

ON THE EXTENSION OF THE CONCEPT OF THE FOUR STAGE MECHANISM. II. APPLICATION IN THE ANALYSIS OF AN EXPERIMENTAL KINETIC CURVE

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The authors carried out the kinetic analysis of an experiment group of the thermal decomposition of the sulphuric oxychloride. Having established the system of rate equations of the reaction the way is illustrated, in which the repeated integration of the rate equations with the variation of the rate constants as parameters leads to significant results; explaining on the one hand the kinetics of the process all along the whole reaction period, determining on the other hand the values of the rate constants in a very sharp splitting. By a number of calculated kinetic curves the way is presented in which the variation of the parameters leads to a better and better approach of experiments. The results are compared with the statements of the previous investigations, and the reason of discrepancies is discussed as well.

In the first part of the paper [1] the system of rate equations was stated, which expresses the kinetics of the thermal decomposition of the sulphuric oxychloride. Owing to the great chain length the contribution of the rupturing reactions in the formation of the end product molecules SO_2 and Cl_2 can be regarded negligible, thus equation (8) of the first part expresses the agreement of the rates $\frac{d(\text{SO}_2)}{dt}$ and $\frac{d(\text{Cl}_2)}{dt}$, consequently $(\text{SO}_2) = (\text{Cl}_2) = c_0 - c$ can be taken, where c_0 denotes the initial concentration of the sulphuric oxychloride, thus the system can be written in the following form:

$$\frac{dn}{dt} = 2k_1c - \frac{k_6\{k_3(c_0 - c) + k_4(2c_0 - c)\} + k_7\{k_2c + k_5(c_0 - c)(2c_0 - c)\}}{\{k_3(c_0 - c) + k_4(2c_0 - c)\} + \{k_2c + k_5(c_0 - c)(2c_0 - c)\}} n, \quad (1)$$

$$\frac{dc}{dt} = \frac{k_2c\{k_3(c_0 - c) + k_4(2c_0 - c)\} - k_5(c_0 - c)\{k_2c + k_5(c_0 - c)(2c_0 - c)\}}{\{k_3(c_0 - c) + k_4(2c_0 - c)\} + \{k_2c + k_5(c_0 - c)(2c_0 - c)\}} n. \quad (2)$$

To be able to integrate this system by means of numerical methods it is advisable to introduce a system of new variables by a suitable transformation, which renders uniform the range of their variation. According to the experiences of the first calculations in the procedure the transformation

$$\frac{c}{c_0} = x, \quad \frac{k_1 n}{c_0} = u \quad \text{and} \quad c_0 t = \tau$$

was found suitable (for units mol, lit and sec). Substituting these variables into equations (1) and (2) one gets:

$$\frac{du}{d\tau} = \frac{2k_1k_4}{c_0} x - \frac{\frac{k_6}{c_0} \left\{ \frac{k_3}{k_4} (1-x) + (2-x) \right\} + \frac{k_7}{c_0} \left\{ \frac{k_2}{k_4} x + \frac{k_5}{k_4} c_0 (1-x)(2-x) \right\}}{\left\{ \frac{k_3}{k_4} (1-x) + (2-x) \right\} + \left\{ \frac{k_2}{k_4} x + \frac{k_5}{k_4} c_0 (1-x)(2-x) \right\}} u, \quad (3)$$

$$\frac{dx}{d\tau} = \frac{\frac{k_2}{k_4} x \left\{ \frac{k_3}{k_4} (1-x) + (2-x) \right\} - \frac{k_3}{k_4} (1-x) \left\{ \frac{k_2}{k_4} x + \frac{k_5}{k_4} c_0 (1-x)(2-x) \right\}}{\left\{ \frac{k_3}{k_4} (1-x) + (2-x) \right\} + \left\{ \frac{k_2}{k_4} x + \frac{k_5}{k_4} c_0 (1-x)(2-x) \right\}} u. \quad (4)$$

