

Numerical Simulation of Concentration Profile in a Pipe Flow Reactor: Modeling of Second-Order Reaction ($A(g) + B(l) \xrightarrow{k_{r2}} R(l)$)

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Abstract

In the classic analysis of gas absorption with chemical reaction, any reaction within the mass transfer film can increase the rate of absorption. This, in the film theory, is represented by an “Enhancement Factor”. Problem can arise in the analysis of gas-liquid mixing in a continuous flow reactor since the conventional approach seeks to quantify the chemical reaction enhancement by an imposition of a bulk liquid phase boundary condition for concentration of the absorbing component A. In reality, this boundary condition is set-up by the balance between film and bulk reaction. Moreover, typical reaction speeds for 2nd order reaction of a gas phase component (A) with a liquid phase reagent (B) which are likely to create an enhancement of absorption rate, are also likely to give rise to spatially variable partial or macro-segregation of the absorbing reagent, so that the bulk concentration varies with position. Hence the bulk boundary condition also varies with position. There is then a complex interaction between film enhancement and bulk liquid phase reaction. The way in which this problem can be tackled for a continuous flow reactor is illustrated for a series of perfectly mixed stages (tanks-in-series model) representation for gas-liquid mixing. The problem is then highlighted for a simplified case: a continuous co-current flow. This question has severe consequences for the proper calculation of chemical selectivity behavior for multiple gas-liquid reactions.

Keywords : enhancement factor, a pipe flow reactor, film and bulk reaction

1. Background and Objectives

In many instances when reagents are fed into the reactor, the concentration fields can exhibit partial or macro-segregation [1-2]. In other words, it seems that in practical case, the reaction rates (fast reaction) will be faster than the mixing rates over macro-scales. When this arises, parts of the reactor volume will be richer in a reagent close to an addition point [3]. It has also been shown that partial segregation effects at different scales can produce paradoxical distortion in product distribution for a triplet reaction sequence [4].

According to Levenspiel [5], if a gas-liquid reactor is sub-divided into a large number of locally backmixed elements (see Figure 1), as in a networks-of-zones approach [6], the proper application of material balances to each zone enables any consequent macro-segregation to be quantified. These difficulties have long been discussed [7-8].

This paper will outline an analysis of the gas-liquid contacting to show the concentration of reactants varying through the reactor axis and to illustrate how film and bulk reaction can be quantitatively computed for a real case. The prediction will be illustrated for the simple configuration of gas-liquid contacting in a pipe flow reactor.

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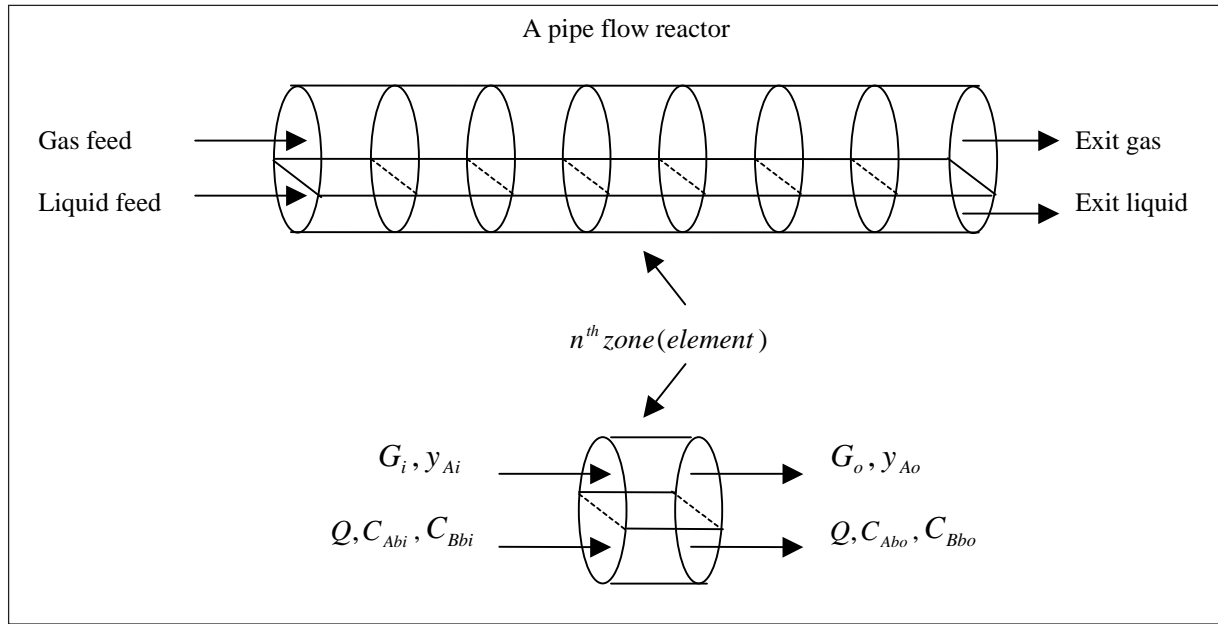


