

SCIENTIFIC PAPERS  
OF THE UNIVERSITY OF PARDUBICE  
Series A  
Faculty of Chemical Technology  
4 (1998)

**DETERMINATION OF RATE CONSTANTS  
OF CHEMICAL REACTIONS  
BY MEANS OF MEASURED TIME BEHAVIOUR  
OF ABSORBANCE**

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Received January 7, 1998

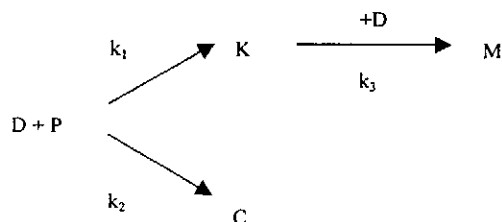
*The calculation procedures of reaction rate constants and absorption coefficients in systems giving coloured products are described. The calculated values are compared with the experimental ones.*

### **Introduction**

In our previous works [1–7] we studied the reaction of diazotized isomers of aminobenzenesulphonic acid (D) and 8-amino-1-naphthol-3,6-disulphonic acid (P)

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The corresponding scheme was solved with the help of the simulation program PPSST [7]. The dependences of concentration vs. time of some components of system with chosen  $k_1$ ,  $k_2$ ,  $k_3$  values were computed. The calculated functions were compared graphically with the measured ones. The best fitted parameters  $k_1$ ,  $k_2$ ,  $k_3$  to these courses were taken as the solution.

### Theoretical and Methods

The Integrated Environment (IE) software was employed with determination of the rate constants as well. The principles of IE are described in Ref. [6]. It enables transformation of any mathematical model (system of kinetic differential equations with initial conditions) into a model of simulation with help of editor. It is possible to use 50 differential equations and 20 rate constants.

For the solution to the problem which is described in this publication, the IE software was transformed into special subprogram CHEMI [8]. We give its parts which are necessary for solution to such a problem.

Let us start from the approved reaction scheme (1) (see Refs [1–6]) which has been completed by the decomposition of component D: ( $D \xrightarrow{k_4}$  products of the decomposition)

The new mathematical model (Model 1) reads as follows

$$\frac{d[M]}{dt} = k_3[D][K]$$

$$\frac{d[K]}{dt} = k_1[D][P] - k_3[D][K]$$

$$\frac{d[C]}{dt} = k_2[D][P]$$

$$\frac{d[D]}{dt} = -k_2[D][P] - k_1[D][P] - k_3[D][K] - k_4[D]$$

$$\frac{d[P]}{dt} = -k_1[D][P] - k_2[D][P]$$

with initial concentrations  $[P]_{t=0}$ ;  $[D]_{t=0}$ ;  $[K]_{t=0} = [M]_{t=0} = [C]_{t=0} = 0$ .

In visible region only components K, C, M absorb and the theoretical absorbance *ABS* is defined

$$ABS = \varepsilon_K l [K] + \varepsilon_C l [C] + \varepsilon_M l [M] \quad (1)$$

where  $\varepsilon_K$ ;  $\varepsilon_C$ ;  $\varepsilon_M$  are absorbance coefficients (unknown), *l* is pathlength, [K], [C], [M] are concentrations of K, C, M in time (*t*) (unknown as well).

We have the experimental dependence *ABSE* vs. *t* at our disposal. Determination of all the unknown constants is carried out by means of program CHEMI. It makes it possible to establish the differential equation whose solution approximates the time behaviour of the measured absorbance values (Eq. (2))

$$\begin{aligned} \frac{d[ABS]}{dt} = & KONI \cdot ABS^2 + KON2 \cdot ABS + KON3 - \\ & - KON4 \cdot \exp[-KON5 \cdot t] \end{aligned} \quad (2)$$

The constants *KONI* through *KON5* in Eq. (2) were established by minimization of the following criterion

$$\frac{100}{m} \sum_{j=1}^m \frac{|(ABSE_j - ABS_j)|}{|ABSE_j|} \rightarrow 0 \quad (3)$$

where *ABSE<sub>j</sub>* is measured absorbance, *ABS<sub>j</sub>* is theoretical absorbance, *m* is the number of *ABSE*, and *j* = (1, 2, ..., *m*) is the *j*-th measurement.