For better arrangement in the sequence of the single calculations on machine, as well as to reduce their number, a further rearrangement of the system is advantageous, namely to write the system by separating the expression

$$\alpha = \frac{\frac{k_3}{k_4} (1-x) + (2-x)}{\left\{ \frac{k_3}{k_4} (1-x) + (2-x) \right\} + \left\{ \frac{k_2}{k_4} x + \frac{k_5}{k_4} c_0 (1-x)(2-x) \right\}},$$

or in a more suitable expanding in terms of $(1-x)$ (verified by the viewpoints of calculation technics)

$$\alpha = \frac{1 + \left(\frac{k_3}{k_4} + 1 \right) (1-x)}{\frac{k_5}{k_4} c_0 (1-x)^2 + \left(1 + \frac{k_3}{k_4} + \frac{k_5}{k_4} c_0 - \frac{k_2}{k_4} \right) (1-x) + \left(1 + \frac{k_2}{k_4} \right)}$$

in the following form:

$$\frac{du}{d\tau} = \frac{2k_1k_4}{c_0} x - \left\{ \frac{k_6}{c_0} \alpha + \frac{k_7}{c_0} (1-\alpha) \right\} u \equiv \frac{2k_1k_4}{c_0} x - \left\{ \frac{k_6 - k_7}{c_0} \alpha + \frac{k_7}{c_0} \right\} u, \quad (5)$$

$$-\frac{dx}{d\tau} = \left\{ \frac{k_2}{k_4} \alpha x - \frac{k_3}{k_4} (1-\alpha)(1-x) \right\} u. \quad (6)$$

This form of the system is very suitable to carry out its numerical integration at given values of its rate constants by the method of RUNGE and KUTTA.

For this purpose the range of the variation of the variable τ expressing the reaction's length of time (a value about 3) will be divided into parts, and the changes Δx and Δu of the variables $x = x(\tau)$ and $u = u(\tau)$ resp. along the single intervals $(\tau, \tau + \Delta\tau)$ of the distribution will be determined by

$$\Delta u = \frac{1}{6} (\Delta u_1 + 2\Delta u_2 + 2\Delta u_3 + \Delta u_4),$$

$$\Delta x = \frac{1}{6} (\Delta x_1 + 2\Delta x_2 + 2\Delta x_3 + \Delta x_4),$$

where the meaning of Δx_i and Δu_i ($i=1, 2, 3, 4$) — denoting the right sides of (5) and (6) for sake of simplicity by $f(x, u)$ and $g(x, u)$ resp. — is given by

$$\begin{aligned}\Delta u_1 &= f(x, u) \Delta \tau, & \Delta x_1 &= -g(x, u) \Delta \tau, \\ \Delta u_2 &= f\left(x + \frac{1}{2} \Delta x_1, u + \frac{1}{2} \Delta u_1\right) \Delta \tau, & \Delta x_2 &= -g\left(x + \frac{1}{2} \Delta x_1, u + \frac{1}{2} \Delta u_1\right) \Delta \tau, \\ \Delta u_3 &= f\left(x + \frac{1}{2} \Delta x_2, u + \frac{1}{2} \Delta u_2\right) \Delta \tau, & \Delta x_3 &= -g\left(x + \frac{1}{2} \Delta x_2, u + \frac{1}{2} \Delta u_2\right) \Delta \tau, \\ \Delta u_4 &= f(x + \Delta x_3, u + \Delta u_3) \Delta \tau, & \Delta x_4 &= -g(x + \Delta x_3, u + \Delta u_3) \Delta \tau.\end{aligned}$$

The beginning of the integration is determined by the initial condition $x_{t=0}=1$ and $u_{t=0}=0$, its continuation by the formulae above. Regarding the choice of the value of $\Delta \tau$ along the range $0 < \tau < 3$, i. e., regarding the density of the distribution there holds the rule that a distribution can be considered suitable, when the result of the approximative integration carried out by its means agrees with that yielded by an other distribution twice as fine — apart from an error negligible in comparison with that of the experiments.

