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# A New Reactive Absorption Model Using Extents of Reaction and Activities.

## I. Application to Alkaline-salts-CO<sub>2</sub> Systems

Submitted to *Chemical Engineering Science*

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### Keywords

Gas-liquid absorption, Kinetic model, Non ideality, Hydroxide solutions, CO<sub>2</sub> absorption

### Abstract

CO<sub>2</sub> absorption into basic aqueous solutions is widely used for CO<sub>2</sub> separation from gas streams (e.g., for natural gas purification). CO<sub>2</sub> loading and ionic strength increase significantly along industrial columns. In absorption modelling, deviation from ideality should then be considered.

This study implements a general steady-state model for reactive gas-liquid absorption. Firstly, equilibrium relations, Nernst-Planck diffusion fluxes and reaction rates are written based on activities. Secondly, local fluxes are related by stoichiometric constraints through extents of reaction.

In a first case study, the model, together with an appropriate thermodynamic representation, was applied with the stagnant film theory (Whitman, 1923) to alkaline salts-water-CO<sub>2</sub> systems. The following Arrhenius expression was found for the direct kinetic constant of reaction  $\text{CO}_2 + \text{HO}^- \leftrightarrow \text{HCO}_3^-$ :  $\ln k \text{ (m}^3 \cdot \text{mol}^{-1} \cdot \text{s}^{-1}\text{)} = 19.84 - 5248.8/T \text{ (K)} - 12\% \text{ overall AAD}$ . This kinetic law can be used in any system involving this reaction (e.g., aqueous amine solutions). This part I paves the way to the further study of CO<sub>2</sub> absorption into aqueous amine solutions.

## Nomenclature

1	A	Logarithm of Arrhenius pre-exponential factor
2	$a_i$	Activity of species $i$ ( $\text{mol.m}^{-3}$ )
3	$a_{1,0}$	Activity of absorbed gas at gas-liquid interface ( $\text{mol.m}^{-3}$ )
4	$c_i$	Molar concentration of species $i$ ( $\text{mol.m}^{-3}$ )
5	$c_{1,0}$	Concentration of absorbed gas at gas-liquid interface ( $\text{mol.m}^{-3}$ )
6	$c_{\text{abs,tot}}$	Total absorptive species concentration ( $\text{mol.m}^{-3}$ )
7	$C_i$	Normalised concentration of species $i$ (-)
8	$c_{b,i}$	Liquid bulk concentration of species $i$ ( $\text{mol.m}^{-3}$ )
9	$c_{N,i}$	Normalisation concentration of species $i$ ( $\text{mol.m}^{-3}$ )
10	$D_i$	Diffusivity of species $i$ in solution ( $\text{mol.m}^{-3}$ )
11	E	Enhancement factor (-)
12	$E_A$	Activation energy ( $\text{J.mol}^{-1}$ )
13	$f_{\text{obj}}$	Optimisation objective function (-)
14	G	Gibbs free energy (J)
15	$H_1$	Henry's constant of absorbed gas at infinite dilution (Pa)
16	$Ha_j$	Hatta number of reaction $j$ (-)
17	$j_i$	Flux of species $i$ through liquid film ( $\text{mol.m}^{-2}.\text{s}^{-1}$ )
18	$j_{1T,0}$	Total absorption flux of absorbed gas ( $\text{mol.m}^{-2}.\text{s}^{-1}$ )
19	$k_j$	Reaction $j$ kinetic constant
20	$K_j$	Reaction $j$ equilibrium constant
21	$K_{N,j}$	Reaction $j$ normalising equilibrium constant
22	$k_{L,1}$	Liquid-side mass transfer coefficient regarding the absorbed gas ( $\text{m.s}^{-1}$ )
23	M	Matrix of the differential problem for concentration-related equations
24	$n_c$	Number of solute constituents in liquid phase
25	$n_i$	mole number of species $i$ (mol)
26	$n_{R,\text{kin}}$	Number of finite-rate reactions in the reaction mechanism
27	$n_{R,\text{eq}}$	Number of reactions at equilibrium in the reaction mechanism
28	$\sigma_{ij}^D$	Direct kinetic order of species $i$ in reaction $j$ (-)
29	$\sigma_{ij}^R$	Reverse kinetic order of species $i$ in reaction $j$ (-)
30	P	Pressure (Pa)
31	$p_{1,0}$	Pressure of absorbed gas at gas-liquid interface (Pa)
32	$r_j$	Reaction rate of reaction $j$ ( $\text{mol.m}^{-3}.\text{s}^{-1}$ )
33	T	Temperature (K)
34	$x_i$	Mole fraction of species $i$ (-)
35	$X_i$	Vector of the differential problem for concentration-related equations
36	z	Distance from interface (m)
37	Z	Normalised distance from interface (z)
38	$z_i$	Number of charges of species $i$ (-)
39	$Z_{Di}$	Diffusion-concentration ratio of species $i$ (-)
40	<i>Constants</i>	
41	$\mathcal{F}$	Faraday constant ( $\text{C.mol}^{-1}$ )
42	R	Ideal gas constant ( $\text{J.mol}^{-1}.\text{K}^{-1}$ )

43 *Greek letters*

44	$\gamma_i$	Activity coefficient of species i (-)
45	$\delta_{ij}$	Kronecker delta between species i and j
46	$\delta_{L,1}$	Film thickness regarding the absorbed gas (m)
47	$\mu_i$	Chemical potential of species i ( $\text{J}\cdot\text{mol}^{-1}$ )
48	$\nu_{ij}$	Stoichiometric coefficient of species i in reaction j (-)
49	$\psi$	Local electric potential (V)
50	$\xi_j$	Extent of reaction j (-)

51 *Subscripts and superscripts*

52	app	Apparent
53	calc	Calculated
54	exp	Experimental
55	REF	Reference state
56	1	Absorbed gas
57	..	Molality-based asymmetric thermodynamic convention (see Supplementary Material section
58	2)	
59	~c	Molar concentration-based symmetric thermodynamic convention

## 60 1. Introduction

61 Chemical absorption into basic solutions has been in use since the 1930s for CO<sub>2</sub> separation from raw  
62 natural gas or from flue gases (Bottoms, 1931). Solvent screening and design are at the heart of the  
63 research effort to increase both CO<sub>2</sub> absorption rate and capacity, and to decrease solvent  
64 regeneration duty (e.g., aqueous amine blends). Industrial absorption column design with a given  
65 solvent requires the identification of the dissolved gas reaction mechanism. To do so, reactions at  
66 equilibrium (e.g., acid-base reactions) and finite-rate reactions need to be studied at pressure,  
67 temperature and composition conditions encountered in the absorption column.

68 Kinetic parameters are typically obtained from absorption or desorption flux measurements in  
69 laboratory gas-liquid contactors of known mass transfer coefficient and interfacial area. Most kinetic  
70 studies deal with absorption experiments into unloaded basic solutions. Only one irreversible  
71 reaction is considered (e.g., (Pohorecki & Moniuk, 1988), (Pani, et al., 1997), (Derks, et al., 2006)).  
72 Such studies disregard the increase in ionic strength and non-ideality when CO<sub>2</sub> is absorbed, due to  
73 bicarbonate, carbonate, and carbamate ion production. However, absorption models based on  
74 activities rather than molarities should lead to more relevant process simulation.

75 CO<sub>2</sub> absorption modelling into aqueous amine solutions first requires the study of CO<sub>2</sub> reaction with  
76 HO<sup>-</sup> ion. Indeed, this reaction takes place in all aqueous systems with CO<sub>2</sub>. Furthermore, kinetic  
77 constants between CO<sub>2</sub> and tertiary amines can be expressed as a function of amine pKa (Couchaux,  
78 et al., 2014). Through molecular simulation, (Rozanska, et al., 2021) show that CO<sub>2</sub> kinetics in  
79 aqueous tertiary amine solutions can be written as a function of CO<sub>2</sub> and HO<sup>-</sup> concentrations only.