The minimization of criterion (3) (which is function of constants *KONI* through *KON5*) was executed by the program CHEMI. The result was the constants *KONI* through *KON5*, which were introduced into Eq. (2) to give Eq. (4)

$$\begin{aligned} \frac{d[ABS]}{dt} = & KONI (\varepsilon_K l [K] + \varepsilon_C l [C] + \varepsilon_M l [M])^2 + KON2 (\varepsilon_K l [K] + \\ & + \varepsilon_C l [C] + \varepsilon_M l [M]) + KON3 - KON4 \exp(-KON5 \cdot t) \end{aligned} \quad (4)$$

In Eq. (4) the constants  $KON1$  through  $KON5$  are already known;  $[K]$ ,  $[C]$ ,  $[M]$  are concentrations which must correspond to MODEL 1. By combining of Eq. (4) with MODEL 1 we get an enlarged model in which the relationship between the time behaviour of the absorbance and the time behaviour of the concentration of the components present in the reaction is comprised. The solution to the enlarged model depends on the rate constants  $k_1, k_2, k_3$  and absorbance coefficients  $\epsilon_K, \epsilon_C, \epsilon_M$ . Their values are calculated in the limits by the minimization of criterion (3) in which  $ABS$  is the solution of Eq. (4). This calculation was carried out by the program CHEMI again.

## Experimental

The reactions of 8-amino-1-naphthol-3,6-disulphonic acid with the following diazonium salts were described in the papers indicated

- diazotized 2-amino-1,4-benzenedisulphonic acid [1,2]
- diazotized 4-aminobenzenesulphonic acid [3]
- diazotized 2-aminobenzenesulphonic acid [4]
- diazotized 3-aminobenzenesulphonic acid [5]

In addition, we present the reaction of 8-amino-1-naphthol-3,6-disulphonic acid (P) with diazotized 2-amino-1,5-naphthalenedisulphonic acid completed by the decomposition of  $D_1$ .

The absorption-time dependence was followed at  $\lambda = 520, 620, 626$  or  $630$  nm because the individual products differ in colour: M is blue, K and C are red. The ratio of initial concentrations  $[D]_{t=0}/[P]_{t=0} \equiv n$  was held at  $n = 1$  or  $n = 2$  according to the rate of formation of products and to the absorption coefficients.

## Chemicals

All the chemicals were purified as described in Refs [1–5]. Adjustment of stock solutions, estimation of concentrations, preparation of diazonium salts and buffer solutions are described in Refs [1–5] as well. In addition, the reaction between diazotized 2-amino-1,5-naphthalenedisulphonic acid ( $D_1$ ) and 8-amino-1-naphthol-3,6-disulphonic acid (P) was studied. Component  $D_1$  was purified by repeated recrystallization from water and filtration through char coal. The product was washed with cold water and dried in air. By elemental analysis, the product contains 85.56 % acid  $D_1$ . The same content was found by titration method with diazotized *p*-nitroaniline. For kinetic experiments,  $0.05 \text{ mol l}^{-1}$  stock solution of  $D_1$  in  $0.1 \text{ mol l}^{-1}$  HCl was prepared.

## Apparatus and Procedures

The formation of coloured products was monitored with the help of a Specol 11 in buffer solutions at pH = 4 or pH = 5 and  $T = 10\text{ }^{\circ}\text{C}$ ,  $25\text{ }^{\circ}\text{C}$  and  $40\text{ }^{\circ}\text{C}$ . The absorbance was measured at definite time intervals at wavelength  $\lambda = 520, 620$  and  $626\text{ nm}$ . The procedure is described in Refs [1–5]. The kinetics of formation of M from P and  $D_1$  was measured as follows: 1 ml  $0.015\text{ mol l}^{-1}$  solution P was added to 25 ml buffer (pH 5) at  $25\text{ }^{\circ}\text{C}$ , and 0.6 ml  $0.05\text{ mol l}^{-1}$  solution  $D_1$  was added thereto at the time  $t = 0$ , whereafter the absorbance was measured at definite time intervals at  $\lambda_{max}$  of product M (630 nm).

## Computing Procedure in CHEMI

As an example we present the process of computing. We chose the reaction between diazotized 2-amino-1,5-naphthalenedisulphonic acid ( $D_1$ ) and 8-amino-1-naphthol-3,6-disulphonic acid (P). The time behaviour of absorbance was monitored. The results of the minimization of the criterion (3) are constants

$$\begin{aligned}KON1 &= 4.946 \times 10^{-6} & KON4 &= 1.001 \times 10^{-8} \\KON2 &= -5.747 \times 10^{-3} & KON5 &= 1.001 \times 10^{-7} \\KON3 &= 1.271 \times 10^{-1} & \text{The average deviation} &= 1.36\%\end{aligned}$$

The limits for the rate constants and for the absorbance coefficients are given in Table I.

