Improved and Generalized Criteria for the Instantaneous Regime for Multiple Parallel Gas-Liquid Reactions

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Abstract

The classic criteria to determine if a second-order irreversible gas-liquid reaction $(A_G + \nu_B B_L \rightarrow \nu_C C_L)$ proceeds in the instantaneous regime are based on the Hatta number, HaA, and the infinite enhancement factor, $E_{A,\infty}$, i.e., $Ha_A > 2$ and $Ha_A \gg E_{A,\infty} - 1$. There is no consensus, however, with respect to the latter threshold value and this work shows that it highly depends on the considered reactant concentrations and rate coefficients, in particular when the non-volatility assumption of the liquid phase component is relieved. Generalizing the original derivation yields an extended expression, which is condensed into a new dimensionless number, $\phi_{A,\infty}$, and allows to rewrite the second criterion as $\phi_{A,\infty} \ge$ 15, where $\varphi_{A,\infty} = \frac{Ha_A}{E_{A,\infty}-1} - E_{A,\infty}$. Next, it is demonstrated that a breakthrough of the gas-phase reactant into the bulk-liquid is readily observed at high interface concentrations of the gas-phase reactant with respect to the bulk concentration of the liquid-phase reactant, even though the classic criteria have been met. Such a situation is quite common in the chemical industry, e.g., in case of the selective reactive removal of an impurity (B_L) from a process stream containing a valuable product by a soluble gaseous component (A_G). The root cause of this deviating behavior results from the position of the reaction plane and an additional criterion, $\phi_{B,\infty} \ge 15$, is needed to resolve this. As such, the set of improved criteria are necessary and sufficient to describe the instantaneous regime for any position of the reaction plane. To conclude, a methodology is presented to apply the modified criteria to multiple

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parallel reactions, and the validity of these improved and generalized criteria is numerically demonstrated.

Keywords

Gas-Liquid mass transfer, instantaneous reaction, enhancement factor, Hatta number

Nomenclature

Abbreviations

BTX	Benzene, Toluene and Xylenes	
PFO	Pseudo-First Order	
vKHa	van Krevelen and Hoftijzer approximation	
Roman		
Al	Hinterland ratio	_
c _A	molar concentration of component A	$mol m_L^{-3}$
${\cal D}$	diffusion coefficient in the liquid phase	$m_L^3 m_L^{-1} s^{-1}$
E	enhancement factor	_
E_{∞}	infinite or instantaneous enhancement factor	_
Fom	Fourier number for mass transfer	_
Н	Henry coefficient	m_L^3 Pa mol ⁻¹
На	Hatta number	_
J	diffusional molar flux	$mol \ m_L^{-2} \ s^{-1}$
[J]	normalized concentration of component j	$\mathrm{mol}_{\mathrm{j}} \mathrm{mol}_{\mathrm{j}}^{-1}$
j	reaction number	_
k	volumetric reaction rate coefficient	s^{-1} or s^{-1} m_L^3 mol ⁻¹
k_L	liquid-phase mass transfer coefficient	$m_L s^{-1}$
Ν	number of reactions	_
	N^{X} number of reactions in the system for which $\text{Ha}_{\text{X},j}>2$	_
r _V	molar rate of production per unit of volume of liquid	$mol \ m_L^{-3} \ s^{-1}$

R _V	net molar rate of production per unit of volume of liquid	$mol \ m_L^{-3} \ s^{-1}$			
S	renewal rate	s^{-1}			
t	clock time	S			
Х	position perpendicular to the interface	m _L			
Z	dimensionless position perpendicular to the interface	$m_Lm_L^{-1}$			
Greek					
$\boldsymbol{\delta}_{f}$	film thickness	m _L			
δ_{R}	position of the reaction plane	m_L			
ν	normalized stoichiometric number	-			
τ	contact time	S			
φ	dimensionless reaction modulus	_			
φ	improved criterion for the instantaneous regime	_			
Sub- and	Sub- and superscripts				
(1)	first order				
(m, n)	m^{th} order in the first component, $n^{th} order$ in the second comp	onent			
0	initial				
А	component A				
В	component B				
b	bulk liquid				
С	concentration				
f	film				
G	gas				
i	interface				
j	species number				
	reaction number				
L	liquid				
R	reaction plane				

r

reactor

3

1 Introduction

For gas-liquid reaction systems, mass transfer accompanied by a chemical reaction has been extensively investigated during the last century, which has resulted in various convection-reaction models based on the stagnant-(two-)film [1–4], penetration or surface-renewal mass transfer theory [5,6]. In these models, the hydrodynamic conditions near the gas-liquid interface are described by a single parameter, i.e., the film thickness δ_f , the contact time τ or the probability of liquid-element replacement s respectively. Furthermore, the Hatta number Ha and the (infinite) enhancement factor $E_{(\infty)}$ are key dimensionless parameters from which the reaction regime can be deduced, see Figure 1. The former is physically proportional to the ratio of the maximal reaction flux to the maximal transferrable flux, whereas the latter corresponds to the ratio of the (maximal) molar flux in the presence of a chemical reaction to the maximal transferrable flux without reaction. In spite of its limited physical meaning, the stagnant-film approximation is extensively used [7] due to its mathematical simplicity and the quantitative similarity with more realistic models [3].



Figure 1 Concentration profiles of A (-) and B (...) for the slow (-), the fast (-) and the instantaneous (-) reaction regime in the film model.

