ARCHIVES OF ACOUSTICS
15, 1–2, 185–192 (1990)

INFORMATION CONTENTS OF THE ACOUSTIC EMISSION EXEMPLIFIED BY THE SELECTED PHYSICO-CHEMICAL PROCESSES

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1. Introduction

The main sources of the acoustic emission (AE) signals in the physico-chemical processes are the phase transitions, gas evolution and heat of the reaction [1, 2]. Measurements of AE signals in solutions are more difficult than in solids because of low energetic levels. Energies of AE measured for the reactions in solutions are not much higher than the noise level of measuring apparatus; beside this, such interferences as wavy motion, liberation of dissolved gas and liquid mixing noise are present. This is why the investigation of chemical reactions in the solution with AE method necessitates for the application of highly sensitive measuring sets and computer data processing systems.

2. Sources of AE signals in chemical reactions

Acoustic emission is generated and can be measured in chemical reactions of various types [1–5]. In general, the relation of the AE signal energy to the number of events as a function of time is recorded. The graphs shapes of these relations are usually close to the distributions of other parameters which are recorded as time – dependent functions with other measuring methods, as e.g. potentiometric, thermal or calorimetric methods. The hitherto experimental results can be treated mainly as qualitative identification of physical effects which result in strain energy generation in the form of AE signals. Batteridge et al. [3] studied about 50 diverse chemical reactions. Among them the exothermic and heterogenic reactions exhibit acoustic activity; particularly acoustically active are the reactions with gas liberation. In the seventies, Biełousow and Żabotyński discovered the reactions in which the system does not tend to the stable state but repeats periodically the dynamical stages of the process. The classical oscillatory reaction (B–Ż) of oxidation of the malonic acid with bromates can be catalyzed by the cerium ions (III), manganium ions (II) or ferroine [6]. In the reaction (B–Ż) catalyzed by cerium (III) four mutually related processes can be distinguished. In the presence of H^+:

$$BrO_3^- + Br^- + 2H^+ \rightarrow HBrO_2 + HOBr \tag{1}$$

$$HBrO_2 + Br^- + H^+ \rightarrow 2HOBr \tag{2}$$

$$HOBr + Br^- + H^+ \rightarrow Br_2 + H_2O \tag{3}$$

$$Br + CH_2(COOH)_2 \rightarrow BrCH(COOH)_2 + Br^- + H^+ \tag{4}$$

The general reaction is represented by the equation

$$BrO_3^- + 2Br^- + 3CH_2(COOH)_2 + 3H^+ \rightarrow 3BrCH(COOH)_2 + 3H_2O \tag{A}$$

The second oscillatory reaction recorded by the authors with the use of AE was the reaction of decomposition of hydrogen peroxide catalyzed by iodates the Bray –Liebhafsky (B – L) reaction. The hydrogen peroxide plays a dual role in this reaction: the role of the oxidation (5) and reduction (6):

$$5H_2O_2 + I_2 \rightarrow 2HIO_3 + 4H_2O \tag{5}$$

$$5H_2O_2 + 2HIO_3 \rightarrow I_2 + 5O_2 + 6H_2O \tag{6}$$

$$H_2O_2 \rightarrow H_2O + \frac{1}{2}O_2 \tag{B}$$

The emerging reaction products periodically drive the system nearer and farther from the balance point. The oscillation period depends on the concentration of substrates. Oscillatory reactions are carried out in closed systems with diffusion reactant transport or with continuous mixting, and also in the systems with the flow of a passive gas which removes the gas products from the vessel [7]. The oscillatory reactions which take place in the presence of redox-type catalysts are tested mainly with the potentiometric, and less frequently with the colorimetric method. The acoustic emission method makes it possible to distinguish a number of processes which take place in these reaction, as the local disturbance of thermal equilibrium and gas phase liberation.

3. Measurements of acoustic emission in physico-chemical reactions

Experimental investigations of the acoustic emission AE in physico-chemical processes are carried out as a cycle of measurements realized in time which include only AE signal measurements or also other parameters transformed into the magnitudes of voltage, as the optic density of liquid, specific resistance, pH and temperature. Regarding the time relations of these signals (as functions of temperature and concentrations) it is necessary to find at the first stage of the experiment, the variations of which of the measured quantities are the quickest. The measuring cycle quantization time should be chosen shorter by an order of magnitude. The results of measurements obtained with such assumptions allow to find, with the numerical methods, the basic parameters of time periodicity of the processes (spectral analysis), or to approximate them with the apperiodic functions (polynomials). The typical scientific measuring data processing software packages make it also possible to study mutual correlations between the magnitudes measured in the experiment.