Figure 1 Series of backmixed zone (for a pipe flow reactor).

2. Modeling of Second-order Reaction in a Local Backmixed Zone

If dissolved gas A reacts with a dissolved reactant B (non-volatile substance) by an irreversible second-order reaction with stoichiometry:



considerations of the interactions of mass transfer and chemical reaction in both the film and the bulk of liquid phases require additional material balances for the reactive component B contained in the liquid phase. The diffusion reaction equations for first-order reaction with respect to A and B are now:

$$\begin{aligned} D_A \frac{d^2 C_A}{dx^2} - k_{r2} C_A C_B &= 0 \\ D_B \frac{d^2 C_B}{dx^2} - z k_{r2} C_A C_B &= 0 \end{aligned} \quad (2)$$

with imposed boundary conditions

$$\begin{aligned} C_A &= C_A^*, x=0 \\ C_A &= C_{Abo}, x=\delta \\ C_B &= C_{Bbo}, x=\delta \end{aligned} \quad (3)$$

(no transfer of reactant B to gas phase)

In providing a general approach to the solution of a single backmixed element, it is essential that the direct solution of the two second order nonlinear equation, ODE's, which are embedded in the algebraic equations governing the overall material balances, are avoided. To do this, it is possible to provide some suitable approximation to the enhancement factor. At low reaction speed, the approximation is to use a value of unity. However, under "infinitely" fast reaction conditions, the overall reaction rate is governed by the diffusion of both A and B to a reaction plane within the liquid film. Thus, at this condition the nature of the kinetics is irrelevant, and the enhancement factor has reached an ultimate asymptotic value.

Considering equation (2), an analytical solution of this set of equations is not available, but van Krevelen and Hoftijzer [9-10] computed an approximate set of solutions for the case $C_{Abo} = 0$ and showed that they could be fitted within about 10% by simple empirical relationships, thus

$$\bar{R} = k_L C_A^* \bar{V} a E_A \quad (4)$$

where

$$E_A = \frac{\sqrt{(M \frac{E_i - E_A}{E_i - 1})}}{\tanh \sqrt{(M \frac{E_i - E_A}{E_i - 1})}}$$

$$M = \frac{D_A k_{r2} C_{Bbo}}{k_L^2}$$

$$E_i = (1 + \frac{D_B C_{Bbo}}{z D_A C_A^*})$$

Van Krevelen and Hoftijzer [9-10] presented their results for the case where $D_A = D_B$ but an inspection of the equations which has been solved shows that if the variables specified above are used, equation (4) is applicable to the case $D_A \neq D_B$.

