

Supplementary Materials

Thermodynamic analysis of the Landolt-type autocatalysis system

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The thermodynamic method used for the derivation of the thermodynamic polynomial (rate equation) originated in a paper by Samohýl and Malihevský [24] and was further developed in subsequent work, particularly in [17, 19].

Equation (4).

The second-degree polynomial approximating the rate function ([17], p. 251; [19]) is in the case of the mixture of A (1), B (2), AB (3), AB₂ (4):

$$\mathbf{J} = \mathbf{k}_{0000} + \mathbf{k}_{1000}c_1 + \mathbf{k}_{0100}c_2 + \mathbf{k}_{0010}c_3 + \mathbf{k}_{0001}c_4 + \mathbf{k}_{2000}c_1^2 + \mathbf{k}_{0200}c_2^2 + \mathbf{k}_{0020}c_3^2 + \mathbf{k}_{0002}c_4^2 + \mathbf{k}_{1100}c_1c_2 + \mathbf{k}_{1010}c_1c_3 + \mathbf{k}_{1001}c_1c_4 + \mathbf{k}_{0110}c_2c_3 + \mathbf{k}_{0101}c_2c_4 + \mathbf{k}_{0011}c_3c_4. \quad (\text{A1})$$

Component numbers instead of symbols were used. The polynomial coefficients -vectors \mathbf{k}_{ijlm} are functions of temperature only and in the end their components represent rate coefficients or constants [17] (p. 251), [19]. In equilibrium, where $\mathbf{J} = 0$, substituting for $c_{1,\text{eq}}$ and $c_{2,\text{eq}}$ from (5), we have:

$$0 = \mathbf{k}_{0000} + (\mathbf{k}_{0010} + \mathbf{k}_{1100}K_1^{-1}K_2^{-1})c_{3,\text{eq}} + (\mathbf{k}_{0020} + \mathbf{k}_{1001}K_2^{-1} + \mathbf{k}_{1000}K_2^{-1}c_{4,\text{eq}}^{-1})c_{3,\text{eq}}^2 + (\mathbf{k}_{0001} + \mathbf{k}_{0110}K_1^{-1} + \mathbf{k}_{0100}K_1^{-2}c_{3,\text{eq}}^{-1} + \mathbf{k}_{0011}c_{3,\text{eq}})c_{4,\text{eq}} + (\mathbf{k}_{0002} + \mathbf{k}_{0101}K_1^{-1}c_{3,\text{eq}}^{-1} + \mathbf{k}_{0200}K_1^{-2}c_{3,\text{eq}}^{-2})c_{4,\text{eq}}^2 + \mathbf{k}_{1010}K_2^{-1}c_{4,\text{eq}}^{-1}c_{3,\text{eq}}^3 + \mathbf{k}_{2000}K_2^{-2}c_{4,\text{eq}}^{-2}c_{3,\text{eq}}^4. \quad (\text{A2})$$

Identity (A2) should be valid in any equilibrium, consequently, expressions in brackets and following coefficients are zero [17] (p. 251), [19]:

$$\mathbf{k}_{0000} = \mathbf{k}_{1000} = \mathbf{k}_{0100} = \mathbf{k}_{0011} = \mathbf{k}_{0002} = \mathbf{k}_{0101} = \mathbf{k}_{0200} = \mathbf{k}_{1010} = \mathbf{k}_{2000} = 0. \quad (\text{A3})$$

From the zero expressions we can derive:

$$\mathbf{k}_{0010} = -\mathbf{k}_{1100}K_1^{-1}K_2^{-1}, \quad \mathbf{k}_{0020} = -\mathbf{k}_{1001}K_2^{-1}, \quad \mathbf{k}_{0001} = -\mathbf{k}_{0110}K_1^{-1}. \quad (\text{A4})$$

Substituting from (A3) and (A4) into (A1), the thermodynamic polynomial (4) is obtained.

Equations (9.1), (9.2).

First, the thermodynamic polynomial (4) is transformed to a function of chemical potentials using $c_\alpha = \exp[(\mu_\alpha - \mu_\alpha^0)/(RT)]$ and $-RT \ln K_p = \sum_\alpha \mu_\alpha^0 P^{p\alpha}$ ([17], pp. 239, 249):

$$\mathbf{J} = \mathbf{k}_{1100} \exp \frac{-\mu_1^0 - \mu_2^0}{RT} \exp \frac{\mu_1 + \mu_2}{RT} \left(1 - \exp \frac{\mu_3 - \mu_1 - \mu_2}{RT}\right) + \mathbf{k}_{0110} \exp \frac{-\mu_2^0 - \mu_3^0}{RT} \exp \frac{\mu_2 + \mu_3}{RT} \left(1 - \exp \frac{\mu_4 - \mu_2 - \mu_3}{RT}\right) + \mathbf{k}_{1001} \exp \frac{-\mu_1^0 - \mu_4^0}{RT} \exp \frac{\mu_1 + \mu_4}{RT} \left(1 - \exp \frac{2\mu_3 - \mu_1 - \mu_4}{RT}\right). \quad (\text{A5})$$

