

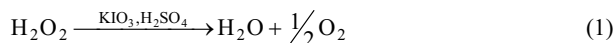
# THE POTENTIOMETRIC STUDY ON BRAY – LIEBHAFSKY REACTION AT HIGH TEMPERATURES

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The oscillatory decomposition of hydrogen peroxide in the presence of potassium iodate and sulphuric acid is analysed potentiometrically with the aid of Pt and Hg/Hg<sub>2</sub>SO<sub>4</sub> electrodes, in the range of temperatures 69.4÷95.1°C. The influence of temperature on the induction period, period of the second oscillation, number, duration and average frequency of oscillations was investigated. The corresponding activation parameters have been determined.

## Introduction

The hydrogen peroxide decomposition in the presence of potassium iodate and sulphuric acid:



known as the Bray-Liebhafsky (shortly BL) oscillatory reaction has been studied for more than eighty years.

Although this reaction is reasonably well known from the beginning of the century, new experimental approaches could be made. Most of the authors report experiments at constant temperatures [1÷15]. There are few papers, which have been an interest for the influence of temperature [16÷19], in the range between 50÷73°C.

Oscillations of iodine concentration over a wide range of temperatures belong to the interval 62.4÷90.0°C were recorded [20] using a spectrophotometric method.

In this paper we report new experimental results concerning BL system by measuring the time variation of the solution potential at different temperatures. Similar considerations concerning Belousov-Zhabotinsky were recently reported [21].

## Experimental

Sulphuric acid (Merck), KIO<sub>3</sub> (Fluka), and H<sub>2</sub>O<sub>2</sub> (Reactivul) were of commercial analytical quality and were used without any further purification.

BL reactions were followed potentiometrically (with a universal polarograph OH-814 Radelkis, Hungary) in a thermostated cell at various temperatures, with a working platinum electrode and a reference Hg/Hg<sub>2</sub>SO<sub>4</sub> electrode.

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A standard solution with concentration:  $4.6 \times 10^{-2} \text{M}$   $\text{KIO}_3$  and  $7.5 \times 10^{-2} \text{M}$   $\text{H}_2\text{SO}_4$  was prepared in bi-distilled water. 20 ml of this solution was thermostated and the solution was stirred by bubbling nitrogen. Before the adding of hydrogen peroxide (0.75ml  $\text{H}_2\text{O}_2$  5.81M), the bubbling was stopped.

The data shown in the tables are the averages of four independent measurements with a standard deviation of 8%.

## Results and discussions

The values for the followed parameters are presented in Table 1.

**Table 1. Values for induction period ( $IP$ ), period of the second oscillation ( $T_2$ ), number ( $N$ ), duration ( $D$ ), and average frequency ( $f$ ) of oscillations**

$t$ ( $^{\circ}\text{C}$ )	$IP$ (min)	$T_2$ (min)	$N$	$D$ (min)	$f = N/D$ ( $\text{min}^{-1}$ )
69.4	6.0	1.6	87	342.0	0.2544
75.0	5.0	1.4	62	216.0	0.2870
80.0	4.0	1.2	49	132.8	0.3689
86.0	3.2	0.92	35	80.0	0.4375
90.0	2.8	0.84	27	45.4	0.5947
95.1	2.2	0.70	20	32.0	0.6250

The induction period here is defined as the time interval elapsing from the beginning of the reaction to the onset of the first oscillation. It was measured the period of the second oscillation because usually the first oscillation is not so reproducible.

It can be easily seen that induction period, period of the second oscillation, number and duration of oscillations depend on temperature in such a manner that they decrease when temperature increases. The average frequency of oscillations increases with increasing temperature.

The temperature dependence of the induction period, period of the second oscillations, number and duration are presented in Figs. 1-4.

From the last two parameters,  $N$  and  $D$ , we could evaluate the average frequency of the oscillation ( $f$ ), which is the ratio between number and duration of oscillations. The temperature dependence of the average frequency is plotted in Fig. 5.