According to Danckwerts [11], the flux of reactant A across the gas-liquid interface into liquid film can be written:

Molar flow rate of reactant A from the film-bulk interface to the bulk of liquid + rate of reactant A entering the bulk of liquid = reaction rate of reactant A with reactant B in the bulk of liquid + rate of component A leaving from the bulk of liquid

$$N_A|_{x=\delta} + QC_{Abl} = k_{r2} C_{Abo} C_{Bbo} V + QC_{Abo} \quad (7)$$

Substituting equation (6) into equation (7) gives:

$$C_{Abo} = \frac{C_A^* + \frac{QC_{Abl} \cosh \sqrt{M}}{V a k_L E_A}}{k_1} \quad (8)$$

where

$$k_1 = (1 + \frac{k_{r2} C_{Bbo}}{a k_L E_A} + \frac{Q}{V a k_L E_A}) \cosh \sqrt{M}$$

Eliminating C_{Abo} by substituting equation (8) into equation (5) and rearranging for C_A^* gives:

$$C_A^* = \frac{N_A|_{x=0} + k_3}{k_2} \quad (9)$$

where

$$k_2 = V k_L a [1 - \frac{1}{k_1 \cosh \sqrt{M}}] E_A$$

$$k_3 = \frac{QC_{Abl}}{k_1}$$

$$N_A|_{x=0} = -D_A (\frac{dC_A}{dx})_{x=0} V a = k_L V a (C_A^* - \frac{C_{Abo}}{\cosh \sqrt{M}}) E_A \quad (5)$$

And the molar flow rate of component A from the film-bulk interface into the local "well mixed" bulk of liquid is expressed as:

$$N_A|_{x=\delta} = -D_A (\frac{dC_A}{dx})_{x=\delta} V a = k_L V a (-\frac{C_A^*}{\cosh \sqrt{M}} - C_{Abo}) E_A \quad (6)$$

The performance of a backmixed element (Figure 2) is then determined by a balanced consumption of component A and component B, where component A is treated exactly as in the single reagent case ($A(g) \xrightarrow{k_{r1}} R(l)$) and conditions for reaction of component B must be additionally satisfied.

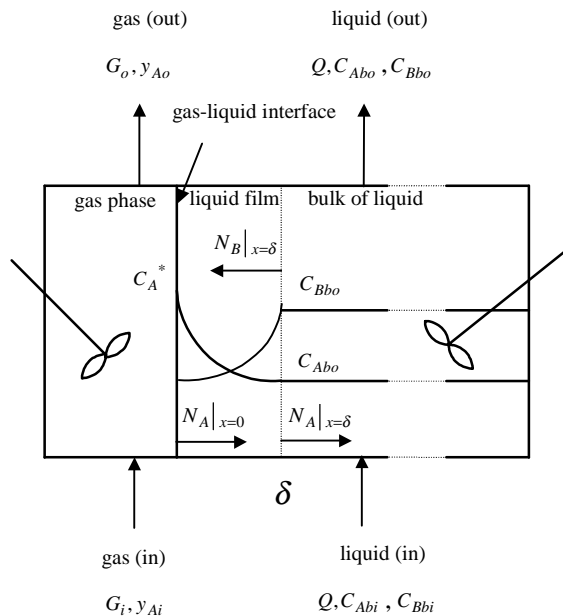


Figure 2 Mass balance (on A and B) over a single perfectly-mixed zone in a pipe flow reactor for the case of bimolecular-type reaction $A(g) + B(l) \xrightarrow{k_{r2}} R(l)$.

