Another rate view on autocatalytic reactions

Miloslav Pekař
Faculty of Chemistry, Brno University of Technology, Purkyňova 118, 612 00 Brno, Czech Republic
E-mail: pekar@fch.vut.cz

Abstract. Discussions on the proper conceptualization and definition of autocatalysis are still lively. Several examples of autocatalytic reaction schemes are analyzed for their concentration and rate time profiles using computer modeling. Autocatalytic features should be inherent in a relevant scheme and its real demonstration further depends on "proper parametrization", i.e., proper values for the rate parameters (their ratios) and relevant concentrations. Flow-through reactors bring a new complication due to the effects of inlet feed on reaction rates. When discussing kinetic features, one should take into account both concentration and rate profiles.

1. Introduction

Even more than 150 years after the first appearance of the autocatalysis concept (Peng et al., 2022) discussions on its proper conceptualization and definition are still lively; see for recent examples, Peng et al. (2022), Horváth (2020, 2021). Schuster (2019) reminds us that the term autocatalysis was introduced by Wilhelm Ostwald in 1890 "for the characterization of reactions that show an acceleration of the rate as a function of time". Peng et al. (2022) point out earlier experimental work on autocatalysis and especially Ostwald's investigations in which the reactant was supposed to be an autocatalytic substance. This contrasts with today's views, in which a product is mostly considered to have an autocatalytic effect; examples of such textbook definitions were presented in an earlier work (Pekař, 2021). Peng et al. (2022) extended Ostwald's original view of an autocatalytic reaction to the definition: "a reaction that can be written as a net reaction equation where reactants and products are non-overlapping sets with at least one reactant or product that has a catalytic effect on the process represented by that equation."

Now, the IUPAC's definition is as follows (IUPAC, 1997a): "A chemical reaction in which a product (or a reaction intermediate) also functions as a catalyst. In such a reaction the observed rate of reaction is often found to increase with time from its initial value." The first part of this definition rests on the definition of catalyst, from which only the first two phrases are cited: "A substance that increases the rate of a reaction without modifying the overall standard Gibbs energy change in the reaction; the process is called catalysis. The catalyst is both a reactant and product of the reaction." (IUPAC, 1997b). Peng et al. (2022) even distinguish recessive and expansive autocatalysis; the former refers to cases in which a reactant provides a catalytic effect whereas in the latter case at least one of the products is the autocatalytic agent.

The situation, therefore, still seems to be confusing. The IUPAC catalyst definition requires the presence of a catalyst among both reactants and products, whereas the IUPAC autocatalysis definition speaks only about a product being a catalyst (that is, autocatalyst). In contrast, Peng et al. (2022) require non-overlapping reactants and products. Evidently, the IUPAC autocatalysis definition tacitly assumes non-equal stoichiometric coefficients for an autocatalyst on both sides of the stoichiometric equation, in contrast to the catalyst definition. More importantly, the IUPAC's definitions speak (also) about rates of reactions and this is essential, because any catalysis is a kinetic phenomenon. It is not clear why the IUPAC catalyst (and catalysis, in fact) definition requires an

https://doi.org/10.32388/ZLDWAU

increase in the rate of a reaction while the IUPAC autocatalysis definition states that the rate increase is observed only frequently, and, therefore, not always.

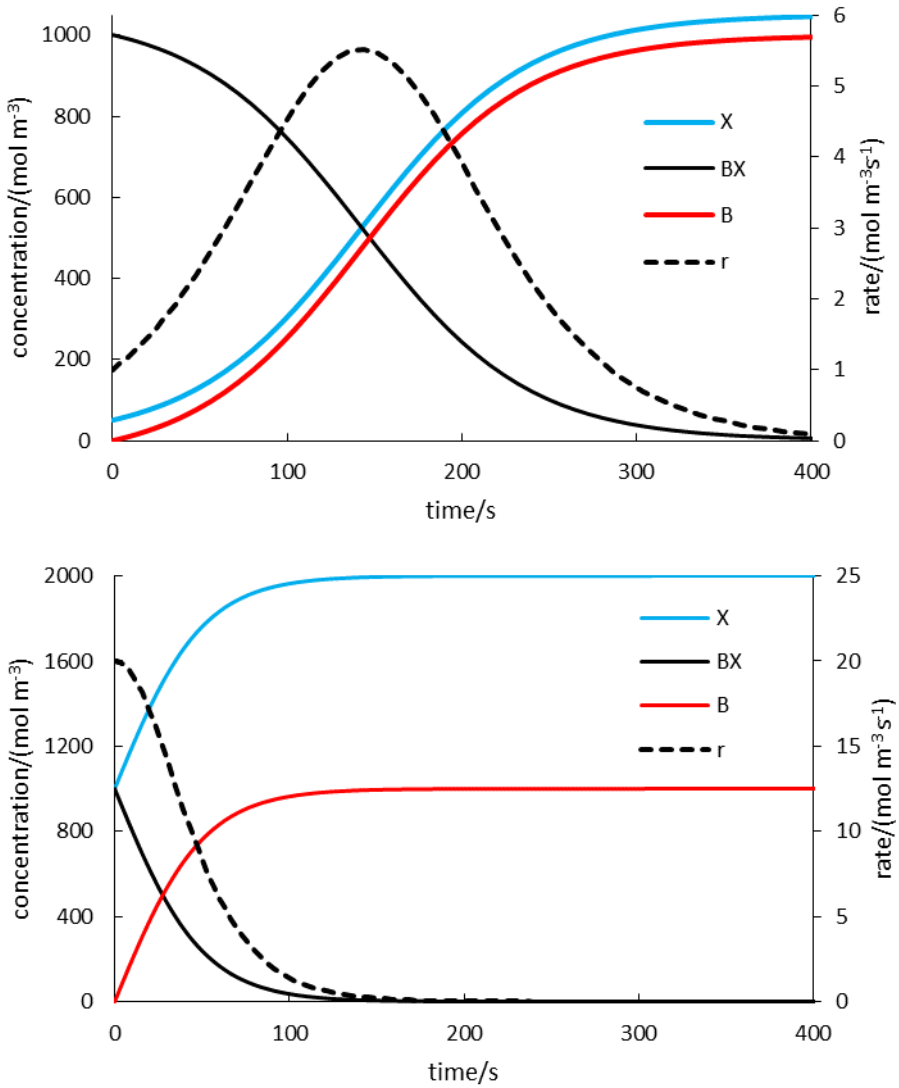

Figure 1. Concentration and rate profiles for reaction R2.
Parameters see Table 1

Recently, I published a brief note on the fruitfulness of not ignoring the inspection of rates when discussing autocatalysis as a part of chemical kinetics (Pekař, 2022). That note extended an example analyzed in papers by Horváth (2020, 2021), who tried to provide a proper classification of autocatalysis. Horváth, in essence, follows the product-based view. For example: "A reaction is called autocatalytic when one of its products enhances the rate of its own formation." (Horváth, 2020) or "autocatalyst (...) [is] a species (...) that increases the rate at which the given process occurs and at the same time it functions as a product of the overall process." Horváth (2021) also claims that if "the addition of a product speeds up its own formation, then the corresponding (...) is indeed autocatalytic."