In the pioneering work of van Krevelen and Hoftijzer [8] on the film model, a reaction A + $\nu_B B \rightarrow \nu_C C$ is considered to proceed in the instantaneous regime when the criteria Ha_A > 2 and Ha_A \gg E_{A,∞} - 1 are fulfilled. In this regime, the reaction takes place in a so-called reaction plane, with a width

that is small compared to the width of the film. Characteristic for this regime is that negligible amounts of component A manage to protrude into the bulk-liquid, i.e., the breakthrough of component A from the liquid film to the liquid bulk (see eq. (1)), is limited to, e.g., 1%. Similarly, if component B can enter the gas phase, its breakthrough (see eq. (2)) is also negligible.

breakthrough of A =
$$\frac{J_{A_L,b}}{J_{A_L,i}} = \frac{\left(\frac{dc_{A_L}}{dx}\right)_{x=\delta_f}}{\left(\frac{dc_{A_L}}{dx}\right)_{x=0}}$$
(1)

breakthrough of B =
$$\frac{J_{B_{L},i}}{J_{B_{j},b}} = \frac{\left(dc_{B_{L}}/dx\right)_{x=0}}{\left(dc_{B_{L}}/dx\right)_{x=\delta_{f}}}$$
(2)

To date, these criteria are widely accepted as necessary and sufficient throughout the entire film [5], even though the original derivation was performed for a narrow zone near the gas-liquid interface, i.e., remote from the bulk liquid.

The limitations of these criteria were demonstrated in a research project at Shell involving the selective removal of an impurity B, present at relatively low concentrations in a liquid product stream containing a valuable product P, by means of a soluble gaseous component A (e.g., oxidation or chlorination). Such systems can be generally represented by a set of parallel reactions: $A_L + v_B B_L \xrightarrow{k_1} v_C C_L$ and $A_L + v_P P_L \xrightarrow{k_2} v_X X_L$.

For such a system, even when the classic criteria are well met, there can be significant breakthrough of the dissolved component A into the bulk liquid, whereas the concept of instantaneous regime hinges on the reaction taking place in a small plane within the film, i.e., near complete depletion of A within the film. The deviating behavior of the criteria results from the liquid-phase concentration of A at the gas-liquid interface being low compared to the concentration of P in the bulk, while being high compared to the bulk concentration of B. This causes the infinite enhancement factor of A to be significantly smaller than 2, i.e., relatively close to 1. Pearson [9] has reported a general solution strategy for both high and low infinite enhancement factors, for a substance diffusing into a semi-infinite medium accompanied by a second-order reaction that did include systems for which $E_{A,\infty} < 2$. However, the

developed theory is only applicable to the penetration theories of Higbie [10] and Danckwerts [11] as it involves a finite diffusion time. To the best of our knowledge, criteria that are applicable throughout the entire boundary layer have not yet been reported for the film model.

In this work, the shortcomings of the classic criteria will first be demonstrated using an elementary three-component diffusion-reaction model, $A_L + v_B B_L \xrightarrow{k_1} v_C C_L$, using identical model assumptions as reported by the aforementioned authors. By revisiting their mathematical derivation, a generalized Hatta number and two new dimensionless numbers ($\varphi_{A,\infty}$ and $\varphi_{B,\infty}$) will be introduced which will allow to adequately determine the reaction regime *a priori*, regardless of the location of the reaction plane in the film. Next, the reaction system is generalized towards the case of multiple parallel reactions, which includes the example for the selective reactive removal of an impurity that had triggered this work.

2 Dimensionless model equations

The diffusion-reaction systems considered in this work are composed of N parallel irreversible reactions. For simplicity, the model-equations are presented for N = 2, corresponding to the case of the selective reactive absorption which will be addressed in detail in section 3.2.3. Assuming homogeneous irreversible reactions of order (1,1), the model system and rate equations are equal to:

gas-liquid mass transfer:
$$A_G \rightarrow A_L$$
 (3)

irreversible impurity removal:
$$A_L + v_B B_L \xrightarrow{k_1^{(1,1)}} v_C C_L$$
 with $r_{V,A_1} = k_1^{(1,1)} c_{A_L} c_{B_L}$ (4)

undesired side reaction:
$$A_L + \nu_P P_L \xrightarrow{k_2^{(1,1)}} \nu_X X_L$$
 with $r_{V,A_2} = k_2^{(1,1)} c_{A_L} c_{P_L}$ (5)

Additional model-assumptions include instantaneous equilibrium at the gas-liquid interface, no advective contributions, unidirectional transport, and non-volatility of the liquid-phase reactants B_L and P_L . These assumptions limit the reaction zone to the liquid phase and therefore the subscripts L denoting this phase are omitted from here on. It is also assumed that a sufficiently large well-mixed liquid bulk

is present, and that the film has reached steady state. The former corresponds to a Hinterland ratio Al = $(1 - \epsilon)/(a\delta_f) \gg 1$, while the latter means that the Fourier number (i.e., Fo_m = $D_A t/\delta_f$) will not affect the value of the enhancement factor [12,13].

The steady-state dimensionless stagnant-film model equations for the reacting species of the irreversible diffusion-reaction system are presented in eq. (10) to eq. (12) as a function of the Hatta numbers Ha_{A_1} and Ha_{A_2} (eq. (6) and eq. (7) resp.), and the infinite enhancement factors $E_{B,\infty}$ and $E_{P,\infty}$ (eq. (8) and eq. (9) resp.).

$$Ha_{A_{1}} = \frac{1}{k_{L}} \sqrt{\mathcal{D}_{A} k_{1}^{(1,1)} c_{B,b}}$$
(6)

$$Ha_{A_2} = \frac{1}{k_L} \sqrt{\mathcal{D}_A k_2^{(1,1)} c_{P,b}}$$
(7)

$$E_{B,\infty} = 1 + \frac{\nu_B \mathcal{D}_A c_{A,i}}{\mathcal{D}_B c_{B,b}}$$
(8)

$$E_{P,\infty} = 1 + \frac{\nu_P \mathcal{D}_A c_{A,i}}{\mathcal{D}_P c_{P,b}}$$
⁽⁹⁾

In the film model, the mass transfer coefficient k_L equals \mathcal{D}_A/δ_f . The dimensionless variables were obtained through normalization of the gas-phase component to its liquid-side interface concentration (which equals the saturation concentration in the absence of gas-side mass transfer resistance) and the liquid-phase components to their respective bulk-liquid concentrations: $A(x) = c_A(x)/c_{A,i}$, $B(x) = c_B(x)/c_{B,b}$, $P(x) = c_P(x)/c_{P,b}$. Finally, the dimensionless spatial coordinate was obtained through normalization to the film thickness: $Z = x/\delta_f$.