80 For CO<sub>2</sub> absorption into aqueous alkaline salts solutions, researchers choose a one-irreversible-  
81 reaction mechanism. In this case, non-ideality is usually included. In early studies such as (Pinsent, et  
82 al., 1956), (Hikita, et al., 1976), (Augugliaro & Rizzuti, 1987), (Pohorecki & Moniuk, 1988), and (Kucka,  
83 et al., 2002), empirical ionic-strength, alkaline-ion-dependent kinetic constant and CO<sub>2</sub> solubility  
84 relations are developed. When studying CO<sub>2</sub> absorption into 30wt% K<sub>2</sub>CO<sub>3</sub> solutions, (Thee, et al.,  
85 2012) fit one Arrhenius-type expression to their kinetic data between 313 and 353 K. The expression  
86 is found coherent with (Knuutila, et al., 2010) correlation when considering identical salt and  
87 concentration range. Under relatively diluted Na<sub>2</sub>CO<sub>3</sub> and K<sub>2</sub>CO<sub>3</sub> concentrations (300 mol/m<sup>3</sup>),  
88 (Penders-van Elk, et al., 2016) find good agreement of their CO<sub>2</sub> absorption data between 283 and  
89 313 K with pKa-dependent Bronsted kinetic law for tertiary amines. Following (Kucka, et al., 2002),  
90 (Haubrock, et al., 2005), (Haubrock, et al., 2007), (Knuutila, et al., 2010) and (Gondal, et al., 2016)  
91 develop an activity-based kinetic rate expression, using Pitzer-Debye-Hückel model, empirical activity  
92 coefficients and e-NRTL model, respectively. Thus, a unique Arrhenius-type expression applies to all  
93 systems (with Li<sup>+</sup>, Na<sup>+</sup> or K<sup>+</sup>).

94 (Sheng, et al., 2019) apply current knowledge on CO<sub>2</sub> absorption into aqueous NaOH solutions to  
95 measure pilot effective mass transfer area. The influence of five literature sources is evaluated for  
96 kinetic and physical properties estimation. According to this study, different Arrhenius parameters  
97 result in large variations for the effective mass transfer area estimation. Additionally, inconsistencies  
98 between kinetics and physical parameter sources should be avoided.

99 Absorption involves reversible finite-rate reactions and acid-base reactions at equilibrium. Species  
100 simultaneously diffuse to and from gas-liquid interface and react. The diffusion driving force is the

101 molar concentration gradient in the widely used semi-empirical Fick diffusion law (e.g., (Versteeg, et  
102 al., 1989), (Bishnoi & Rochelle, 2002), (Derks, et al., 2006)). However, Maxwell-Stefan theory  
103 (Ahmadi, et al., 2010), or Nernst-Planck equation in case of unknown binary diffusivities (e.g.,  
104 (Glasscock & Rochelle, 1989) and (Littel, et al., 1991)) are more suitable to highly non ideal  
105 multiconstituent electrolytic systems. The diffusion driving force is then the chemical potential  
106 gradient (Taylor & Krishna, 1993). (Thomas, et al., 2016) model CO<sub>2</sub> diffusion-reaction into stagnant  
107 water and aqueous alkaline salt solutions with one irreversible reaction. Instead of individual ion  
108 diffusion, salt diffusion across the liquid medium is represented. Thus, diffusivities are decoupled  
109 without the need for an electric potential gradient to keep electroneutrality.

110 Mass transfer problem formulation with any transient or steady-state mass transfer theory results in  
111 a set of local balances of each species. The differential problem is a boundary value problem. At the  
112 gas-liquid interface, absorbed gas physical equilibrium is assumed and in the liquid bulk, chemical  
113 equilibrium is assumed. In some models, acid-base reactions are represented as reversible reactions  
114 with a very high reaction rate constant (e.g., (Glasscock & Rochelle, 1989), (Versteeg, et al., 1989),  
115 (Ahmadi, et al., 2010)). The problem then includes a system of  $n_c$  second order ordinary or partial  
116 differential equations. In other models, diffusion-reaction flux coupling is explicitly considered. The  
117 number of differential equations decreases, but this formulation lacks generality (e.g., (Rinker, et al.,  
118 1995), (Bishnoi & Rochelle, 2002), (Servia, et al., 2014)). This second formulation ensures the  $n_{eq}$  acid-  
119 base equilibria by the addition of  $n_{eq}$  algebraic equations: a differential-algebraic problem needs to  
120 be solved.

121 The purpose of this article is to propose a general reactive absorption model entirely based on  
122 activities, unlike previous reactive absorption models. Indeed, previous models are either based on  
123 Nernst-Planck diffusion with a complete mass transfer model, but activity coefficients are assumed  
124 equal to unity or, like (Gondal, et al., 2016), use a simplified mass transfer model with Fick's diffusion  
125 law and constant activity coefficients. Activity coefficients are then calculated at equilibrium with a  
126 thermodynamic model. For steady-state absorption, extent-of-reaction variables are introduced to  
127 take advantage of flux coupling (section 2). This has two advantages compared to usual model  
128 formulations: (1) the number of equations is reduced while still maintaining a general formulation,  
129 and (2) solving a system of algebraic equations and substituting the results into the differential  
130 equations takes care of acid-base equilibria. Extents of reactions have yet to be implemented in  
131 reactive absorption problems.

132 This model is then applied to CO<sub>2</sub> absorption in aqueous alkaline salts solutions with a full reaction  
133 mechanism considering two reversible reactions. This third section aims at fitting a unique Arrhenius-  
134 type expression for the direct kinetic constant of reaction  $\text{CO}_2 + \text{HO}^- \leftrightarrow \text{HCO}_3^-$  to literature CO<sub>2</sub>  
135 absorption flux data with all three alkaline salt counter ions. This part I paves the way to the further  
136 study of CO<sub>2</sub> absorption into aqueous amine solutions. Indeed, this reaction takes place in all  
137 aqueous solvents. It is necessary to characterise it before focusing on more complex systems.

## 138 2. Modelling framework

### 139 2.1. Activity-based diffusion, fluxes, rates of reaction and equilibria

140 Equation 1 gives the Nernst-Planck expression for the diffusion flux of a given species  $i$  (Taylor &  
141 Krishna, 1993).

$$j_i = -\frac{D_i c_i}{RT} (\nabla \mu_i + z_i F \nabla \psi) \quad \text{Eq. (1)}$$

142 In case of different diffusion coefficients of ionic species, the electric potential  $\psi$  is to ensure local  
143 electroneutrality through the liquid film ( $\sum_{i \text{ species}} z_i j_i = 0$ ):

$$\nabla \psi = -\frac{\sum_{i \text{ species}} z_i D_i c_i \nabla \mu_i}{F \sum_{i \text{ species}} z_i^2 D_i c_i} \quad \text{Eq. (2)}$$

144 The chemical potential of a given species  $i$ ,  $\mu_i$ , is defined as its partial molar Gibbs free energy  
145 (Prausnitz, et al., 1998). A thermodynamic convention consists in defining a reference state, then the  
146 activity  $a_i$  (eq. 3) and the activity coefficient (eq. SM16 in Supplementary Material) of the species  $i$ .

$$\mu_i(T, P, \mathbf{n}) = \left( \frac{\partial G}{\partial n_i} \right)_{T, P, n_{j \neq i}} = \mu_i^{REF}(T, P) + RT \ln(a_i) \quad \text{Eq. (3)}$$

147  $\mu_i^{REF}$  and  $a_i$  are expressed in the same chosen thermodynamic convention. The dimension of the  
148 activity depends on the composition scale, such as molalities, molarities, mass fractions, etc. We  
149 express reaction rates as functions of activities as well (eq. 4).

$$r_j = k_j \left( \prod_{i \text{ species}} a_i^{o_{ij}^D} - \frac{1}{K_j} \prod_{i \text{ species}} a_i^{o_{ij}^R} \right) \quad \text{Eq. (4)}$$

150 Kinetic constants  $k_j$  and equilibrium constants  $K_j$  also need to be expressed according to the chosen  
151 thermodynamic convention. For reactions assumed to be at equilibrium:

$$K_j = \prod_{i \text{ species}} a_i^{v_{ij}} \quad \text{Eq. (5)}$$

152  $v_{ij}$  is the stoichiometric coefficient of species  $i$  in reaction  $j$ . Consistency between orders of reaction  
153 and stoichiometric coefficients (eq. 4 and 5) yields  $o_{ij}^R - o_{ij}^D = v_{ij}$ .

