

IDENTIFICATION OF REACTION AND MASS-TRANSFER RATES IN GAS-LIQUID REACTION SYSTEMS

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ABSTRACT

This paper deals with the identification of reaction and mass-transfer rates from concentrations measured in gas-liquid reaction systems. It is assumed that the reactions take place in the liquid bulk only. The identification proceeds in two steps: (i) estimation of the extents of reaction and mass transfer from concentration measurements, and (ii) estimation of the parameters of the individual reaction and mass-transfer rates from the extents. For the estimation of the individual extents, two cases are considered: if the concentrations of all the species in the liquid phase can be measured, a linear transformation is used; otherwise, if the concentrations of only subsets of the species can be measured in the gas and liquid phases, an approach as an extension of the linear transformation is proposed. The approach is illustrated in simulation via the chlorination of butanoic acid.

1 INTRODUCTION

Gas-liquid (G-L) reaction systems such as hydrogenations, oxidations and fermentations are employed in the production of various important chemical and biochemical products. Detailed kinetic models of such reaction systems are useful for process development, control, monitoring and optimization. However, the identification of reliable models is a challenging task because of the couplings between the reaction and mass-transfer phenomena.

An incremental identification approach has been proposed to identify reaction systems from concentration data by solving a sequence of subproblems [1]. For each subproblem, the number of model candidates can be considerably reduced, which results in an efficient and computationally less expensive identification procedure. This approach is closely related to the *differential method* for identifying the reaction kinetics, whereby reaction and mass-transfer rates are obtained by differentiation of concentration data [2].

The concept of extent of reaction is useful to describe the behavior of chemical reactions. For a particular reaction, the change in extent of reaction is given by the change in the number of moles of any species due to that reaction divided by the corresponding stoichiometric coefficient. Recently, Amrhein et al. [3] proposed a linear transformation to compute individual extents of reaction and inlet flow from the numbers of moles in homogeneous reaction systems. This transformation uses only information regarding the stoichiometry, the inlet composition and the initial conditions and, furthermore, it does not require any constitutive relationships such as kinetic expressions. The approach has also been extended to compute the extents of reaction, mass transfer and flow in G-L reaction systems by Bhatt et al. [4]. Then, in subsequent steps, the rate laws can be investigated *individually* for each reaction and each mass transfer based on the computed extents.

The main contribution of this paper is the estimation of the extents of reaction and mass transfer from measurements in G-L reaction systems. Two cases are considered: (a) the concentrations of all the species in the liquid phase are measured, and (b) the concentrations of subsets of the species are

measured in the gas and liquid phases. For Case a, a linear transformation is proposed to estimate the extents of reaction, mass transfer and flow based on the stoichiometry, the inlet composition and the initial conditions. The inlet and outlet flowrates need not be known. For Case b, an approach is proposed to estimate the extents of reaction and mass transfer as an extension of the linear transformation. In both cases, the unknown rate parameters can be estimated individually for each reaction and mass transfer from the corresponding extent. This work can be seen as a two-fold extension of the incremental approach given in [5]: extension from homogeneous to G-L reaction systems, and using the integral instead of the differential method.

The paper is organized as follows. In Section 2, the mole balance equations of G-L reaction systems are revisited. Section 3 presents the estimation of the extents of reaction and mass transfer from measured concentrations. Based on these extents, Section 4 estimates the parameters of the individual reaction and mass-transfer rates using *the integral method*, which is proven to have statistical advantages over the differential method. Finally, Section 5 concludes the paper.

2 MOLE BALANCE EQUATIONS IN G-L REACTION SYSTEMS

Consider a G-L reaction system involving S species. Among these S species, S_g species live in the gas phase, S_l species live in the liquid phase, $S_m = S_{gl} + S_{lg}$ species transfer between the two phases, with S_{gl} species transferring from the gas to the liquid and S_{lg} species transferring from the liquid to the gas. Let us consider the following assumptions:

- (A1) The gas and liquid phases are homogeneous.
- (A2) The G-L reactor has a constant total volume.
- (A3) The reactions take place in the liquid bulk only.
- (A4) The mass-transfer phenomena are described by the two-film theory with no accumulation in the boundary layer. This assumption is made here for simplicity of presentation, and Appendix A in [4] discusses the case of unsteady-state mass transfer.

