A FEEDBACK REACTOR FOR DISCONTINUOUS FEED OF A REACTION COMPONENT WITH SPECTROPHOTOMETRIC INDICATION

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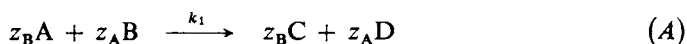*Institute of Chemical Technology, 532 10 Pardubice*

The absorbance-time dependence has been derived for a repeated arbitrary feed of one reaction component into solution of the other component controlled by the feedback. On the basis of the expressions derived, methods have been suggested for determination of the rate constant of irreversible reaction of the IInd order, and they have been experimentally tested on two reactions.

Kinetic studies of reactions in a discontinuous reactor suffer from the drawback that the measurements must be repeated with various concentrations of the starting substances. The method suggested makes it possible to carry out an analogy of such measurements in a single sequence from a certain concentration of the starting substance to its complete exhaustion. The method is analogous to the kinetic titrations[1-3] in which the titrant is added at chosen time intervals or at a constant volume rate[4-7].

The method is based on the following principles: one component is placed in the reactor, and the other component is added thereto gradually in any arbitrary amount, the absorbance of the reaction mixture being followed with time. The second component is added always at such moment when the reaction mixture attains a certain constant absorbance level chosen in advance. Hence this addition is controlled by the reaction course itself by means of a feedback. The method can be used not only for kinetic measurements but also for quantitative analytical purposes. The time course of absorbance of the reaction mixture (the saw-tooth curve) and that of volume amount of the component added (the step-shaped curve) are given schematically in Fig. 1.

THEORETICAL

For the irreversible reaction of the IInd order

$$z_B A + z_A B \xrightarrow{\ k_1\ } z_B C + z_A D \qquad (A)$$

it is

$$C_{A_i} = \frac{b_i - va_i}{(b_i/a_i)\exp\left(\tau_i(b_i - va_i)/b_p\right) - v},$$ (1)

$$v(a_i - C_{A_i}) = b_i - C_{B_i} = v(C_{C_i} - c_i) = C_{D_i} - d_i,$$

where b_p means concentration of the substance B placed in the reactor, a_i, b_i, c_i, d_i stand for the initial concentrations of the compounds A, B, C, D, respectively, $C_{A_i}, C_{B_i}, C_{C_i}, C_{D_i}$ mean the actual concentrations of the substances A, B, C, D, resp. for the i-th addition; $v = z_A/z_B$; $\tau_i = t_B b_p k_1 t_i$ is the dimensionless time of the i-th addition; k_1 is the rate constant of the reaction (A); t_i means the time from the moment of the feed up to the i-th addition.

Presuming the quantity measured to be linearly dependent on concentration (*e.g.* the absorbance at a constant wavelength), it follows:

$$A_i = \sum_j C_{ji} \varkappa_j,$$ (2)

where A_i means the actual absorbance of the *i*-th addition, C_{ji} are the actual concentrations of the compounds A, B, C, D, and $\varkappa_j$ stands for their molar absorption coefficient multiplied by the length of the optical path.

For the initial concentrations a_0, b_0, c_0, d_0, after mixing the volume ΔV_0 of compound A of concentration c_A with the volume V_s of compound B of concentration b_p,
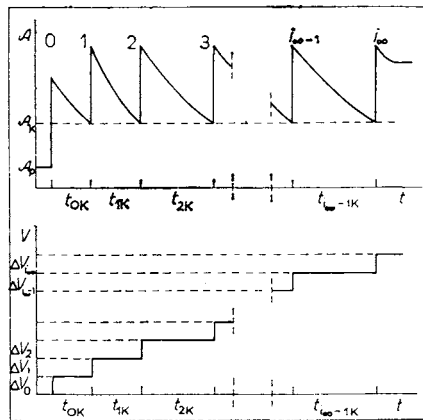