The chemical affinities in this simplified scheme are obtained from their general definition $A^p = \sum_\alpha \mu_\alpha P^{p\alpha}$ ([17], p. 181) as:

$$A^1 = -\mu_2 - \mu_3 + \mu_4, \quad A^2 = -\mu_1 + 2\mu_3 - \mu_4. \quad (\text{A6})$$

The basis vectors necessary to express the constitutional affinities ([17], p. 152) are $\mathbf{f}_\sigma = \sum_\alpha S_{\sigma\alpha} \mathbf{e}^\alpha$:

$$\mathbf{f}_1 = (1,0,1,1), \quad \mathbf{f}_2 = (0,1,1,2). \quad (\text{A7})$$

The contravariant components $f^{\sigma\tau}$ of the metric tensor ([17], p. 295) obtained by inverting the metric tensor in covariant components ($f_{\sigma\tau} = \mathbf{f}_\sigma \cdot \mathbf{f}_\tau$), are also necessary to express the constitutional constitutive affinities. In matrix form, these contravariant components are:

$$\begin{bmatrix} 4/3 & -1 \\ -1 & 1 \end{bmatrix}. \quad (\text{A8})$$

The constitutional affinities $B^\sigma = \sum_\alpha \sum_\tau \mu_\alpha S_{\tau\alpha} f^{\sigma\tau}$ ([17], p. 182) then are:

$$\begin{aligned} B^1 &= \frac{4}{3}\mu_1 - \mu_2 + \frac{1}{3}\mu_3 - \frac{2}{3}\mu_4, \\ B^2 &= -\mu_1 + \mu_2 + \mu_4. \end{aligned} \quad (\text{A9})$$

From eqs. (A6) and (A9) the decomposition of the chemical potentials into affinities ([17], p. 181) is obtained:

$$\begin{aligned} \mu_1 &= -\frac{1}{3}A^1 - \frac{1}{3}A^2 + B^1 + \frac{2}{3}B^2, \\ \mu_2 &= -\frac{2}{3}A^1 - \frac{1}{3}A^2 + \frac{1}{3}B^2, \\ \mu_3 &= \frac{1}{3}A^2 + B^1 + B^2, \\ \mu_4 &= \frac{1}{3}A^1 + B^1 + \frac{4}{3}B^2. \end{aligned} \quad (\text{A10})$$

The relationships in (A10) are introduced into (A5); equations (9) in the main text follow.

Modeling rate time profiles in CSTR.

The same cases as in Figures 1 and 2 (main text) were modeled also in a continuous stirred tank reactor (CSTR) of constant volume (1 liter) and constant flow rate (1 liter per minute). For readers' convenience the balance equation used in modeling is reported here:

$$V \frac{dc_i}{dt} = F(c_i^0 - c_i) + VJ_i.$$

V is the reactor volume, F is the flow rate, J_i represents the reaction rate of the component i and superscript 0 refers to the input flow.

Figure S1 shows profiles corresponding to the same kinetic parameters as in Figure 1 in the main text. Also here a maximum on r_2 and r_3 profiles is observed. However, the shape of r_1 is completely different, this rate has a maximum around the time point when the steep increase of the other two rates begins. Even the maximum on r_2 and r_3 profiles is interesting, because it cannot be caused by exhaust of reactants as was the case in the batch reactor. It is a kind of “over-shooting” the subsequent stationary value by the autocatalytic route with a very high rate constant. The feed into the reactor is not sufficient to maintain such high rates and their values drop to stationary values reflecting the inflow (model equation with zero derivative).

In the second modeling case (Figure S2) the two rates of the catalytic route are never higher than that of the direct pathway. In the stationary state the latter are several times slower. Although the rate constant of the autocatalytic product formation (k_3) is much higher than the rate constant of the direct pathway the continuous feed of reactants maintains the direct route faster, in contrast to the situation in the batch reactor. There is also no maximum on r_2 and r_3 profiles as observed in the batch system.

These are other examples of the importance of concentration values when discussing the kinetics of reactions and comparing their rates.

These rate profiles also demonstrate that coefficients a and b in (15) are not constants throughout the whole profile. Equation (15) thus has theoretical significance and does not simplify experiments or data evaluation.

