Sustained oscillations in a simple reaction model

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It is shown that the reaction sequence comprising steps (i) and (ii) and undergoing in a continuous flow stirred tank reactor generates oscillations (A and B represent the concentration of reactant A and intermediate B)

A + B → 2B
B → C

The reaction (i) is autocatalytic and reaction (ii) obeys half-order kinetics.

The need for ‘a very simple example of a kinetic mechanism’, through which oscillatory reactions can be understood, has been reemphasised recently \(^1\). Although, Lotka-Volterra scheme \(^2\) first put forward in 1920, accounted for oscillatory behaviour, it did not provide stable limit cycle behaviour characteristic of self-oscillating systems. Versions of cubic autocatalator were later suggested by Sel’kov \(^3\) and also by Lefever \(^4\) involving the core

A + 2B → 3B
B → C

Prigogine and Lefever \(^4\) while retaining the core, suggested a scheme known as Brusselator where a few steps were added. This has been extensively used to investigate temporal and spatio-temporal oscillations including dissipative structures in model systems \(^1\).\(^2\).\(^3\).

A number of simple reaction schemes have been proposed in the literature \(^6\)-\(^12\), which show oscillatory behaviour under certain conditions. Very recently a two-step model \(^11\), containing an autocatalytic step and a decay step, has been proposed which shows sustained oscillations in a continuous flow stirred tank reactor (CSTR). The model consists of the following steps:

A + B → 2B
B → C

where A and B are the reactants and C is the product. Damped oscillations are obtained when linear decay of B is assumed. However sustained oscillations are obtained when Michaelis-Menten type of rate law \(^1\) for step (ii) is assumed, i.e.

\[
\text{Rate} = \frac{kB}{(1 + rB)}
\]

where \(k\) is the rate constant and \(r\) is another constant, B denotes the concentration of the reactant B itself.

We propose to examine in this paper the consequences of assuming half order kinetics for step (ii), i.e.

\[
\text{Rate} = k_2B^{1/2}
\]

Search for simple schemes is desirable for understanding the basic control of oscillatory behaviour and hence the present investigation was undertaken. It may be noted that fractional order kinetics is quite common in heterogeneous reactions and the rate can be expressed by the relation \(3\)

\[
\text{Rate} = \dot{k}p^n (1 > n > 0)
\]

where \(\dot{k}\) is a constant, \(p\) is the pressure and \(n\) denotes the order. Further, \(n = 1\) when the surface is sparsely covered while \(n = 0\) when the surface is completely covered. An illustrative example \(^13\) is the decomposition of arsine on metallic arsenic for which \(n = 0.6\).

Analysis of simple reaction model

According to the present model, the rates of step (i) and (ii) would be given by:

\[
\text{Rate (i)} = k_1AB
\]

\[
\text{Rate (ii)} = k_2B^{1/2}
\]

We can consider step (i) as simple A → B with the rate law given by Eq. (4) as pointed out by Cook et al.\(^2\) Considering A and B as dynamic variables, for an open system (flow reactor) the kinetic equations can be expressed by Eqs (6) and (7)

\[
\frac{dA}{dT} = -k_1AB + k_i(A_0 - A)
\]

\[
\frac{dB}{dT} = k_1AB - k_2B^{1/2} + k_i(B_0 - B)
\]

where \(k_i\) is the inverse of residence time and \(A_0\) and \(B_0\) are concentrations of reactant and radical re-
respectively. In dimensionless form, Eqs (6) and (7) may be written as:
\[
\frac{dx}{dt} = -yx + \frac{(1-x)}{t_{res}} \quad \ldots (8)
\]
\[
\frac{dy}{dt} = xy - \frac{y^{1/2}}{t_2} + \frac{(y_0 - y)}{t_{res}} \quad \ldots (9)
\]
where \( x = \frac{A}{A_0}; \ y = \frac{B}{B_0}; \ y_0 = \frac{B_0}{A_0}; \ t = k_1A_0T; \ t_{res} = k_1A_0/k_1 \) and \( t_2 = k_1A_0^{3/2}/k_2 \) (where \( t_{res} \) is residence time).

Computer solution shows that when \( t_{res} = \infty \) (batch reactor condition) or when \( y_0 = 0 \) oscillations are not obtained. However for CSTR under certain condition sustained oscillations are obtained.

From Eq. (8), we obtain for the steady state when
\[
\frac{dx}{dt} = 0,
\]
\[
y = \frac{(1-x)}{(xt_{res})} \quad \ldots (10)
\]
Now, combining Eq. (9) with Eq. (8) for the steady state situation when both \( \frac{dx}{dt} \) and \( \frac{dy}{dt} \) are zero, we get
\[
x^3t_{res}^2t_2^2 - x^2 \left( 2t_{res}^2t_2^2 + t_{res}t_2 + y_0t_{res}^2t_2^2 \right) + x^2 \left( t_{res}^2 + 2yt_{res}t_2 + 3y_0t_{res}^2t_2 + 4t_{res}t_2^2 \right) + t_{res}^3 + t_2^2 - x \left( t_{res}^3 + 2t_2^2 + 2y_0t_{res}t_2^2 + 2t_{res}t_2^2 \right) + t_2^3 = 0. \quad \ldots (11)
\]
Solution of equation (11) gives the steady state values of \( x \) and \( y \) at different values of \( t_{res} \) and \( t_2 \). Obviously Eq. (11) will give four roots indicating the possibility of multistability.