FIG. 1
The time course of the absorbance. A_k the chosen constant absorbance level, A_p the absorbance of the substance charged in the reactor, $t_{0k}, t_{1k}, \ldots, t_{i-1,k}$ — the times between the individual additions, $\Delta V_0, \Delta V_1, \ldots$ $\ldots, \Delta V_i$ volume amounts of the second component injected, i_∞ total number of the additions

we obtain for $i = 0$:

$$a_0 = c_A \, \Delta V_0 / (V_s + \Delta V_0),$$
$$b_0 = b_p V_s / (V_s + \Delta V_0),$$
$$c_0 = d_0 = 0. \tag{3}$$

The reaction course from the moment of mixing for $i = 0$ (the 0-th addition) can be described by the absorbance-time dependence obtained by combination of Eqs (1) and (3) and introduction into Eq. (2):

$$\tau_0 \cdot \frac{b_p V_s - v c_A \, \Delta V_0}{b_p (V_s + \Delta V_0)} = \ln \frac{v c_A \, \Delta V_0}{b_p V_s} \cdot$$

$$\cdot \frac{1 + (v A_0 - b_p(\varkappa_C + v\varkappa_D))/b_p \varkappa_A - (v c_A \, \Delta V_0 / b_p V_s)(1 - A_0 / c_A \varkappa_A)}{(\varkappa_C + v\varkappa_D - v\varkappa_B)/\varkappa_A + (v A_0 - b_p(\varkappa_C + v\varkappa_D))/b_p \varkappa_A - (v c_A \, \Delta V_0 / b_p V_s)((\varkappa_C + v\varkappa_D - v\varkappa_B)/\varkappa_A - A_0 / c_A \varkappa_A)} \cdot \tag{4}$$

This reaction phase can be considered to represent the start of the proper repeated discontinuous feed of the compound A into the reactor. The following notation can be introduced for simplification:

$$P = (\varkappa_C + v\varkappa_D - v\varkappa_B)/\varkappa_A,$$
$$P_i = (v A_i - b_p(\varkappa_C + v\varkappa_D))/b_p \varkappa_A,$$
$$\Delta n_i = v c_A \, \Delta V_i / b_p V_s. \tag{5}$$

The P_i expression implicitly involves the dependence of the actual absorbance for the i-th addition. At the time τ_{0k} when the absorbance of the reaction mixture reaches the chosen constant level A_k, it is

$$P_i = P_k. \tag{5a}$$

The following considerations and generalizations will apply to the repeated addition of the compound A into the reaction mixture. In the case of the first addition, the state of the reaction at the time τ_{0k} together with the added volume ΔV_1 of the compound A will represent the initial state for the further reaction course, *i.e.* in the new time from $\tau_1 = 0$. The initial concentrations a_1, b_1, c_1, d_1 of the compounds A, B, C, D, are then given by the following relations:

$$a_1 = C_{A0k}(V_s + \Delta V_0)/(V_s + \Delta V_0 + \Delta V_1) + c_A \, \Delta V_1 / (V_s + \Delta V_0 + \Delta V_1)$$
$$b_1 = C_{B0k}(V_s + \Delta V_0)/(V_s + \Delta V_0 + \Delta V_1)$$
$$c_1 = d_1 / v = C_{C0k}(V_s + \Delta V_0)/(V_s + \Delta V_0 + \Delta V_1). \tag{6}$$

The concentrations $C_{A_{0k}}$, $C_{B_{0k}}$, $C_{C_{0k}}$, $C_{D_{0k}}$ are given by the expressions (1) at the time τ_{0k}. By elimination of τ_{0k} by means of Eqs (4) and after substitution (5), the Eq. (6) are transformed into:

$$
a_1 = \frac{P_k + P + (1 - P)(\Delta n_0 + \Delta n_1) - \Delta n_0(1 - A_k/c_A\varkappa_A)}{(1 - P)(v/b_p + (\Delta n_0 + \Delta n_1)/c_A)}
$$

$$
b_1 = \frac{v(1 + P_k - \Delta n_0(1 - A_k/c_A\varkappa_A))}{(1 - P)(v/b_p + (\Delta n_0 + \Delta n_1)/c_A)}
$$

$$
c_1 = \frac{d_1}{v} = \frac{\Delta n_0(1 - A_k/c_A\varkappa_A) - P_k - P}{(1 - P)(v/b_p + (\Delta n_0 + \Delta n_1)/c_A)} . \tag{6a}
$$