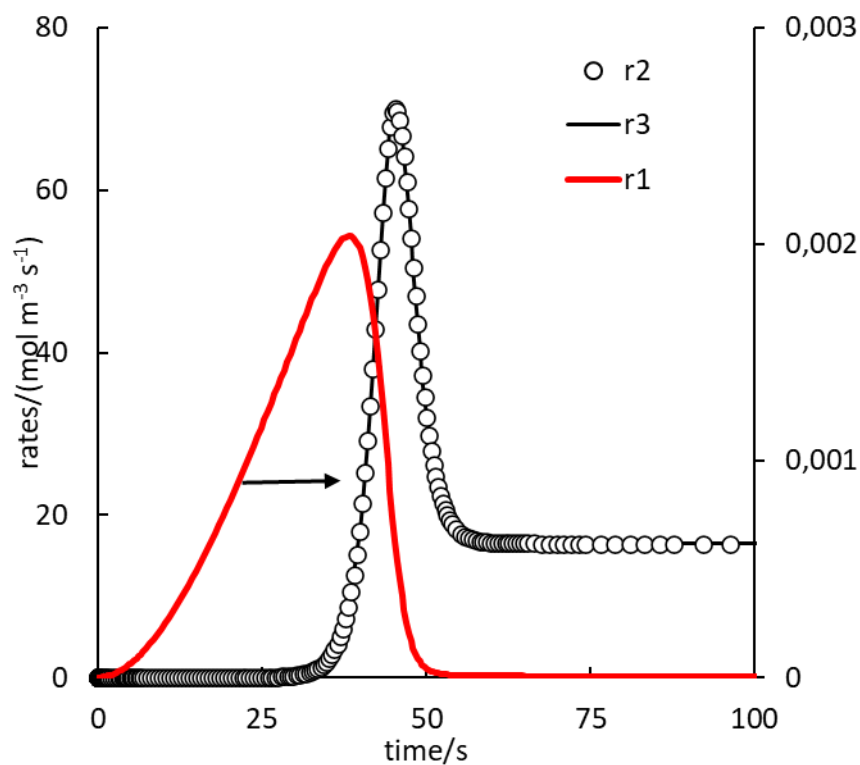


Figure S1. Modeled rate time profiles. Reaction scheme (R1), rates (1), CSTR system. Rate constants correspond to the black curve in Figure 1 in [14] and to Figure 1 in the main text: $k_1 = 10^{-8}$, $k_2 = 10^{-3}$, $k_3 = 10^4$ (all $\text{m}^3 \text{mol}^{-1} \text{s}^{-1}$).

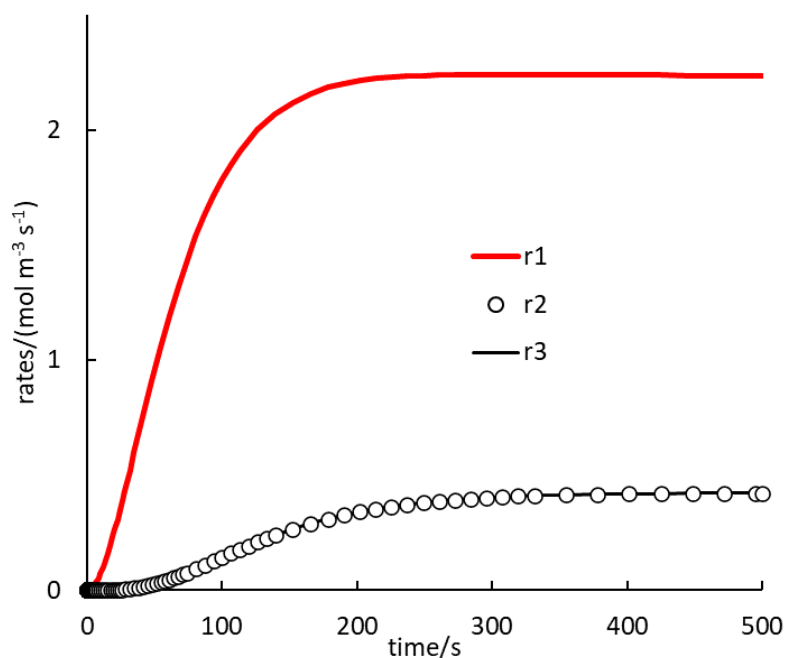


Figure S2. Modeled rate time profiles. Reaction scheme (R1), rates (1), CSTR system. Rate constants correspond to the cyan curve in Figure 1 in [14] and to Figure 2 in the main text: $k_1 = k_2 = 3.1623 \times 10^{-8}$, $k_3 = 10^4$ (all $\text{m}^3 \text{mol}^{-1} \text{s}^{-1}$).

References (from the main text)

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