The gas and liquid phases will be modeled separately, with the mass-transfer rates ζ_{gl} and ζ_{lg} connecting the two phases. The gas phase also contains p_g inlets and one outlet, while the liquid phase contains p_l inlets and one outlet. There are p_{gl} ($= S_{gl}$) mass-transfer fluxes from the gas to the liquid, p_{lg} ($= S_{lg}$) mass-transfer fluxes from the liquid to the gas, i.e. a total of p_m ($= S_m$) mass-transfer fluxes. The mass-transfer rates ζ_{gl} and ζ_{lg} are positive or zero. Since, by convention, the positive sign (+) is assigned to the mass transfer from the gas to the liquid, the p_m -dimensional mass-transfer rate vector is $\zeta = \begin{bmatrix} \zeta_{gl} \\ -\zeta_{lg} \end{bmatrix}$. With these assumptions, the mole balances for the gas and liquid phases read:

$$\text{Gas Phase: } \dot{\mathbf{n}}_g(t) = \mathbf{W}_{in,g} \mathbf{u}_{in,g}(t) - \mathbf{W}_{m,g} \zeta(t) - \frac{u_{out,g}(t)}{m_g(t)} \mathbf{n}_g(t), \quad \mathbf{n}_g(0) = \mathbf{n}_{g0}, \quad (1)$$

$$\text{Liquid Phase: } \dot{\mathbf{n}}_l(t) = \mathbf{N}_l^T V_l(t) \mathbf{r}(t) + \mathbf{W}_{in,l} \mathbf{u}_{in,l}(t) + \mathbf{W}_{m,l} \zeta(t) - \frac{u_{out,l}(t)}{m_l(t)} \mathbf{n}_l(t), \quad \mathbf{n}_l(0) = \mathbf{n}_{l0}, \quad (2)$$

where \mathbf{n}_i is the S_i -dimensional vector of numbers of moles in the i^{th} phase, $i \in \{g, l\}$, \mathbf{N}_l the $R \times S_l$ stoichiometric matrix, R the number of reactions, $\mathbf{W}_{in,i} = \mathbf{M}_{w,i}^{-1} \check{\mathbf{W}}_{in,i}$ the $S_i \times p_i$ inlet matrix expressing the composition of the inlets to the i^{th} phase, $\mathbf{M}_{w,i}$ the S_i -dimensional diagonal matrix of molecular weights, and $\check{\mathbf{W}}_{in,i} = [\check{\mathbf{w}}_{in,i}^1 \ \cdots \ \check{\mathbf{w}}_{in,i}^{p_i}]$ with $\check{\mathbf{w}}_{in,i}^j$ being the S_i -dimensional vector of weight fractions of the j^{th} inlet to the i^{th} phase, $\mathbf{u}_{in,i}$ the p_i -dimensional inlet mass flowrate to the i^{th} phase, and \mathbf{n}_{i0} the vector of initial moles in the i^{th} phase. $\mathbf{W}_{m,i} = \mathbf{M}_{w,i}^{-1} \check{\mathbf{E}}_{m,i}$ is the $S_i \times p_m$ mass-transfer matrix to the i^{th} phase, $\check{\mathbf{E}}_{m,i} = [\check{\mathbf{e}}_{m,i}^1 \ \cdots \ \check{\mathbf{e}}_{m,i}^{p_m}]$ with $\check{\mathbf{e}}_{m,i}^j$ being the S_i -dimensional vector with the element corresponding to the j^{th} transferring species equal to unity and the other elements equal to zero. V_l is the volume of the liquid phase. Note that the reactor masses $m_g(t)$ and $m_l(t)$ can be inferred from the numbers of moles as: $m_i(t) = \mathbf{1}_{S_i}^T \mathbf{M}_{w,i} \mathbf{n}_i(t)$, $i \in \{g, l\}$, where $\mathbf{1}_{S_i}$ is a S_i -dimensional vector filled with ones.

