

## GRASPING COMPLEXITY IN CHEMICAL KINETICS: TOP-DOWN, BOTTOM-UP AND SOME MORE

Gregory S. Yablonsky\*, Denis Constaes<sup>o</sup>, Guy B. Marin\*\*

\*Parks College of Engineering, Aviation, and Technology, Department of Chemistry, Saint Louis University, St. Louis MO, 63103, USA

<sup>o</sup>Department of Mathematical Analysis, Ghent University, Galglaan 2, B-9000, Ghent (Belgium)

\*\*Laboratory for Chemical Technology, Ghent University, Krijgslaan, S5, B-9000, Ghent (Belgium)

### EXTENDED ABSTRACT

The analysis of complex reaction networks can be performed in two complementary ways:

- (a) Insight in the chemistry of the investigated process can be translated into so-called chemical rules. This can be implemented as algorithms in computer code, allowing the automatic generation of reaction networks consisting of several thousands of elementary steps. Databases, which are based either on experiments or on the quantum chemical calculation of model reactions, then provide the corresponding thermodynamic and kinetic parameters.

Numerical integration techniques and kinetic Monte-Carlo simulations finally allow, e.g. via a sensitivity analysis, to assess the significance of each elementary reaction family considered, and the effects of the reaction conditions on them.

Recent results by Gorban et al. [1-2] provide the means for a rigorous asymptotic analysis of complex kinetic models for both reversible and irreversible mechanisms. This first way can be interpreted as a *top-down* approach.

- (b) Alternatively, under the *bottom-up* approach, the so-called minimal reaction networks and mechanisms are the starting point. For the steady-state kinetics of catalytic reactions a general, a thermodynamically consistent rate equation can be constructed using algebraic methods and/or graph theory [3]. For linear reaction mechanisms this rate equation consists of a driving force, which ensures thermodynamic consistency, and a resistance, which is the inverse of the total weight of the node-spanning trees of the graph corresponding to the reaction mechanism. This resistance can actually be measured as the ratio of the driving force to the reaction rate.

The analysis of the concentration and temperature dependence of the resistance then provides direct information on the nature of the elementary steps involved in the reaction mechanism. For nonlinear reaction mechanisms an implicit equation for the reaction rate can conveniently be used to obtain insights. This so-called *kinetic polynomial* is a generalization of the well-known Langmuir-Hinshelwood-Hougen-Watson (LHHW) rate equation for linear reactions mechanisms.

In the non-steady-state kinetic description, data from pulse-response experiments with insignificant perturbation (data obtained from Temporal Analysis of Products) can be used to construct the model in the bottom-up style. In such cases, the model is built using decision tree procedures.

A new, additional form of pattern analysis exists that lies beyond the alternative between the top-down and bottom-up approaches:

- (c) It is based on the following new kinetic phenomena that were discovered theoretically [4-8] and experimentally confirmed [8].
- (1) Intersections of concentration dependencies, coincidences of such intersections, and the structure of possible orderings of concentration and time values defined by intersections.

The intersections under consideration are defined by the concentration dependencies of the system when started from special, extreme initial conditions. For instance, the two-step reversible-irreversible mechanism  $A \rightleftharpoons B \rightarrow C$  can be studied for an initial state where all substance is A and no B or C occur (the A-trajectory) and from the initial state where all substance is B and no A or C occur (the C-trajectory). We then denote by  $C_{AA}(t)$  the time evolution of the concentration of A in the A trajectory, by  $C_{AB}(t)$  that of A in the B trajectory, etc.

As examples of intersections, we can investigate whether  $C_{AA}(t)$  and  $C_{BA}(t)$  intersect, and whether  $C_{BA}(t)$  intersects with  $C_{CB}(t)$ . Given two such intersections, we consider their ordering, either in time or in concentration value: for some choices of the parameters the first will come before the second, or vice versa. At the boundary between both parameter domains there occurs a coincidence: the two intersections coincide in their time or concentration value.

