

SIMULATION OF ELECTROCHEMICAL DATA ASSOCIATED TO THE EVOLUTION OF BRAY-LIEBHAFSKY SYSTEM AT 86°C

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abstract: The Bray – Liebhafsky (BL) oscillatory reaction (the decomposition of hydrogen peroxide in the presence of potassium iodate and sulphuric acid) at 86°C is analysed. The reaction was followed potentiometrically with the aid of platinum and Hg/Hg₂SO₄ electrodes. In order to simulate the recorded experimental data, a polynomial function E(t) was established. The simulation was made in time interval 36÷70 minute. The simulated data are presented in 3 tables. The final polynomial established function fitted with good approximation the experimental data.

Introduction

In systems, which are far from equilibrium, the oscillations in concentration of species participating in a complex chemical reaction may appear. These oscillations are sensitive to fluctuations in the parameters of the systems [1,2]. The behaviour of these oscillatory chemical reactions is a deterministic phenomenon, which depends on the initial concentrations of the reactants and the temperature of the systems.

The Bray-Liebhafsky (BL) oscillatory reaction of the decomposition of hydrogen peroxide into water and oxygen in the presence of potassium iodate and sulphuric acid is an example of a system with the above characteristics [3]. The BL reaction is one of the most known homogeneous oscillating reactions. Generally, the mechanism of such reactions is not conclusive; this behavior is attributed to their uncommon peculiarities: they don't respect the stoichiometry or the regularities of the traditional reactions [4÷14]. Because the domain is situated at the frontier between several fields of research, it is necessary to investigate these systems by using physique-mathematical analysis and simulate the experimental data [15].

Experimental

Sulphuric acid (Merck), KIO₃ (Fluka) and H₂O₂ (Reactivul Bucharest) were of commercial analytical quality and were used without any further purification.

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The time evolution of the decomposition of hydrogen peroxide in the presence of potassium iodate and sulphuric acid was followed potentiometrically (with a universal polarograph OH – 814 Radelkis, Hungary) in a closed thermostated cell at various temperatures, with a working platinum electrode and a reference Hg/Hg₂SO₄ electrode. A Lauda K4R thermostat with the precision of 0.02°C/skt was used.

The reaction commenced when hydrogen peroxide (0.75 mL with different concentrations) was added to a standardised mixture of potassium iodate (4.6x10⁻²M) and sulphuric acid (7.5x10⁻²M). 20 mL of this mixture was thermostated and the solution was stirred magnetically (900 rpm) and by bubbling nitrogen. Before the adding of hydrogen peroxide, the bubbling was stopped. The initial concentrations of the reactants in the reaction mixture were: [KIO₃]₀ = 4.43x10⁻²M, [H₂SO₄]₀ = 7.23x10⁻²M and initial concentration of [H₂O₂]₀ = 8.4x10⁻²M. Detailed data concerning the experimental set up, the variation of BL parameters with temperature and hydrogen peroxide concentration and some considerations about reaction mechanism were given before [16-20].

Results and discussions

As a rule, the BL reaction is preceded by an induction period, in all cases with an initial hydrogen peroxide concentration not exceeding 2.1x10⁻¹ mole/L. The induction period is defined as the interval elapsing from the beginning of the reaction to the onset of the first oscillation). The time dependence of platinum electrode potential in a BL system is given in Fig. 1.

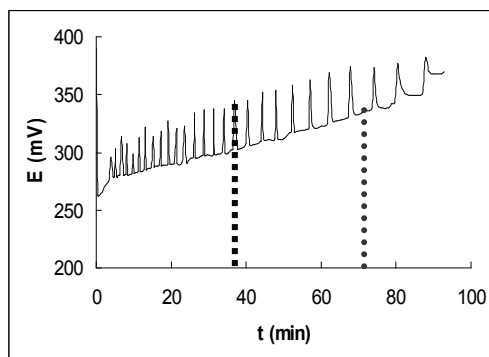


Fig. 1 Time variation of platinum electrode potential in a BL system, at 86°C and following composition: [KIO₃]₀ = 4.43x10⁻² M; [H₂SO₄]₀ = 7.23x10⁻¹ M and ; [H₂O₂]₀ = 8.4x10⁻² M.