Model (1)-(2) holds for both isothermal and non-isothermal reactors since the specificities regarding the reactor type and its operation are hidden in the liquid volume $V_l(t)$, the reaction rate vector $\mathbf{r}(t)$, the mass-transfer rate vector $\boldsymbol{\zeta}(t)$, and the specified inlet and outlet streams $\mathbf{u}_{in,i}(t)$ and $u_{out,i}(t)$. The reader can find the specificities for both gas-phase and liquid-phase reaction systems in Appendix A of [3]. Throughout this paper, the R reactions, the p_i inlets and the p_m mass transfers are assumed to be independent, according to the definitions given in [4].

3 ESTIMATION OF EXTENTS OF REACTION AND MASS TRANSFER FROM MEASURED CONCENTRATIONS

The objective of this section is to estimate the extents of reaction and mass transfer from concentration measurements. Note that the extents of mass transfer can be estimated from either the gas or the liquid concentrations. However, the extents of reaction can only be estimated from the liquid concentrations. Here, two cases will be distinguished depending upon the measurements available in the gas and liquid phases.

A. All liquid-phase concentrations measured

Let $\mathbf{c}_l(t)$ be the molar concentrations measured at the time instant t for the S_l species in the liquid phase. The following proposition describes the conditions required to be able to estimate the extents of reaction, mass transfer and flows from $\mathbf{c}_l(t)$.

Proposition 1 *If (i) the matrices \mathbf{N}_l , $\mathbf{W}_{m,l}$, $\mathbf{W}_{in,l}$ and \mathbf{n}_{l0} are known, (ii) $\text{rank}([\mathbf{N}_l^T \ \mathbf{W}_{m,l} \ \mathbf{W}_{in,l} \ \mathbf{n}_{l0}]) = R + p_l + p_m + 1$, and (iii) $\mathbf{c}_l(t)$ and $V_l(t)$ are measured, then the R -dimensional extents of reaction $\mathbf{x}_r(t)$, the p_m -dimensional extents of mass transfer in the liquid phase $\mathbf{x}_{m,l}(t)$, the p_l -dimensional extents of inlet $\mathbf{x}_{in,l}(t)$, and the discounting of the initial conditions $\lambda_l(t)$ can be estimated using the following linear transformation:*

$$\begin{bmatrix} \mathbf{x}_r(t) \\ \mathbf{x}_{m,l}(t) \\ \mathbf{x}_{in,l}(t) \\ \lambda_l(t) \end{bmatrix} = \begin{bmatrix} \mathbf{S}_{l0}^T \\ \mathbf{M}_{m,l0}^T \\ \mathbf{M}_{in,l0}^T \\ \mathbf{q}_{l0}^T \end{bmatrix} V_l(t) \mathbf{c}_l(t), \quad (3)$$

with

$$\begin{aligned} \mathbf{S}_{l0}^T &= \mathbf{S}_l^T (\mathbf{I}_{S_l} - \mathbf{n}_{l0} \mathbf{q}_{l0}^T), & \mathbf{M}_{m,l0}^T &= \mathbf{M}_{m,l}^T (\mathbf{I}_{S_l} - \mathbf{n}_{l0} \mathbf{q}_{l0}^T), \\ \mathbf{M}_{in,l0}^T &= \mathbf{M}_{in,l}^T (\mathbf{I}_{S_l} - \mathbf{n}_{l0} \mathbf{q}_{l0}^T), & \mathbf{q}_{l0}^T &= \frac{\mathbf{I}_{S_l - R - p_m - p_l}^T \mathbf{Q}_l^T}{\mathbf{I}_{S_l - R - p_m - p_l}^T \mathbf{Q}_l^T \mathbf{n}_{l0}}. \end{aligned} \quad (4)$$

The matrices \mathbf{S}_l , $\mathbf{M}_{m,l}$, $\mathbf{M}_{in,l}$ and \mathbf{Q}_l are of dimensions $S_l \times R$, $S_l \times p_m$, $S_l \times p_l$ and $S_l \times (S_l - R - p_m - p_l)$, respectively. These matrices can be constructed using the algorithm given in Appendix B of [4]. (Proof see full paper)

Alternatively, one can estimate the extents of mass transfer $\mathbf{x}_{m,g}(t)$, the extents of inlet flow $\mathbf{x}_{in,g}(t)$ and the discounting of the initial conditions $\lambda_g(t)$ in the gas phase by applying a similar linear transformation to the numbers of moles in the gas phase as shown in [4]. Note that $\mathbf{x}_{m,l}(t)$ and $\mathbf{x}_{m,g}(t)$ differ slightly since the extents express the mass transferred between the two phases corrected for the amount that has left the corresponding phase (which is different in the liquid and gas phases).