Tab. I Constants and interval

Constants	Interval	Absorb. coefficients, $\text{l mol}^{-1}\text{ cm}^{-1}$	Interval
$k_1, \text{l mol}^{-1}\text{ min}^{-1}$	10 – 50	$\epsilon_K$	0
$k_2, \text{l mol}^{-1}\text{ min}^{-1}$	200 – 850	$\epsilon_C$	0
$k_3, \text{l mol}^{-1}\text{ min}^{-1}$	1 – 20	$\epsilon_M$	20000 – 70000
$k_4, \text{min}^{-1}$	0.001 – 0.01		

The absorbance coefficients  $\epsilon_C, \epsilon_K$  are negligible because only M absorbs at  $\lambda = 630\text{ nm}$ .

Values of the constants and the coefficients were calculated by means of the minimization of criterion (3). This calculation was carried out by the program CHEMI again. The results are given in Table II.

For easier comparison of the results the values of measured and computed absorbance are given in Table III.

Tab. II Results of computation

Constants	Values of constants	Absorb. coefficients, $\text{l mol}^{-1} \text{cm}^{-1}$	Values of absorb. coefficients
$k_1, \text{l mol}^{-1} \text{min}^{-1}$	20.75	$\epsilon_K$	0
$k_2, \text{l mol}^{-1} \text{min}^{-1}$	25.0	$\epsilon_C$	0
$k_3, \text{l mol}^{-1} \text{min}^{-1}$	10.0	$\epsilon_M$	31250
$k_4, \text{min}^{-1}$	0.0024		

The average deviation  $\sigma = 1.9$

Tab. III Comparison of absorbance

$t, \text{min}$	$ABS_{\text{calculated}}$	$ABS_{\text{measured}}$	$t, \text{min}$	$ABS_{\text{calculated}}$	$ABS_{\text{measured}}$
0	0	0	195	0.608	0.606
15	0.073	0.065	210	0.624	0.625
30	0.140	0.135	225	0.644	0.642
45	0.202	0.195	240	0.664	0.659
60	0.258	0.259	255	0.684	0.682
75	0.310	0.309	270	0.704	0.695
90	0.358	0.359	285	0.716	0.718
105	0.400	0.402	300	0.732	0.728
120	0.440	0.443	315	0.748	0.747
135	0.480	0.482	330	0.760	0.755
150	0.512	0.515	345	0.768	0.770
165	0.544	0.555	360	0.780	0.780
180	0.572	0.581			

In Figs 1 – 5 we present the calculated concentration-time dependences with the calculated rate constants. Figure 6 presents the absorbance-time dependence of the same reaction. Comparison of the experimental values with the calculated ones showed that they are nearly identical.