In order to simulate the recorded experimental data, a polynomial function E(t) was established, with certain values in t₁, t₂, ..., t_n. If we note by E(t₁), E(t₂), ..., E(t_n), the values of the potential in t₁, t₂, ..., t_n, then the time variation of the platinum electrode potential can be written in this form:

$$E(t) = \sum_{k=1}^n E(t_k) \frac{(t-t_1)(t-t_2)\dots(t-t_{k-1})(t-t_{k+1})\dots(t-t_n)}{(t_k-t_1)(t_k-t_2)\dots(t_k-t_{k-1})(t_k-t_{k+1})\dots(t_k-t_n)} \quad (1)$$

The simulation was made in time interval 36.76÷70.15 minute. The abscisa values, for 16 points, are given in Table 1.

Table 1. The abscisa values

t₁	t₂	t₃	t₄	t₅	t₆	t₇	t₈
36.76	38.76	40.3	42.61	44	45.24	47.58	49.69
t₉	t₁₀	t₁₁	t₁₂	t₁₃	t₁₄	t₁₅	t₁₆
51.53	54.3	56.46	58.76	61.53	64.76	67.07	70.15

If we note:

$$\begin{aligned}
 p_1 &= (t_1 - t_2) \cdot (t_1 - t_3) \cdot \dots \cdot (t_1 - t_{16}) \\
 p_2 &= (t_2 - t_1) \cdot (t_2 - t_3) \cdot \dots \cdot (t_2 - t_{16}) \\
 p_3 &= (t_3 - t_1) \cdot (t_3 - t_2) \cdot \dots \cdot (t_3 - t_{16}) \quad \text{with } k = \overline{1,16} \\
 &\dots\dots\dots \\
 p_k &= (t_k - t_1) \cdot (t_k - t_2) \cdot \dots \cdot (t_k - t_{16})
 \end{aligned} \tag{2}$$

than eqn. (1) can be written in this form:

$$E(t) = \sum_{k=1}^{16} \frac{(t-t_1)(t-t_2)\dots(t-t_{k-1})(t-t_{k+1})\dots(t-t_{16})}{\frac{p_k}{E(t_k)}} \tag{3}$$

Values for E(t_k), p_k and p_k/E(t_k) are listed in Tables 2 and 3.

Table 2. Values of E(t_k)

E(t₁)	E(t₂)	E(t₃)	E(t₄)	E(t₅)	E(t₆)	E(t₇)	E(t₈)
348.85	303.44	348.85	308.62	354.02	311.49	356.89	314.36
E(t₉)	E(t₁₀)	E(t₁₁)	E(t₁₂)	E(t₁₃)	E(t₁₄)	E(t₁₅)	E(t₁₆)
359.77	319.54	366.09	324.13	371.83	329.88	377.58	334.48

Table 3. Values of p_k and p_k/E(t_k)

