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What is and what isn't a clock reaction?

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Clear distinction should be made between the several dierent causes that may lead to an induction period in a kinetic experiment, and the term 'clock reaction' should be used only when an abrupt increase occurs in the concentration of one or more products due to the total consumption of a limiting reagent.

The formation rate of a product in a kinetic experiment usually gradually decreases because the concentrations of the reagents fall. However, numerous examples are known where the product appears in considerable concentration only after some initial delay called the 'induction period'. After this period, the rate of product formation increases for a limited time and reaches a local maximum before the end of the reaction. This phenomenon may be observed in processes with fundamentally different mechanisms. Unfortunately, there is a growing number of publications[1–5] in which a reaction exhibiting an induction period is termed a 'clock reaction' without considering the mechanistic background of the phenomenon. The purpose of this paper is to make a clear distinction between the different types of reactions featuring induction periods.

In general, we distinguish five different reasons why a reaction rate may temporarily increase as a function of time in a batch system.

1. In a **clock reaction**, a product suddenly appears with a well defined time lag after mixing the reactants.[6] This typical clock behavior occurs only if certain stoichiometric and kinetic conditions are met. The following scheme gives a simple example:

$$\mathrm{A} + \ldots \rightarrow \mathrm{P} + \ldots \quad \text{slow, rate determining}$$

$$\mathrm{B} + \mathrm{P} \rightarrow \ldots \qquad \text{fast}$$

Clock behavior occurs if $[\mathrm{A}]_0 > [\mathrm{B}]_0$ and P produced in the first step is consumed very rapidly in the second. In this clock period, the two parallel reactions have essentially the same rates resulting in $[\mathrm{P}] \sim 0$. After B is consumed, the concentration and the formation rate of P increases rapidly. The length of the induction period, often called Landolt-time, is defined by the rate of the first step and $[\mathrm{B}]_0$. When $[\mathrm{B}]_0$ is increased, the Landolt-time increases.

2. **Autocatalysis** is a well known and thoroughly studied kinetic phenomenon where a product catalyzes its own production.[7] This is an example of positive feedback. The simplest scheme of autocatalysis is the following:

$$\mathrm{A} + \mathrm{P} \rightarrow 2\mathrm{P} \qquad \mathrm{d}[\mathrm{P}]/\mathrm{d}t = k[\mathrm{A}][\mathrm{P}] \quad (1)$$

At the beginning, the product P is either present in very low $[\mathrm{P}]_0$ concentration or is formed in one or more much slower reactions, *e.g.* $\mathrm{A} + \ldots \rightarrow \mathrm{P}$. As time passes, an increase in the rate occurs because [A] is still relatively high and [P] increases. In the last stage, the rate decreases as A is consumed. The [P] *vs.* t curve shows a sigmoidal shape and has an inflection point where the rate ($\mathrm{d}[\mathrm{P}]/\mathrm{d}t$) has its maximum. In most autocatalytic processes, the length of the induction period is poorly defined. However, higher-order autocatalysis may give rise to a change that is rather abrupt and seemingly similar to clock reactions. When $[\mathrm{P}]_0$ is increased, the induction period decreases.

3. In a **consecutive reaction mechanism**, the product(s) of the second or later steps appear with some sort of delay only. The most common textbook example is a sequence of first-order steps:

$$\mathrm{A} \rightarrow \mathrm{B} \rightarrow \mathrm{P}$$

If $[\mathrm{B}]_0 = 0$, the formation rate of P at $t = 0$ is 0, thus, it necessarily increases for some time and, after reaching a maximum, decreases gradually. The induction period is not usually sharp, although it can be more pronounced if more than one intermediate is involved.

4. **Branching chain reactions** may be considered formally as autocatalytic in nature because the branching step increases the number of chain carriers similarly to P in case 2. As a consequence, an induction period is followed by a huge increase in the rate, leading to a nonthermal explosion. The explosion is a sharp indicator of the length of the induction period.

5. In **thermal explosions**, the increase of temperature in an adiabatically closed system exponentially increases the rate constant(s) of an exothermic reaction, which yields a maximum in the reaction rate as a function of time. Consequently, the kinetic traces of product formation also feature some sort of time lag. Generally speaking, heat acts as an autocatalyst in these processes.

Autocatalysis and clock behavior are often confused, although they possess distinct kinetic and mechanistic features. A single reaction in itself can be autocatalytic, whereas clock behavior implies at least two parallel reaction steps coupled properly without positive feedback. Moreover, autocatalysis does not imply any stoichiometric constraints, whereas clock behavior does. Individual steps of a clock reaction may be autocatalytic, but this is not a necessary condition.

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