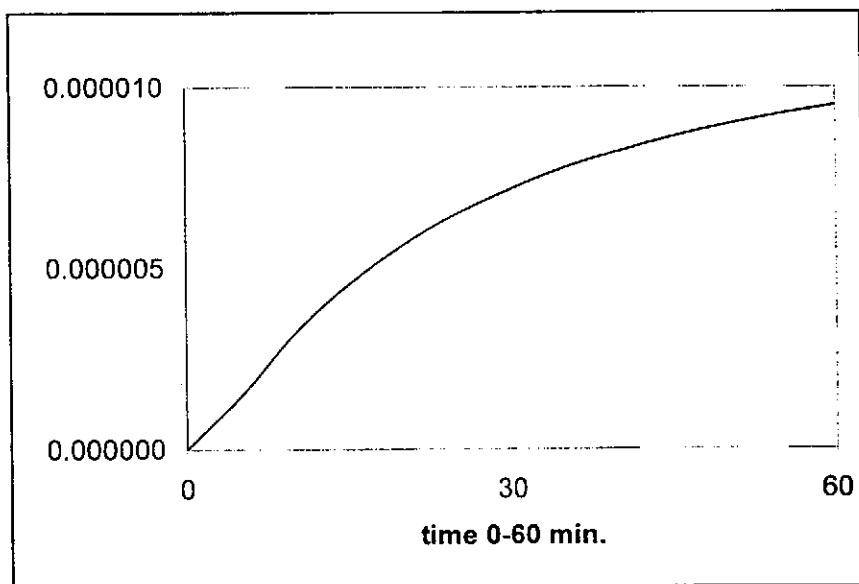


Fig. 1 The time dependence of M concentration

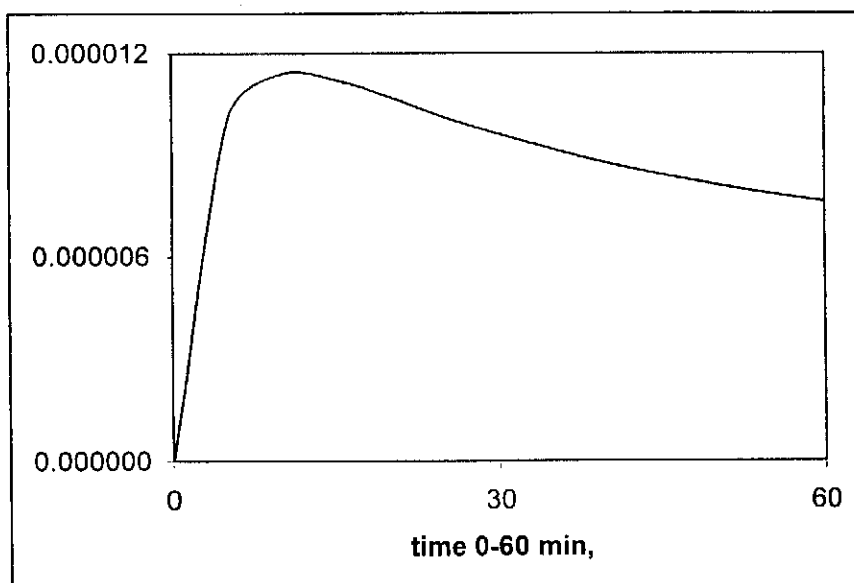


Fig. 2 The time dependence of K concentration

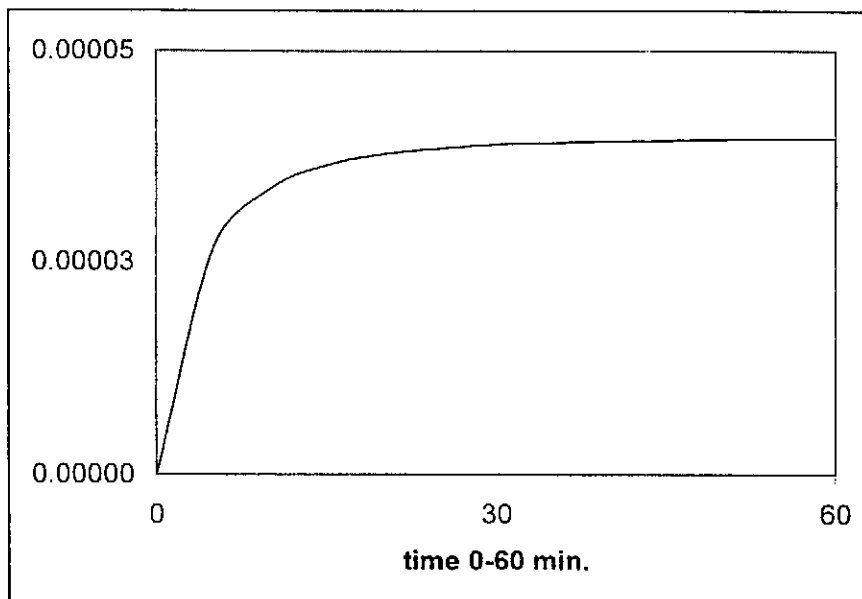


Fig. 3 The time dependence of C concentration

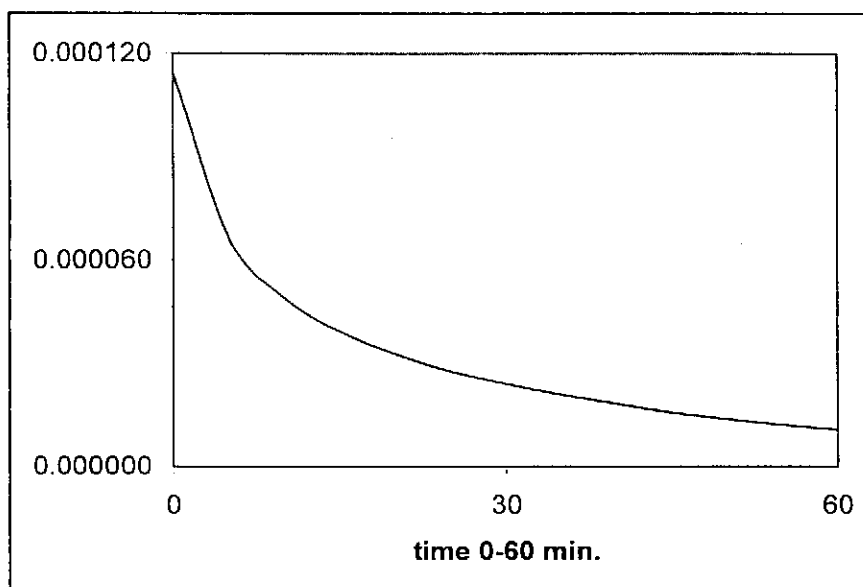


Fig. 4 The time dependence of D concentration



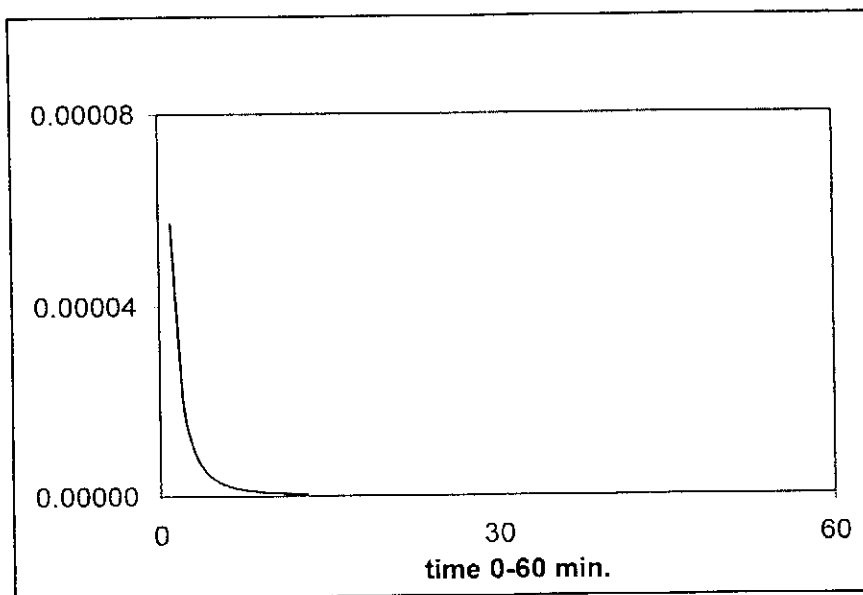


Fig. 5 The time dependence of P concentration