In this work, I further elaborate on the rate view of autocatalysis and extend the previous, brief note (Pekař, 2022). Owing to some responses to that previous text I also try to apply a pedagogical approach. Besides the traditional batch system, also a flow-through arrangement is included. The

tool is, again, computer modeling, which was performed with the Chemical Reaction Engineering Module of the COMSOL Multiphysics package, version 6.0 or 6.1.

2. Results

2.1 Simple reaction

The simplest autocatalytic reaction is probably (Schuster, 2019):

$$\mathrm{A} + \mathrm{X} \rightarrow 2\mathrm{X}. \qquad \text{(R1)}$$

It can be rewritten into an atom-conserving (the conservative approach (Érdi and Tóth, 1989)) but still general form as (Pekař, 2021):

$$\mathrm{BX} + \mathrm{X} \rightarrow 2\mathrm{X} + \mathrm{B}. \qquad \text{(R2)}$$

The autocatalytic specie should be the component X, which is consumed (as a reactant) and at the same time produced (as a product) but in a larger amount. Examples of the behavior of (R2) in a

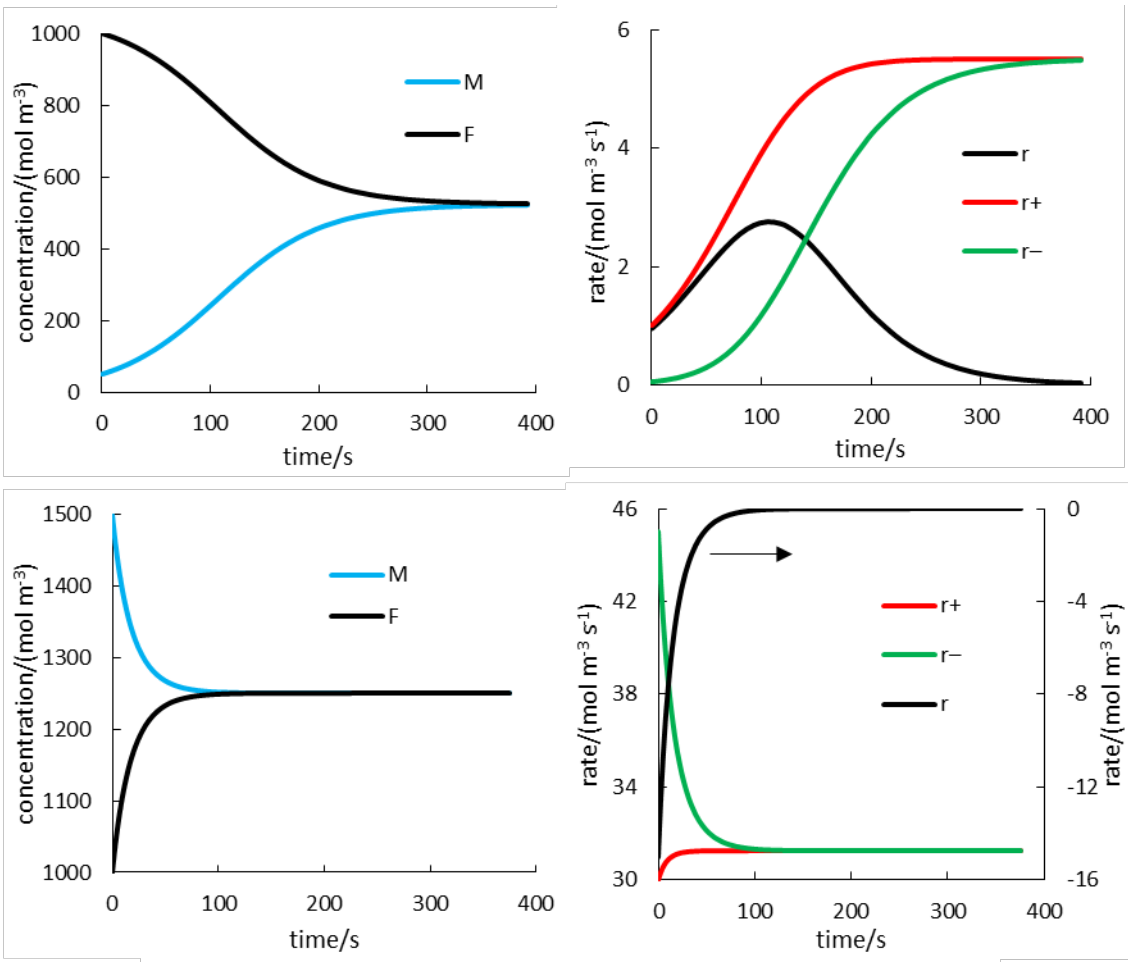

Figure 2. Concentration and rate profiles for reversible reaction R1. M≡X, F≡A. Parameters see Table 2

batch reactor are given in Fig. 1 for an increased initial concentration of X (c_{X}^{0}) at a constant initial concentration of BX (orA) ($c_{\mathrm{BX}}^{0} = 1000\ \mathrm{mol\ m^{-3}}$) and with the rate constant (k) equal to 2×10^{-5} $\mathrm{mol^{-1}m^{3}s^{-1}}$. For the lower X initial concentration, we see a typical S-shaped concentration-time profile for both products (Fig. 1 upper). This shape is "smoothed" with increasing X initial concentration to a parabolic-like shape (cf. Fig. 1 lower). The reaction rate for the lower X initial concentration has a time profile with a clear and high maximum – up to this maximum, the reaction really accelerates

throughout its course. An increased X initial concentration decreased the maximum and shortened the duration of the increasing reaction rate. For the highest used (and the other shown) X initial concentration (equal initial concentrations of both reactants), no maximum is seen and the rate decreases continuously throughout the whole course of the reaction (Fig. 1 lower) – i.e., no acceleration is observed. It should be noted that the inflection point on the S-shape corresponds to the maximum on the reaction rate profile.