B. Concentrations of subsets of species measured in the gas and liquid phases

Let $\mathbf{c}_{g_k}(t)$ and $\mathbf{c}_{l_k}(t)$ be the S_{g_k} - and S_{l_k} -dimensional vectors of measured concentrations in the gas and liquid phases at time instant t , respectively. The subscript " k " indicates that the corresponding quantity is known or measured in the corresponding phase. Without loss of generality, it is assumed that the S_{g_k} species measured in the gas phase are involved in mass transfer.

The extents of mass transfer will be computed from information stemming from both phases: $p_{m_g} = S_{g_k}$ extents will be computed from the gas phase, while the remaining $p_{m_l} = p_m - p_{m_g}$

extents will be computed from the liquid phase. The extents of mass transfer and the mass-transfer matrices are noted accordingly: for instance, $\mathbf{x}_{m_g,g}$ and $\mathbf{x}_{m_g,l}$ represent the p_{m_g} -dimensional vectors of extents of mass transfer computed from gas-phase measurements for the gas and the liquid phase, respectively; $\mathbf{x}_{m_l,l}$ is the p_{m_l} -dimensional vector of extents of mass transfer computed from and for the liquid phase; \mathbf{W}_{m_g,g_k} is the $S_{g_k} \times p_{m_g}$ mass-transfer matrix associated with the p_{m_g} mass transfers and the S_{g_k} species; \mathbf{W}_{m_l,l_k} is the $S_{l_k} \times p_{m_l}$ mass-transfer matrix associated with the p_{m_l} mass transfers and the S_{l_k} species; \mathbf{W}_{m_g,l_k} is the $S_{l_k} \times p_{m_g}$ mass-transfer matrix associated with the p_{m_g} mass transfers and the S_{l_k} species.

Proposition 2 *Let the matrices \mathbf{N}_{l_k} , \mathbf{W}_{m_g,g_k} , \mathbf{W}_{m_l,l_k} , \mathbf{W}_{m_g,l_k} , \mathbf{W}_{in,l_k} , \mathbf{W}_{in,g_k} , the reactor volume V_r , and the initial conditions $\mathbf{n}_{l_k,0}$ and $\mathbf{n}_{g_k,0}$ be known. Furthermore, let the quantities $\mathbf{c}_{g_k}(t)$, $\mathbf{c}_{l_k}(t)$, $\mathbf{u}_{in,l}(t)$, $\mathbf{u}_{in,g}(t)$, $u_{out,l}(t)$, $u_{out,g}(t)$, $V_l(t)$, $m_l(t)$ and $m_g(t)$ be measured. If (i) $S_{l_k} + S_{g_k} \geq R + p_m$, (ii) $\text{rank}(\mathbf{N}_{l_k}) = R$, and (iii) $\text{rank}([\mathbf{N}_{l_k}^T, \mathbf{W}_{m_l,l_k}]) \geq R + p_{m_l}$, then the extents of reaction and mass transfer can be estimated in three steps as follows:*

1. Estimation of extents of mass transfer $\mathbf{x}_{m_g,g}$ in the gas phase:

$$\dot{\mathbf{x}}_{in,g} = \mathbf{u}_{in,g} - \frac{u_{out,g}}{m_g} \mathbf{x}_{in,g}, \quad \mathbf{x}_{in,g}(0) = \mathbf{0}_{p_g}, \quad (5a)$$

$$\dot{\lambda}_g = -\frac{u_{out,g}}{m_g} \lambda_g, \quad \lambda_g(0) = 1, \quad (5b)$$

$$\mathbf{W}_{m_g,g_k} \mathbf{x}_{m_g,g}(t) = (V_r - V_l(t)) \mathbf{c}_{g_k}(t) - \mathbf{W}_{in,g_k} \mathbf{x}_{in,g}(t) - \lambda_g(t) \mathbf{n}_{g_k,0}. \quad (5c)$$