The aim followed by the numerical integration of the system (5) and (6) is to bring into accordance the kinetics of the reaction with its mechanism mentioned in the first part of the paper. Due to the fact that the previous investigations of the reaction did not give all the values of the rate constants by means of the kinetic analysis of the reaction, as a matter of fact they were determined partly by thermodynamical considerations, it seemed suitable to base the following analysis of the process on the statements of the previous studies obtained from the kinetic analysis carried out by the application of the steady state method. As the kinetic analysis mentioned

resulted only in the determination of $\frac{2k_1 k_4}{k_7}$, $\frac{2k_1 k_3 k_5}{k_7 k_2}$, $\frac{k_3 k_6}{k_2 k_7}$, i. e., three complexa of the rate constants, there remained to determine the values of the other constants of the equations (5) and (6) the way connected with the numerical integration of the system of the rate equations varying its constant complexa as parameters, as long as the kinetic curves $x = x(\tau)$ and $-\frac{dx}{d\tau} = w = w(\tau)$

cover the analogous experimental ones. (As the expression $-\frac{dx}{d\tau}$ is proportional to $-\frac{dc}{dt}$ the rate of the reaction, it can be regarded as the reaction rate in a new system of units, thus for sake of simplicity the curve $w = w(\tau)$ will be called also as the rate curve of the process.)

In the following the variation method will be illustrated in comparison with the experiments carried out at the temperature 300°C and at the initial pressure 60 mm Hg ($c_0 = 1,6787 \cdot 10^{-3} \text{ mol/lit}$). Concerning the values of the constant complexa in question the previous investigations of Z. G. SZABÓ and T. BÉRCES [2] furnished the following data as results of the kinetic analysis (for units mol, lit and sec):

$$\frac{2k_1 k_4}{k_7} = 0,691, \quad \frac{2k_1 k_3 k_5}{k_7 k_2} = 174, \quad \frac{k_3 k_6}{k_2 k_7} = 0.20.$$

Besides these three data a further estimation is possible based on the initial slope of the curve $w = w(\tau)$ deducible from the equations (5) and (6) according to the initial conditions in the form

$$\left(\frac{d}{d\tau} \left(-\frac{dx}{d\tau} \right) \right)_{\tau=0} = \frac{2k_1 k_2 k_4}{c_0 (k_2 + k_4)} \quad (7)$$

The comparison with the experiments gives $\frac{2k_1 k_2 k_4}{(k_2 + k_4)c_0} = 4,6$. Based on these informations regarding the values of the rate constant — completed with some statements of BODENSTEIN, LAUNER and WINTER referring to the rate of the elementary reactions [3], [4] — the integration of the system has been begun with the following values:

$$\frac{2k_1 k_4}{c_0} = 4,8; \quad \frac{k_2}{k_4} = 9,2; \quad \frac{k_3}{k_4} = 1,5; \quad \frac{k_5}{k_4} c_0 = 2,8; \quad \frac{k_6}{c_0} = 2,4; \quad \frac{k_7}{c_0} = 3,5$$

and continued with such variations in the system of the parameters, which resulted in the covering of the experimental curve $w = w(\tau)$ by the corresponding calculated one up to the neighborhood of the rate maximum. This introducing section of the procedure is illustrated in Tables I and II and by Fig. 1.

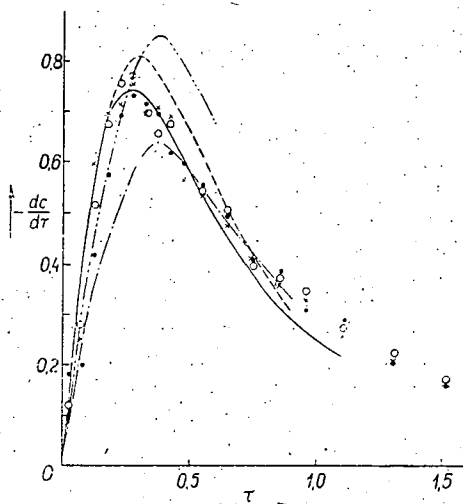


Fig. 1. Comparison of the empirical and calculated kinetic rate curves by plot of the data of Tables I and II.