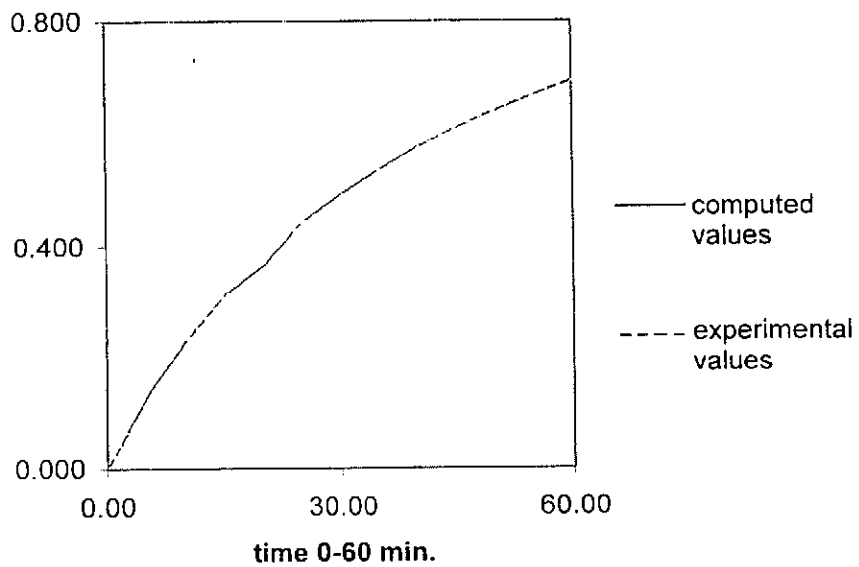


Fig. 6 The calculated and experimental absorbance

## Results

The comparison of values of reaction constants determined experimentally with the calculated constants (programs PPSSS, IE and CHEMI) is given in Tab. IV – Tab. VIII. In the case of program PPSSS we compared the experimental and calculated values of concentration-time courses. Programs IE and CHEMI calculated the values of rate constants.