The various cases are best presented in graphical form, as in Fig. 1, where the black means neither intersection occurs, the dark yellow only the first, the dark blue only the second, the blue that the first intersection occurs before the second, and the yellow that the first occurs after the second. See [6] for the detailed study of this two-step mechanism.

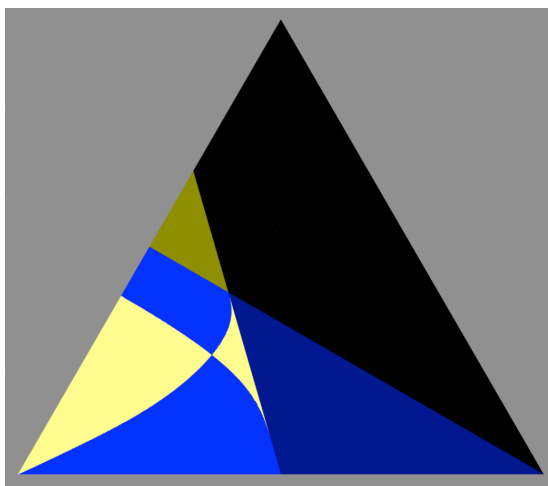


Figure 1: Example parameter domain for intersections.

- (2) Invariances of a special type observed in so-called dual experiments.

When studying these intersections, a remarkable property arises: some of the concentration dependencies are always proportional to each other, so that their intersection is either empty (in positive time) or they coincide at all points in time. In our simple example  $A \rightleftharpoons B \rightarrow C$  this is the case for  $C_{AB}(t)$  and  $C_{BA}(t)$ : at all  $t > 0$ ,  $C_{BA}(t)/C_{AB}(t) = k^+ / k^-$ , the equilibrium constant of the first reaction step. Closer analysis reveals that this property holds in all linear reaction schemes for each pair of substances A and B between which a reversible reaction occurs, and that it is a consequence of Onsager reciprocity (see [7]).

## ACKNOWLEDGMENT

Financial support from the Long Term Structural Methusalem Funding by the Flemish Government is gratefully acknowledged.

## REFERENCES

- [1] A.N. Gorban, and G.S. Yablonsky, Extended Detailed Balance for Systems with Irreversible Reactions, *Chem. Eng. Sci.*, vol. 66, pp. 5388-5399, 2011.
- [2] A.N. Gorban, E.M. Mirkes, and G.S. Yablonsky, Thermodynamics in the Limit of Irreversible Reactions, *Physica A*, vol. 392, pp. 1318-1335, 2013.
- [3] G.B. Marin and G.S. Yablonsky, *Kinetics of Chemical Reactions: Decoding Complexity*, Wiley-VCH, 2011.
- [4] G.S. Yablonsky, D. Constaes, G.B. Marin, Equilibrium relationships for non-equilibrium chemical dependencies. *Chem. Eng. Sci.*, vol. 66, pp. 111-114, 2011.
- [5] D. Constaes, G.S. Yablonsky, G.B. Marin, Thermodynamic time invariances for dual kinetic experiments: nonlinear single reactions and more, *Chem. Eng. Sci.*, vol. 73, pp. 20-29, 2012.
- [6] D. Constaes, G.S. Yablonsky, and G.B. Marin, Intersections and coincidences in chemical kinetics: linear two-step reversible-irreversible reaction mechanism, accepted by *Computers and Mathematics with their Applications*, 2013.
- [7] G.S. Yablonsky, A.N. Gorban, D. Constaes, V.V. Galvita, G.B. Marin, Reciprocal relations between kinetic curves. *EPL - Europhysics Letters*, vol. 93, 20004, 2011.
- [8] D. Constaes, G.S. Yablonsky, V.V. Galvita, G.B. Marin, Thermodynamic time-invariances: theory of TAP pulse-response experiments. *Chem. Eng. Sci.*, vol. 66, 4683-4689, 2011.