The model equations, hence, are:

$$\frac{d^2 A}{dZ^2} = Ha_{A_1}^2 A B + Ha_{A_2}^2 A P$$
(10)

$$\frac{\mathrm{d}^2 \mathrm{B}}{\mathrm{d} \mathrm{Z}^2} = \left(\mathrm{E}_{\mathrm{B},\infty} - 1\right) \mathrm{Ha}_{\mathrm{A}_1}^2 \mathrm{A} \mathrm{B} \tag{11}$$

$$\frac{d^2 P}{dZ^2} = (E_{P,\infty} - 1) Ha_{A_2}^2 A P$$
(12)

Similar to the theory described by Westerterp et al. [5], the gas-phase component A is assumed to absorb in the liquid film and chemically react with the non-volatile reactants B and P [5]. This yields the following boundary conditions at the gas-liquid interface:

At Z = 0: A = 1,
$$\frac{dB}{dZ} = 0$$
, $\frac{dP}{dZ} = 0$ (13)

The boundary conditions near the film-bulk boundary are open, i.e., all concentrations are set to their corresponding bulk concentrations while A is set to zero, see eq. (14).

At
$$Z = 1$$
: $A = 0, B = 1, P = 1$ (14)

The solution of this set of ordinary differential equations allows to calculate the flux across the gasliquid interface and the film-bulk boundary liquid of, e.g., A (eq. (15)) and B (16). From which the breakthrough of these components into the bulk-liquid and gas phase is obtained using eq. (1) and eq. (2) resp.

breakthrough of A in the bulk liquid =
$$\frac{J_{A,b}}{J_{A,i}}$$
 (15)
with $J_{A,b} = -\mathcal{D}_A \left(\frac{dA}{dZ}\right)_{Z=1}$ and $J_{A,i} = -\mathcal{D}_A \left(\frac{dA}{dZ}\right)_{Z=0}$
breakthrough of B in the gas phase = $\frac{J_{B,i}}{J_{B,b}}$
with $J_{B,i} = -\mathcal{D}_B \left(\frac{dB}{dZ}\right)_{Z=0}$ and $J_{B,b} = -\mathcal{D}_B \left(\frac{dB}{dZ}\right)_{Z=1}$

The equations were investigated using parameter values and variable ranges to cover a sufficiently wide range of Hatta numbers (Ha = $10^{-2} - 10^3$) and enhancement factors (E_{∞} - 1 = $10^{-5} - 10^5$). The

values of the diffusion coefficients ($\mathcal{D} = 10^{-9} \text{ m}_{\text{L}}^3 \text{ m}_{\text{L}}^{-1} \text{ s}^{-1}$) and the liquid mass transfer coefficient ($k_{\text{L}} = 5 \ 10^{-5} \text{m}_{\text{L}} \text{ s}^{-1}$) were taken from the literature reports of Schumpe et al. [14] and Van Elk et al. [15] resp. The rate coefficients ($k = 10^{-1} - 10^3 \text{ m}_{\text{L}}^3 \text{ mol}^{-1} \text{ s}^{-1}$) and component concentration ($c = 10^{-2} - 10^3 \text{ mol} \text{ m}_{\text{L}}^{-3}$) were varied within an arbitrary but physically meaningful range, to yield the aforementioned Hatta numbers and enhancement factors.

3 Revision classic criteria

The classic criteria for the fast and instantaneous reaction regimes originate from van Krevelen and Hoftijzer [8] and their validity for $E_{\infty} < 2$ is first assessed for a single irreversible second-order reaction to clearly demonstrate that the deviating behavior is not caused by the occurrence of several reactions in parallel.

3.1 Single reaction
$$A_L + v_B B_L \xrightarrow{k_1} v_C C_L$$

3.1.1 Classic criteria 1 and 2 for $E_{A,\infty} > 2 (c_{B,b} > v_B c_{A,i})$

A key assumption in the derivation of the classic criteria for the instantaneous regime is that the reaction plane (δ_R) in the liquid film is located near the gas-liquid interface, see Figure 2. For equal diffusivities of both components, this corresponds to an infinite enhancement factor well above 2 as the liquid-phase concentration of A is substantially smaller than that of B.



Figure 2 Schematic representation of the van Krevelen and Hoftijzer approximation near the gasliquid interface for a single irreversible reaction of order (1,1).

The first assumption in the van Krevelen and Hoftijzer approximation (vKHa) is the non-reactive transport of component B to the gas-liquid interface (Figure 2, assumption 1), followed by a pseudo-first order (PFO) approximation on the reacting system by considering the concentration of component B to be constant throughout the entire reaction zone (Figure 2, assumption 2). For the irreversible bimolecular model-reaction $A + v_B B \rightarrow v_C C$ of order (1,1), imposing a complete diffusion limited transport of B then yields the classic criteria for the instantaneous regime [5].

classic criterion 1:
$$Ha_A > 2$$
 (17)

with
$$\text{Ha}_{A}=\frac{1}{k_{L}}\sqrt{\mathcal{D}_{A}\;k_{1}^{(1,1)}c_{B,b}}$$

classic criterion 2: $\operatorname{Ha}_{A}(E_{A,\infty}-1)^{-1} \gg 1$ (18)

with
$$E_{A,\infty} = 1 + \frac{\mathcal{D}_B c_{B,b}}{\nu_B \mathcal{D}_A c_{A,i}}$$

According to Westerterp et al. [5], by taking Ha_A 10 times larger than $E_{A,\infty} - 1$ in eq. (18), these criteria are necessary and sufficient to describe the instantaneous regime because the breakthrough of reactant A into the bulk liquid was limited to 1% (Figure 3, left). Several authors have put forward alternative

expressions and numeric values for the second criterion such as $Ha_A > 10 E_{A,\infty}$ (Sebastia-Saez et al. [16]) or $Ha_A > 10$ (Kale et al. [17]).