154 Absorption problems are typically one dimension. At gas-liquid interface, the partial pressure and the  
155 activity of the absorbed gas (subscript 1) are assumed at equilibrium. A Henry's relation is obtained  
156 (Prausnitz, et al., 1998), assuming asymmetric thermodynamic convention for the absorbed gas (eq.  
157 6).

$$H_1 = \frac{p_{1,0}}{a_{1,0}} \quad \text{Eq. (6)}$$

158

## 159 2.2. Extents of reaction and resulting system of equations

160 For a steady-state mass transfer model such as the film model, a new algebraic variable is  
161 introduced: the extent of each reaction. The extent  $\xi_j$  of a given reaction  $j$  measures its progress in  
162 the liquid film from the interface to a distance  $z$ . The relation between fluxes and extents of reaction  
163 is dictated by stoichiometric constraints. The flux of a given species  $i$  through the film, as a function of  
164 the extents of reaction, is given in eq. 7.

$$j_i = j_{1T,0} \left( \delta_{1i} + \sum_{j \text{ reactions}} \nu_{ij} \xi_j \right) \quad \text{Eq. (7)}$$

165 Where  $j_{1T,0}$  is the total flux of gas absorbed. Due to the normalisation by  $j_{1T,0}$ ,  $\xi_j$  is dimensionless. This  
 166 expression sums up the contribution of extents both finite-rate reactions and reactions assumed at  
 167 equilibrium where species  $i$  is either a reactant or a product. At the gas-liquid interface ( $z=0$ ), only  
 168 reactions at equilibrium may have a non-zero extent. For non-volatile species, the extents of all  
 169 finite-rate reactions must be zero. Eq. 7 then becomes eq. 8 at the gas-liquid interface.

$$j_i(z=0) = j_{1T,0} \left( \delta_{1i} + \sum_{k \text{ reactions}} \nu_{ik} \xi_k(z=0) \right) \quad \text{Eq. (8)}$$

170 Where index  $k$  refers to a reaction assumed at equilibrium. As a result, the flux  $j_1(z=0)$  is not only the  
 171 flux of 1 crossing the interface,  $j_{1T,0}$ . It is modified by all reactions at equilibrium with a non-zero  
 172 extent of reaction at the gas-liquid interface (eq. 9).

$$j_1(z=0) = j_{1T,0} \left( 1 + \sum_{k \text{ reactions}} \nu_{1k} \xi_k(z=0) \right) \quad \text{Eq. (9)}$$

173 The local variation of the extent of a finite-rate reaction, is by definition proportional to its local rate  
 174 (eq. 10).

$$\nabla \xi_j = \frac{r_j}{j_{1T,0}} \quad \text{Eq. (10)}$$

175 Combining equations 3 and 7 yields eq. 11.

$$j_i = j_{1T,0} \left( \delta_{1i} + \sum_{j \text{ reactions}} \nu_{ij} \xi_j \right) = -\frac{D_i c_i}{RT} (\nabla \mu_i + z_i F \nabla \psi) \quad \text{Eq. (11)}$$

176 Differentiation of equilibrium relation (eq. 5) of reaction  $k$  generates an algebraic relation between  
 177 its extent of reaction and the extents of other reactions. Substituting the expression of  $\nabla \mu_i$  from eq.  
 178 11:

$$0 = \sum_{i \text{ species}} \nu_{ik} \left( j_{1T,0} \frac{(\delta_{1i} + \sum_{j \text{ reactions}} \nu_{ij} \xi_j)}{D_i c_i} - z_i F \nabla \psi \right) \quad \text{Eq. (12)}$$

179 Where index  $k$  refers to a given reaction at equilibrium. The resulting system of  $n_{R,eq}$  algebraic  
 180 equations can be solved separately. The resulting extents  $\xi_k$  of reactions at equilibrium are  
 181 substituted back into the differential equations.

### 182 2.3. Thermodynamic framework and mass transfer and diffusion assumptions

183 The mass transfer framework used in this work is the stagnant film theory (Whitman, 1923). In  
 184 aqueous solution, the asymmetric convention is more relevant for solute species. The selected  
 185 thermodynamic model is described in the Supplementary Material section 2. Ionic diffusivities are  
 186 known only in water at infinite dilution at 25°C. As a first application, equal diffusivities are assumed



187 for all ions in solution (as did e.g., (Derks, et al., 2006), (Ahmadi, et al., 2010), (Luo, et al., 2015)). The  
 188 electric potential term is thus neglected. Since the problem is spatially one-dimensional (in z), eq. 13  
 189 is obtained.

$$j_i = -D_i \sum_{k \text{ species}} \left( \delta_{ik} + c_i \frac{\partial \ln \dot{\gamma}_i}{\partial c_k} \right) \frac{dc_k}{dz} \quad \text{Eq. (13)}$$

190 Where  $\dot{\gamma}_i$  is the activity coefficient of species i in the molality-based asymmetric convention, and  $\delta_{ik}$  is  
 191 the Kronecker delta (1 if i=k, 0 otherwise). Reactions rates can be expressed as:

$$r_j = \tilde{k}_j^c \left( \prod_{i \text{ species}} (\tilde{\gamma}_i c_i)^{o_{ij}^D} - \frac{1}{\tilde{K}_j^c} \prod_{i \text{ species}} (\tilde{\gamma}_i c_i)^{o_{ij}^R} \right) \quad \text{Eq. (14)}$$

192 Where  $\tilde{\gamma}_i = \frac{\dot{\gamma}_i}{x_{\text{H}_2\text{O}}}$  is the activity coefficient of species i in the molarity-based asymmetric convention.

193  $\tilde{k}_j^c(T)$  is the forward kinetic constant of reaction j ( $(\text{m}^3 \cdot \text{mol}^{-1})^{\sum o_{ij}^D} \cdot \text{s}^{-1}$ ) and  $\tilde{K}_j^c(T)$  is the

194 equilibrium constant of reaction j ( $(\text{m}^3 \cdot \text{mol}^{-1})^{\sum v_{ij}}$ ). Both are written in the same convention.

195 Reaction equilibrium equations are then written as follows.

$$\tilde{K}_j^c = \prod_{i \text{ species}} (\tilde{\gamma}_i c_i)^{v_{ij}} \quad \text{Eq. (15)}$$

196 Combining equations 3 and 14 yields eq. 16.

$$j_i = j_{1T,0} \left( \delta_{1i} + \sum_{j \text{ reactions}} v_{ij} \xi_j \right) = -D_i \sum_{k \text{ species}} \left( \delta_{ik} + c_i \frac{\partial \ln \dot{\gamma}_i}{\partial c_k} \right) \frac{dc_k}{dz} \quad \text{Eq. (16)}$$

197 Without electric potential gradient, the system of equations defined by eq. 12 becomes linear  
 198 regarding the extents of reactions at equilibrium:

$$0 = \frac{v_{1k}}{c_1 D_1} + \sum_{i \text{ species}} \frac{v_{ik}}{c_i D_i} \sum_{j \text{ reactions}} v_{ij} \xi_j \quad \text{Eq. (17)}$$

199 In the chosen thermodynamic convention, Henry's relation for the absorbed gas at the interface  
 200 (z=0) is expressed as follows:

$$p_{1,0} = \frac{H_1(T, P, \mathbf{n})}{c_{\text{H}_2\text{O}}} \dot{\gamma}_1 c_{1,0} \quad \text{Eq. (18)}$$

201 As experimental pressure is lower than 1 bar in the data considered in section 3, gas-phase is  
 202 assumed ideal.

## 203 2.4. Solution

204 Before writing the differential problem to solve, dimensionless variables (eq. 19) and parameters (eq.  
 205 20) are introduced.

$$Z = \frac{z}{\delta_{L,1}} = \frac{k_{L,1}}{D_1} z$$

$$C_i = \frac{c_i}{c_{N,i}}$$
Eq. (19)

206 Where  $c_{N,i}$  is the normalising concentration, such as if  $i=1$ ,  $c_{N,i} = c_{1,0}$ , and  $c_{N,i} = c_{\text{abs,tot}}$  otherwise.  $c_{\text{abs,tot}}$   
 207 is the total absorptive species concentration ( $\text{mol.m}^{-3}$ ).

$$Z_{D,i} = \frac{c_{N,i} D_i}{c_{1,0} D_1}$$

$$E = \frac{j_{1T,0}}{k_{L,1} c_{1,0}}$$

$$\text{Ha}_j^2 = \frac{D_1 \tilde{k}_j^c \left( \prod_i (c_{N,i})^{o_{ij}^D} \right)}{k_{L,1}^2 c_{1,0}}$$

$$K_{N,j} = \prod_i (c_{N,i})^{v_{ij}}$$
Eq. (20)

208 Therefore, the flux of species  $i$  is expressed as a matrix product (eq. 21).

$$j_i = j_{1T,0} \left( \delta_{1i} + \sum_{j \text{ reactions}} v_{ij} \xi_j \right) = -j_{1T,0} \frac{Z_{D,i}}{E} \sum_{k \text{ species}} M_{ik} \frac{dC_k}{dZ}$$

$$M_{ik} = \left( \delta_{ik} + C_i \frac{\partial \ln \tilde{y}_i}{\partial C_k} \right)$$
Eq. (21)

209 Square matrix  $M$  inversion yields:

$$\frac{dC_k}{dZ} = -E \left( \sum_{i \text{ species}} (M^{-1})_{ki} X_i \right) \quad k = 1..n_c$$

$$\frac{d\xi_j}{dZ} = \frac{\text{Ha}_j^2}{E} \left( \prod_{i \text{ species}} (\tilde{y}_i C_i)^{o_{ij}^D} - \frac{K_{N,j}}{\tilde{K}_j^c} \prod_{i \text{ species}} (\tilde{y}_i C_i)^{o_{ij}^R} \right) \quad j = 1..n_{R,\text{kin}}$$
Eq. (22)

210 Where  $M^{-1}$  is the inverse of matrix  $M$  and vector  $X$  is defined as  $X = \left( \frac{\delta_{1i} + \sum_j \text{reactions } v_{ij} \xi_j}{Z_{D,i}} \right)_i$ .