Table 1. Parameters used to simulate reaction (R2) in a batch reactor

Figure 1	k/(mol^{-1}m^{3}s^{-1})	c_X^0/(mol m^{-3})
upper	2×10^{-5}	50
lower	2×10^{-5}	1000

Table 2. Parameters used to simulate reversible reaction (R1) in a batch reactor

Figure 2	k^+/(mol^{-1}m^{3}s^{-1})	K	c_M^0/(mol m^{-3})	c_F^0/(mol m^{-3})
upper	2×10^{-5}	1	50	1000
lower	2×10^{-5}	1	1500	1000

The simple reaction (R1) or (R2) is identical to that given by Peng et al. (2022), except that Peng et al. also considered the reversed direction and used different symbols ($\mathrm{M} \equiv \mathrm{X}, \mathrm{F} \equiv \mathrm{A} \equiv \mathrm{BX}$; $\mathrm{M} + \mathrm{F} \rightleftarrows 2\mathrm{M}$). Here, we retain the original symbols of Peng et al. (2022). The reversed direction did not bring anything substantially new. Of course, both concentration profiles end at equilibrium concentrations; the reactant (F) is not fully consumed, as in the irreversible case. S-shaped concentration profiles can be found for both components (see the example in Fig. 2) as well as a maximum on the (overall) rate profile (Fig. 2). What is new and specific is the possibility to decompose the overall rate into forward and reversed rates (remember that $r = r^+ - r^-$). In the same example, both rates increased with time and no maximum was observed for either of them. This is quite standard for the reversed rate, because the amount of its reactant (the overall product M) continuously increases by means of the forward reaction. This is less expected for the forward direction because its reactants (M and F) are consumed in this direction. However, just due to the autocatalytic feature, more M is produced than consumed at the same time.

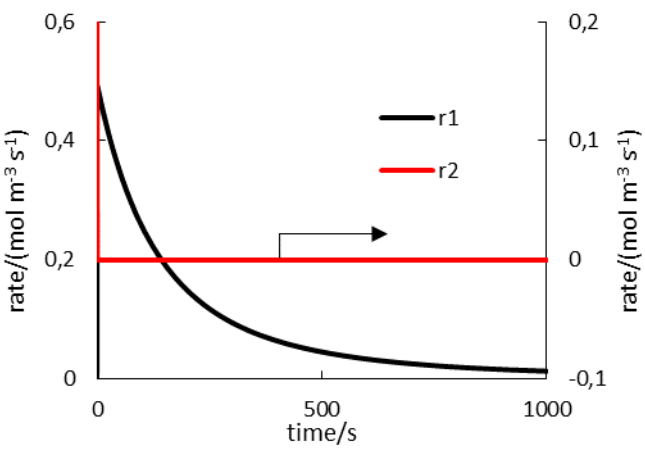

Figure 3. Rate profiles for reaction R3. Parameters see Table 3

Increasing the initial concentration of M changes the shape of the concentration profiles to a parabolic-like form and erases the increasing part of the overall rate profile, i.e., its maximum is at time zero and the rate continuously decreases. This means that the autocatalytic behavior is eliminated. When the initial concentration of M exceeds that of F, the sign of the overall rate is reversed; i.e., the reaction runs, in fact, in the reversed direction and the absolute value of the overall rate continuously decreases (Fig. 2 lower). No autocatalytic behavior is thus seen. The reversed rate continuously decreases due to the

continuous depletion of its reactant (M), whereas the forward rate increases because the production of F exceeds the consumption of M. The concentration profiles are parabolic-like (Fig. 2 lower). The magnitude of the equilibrium constant has no significant qualitative effect relevant to this discussion; the interested reader can check it in his own simulations. Similar comments can be ascribed to a slightly more complex reaction found in Peng et al. (2022): $\mathrm{P} + 2\mathrm{Q} \rightleftarrows 2\mathrm{P} + \mathrm{Q}$.

2.2 Ostwald's lactonization example

Ostwald's valerolactone example (Ostwald, 1890) can be formally written as

$$\mathrm{HA} \rightarrow \mathrm{L} + \mathrm{H_2O}, \tag{R3.1}$$

$$\mathrm{HA} \rightarrow \mathrm{A^-} + \mathrm{H^+}, \tag{R3.2}$$

where HA is γ-hydroxyvaleric acid and L is γ-valerolactone. The autocatalyzed reaction should be (R3.1), which is known to be catalyzed by hydrogen ions. Ostwald gives no rate equation; perhaps the simplest one should be:

$$r_{\mathrm{VL}} = k_{\mathrm{VL}} c_{\mathrm{HA}} c_{\mathrm{H^+}}. \tag{1}$$

However, this form means no reaction without the presence of hydrogen ions, that is, there is no non-(auto)catalytic path. A more appropriate general form could thus be

$$r_{\mathrm{VL}} = k_{\mathrm{VL0}} c_{\mathrm{HA}} + k_{\mathrm{VL}} c_{\mathrm{HA}} c_{\mathrm{H^+}}. \tag{2}$$

The first term in (2) represents the "ordinary", non-autocatalytic path, while the second term expresses the (auto)catalytic action of protons formed in (R3.2).

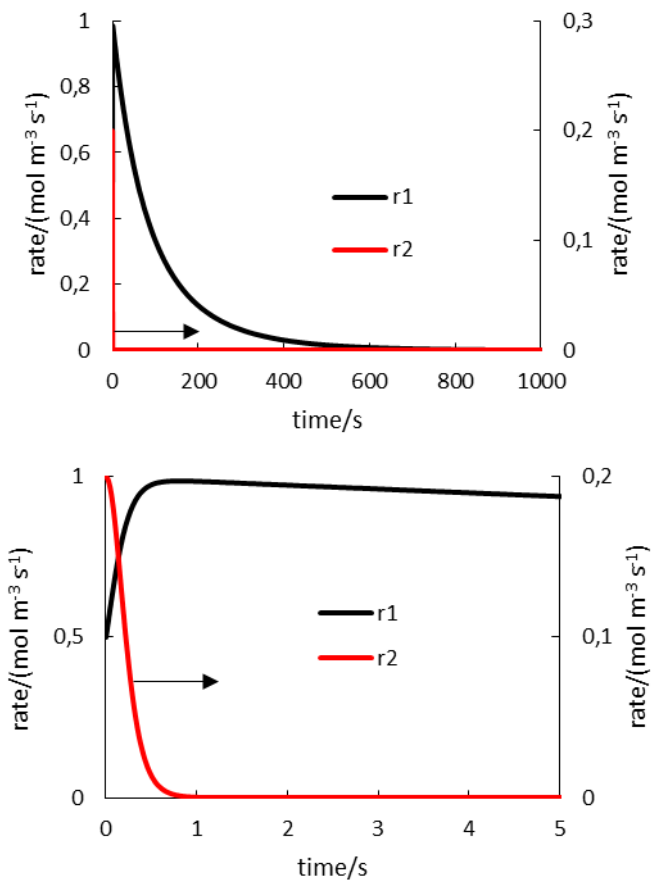

Figure 4. Rate profiles for reaction R3. Parameters see Table 3

There is a problem with the dissociation of γ-hydroxyvaleric acid as a weak acid. SciFinder[1] estimates its pK_a as 4.61 (Henry (1892) published a value which gives pK_a = 4.69). The (equilibrium) concentration of protons is thus very low (cf Ostwald´s: "*...der dissociirte Antheil der Säure nicht gross ist*..."[2] (Ostwald, 1890)) and the reaction (R3.2) quickly attains equilibrium. Thus, unless the value of k_{VL} is really very high, the catalytic effect of H^+ is hardly seen. This accords with Ostwald's qualitative statement: "*...bei Gegenwart des Neutralsalzes behält die γ-Oxyvaleriansäure ihren Säuretiter tagelang fast unverändert bei und lässt nur einen äusserst langsamen Uebergang in das Lacton erkennen*."[2] (Ostwald, 1890).