However, numerical screening of the reactant concentrations and rate coefficients showed that the limiting value for the second criterion is a function of the physical parameters of the simulated system. Figure 3 (left) shows that using a value of 10 in eq. (18), as recommended by Westerterp, usually works well for $E_{A,\infty}>2$ because there are virtually no points in the upper right quadrant for a breakthrough-limit of 1%. The parameter-dependency of this value becomes clear when the non-volatility boundary condition for B is relaxed, i.e., when it is no longer imposed that $\frac{dB}{dz}(Z = 0) = 0$ but B(Z = 0) = 0, thus allowing a potential flux of the liquid-phase component B into the gas phase. As shown in Figure 3 (right), Ha_A should then be at least 35 times the value of $E_{A,\infty} - 1$ to limit the breakthrough of B into the gas-phase to 1%. It can therefore be concluded that the non-volatile nature of B limits the impact of criterion 2 on the full assessment of the reaction regime. The figure also shows that the obtained *in silico* data is composed of subsets which appear to be a function of $E_{A,\infty}$.



Figure 3 Numerical evaluation of the breakthrough of reactant A into the bulk-liquid (left) and of reactant B into the gas-phase (right) as a function of $Ha_A(E_{A,\infty} - 1)^{-1}$ for $E_{A,\infty} > 2$ (×) and $E_{A,\infty} = 2$ (-D-). The thresholds of 1% (···) and the threshold values for criterion 2 (-) are shown as well. Numerical simulations were performed for $\mathcal{D}_A = \mathcal{D}_B$: $10^{-9} m_L^3 m_L^{-1} s^{-1}$, k_L :

 $5 \ 10^{-5} m_L s^{-1}$, k: 1 to $10^3 m_L^3 mol^{-1} s^{-1}$, $c_{A,i}$ and $c_{B,b}$: 10^{-2} to $10^3 mol m_L^{-3}$. Reactant B was considered volatile.

3.1.2 Limitations of classic criterion 2 for $E_{A,\infty} < 2 (c_{B,b} < v_B c_{A,i})$

With increasing interface-concentration of A, $E_{A,\infty}$ is reduced and the reaction plane (δ_R) shifts more towards the film-bulk boundary of the film (for which $E_{A,\infty} < 2$). As a result, the assumptions on which the original vKHa was based are no longer valid. The breakthrough of the gas-phase component A was evaluated for a large number of parameter values and, hence, various positions of the reaction plane while the first criterion (Ha_A > 2) was always fulfilled. The results are shown in Figure 4.

If the classic criteria are fulfilled, the reaction should operate in the instantaneous regime (i.e., less then 1% breakthrough), regardless of the selected reaction-parameter combinations. However, the datapoints in the red quadrant correspond to reaction conditions for which a significant or even large breakthrough of A into the bulk-liquid occurs, despite meeting the classic criteria shown in equations (17) and (18).

Figure 4 also clearly demonstrates that, the center of the film ($E_{A,\infty} = 2$) plays a pivotal role; for $E_{A,\infty} < 2$, the classic criteria are often no longer sufficient due to the shifted position of the reaction plane resulting from a significantly higher concentration of component A compared to that of component B. Furthermore, solely increasing the threshold of criterion 2 would not suffice to cope with its deviating behavior as the criterion's value inherently increases with decreasing $E_{A,\infty}$. It should be noted that the simulation results presented in Figure 4 are obtained by applying the standard boundary conditions as shown in eq. (13) and eq. (14). A qualitative analysis of the parameter values showed that the breakthrough-likelihood increased for decreasing rate coefficients and increasing ratios of the interface-concentrations of A to the bulk concentration of B.



Figure 4 Breakthrough of reactant A into the bulk-liquid for which the classic criteria for the instantaneous regime are fulfilled. The data was categorized according to the infinite enhancement factor: $E_{A,\infty} > 2$ (×), $E_{A,\infty} = 2$ (-□-) and $E_{A,\infty} < 2$ (Δ). The thresholds of 1% (…) as well as $Ha_A(E_{A,\infty} - 1)^{-1}$ (¬) are also shown. The simulations were performed for $\mathcal{D}_A = \mathcal{D}_B$: $10^{-9} \text{ m}_L^3 \text{ m}_L^{-1} \text{ s}^{-1}$; $k_L = 5 \ 10^{-5} \text{m}_L \text{ s}^{-1}$; $k = 1 \text{ to } 10^3 \text{ m}_L^3 \text{ mol}^{-1} \text{ s}^{-1}$, $c_{A,i}$ and $c_{B,b} = 10^{-2}$ to $10^3 \text{ mol} \text{ m}_L^{-3}$. Reactant B was considered non-volatile. Data points inside the red quadrant are instantaneous according to the classic criteria even though a significant breakthrough in the bulk-liquid will occur.

3.1.3 Revisiting criterion 2 for
$$E_{A,\infty} > 2 (c_{B,b} > v_B c_{A,i})$$

Before deriving the additional criterion needed for the $E_{A,\infty} < 2$ cases, the parameter-dependence of the second criterion near the gas-liquid interface is resolved (cf. Figure 3, right).

