3}$
B_{bulk} = concentration of the liquid-phase reactant in the bulk liquid, $\text{kmol} \cdot \text{m}^{-3}$
D_A, D_B = diffusivities of A and B, respectively, $\text{m}^2 \cdot \text{s}^{-1}$
E = enhancement factor = $R_A a / [k_L a (A^* - A_{\text{bulk}})]$, dimensionless
E_i = instantaneous enhancement factor = $(D_A/D_B)^{1/2} \times (1 + z D_B B_{\text{bulk}} / D_A A^*)$, dimensionless
$k_L a$ = volumetric mass transfer coefficient, s^{-1}
k_r = second-order rate constant, $\text{m}^3 \cdot \text{kmol}^{-1} \cdot \text{s}^{-1}$
$M^{1/2}$ = Hatta number = $[(D_A k_r B_{\text{bulk}})^{1/2}\ k_L^{-1}]$, dimensionless
R_A = absorption rate per unit interfacial area, $\text{kmol} \cdot \text{s}^{-1} \cdot \text{m}^{-2}$
t' = age of a surface element, s
z = stoichiometric coefficient in E_i, dimensionless

Literature Cited

Astarita, G., *Mass Transfer with Chemical Reaction*, Elsevier, New York (1967).

Bhakuri, S., S. C. Bhunia, and R. N. Sharma, "Studies of Interfacial Area in Gas Sparged Mechanically Agitated Vessels," Mixing XI, Engineering Foundation Conf., Henniker, NH (1987).

Brian, P. L. T., J. F. Hurley, and E. H. Hasseltine, "Penetration

Theory for Gas Absorption by a Second-Order Chemical Reaction," *AIChE J.*, **8**, 226 (1961).

Danckwerts, P. V., *Gas-Liquid Reactions*, McGraw-Hill, New York (1970).

Mehta, V. D., and M. M. Sharma, "Mass Transfer in Mechanically Agitated Gas-Liquid Contactors," *Chem. Eng. Sci.*, **26**, 461 (1971).

Pearson, J. R. A., "Diffusion of One Substance into a Semiinfinite Medium Containing Another with Second-Order Reaction," *Appl. Sci. Res.*, Sect. A, **11**, 321 (1961).

Ridgway, D., R. N. Sharma, and T. R. Hanley, "Determination of Mass Transfer Coefficients in Agitated Gas-Liquid Reactors By Instantaneous Reaction," *Chem. Eng. Sci.*, **44**, 2935 (1989).

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