Experimental data: \circ exp. 35. \times exp. 37. \bullet exp. 38.
Calculated curves: \cdots table II a) $- \cdot -$ table II b)
 — table II c) $- - -$ table II d)

Regarding the viewpoints of the first variations within the system of parameters the equation of SEMENOV [5] expressing the development of the chains

$$n = \frac{n_0}{g} (1 - e^{-gt}) \quad (8)$$

Table I.
 The empirical kinetic curves $x = x(\tau)$ and $w = w(\tau)$ of the experiments
 carried out at $T = 320^\circ \text{C}$ and at the initial pressure
 $p_0 = 60 \text{ mm Hg}$ ($c_0 = 1,6787 \cdot 10^{-3} \text{ mol/lit}$).

τ	exp. 35.		exp. 37.		exp. 38.	
	x	w	x	w	x	w
0,00	1,000		1,000		1,000	
0,05	0,995	0,119	—	—	0,992	0,179
0,10	0,982	0,278	0,986	0,252	0,982	0,199
0,15	0,956	0,516	0,943	0,596	0,961	0,417
0,20	0,922	0,675	0,908	0,695	0,932	0,576
0,25	0,884	0,755	0,872	0,715	0,897	0,695
0,30	0,845	0,774	0,834	0,755	0,860	0,731
0,35	0,810	0,695	0,799	0,695	0,834	0,715
0,40	0,777	0,655	0,763	0,708	0,799	0,695
0,45	0,743	0,675	0,728	0,682	0,768	0,616
0,50	0,710	—	0,701	0,566	0,738	0,596
0,60	0,655	0,546	0,646	0,536	0,682	0,556
0,70	0,604	0,506	0,598	0,477	0,632	0,496
0,80	0,564	0,397	0,557	0,407	0,591	0,407
0,91	0,526	0,377	0,521	0,357	0,552	0,387
1,01	0,491	0,348	0,488	0,328	0,521	0,308
1,21	0,436	0,273	0,436	0,258	0,463	0,288
1,41	0,391	0,223	0,395	0,204	0,422	0,204
1,61	0,357	0,169	0,362	0,164	0,389	0,164
1,81	—	—	—	—	0,358	0,154
1,91	0,320	0,122	0,328	0,113	—	—
2,01	—	—	—	—	0,334	0,119
2,32	0,280	0,099	0,293	0,088	—	—
2,42	—	—	—	—	0,308	0,060
2,72	—	—	0,274	0,048	—	—
2,82	0,278	0,079	—	—	—	—

Table II

The results of the numerical integration carried out at the values of the constant complexa below:

	$\frac{2k_1k_4}{c_0}$	$\frac{k_2}{k_4}$	$\frac{k_3}{k_4}$	$\frac{k_5}{k_4} c_0$	$\frac{k_6}{c_0}$	$\frac{k_7}{c_0}$
a)	6,0	9,2	1,8	2,8	3,2	4,8
b)	6,0	2,5	0,4	2,8	3,2	4,8
c)	10,0	3,0	0,46	2,8	5,3	8,0
d)	9,0	3,0	0,46	2,8	4,0	6,0

(The values of w given in the spaces between the rows of the concentration data denote the average rate of the change of x in the corresponding intervals.)