The textbook derivation of the second criterion applies the PFO approximation throughout the reaction zone (cf. 3.1.1) after which a flux balance over the reaction zone is made. Balancing the reactant fluxes J_A and J_B over the reaction zone $[0, \delta_R]$ (cf. Figure 2) yields,

$$(J_A)_{x=0} = \left(\frac{J_B}{\nu_B}\right)_{x=\delta_R}$$
(19)

The vKHa entails that all B will diffuse to the interface as well as that its concentration is constant throughout the reaction zone (see supporting information, chapter A) [5]. Therefore,

$$\mathcal{D}_{A}c_{A,i}Ha_{A} \approx \frac{\mathcal{D}_{B}}{\nu_{B}} \left(c_{B,b} - c_{B,i} \right)$$
(20)

The original derivation of criterion 2 introduces the PFO assumption into the equation, i.e., $\frac{c_{B,b}-c_{B,i}}{c_{B,b}} \ll 1$, which converges into an expression which validates this approximation: $Ha_A(E_{A,\infty} - 1)^{-1} \ll 1$. The opposite of this corresponds to other limiting case: the maximum diffusion-limited transport of B. This yields the second criterion for the instantaneous regime: $Ha_A(E_{A,\infty} - 1)^{-1} \gg 1$.

The parameter-dependence of this second criterion, i.e., how much Ha_A needs to be larger than $(E_{A,\infty} - 1)$, results from several mathematical cancellations made during the initial derivation (cf. Westerterp et al. [5]). Excluding such rigorous cancellations yields a different version of criterion 2; first, eq. (20) is rearranged into:

$$\mathcal{D}_{A}c_{A,i}Ha_{A} - \frac{\mathcal{D}_{B}}{\nu_{B}}c_{B,b} \approx -\frac{\mathcal{D}_{B}}{\nu_{B}}c_{B,i}$$
(21)

Substituting $\frac{\delta_R}{\delta_f} = \frac{-c_{B,i}}{c_{B,b}-c_{B,i}}$ (supporting information, eq. C-1), rearranging and simplifying then yields:

$$\frac{\delta_{\rm f}}{\delta_{\rm R}} \left(\frac{\nu_{\rm B} \mathcal{D}_{\rm A} c_{\rm A,i}}{\mathcal{D}_{\rm B} c_{\rm B,b}} {\rm Ha}_{\rm A} - 1 \right) \approx \frac{c_{\rm B,b} - c_{\rm B,i}}{c_{\rm B,b}}$$
(22)

As such, for the limiting case of the maximum diffusion-limited transport of B, it should hold that:

$$\frac{\delta_{\rm f}}{\delta_{\rm R}} \left(\frac{\nu_{\rm B} \mathcal{D}_{\rm A} c_{\rm A,i}}{\mathcal{D}_{\rm B} c_{\rm B,b}} {\rm Ha}_{\rm A} - 1 \right) \gg 1$$
(23)

Substituting $E_{A,\infty} - 1 = \frac{v_B \mathcal{D}_B c_{B,b}}{\mathcal{D}_A c_{A,i}}$ and $\frac{\delta_R}{\delta_f} = E_{A,\infty} - 1$ (supporting information, eq. C-2) then yields:

$$\frac{\mathrm{Ha}_{\mathrm{A}}}{\mathrm{E}_{\mathrm{A},\infty}-1} - \mathrm{E}_{\mathrm{A},\infty} \gg 0 \tag{24}$$

The left-hand side of equation (24) accounts for A's reactivity (Ha_A) and its concentration relative to that of B ($E_{A,\infty}$), and is condensed into a new dimensionless number $\varphi_{A,\infty}$. The dimensionless number

can therefore be seen as the potential of A to impose maximum diffusion limitations on the transport of B (denoted by ∞). Hence, the modified criterion 2 becomes:

improved criterion 2: $\phi_{A,\infty} \gg 0$ (25)

with
$$\varphi_{A,\infty} = \frac{Ha_A}{E_{A,\infty} - 1} - E_{A,\infty} \gg 0$$

. When plotting the data from Figure 3 (right) as a function of $\varphi_{A,\infty}$, a clear convergence is obtained, virtually independent of the parameter values (Figure 5). An analytical relationship between the numeric values of the breakthrough of B and $\varphi_{A,\infty}$ could not be derived from the model equations. Figure 5 shows that, for approximately $\varphi_{A,\infty} \ge 15$, the breakthrough of B into the gas phase is sufficiently below 1% and this empirical threshold value is therefore taken as a benchmark in the following sections.



Figure 5 Breakthrough of reactant B into the gas-phase as a function of $\varphi_{A,\infty}$ for $E_{A,\infty} > 2$ (×) and $E_{A,\infty} = 2$ (-D-). The threshold of 1% (···) and the limiting value for $\varphi_{A,\infty}$ (–) are shown as well. Numerical simulations were performed for $\mathcal{D}_A = \mathcal{D}_B: 10^{-9} \text{ m}_L^3 \text{ m}_L^{-1} \text{ s}^{-1}$, $k_L: 5 \ 10^{-5} \text{m}_L \text{ s}^{-1}$, k: 1 to $10^3 \text{ m}_L^3 \text{ mol}^{-1} \text{ s}^{-1}$, $c_{A,i}$ and $c_{B,b}: 10^{-2}$ to $10^3 \text{ mol} \text{ m}_L^{-3}$. Reactant B was considered volatile.

3.1.4 Additional criteria for $E_{A,\infty} < 2 (c_{B,b} < v_B c_{A,i})$

For high concentrations of A relative to B, the infinite enhancement factor is substantially smaller than 2. To prevent the breakthrough of A into the bulk liquid, additional criteria are needed to impose

transport limitations on A. Apparent symmetry arguments could rationalize a formulation similar to that of $\varphi_{A,\infty}$ in addition to Ha_B > 2, however, the boundary behavior of A and of B are quite different. As B is assumed non-volatile in many applications, there is no flux through the gas-liquid interface for that component. Conversely, there usually is a flux of component A into the bulk-liquid and the symmetry argument does not fully hold and a more deductive approach is needed.

