

Absorption of CO₂ by a two reactions system: how to access the kinetics constant of the main reaction?

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Highlights

- Influence of the secondary reaction in CO₂ absorption rate
- Estimation of the difference between the CO₂ absorption rate with pseudo-first order regime and actual rate in a two reactions system
- Proposal of variables to characterise reaction competition

1. Introduction

According to the IPCC, CO₂ is the main greenhouse gas in terms of concentration and emissions. Human activities are primarily responsible for these emissions, and we can no longer wait to drastically reduce them. Part of the solution is to capture CO₂. The most successful process today is capture by basic solutions such as aqueous solutions of monoethanolamine. However, these solutions have a number of drawbacks, including toxicity, thermal degradation and loss during regeneration. The replacement of these solvents is crucial, and we need to evaluate the ability of new solvents through certain properties. One of these is reaction kinetics. Indeed, Sheng et al¹ demonstrate, with the capture of CO₂ by NaOH solutions, the importance of using very accurate values of reaction kinetics. Inaccurate values can lead to over- or under-design of industrial contactors or absorbers. However, during CO₂ chemical absorption, the system is rarely the seat of a single reaction. In this work, we focus on the system with two irreversible reactions. Some researchers refer to Westerterp et al² to select the CO₂ pressure range in order to set the system in pseudo-first order regime according to criteria. In this way, the expression of the transfer rate does not depend on the partial transfer constant k_{liq} , and the evaluation of the kinetic constant has less uncertainty. Those criteria seem very strict and not easy to respect. Other researchers neglect the second reactions to estimate the main reaction.

When studying this kind of system, certain questions come to mind: can we neglect the second reaction? If not, how can we estimate the kinetic constant of the main reaction? How do we define the Hatta number? Are there several Hatta numbers? Are there any criteria for considering the system as pseudo-first-order?

2. Methods

To answer these questions, we first establish a microscopic balance on CO₂ and other chemical reagents within the framework of non-steady-state double-film theory. We solve the system of equations with a mesh method and obtain the stationary regime for a relatively long time. The reactions are:



The Hatta numbers and limit enhancement factors relative to this system are defined as:

$$\begin{aligned} Ha &= \frac{\sqrt{k_1 \cdot D_{a,liq} \cdot C_{B,L} + k_2 \cdot D_{a,liq} \cdot C_{P,L}}}{k_{liq}} \\ Ha_1 &= \frac{\sqrt{k_1 \cdot D_{a,liq} \cdot C_{B,L}}}{k_{liq}} & Ha_2 &= \frac{\sqrt{k_2 \cdot D_{a,liq} \cdot C_{P,L}}}{k_{liq}} \\ E_{al,1} &= 1 + \frac{D_{b,liq} \cdot C_{B,L}}{\nu_B \cdot D_{a,liq} \cdot C_{A,int}} & E_{al,2} &= 1 + \frac{D_{p,liq} \cdot C_{P,L}}{\nu_P \cdot D_{a,liq} \cdot C_{A,int}} \end{aligned}$$

Janssens et al³ have worked on the same system, but to discuss the instantaneous regime. We use their solving resolution to study the system in the pseudo-first-order regime. Indeed, their method converge to the same solution in a faster way.

3. Results and discussion

According to Westerterp et al², the pseudo-first order, is reached if $Ha \ll Eal_1$ and $Ha \ll Eal_2$. In order to find a less strict condition, we calculate the relative difference between the real flux and the flux calculated if the system is in a pseudo-first order regime (PFO). As might be expected, the actual flow is always lower than the theoretical flow, and the less Ha_1/Eal_1 , the less the difference (see figure 1.) Considering the Westerterp criteria, the entire ratio Ha / Eal_2 of the simulations in figure 1 are higher than 0.10 and one could consider that the system is not in a PFO regime. However, figure 2 shows that normalized B concentrations are relatively close to 1, whatever the Ha_2/Eal_2 ratio for $Ha_1/Eal_1 = 0.05$. Concerning P, interface concentrations decrease with the increase of Ha_2/Eal_2 as expected, but are above 0.90 for $Ha_2/Eal_2 < 0.2$. It is confirmed that the criteria of Westerterp et al are too strict in practice.

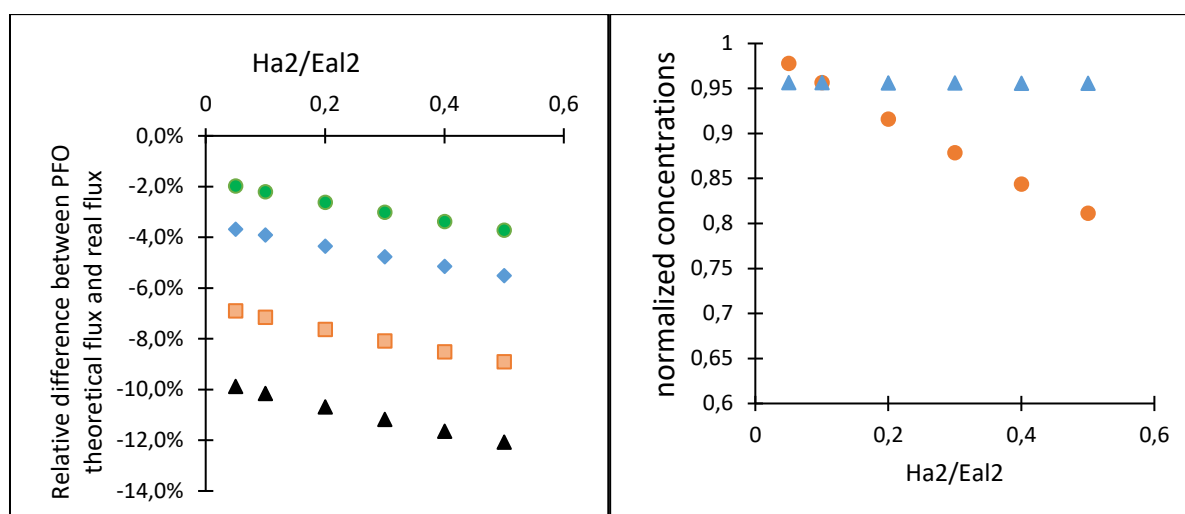


Figure 1. Relative difference between theoretical PFO flux and real flux as a function of Ha_2/Eal_2 for different ratio Ha_1 / Eal_1 (Ratio Ha_1 / Eal_1 : ●, 0.050; ◆, 0.100; ■, 0.200; ▲, 0.300) – $Ha_1 = 200$ and $Ha_2 = 100$

Figure 2. Normalized concentrations at the interface as a function of Ha_2/Eal_2 for $Ha_1/Eal_1 = 0.050$. (normalized concentrations: ▲, concentration of B; ●, concentration of P) Normalized concentration in the bulk of liquid = 1 for both B and P.

These curves are part of this work, and we have drawn generalized curves from over 300 simulations which can be useful to assess the influence of the secondary reactions on the CO_2 absorption rates and finally to determine the kinetics constant of the main reaction.

4. Conclusions

Westerterp et al.'s double criteria for considering a system in a pseudo-first-order (PFO) regime is strict and not often used in practice. We propose with our results to estimate by using the curves if the system is in PFO regime. Moreover, these simulations allow knowing the proportion of CO_2 absorption rates due to the main reaction and due to the secondary reaction.

References

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Keywords

Hatta numbers, Enhancement factors, Pseudo-first order criteria, generalized curves