2. Estimation of extents of mass transfer $\mathbf{x}_{m_g,l}$ in the liquid phase:

$$\dot{\Phi}(t) = -\frac{u_{out,l}(t)}{m_l(t)} \Phi(t) + \left(\frac{u_{out,l}(t)}{m_l(t)} - \frac{u_{out,g}(t)}{m_g(t)} \right) \mathbf{x}_{m_g,g}(t), \quad \Phi(0) = \mathbf{0}_{p_{m_g}}, \quad (6a)$$

$$\mathbf{x}_{m_g,l}(t) = \mathbf{x}_{m_g,g}(t) - \Phi(t), \quad (6b)$$

where Φ is a p_{m_g} -dimensional vector expressing the differences in mass-transfer extents in the gas and liquid phases.

3. Estimation of extents of reaction \mathbf{x}_r and mass transfer $\mathbf{x}_{m_l,l}$ in the liquid phase:

$$\dot{\mathbf{x}}_{in,l} = \mathbf{u}_{in,l} - \frac{u_{out,l}}{m_l} \mathbf{x}_{in,l}, \quad \mathbf{x}_{in,l}(0) = \mathbf{0}_{p_l}, \quad (7a)$$

$$\dot{\lambda}_l = -\frac{u_{out,l}}{m_l} \lambda_l, \quad \lambda_l(0) = 1, \quad (7b)$$

$$\mathbf{W}_{m_l,l_k} \mathbf{x}_{m_l,l}(t) + \mathbf{N}_{l_k}^T \mathbf{x}_r(t) = V_l(t) \mathbf{c}_{l_k}(t) - \mathbf{W}_{in,l_k} \mathbf{x}_{in,l}(t) - \lambda_l(t) \mathbf{n}_{l_k,0} - \mathbf{W}_{m_g,l_k} \mathbf{x}_{m_g,l}(t). \quad (7c)$$

(See full paper for proof)

Remarks

1. In the first step, the matrix \mathbf{W}_{m_g,g_k} is of full rank by construction.
2. Conditions (i)–(iii) specify the minimum numbers of concentration measurements required to estimate the extents of reaction and mass transfer.

4 PARAMETER ESTIMATION USING INDIVIDUAL EXTENTS

For given model structures of the reaction and mass-transfer rates, the unknown parameters can be estimated from experimental data. In this section, the estimated extents of reaction and mass transfer will be used to estimate these parameters. The unmeasured concentrations in the liquid phase, \mathbf{c}_{l_u} , can be reconstructed from the various extents as follows:

$$\mathbf{c}_{l_u}(t) = V_l^{-1}(t) \left(\mathbf{N}_{l_u}^T \mathbf{x}_r(t) + \mathbf{W}_{m_l,l_u} \mathbf{x}_{m_l,l}(t) + \mathbf{W}_{in,l_u} \mathbf{x}_{in,l}(t) + \lambda_l(t) \mathbf{n}_{l_u,0} \right), \quad (8)$$

where $\mathbf{x}_{m,l} = \begin{bmatrix} \mathbf{x}_{m_g,l} \\ \mathbf{x}_{m_l,l} \end{bmatrix}$ and \mathbf{c}_{l_u} is the $S_{l_u} (= S_l - S_{l_k})$ -dimensional vector of unmeasured species, with the subscript "u" indicating an unknown or unmeasured species.