Tab. IV Values of rate constants of reaction between diazotized 2-amino-1,4-benzenedisulphonic acid [1,2] and component P.  $[P]_{t=0} = 2.403 \times 10^{-5} \text{ mol l}^{-1}$ ;  $n = 1$ ;  $\lambda = 626 \text{ nm}$ ;  $\text{pH} = 4$ ;  $T = 10 \text{ }^\circ\text{C}$

	Experimental values	IE program	CHEMI program
$k_1, \text{ l mol}^{-1} \text{ min}^{-1}$	55.54	60.0	55.54
$k_2, \text{ l mol}^{-1} \text{ min}^{-1}$	11.22	9.4	11.20
$k_3, \text{ l mol}^{-1} \text{ min}^{-1}$	1.58	1.9	1.66
$\epsilon_M^{626}, \text{ l mol}^{-1} \text{ cm}^{-1}$	32500		38000
$\sigma, \%$		4.6	5.10

Experimental values were confirmed by program PPSSS

Tab. V Values of rate constants of reaction between diazotized 4-aminobenzenesulphonic acid [3] and component P.  $n = 2$ ;  $\text{pH} = 4$ ;  $T = 10 \text{ }^\circ\text{C}$ . Part A

	Experiment	PPSSS	IE
$k_1, \text{ l mol}^{-1} \text{ min}^{-1}$	$343 \pm 11$	values confirmed	349.7
$k_2, \text{ l mol}^{-1} \text{ min}^{-1}$	$857 \pm 11$	values confirmed	855.4
$k_3, \text{ l mol}^{-1} \text{ min}^{-1}$		137.5	149.2
$\epsilon_M^{620}, \text{ l mol}^{-1} \text{ cm}^{-1}$			41000
$\sigma, \%$			9.04

In the experiment with  $\lambda = 520$  it was found:  $\epsilon_K = 4.0 \times 10^4$ ;  $\epsilon_C = 2.665 \times 10^4$ ;  $\epsilon_M = 2.001 \times 10^4$

## Discussion

We consider the determination of constants *KON1* through *KON5* in Eq. (2) as the most important procedure in computing. The average deviation should be as small as possible. This value influences the next procedure—the determination of rate

Tab. V Values of rate constants of reaction between diazotized 4-aminobenzenesulphonic acid [3] and component P.  $n = 2$ ; pH = 4;  $T = 10$  °C. Part B

	CHEMI		
	$[P]_0 = 1.45 \times 10^{-5}$ , mol l <sup>-1</sup>	$[P]_0 = 5.72 \times 10^{-5}$ , mol l <sup>-1</sup>	$[P]_0 = 5.72 \times 10^{-5}$ , mol l <sup>-1</sup>
	$\lambda = 520$ nm	$\lambda = 620$ nm	$\lambda = 620$ nm <sup>1)</sup>
$k_1$ , l mol <sup>-1</sup> min <sup>-1</sup>	350	350	800
$k_2$ , l mol <sup>-1</sup> min <sup>-1</sup>	857	850	1850
$k_3$ , l mol <sup>-1</sup> min <sup>-1</sup>	120	140	550
$k_4$ , min <sup>-1</sup>			0.0249
$\epsilon_M^{620}$ , l mol <sup>-1</sup> cm <sup>-1</sup>		37560	35000
$\sigma$ , %	1.18	3.05	0.99

<sup>1)</sup>  $T = 40$  °C, the decomposition of D<sub>1</sub> takes place

Tab. VI Rate constants of reaction between diazotized 2-aminobenzenesulphonic acid [4] and component P.  $n = 2$ ;  $T = 10$ ; pH = 4;  $[P]_0 = 1.775 \times 10^{-3}$  mol l<sup>-1</sup>