211 At each resolution step, an algebraic system of equations is solved independently to obtain the  
 212 extents of acid-base reactions (eq. 23). These values are used in the differential equations.

$$0 = \frac{v_{1k}}{C_1} + \sum_{i \text{ species}} \frac{v_{ik}}{Z_{D,i} C_i} \sum_{j \text{ reactions}} v_{ij} \xi_j$$
Eq. (23)

213 Boundary conditions are presented in Table 1.

214 **Table 1** Film model boundary conditions with dimensionless variables

$Z = 0 (z = 0)$	$Z = 1 (z = \delta_{L,1})$
$C_1 = 1$	$C_i = \frac{C_{b,i}}{C_{N,i}}, \forall i$ species in solution
$\xi_j = 0, \forall j$ finite-rate reaction	-

215

216 This formulation with Nernst-Planck equation for molecular diffusion and activity-based rate  
 217 expressions consists in a system of  $n_C + n_{R,kin}$  *first-order* ordinary differential equations, thanks to  
 218 steady-state extents of reaction, whereas writing local balances per species leads to a system of  $n_C$   
 219 *second-order* differential equations. Extents of reactions at equilibrium are calculated from a set of  
 220  $n_{R,eq}$  algebraic equations (eq. 23). Equilibrium relations, Nernst-Planck diffusion fluxes and reaction  
 221 rates are activity-based. Therefore, this model reconciles kinetics and thermodynamics especially  
 222 close to equilibrium. Simulations are performed in Matlab R2013a. The `bvp4c` function available in  
 223 the software is used to solve the differential problem (Kierzenka & Shampine, 2001).

### 224 3. Application to alkaline salts-water-CO<sub>2</sub> systems

225 Four species are considered: CO<sub>2</sub>, HCO<sub>3</sub><sup>-</sup>, CO<sub>3</sub><sup>2-</sup> and HO<sup>-</sup> ( $n_C=4$ ). The alkaline ion does not take part in  
 226 the reaction scheme, so that its concentration is constant through the film because the electric  
 227 potential is disregarded. However, this ion contributes to non-ideality. The mechanism consists in  
 228 two reversible reactions ( $n_R=2$ ):



229 Reaction R-I is reversible and finite-rate ( $n_{R,kin}=1$ ):

$$r_I = r_{(\text{CO}_2, \text{HO}^-)} = \tilde{k}_{(\text{CO}_2, \text{HO}^-)}^c \left( \tilde{Y}_{\text{CO}_2} \tilde{Y}_{(\text{HO}^-)} c_{\text{CO}_2} c_{(\text{HO}^-)} - \frac{\tilde{Y}_{(\text{HCO}_3^-)} c_{(\text{HCO}_3^-)}}{\tilde{K}_{(\text{CO}_2, \text{HO}^-)}^c} \right) \quad \text{Eq. (24)}$$

230 Where  $\tilde{k}_{(\text{CO}_2, \text{HO}^-)}^c$  is its forward kinetic constant – to determine – ( $\text{m}^3 \cdot \text{mol}^{-1} \cdot \text{s}^{-1}$ ) and  $\tilde{K}_{(\text{CO}_2, \text{HO}^-)}^c$  its  
 231 equilibrium constant ( $\text{m}^3 \cdot \text{mol}^{-1}$ ).

232 In addition, the acid-base equilibrium between HCO<sub>3</sub><sup>-</sup> and CO<sub>3</sub><sup>2-</sup> is considered (reaction R-II;  $n_{R,eq}=1$ ).

233 The equilibrium constant parameters are taken from (Kamps, et al., 2001). Solution density is taken  
 234 from (Laliberté & Cooper, 2004). Liquid phase CO<sub>2</sub> diffusivity is calculated with the Stokes-Einstein  
 235 relation (Versteeg & Van Swaaij, 1988). (Knuutila, et al., 2010) use this relation as well in combination  
 236 with CO<sub>2</sub> diffusivity in pure water from (Danckwerts & Lannus, 1970). Viscosity is taken from  
 237 (Laliberté, 2007). Hydroxide ion diffusivity is set to  $1.7 \times D_{\text{CO}_2}$  based on the ratio proposed by (Hikita,  
 238 et al., 1976), and  $D_{(\text{HCO}_3^-)}$  and  $D_{(\text{CO}_3^{2-})}$  are supposed equal to  $D_{(\text{HO}^-)}$  (see Supplementary Material section  
 239 1 for detailed correlations).

240 As a base case, the mass transfer model was tested with no deviation from ideality ( $\gamma=1$ ) and  
 241 (Weisenberger & Schumpe, 1996) CO<sub>2</sub> apparent solubility (“concentration-based model”). Secondly,  
 242 the activity-based model was implemented.

243 Few CO<sub>2</sub> absorption flux measurements are available in these systems. (Kucka, et al., 2002),  
 244 (Pohorecki & Moniuk, 1988) and (Knuutila, et al., 2010) do not publish raw experimental data, such  
 245 as CO<sub>2</sub> partial pressure. (Gondal, et al., 2016) use raw absorption flux data from (Gondal, et al., 2015)  
 246 in alkaline hydroxide solutions and from (Knuutila, et al., 2010) in alkaline carbonate solutions. Note  
 247 that data from (Knuutila, et al., 2010) is not available in open literature. The only other raw dataset  
 248 on CO<sub>2</sub> absorption in sodium hydroxide and carbonate solutions was found in (Hikita, et al., 1976)  
 249 (see Table 2).

250 **Table 2** Available CO<sub>2</sub> absorption flux data in alkaline hydroxide and carbonate aqueous solutions

Ref, apparatus	Alk <sup>+</sup>	x(Alk <sup>+</sup> ,app)	x(HO <sup>-</sup> ,app)	x(CO <sub>2</sub> ,app)	T (K)	P <sub>CO2</sub> (kPa)	n <sub>data</sub>
(Gondal, et al., 2015), SDC	Li <sup>+</sup>	1.8.10 <sup>-4</sup> -0.035	1.8.10 <sup>-4</sup> -0.035	0-3.5.10 <sup>-4</sup>	298-338	0.17-0.28	30
(Hikita, et al., 1976), Jet & WWC	Na <sup>+</sup>	2.3.10 <sup>-3</sup> -0.025	0-9.0.10 <sup>-3</sup>	2.3.10 <sup>-7</sup> -0.017	298-303	100	157
(Gondal, et al., 2015), SDC	Na <sup>+</sup>	1.8.10 <sup>-4</sup> -0.036	1.8.10 <sup>-4</sup> -0.036	0-3.6.10 <sup>-4</sup>	298-333	0.18-0.32	38
(Gondal, et al., 2015), SDC	K <sup>+</sup>	1.6.10 <sup>-4</sup> -0.033	1.6.10 <sup>-4</sup> -0.033	0-3.6.10 <sup>-4</sup>	298-337	0.16-0.29	35

SDC: "String of Discs Column", Jet: "Laminar Jet Absorber", WWC: "Wetted-Wall Column", Alk<sup>+</sup>: alkaline ion.

251

252 For kinetic constant regression, (Gondal, et al., 2015) data was used, as it encompasses all three  
 253 alkaline ions between 298 and 338 K. To keep datasets with each counter ion approximately to the  
 254 same size, (Hikita, et al., 1976) data for sodium hydroxide and carbonate solutions between 298 and  
 255 303 K was used as a validation dataset. (Hikita, et al., 1976) data therefore also serves as a model  
 256 prediction test. Modelling each flux measurement requires the value of the liquid-side mass transfer  
 257 coefficient, which is taken from each study.