From Henry's law, the solubility relationship between the partial pressure of component A (p_A) and the concentration of component A (C_A^*) at gas-liquid interface can be expressed by:

$$p_A = H_A C_A^* = y_{Ao} P \quad (10)$$

Substituting C_A^* from equation (9) into equation (10) gives:

$$N_A|_{x=0} = \frac{y_{Ao} P k_2}{H_A} - k_3 \quad (11)$$

According to the material balance of reactant A over the gas phase,

$$N_A|_{x=0} = G_i \frac{(y_{Ai} - y_{Ao})}{(1 - y_{Ao})} \quad (12)$$

Equating equation (11) with equation (12) and rearranging gives:

$$\left(\frac{k_2 P}{H_A}\right) y_{Ao}^2 - (G_i + \frac{k_2 P}{H_A} + k_3) y_{Ao} + (k_3 + G_i y_{Ai}) = 0 \quad (13)$$

If the inlet conditions are given, the quadratic equation above can be solved for outlet gas compositions. However, for the reaction between component A and component B, the value of E_i depends on the outlet composition, then, it is necessary to initially estimate by using the inlet composition and then update with each iteration until it converges within a specified tolerance. In order to calculate other parameters, it can be then back substituted into the previous equations.

3. Modeling of Strings of Backmixed Zone in a Pipe Flow Reactor

Modeling a simple pipe flow reactor used for contacting 10% ozone in gas stream with a liquid stream containing a reactive substrate is one of the objectives of this research. After a single backmixed element model has been developed, a series of backmixed elements (zones) can be arranged in a

configuration which will simulate the characteristics of a pipe flow reactor.

3.1 Model Formulation

According to Levenspiel [5], if the reactor is divided into equal volume backmixed elements (volumes), each volume is actually equal to $\frac{V}{N}$. For illustration in this case, N is assumed to be 10 and Moreover, the property of each zone before operating is exactly the same.

Gas stream containing reactant A and liquid stream containing substrate B are continuously fed from the bottom to the top of the reactor. After being contacted together, the gas and liquid streams at the outlet of the 1st zone will enter the 2nd zone. This will continue till the zone. On reaching the N^{th} zone, these two streams then leave from the system.

Table 1 Illustrative parameters for an ozone reaction simulation (2nd - order reaction)

Parameters	Values
N	10 zone
D_A	$2.0 \times 10^{-9} \text{ m}^2 \text{ s}^{-1}$
D_B	$2.0 \times 10^{-9} \text{ m}^2 \text{ s}^{-1}$
\bar{a}	$70 \text{ m}^2 \text{ m}^{-3}$
k_L	$2.14 \times 10^{-5} \text{ m s}^{-1}$
H_A	$7.6 \times 10^6 \text{ N kmol}^{-1} \text{ m}^{-5}$
P	$1.01 \times 10^5 \text{ N m}^{-2}$
V	1 m^3
y_{Ai}	0.1
G_i	$5.0 \times 10^{-6} \text{ kmol s}^{-1}$
C_{Abi}	0 kmol m^{-3}
C_{Bbi}	1 kmol m^{-3}
Q	$5.0 \times 10^{-7} \text{ m}^3 \text{ s}^{-1}$
k_r	$1.0 \times 10^{-6} \text{ to } 1.0 \times 10^3 \text{ m}^3 \text{ kmol}^{-1} \text{ s}^{-1}$

Source : Perry and Green [12]

3.2 Method of Solving

The outlet “parameters” of each zone connecting in series can be found by solving the same algorithm already discussed in previous section. For example, if the algorithm is run using 10 zones, it solves for the outlet parameters at the first zone (by using data in Table 1) first and then uses these output parameters as the inlet values for the next zone. This procedure obviously continues till the final zone is reached. The overall results show how the relative amounts of film and bulk reaction may vary through the reactor.

3.3 Results and Discussion

For N=10, considering the first zone, before reactant A can react with substrate B in the liquid phase, it must pass through the gas-liquid interface. And it then has the opportunity to react with substrate B in the liquid film. Any unreacted A transports across the film-bulk liquid boundary to react with substrate B in the bulk liquid phase before convecting out of the zone and entering again as the fresh feed of liquid into the next zone. Back to the gas phase again, while some reactant A absorbs and dissolves into the liquid phase, the rest must leave and then directly enter the next zone. As a result the concentration of gas A from each zone will be decreased with the zone number.