Combination of Eq. (1) for $i = 1$ with Eq. $(6a)$ and introduction into Eq. (2) with application of (5) gives the absorbance–time dependence for the first addition (implicitely in P_1):

$$
\tau_1 \frac{1 - \Delta n_0 - \Delta n_1}{1 + \Delta V_0/Vs + \Delta V_1/V_s} = \ln \frac{P_k + P - \Delta n_0(P - A_k/c_A\varkappa_A) + \Delta n_1(1 - P)}{P_k + 1 - \Delta n_0(1 - A_k/c_A\varkappa_A)} .
$$

$$
\cdot \frac{P_1 + 1 - (\Delta n_0 + \Delta n_1)(1 - A_1/c_A\varkappa_A)}{P_1 + P - (\Delta n_0 + \Delta n_1)(P - A_1/c_A\varkappa_A)} . \tag{7}
$$

The same way can be applied also to the further additions of the compound A into the reaction mixture at a constant absorbance A_k, and, hence, it can be general for the initial concentrations of the compounds A, B, C, D for the i-th addition:

$$
a_i = \left(C_{A_{i-1,k}}\left(V_s + \sum_{i=0}^{i-1} V_i\right) + \Delta V_i c_A\right)\Big/\left(V_s + \sum_{i=0}^{i} V_i\right)
$$

$$
b_i = C_{B_{i-1,k}}\left(V_s + \sum_{i=0}^{i-1} \Delta V_i\right)\Big/\left(V_s + \sum_{i=0}^{i} \Delta V_i\right)
$$

$$
c_i = d_i/v = C_{C_{i-1,k}}\left(V_s + \sum_{i=0}^{i-1} \Delta V_i\right)\Big/\left(V_s + \sum_{i=0}^{i} \Delta V_i\right) . \tag{8}
$$

In analogy to the case of the relation (6) it can be obtained by modification with the use of (5):

$$
a_i = \frac{P_k + P + (1 - P)\sum_{i=0}^{i} \Delta n_i - \left(1 - \dfrac{A_k}{c_A\varkappa_A}\right)\sum_{i=0}^{i-1} \Delta n_i}{(1 - P)\left(\dfrac{v}{b_p} + \dfrac{1}{c_A}\sum_{i=0}^{i} \Delta n_i\right)}
$$

$$b_i = v \frac{1 + P_k - \left(1 - \frac{A_k}{c_A \varkappa_A}\right) \sum_{i=0}^{i-1} \Delta n_i}{(1 - P)\left(\frac{v}{b_p} + \frac{1}{c_A} \sum_{i=0}^{i} \Delta n_i\right)}$$

$$c_i = \frac{d_i}{v} = \frac{\left(1 - \frac{A_k}{c_A \varkappa_A}\right) \sum_{i=0}^{i-1} \Delta n_i - P_k - P}{(1 - P)\left(\frac{v}{b_p} + \frac{1}{c_A} \sum_{i=0}^{i} \Delta n_i\right)} . \tag{8a}$$

Combination of the expressions (1) for any arbitrary i with Eq. (8a) and introduction into Eq. (2) with application of Eq. (5) gives Eq. (9),

$$\tau_i \frac{1 - \sum_{i=0}^{i} \Delta n_i}{1 + \sum_{i=0}^{i} \frac{\Delta V_i}{V_s}} = \ln \frac{P_k + P - \left(P - \frac{A_k}{c_A \varkappa_A}\right) \sum_{i=0}^{i-1} \Delta n_i + \Delta n_i (1 - P)}{P_k + 1 - \left(1 - \frac{A_k}{c_A \varkappa_A}\right) \sum_{i-1}^{i=0} \Delta n_i} .$$

$$. \frac{P_i + 1 - \left(1 - \frac{A_i}{c_A \varkappa_A}\right) \sum_{i=0}^{i} \Delta n_i}{P_i + P - \left(P - \frac{A_i}{c_A \varkappa_A}\right) \sum_{i=0}^{i-1} \Delta n_i} \tag{9}$$

which represents the equation (for $i = 1, 2, \ldots$) of the saw-tooth shaped curve of the absorbance–time dependence (Fig. 1).