258 Kinetic parameter optimisation of reaction R-I direct kinetic constant is achieved using the objective  
 259 function specified in eq. 25.

$$f_{\text{obj}} = \sum_{i \text{ data}} \frac{1}{2} \left( \left( \frac{j_i^{\text{calc}} - j_i^{\text{exp}}}{j_i^{\text{exp}} + \varepsilon} \right)^2 + \left( \frac{j_i^{\text{calc}} - j_i^{\text{exp}}}{j_i^{\text{calc}} + \varepsilon} \right)^2 \right) \quad \text{Eq. (25)}$$

260  $\varepsilon$  is a constant set to 1.10<sup>-4</sup> mol.m<sup>-2</sup>.s<sup>-1</sup> to mitigate the error value for very small absorption fluxes.  
 261 The two terms in the objective function (eq. 25) give this function a symmetrical behaviour for flux  
 262 underestimation and overestimation. Optimisation function fminsearch from Matlab R2013a was  
 263 used to fit the Arrhenius parameters of the kinetic constant (eq. 26). In fminsearch, the simplex  
 264 algorithm by (Lagarias, et al., 1998) is used.

$$\ln k_{(\text{CO}_2, \text{HO}^-)} = A + \frac{E_A}{RT} \quad \text{Eq. (26)}$$

265 The fitted Arrhenius parameters as well as model performance is presented in Table 3: the average  
 266 absolute deviation (AAD, eq. 27) and the bias (eq. 28) of regression (Gondal, et al., 2015) and  
 267 validation (Hikita, et al., 1976) datasets. Model performance is also compared to (Gondal, et al.,  
 268 2016).

$$\text{AAD} = \frac{1}{n_{\text{data}}} \sum_{i \text{ data}} \left| \frac{j_i^{\text{calc}} - j_i^{\text{exp}}}{j_i^{\text{exp}}} \right| \times 100 \quad \text{Eq. (27)}$$

$$\text{bias} = \frac{1}{n_{\text{data}}} \sum_{i \text{ data}} \frac{j_i^{\text{calc}} - j_i^{\text{exp}}}{j_i^{\text{exp}}} \times 100 \quad \text{Eq. (28)}$$

269 Parameter standard errors are calculated by variance-covariance analysis, as described in the  
 270 Supplementary Material section 3.

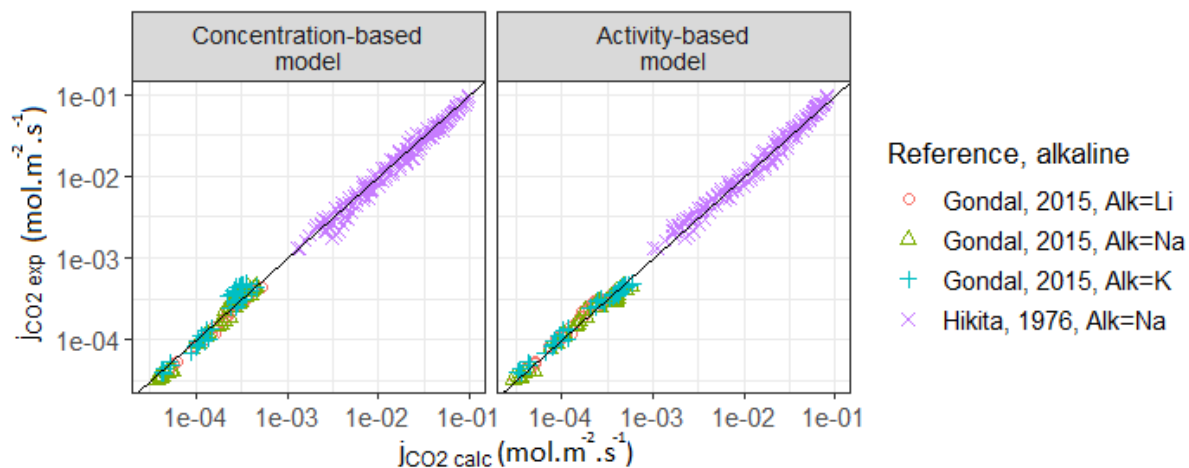
271 **Table 3** Optimised Arrhenius parameters of reaction R-I direct kinetic constant over (Gondal, et al.,  
 272 2015) CO<sub>2</sub> absorption flux data in alkaline hydroxide solutions and performance

Model		Concentration-based	Activity-based	(Gondal, et al., 2016)
Reference	A	19.387 ± 0.004	19.841 ± 0.003	19.53
	E <sub>A</sub> /R (K)	-5020.99 ± 0.07	-5248.77 ± 0.05	-5111.2
(Gondal, et al., 2015) (Li <sup>+</sup> , Na <sup>+</sup> , K <sup>+</sup> )	AAD (%)	14	10	15
	Bias (%)	6.2	-2.1	-
(Hikita, et al., 1976) (Na <sup>+</sup> )	AAD (%)	17	14	-
	Bias (%)	12	-0.23	-

Remark: (Gondal, et al., 2016) do not provide parameter standard deviations.

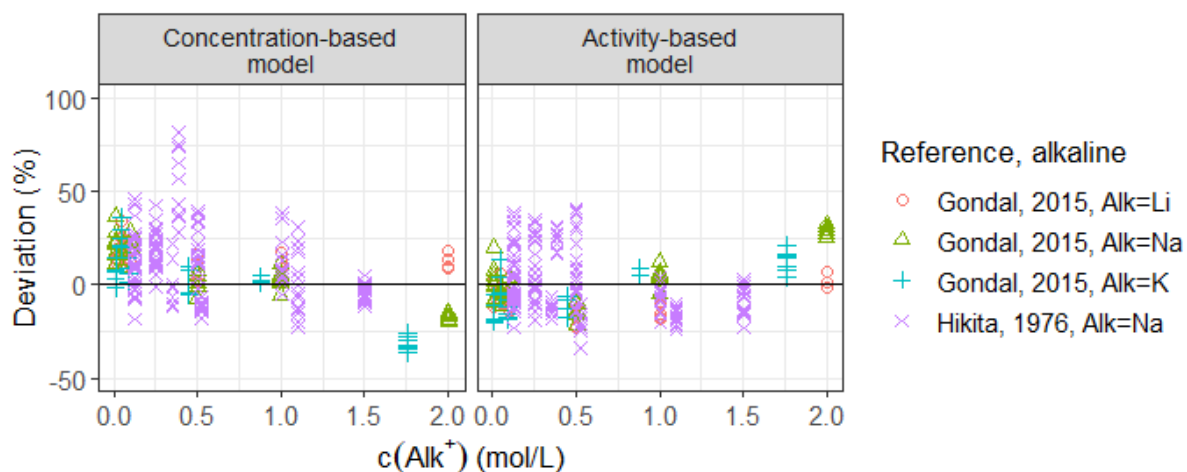
273

274 Parity and deviation plots are shown in Figure 1 and Figure 2, respectively.



275

276 **Figure 1** Reactive absorption model parity plot for alkaline salts-water-CO<sub>2</sub> systems



277

278 **Figure 2** Reactive absorption model deviations for alkaline salts-water-CO<sub>2</sub> systems

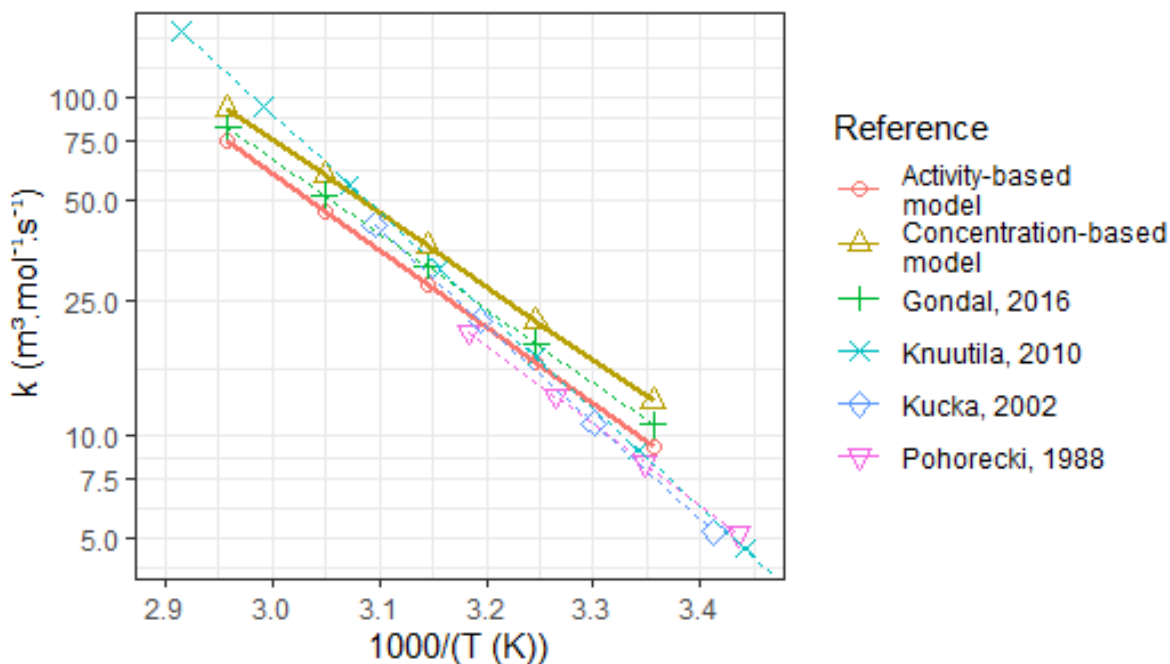
279 Considering solution non-ideality improves model performance for all three types of salts. The only  
 280 exception is the data of (Gondal, et al., 2015) with NaOH data at 2 mol.L<sup>-1</sup>. All data from (Gondal, et  
 281 al., 2015) for all three salts (Li, Na and K-based) and most of the data from (Hikita, et al., 1976) are  
 282 represented within a +/-30% relative deviation by the activity-based model. Only 13 of all 157  
 283 validation data points have a relative deviation exceeding +/-30%. AAD over validation dataset is  
 284 13,7% and bias -0,2%, which is on par with the model performance of (Gondal et al., 2016).  
 285 Concentration-based model performance is on par with that of (Gondal, et al., 2016) when  
 286 considering the data of (Gondal, et al., 2015). Ideal solution is assumed in the concentration-based  
 287 model for reaction rate, diffusion flux, and chemical equilibria, but uses a correlation for CO<sub>2</sub> physical  
 288 solubility at gas-liquid interface. Salting-out effect on CO<sub>2</sub> solubility due to increasing ionic strength is  
 289 represented in both models: in the concentration-based model, by ion-concentration-dependent  
 290 (Weisenberger & Schumpe, 1996) correlation, and in the activity-based model, by the developed  
 291 thermodynamic model (see Supplementary Material section 2). Finally, only the activity-based model  
 292 unifies the representation of all equilibria with the chosen thermodynamic model, whereas the  
 293 concentration-based model is correlation-dependent.