The shortcomings of the classic criteria near the liquid film-bulk boundary (Z=1) can also be interpreted as follows. For $E_{A,\infty} > 2$, the criterion $\phi_{A,\infty} \ge 15$ essentially imposes restrictions on the mass-transfer of reactant B. However, $\phi_{A,\infty}$ does not impose such restrictions on reactant A. As there are no boundary conditions that force the flux of A into the bulk liquid to be zero, the likelihood of a breakthrough of A into the bulk liquid increases when the reaction plane moves towards the liquid film-bulk boundary. Such a situation is readily encountered when the film-concentration of A greatly exceeds the bulkconcentration of B, i.e., for $E_{A,\infty} < 2$.

Analogous to the derivation in section 3.1.3, a vKHa was applied to conditions where the reaction plane is not close to the gas-liquid interface but rather near the film-bulk boundary (see Figure 6). This allows to derive an additional criterion to determine whether breakthrough of A into the bulk-liquid occurs or not.



Figure 6 Schematic representation of the vKHa applied to the film and bulk-liquid boundary for a single irreversible reaction of order (1,1) and $E_{A,\infty} < 2$. The key assumptions involved in the approximation are shown in orange.

Like the classic criterion 1 at the gas-liquid interface, a fast consumption of B is the first prerequisite for the instantaneous regime, eq. (26).

criterion 3:
$$Ha_B > 2$$
 (26)

with
$$Ha_B = \frac{1}{k_L} \sqrt{D_B k_1^{(1,1)} c_{A,i}}$$

Next, imposing a zero-order approximation on reactant A throughout the reaction zone allows to derive an final criterion for the instantaneous regime which accounts for the limiting case of the complete diffusion-limited mass transfer of reactant A, see eq. (27). This third criterion is now also coined in a dimensionless number $\varphi_{B,\infty}$, which is a function of Ha_B and E_{B,∞}, and therefore a measure of B's potential to enforce diffusion-limitations on the transport of A through the film.

criterion 4:
$$\varphi_{B,\infty} \gg 0$$
 (27)

with
$$\varphi_{B,\infty} = \frac{Ha_B}{E_{B,\infty} - 1} - E_{B,\infty}$$
 and $E_{B,\infty} = 1 + \frac{\nu_B \mathcal{D}_A c_{A,i}}{\mathcal{D}_B c_{B,b}}$

The mathematical analogy between equations (25) and (27) is obvious, provided that identical boundary conditions at both sides of the liquid film are considered. Nevertheless, even for a non-volatile component B, both equations are valid and useful from a practical point of view as shown in Figure 7; if the reaction plane is located near the film-bulk boundary (i.e., $E_{A,\infty} < 2$), $\varphi_{B,\infty}$ is well-suited to exclude the reactions that result in a significant breakthrough of A while the classic criteria are fulfilled (cf. Figure 4, red quadrant).



Figure 7 Breakthrough of A into the bulk-liquid as a function of $\varphi_{B,\infty}$ for the instantaneous regime for a single irreversible instantaneous reaction of order (1,1), shown for $E_{A,\infty} < 2$ (Δ). The thresholds of 1% (...) and 15 (–) are also shown. Numerical simulations were performed for $\mathcal{D}_A = \mathcal{D}_B$: $10^{-9} \text{ m}_L^3 \text{ m}_L^{-1} \text{ s}^{-1}$, k_L : $5 \ 10^{-5} \text{m}_L \text{ s}^{-1}$, k: 1 to $10^3 \text{ m}_L^3 \text{ mol}^{-1} \text{ s}^{-1}$, $c_{A,i}$ and $c_{B,b}$: 10^{-2} to $10^3 \text{ mol} \text{ m}_L^{-3}$. Reactant B was considered non-volatile.

In summary, the improved criteria to describe the instantaneous regime (i.e., to limit the breakthrough of both reactants to 1%) for a single irreversible reaction are $Ha_A > 2$, $\phi_{A,\infty} \ge 15$, $Ha_B > 2$ and $\phi_{B,\infty} \ge 15$.

3.2 Multiple parallel reactions

In this work, a system of multiple parallel reactions corresponds to the simultaneous reaction of a gasphase component A with N liquid-phase reactants, arbitrary denoted B_1 to B_N (Figure 8). Such a reaction network is encountered in the chemical industry in, for instance, the oxidative conversion of trace amounts of sulfides to disulfides (crude oil "sweetening") [18] or the Co/Mn/Br catalyzed aerobic oxidation of benzyl alcohol to benzaldehyde [19]. Another example is the regiospecific transformation of BTX-derived product streams such as the selective chlorination of m-xylene over p-xylene in acetic acid [20,21].



Figure 8 Conceptual representation of a system of N irreversible reactions of order (1,1).

The resulting flux-balance over the reaction zone then equals to equation (28), from which the generalized criteria are obtained through an extended vKHa near the gas-liquid interface ($E_{A,\infty} > 2$) and the liquid film-bulk boundary ($E_{A,\infty} < 2$).

$$J_{A,i} = \frac{J_{B_1}}{\nu_{B_1}} + \dots + \frac{J_{B_N}}{\nu_{B_N}} = \sum_{j=1}^{N} \frac{J_{B_j}}{\nu_{B_j}}$$
(28)