This expression is rather complicated for practical applications. Presuming that all additions are the same, *i.e.* $\Delta n_i = \Delta n$, that the overall volume of the compound A added is negligible with respect to the total volume of the reaction mixture, *i.e.*

$$\sum_{i=0}^{i} \Delta V_i \ll V_s ,$$

and if it is $A_k \ll c_A \varkappa_A$, then the expression (9) can be rewritten in the following simplified form:

$$\tau_{ik}\big(1 - (i + 1) \Delta n\big) = \ln \frac{P_k + P(1 - (i + 1) \Delta n) + \Delta n}{P_k + P(1 - (i + 1) \Delta n)} \cdot \frac{P_k + 1 - (i + 1) \Delta n}{P_k + 1 - i \Delta n} =$$

$$= \ln Y . \tag{10}$$

The rate constant k_1 can be determined either graphically from the slope after linearization of the relation (10) or, more advantageously, by some numerical optimizing procedure.

The expression (10) can be further simplified in the case that for the reaction (A) it will be $\varkappa_A \neq 0$ and the other $\varkappa = 0$. Then it is $P = 0$, and $P_k = \nu C_{Ak}/b_p = \text{const.}$ for all the additions, which in fact means the adjustable relative concentration of compound A with respect to compound B. Then it is possible to write

$$z_B k_1 b_p t_{ik}(1 - (i + 1)\Delta n) = \ln\left(1 + \frac{\Delta n}{P_k}\right)\frac{1 + P_k - (i + 1)\Delta n}{1 + P_k - i\Delta n}, \qquad (11)$$

where the parameters Δn and P_k are easily accessible experimentally. They can be determined as follows: for the last i_∞-th addition it must be $\lim_{i \to i_\infty} t_i \to \infty$, hence from Eq. (11) it follows:

$$i_\infty = \frac{1 + P_k}{\Delta n} - 1. \qquad (12)$$

After introduction into Eq. (11) for $\Delta n \ll P_k$ it is obtained:

$$z_B k_1 b_p t_{ik}\left(1 - (i + 1)\frac{1 + P_k}{1 + i_\infty}\right) = \ln\frac{i_\infty - i}{i_\infty - i + 1}\left(1 + \frac{1 + P_k}{P_k(i_\infty + 1)}\right). \qquad (13)$$

Thus the relatively laborious determination of Δn from its definition (5) is unnecessary, and it is possible — from a single feed sequence — to determine, repeatedly, the rate constant from each decrease of the saw-tooth shaped curve of the absorbance-time dependence.

EXPERIMENTAL

Apparatus. The apparatus used is schematically represented in Fig. 2. It is composed of a monochromator with the reactor, a doser for discontinuous injecting and a recorder. The reactor itself 1 with the photo-electric cell 2 are placed in the single-beam monochromator Specol 6 3 with a tungsten lamp 4 fed by a stabilizer 5. The reactor is a double-jacketed thermostated block made of brass in which there is a glass cell of 30 cm³ volume. Length of optical path is 2 cm, the beam width and intensity being adjusted by means of a diaphragm. The beam intensity is indicated by means of the photo-electric cell whose signal is led directly to the recorder G1B1 6.

The brass block is covered with a lid through which the following accessories are led into the glass cuvette: a glass spiral mixer 7 whose speed is chosen so as not to produce bubbles in the cuvette; the nozzle 8 of the discontinuous doser of the feed is immersed immediately below the surface of the liquid and as close to the mixer as possible; the other inlets of the reaction components, medium, inert gas from the respective reservoirs 9, 10, 11 are placed close above the surface of the liquid.