294 The activity-based model is better at predicting (Hikita, et al., 1976) measurements in NaOH and  
 295 Na<sub>2</sub>CO<sub>3</sub> aqueous solutions than the concentration-based model. This suggests the activity-based  
 296 model can more easily be extrapolated outside regression area than the concentration-based model.

297 Arrhenius parameters are compared to previous studies in Figure 3, specifically (Pohorecki & Moniuk,  
 298 1988), (Kucka, et al., 2002), (Knuutila, et al., 2010) and (Gondal, et al., 2016). All these studies  
 299 consider the solution non ideality in the reaction rate expression. Both concentration-based and  
 300 activity-based models lead to close kinetic constants compared to (Gondal, et al., 2016). The  
 301 Arrhenius law obtained with the activity-based model displays a -14% to -9% difference in the  
 302 regression temperature range.

303 Fitted Arrhenius law extrapolation to higher temperatures leads to significant underestimation  
 304 compared to the kinetic constant obtained by (Knuutila, et al., 2010) with their own experimental  
 305 data and methodology – 94 vs. 157 m<sup>3</sup>.mol<sup>-1</sup>.s<sup>-1</sup> at 343 K. The value remains close to that of (Gondal,  
 306 et al., 2016) – 102 m<sup>3</sup>.mol<sup>-1</sup>.s<sup>-1</sup>. Temperatures of 343 K and higher occur in industrial absorption

307 columns. Therefore, having access to raw absorption flux data at higher temperatures (e.g., found in  
 308 (Knuutila, et al., 2010)) is of interest to extend kinetic law application range.



309  
 310 **Figure 3** Arrhenius plot and comparison to previous studies

311 Activity-based model results at specific conditions are then examined. These conditions are listed in  
 312 in Table 4. The four selected points cover the examined data experimental conditions (type and  
 313 concentration of salt, temperature, CO<sub>2</sub> partial pressure). As a reminder, CO<sub>2</sub> concentration is  
 314 normalised by  $c_{1,0}$ , its concentration at the interface, while all other concentrations are normalised by  
 315  $c_{abs,tot} = c_{(Alk+)}$ .

316 **Table 4** Selected points for concentration, extent of reaction and activity coefficient profile  
 317 simulation: system and conditions

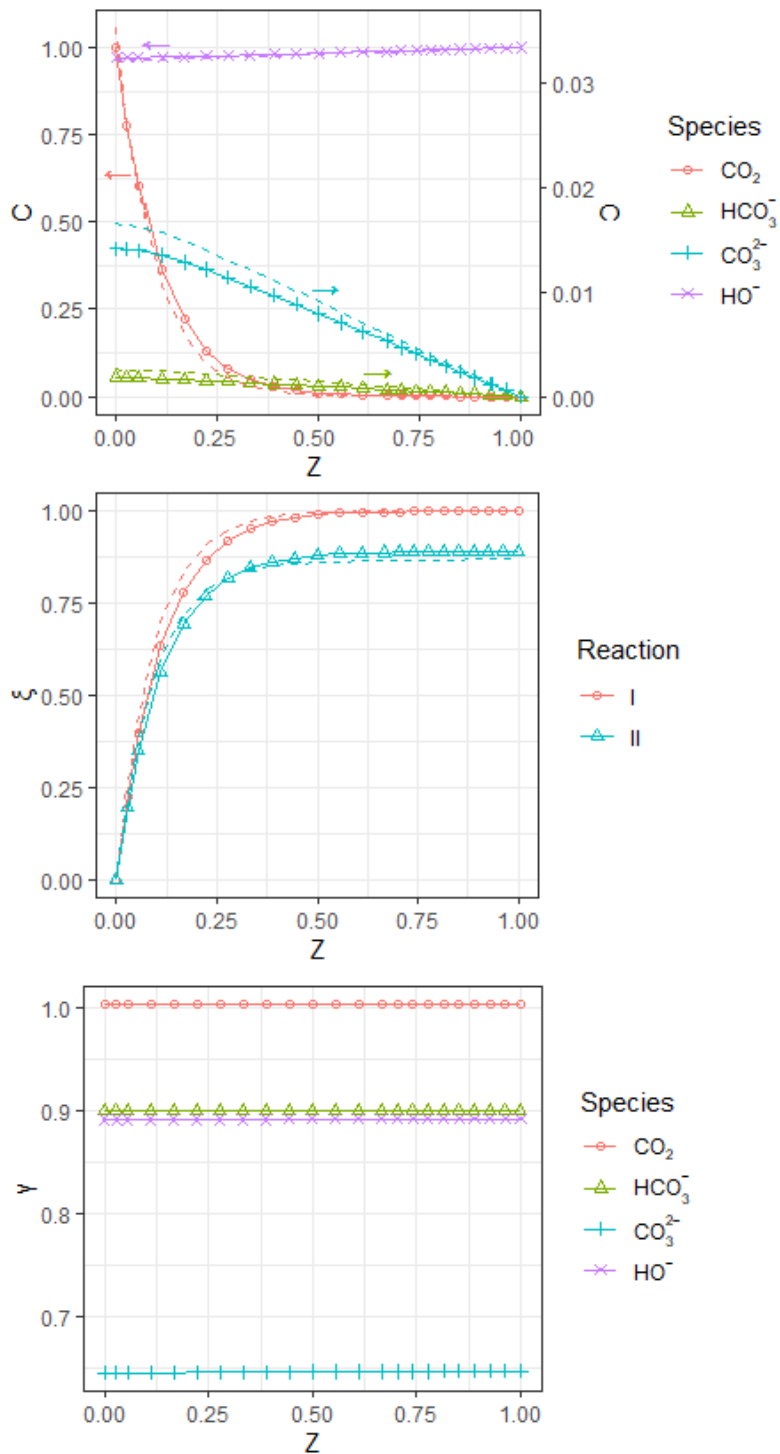
Figure	Reference	Salt	$c_{salt}$ (mol.L <sup>-1</sup> )	T (K)	$P_{CO_2}$ (kPa)	$k_{L,1}$ (m.s <sup>-1</sup> )	$c_{1,0}$ (mol.L <sup>-1</sup> )*
Figure 4	(Gondal, et al., 2015)	LiOH	0.01	336	0.2	$1.7 \cdot 10^{-4}$	$3.1 \cdot 10^{-5}$
Figure 5	(Gondal, et al., 2015)	KOH	1.76	317	0.2	$1.1 \cdot 10^{-4}$	$2.6 \cdot 10^{-5}$
Figure 6	(Hikita, et al., 1976)	Na <sub>2</sub> CO <sub>3</sub>	0.06	298	100	$5.0 \cdot 10^{-5}$	$32.0 \cdot 10^{-3}$
Figure 7	(Hikita, et al., 1976)	NaOH	0.13	303	100	$4.5 \cdot 10^{-5}$	$28.2 \cdot 10^{-3}$

\*Calculated variable (eq. 18), in the activity-based model

318  
 319 Concentration and extent of reaction profiles calculated with non-ideality consideration (solid lines  
 320 and symbols in Figure 4 to Figure 7) or with ideal solution hypothesis (dashed lines in Figure 4 to  
 321 Figure 7) display similar trends. CO<sub>2</sub> concentration profiles are especially close in both models.  
 322 Consequently, resulting Arrhenius parameters are very close in both models as well. As expected, in  
 323 these systems and at these conditions, calculated activity coefficient profiles are mostly constant but  
 324 largely different from unity. Other more complex systems, such as acid gas absorption into aqueous  
 325 amine solutions, could lead to higher non-ideality influence.