τ	a)		b)		c)		d)	
	x	w	x	w	x	w	x	w
0,0	1,0000		1,0000		1,0000		1,0000	
0,1		0,4062		0,3207	0,9703	0,2966	0,9719	0,2810
0,2	0,9188		0,9359		0,9065	0,6385	0,9072	0,6475
0,3		0,8021		0,6061	0,8326	0,7389	0,8282	0,7897
0,4	0,7584		0,8147		0,7614	0,7121	0,7496	0,7864
0,5		0,7664		0,5798	0,6982	0,6321	0,6789	0,7071
0,6	0,6051		0,6987		0,6442	0,5398	0,6187	0,6024
0,7				0,4559	0,5987	0,4555		0,4562
0,8			0,6075		0,5604	0,3831	0,5275	
0,9				0,3382	0,5281	0,3234		0,3105
1,0			0,5399		0,5006	0,2751	0,4655	
1,1								0,2176
1,2							0,4220	

presents a very applicable basis (where n_0 is the rate of the creation of the active radicals, g the rate constant of their rupturing reaction regarded as monomolecular). Although in the case studied now the equation (5) expressing the development of the chain differs significantly from that of SEMENOV

$$\frac{dn}{dt} = n_0 - gn \quad (9)$$

involving (8), some comparison is still possible, which enables us to designate the right direction of the variation within the set of the constants $\frac{2k_1k_4}{c_0}$, $\frac{k_6}{c_0}$ and $\frac{k_7}{c_0}$. The basis of this comparison is the correspondence of the

expressions $\left\{ \frac{k_6}{c_0} \alpha + \frac{k_7}{c_0} (1-\alpha) \right\}$ and $\frac{2k_1k_4}{c_0} x$ to the terms g and n_0 of the

SEMENOV's equation. Thus, considering that in equation (8) the decreasing of the term e^{-gt} is responsible for the rate of approaching the stationary state, at first it seems that the place of the rate maximum of the calculated kinetic rate curves $w = w(\tau)$ can be governed by the variation of the constants k_6 and k_7 .

On the other hand the (8)-like expression $u_{\text{stat.}} = \frac{2k_1 k_4}{c_0 g} x$ (where the coefficient of u in (5) is denoted by g) shows that at given values of the other constants the increasing of u in the initial section of the curve is the higher the greater the value of $\frac{2k_1 k_4}{c_0}$ is, consequently it can be said that the increasing of $k_1 k_4$ against k_6 and k_7 results in such kinetics, in which the maximal value of the rate also increases compared with the earlier one. At the same time this behaviour of the expression of $u_{\text{stat.}}$ exerts its effect also along the whole descending section of the rate curve, which is in the neighborhood of the rate maximum similar as explained before, however, it turns to the opposite direction due to the more rapid decreasing of x in the earlier period.

It is natural that the effect of the variation of the parameters appears not quite in such a simple way in the structure of the corresponding kinetic curves, and thus the determination of the subsequent variations can occur more exactly only based on the comparison of the kinetic curves $x = x(\tau)$ and $w = w(\tau)$ with the preceding ones. The explanation of this statement can be given in the circumstance that the further parameters taking place in the procedure, however not discussed hitherto, have no such a definite effect as the previous ones. As these constants playing role in the expressions of α and $(1-\alpha)$ they have the effect of involving some deviations compared with the feature of the above conclusions concerning equation (8) and (9), which deviations, however, have also special characteristics, and enable to carry out refinements in the system of the parameters allowing to govern the procedure in the direction of more exact covering of the experimental kinetic curves by the calculated ones. These very relations are not suitable to be judged correctly by qualitative analysis of equations (5) and (6); within them the right orientation can be based only on the comparison of the different calculated kinetic curves.

The continuation of the procedure in this phase is illustrated in Tables III and IV and by Figures 2 and 3. Table II contains the kinetic curves $x = x(\tau)$ and $w = w(\tau)$ determined at two different system of the parameters, Table IV shows quite detailed the carrying out of the integration at such values of the parameters which resulted in covering of the empirical and calculated data. In this latter the data of the column $x_{\text{contr.}}$ and $u_{\text{contr.}}$ denote the results of the calculations made by the density $\Delta\tau = 0,05$ of the distribution (with the exactness of five decimal ciphers) belonging to the same point of the distribution. They show at any rate the agreement of the two calculations to a degree of error negligible in comparison with that of the experiments. (In the case studied the error of the experiments regarding x is about 1%.) Contemporaneously it can be also stated that the calculated curves and the experimental results are in very good agreement.

