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Activation Energies as the Validity Criterion of a Model for Complex Reactions that can be in Oscillatory States

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Abstract:

Modeling of any complex reaction system is a difficult task. If the system under examination can be in various oscillatory dynamic states, the apparent activation energies corresponding to different pathways may be of crucial importance for this purpose. In that case the activation energies can be determined by means of the main characteristics of an oscillatory process such as pre-oscillatory period, duration of the oscillatory period, the period from the beginning of the process to the end of the last oscillation, number of oscillations and others. All is illustrated on the Bray-Liebhafsky oscillatory reaction.

Keywords: Modeling, Complex reaction, Oscillatory reaction, Activation energy, Bray-Liebhafsky reaction.

Introduction

It is well known that modeling of any complex reaction system is a difficult task. For this purpose, the activation energy, or energies, determined experimentally, can be of crucial importance, although in these systems, they do not have values corresponding to particular reactions, but apparent ones corresponding to the overall process or to one reaction pathway. They would be in relation with the activation energies obtained by numerical simulations of a process based on the proposed model. If the complex process under examination is in an oscillatory dynamic state, the general discussion is similar. However, one oscillatory chemical reaction, beside the rate constants having any other reaction, possess the ones essentially related with an oscillatory. Hence, the apparent activation energies in such a system can be determined by means of kinetic values, or their analogs, which are, actually, the main characteristics of an oscillatory process such as pre-oscillatory period, duration of the oscillatory period, the period from the beginning of the process to the end of the last oscillation, number of oscillations, their periods and others.

The above general discussion will be illustrated on hydrogen peroxide decomposition in the presence of iodate and hydrogen ions,
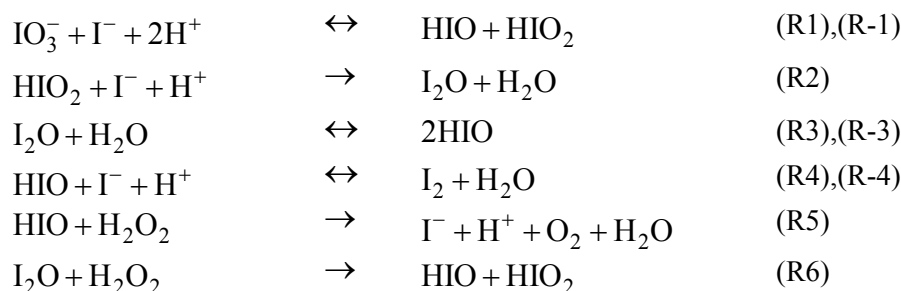
$$2H_2O_2 \xrightarrow{\quad IO_3^-, H^+ \quad} 2H_2O + O_2 , \tag{D}$$

that is, the Bray-Liebhafsky oscillatory reaction. [1,2] Experimental investigations of this

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reaction system at different temperatures have been known for a long time. [3-12] Systematic analysis of the experimental results obtained by different methods together with the new ones, is given in ref [6]. Here, the same methods are applied on oscillograms simulated by the proposed model for the Bray-Liebhafsky oscillatory reaction [14-16]. The analyzed variant of the model consists of the following six reactions [14]:

$IO_3^- + I^- + 2H^+$	$\leftrightarrow$	$HIO + HIO_2$ (R1),(R-1)
$HIO_2 + I^- + H^+$	$\rightarrow$	$I_2O + H_2O$ (R2)
$I_2O + H_2O$	$\leftrightarrow$	$2HIO$ (R3),(R-3)
$HIO + I^- + H^+$	$\leftrightarrow$	$I_2 + H_2O$ (R4),(R-4)
$HIO + H_2O_2$	$\rightarrow$	$I^- + H^+ + O_2 + H_2O$ (R5)
$I_2O + H_2O_2$	$\rightarrow$	$HIO + HIO_2$ (R6)