In all above graphic representations the initial concentrations of the reactants were:  $[\text{KIO}_3] = 4.43 \times 10^{-2} \text{M}$ ,  $[\text{H}_2\text{SO}_4] = 7.23 \times 10^{-2} \text{M}$ ,  $[\text{H}_2\text{O}_2] = 2.10 \times 10^{-1} \text{M}$ . From the presented figures one can see that we obtained Arrhenius plots with good correlation factors.

Using Eyring equations and instead of rate constants we introduced the values for induction period, period of the second oscillations, number, duration and average frequency of oscillations, the corresponding activation parameters have been determined and are presented in Table 2.

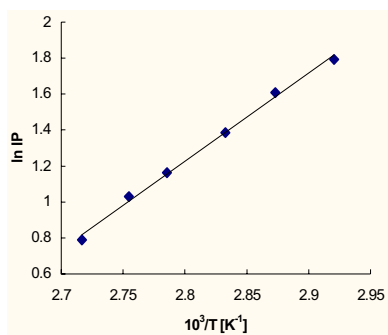


Fig. 1: Temperature dependence of the induction period.

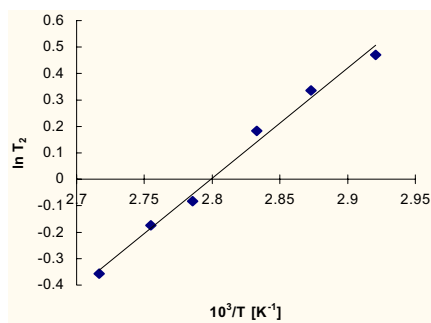


Fig. 2: Temperature dependence of the period of the second oscillations.

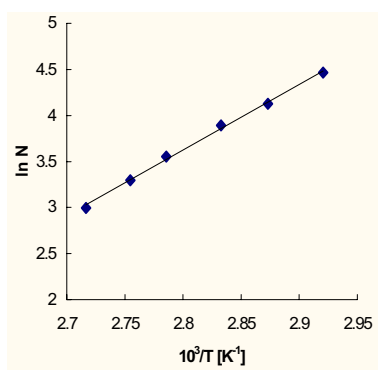


Fig. 3: Temperature dependence of the Number of oscillations.

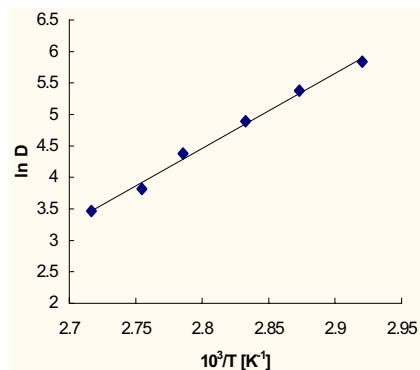


Fig. 4: Temperature dependence of the duration of oscillations.

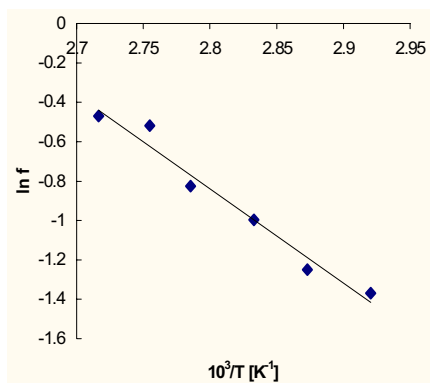


Fig. 5: Temperature dependence of the average frequency of oscillations.

**Table 2. Activation parameters derived from induction period (*IP*), period of the second oscillation (*T*<sub>2</sub>), number (*N*), duration (*D*), and average frequency (*f*) of oscillations.**

Parameter	<i>IP</i>	<i>T</i> <sub>2</sub>	<i>N</i>	<i>D</i>	<i>f</i> = <i>N/D</i>
$\Delta H^\ddagger$ , kJ mol <sup>-1</sup>	-43.86	-37.65	-62.39	-100.26	36.90
$\Delta S^\ddagger$ , kJ mol <sup>-1</sup> K <sup>-1</sup>	-363.48	-356.25	-395.41	-500.06	-154.1-53

[KIO<sub>3</sub>] = 4.43×10<sup>-2</sup>M, [H<sub>2</sub>SO<sub>4</sub>] = 7.23×10<sup>-2</sup>M, [H<sub>2</sub>O<sub>2</sub>] = 2.10×10<sup>-1</sup>M.

