Isothermal Characterization of Linear Catalytic Reaction Networks from Transient Experiments

Raf Roelant[a]   Denis Constales[b]   Roger Van Keer[b]   Guy B. Marin[a*]

1   Introduction

To reveal chemical reaction networks, scientists rely primarily on kinetic experiments. Working in a transient regime provides especially valuable information. Usually, the analysis of the data is facilitated by keeping the reactor isothermal in time and space. For catalytic reactions, similarly, variations in time and space of the catalyst surface state are often kept insignificant. In many cases, this condition ensures that the mass power law, expressing the rate of the elementary reaction steps, degenerates everywhere to pseudolinear.

Classically, some candidate reaction networks are postulated which are then tested against the experimental data until a representative one is selected. Suppose however that experimental data have been collected as mentioned above, over a heterogeneous catalyst at a single temperature. Under this constraint, multiple networks are often indistinguishable because the concentration of surface intermediates is not measured (Walter et al., 1989). This contribution will explain how the data can still be used to derive features of the reaction network. As opposed to the classical approach, this can be done in a model-free manner.

2   Kinetic transfer functions

Consider an example of a pseudolinear reaction network in Fig. 1. Those species marked with * represent surface intermediates, the others liquid or gaseous reactants or reaction products. The kinetics of the reaction are most easily described in the Laplace domain. Indeed, abstracting the responsible transport phenomena, suppose a molar flow F_{A_i} of

[a]Laboratory for Chemical Technology, Department of Chemical Engineering and Technical Chemistry, Ghent University, Krijgslaan 281 (S5), B–9000 Gent, Belgium

[b]Department of Mathematical Analysis, Ghent University, Galglaan 2, B–9000 Gent, Belgium

*Corresponding author.

E-mail addresses: Raf.Roelant@UGent.be, Denis.Constales@UGent.be, Roger.VanKeer@UGent.be, Guy.Marin@UGent.be
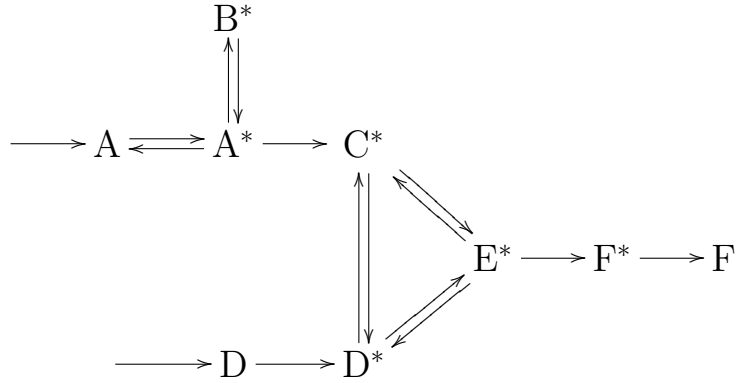
Figure 1: A linear heterogeneous-catalytic reaction network. Species labelled with * represent surface intermediates.

a gas/liquid A_i is admitted to the catalyst. As a response, the concentration C_{A_j} of all gases/liquids will evolve in a predetermined way. Again, abstraction is made of the transport phenomena responsible for their removal. The Laplace transform $\mathscr{L}C_{A_j}$ of the evolutions can be found by multiplying the Laplace transform $\mathscr{L}F_{A_i}$ of the inflow by a transfer function $H_{A_i \to A_j}$. Obviously the transfer function depends on the values of the rate coefficients (including adsorption and desorption coefficients). However, its functional form depends solely on the reaction network. Indeed, the transfer function is a polynomial quotient

$$H_{A_i \to A_j}(s) = \frac{\sum_{k=0}^{m} \alpha_k s^k}{s^n + \sum_{l=0}^{n-1} \beta_l s^l}, \tag{1}$$

in which the coefficients α_k and β_l are positive functions of the rate coefficients. n is the total number of components involved in the production of A_j out of A_i, including reactant and product. $n - m$ is the minimal number of components involved, i.e. the number of components along the shortest reaction path(s) from A_i to A_i, these latter included. In Fig. 1, all components except D are involved in the production of F out of A, so $n = 8$ in $H_{A \to F}(s)$. Moreover, the shortest reaction path is $AA^*C^*E^*F^*F$. Therefore $n - m = 6$ or $m = 2$.

3 Characterization of reaction networks

The kinetics of the production of A_j out of A_i is uniquely determined by the transfer function $H_{A_i \to A_j}$ in Eq. (1). It has been proved that the number of linearly independent coefficients α_k and β_l in Eq. (1) is always greater than or equal to the number of rate coefficients, i.e. the number of elementary steps. As a result it is often impossible to identify the rate coefficients from the measurement of the concentration of A_j alone. Obviously,

different reaction networks can also give rise to transfer functions with the same functional form. Application of a theorem by Vajda (1981) shows that this makes it impossible to distinguish between these networks in at least some open sets of the parameter spaces on the basis of a measurement of the concentration of A_j at a single temperature.

Unidentifiability and indistinguishability are characteristics that often prevail even when multiple reactants and/or products are measured. This is the price to pay for not being able to measure the concentration of the surface intermediates. Luckily, this uncertainty is greatly diminished if one simultaneously processes data collected at multiple temperatures, assuming that the reaction network remains valid in the whole range and knowing that the rate coefficients have an Arrhenius kind of dependence on temperature. However, as a first step in the determination of the reaction network it is still interesting to perform isothermal analyses. These should allow a model-free estimation of m and n for each transfer function $H_{A_i \to A_j}$ in Eq. (1), leading to an estimate of the (minimal) number of observable surface intermediates along which reactants A_i react to products A_j. Furthermore, comparison of the poles and zeros of different transfer functions $H_{A_i \to A_j}$ and $H_{A_k \to A_l}$ can provide such information about the parts of the reaction networks commonly traversed from A_i to A_j and from A_k to A_l.

4 Conclusion

Data from catalytic experiments collected at a single temperature allow the extraction of limited information about the reaction network in a model-independent way. This information is the total and minimal number of observable surface intermediates to traverse for reaction. If applicable, such information can also be extracted about parts of the reaction network shared by reaction pathways between multiple measured species.

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