Summing all the reactions, one can see that this model can be represented by one net stoichiometric equation (D). The same process can also be described by the following two complex reactions denoting the reduction of iodate by hydrogen peroxide (R) and oxidation of iodine by the same agent (O)

$$2IO_3^- + 2H^+ + 5H_2O_2 \rightarrow I_2 + 5O_2 + 6H_2O \qquad\qquad (R)$$

$$I_2 + 5H_2O_2 \rightarrow 2IO_3^- + 2H^+ + 4H_2O . \qquad\qquad (O)$$

The sum of reactions R and O gives the overall decomposition, D. In the narrow region of concentrations and other external parameters, it is possible that processes R and O alternately dominate; the iodine concentration increases and decreases alternately, and the reaction is periodic. The kinetics and the apparent activation energies depend on overall reaction and domination of particular pathways. [6,7,17-21]
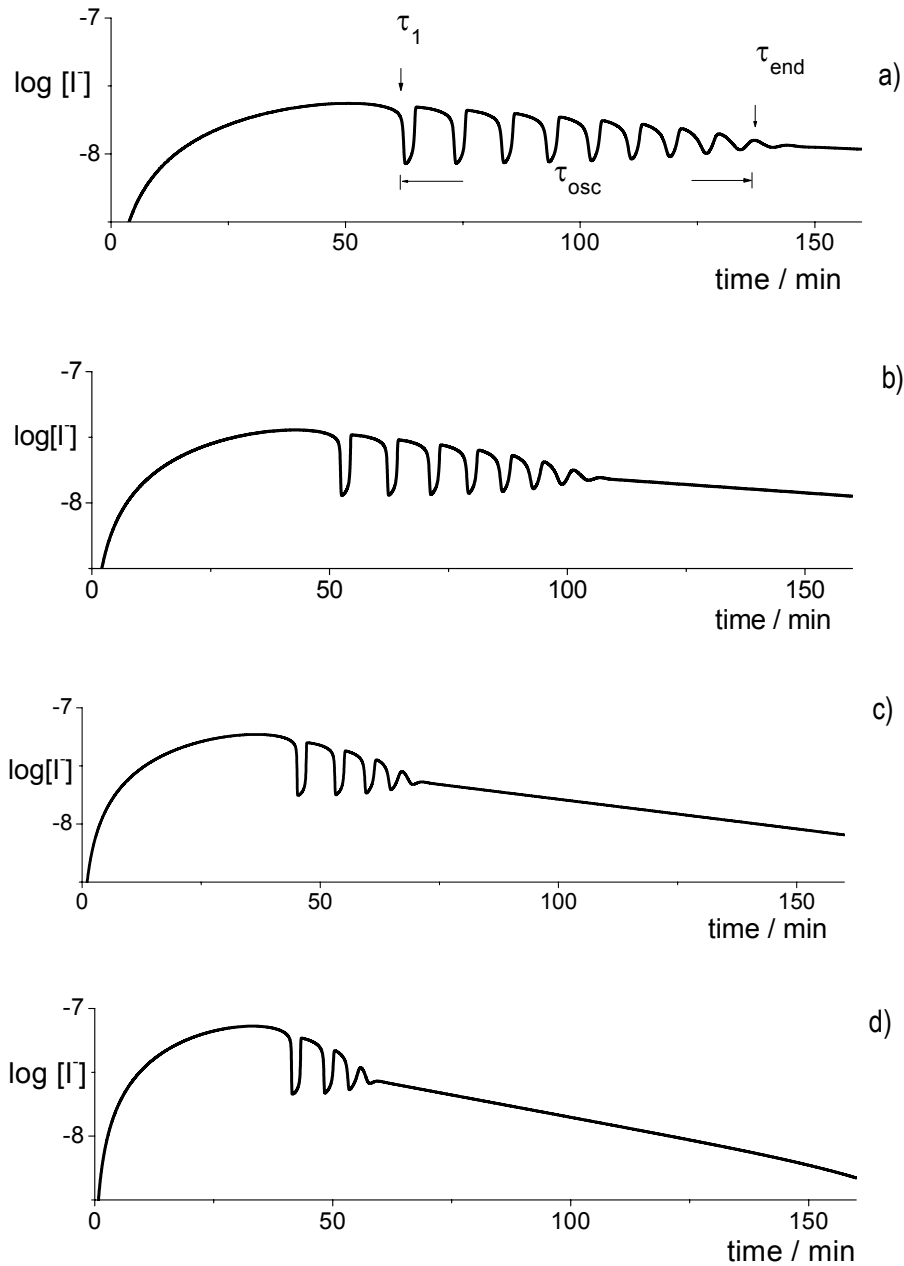
Numerical simulations