p₁	-3.0004908*10 ¹⁶	p₁/E(t₁)	-8.60109*10 ¹³
p₂	1.6395684*10 ¹⁵	p₂/E(t₂)	5.403322*10 ¹²
p₃	-3.341104*10 ¹⁴	p₃/E(t₃)	-9.57748*10 ¹¹
p₄	5.2599733*10 ¹³	p₄/E(t₄)	1.7043526*10 ¹¹
p₅	-2.2251052*10 ¹³	p₅/E(t₅)	-6.449206*10 ¹⁰
p₆	1.3821366*10 ¹³	p₆/E(t₆)	4.437178*10 ¹⁰
p₇	-1.24402091*10 ¹³	p₇/E(t₇)	-3.485726*10 ¹⁰
p₈	1.4526273*10 ¹³	p₈/E(t₈)	4.620903*10 ¹⁰
p₉	-2.2333503*10 ¹³	p₉/E(t₉)	-6.207716*10 ¹⁰
p₁₀	4.8945115*10 ¹³	p₁₀/E(t₁₀)	1,5317367*10 ¹¹
p₁₁	-9.3611584*10 ¹³	p₁₁/E(t₁₁)	-2.5570647*10 ¹¹
p₁₂	2.9557962*10 ¹⁴	p₁₂/E(t₁₂)	9,119168*10 ¹¹
p₁₃	-1.6057013*10 ¹⁵	p₁₃/E(t₁₃)	-4.318374*10 ¹²
p₁₄	4.52298688*10 ¹⁴	p₁₄/E(t₁₄)	1.3711006*10 ¹²
p₁₅	-6.358112*10 ¹⁶	p₁₅/E(t₁₅)	-1.6839112*10 ¹⁴
p₁₆	1.6512293*10 ¹⁸	p₁₆/E(t₁₆)	4.936705*10 ¹⁵

The expression of the polynomial function which simulates the platinum electrode potential is:

$$\begin{aligned}
 E(t) = & -\frac{(t-t_2)(t-t_3)\dots(t-t_{16})}{8.60109 \times 10^{13}} + \frac{(t-t_1)(t-t_3)(t-t_4)\dots(t-t_{16})}{5.403322 \times 10^{12}} - \\
 & \frac{(t-t_1)(t-t_2)(t-t_4)\dots(t-t_{16})}{9.57748 \times 10^{11}} + \frac{(t-t_1)(t-t_2)(t-t_3)(t-t_5)\dots(t-t_{16})}{1.7043526 \times 10^{11}} - \\
 & \frac{(t-t_1)(t-t_2)(t-t_3)(t-t_4)(t-t_6)\dots(t-t_{16})}{6.449206 \times 10^{10}} + \frac{(t-t_1)\dots(t-t_4)(t-t_5)(t-t_7)\dots(t-t_{16})}{4.437178 \times 10^{10}} - \\
 & \frac{(t-t_1)\dots(t-t_5)(t-t_6)(t-t_8)\dots(t-t_{16})}{3.485726 \times 10^{10}} + \frac{(t-t_1)\dots(t-t_6)(t-t_7)(t-t_9)\dots(t-t_{16})}{4.620903 \times 10^{10}} - \\
 & \frac{(t-t_1)\dots(t-t_7)(t-t_8)(t-t_{10})\dots(t-t_{16})}{6.207716 \times 10^{10}} + \frac{(t-t_1)\dots(t-t_8)(t-t_9)(t-t_{11})\dots(t-t_{16})}{1.5317367 \times 10^{11}} - \\
 & \frac{(t-t_1)\dots(t-t_9)(t-t_{10})(t-t_{12})\dots(t-t_{16})}{2.5570647 \times 10^{11}} + \frac{(t-t_1)\dots(t-t_{10})(t-t_{11})(t-t_{13})\dots(t-t_{16})}{9.119168 \times 10^{11}} - \\
 & \frac{(t-t_1)\dots(t-t_{11})(t-t_{12})(t-t_{14})\dots(t-t_{16})}{4.318374 \times 10^{12}} + \frac{(t-t_1)\dots(t-t_{12})(t-t_{13})(t-t_{15})(t-t_{16})}{1.3711006 \times 10^{12}} - \\
 & \frac{(t-t_1)\dots(t-t_{13})(t-t_{14})(t-t_{16})}{1.6839112 \times 10^{14}} + \frac{(t-t_1)\dots(t-t_{14})(t-t_{15})}{4.936705 \times 10^{15}}
 \end{aligned} \tag{4}$$

The final polynomial established function fitted with good approximation the experimental data.

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