The doser **12** for discontinuous injecting of the starting substance into the reactor is represented schematically in Fig. 3. In principle, this is a single acting plunger pump. It is composed of a glass injection syringe **1**, closing device **2**, and the electromagnet **3**. The closing device consists of ground--glass non-return valves. Motion of the plunger of the syringe is ensured by a mechanical connection with the magnet core **4**. When the electromagnet is switched on, the plunger is drawn into the syringe, whereby a certain volume of the compound is injected through the nozzle **8** into the reactor. After the electromagnet is switched off, the plunger is returned to the initial position by means of a spring, whereby an equal volume of the compound is taken from the reservoir **5**. The magnitude of the volume injected is adjusted by means of the micrometer screw **6**. The switching-on and -off of the electromagnet can be carried out either by means of a manual press button or by a microswitch located below the slider of the recorder. The microswitch can be shifted and thus adjusted along the transparence scale. At a chosen transparance (absorbance) value, the recorder slider switches on the microswitch, and it switches off after injection. An electromagnetic numerical counter **7** is located parallel to the electromagnet to provide information about number of injections during a measurement.

Measurement procedure. The chosen wavelength is adjusted, and the glass cell is charged with one reaction component and the reaction medium. After tempering with continuous stirring, the other reaction component is injected manually (whereby the reaction is started). After switching over to automatic dosing, equal amounts of the second component are gradually injected at the chosen transparence (absorbance) value. The constant transparence value is adjusted in advance by the position of the microswitch in the recorder. The automatic dosing can be finished after any arbitrary addition. It is, however, advantageous to continue the dosing until complete exhaustion of the first reaction component. In this case the automatic dosing cannot
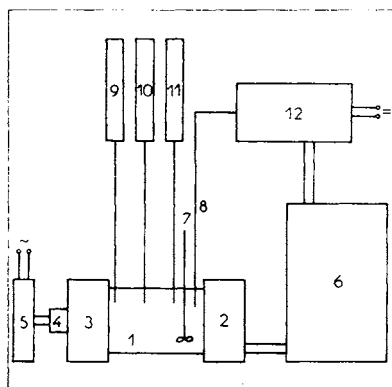

FIG. 2

The experimental arrangement of the feedback reactor. **1** reactor, **2** photoelectric cell, **3** monochromator, **4** lamp, **5** stabilizer, **6** recorder, **7** mixer, **8** the doser nozzle, **9**–**11** inlets of the reaction components, reaction medium, and inert gas, **12** doser
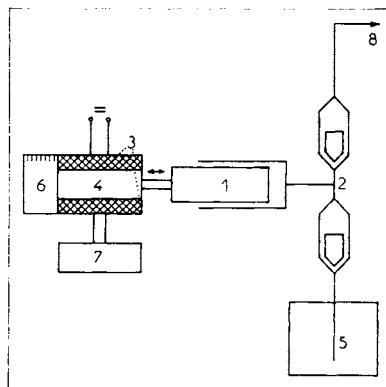
FIG. 3

Schematic representation of operation of the doser. **1** injection syringe, **2** the closing device, **3** electromagnet, **4** the magnet core, **5** reservoir, **6** micrometer screw, **7** electromagnetic counter, **8** the nozzle

supply any further injection, and the measurement is practically finished; moreover it is possible to use this procedure for determination of the starting concentration of one of the reaction components. After the measurement is finished, the reaction mixture is removed from the reactor, the cell is cleaned, whereby the apparatus is ready for the next experiment.

Reagents. Ferric sulphate of *p.a.* purity grade (Lachema, Brno). Solution of vanadium(III) sulphate in 1M sulphuric acid (*p.a.*; Lachema, Brno) was prepared by combining equal volumes of equally concentrated solutions of vanadyl sulphate and vanadium(II) sulphate. The vanadyl sulphate was prepared from ammonium metavanadate(V) (pure; Lachema, Brno) by reduction with sulphur dioxide in 1M sulphuric acid; the excess sulphur dioxide was removed by boiling with simultaneous bubbling carbon dioxide through the mixture[8]. The vanadium(II) sulphate was prepared by reduction of vanadyl sulphate in a reductor filled with amalgamated zinc[9]. Cerium(IV) sulphate of *p.a.* purity grade. Stannous sulphate was prepared by precipitation of saturated solution of stannous chloride (pure; Lachema, Brno) in sulphuric acid with acetone. All the solutions were standardized potentiometrically[9].