The first example involving only the autocatalytic rate contribution, i.e. with $k_{\mathrm{VL0}} = 0$, (Fig. 3) shows a very fast increase in the dissociation rate and the rapid attainment of dissociation equilibrium. The former is accompanied by a very fast increase also in the lactonization step rate, which demonstrates (auto)catalysis. However, the lactonization rate quickly reaches a maximum and continuously decreases due to the depletion of the acid supply, as in the case of a general, non-catalyzed reaction in a batch system. The concentration profiles of the acid and lacton do not show any specific (autocatalytic) features. Both change smoothly and parabolically, the acid decreasing, the lactone increasing (not shown). The concentration of H^+ is very low (and equal to the acid anion concentration) due to the low value of the dissociation constant. Its time profile also has a maximum as a result of equilibrium (R3.2) responding to the depletion of the acid concentration.

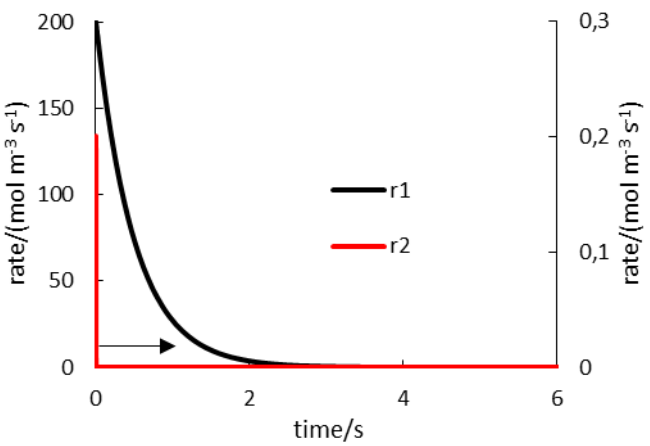

Figure 5. Rate profiles for reaction R3. Parameters see Table 3

Adding the direct rate step ($k_{\mathrm{VL0}} > 0$) increased the initial rate of lactone formation while not depressing the height of the maximum (measured as the difference to the value at time zero) in the autocatalytic phase (Fig. 4), at least for the (low) value of k_{VL0} used in the simulation. The effect of adding hydrogen ions to the initial mixture on the lactone formation rate is clear (Fig. 5) when compared with the same situation with no added hydrogen ions. However, even in the former case, the rate can continuously decrease throughout the course of time (Fig. 5), as in the case of a non-autocatalytic reaction.

Perhaps surprisingly, the increased rate of formation of the autocatalytic species (the increased rate constant of hydroxyvaleric acid dissociation) barely changed the rate of lactone formation; on the other hand, the rate of acid dissociation was increased by several orders (data not shown). Yet, the concentration of H^+ was determined mainly by the equilibrium constant, which remained unchanged in this example. A clearly visible S-shaped lactone concentration profile can be obtained for sufficiently high values of k_{VL} (Fig. 6). The lactonization rate had, here, a maximum at the time corresponding to the inflection point on the S-shape; the dissociation rate decreased up to the

[1] https://www.cas.org/solutions/cas-scifinder-discovery-platform/cas-scifinder
[2] English translation can be found in supplementary to Peng et al. 2022

reversed direction and then attained a minimum, these results indicating responses of the dissociation equilibrium to the consumption of the acid in the lactonization step.

Table 3. Parameters used to simulate reaction (R3) in a batch reactor. Rate constants $k_{\mathrm{HA}}^{\pm}$ refer to the dissociation step (R3.2)

Fig.	k_{VL0}/s^{-1}	k_{VL}/(mol^{-1}m^{3}s^{-1})	k_{HA}^{+}/ s^{-1}	k_{HA}^{-}/(mol^{-1}m^{3}s^{-1})	c_{HA}^{0}/(mol m^{-3})	$c_{\mathrm{H*}}^{0}$/(mol m^{-3})
3	0	10^{-1}	2×10^{-3}	80	100	0
4	5×10^{-3}	10^{-1}	2×10^{-3}	80	100	0
5	5×10^{-3}	10^{-1}	2×10^{-3}	80	100	20
6	1×10^{-9}	10	2×10^{-4}	8	100	0
7[a]	0	12×10^{-5}	22×10^{-7}	88×10^{-3}	37	0

[a]units as in original source, Henry (1892)

Ostwald´s note (1890) is reflective not experimental; he refers to experimental work by Henry, published (later) in Henry (1892). Only a minor part of Henry´s paper deals with autocatalysis; as an example of the fitting of his data by model (R3) and (2) ((1), in fact, cf. Table 3), Fig. 7 is presented (x is the lactone amount per cm^3).

Henry used the following equation to describe the kinetics of autocatalytic lactonization:

$$dx/dt = Cy(A-x)^2. \quad (3)$$

In it, x is the amount of lactone formed in time t, C is the rate coefficient (determined from experimental data), A is the initial amount of hydroxyacid, and y denotes a function which gives the amount of hydrogen ions. Henry derived the function y from considerations on the hydroxyacid dissociation equilibrium. Because y is then proportional to $(A-x)^{-1}$ and $A-x$ is proportional to the amount of hydroxyacid reacted to lacton, Henry´s equation is not far from (1).