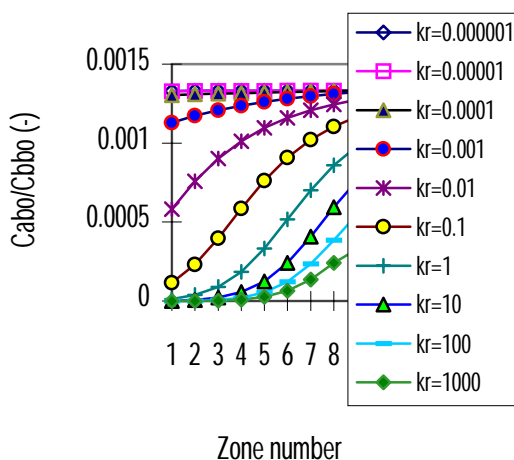


Figure 3 Ratio of C_{Abo} and C_{Bbo} with zone number.

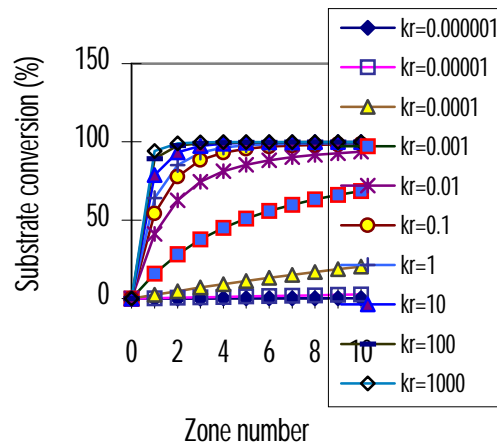


Figure 4 Increase in percentage conversion of reactant A along the zone number (or the length of the reactor).

Figure 3 shows the ratio of the outlet concentration of component A and B in the bulk of liquid phase which increases and varies according to the reaction rate constant. Because at the outlet liquid stream, the concentration of reactant B decreases from the first zone to the final zone, certainly this ratio increases.

According to the definition of the fractional conversion of reactant A, X_A , defined as below [7]:

$$X_A = \frac{N_{Ao} - N_A}{N_{Ao}}$$

where N_{Ao} is moles of reactant A entering the system and N_A is moles of reactant A leaving the system. Thus percentage conversion of reactant A for each zone can be expressed as:

$$\% \text{ conversion of A} = 100 * (\text{Mole A reacted} / \text{Mole A entering the system})$$

Figure 4 illustrates an increase in percentage conversion of reactant A with the number of zones (the reactor length). From the same figure, the higher the reaction rate constant, the greater the substrate conversion becomes.

The calculated result for the percentage film reaction taking place in each zone is then presented

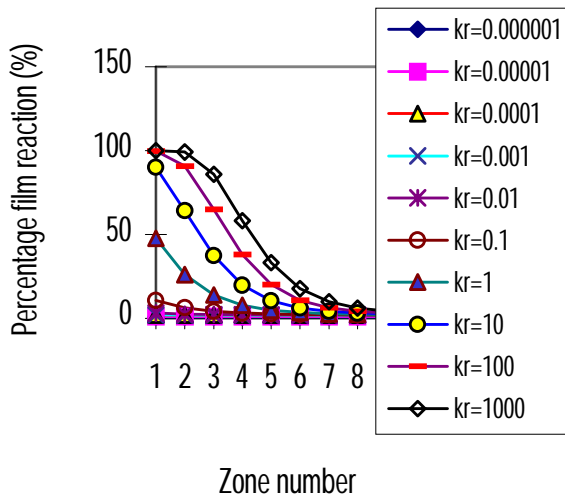


Figure 5 Depletion of percentage film reaction versus zone number.

in Figure 5. As expected, the reaction between reactant A and B in the liquid film is a maximum in the first zone and then decreases dramatically at the next zone until the last zone. Interestingly, the percentage film reaction is usually high when the ratio $(\frac{C_{Abo}}{C_{Bbo}})$ is low (see Figure 3).