3.2.1 Generalized criteria for $E_{A,\infty} > 2 (c_{B,b} > v_B c_{A,i})$

Within the considered N parallel reactions, the consumption of the reactants can be slow, fast, or instantaneous and it is important to limit the system to those reactions that significantly affect the flux balance. When the reaction zone is located near the gas-liquid interface, any reaction that involves a slow consumption of A (i.e., $Ha_{A_j} < 2$) is therefore excluded because such a reaction induces a negligible transport of A to the reaction zone as compared to fast and instantaneous reactions. Furthermore, as the infinite enhancement factor of A is solely determined by the interface and bulk-liquid concentration of the reactants, excluding these slow reactions is key to obtain an accurate value for $E_{A,\infty}$. The system of N parallel reactions is thus reduced to a system of N^A parallel reactions for which $Ha_{A_j} > 2$. These Ha_{A_j} allowed to derive an expression for the overall Hatta number (see supporting information, section D), from which the generalized first criterion was obtained:

generalized criterion 1: $Ha_A > 2$

with
$$\operatorname{Ha}_{A} = \left(\sum_{j=1}^{N^{A}} \operatorname{Ha}_{A_{j}}^{2}\right)^{\frac{1}{2}}$$
 and $N^{A} = \left\{j \in N \mid \operatorname{Ha}_{A_{j}} > 2\right\}$

Returning to the flux balance over the reaction zone (cf. equation (28)), the PFO approximation allows to introduce an analytical expression (cf. reference [5] and supporting information, section E) for the interphase-flux of A.

$$J_{A,i} = -\mathcal{D}_A \left(\frac{dc_A}{dx}\right)_{x=0} = \frac{\mathcal{D}_A}{\delta_f} \left(c_{A,i} - \frac{c_{A,b}}{\cosh \phi_A}\right) \frac{\phi_A}{\tanh \phi_A}$$
(30)

For the film model, the reaction modulus ϕ_A equals Ha_A and equation (30) allows to approximate equation (28) as:

$$\frac{\mathcal{D}_{A}}{\delta_{f}} \left(c_{A,i} - \frac{c_{A,b}}{\cosh Ha_{A}} \right) \frac{Ha_{A}}{\tanh Ha_{A}} \approx \sum_{j=1}^{N^{A}} \frac{\mathcal{D}_{B_{j}}}{\nu_{B_{j}} \delta_{f}} \left(c_{B_{j},b} - c_{B_{j},i} \right)$$
(31)

Eq. (31) is significantly simplified by applying the first criterion:

$$\mathcal{D}_{A}c_{A,i}Ha_{A} \approx \sum_{j=1}^{N^{A}} \frac{\mathcal{D}_{B_{j}}}{\nu_{B_{j}}} \left(c_{B_{j},b} - c_{B_{j},i} \right)$$
(32)

Conceptually, the collection of liquid-phase reactants B_j can be considered as a single species with total concentration $c_{B,b}/\nu_B = \sum_{j=1}^{N^A} c_{B_j,b}/\nu_{B_j}$ and weight-averaged diffusion coefficient $\mathcal{D}_B = \frac{\sum_{j=1}^{N^A} \mathcal{D}_{B_j} c_{B_j,b}/\nu_{B_j}}{\sum_{j=1}^{N^A} c_{B_j,b}/\nu_{B_j}}$. This is because the instantaneous reaction of A should result in a single reaction plane and its location is fixed according to equation (33) (cf. supporting information, equations C-2 and C-

$$\frac{\delta_{\rm R}}{\delta_{\rm f}} = \frac{\mathcal{D}_{\rm B}c_{\rm B,b}}{\nu_{\rm B}\mathcal{D}_{\rm A}c_{\rm A,i}} \text{ and } \frac{\delta_{\rm R}}{\delta_{\rm f}} = E_{\rm A,\infty} - 1$$
(33)

Eq. (32) is therefore transformed into:

$$\mathcal{D}_{A}c_{A,i}Ha_{A} \approx \frac{\mathcal{D}_{B}}{\nu_{B}} \left(c_{B,b} - c_{B,i} \right)$$
(34)

A similar derivation as outlined in section 3.1.3 then yields the generalized expression for $\phi_{A,\infty}$:

generalized criterion 2: $\phi_{A,\infty} \gg 0$

with
$$\varphi_{A,\infty} = \frac{Ha_A}{E_{A,\infty} - 1} - E_{A,\infty}$$
 and $E_{A,\infty} = 1 + \sum_{j=1}^{N^A} \left(E_{A_j,\infty} - 1 \right)$

3.2.2 Generalized criteria for $E_{A,\infty} < 2 (c_{B,b} < v_B c_{A,i})$

An analogous approach is subsequently performed near the liquid film-bulk boundary (see supporting information). The system of N parallel reactions is first reduced to a system of N^B parallel reactions for which $Ha_{B_j} > 2$:

generalized criterion 3:
$$\operatorname{Ha}_{B_j} > 2$$
 (36)
with $\operatorname{Ha}_{B_j} = \frac{1}{k_L} \sqrt{\mathcal{D}_{B_j} k_j^{(1,1)} c_{A,i}}$

The equivalent of equation (31) at the film-bulk boundary is shown in equation (37).

$$\frac{\mathcal{D}_{A}}{\delta_{f}}(c_{Ai} - c_{Ab}) \approx \sum_{j=1}^{N^{B}} \frac{\mathcal{D}_{B_{j}}}{v_{B}\delta_{f}} c_{B_{j},b} \left(1 - \frac{c_{B_{j},i}}{c_{B_{j},b}\cosh Ha_{B_{j}}}\right) \frac{Ha_{B_{j}}}{\tanh Ha_{B_{j}}}$$
(37)

for $N^B = \left\{ j \in N \mid Ha_{B,j} > 2 \right\}$

Which yields the generalized $\phi_{B,\infty}$ as shown in equation (38):

generalized criterion 4: $\phi_{B,\infty} \gg 0$

with
$$\phi_{B,\infty} = \sum_{j=1}^{N^B} \left(\frac{Ha_{B_j}}{E_{B_j,\infty} - 1} \right) - E_{B,\infty} \text{ and } E_{B,\infty} = 1 + \sum_{j=1}^{N^B} \left(E_{B_j,\infty} - 1 \right)$$

