

CHEMICAL OSCILLATIONS IN HOMOGENEOUS SYSTEMS

1. ESSENTIAL THERMODYNAMIC AND KINETIC CONDITIONS FOR THE OCCURRENCE OF OSCILLATIONS

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abstract: This manuscript reviews the understanding of homogeneous chemical oscillations, the conditions in which a chemical reaction will undergo oscillations and presents a schematic classification scheme for homogeneous-phase chemical oscillations.

General background

Oscillating reactions are a subset of phenomena in a wide field which deal with the formation of structures ordered in space and/or time in physical and chemical systems. Such structures are maintained as long as matter and/or energy flow through the system assuring the highest rate of entropy production. For this reason are called dissipative structures.

In an oscillating chemical reaction the concentrations of catalyst and/or intermediate species undergo oscillations in time. The behaviour of the system is determined by the decreasing in Gibbs free energy of an overall reaction, which occurs far from thermodynamic equilibrium.

Compared to the variety of oscillatory systems, they show a surprising similarity in the general shape of their response curves or oscillograms (time variation of the intermediate species concentrations or time variation of the potential or pH of the system etc). This fact suggests that there may exist a common kinetic principle for their occurrence. The oscillograms consist in periodic transition of the system between two distinct quasi states. Chemical oscillations look like non-linear flip-flop oscillations or can have saw-tooth shape (Fig. 1). The sinusoidal oscillograms recorded sometimes are due to particularly simple processes.

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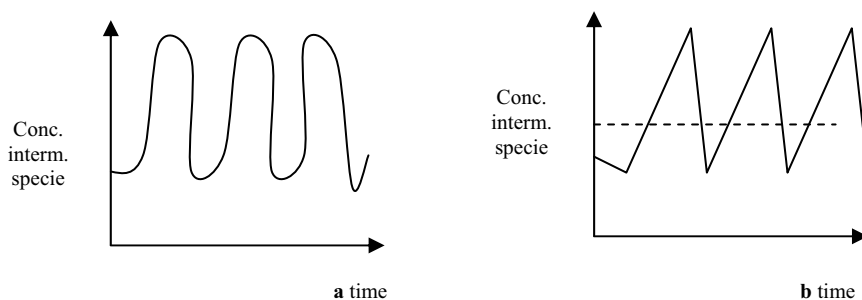


Fig. 1: Examples of flip-flop (a) and saw-tooth (b) oscillations

The kinetics of most chemical oscillations is not completely well understood, but the phenomenology of these systems shows that there are certain thermodynamic and kinetic conditions for the producing of spontaneous oscillations.

- The oscillatory processes can occur only in thermodynamic systems which are far from equilibrium;
- The oscillatory systems consist from a network of reactions and the behaviour of these systems requires a corresponding set of simultaneous differential equations. Therefore it can't exist direct functions like $y = f(x, y, \dots)$ but only set of equations of the kind:

$$\frac{dx}{dt} = f_x(x, y, \dots), \quad \frac{dy}{dt} = f_y(x, y, \dots) \quad (1)$$

Hence, the dynamics of the oscillatory systems is described by equations:

$$\frac{dx(t)}{dt} = F(x, u, t) \quad (2)$$

In the case of a system with a set of chemical reactions, the equation (2) represents the expression of the rates of change. We note by: x – the vector of system variables (which can be represented by concentrations and/or temperature); F – the vector of functions obtained from the kinetic model; u – the vector of system parameters (which can be represented by rate constants, stoichiometric coefficients, temperature, pressure, etc; t – time.

In order for the system to present oscillations, the x vector must be at least bidimensional (two concentrations or one concentration and temperature).

- The relationships between driving forces and driven fluxes are extremely non-linear. The function from F must be non-linear. Non-linearity are due to the type of feedback, the oscillatory processes contain autocatalytic or autoinhibitory reactions, or they can appear because of the exponential dependence of the rate constant with the temperature (in the systems with temperature variation);
- Oscillatory systems always contain unstable states;
- Several kinetic variables participate in the periodic process and oscillations are the results of mutual coupling between processes. The variables are not directly interdependent but they are kinetically coupled with one another;

- In physicochemical systems, sometimes the oscillations are accompanied by periodically occurrence spatial propagation processes (an example can be the Belousov-Zhabotinsky reaction). Therefore they are temporal and spatial phenomena at the same time [1÷9].

The feedback in chemical oscillations

Oscillatory systems contain at least two simultaneous processes. The total coupling effect between these processes forms closed feedback loops for each kinetic variable involved. Feedback occurs when a process acts kinetically upon itself and consists in a closed chain of action, which causes:

- effects of self-enhancement in case of positive feedback;
 - effects of self-inhibition in case of negative feedback.
- a) When the output of transmission systems acts upon the input of the same systems (an effect is influencing its own cause) than this type of feedback has no effect upon the properties of the transmission systems or upon the rate constant of the reaction. This kind of feedback is named “non-systemic” feedback (Fig. 2). The chemical analogy is stoichiometric autocatalysis. In an autocatalytic reaction the product is also a reactant.

