

# Review of: "Reaction rate view on autocatalysis"

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This article reports valid kinetic simulations in a scheme used in two previous articles. I think there is a fundamental error in the interpretation.

In the second paragraph of the 'Results and Discussion', the simple second order  $A + B \rightarrow C$  process is discussed briefly. Clearly, no kineticist would call this single-step scheme autocatalytic.

However, the text still claims "It is noteworthy that, being proportional to the concentration of the product,...". I do not think experienced kineticists agree with this sentence in general.

In this reaction, the rate is independent of the concentration of the product. The presented derivation re-wrote the rate equation using only the concentration of C (product) based on stoichiometric constraints. The smaller problem is that even within the line of thought of the text, this is not proportionality. In common usage, proportionality between dependent variable  $y$  and independent variable  $x$  means an  $y = Cx$  dependence, where parameter  $C$  is positive. Instead, the presented case would be commonly called a second-order polynomial dependence with non-zero intercept and negative first-order term.

The larger problem is that this dependence is not caused by the change in the concentration of C. The rate change is caused by the fact that the analysis imagines a change in the concentration of C that is simultaneous with changes in the concentrations of A and B. In other words, if the concentration of C is changed in a way that leads the concentrations of A and B unchanged, no change in the rate would be seen. This is quite viable experimentally: a kinetic curve monitored by the concentration of A does not depend on how much C is initially present. Also, this effect is the theoretical reason why partial derivatives are necessary for multivariate functions.

I feel that this fundamental error is carried through the entire analysis. This is the reason why Figure 3 does not show a function in the mathematical sense (in a function, it would not be possible to obtain two different rate values for a single concentration C). A concentration is always a function of time, but in this example, the concentration of C shows an extremum in time, so anything that is normally a function of time plotted against the concentration of C on the x axis runs the risks of not being a function. The reason why this is a fundamental problem is that the results of mathematical analysis are mostly stated for functions and extra considerations would be necessary for cases like this.

I also disagree with the last two sentences of the conclusion 'The rates should not be ignored in favor of concentrations. The concentration-time profiles should be used as an additional tool.' I would like to remind that experimentally, rates are very rarely measurable directly. In fact, they are mostly calculated from the numerical analysis of concentration-time profiles.