**Normal mode analysis**

Applying normal mode analysis\(^{10}\) the secular equation (12) is obtained, when \( y_0 = 0 \) or \( y_0 \neq 0 \)
\[
\begin{vmatrix}
\omega + \frac{1}{t_{res}} + y_s
\end{vmatrix} \begin{vmatrix}
x_s
\end{vmatrix} = 0
\]
\[
\begin{vmatrix}
y_s
\end{vmatrix} \begin{vmatrix}
\left( x_s - \frac{1}{(2y_s^{1/2})} \right) - \frac{1}{t_{res}} - \omega
\end{vmatrix} = 0
\]
where \( \omega \) is the frequency. \ldots (12)

Equation (12) can be rewritten as
\[
\omega^2 = \omega \left( x_s - y_s - \frac{2}{t_{res}} - \frac{1}{(2t_2y_s^{1/2})} \right) + \left[ \frac{1}{t_{res}} \left( -x_s + \frac{1}{t_{res}} + y_s \right) \right] + y_s^{1/2} / 2t_2 \left( 1 + \frac{1}{(t_{res}y_s)} \right) = 0
\]
\ldots (13)
where \( x_s \) and \( y_s \) are steady state values of \( x \) and \( y \) respectively.

Or \( \omega^2 - p \omega + q = 0 \)

where
\[
p = x_s - y_s - \frac{2}{t_{res}} - \frac{1}{(2t_2y_s^{1/2})}
\]
and
\[
q = \left[ \frac{1}{t_{res}} \left( -x_s + \frac{1}{t_{res}} + y_s \right) \right] + y_s^{1/2} / 2t_2 \left( 1 + \frac{1}{(t_{res}y_s)} \right)
\]

![Fig. 1 — Plot of computed values of (a) log x and (b) log y versus time for \( t_{res} = 500 \), \( t_2 = 100 \) and \( y_0 = 0.0 \).](image-url)
Bifurcation would occur when \( q > 0 \) and \( p = 0 \) so that at the bifurcation point,
\[
x_1 - y_1 - 2/t_{rev} - 1/(2t_2y_0^{1/2}) = 0
\]  \( \ldots (14) \)

**Numerical solution**

Numerical solution of Eqs (8) and (9) were obtained for different values of \( t_2 \) and \( t_{rev} \), and typical results for \( t_2 = 100, t_{rev} = 500 \) and \( y_0 = 0 \) are plotted in Fig. 1. In this situation damped oscillations are obtained. Now, if we consider the case when \( y_0 \) is finite, computer solution gives oscillatory behaviour as shown in Fig. 2, when \( t_{rev} = 700, t_2 = 100 \) and \( y_0 = 0.1 \). In all the cases when \( t_{rev} \geq 700 \) sustained oscillations are obtained. We also computed numerically the nature of stability/instability when \( t_2 = 100, y_0 = 0.1 \) and \( t_{rev} \) is varying. The results are given in Table 1.

Equation (11) was also solved for \( t_2 = 100, y_0 = 0.1 \) and for varying values of \( t_{rev} \), and accepted solutions of \( x \) and \( y \) i.e. \( 0 < x < 1; 0 < y < 1 \) were obtained. These values were then substituted in Eq. (14) in order to find out when the left hand side of the Eq. (14) is negative, zero or positive in order to identify the bifurcation point for particular values of \( t_{rev} \). It is found that when \( t_{rev} \geq 723 \), instability occurs.

The finding that an autocatalytic reaction followed by a reaction obeying half-order kinetics displays oscillatory behaviour in a CSTR may have some implication in oscillations in heterogeneous reaction system. Experimental observations reveal that under certain conditions, the rate of several oxidation reactions oscillate continuously and never attain a steady state\(^{14}\). Some of the examples are: (a) oxidation of hydrogen by oxygen on nickel\(^{15}\); (b) oxidation of hydrogen on supported Pt-catalyst\(^{16a}\); and (c) oxidation of CO on supported catalyst\(^{16b,16c}\).

Combustion instability in solid propellant rocket motors using ammonium perchlorate (AP) as an oxidizer can also be possibly understood on the basis of the above model since it is widely accepted that burning rate of composite propellants is primarily governed\(^{17}\) by the autocatalytic production of \( \text{HClO}_4 \) by the decomposition of AP which is followed by heterogeneous decomposition of \( \text{HClO}_4 \).

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