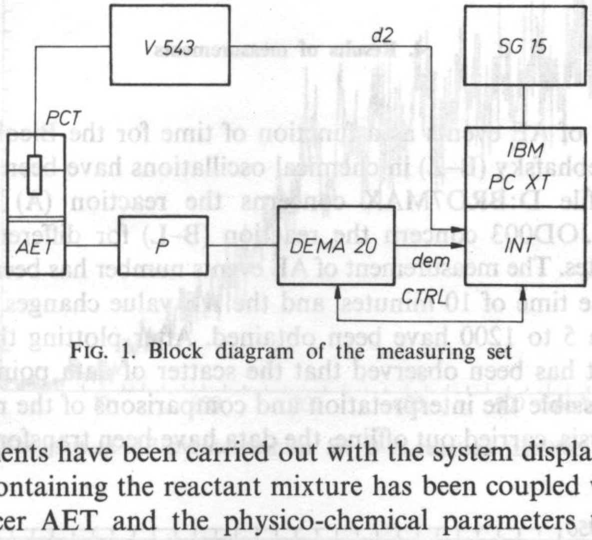

FIG. 1. Block diagram of the measuring set

The measurements have been carried out with the system displayed in the Fig. 1. The glass vessel containing the reactant mixture has been coupled with the acoustic emission transducer AET and the physico-chemical parameters transducer PCT, which co-operates with the numerical voltage or resistance meter, type MERATRONIK V 543. The AET transducer co-operates with the DEMA 20 analyzer through preamplifier P. Both measuring devices have 5–digit numerical outputs in the BCD code and a set of control signals. As an output, the three data blocks are obtained:

dem – block of data on the number of AE events counted in the intervals of 0.1, 1 or 10 s;

d2 – block of data on the physical quantity defined by the type of the PCT transducer, which varies much slower then the AE and is measured at the time of transmission of DEM data;

CTRL – block of the signals which control the cycle of transmission, dependent in time on the signals which control DEM; these signals, in turn, are software controlled by the *I/O* parallel interface of the IBM PC/XT. The parallel interface card, designed and manufactured specially for this purpose, enables simultaneous transmission of 12 bytes of data and 2 bytes of control signals in both directions.

The real-time process of measuring and storing the data during the experiment is realized by the program DEMASCII, which contains the following functional blocks:

1. Automatic measurement and loading the data to the operating memory.
2. Plotting the graph on a parameter-time or parameter-parameter plane.
3. Printout of the plot in the graphic mode.
4. Storing the data as a binary disk file with a chosen name.
5. Reading the data from the disk file to the memory buffer.
6. Conversion of the binary data sers to the ASCII code with separators between data and writing such strings with a name to the disk file.

4. Results of measurements

The numbers of AE events as a function of time for the Bieołusow–Żabotyński (A) and Bray–Liebhafsky (B–Ż) in chemical oscillations have been displayed in Figs. 2–8. The data file D:BRO7MAX concerns the reaction (A) whereas the files D:JOD103 and JOD003 concern the reaction (B–L) for different initial concentrations of substrates. The measurement of AE events number has been carried out every second during the time of 10 minutes, and the AE value changes from 5 to 400 for iodates and from 5 to 1200 have been obtained. After plotting the distributions of measured data, it has been observed that the scatter of data points was very large, what made impossible the interpretation and comparisons of the results. In the next stage of the analysis, carried out offline, the data have been transformed to the ASCII

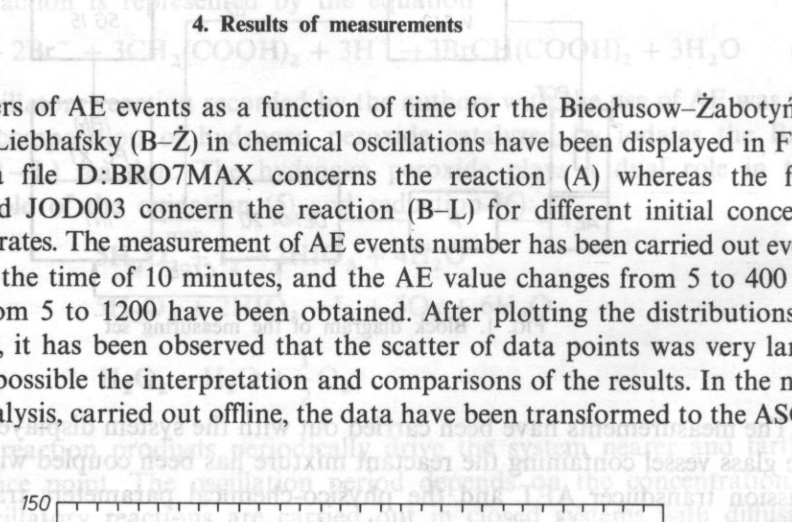

FIG. 2. The plot of AE events number for B–L reaction (D:JOD103)

code and subjected to some numerical processing. In the Figs. 2 and 3 the graphs of numbers of AE events for the data D:JOD103 and D:BRO7MAX have been shown. The plots were obtained by connecting the subsequent data points with sectors. The general AE increase tendency in time can be observed; the differences consist in that for bromium the AE increase is quicker and the oscillations take place after 5 minutes. In order to discriminate the periodical AE changes the moving average