Table III

The results of the numerical integration carried out at the values of the parameters below:

	$\frac{2k_1k_4}{c_0}$	$\frac{k_3}{k_4}$	$\frac{k_5}{k_4}$	$\frac{4_3}{k_4} c_0$	$\frac{k_6}{c_0}$	$\frac{k_7}{c_0}$
a)	8,1	2,4	0,16	2,2	3,6	5,5
b)	9,0	2,4	0,16	2,2	4,3	6,6

τ	a)		b)	
	x	w	x	w
0,0	1,0000		1,0000	
0,1	0,9758	0,2425	0,9738	0,2616
0,2	0,9183	0,5753	0,9141	0,5970
0,3	0,8454	0,7287	0,8411	0,7296
0,4	0,7696	0,7580	0,7670	0,7406
0,5	0,6983	0,7131	0,6989	0,6807
0,7	0,5800	0,5913	0,5875	0,5572
0,9	0,4942	0,4292	0,5064	0,4053
1,1	0,4323	0,3093	0,4471	0,2967
1,4	0,3680	0,2142	0,3839	0,2106
1,8	0,3125	0,1387	0,3277	0,1404
2,2	0,2757	0,0927	0,2893	0,0959

Comparing the results of the previous kinetic analysis with those of the present calculations, obtainable from the values of the parameters of the last calculation, it can be seen that they differ fairly from each other. In fact the data of the last calculation give for the values z_1 , z_2 and z_3

$$z_1 = \frac{2k_1k_4}{k_7} = 1,9 \text{ instead of } 0,691; \quad z_2 = \frac{2k_1k_3k_5}{k_2k_7} = 138 \text{ instead of } 174;$$

$$z_3 = \frac{k_3k_6}{k_2k_7} = 0,128 \text{ instead of } 0,20.$$

The discrepancies arise from the divergency of the two methods of the kinetic analysis, as a matter of fact the previous investigations are based on the steady state method taking into account only the rate curve of the reaction in its approximate rate equation representation $w = F(c)$, even this curve only along the descending section of the experimental rate curve, whereas the present analysis is supported by the covering of both kinetic curves of the

Table IV.

The result of the numerical integration at the following values of the parameters:

$$\frac{2k_1 k_4}{c_0} = 9,5; \quad \frac{k_2}{k_3} = 2,7; \quad \frac{k_3}{k_4} = 0,15; \quad \frac{k_5}{k_4} c_0 = 2,2; \quad \frac{k_6}{c_0} = 11,5; \quad \frac{k_7}{c_0} = 5,0.$$