For the a^{th} reaction, let $\hat{\mathbf{x}}_{r,a}$ and $\mathbf{x}_{r,a}$ denote the K -dimensional vectors of estimated (according to the procedure of Section 3) and simulated (according to a postulated rate law involving the parameters $\boldsymbol{\theta}_{r,a}$) extents of reaction at K time instants, respectively. A parameter estimation problem of the following form can be formulated:

$$\begin{aligned} \min_{\boldsymbol{\theta}_{r,a}} J_a &= (\hat{\mathbf{x}}_{r,a} - \mathbf{x}_{r,a}(\boldsymbol{\theta}_{r,a}))^T (\hat{\mathbf{x}}_{r,a} - \mathbf{x}_{r,a}(\boldsymbol{\theta}_{r,a})) \\ \text{s.t.} \quad \dot{x}_{r,a}(t) &= r_a(\mathbf{c}_l(t), \boldsymbol{\theta}_{r,a}) V_l(t) - \frac{u_{out,l}(t)}{m_l(t)} x_{r,a}(t), \quad x_{r,a}(0) = 0, \\ \boldsymbol{\theta}_{r,a}^L &\leq \boldsymbol{\theta}_{r,a} \leq \boldsymbol{\theta}_{r,a}^U, \end{aligned} \quad (9)$$

where J_a is the cost to minimize, r_a is the rate of the a^{th} reaction, which is a known function of the molar concentration \mathbf{c}_l and of the l -dimensional unknown parameters $\boldsymbol{\theta}_{r,a}$ that can vary between the bounds $\boldsymbol{\theta}_{r,a}^L$ and $\boldsymbol{\theta}_{r,a}^U$.

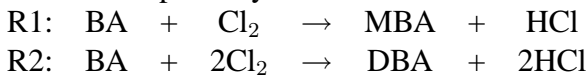
Similarly, let $\hat{\mathbf{x}}_{m,l,b}$ and $\mathbf{x}_{m,l,b}$ denote the K -dimensional vectors of the estimated and simulated extents of the b^{th} mass-transfer in the liquid phase. The parameter estimation problem for the mass transfer rates can be formulated as:

$$\begin{aligned} \min_{\boldsymbol{\theta}_{m,b}} J_b &= (\hat{\mathbf{x}}_{m,l,b} - \mathbf{x}_{m,l,b}(\boldsymbol{\theta}_{m,b}))^T (\hat{\mathbf{x}}_{m,l,b} - \mathbf{x}_{m,l,b}(\boldsymbol{\theta}_{m,b})) \\ \text{s.t.} \quad \dot{\mathbf{x}}_{m,l,b}(t) &= \zeta_b(\mathbf{c}_l(t), \mathbf{c}_g(t), \boldsymbol{\theta}_{m,b}) - \frac{u_{out,l}(t)}{m_l(t)} \mathbf{x}_{m,l,b}, \quad \mathbf{x}_{m,l,b}(0) = 0, \\ \boldsymbol{\theta}_{m,b}^L &\leq \boldsymbol{\theta}_{m,b} \leq \boldsymbol{\theta}_{m,b}^U, \end{aligned} \quad (10)$$

where ζ_b is the b^{th} mass-transfer rate, which is a known function of both \mathbf{c}_l and \mathbf{c}_g and of the q -dimensional parameter vector $\boldsymbol{\theta}_{m,b}$ that can vary between the bounds $\boldsymbol{\theta}_{m,b}^L$ and $\boldsymbol{\theta}_{m,b}^U$.

5 SIMULATION STUDY: CHLORINATION OF BUTANOIC ACID

The chlorination of butanoic acid (BA) is a G-L reaction system. The reaction, which takes place in the organic liquid phase with ethanol (Q) as solvent, involves two parallel auto-catalytic reactions that consume dissolved Cl_2 [6]. The main reaction produces the desired product α -monochlorobutanoic acid (MBA) and hydrochloric acid (HCl), the latter being a highly volatile product that is found in both phases. The second reaction produces the side product α -dichlorobutanoic acid (DBA) and HCl. The reaction pathway reads:



with the kinetic expressions:

$$\begin{aligned} r_1 &= k_{r,1} c_{l,BA} c_{l,\text{Cl}_2} \sqrt{c_{l,\text{MBA}}}, \\ r_2 &= k_{r,2} r_1 c_{l,\text{Cl}_2}. \end{aligned} \quad (11)$$