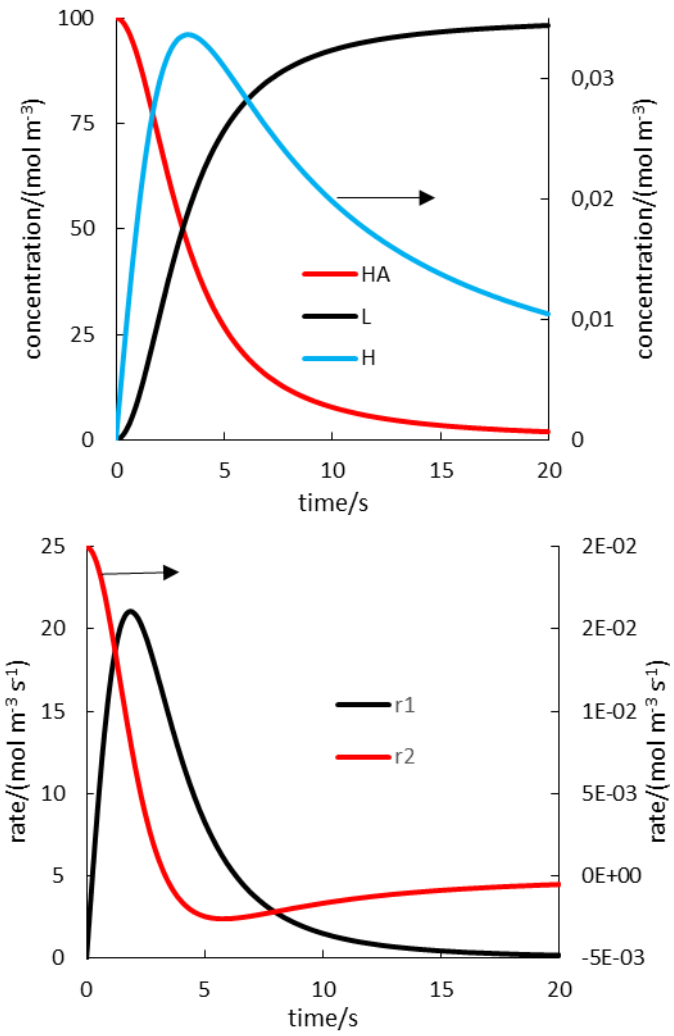

Figure 6. Rate profiles for reaction R3. Parameters see Table 3

2.3 Landolt reaction scheme

Horváth suggested using (the visualization of) "the effect of the initially added product on the concentration–time profiles" as "a simple tool to decide whether the experimental system or the theoretical model has an autocatalytic feature or not" (Horváth, 2021). He presented an example of a parabolic-like profile in the Landolt mechanism fulfilling this criterion (Figure 1a in ref. Horváth (2021)). Let us look at a very similar

example from the viewpoint of rates – that of the cyan curve of Figure 1B in Horváth's other work with the same mechanism (Horváth, 2020) and probably demonstrating the suppression of the autocatalytic feature by "improper parametrization". Because the reference Horváth (2020) was commented in the previous note (Pekař, 2022), only the reaction scheme is given here:

$$\mathrm{A} + \mathrm{B} \rightarrow \mathrm{C}, \quad \text{(R4.1)}$$

$$\mathrm{B} + \mathrm{C} \rightarrow \mathrm{D}, \quad \text{(R4.2)}$$

$$\mathrm{A} + \mathrm{D} \rightarrow 2\mathrm{C}. \quad \text{(R4.3)}$$

When no product C is initially present in a batch system, the rate of its formation continuously decreases during the course of the reaction and no autocatalytic behavior is observed (Pekař, 2022). If the product is present initially, its formation rate increases over a very short initial time interval and then decreases continuously (Fig. 8). That very short interval can be considered as an autocatalytic feature evoked by the non-zero initial concentration of the product. If the initial product concentration is sufficiently high, its initial formation rate can even be negative, i.e., its destruction outweighs its formation (Fig. 9). Paradoxically, the initial rate of C formation is thus decreased by adding this autocatalyzing product into the initial mixture, because it is consumed in the second step at the same time. Apparently, the product concentration profiles remain parabolic-like (data not shown).

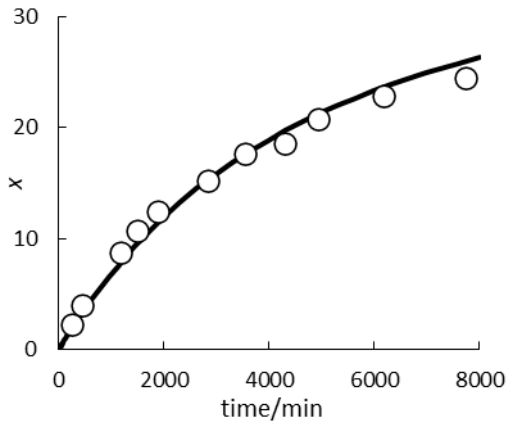

Figure 7. Fitting of Henry´s data by model R3

The example in ref. Horváth (2021) is suitable also for demonstrating the role of the inspection of rates in the discussion of S-shaped/parabolic concentration profiles. The curves in Fig. 1a of that reference are of parabolic shape and show increasing order with the increasing initial concentration of product C, similarly to the curves in Fig. 1b of Horváth (2021), which are, however, S-shaped. The S-shape of the concentration profile actually means the existence of an inflection point at which the first derivative possesses an extreme. In this example, this means an extreme on the rate profile, because here $r_{\mathrm{C}} = dc_{\mathrm{C}}/dt$. A maximum on the rate profile is observed already in the case of a zero initial concentration of C and for the (black) curve from Fig. 1b of Horváth (2021); see Fig. 10 here. However, the corresponding inflex point on the concentration profile is featureless and impossible to see in the small drawing presented in Fig. 1b of ref. Horváth (2021). Even an enlarged figure requires careful inspection, cf. Fig. 10 (lower). The S-shape thus need not be attributed only to curves on which it is easily recognizable.

Table 4. Parameters used to simulate reaction (R4) in a batch reactor; $c_{\mathrm{A}}^0 = c_{\mathrm{B}}^0 = 1000$ mol m^{-3}, no D at $t = 0$.

Fig.	k_1/(mol^{-1}m^{3}s^{-1})	k_2/(mol^{-1}m^{3}s^{-1})	k_3/(mol^{-1}m^{3}s^{-1})	c_{C}^0/(mol m^{-3})
8	32×10^{-7}	32×10^{-7}	10^4	25
9	32×10^{-7}	32×10^{-7}	10^4	1200
10	6×10^{-6}	2×10^{-5}	10^4	0

2.4 CSTR as an example of flow system

CSTR (continuous stirred tank reactor) systems bring new aspects to (not only) autocatalysis. Reaction rates are affected by the continuous feed into the reactor. For example, in a batch system, the concentration profiles of the Landolt scheme (R4), the cyan curve in Fig. 1 of Horváth (2020), are parabolic-like and r_{C} is decreasing (Pekař, 2022), whereas in CSTR the former profile is S-shaped and the latter is increasing; r_{C} is increasing also when plotted against c_{C} – thus apparently indicating autocatalysis (data not shown). In a batch system, the r_1 profile is decreasing and the r_2 and r_3 profiles are almost equal and with a maximum. In contrast, in CSTR, all rate profiles are increasing (and S-shaped) and r_1 is evidently higher than the other two rates (which are also almost equal and thus causing an extremely low concentration of intermediate D), including their steady state values.

When the product C is also present in the inlet stream, its concentration profile changes from S-shaped to parabolic-like (Fig. 11), while the autocatalytic effect of the product is demonstrated by its formation rate increasing in time and being higher than when no product is injected (Fig. 12). It should be noted that the corresponding rate parameters ratio (k_2/k_1) in the original work (Horváth, 2020) was probably considered as an example of non-autocatalytic parametrization.