	Experiment	PPSSS	IE	CHEMI
$k_1$ , l mol <sup>-1</sup> min <sup>-1</sup>	8.65	76	70.20	73.95
$k_2$ , l mol <sup>-1</sup> min <sup>-1</sup>	41.35	44	49.97	35.00
$k_3$ , l mol <sup>-1</sup> min <sup>-1</sup>	~1.5	3.5	3.12	6.74
$\epsilon_M^{620}$ , l mol <sup>-1</sup> cm <sup>-1</sup>	53400 ± 3300	confirmed 53400	confirmed 53500	75000
$\sigma$ , %			6.99	0.96

Tab. VII Rate constants of reaction between diazotized 3-aminobenzenesulphonic acid [5] and component P.  $n = 2$ ;  $T = 10$ ; pH = 4;  $[P]_0 = 8.86 \times 10^{-3}$  mol l<sup>-1</sup>

	Experiment	PPSSS	IE	CHEMI
$k_1$ , l mol <sup>-1</sup> min <sup>-1</sup>	79.43 ± 3.97	94	85.31	80
$k_2$ , l mol <sup>-1</sup> min <sup>-1</sup>	1461.5 ± 69.7	1455	1376.9	1405
$k_3$ , l mol <sup>-1</sup> min <sup>-1</sup>	127.39 ± 2.84	137	142.5	142.6
$\epsilon_M^{620}$ , l mol <sup>-1</sup> cm <sup>-1</sup>	1.588 × 10 <sup>5</sup> ± 3210			1.749 × 10 <sup>5</sup>
$\sigma$ , %			4.97	0.79

Tab. VIII Rate constants of reaction between diazotized 2-amino-1,5-naphthalenedisulphonic acid and component P.  $T = 25$ ;  $\text{pH} = 5$ ;  $\lambda = 630 \text{ nm}$

	Experiment	CHEMI	
		$[\text{P}]_0 = 1.06 \times 10^{-3} \text{ mol l}^{-1}$	$[\text{P}]_0 = 5.64 \times 10^{-5} \text{ mol l}^{-1}$
$k_1, \text{ l mol}^{-1} \text{ min}^{-1}$		18.24	20.75
$k_2, \text{ l mol}^{-1} \text{ min}^{-1}$		25.0	25.0
$k_3, \text{ l mol}^{-1} \text{ min}^{-1}$		9.97	10.0
$k_4, \text{ min}^{-1}$	0.0023	0.0034	0.0024
$\epsilon_M^{630}, \text{ l mol}^{-1} \text{ cm}^{-1}$		$6.25 \times 10^4$	$6.25 \times 10^4$
$\sigma, \%$		0.34	1.9

Two parallel experiments were carried out. All the absorbance values were monitored 3 times. For computation the mean value was taken

constants. We consider the comparison of the measured values and computed values of absorbances for the main criterion of accuracy.

There is a possibility to solve any system described by 50 differential equations with 20 rate constants at most. The calculation lasts only few minutes and it is possible to modify the reaction scheme quickly. It was not necessary to know the approximate values of rate constants. The first approximation was carried out in a wide interval with great average deviation. The intervals were stepwise contracted till the deviation reached the end value.

## Conclusion

Since we are not able to measure the concentrations of the reactions experimentally, the simulation on computer enables us to provide it for any type of reaction-kinetic scheme. We are convinced that the research of the reaction kinetics should continue by experimental works and parallel simulation on computer. If the experimental and theoretical results of the corresponding parts of research are in agreement, they should be considered satisfactory.

## References

1. Plocek J., Dlask V.: *Dyes and Pigments* **26**, 307 (1994).
2. Dlask V., Plocek J.: *Dyes and Pigments* **27**, 71 (1995)
3. Dlask V., Plocek J., Královský J.: *Dyes and Pigments* **27**, 163 (1995).

4. Dlask V., Plocek J., Královský J., Němcová A.: *Dyes and Pigments* **28**, 165 (1995).
5. Dlask V., Plocek J., Královský J., Němcová A.: *Dyes and Pigments* **30**, 253 (1995).
6. Němcová A., Plocek J., Dlask V.: *Sci. Pap. Univ. Pardubice, Ser. A* **2**, 103 (1996).
7. FEL Faculty VÚT Brno, Dept. of Computers: PPSSS program.
8. FEL Faculty VÚT Brno, Dept. of Computers: CHEMI - Program for simulation of Chemical Reaction Kinetics (1995).