The oscillograms obtained by numerical calculations based on the model consisting of reactions (R1)-(R6) with rate constants and activation energies of particular reactions given in Tab. I, are presented in Fig. 1

The temperature dependence on the time evolution of the process under consideration is obvious. Thus, the number of oscillations, preoscillatory period, duration of the oscillatory state and other characteristics of an oscillatory process change with temperature.

Discussion

The simulated oscillograms presented in Fig. 1 correspond to the experiments generated under batch conditions. Then, one can analyze the temperature dependence of several kinetic parameters such as: the pre-oscillatory period (τ_1), the average of the oscillatory period ($\bar{\tau}$), the total number of oscillations (n), the duration from the beginning of the reaction to the end of the oscillatory state (τ_{end}) and the duration of the oscillatory state (τ_{end} - τ_1). Although phenomenological, kinetic analysis holds for these reactions as for any other [22-25], the relations between the above mentioned values and temperature have specific properties based on specific features of oscillatory processes.

Fig. 1 Logarithmic dependence of the iodide ion concentration vs. time, obtained by numerical simulation for the model (R1)-(R6) of the Bray-Liebhafsky reaction at different temperatures: a) 328K, b) 333K, c) 339K and d) 342K. $[H_2SO_4]_0 = 4.9\times10^{-2}$ mol/dm^3; $[KIO_3]_0 = 7.35\times10^{-2}$ mol/dm^3; $[H_2O_2]_0 = 4.00\times10^{-3}$ mol/dm^3.

In the case of the Bray-Liebhafsky oscillatory reaction, it was found that the overall reaction, independently of its complexity, was pseudo-first order with respect to hydrogen peroxide

$$-\frac{d[H_2O_2]}{dt} = k_D[H_2O_2],$$

(1)

Tab. I Activation energies and rate constants of the reactions (R1)-(R6), used for numerical simulation of the Bray-Liebhafsky reaction. [6,16]

Reaction	Rate	Rate constants at T = 60°C	E_a kJ/mol
R1	$k_1^0\left[I^-\right]\left[IO_3^-\right]\left[H^+\right]^2 = k_1\left[I^-\right]$	$k_1^0 = 3.18\times10^5\,M^{-3}\,min^-$	30.4
R-1	$k_{-1}^0\left[HIO\right]\left[HIO_2\right] = k_{-1}\left[HIO\right]\left[HIO_2\right]$	$k_{-1}^0 = 7.91\times10^7\,M^{-1}\,min$	50
R2	$k_2^0\left[HIO_2\right]\left[I^-\right]\left[H^+\right] = k_2\left[HIO_2\right]\left[I^-\right]$	$k_2^0 = 5.00\times10^{11}\,M^{-2}\,min$	51.5
R3	$k_3^0\left[I_2O\right] = k_3\left[I_2O\right]$	$k_3^0 = 5.00\times10^3\,min^{-1}$	100
R-3	$k_{-3}^0\left[HIO\right]^2 = k_{-3}\left[HIO\right]^2$	$k_{-3}^0 = 3.15\times10^8\,M^{-1}\,min$	40
R4	$k_4^0\left[HIO\right]\left[I^-\right] = k_4\left[HIO\right]\left[I^-\right]$	$k_4^0 = 3.00\times10^{11}\,M^{-1}\,min$	10.5
R-4	$k_{-4}^0\left[I_2\right]/\left[H^+\right] = k_{-4}\left[I_2\right]$	$k_{-4}^0 = 4.50\,M\,min^{-1}$	69.0
R5	$\left(k_5' + k_5''\left[H^+\right]\right)\left[HIO\right]\left[H_2O_2\right] = k_5\left[HIO\right.$	$k_5' = 12\times10^3\,M^{-1}\,min^{-1}$ $k_5'' = 30\times10^3\,M^{-2}\,min^{-1}$	34.0 34.0
R6	$k_6^0\left[I_2O\right]\left[H_2O_2\right] = k_6\left[I_2O\right]\left[H_2O_2\right]$	$k_6^0 = 5.00\times10^5\,M^{-1}\,min^-$	22