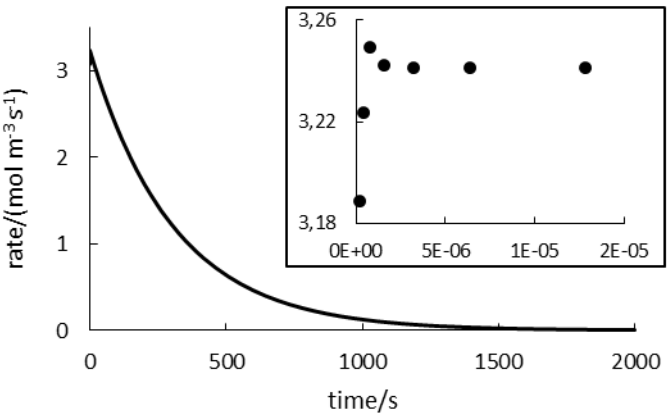

Figure 8. Product C formation rate, reaction R4. Parameters see Table 4

In the standard CSTR model, it is impossible to separate the effect of continuous feeding from the pure autocatalytic effect on reaction rates. To achieve such separation, we can explore the ideas published by Rodrigues et al. (2017). The standard molar balance of a constant volume CSTR is (Scott Fogler, 1997):

$$\tau\, dc_i/dt = c_i^{\mathrm{o}} - c_i + \tau r_i; \quad \tau = V/v, \tag{4}$$

where τ is the space time (V is the constant volume and v is the constant volumetric flow rate) and c_i^{o} is the component concentration at the reactor inlet. The concentration of component i (in fact, its change in time) is divided into two parts – the "purely flowing" and the "reacting": $c_i = c_{i\mathrm{f}} + c_{i\mathrm{r}}$. The balances for these two parts are then:

$$\tau\, dc_{i\mathrm{f}}/dt = c_i^{\mathrm{o}} - c_{i\mathrm{f}}, \tag{5}$$

$$\tau\, dc_{i\mathrm{r}}/dt = -c_{i\mathrm{r}} + \tau r_i. \tag{6}$$

Note that $c_{i\mathrm{f}}^{\mathrm{o}} = c_i^{\mathrm{o}}$, $c_{i\mathrm{r}}^{\mathrm{o}} = 0$ and the sum of (5) and (6) is (4). Rate equations for r_i are formulated in c_i´s, of course.

Decomposition of the concentration of product C for the previous example is shown in Fig. 13. The c_{Cf} profile is parabolic, as is the overall c_{C} profile, whereas the c_{Cr} is sigmoidal, as in the case when there is no C at the inlet. The rate profiles remain unchanged, of course.

5. Discussion

Autocatalysis is a kinetic phenomenon and as such is very tightly linked to the rate of reaction. Autocatalytic analyses thus should also include the inspection of rates. This does not mean that concentrations and their (time) profiles can then be ignored. On the contrary, none of these two

insights should be ignored, but they have to be combined. This, hopefully, was clearly illustrated by examples in the previous note (Pekař, 2022) and in the Results section here.

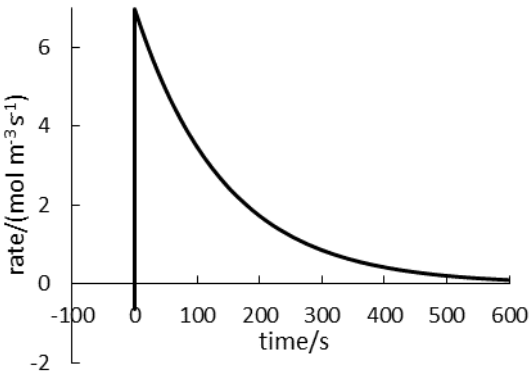

Figure 9. Product C formation rate, reac. R4. Parameters see Table 4

In a discussion of autocatalysis, we should clearly state which reaction we have in mind and what its rate is. In the case of a single(-step) reaction, the reaction in mind is clear and unambiguous. In the case of multi-step reactions, the individual steps generally have different rates, and we should clearly state which one we are discussing. For example, the simple reaction from section 2.1 is a single reaction and its rate is considered. The Landolt scheme from section 2.3 is an example of a multi-step reaction (with three steps) and we discussed the product reaction (formation) rate. It should be noted that that rate is a combination of all three step rates: $r_{\mathrm{C}} = r_1 - r_2 + 2r_3$. In the case of lactonization, we focused on the rate of (R3.1), while (R3.2) was a side reaction producing the autocatalytic specie in the system as a whole.

A catalyst affects the reaction rate and thus has to occur in the rate equation. Rate equations generally describe the effects of two principal factors determining the reaction rate: temperature and concentrations. The temperature effect is described by the rate constant (coefficient) and is outside the scope of this discussion (it is sufficient to restrict the discussion to isothermal cases). Concentrations are present in the rate equation *per se*, often raised to a power (the reaction order). The catalyst concentration thus appears in the rate equation. An "ordinary" catalyst is a substance "external" to the catalyzed reaction, not among its "ordinary" reactants. The reaction can proceed without its presence, though possibly at a very small (negligible) rate. When the catalyst is added (externally), the reaction rate increases (appreciably) and the reaction usually follows another, faster pathway. For example, a slow synthesis $\mathrm{A} + \mathrm{B} \rightarrow \mathrm{AB}$ may be switched to a faster, catalytic route $\mathrm{A} + \mathrm{cat} \rightarrow \mathrm{A} \cdot \mathrm{cat}; \mathrm{A} \cdot \mathrm{cat} + \mathrm{B} \rightarrow \mathrm{AB} + \mathrm{cat}$, at the end, from which the catalyst is released "unchanged". The rate of AB formation can be expressed in the former case as

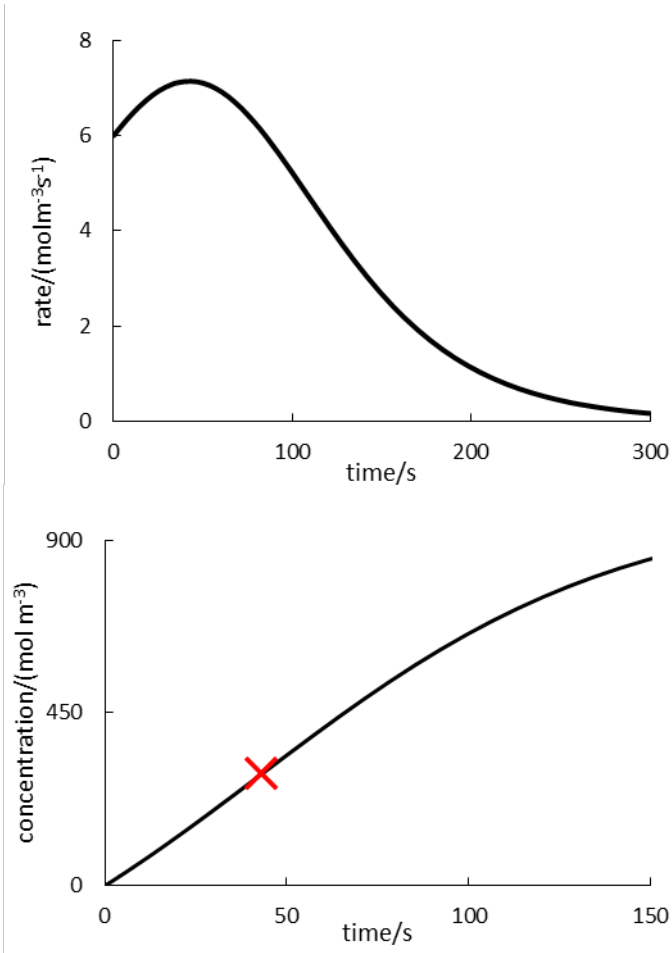

Figure 10. Product C formation rate and concentration, reaction R4; cross=inflex point. Parameters see Table 4