The thermodynamic parameters are given in Appendix D of [4]. The mass-transfer rates (in kg s^{-1}) are calculated using the following equations:

$$\begin{aligned} \zeta_{g,l,\text{Cl}_2} &= k_{\text{Cl}_2} A_s V_l M_{w,\text{Cl}_2} (c_{\text{Cl}_2}^* - c_{l,\text{Cl}_2}), \quad c_{\text{Cl}_2}^* = \mathcal{P}_{\text{Cl}_2} / H_{\text{Cl}_2}, \\ \zeta_{g,l,\text{HCl}} &= k_{\text{HCl}} A_s V_l M_{w,\text{HCl}} (c_{l,\text{HCl}} - c_{\text{HCl}}^*), \quad c_{\text{HCl}}^* = \mathcal{P}_{\text{HCl}} / H_{\text{HCl}}, \end{aligned} \quad (12)$$

where A_s is the specific interfacial area, $c_{\text{Cl}_2}^*$ and c_{HCl}^* are the equilibrium molar concentrations at the interface, c_{l,Cl_2} and $c_{l,\text{HCl}}$ are the molar concentrations in the liquid bulk, H_{Cl_2} and H_{HCl} are Henry's

law constants, \mathcal{P}_{Cl_2} and \mathcal{P}_{HCl} are the partial pressures in the gas phase and are calculated using the ideal gas law from the numbers of moles in the gas phase.

Case b in Section is considered for this simulation study. The data are generated by simulating the chlorination of butanoic acid with inlets and outlets and adding zero-mean Gaussian noise with $\sigma = 0.02$. The species Cl_2 and BA are continuously fed to the gas and the liquid, respectively. The concentration of Cl_2 in the gas phase ($c_{Cl_2,g}$, $S_{gk} = 1$), the concentrations of BA, MBA and HCl in the liquid phase ($c_{l,BA}$, $c_{l,MBA}$, $c_{l,HCl}$, $S_{lk} = 3$), the flowrates and masses in the liquid and gas phases and the liquid volume are taken as measurements. The measurements satisfy Conditions (i)-(iii). Hence, in Step 1, the extents of reaction R1 ($x_{r,1}$) and R2 ($x_{r,2}$) and the extents of mass transfer for Cl_2 (x_{m,g,l,Cl_2}) and HCl ($x_{m,l,HCl}$) can be estimated from the measurements as mentioned in Proposition 2 (the plots of the estimated extents are not shown here). In Step 2, the kinetic rate constants ($k_{r,1}$ and $k_{r,2}$) and mass-transfer rate constants (k_{Cl_2} and k_{HCl}) are estimated by solving the parameter estimation problem given in Eq. (9). The true and estimated rate constants are presented in Table 1 along with the initial guesses to the estimation problem.

Table 1: True values, initial guesses and estimated values of the kinetic rate constants ($k_{r,i}$, $i \in \{1, 2\}$) and mass-transfer rate constants (k_j , $j \in \{Cl_2, HCl\}$).

	$k_{r,1}$ [m ³ kmol ⁻¹]	$k_{r,2}$ [-]	k_{Cl_2} [m s ⁻¹]	k_{HCl} [m s ⁻¹]
True values	1.3577	0.100	6.66×10^{-5}	8.45×10^{-5}
Initial guesses	0.0800	0.020	2.00×10^{-2}	2.00×10^{-2}
Estimated values	1.3603	0.105	6.91×10^{-5}	8.34×10^{-5}

6 CONCLUDING REMARKS

Being able to estimate the extents of reaction and mass transfer helps in the investigation of G-L reaction systems. In this paper, a linear transformation has been proposed to estimate the extents of reaction, mass transfer and flow from the concentration measurements of all the species in the liquid phase. The key feature of the transformation is the ability to estimate the various extents using only the stoichiometry, the inlet composition and the initial conditions, i.e. independently of the (unknown) reaction and mass-transfer rates. When the concentrations are measured only for subsets of the species in the gas and liquid phases, an approach has been proposed to estimate the extents of reaction and mass transfer by solving a set of differential-algebraic equations. The possibility of estimating the unknown rate parameters individually for each reaction and mass transfer from the corresponding extent has been illustrated using the chlorination of butanoic acid. The approaches presented in this paper can be extended to include spectral and calorimetric data for estimating the various extents.

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