τ	w	x	$x_{\text{contr.}}$	w_{it}	u	$u_{\text{contr.}}$	α
		1,0000	1,00000		0,0000	0,00000	0,2703
	0,0000	1,0000		9,5000	0,4750		0,2703
0,0—	0,3467	0,9827		6,2904	0,3145		0,2748
0,1	0,2287	0,9771		7,2014	0,7201		0,2762
	0,5229			4,4313			
	0,2790			6,8192			
		0,9721	0,97214		0,6819	0,68188	0,2774
	0,4944	0,9474		4,5959	0,9117		0,2835
0,1—	0,6560	0,9393		2,7618	0,8200		0,2855
—0,2	0,5884	0,9133		3,3016	1,0121		0,2915
	0,7182			1,6982			
	0,6169			3,0702			
		0,9104	0,91052		0,9889	0,98939	0,2921
	0,7006	0,8754		1,8267	1,0802		0,2997
0,2—	0,7510	0,8728		0,8110	1,0295		0,3002
—0,3	0,7146	0,8389		1,1352	1,1015		0,3069
	0,7472			0,2647			
	0,7298			0,9973			
		0,8374	0,83753		1,0886	1,08917	0,3072
	0,7377	0,8005		0,3386	1,1055		0,3139
0,3—	0,7273	0,8010		—0,1784	1,0797		0,3138
—0,4	0,7106	0,7663		0,0087	1,0895		0,3194
	0,6940			—0,4296			
	0,7179			—0,0717			
		0,7656	0,76573		1,0814	1,08203	0,3195
	0,6883	0,7312		—0,3796	1,0624		0,3245
0,4—	0,6517	0,7330		—0,6065	1,0511		0,3243
—0,5	0,6462	0,7010		—0,5077	1,0306		0,3285
	0,6097			—0,6941			
	0,6490			—0,5504			
		0,7007	0,70080		1,0264	1,02685	0,3285
	0,6070	0,6704		—0,6670	0,9931		0,3320
0,5—	0,5640	0,6725		—0,7398	0,9894		0,3318
—0,6	0,5636	0,6443		—0,6921	0,9572		0,3347
	0,5233			—0,7476			
	0,5643			—0,7131			

τ	w	x	$x_{\text{contr.}}$	w_{it}	u	$u_{\text{contr.}}$	α
		0,6443	0,64432		0,9551	0,95541	0,3347
	0,5222	0,5921		-0,7325	0,8819		0,3392
0,6—	0,4426	0,6000		-0,7275	0,8823		0,3386
-0,8	0,4490	0,5545		-0,6534	0,8244		0,3417
	0,3855			-0,6853			
	0,4485			-0,6966			
		0,5546	0,55467		0,8158	0,81667	0,3417
	0,3815	0,5165		-0,6222	0,7536		0,3436
0,8—	0,3252	0,5221		-0,5443	0,7614		0,3434
-1,0	0,3327	0,4881		-0,5466	0,7065		0,3456
	0,2863			-0,4826			
	0,3306			-0,5478			
		0,4885	0,48855		0,7062	0,70671	0,3456
	0,2864	0,4599		-0,4767	0,6585		0,3454
1,0—	0,2475	0,4638		-0,4018	0,6660		0,3454
-1,2	0,2530	0,4379		-0,4191	0,6224		0,3458
	0,2201			-0,3509			
	0,2513			-0,4116			
		0,4383	0,43829		0,6239	0,62395	0,3458
	0,2209	0,4052		-0,3580	0,5702		0,3462
1,2—	0,1827	0,4109		-0,2847	0,5812		0,3461
-1,5	0,1896	0,3814		-0,3099	0,5309		0,3462
	0,1570			-0,2259			
	0,1871			-0,2955			
		0,3822	0,38214		0,5352	0,53473	0,3462
	0,1588	0,3584		-0,2495	0,4978		0,3460
1,5—	0,1353	0,3619		-0,2037	0,5046		0,3461
-1,8	0,1391	0,3405		-0,2201	0,4692		0,3458
	0,1188			-0,1659			
	0,1377			-0,2105			
		0,3409	0,34085		0,4721	0,47160	0,3458
	0,1197	0,3170		-0,1831	0,4355		0,3453
1,8—	0,0995	0,3210		-0,1435	0,4434		0,3454
-2,2	0,1032	0,2996		-0,1630	0,4069		0,3449
	0,0855			-0,1005			
	0,1018			-0,1494			
		0,3002	0,30014		0,4123	0,41123	

experiments $x = x(\tau)$ and $w = w(\tau)$ with the solution of the exact rate equations' system derived from the mechanism assumed of the reaction all along the whole reaction period. Due to the differences in the characteristics of the analysing methods the discrepancy can be regarded as expressing the more exactness of the latter method, and the values of α_1 , α_2 and α_3 as refinements of the previous results.