$r_{AB} = kc_A c_B$, in the latter as $r_{AB} = k_2 c_{A\cdot cat} c_B$, where the catalyst amount is hidden in $c_{A\cdot cat}$ (the formation rate of $A \cdot cat$ in the first step is given by $k_1 c_A c_{cat}$).

Autocatalysis is specific by the fact that the catalyst is not an "external" but an "internal, intrinsic" substance, one of the "ordinary" reactants or products. The occurrence of an autocatalyst in the rate equation must be inspected carefully, because "ordinary" reactants (and products in the case of reversible reactions) are normally present in rate equations. In other words, an (increased) reactant concentration always has an accelerating effect on the rate of reaction, providing it is of the form $r = c_{reactant} f(T, c)$, where $f(T, c)$ is a function of temperature and (other) concentrations. Thus, recessive autocatalysis (Peng et al. 2022) remains unclear unless the reactant, the accelerated reaction, and its rate equation are specified precisely.

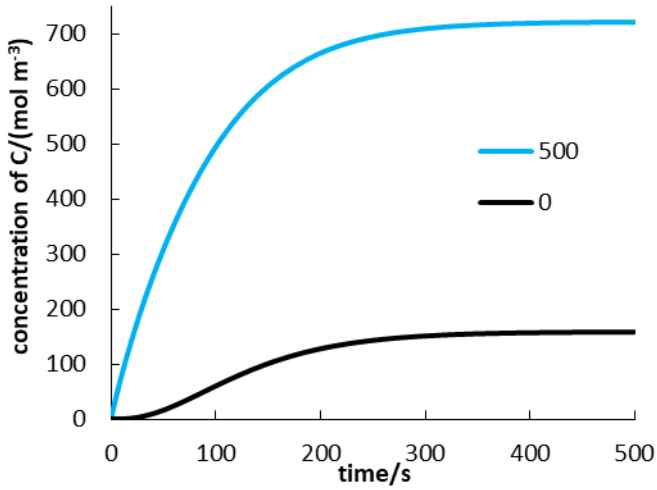

Figure 11. Product C concentration profile in CSTR for its various inlet concentrations, reaction R4. Kinetic parameters as in Fig. 8

Further, we should clearly state the aspect or thing, relative to which the increased, catalyzed, rate is considered. In the case of standard, "external" catalysis, it is relative to the uncatalyzed reaction; that is, the reaction without the addition of a catalyst. See, for example, the discussion of the lactonization example in sec. 2.3. In the case of autocatalysis, the situation is more intricate because the catalyst is inherently present in the reacting mixture. We can play with its concentration as Henry did in the lactonization experiments or Horváth, in the simulation of Landolt scheme, and compare the relevant time profiles. We can thus make a relative comparison of the profiles detected for the varying concentration. In all cases, we can and should simply watch the time profile of the relevant reaction rate and its relation to the (auto)catalyst concentration. Playing with the (initial) concentration can be ambiguous in revealing autocatalytic behavior, as noted in (the middle of) section 2.3.

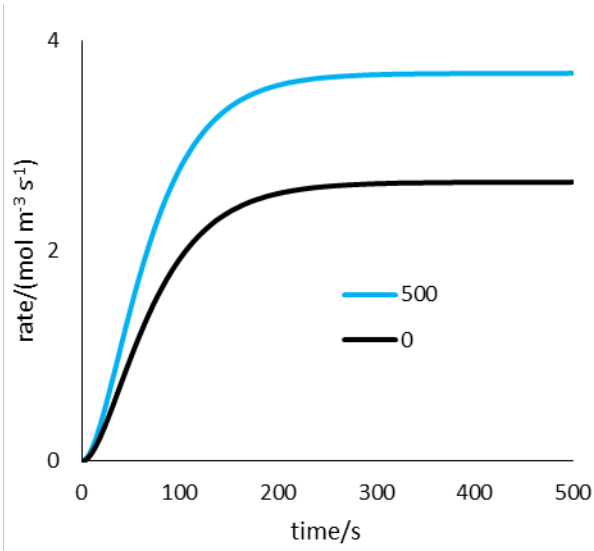

Figure 12. Product C formation rate profile in CSTR for its various inlet concentrations, reaction R4. Kinetic parameters as in Fig. 8

Briefly, an autocatalytic reaction scheme should inherently contain an autocatalytic feature – the formation of a specie which could really increase the rate of the relevant reaction under consideration. This is a necessary condition determining autocatalytic reactions, though it may not be a sufficient one, as pointed out, for example, by Horváth in his note on proper parametrization (Horváth, 2020). However, as the rate equation teaches us, parametrization includes not only the rate

coefficients but also the concentrations of the constituents of the reacting mixture (and, probably, also the temperature, especially in non-isothermal reacting mixtures). In the simple reaction, the autocatalytic feature is the formation of $2\mathrm{X}$ when one X is consumed at the same time. Similarly, in the Landolt scheme, the autocatalytic feature is the formation of $2\mathrm{C}$ when one C is consumed – but in two different steps. In these two examples, a product is a reactant at the same time. In the lactonization example, the autocatalytic feature is the accelerating effect of hydrogen ions (on lactone formation) which are formed from the reactant by a side reaction; i.e., one (side) product, not (necessarily) a reactant, is the catalyst. This catalyst, hydrogen ions, can also be added externally, as in most experiments described by Henry (1892).

The role of concentrations in the "proper parametrization" was illustrated by Fig. 1 (simple reaction) and Fig. 2 (reversible simple reaction).