It was also found that a correspondence exists between the rate constants of the reactions D, R and O, and the characteristic kinetic parameters such as τ_1, $\overline{\tau}$, n, τ_{end} and τ_{osc}. [4,6,7,19] given by the following relations

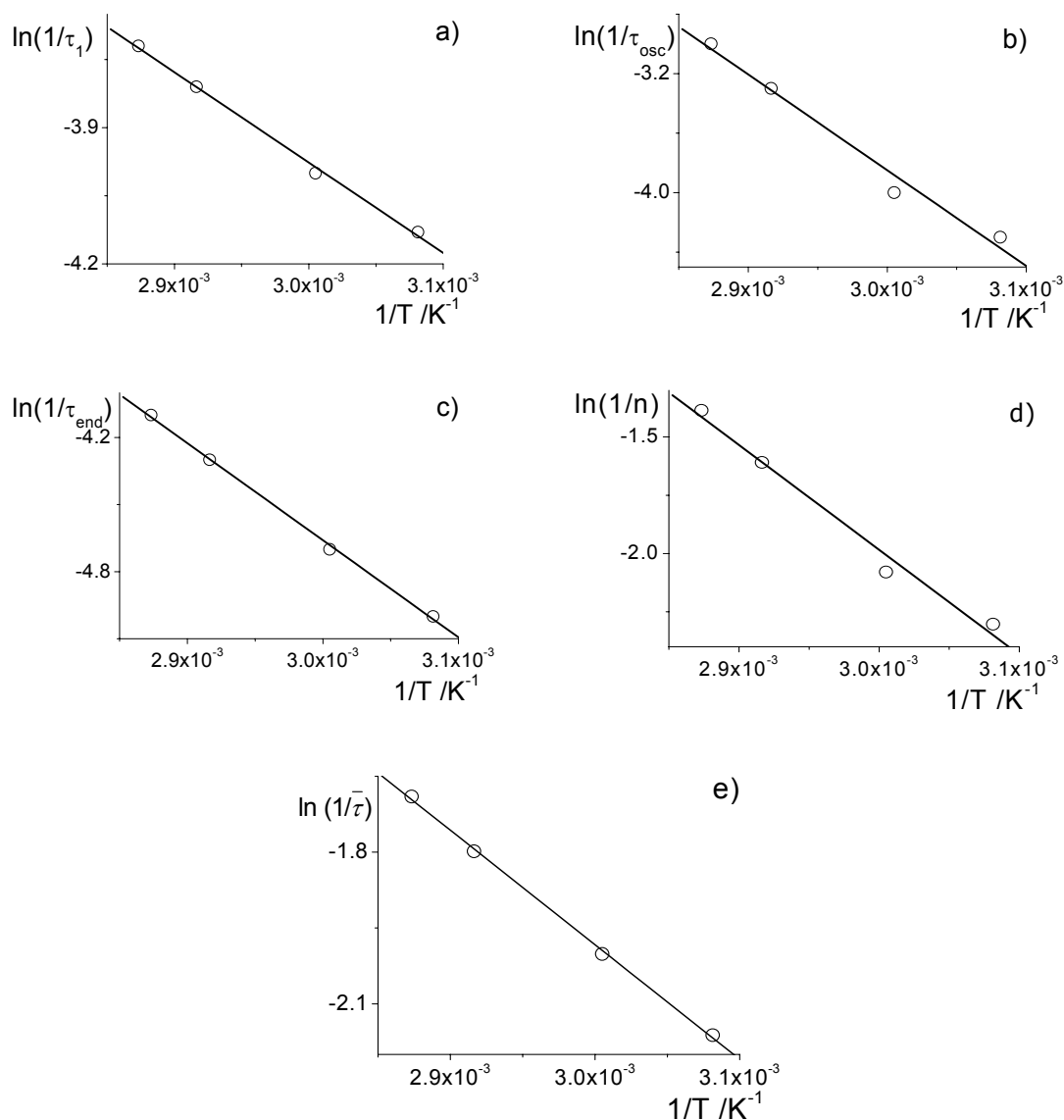$$k_D = C_1\frac{1}{t_{end}}, \tag{2}$$

$$k_D = C_2\frac{1}{\overline{\tau}} \tag{3}$$

$$k_D = C_3\frac{1}{n}, \tag{4}$$

$$k_R = C_4\frac{1}{\tau_1}, \tag{5}$$

$$k_D = C_5\frac{1}{\tau_{osc}} \tag{6}$$

where C_1, C_2, C_3, C_4 and C_5 are constants characteristic for considered system. [6,7,26]

The Arrhenius relation between analogues of rate constants and temperature is presented in Fig. 2.

Fig. 2 The Arrhenius dependence between a) $\ln(1/\tau_1)$, b) $\ln(1/\tau_{osc})$, c) $\ln(1/\tau_{end})$,
d) $\ln(1/n)$ and e) $\ln(1/\bar{\tau})$ and 1/T for the Bray-Liebhafsky system in the temperature region between 328K and 342K (see fig. 1).

      The obtained values for activation energies are given in Tab. II. They are similar to the experimentally obtained ones in all five cases. However, analyzing experimental results we were able to determine activation energies by two manners more. Two additional ones are related to analysis of maximum and minimum iodide concentrations in the oscillatory region [6]. The last two methods cannot be simply applied on the simulated oscillograms. Their application demands additional adjustment of parameters or correction of the model. The most sensitive parameters for further analysis of the temperature dependence of the considered oscillatory system are the activation energies of particular reactions (R1)-(R6). Only some of them are determined experimentally, since reactions in such a complex system cannot be simply isolated from one another. Some of these reactions are even complex ones.