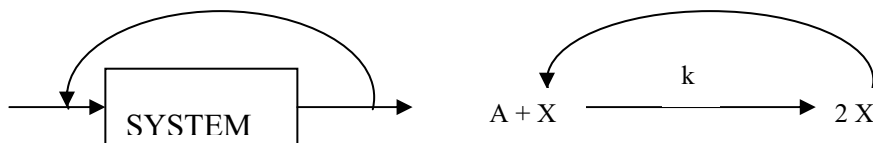


Fig. 2: *Non-systemic feedback.*

- b) Another type of feedback is the “systemic” feedback, which acts upon the properties of the systems and has no effect upon the input (Fig. 3). This kind of feedback can arise in heterogeneous systems (at electrodes, contact catalysts and membranes etc) and also in homogeneous systems (in thermochemical reactions, in enzymatic systems). Systemic feedback is usually non-stoichiometric (non-linear) being more favourable to oscillations than non-systemic feedback (which is linear).

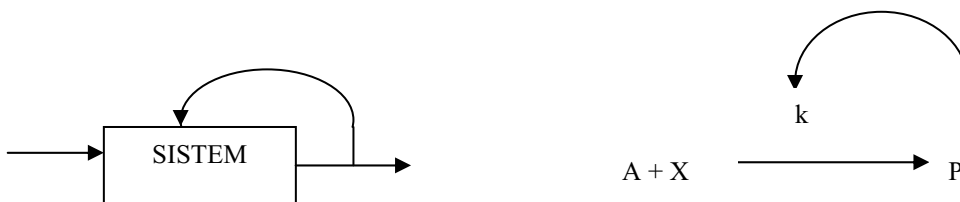


Fig. 3: *Systemic feedback*

Search for new oscillators

The first chemical oscillators (Bray-Liebafsky and Belousov-Zhabotinsky reactions) were discovered by accident, and before 1980 it was believed that homogeneous oscillating reactions were impossible. The Bray – Liebafsky [10÷13] (shortly BL) oscillatory reaction

has been studied for more than eighty years and consists in hydrogen peroxide decomposition in the presence of potassium iodate and sulphuric acid. Although this reaction is reasonably well known from the beginning of the century, new experimental approaches could be made.

The Belousov [14] – Zhabotinsky [15,16] (BZ) reaction is one of the most studied and best-understood chemical oscillating reactions. Even in a closed system the reaction exhibits an unexpected wealth of dynamic behaviors ranging from sustained oscillations [14÷18], excitabilities [19÷21] and chemical wave activity [22÷24] to bistability [20,15÷27]. In general, a BZ reaction is the simultaneous bromination and oxidation of an organic substrate by bromate in the presence of metal ion catalyst in aqueous media [28,29]. Malonic acid is the most common substrate used in the studies of the BZ reaction and it plays a dual role: the reduction of the metal ion catalyst and the removal of bromine.

Oscillatory phenomena in biochemical systems were also becoming a subject of intensive study (glycolytic oscillation).

An important step in understanding the bromate oscillators was the formulation by Noyes [30] of a classification scheme for the known bromate oscillators. Since that time, another oxyhalogen (bromate, chlorite, iodide) systems have been shown to oscillate. In Fig. 4 we present a preliminary attempt of a classification scheme for homogeneous chemical oscillators [31,32]. In that scheme we noted: R = reductant, R(In) = inorganic reductant, R(Or) = organic reductant, R (Ar) = aromatic reductant, Ox = oxidant, MB = methylene blue, M^+ = metal ion catalyst, Sulfur species = $S_2O_3^{2-}$, SCN^- , S^{2-} , SO_3^{2-} , thiourea. Solid lines link related systems within families or chemical oscillators. Broken lines connect systems that share certain features.

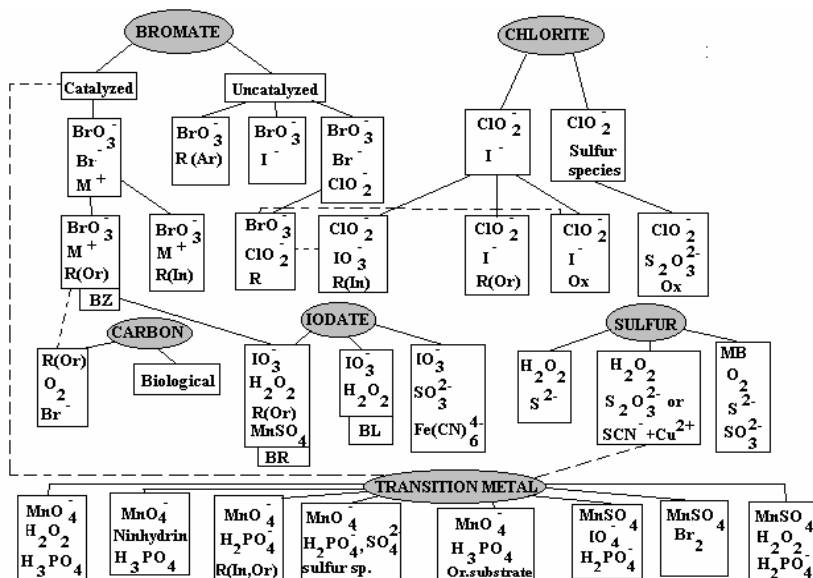


Fig. 4 Schematic classification scheme for homogeneous chemical oscillators

In a next paper we will present the most important and studied chemical oscillators in homogeneous medium (Bray-Liebhafsky and Belousov-Zhabotinsky reactions). Details about the types of systems and adopted mechanisms for the explanation of their periodic behaviour will be given. The most used experimental techniques and some of our results concerning these two systems will be reviewed.

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