Response by
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Autocatalysis — A Misnomer?

Oscillatory reactions form the backbone for any kind of 'self-organizing system'. For the sustenance and persistence of oscillatory reactions, there should be at least one 'autocatalytic step' – i.e.,

$$A + X \rightarrow 2X$$
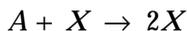
With the advent of ultra-short pulse lasers, the traditional notions of a 'transition state' have been challenged and it has been possible to visualize the structure of the 'transient activated complex'. In this context my queries are –

1. In the above type of reaction, does the rate increase due to increase in concentration of X, or does it actually catalyze the reaction? Is *autocatalysis* really a misnomer?

2. How does one visualize the structure of the transition state for such an autocatalytic reaction?

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Response

Oscillatory reactions have attracted both experimental and theoretical attention due to the recognition of the fact that so many life processes are periodic – from heart's beat to the leopard's spots. Let us consider the famous Lotka–Volterra mechanism (see *Box* 1), which has three simple steps.
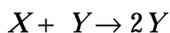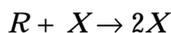
$$R + X \rightarrow 2X$$
$$X + Y \rightarrow 2Y$$
$$Y \rightarrow P$$

Although no chemical reaction follows this mechanism, we can think of some analogous situations where this is applicable. Let R be food, X be ducks, Y be wolves, and P be dead wolves.

Ducks eat food, prosper and reproduce (step 1). Wolves eat ducks, prosper and reproduce (step 2) but wolves are mortal (step 3). The overall transformation is food → dead wolves, given a constant supply of food. The first two steps of this scheme could be written $R \rightarrow X$ and $X \rightarrow Y$ if we are interested in only the net transformations. If we assume that all the steps are elementary in the above mechanism, the reaction rates must reflect the second order nature of these steps. The rates of the first two elementary steps may be written as $k_1[R][X]$ and $k_2[X][Y]$, respectively. Processes/reactions for which the forward rate depends on the concentration of a product are called '*autocatalytic*'. Instead of a simple first order growth, an autocatalytic step has a characteristic 'S' shaped curve (*Figure* 1). Thus, from the nature of the time variation of the product concentration an autocatalytic process can be distinguished from a simple first order one. The positive feedback mechanism in the autocatalytic process leads to a difference in the time dependence of the product concentration.

To address the question as to whether autocatalysis is a misnomer, let us look at the definition of catalysis. A recent textbook titled *Chemical Kinetics and Dynamics* by J I Steinfeld, J S Francisco and W L Hase, gives the following definition: "A catalyst is defined as a chemical substance which increases the rate of a chemical reaction without itself being consumed by the reaction." The same book goes on to explain the action of a catalyst as resulting from a reduction of the activation barrier. The other

Box 1

Lotka who was a statistician, discovered in the early part of the last century that number of scientific papers published per author followed an inverse square law: for every 100 authors who have published only 1 paper, there are roughly 25 who publish 2, 11 who publish 3, and so on. This phenomenon has autocatalytic aspects to it and may be generalized in the form of the maxim, "it takes money to make more money".
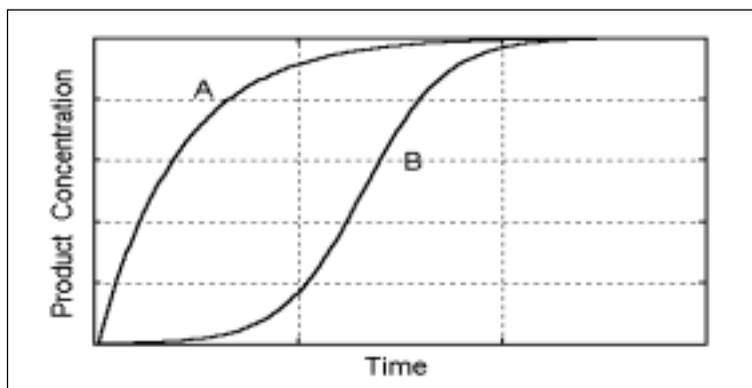
Figure 1. Curve A will be observed if the steps are just normal first order steps. Curve B is typical of an autocatalytic reaction.

Autocatalysis is not a misnomer. However, except for autocatalytic reactions, all the catalytic reactions become faster compared to un-catalyzed reactions due to a reduction in activation energy.

popular text book on *Chemical Kinetics* by K J Laidler gives the following definition: "A catalyst is a substance that is both a reactant and product of reaction; its concentration enters into the kinetic equation but not into the equilibrium constant for the reaction"

Consider an elementary reaction catalyzed by a catalyst:

$$A + X \rightarrow B + X$$
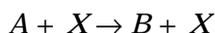
The rate of formation of B is –

$$d[B]/dt = k_2 [A][X]$$

The rate constant k_2 can be given in Arrhenius form as $k_2 = A$ exp $(-E_a/RT)$. In general, a catalyst reduces E_a leading to an increase in k_2 and hence the rate. The $A \rightarrow B$ transformation could occur without the catalyst as well, but at a slower rate. Now let us look at the autocatalytic reaction in question:

$$A + X \rightarrow 2 X$$
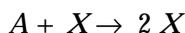
Let us ignore for the present moment that autocatalytic and oscillatory reactions are not elementary reactions. The rate of formation of X is –

$$d[X]/dt = 1/2 \, k_2[A][X]$$

Naturally, the rate increases in this case as well but now due to increasing [X]. Thus, the term *autocatalysis* is used when one of the product catalyses i.e. increases the rate of the reaction. With the two definitions given above, it is clear that the *autocatalysis* is not a misnomer. However, except for autocatalytic reactions, all the catalytic reactions become faster compared to un-catalyzed reactions due to a reduction in activation energy.

Autocatalysis and oscillatory reactions are fascinating subjects. There are several real life examples as mentioned earlier. The Lotka mechanism discussed in the beginning does not correspond to any chemical system that is known. However, there are several known 'chemical oscillators' of which the Belousov–Zhabotinsky reaction is the most extensively studied (Look at

Steinfeld, Francisco and Hase for details). This has at least nine coupled reactions. None of these reactions has any reagent as both reactant and product. This highlights the most important thing about oscillatory reactions, which is that they are not *elementary reactions.* It is therefore, important to remember that *there is no known elementary reaction in which a product can catalyze its formation in one step.* Transition state theory is applicable to elementary reactions only. To answer the second question directly, there is no transition state structure, comprehending which can help in rationalizing the stoichiometry of X.

To conclude, it may be worthwhile to remember that chronologically the term *catalysis* precedes the term *activation energy*, and when coined, it simply reflected an observed increase in the rate of the reaction in the presence of the species termed as a *catalyst*. The explanation for such an observation, in most cases, was later shown to be due to a decrease in the activation barrier. *Autoacceleration* is another term that is often used to describe such processes wherein the rate increases as the reaction proceeds – the S-shaped curve. Here the term simply restates the observation of enhanced rate without presupposing a cause.

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From:
Gene Antics

"We finished the genomic map, now we can't figure out how to fold it."