The values from enthalpy and entropy of activation, determined using Eyring equation are apparent or experimental values that do not correspond to any elementary reaction step, but do provide information about the extent of temperature influence on BL oscillating system.

## Conclusions

As to the possibility of temperature compensation in Bray – Liebhafsky reaction, we can say that all parameters (induction period, period of the second oscillations, number, duration and average frequency of oscillations) fulfil the Arrhenius and/or Eyring equations and we have not found the temperature compensation of its oscillatory behaviour.

## REFERENCES

1. Degn, H. (1967), *Acta Chem. Scand.* **21**, 1057-1066
2. Matsuzaki, I., Simic, R., Liebhafsky, H. A. (1972), *Bull. Chem. Soc. Japonia*, **45**, 3367-3371
3. Liebhafsky, H. A., McGavock, W. C., Reyes, R. J., Roe, G. M., Wu, L. S. (1978), *J. Am. Chem. Soc.* **100**, 87-91.
4. Liebhafsky, H. A., Furuichi, R., Roe, G. M., (1981), *J. Am. Chem. Soc.* **103**, 51-56
5. Anic, S., Mitic, D., Kolar-Anic, Lj. (1985), *J. Serb. Chem. Soc.* **50**, 53-59
6. Anic, S., Mitic, D., Veselinovic, D., Kolar-Anic, Lj. (1985), *J. Serb. Chem. Soc.* **50**, 529-533
7. Anic, S., Kolar-Anic, Lj. (1986), *Ber. Bunsenges. Phys. Chem.* **90**, 539-542
8. Anic, S., Kolar-Anic, Lj. (1986), *Ber. Bunsenges. Phys. Chem.* **90**, 1084-1086
9. Anic, S., Kolar-Anic, Lj. (1987), *Ber. Bunsenges. Phys. Chem.* **91**, 1010-1013
10. Anic, S., Mitic, D., Curcija, M. (1987), *J. Serb. Chem. Soc.* **52**, 575-579
11. Anic, S., Kolar-Anic, Lj. (1988), *J. Chem. Soc., Faraday Trans. 1*, **84**, 3413-3421
12. Anic, S., Mitic, D. (1988), *J. Serb. Chem. Soc.* **53**, 371-376
13. Kolar-Anic, Lj., Stanisavljev, D., Krnjajski Belovljjev, G., Peeters, Ph., Anic, S. (1990) *Computers Chem.*, **14**, 345-347
14. Buchholtz, F. G., Broecker, S. (1998), *J. Phys. Chem. A* **102**, 1556-1559
15. Sevcik, P., Adamcikova, L. (1998) *J. Phys. Chem. A* **102**, 1288-1291
16. Anic, S., Stanisavljev, D., Krnjajski Belovljjev, G., Kolar-Anic, Lj. (1989) *Ber. Bunsenges. Phys. Chem.* **93**, 488-491
17. Anic, S., Kolar-Anic, Lj., Stanisavljev, D., Begovic, N., Mitic, D. (1991) *React. Kinet. Catal. Lett.* **43**, 155-162
18. Anic, S., Stanisavljev, D. (1995) *J. Serb. Chem. Soc.* **61**, 125-127
19. Stanisavljev, D., Begovic, N., Vukojevic, V. (1998) *J. Phys. Chem. A* **102**, 6887-6891.
20. Vilcu, R., Danciu, T., Bala, D. (1998) *Discrete Dynamics in Nature and Society*, **2**, 195-201.
21. Vilcu, R., Bala, D. (2001) 12<sup>th</sup> Romanian International Conference on Chemistry and Chemical Engineering RICCE 12, 97-102.