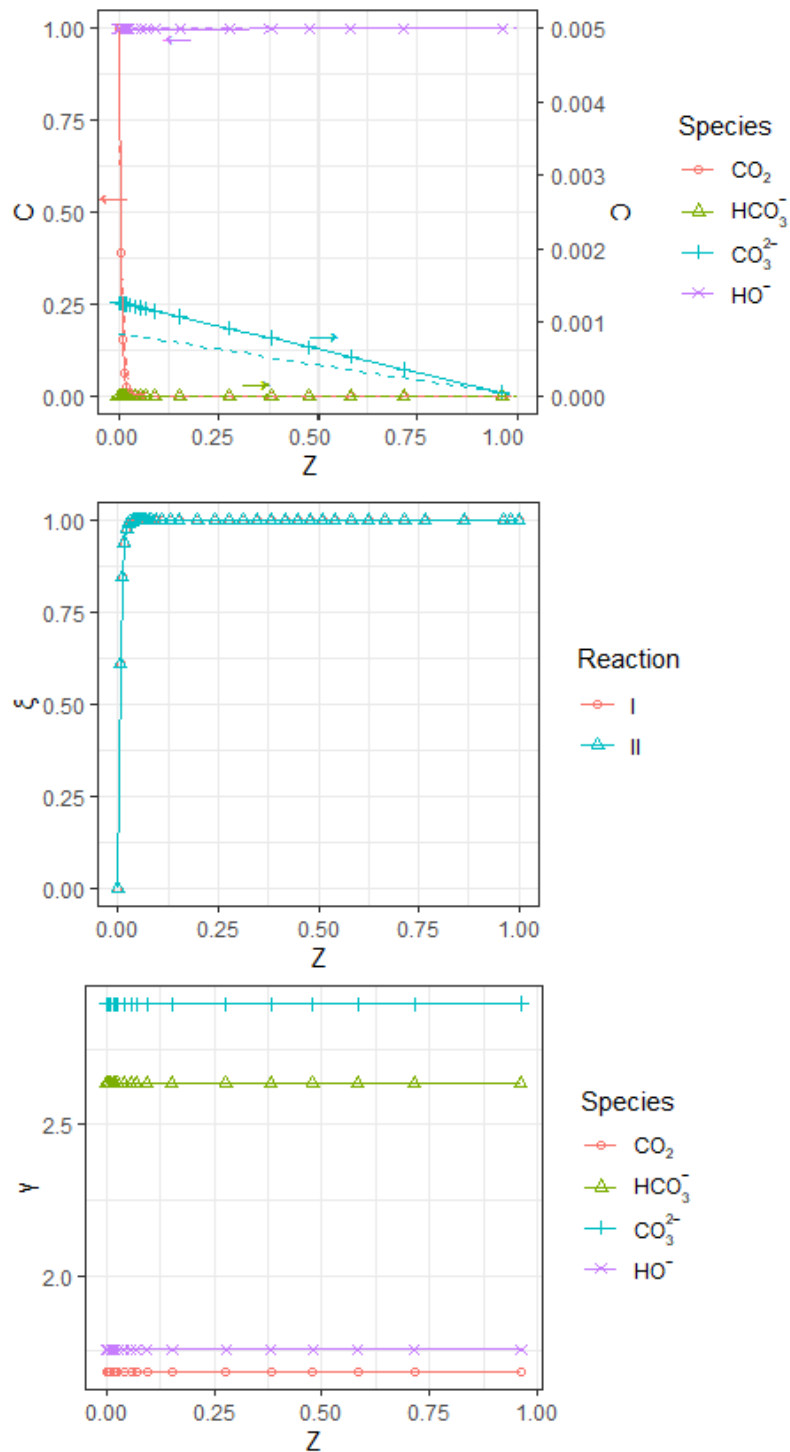
326 (Gondal, et al., 2015) experiments are compatible with pseudo-first order absorption regime  
327 assumption (Figure 4 and Figure 5). Concentration profiles are compatible with this assumption: HO<sup>-</sup>  
328 concentration barely drops at the interface. The main reaction product is not HCO<sub>3</sub><sup>-</sup>, but CO<sub>3</sub><sup>2-</sup>, and  
329 extents of both reactions are close along the liquid film. They are even the equal in Figure 5. This is  
330 because CO<sub>3</sub><sup>2-</sup> (pK<sub>b</sub>(25°C) = 3,7) is more basic than HCO<sub>3</sub><sup>-</sup> (pK<sub>b</sub>(25°C) = 7,3). At these conditions,  
331 activity coefficients are constant, as the overall solution composition remains close to bulk  
332 composition everywhere. Still, activity coefficients differ significantly from unity and non ideality  
333 needs to be considered. Therefore, according to the model, (Gondal, et al., 2015) absorption flux  
334 measurements can be interpreted with constant activity coefficients (as done by (Gondal, et al.,  
335 2015) and (Gondal, et al., 2016)). The same behaviour, but amplified, is displayed in Figure 5. HO<sup>-</sup>  
336 excess is much more important, therefore, reaction R-II equilibrium shifts toward CO<sub>3</sub><sup>2-</sup> formation.  
337 Activity coefficient divergence from unity is significantly higher, due to very high ionic strength.





338

339 **Figure 4** Simulated absorption of CO<sub>2</sub> in LiOH aqueous solution at 0.01 mol.L<sup>-1</sup>, 336 K and P<sub>CO2</sub> = 0.2  
 340 kPa measured by (Gondal, et al., 2015). C: normalised concentration, ξ: extent of reaction, γ: activity  
 341 coefficient. Solid line & symbol: activity-based model, dashed line: concentration-based model (C and  
 342 ξ). γ<sub>Li+</sub> = 0.88



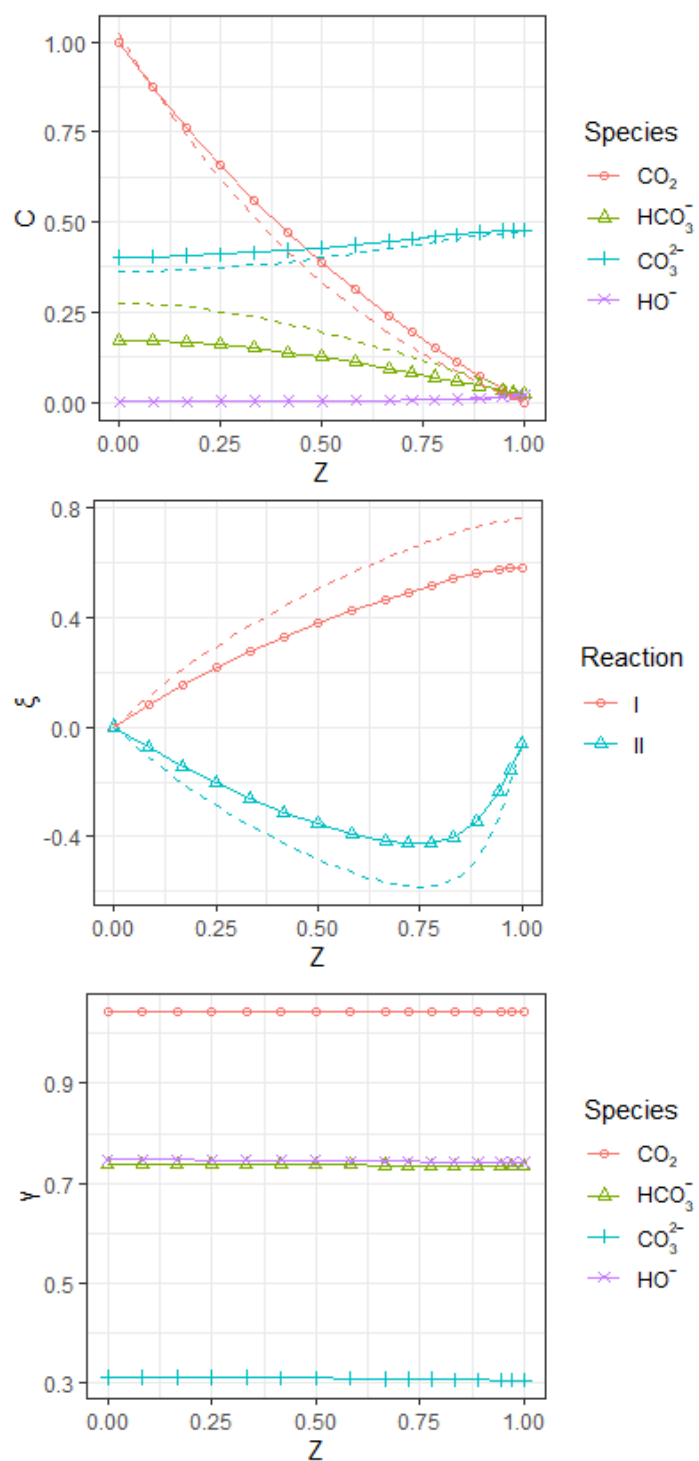
343

344 **Figure 5** Simulated absorption of  $\text{CO}_2$  in  $\text{KOH}$  aqueous solution at  $1.76 \text{ mol.L}^{-1}$ ,  $317 \text{ K}$  and  $P_{\text{CO}_2} = 0.2$   
 345  $\text{kPa}$  measured by (Gondal, et al., 2015).  $C$ : normalised concentration,  $\xi$ : extent of reaction,  $\gamma$ : activity  
 346 coefficient. Solid line & symbol: activity-based model, dashed line: concentration-based model ( $C$  and  
 347  $\xi$ ).  $\gamma_{\text{K}^+} = 1.48$