(38)

(35)

3.2.3 Validation

The generalized criteria, i.e., $Ha_A > 2$, $\varphi_{A,\infty} \gg 0$, $Ha_{B_j} > 2$ and $\varphi_{B,\infty} \gg 0$, were numerically validated by screening of the reactant concentrations and rate coefficients for a system of two parallel irreversible reactions (see equations (4) and (5)) with unitary stoichiometric coefficients. The fixed parameters during this screening were the diffusion coefficients $(10^{-9} \text{ m}_L^3 \text{ m}_L^{-1} \text{ s}^{-1}$ for each component) and the mass transfer coefficient (5 $10^{-5} \text{ m}_L \text{ s}^{-1}$). The investigated rate coefficients were varied from 10^{-1} to $10^3 \text{ m}_L^3 \text{ mol}^{-1} \text{ s}^{-1}$ while the concentrations ranged from 10^{-2} to $10^3 \text{ mol} \text{ m}_L^{-3}$ for components A, B and P. The rate coefficients and interface and concentrations were allowed to take on any value within these ranges and, as such, the evaluated parameter space covered the case of both reactions being slow, the case of a selective removal (i.e., only the fast reaction is accounted for), as both reactions being fast.

The numeric results for the film model clearly show the divergent behavior of $\varphi_{A,\infty}$ near the film-bulk boundary (Figure 9). Conversely, $\varphi_{B,\infty}$ effectively excludes specific sets of parameter values from the instantaneous regime and limits the breakthrough of the gas-phase component into the bulk-liquid well below 1% if its numeric threshold is set to 15. In Figure 5 and Figure 7, subsets within the simulated data are clearly visible and could be related to the value of the enhancement factor (e.g., the line connecting the data corresponding to $E_{\infty} = 2$). While a similar boundary emerges with respect to a potential breakthrough and, hence, supports the validity of the derived criteria, the presence of such subsets is less clear from Figure 9 due to the second reaction that is considered. These features are expected to become more pronounced for systems with more than two parallel reactions.



Figure 9 Validation of the proposed third criterion for a system of two parallel irreversible reactions of order (1,1) in the instantaneous regime according to the film model. The breakthrough of component A into the bulk-liquid as a function of $\varphi_{A,\infty}$ (×) and $\varphi_{B,\infty}$ (Δ). Whereas $\varphi_{A,\infty}$ is unable to limit the breakthrough of A into the bulk-liquid, with $\varphi_{B,\infty} = 15$ (–), this is effectively constrained to 1% (…) as no orange data points were found in the red quadrant. Data for which Ha_A \leq 2 and/or $\varphi_{A,\infty} < 15$ were excluded from the dataset.

Future work on the validity of these generalized and improved criteria in systems with complex kinetics (e.g., irreversible reactions of order (m,n) and cascade reactions) will be communicated in the near future. Additional research is also required to evaluate the robustness of these criteria in mass transfer models based on the penetration or surface-renewal theory as well to validate them using experimental data. The latter is particularly challenging, and direct numerical simulations (e.g., solving of the Navier-Stokes and species mass transport equations around a single rising bubble) could already provide important insights in this direction.

4 Conclusions

It was demonstrated that the classic criteria for instantaneous regime in gas-liquid reactions, i.e., $Ha_A > 2$ and $Ha_A(E_{A,\infty} - 1)^{-1} \gg 1$, are necessary but not sufficient in case the infinite enhancement factor $E_{A,\infty}$ is below 2. It was also shown that the numeric value of the second criterion, i.e., how much larger

than one $\text{Ha}_{A}(\text{E}_{A,\infty} - 1)^{-1}$ must be, highly depends on the value of the infinite enhancement factor $\text{E}_{A,\infty}$, especially when the non-volatility assumption of the liquid phase component is relieved.

The original derivation of these criteria (which was performed on a single-reaction system) was reassessed and resulted in an expression that was captured in a new dimensionless number, $\varphi_{A,\infty}$, which accounts for A's reactivity as well as its interface concentration relative to the bulk concentration of the co-reactant B. The value of $\varphi_{A,\infty}$ is therefore related to the potential of A to impose maximum diffusion limitations on the transport of B. As such, the breakthrough of a volatile liquid-phase component into the gas phase could be limited to 1% for a single reaction for any value of $E_{A,\infty}$ if:

$$Ha_A > 2 \text{ and } \phi_{A,\infty} \ge 15 \text{, with } \phi_{A,\infty} = \frac{Ha_A}{E_{A,\infty} - 1} - E_{A,\infty} \text{ and } E_{A,\infty} = 1 + \frac{\mathcal{D}_B c_{B,b}}{\nu_B \mathcal{D}_A c_{A,i}}$$

However, these criteria are still not sufficient to assess the breakthrough of the gas-phase component into the bulk-liquid. By performing an analogous derivation near the film-bulk boundary, two additional criteria emerged which impose maximum diffusion limitations on the transport of A. These additional criteria for the instantaneous regime are critical when $E_{A,\infty} < 2$ and effectively limit the breakthrough of the gas-phase component to 1% if:

$$Ha_B > 2 \text{ and } \phi_{B,\infty} \ge 15 \text{, with } \phi_{B,\infty} = \frac{Ha_B}{E_{B,\infty} - 1} - E_{B,\infty} \text{ and } E_{B,\infty} = 1 + \frac{\mathcal{D}_A c_{A,i}}{\nu_B \mathcal{D}_B c_{B,b}}$$

These expressions were extended to systems of N parallel reactions of which the selective removal of an impurity from a product stream is a specific example. The set of generalized criteria was numerically validated as needed and sufficient to limit the breakthrough of the gas phase component into the liquid bulk and, as such, *a priori* calculate if the system proceeds in the instantaneous regime.

Declaration of interests

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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