And, of course, for higher reaction rate constants the effect on percentage film reaction is more obvious. For low reaction rate constants, the reaction between A and B occurs solely in the bulk liquid phase. For example at $k_r = 1.0 \times 10^{-6}$, 1.0×10^{-5} and $1.0 \times 10^{-4} \text{ m}^3 \text{ kmol}^{-1} \text{ s}^{-1}$, the percentage film reaction is very close to zero. It means that there is negligible reaction taking place within the liquid film. Almost all reaction then occurs in the bulk of the liquid phase. Again, the two extremes of “all film” and “all bulk” reaction apply over a large range of reaction rate constant. For instances, the proportion of film reaction for the reaction rate constant of 1.00×10^{-2} and $1.00 \times 10^{-3} \text{ m}^3 \text{ kmol}^{-1} \text{ s}^{-1}$ falls with the length of the reactor (zone number) from an initial value of 100% down to about 2 to 3%. So again, at the bottom of the contactor the absorption behavior is largely in the liquid film whereas it is nearly completely in the liquid bulk at the top of the reactor.

4. Conclusion

The model of a simple pipe flow reactor has been developed without making any prior assumption which is imposed upon the reaction-diffusive regime within the mass transfer film (fast, slow, etc.). By means of the film theory, a full analysis of gas-liquid absorption for the 2nd-order reaction in a single backmixed element has been made first then used it as a basis in developing a pipe flow reactor model using interconnecting backmixed elements.

By the approach developed, the profile of the reactant (and other parameters involved in gas-liquid absorption with chemical reaction) through the reactor axis can be computed. The reactant A and B decrease from the bottom to the top of the vessel. The variation of film and bulk reaction which depends on the ratio of liquid bulk concentration of reactant A to substrate B has also been calculated.

5. Nomenclature

\bar{a}	Interfacial area	$\text{m}^2 \text{ m}^{-3}$
A	Reactant A	
B	Reactant B (non-volatile substance)	
C_A	Concentration of reactant A	kmol m^{-3}
C_A^*	Concentration of A at gas-liquid interface	kmol m^{-3}
C_{Abi}	Initial concentration of reactant A	kmol m^{-3}
C_{Abo}	Liquid bulk concentration of reactant A	kmol m^{-3}
D_A	Diffusivity of reactant A	$\text{m}^2 \text{ s}^{-1}$
D_B	Diffusivity of reactant	$\text{m}^2 \text{ s}^{-1}$
E_A	Enhancement factor, reaction factor	-
E_i	Enhancement factor for an infinitely fast reaction	-
G_i	Total gas molar flow rate (inlet)	kmol s^{-1}
G_o	Total gas molar flow rate (outlet)	kmol s^{-1}
Ha	Hatta number	-
H_A	Henry constant	$\text{N kmol}^{-1} \text{ m}^5$
k_1, k_2, k_3	Constant	-
k_{r2}	Reaction rate constant for 2 nd order reaction	

		$\text{m}^3 \text{ kmol}^{-1} \text{ s}^{-1}$
k_L	Liquid side mass transfer coefficient	m s^{-1}
M	Film conversion parameter	-
$N_A _{x=0}$	Molar flow rate of A at gas-liquid interface	kmol s^{-1}
$N_A _x$	Molar flow rate of A at outer-liquid film interface	kmol s^{-1}
P	Total pressure of the system	N m^{-2}
p_A	Partial pressure	N m^{-2}
Q	Liquid volumetric flow rate	$\text{m}^3 \text{ s}^{-1}$
r	Local rate of reaction (2^{nd} order)	
		$\text{kmol m}^{-3} \text{ s}^{-1}$
\bar{R}	Absorption rate	kmol s^{-1}
V	Liquid volume	m^3
X_A	Fractional conversion of reactant A	-
y_{Ai}	Mole fraction of reactant A (inlet)	-
y_{Ao}	Mole fraction of reactant A (outlet)	-

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