A note to the paper by Peng et al. (2022): the reaction $\mathrm{M} + \mathrm{F} \rightleftarrows 2\,\mathrm{M}$ is rewritten there as $\mathrm{F} \rightleftarrows \mathrm{M}$, said to be catalyzed by M and then decomposed in two steps: $\mathrm{F} \rightarrow \mathrm{M}$, catalyzed by M, and $\mathrm{M} \rightarrow \mathrm{F}$, catalyzed by M. No more specification is given. The rate of the catalyzed first step would probably be $k_\mathrm{F} c_\mathrm{F} c_\mathrm{M}$, of the catalyzed second step, probably $(k_\mathrm{M} + k_\mathrm{Ma} c_\mathrm{M}) c_\mathrm{M}$. The kinetic equilibrium constant of the summary reaction, obtained according to the kinetic equilibrium condition $\vec{r}_\mathrm{eq} = \overleftarrow{r}_\mathrm{eq}$, is then $K = k_\mathrm{F} c_\mathrm{M,eq} / \left(k_\mathrm{M} + k_\mathrm{Ma} c_\mathrm{M,eq}\right) = c_\mathrm{M,eq} / c_\mathrm{F,eq}$. This expression was written to be basically consistent with the expression for the thermodynamic equilibrium constant ($a_\mathrm{M,eq} / a_\mathrm{F,eq}$; a denotes the activity). The thermodynamic equilibrium constant is "hidden" in the standard reaction Gibbs energy mentioned in the IUPAC definition of catalyst (see Introduction). The standard mass-action kinetics used for this reaction in the Results section seems to be fully adequate and sufficient for describing this reaction, including its autocatalytic behavior.

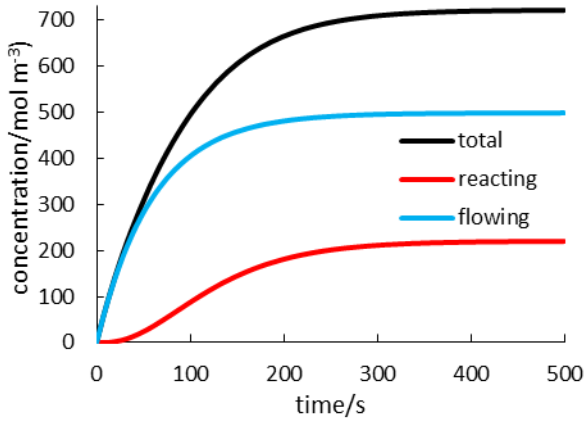

Figure 13. Decomposition of product C concentration from Figure 11, blue curve

The statement on the permanent reaction rate increase, cited in Peng et al. (2022), is evidently not valid, particularly in batch systems, cf., as examples, Figs. 1 and 6.

The S-shaped product concentration time profile can be a strong indicator of autocatalysis but is not unambiguous, as pointed out, for example, by Horváth (2021); see also the discussion of the lactonization example in sec. 2.3. In the case of a simple, single reaction in a batch system, it is a result of autocatalysis, because it reflects the (temporarily) accelerated product formation. At the same time, it (its inflection point) indicates the existence of a rate maximum, i. e., not a continuous reaction rate increase. In the case of a multi-step reaction scheme, the S-shaped product concentration time profile can be a consequence also of other kinetic features like the consecutiveness of reactions leading to that product formation. A typical example of the latter is the consecutive transformation of A to C: $\mathrm{A} \rightarrow \mathrm{B} \rightarrow \mathrm{C}$. Here, the S-shape of the c_C time profile in the batch reactor is accompanied by a maximum on the c_B time profile.

Flow-through systems like CSTR add new complications – instantaneous feed in (and out) affect the rates of reaction steps and can interfere with "pure" autocatalysis and suppress it regardless of the presence of autocatalytic features in the underlying reaction scheme. In other words, the reactor

inlet and outlet should be considered in the "proper parametrization". Flow-through systems are often operated under steady state (ss) conditions where rates and concentrations do not change in time. This special case is not discussed here; let it only be noted that CSTR steady state balance $r_i^{ss} = (c_i^{ss} - c_i^{o})/\tau$ shows that a stationary rate depends on both inlet and initial concentrations, generally.

Conclusions

The IUPAC definition of a catalyst is not bad but should be used carefully in the case of autocatalysts and in discussions of autocatalysis. An autocatalytic feature should be present in the reaction scheme – the formation of a specie which acts, at the same time, as a reactant in a relevant step and whose formation outweighs (temporarily) its consumption, or which participates in the rate equation of some step (while not necessarily being a standard reactant in the stoichiometric equation of that step). This still may not be sufficient, as proper values of relevant rate coefficients and concentrations are important for autocatalysis to really appear. Special attention should be devoted to flow-through systems in which reaction rates are affected by a continuous inlet of standard reactant(s).

References

Érdi P., Tóth J. (1989). *Mathematical models of chemical reactions*. Princeton: Princeton University Press.

Henry P. (1892). Über die wechselseitige Umwandlung der Laktone und der Oxysäuren. *Zeitschrift für Physikalische Chemie* **10U**(1), 96-129.

Horváth A. K. (2020) Law of Mass Action Type Chemical Mechanisms for Modeling Autocatalysis and Hypercycles: Their Role in the Evolutionary Race, *ChemPhysChem* **21**(15), 1703-1710.

Horváth A. K. (2021). Correct classification and identification of autocatalysis, *Physical Chemistry Chemical Physics* **23**(12), 7178-7189.

IUPAC (1997a) *Compendium of Chemical Terminology*, 2nd ed. (the "*Gold Book*"). Compiled by A. D. McNaught and A. Wilkinson. Blackwell Scientific Publications, Oxford. Online version (2019-) created by S. J. Chalk. https://goldbook.iupac.org/terms/view/A00525.

IUPAC (1997b) *Compendium of Chemical Terminology*, 2nd ed. (the "*Gold Book*"). Compiled by A. D. McNaught and A. Wilkinson. Blackwell Scientific Publications, Oxford. Online version (2019-) created by S. J. Chalk. https://goldbook.iupac.org/terms/view/C00876.

Ostwald W. (1890). Ueber Autokatalyse. *Berichte über die Verhandlungen der Königlich Sächsischen Gesellschaft der Wissenschaften zu Leipzig, Mathematisch-Physische Classe* **42**, 189–191.

Pekař M. (2021). Non-Equilibrium Thermodynamics View on Kinetics of Autocatalytic Reactions—Two Illustrative Examples. *Molecules* **26**(3), article 585.

Pekař M. (2022). Reaction rate view on autocatalysis. *Qeios*, https://doi.org/10.32388/IR2WXP.

Peng Z., Paschek K., Xavier J.C. (2022). What Wilhelm Ostwald meant by "Autokatalyse" and its significance to origins-of-life research. *BioEssays* **44**, 2200098.

Rodrigues D., Billeter J., Bonvin D. (2017). Generalization of the concept of extents to distributed reaction systems. *Chemical Engineering Science* **171**, 558-575.

Schuster P. (2019). What is special about autocatalysis? *Monatshefte für Chemie - Chemical Monthly* **150**(5),763–775.

Scott Fogler H. (1992). *Elements of Chemical Reaction Engineering*, 2nd ed. Englewood Cliffs: Prentice-Hall.