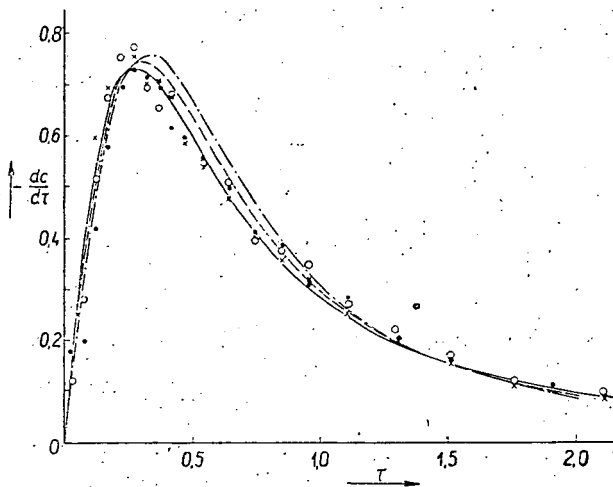


Fig. 2. Comparison of the empirical and calculated kinetic curves $w = w(\tau)$ by plot of the data of Tables I, III and IV.
 Experimental data: \circ exp. 35. \times exp. 37. \bullet exp. 38.
 Calculated curves: $-\cdot-$ table III a) $- - -$ table III b)
 $—$ table IV.

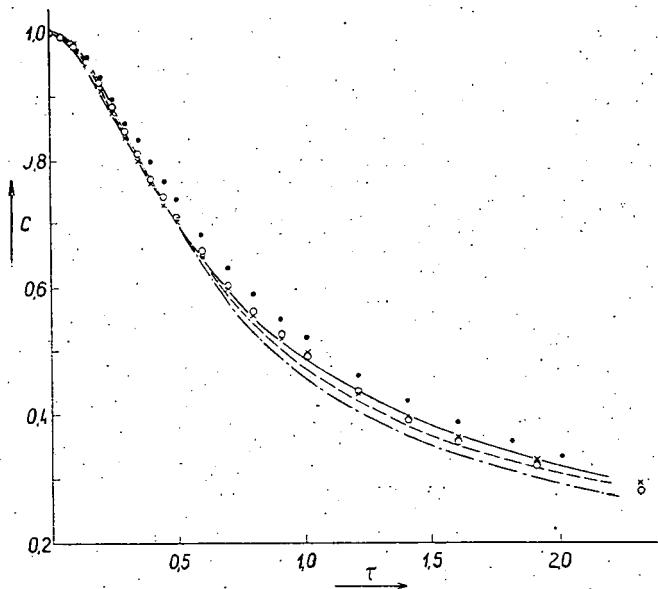


Fig. 3. Comparison of the empirical and calculated kinetic curve $x = x(\tau)$ by plot of the data of Tables I, III and IV.
 Experimental data: \circ exp. 35. \times exp. 37. \bullet exp. 38.
 Calculated curves: $-\cdot-$ table III a) $- - -$ table III b)
 $—$ table IV.

Comparing the results of the recent analysis with that of the earlier one can be stated as follows. It is doubtless that this new method of treatment requires a greater apparatus than the steady state method applied in the previous investigation, at the same time also its results overgrow those of the BODENSTEIN's method. First it leads nearer to the real values of the constants, thus to the concentration of the active radicals. Further it can explain the kinetics of the reaction along both the ascending and descending section of the rate curve. Finally it offers a very good splitting for the seven rate constants determining two of them immediately, the five others split into four simple complexa (against the three complexa α_1 , α_2 and α_3 furnished by the steady state method), thus requires further considerations (of thermodynamical or similar nature) to obtain a total splitting only in the relation of one of the rate constants. The explanation of the kinetics along a wider range and the determination of the rate constants in a sharper splitting can be regarded on the one hand a more effective support of the mechanism, on the other hand its more profound interpretation.

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