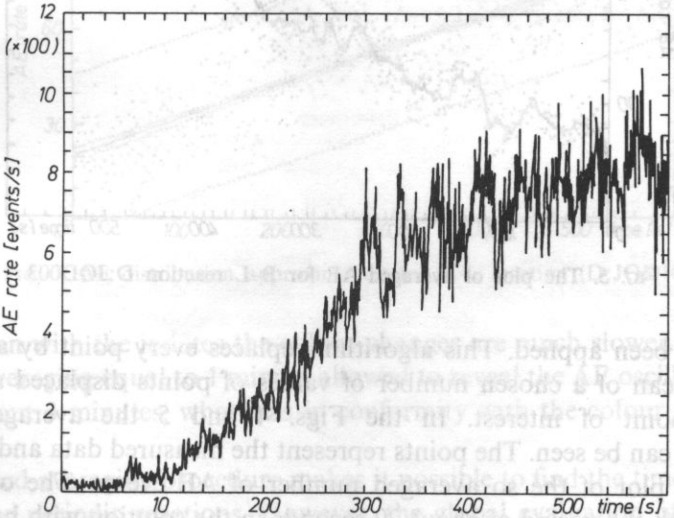

FIG. 3. The plot of AE events number for B–Ż reaction (D:BRO7MAX)

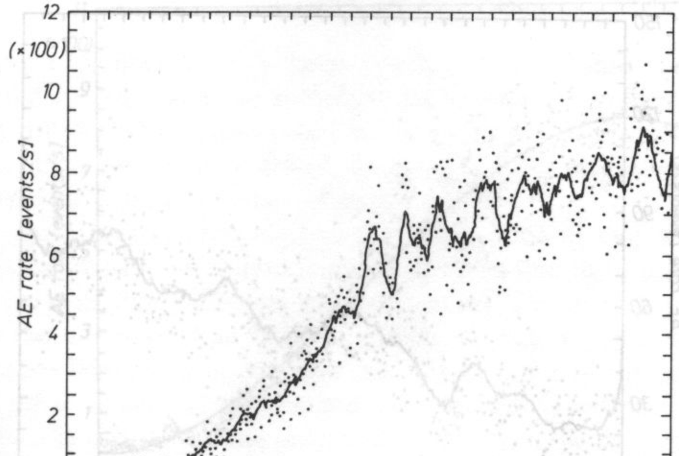

FIG. 4. The plot of averaged AE for B–Ż reaction (D:BRO7MAX)

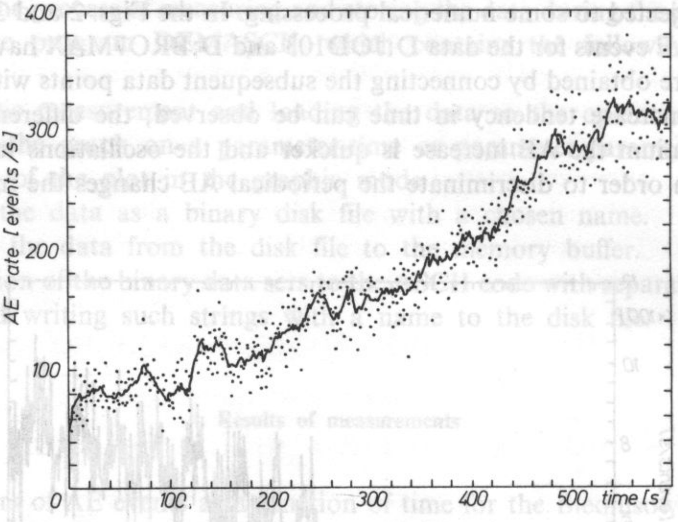

FIG. 5. The plot of averaged AE for B–L reaction D:JOD003

algorithm has been applied. This algorithm replaces every point by a point which value is the mean of a chosen number of values of points displaced symmetrically around the point of interest. In the Figs. 4 and 5 the averaged results of measurements can be seen. The points represent the measured data and the solid line represents the plot of the so averaged number of AE events. The observation of oscillations with the period of about 20 seconds in the solution with bromates takes place simultaneously with the emergence of periodic change of the solution colour.