348 In Figure 6, resulting  $\text{CO}_2$  absorption profiles are shown in aqueous  $\text{Na}_2\text{CO}_3$  at conditions researched  
 349 by (Hikita, et al., 1976). In this case, the main reaction product is  $\text{HCO}_3^-$  from  $\text{CO}_3^{2-}$  conversion. This is  
 350 also coherent with a negative extent of reaction R-II. Here, reversibility needs to be considered,

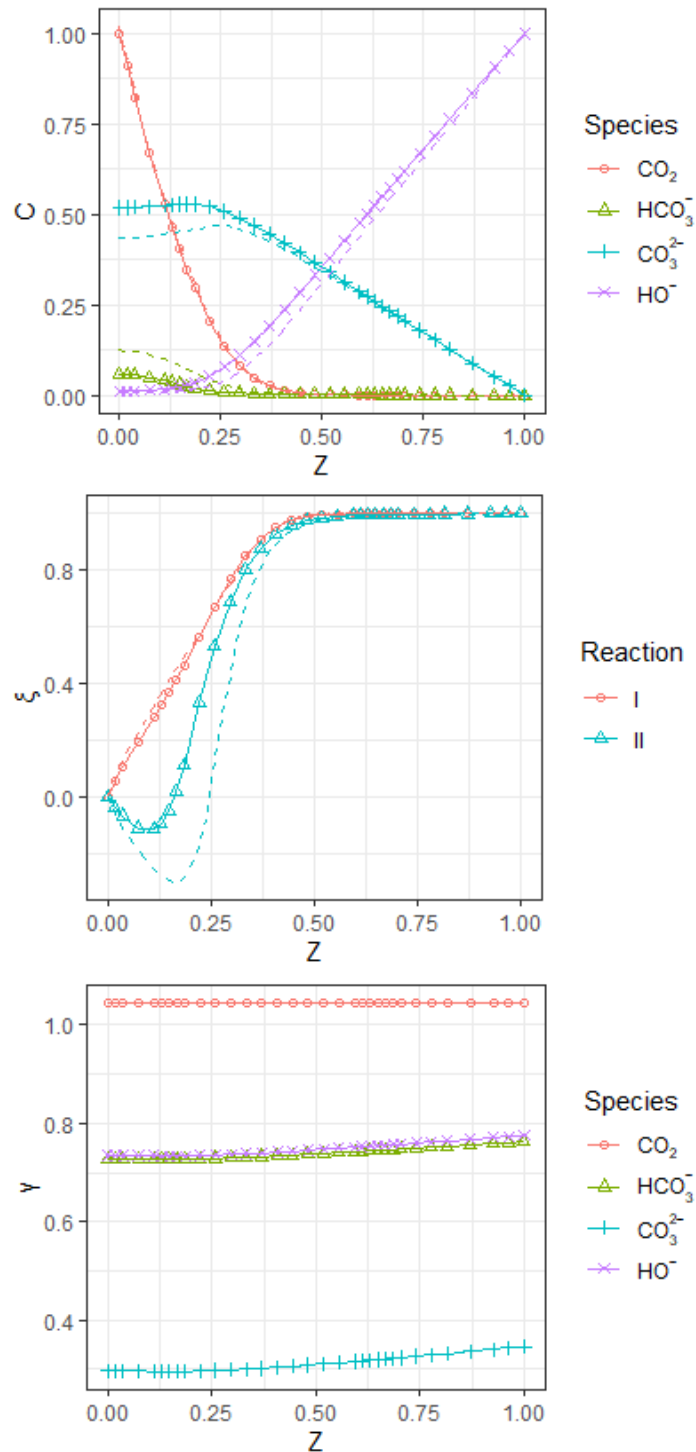
351 which the model does, unlike models from the literature (e.g., (Knuutila, et al., 2010), (Gondal, et al.,  
352 2016)).

353 Activity coefficients display a gradient along the liquid film in Figure 7, with a maximum of 14%  
354 decrease from liquid bulk to interface for  $\gamma_{(\text{CO}_3^{2-})}$ . In (Hikita, et al., 1976), experimental  $\text{CO}_2$  partial  
355 pressure is of several orders of magnitude higher than in (Gondal, et al., 2015) – 100 vs. 0.2 kPa.  $\text{HO}^-$   
356 concentration drops significantly along the liquid film, more so close to the interface, in a similar  
357 behaviour to the instantaneous absorption regime.  $\text{CO}_3^{2-}$  is consumed in the vicinity of the interface.  
358 At these experimental conditions, it is important to consider the reaction mechanism with both  
359 reactions and varying activity coefficients along the liquid film. The high absorption driving force  
360 results in ionic strength variation. These conditions are closer to those expected in an industrial  
361 setting. This shows how the model could accurately represent mass transfer phenomena at industrial  
362 conditions.



363

364 **Figure 6** Simulated absorption of CO<sub>2</sub> in Na<sub>2</sub>CO<sub>3</sub> aqueous solution at 0.06 mol.L<sup>-1</sup>, 298 K and P<sub>CO<sub>2</sub></sub> =  
 365 100 kPa measured by (Hikita, et al., 1976). C: normalised concentration, ξ: extent of reaction, γ:  
 366 activity coefficient. Solid line & symbol: activity-based model, dashed line: concentration-based  
 367 model (C and ξ). γ<sub>Na<sup>+</sup></sub> = 0.68



368

369 **Figure 7** Simulated absorption of CO<sub>2</sub> in NaOH aqueous solution at 0.13 mol.L<sup>-1</sup>, 303 K and P<sub>CO<sub>2</sub></sub> = 100  
 370 kPa measured by (Hikita, et al., 1976). C: normalised concentration, ξ: extent of reaction, γ: activity  
 371 coefficient. Solid line & symbol: activity-based model, dashed line: concentration-based model (C and  
 372 ξ). γ<sub>Na<sup>+</sup></sub> = 0.76

#### 373 4. Conclusion

374 This study implements a steady-state reactive absorption model applied to the stagnant film theory  
 375 and focusing on solution non-ideality representation in equilibrium relations, Nernst-Planck diffusion  
 376 fluxes and reaction rates. This approach is more complete than literature models where activity

377 coefficients are assumed constant, and most often equal to unity. Extents of reactions, a new feature  
378 for reactive absorption models, reduces the number of differential problem variables while  
379 maintaining a general formulation. This formulation with Nernst-Planck equation for molecular  
380 diffusion and activity-based rate expressions consists in a system of  $n_C+n_{R,kin}$  *first-order* ordinary  
381 differential equations, whereas writing local balances per species leads to a system of  $n_C$  *second-*  
382 *order* differential equations. The relation between fluxes and extents of reactions is dictated by  
383 stoichiometric constraints.

384 This model is first applied to alkaline salts-water-CO<sub>2</sub> systems and the CO<sub>2</sub> absorption flux data from  
385 the literature. Arrhenius parameters for CO<sub>2</sub> + HO<sup>-</sup> ↔ HCO<sub>3</sub><sup>-</sup> direct kinetic constant are fitted. This is  
386 a necessary step to study amine-based systems in the same modelling framework. This progressive  
387 approach is made possible by the kinetic data availability in alkaline salts-water-CO<sub>2</sub> systems. The  
388 obtained Arrhenius parameters are coherent to previous studies in the regression temperature  
389 interval. Overall AAD is 12%. Besides, the consideration of activity coefficient variation along the  
390 liquid film is shown to be relevant when experimental conditions diverge from the simple pseudo-  
391 first order absorption regime. These conditions are closer to the industrial setting.

392 Model improvement perspectives include extending mass transfer representation to steady-state  
393 eddy-diffusivity theory, and assessing uncoupled ion diffusivities influence.

394 With this model, reaction mechanism investigation in any reactive absorption system is possible. Our  
395 further goal is to apply the model to CO<sub>2</sub> absorption in aqueous amines solutions (namely MDEA),  
396 especially for increasing CO<sub>2</sub> partial pressure and loading. In these solutions, the more complex  
397 reaction scheme could lead to higher variations in ionic strength and activity coefficients through the  
398 liquid film.

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