Tab. II The apparent activation energies E_a (in kJ/mol) obtained for the equiconcentartion BL systems: from experimental [6,7] and simulated oscillograms (see fig. 1).

	E_a Calculated	E_a Experimental
$E_a(\tau_1)$	28	34
$E_a(\bar{\tau})$	31	31
$E_a(\tau_{end})$	60	78
$E_a(n)$	62	77
$E_a(\tau_{osc})$	89	96

Conclusion

Already proposed methods for determination of apparent activation energies of an oscillatory reaction from experimentally obtained oscillograms are applied on the oscillograms obtained by the offered model. It is found that, on one hand, the methods are very appropriate for such calculations, and, on the other hand, the proposed model is good but not excellent and demands, at least parameter adjustment.

Acknowledgement

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Садржај: *Моделирање ма ког комплексног рекакционог система је тежак задатак. Ако испитивани систем може да постоји у различитим осцилаторним динамичким стањима, привидне енергије активације, које одговарају различитим реакционим путевима, могу бити од битне важности за моделирање. У том случају енергије активације могу бити одређене помоћу основних особина осцилаторног процеса као што су предосцилаторни период, трајање осцилаторног периода, период од почетка процеса до зарщетка задње осцилације, број осцилација и других. Све ово је објашњено на Bray-Liebhfasky осцилаторној реакцији.*
Кључне речи: *Моделирање, сложена реакција. осцилаторна реакција, енергија активације, реакција Bray-Liebhfasky.*