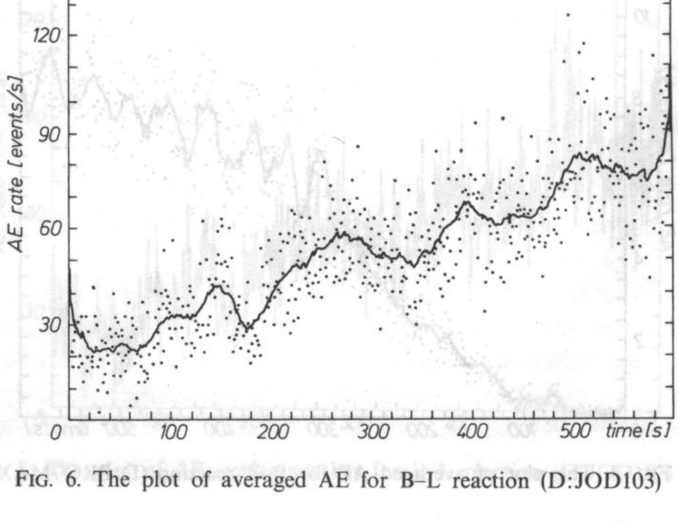

FIG. 6. The plot of averaged AE for B–L reaction (D:JOD103)

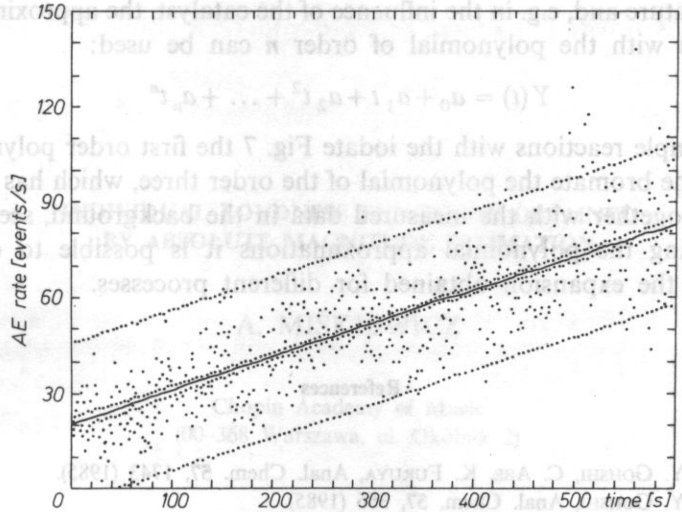

FIG. 7. AE distribution approximation for B–L reaction (D:JOD103)

In the solution with the iodates the colour changes are much slower. Application of the time of averaging equal to 1 minute allowed to reveal the AE oscillations with the period of about 3 minutes, what was in conformity with the colour changes period (Fig. 6).

The applied averaging procedure makes it possible to find the time parameters of the AE in the periodic reactions. However, the global evaluation of the process is difficult. To enable the comparison of various experiments which differ in concent-

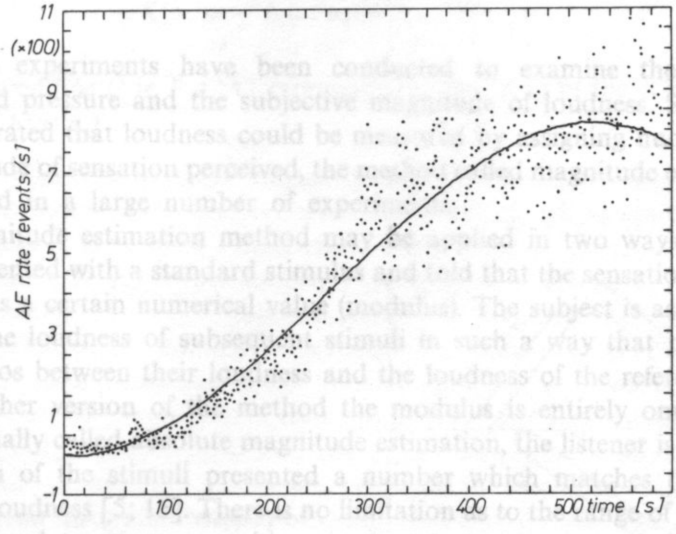

FIG. 8. AE distribution approximation for B–Z reaction (D:BRO7MAX)

ration, temperature and, e.g. in the influence of the catalyst, the approximation of the AE (t) process with the polynomial of order n can be used:

$$Y(t) = a_0 + a_1 t + a_2 t^2 + \ldots + a_n t^n$$

In the example reactions with the iodate Fig. 7 the first order polynomial is the best, and for the bromate the polynomial of the order three, which has been plotted in the Fig. 8 together with the measured data in the background, seems the most expedient. Using the polynomial approximations it is possible to compare the coefficients of the expansion obtained for different processes.

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Received on March 20, 1989