RESULTS AND DISCUSSION

The reaction $Fe(III) + V(III) \xrightarrow{k_1} Fe(II) + V(IV)$ was measured in 1M sulphuric acid at 25°C in the inert atmosphere of argon. The reactor was charged with the V(III) solution of the initial concentrations within the interval from 0·002 to 0·018 mol l^{-1}. The solution injected contained Fe(III) of the concentrations from 0·1 to 0·3 mol l^{-1}. At the wavelengths of 370 nm and 380 nm, the constant absorbance levels were chosen within the interval from 0·05 to 0·3. Magnitude of the individual injections was chosen in such way that their total number was 10 to 25, *i.e.* the Δn parameter value was within the interval from 0·1 to 0·04.

The relation (*10*) was verified numerically by linear regression, Fig. 4 shows an example of experimental record and linearization of Eq. (*10*). Table I gives values

TABLE I
Values of the rate constants of the reaction $Fe(III) + V(III) \xrightarrow{k_1} Fe(II) + V(IV)$; $k_1 = 2\cdot92$ l mol^{-1} s^{-1} (ref.[10])

λ, nm	b_p, M	P	k_1, M^{-1} s^{-1}
370	0·00284	$-0\cdot0512 \pm 0\cdot0079$	$3\cdot12 \pm 0\cdot18$
	0·00455	$-0\cdot0521 \pm 0\cdot0057$	$2\cdot81 \pm 0\cdot22$
	0·00568	$-0\cdot0489 \pm 0\cdot0045$	$3\cdot01 \pm 0\cdot22$
380	0·00852	$-0\cdot1213 \pm 0\cdot0126$	$2\cdot69 \pm 0\cdot10$
	0·0136	$-0\cdot1096 \pm 0\cdot0156$	$2\cdot91 \pm 0\cdot16$
	0·0174	$-0\cdot1259 \pm 0\cdot0090$	$2\cdot87 \pm 0\cdot11$

of the rate constants from the linear regression and of the P parameter determined from the definition for the two mentioned wavelengths and various initial concentrations.

The correlation coefficient of the linear regression is 0·9998 to 0·9999. The values of the P parameter only depend on the wavelength in accordance with the definition of this parameter. The difference between the rate constant value found by the method suggested and that found by the independent stopped-flow method with spectrophotometric and potentiometric indication[10] is statistically insignificant.

The reaction $Ce(IV) + Sn(II) \xrightarrow{k_1} Ce(III) + Sn(IV)$ was measured in 1M sulphuric acid medium at 20 and 25°C under argon. The reactor was charged with the Sn(II) solution of initial concentrations within the interval from $4·5 . 10^{-4}$ to $3 . 10^{-3}$ mol . $. l^{-1}$. The solution injected contained $Ce(IV)$ of the concentrations from 0·027 to 0·1 mol l^{-1}. At the wavelength of 390 nm and 420 nm the constant absorbance levels were chosen within the interval from 0·05 to 0·2. Volume of the individual
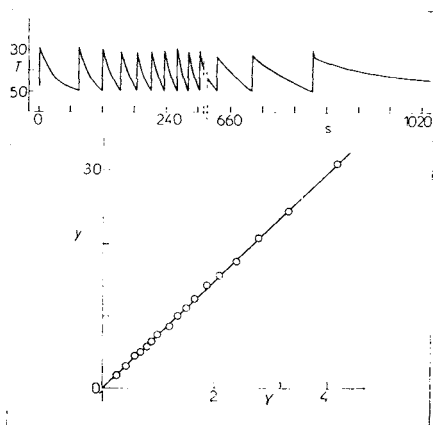

FIG. 4

Experimental record of the course of the reaction $Fe(III) + V(III) \rightarrow Fe(II) + V(IV)$. Temperature 25°C, wavelength 380 nm, optical path length 4 cm, the first component charge 37 cm³ of 0·018 mol.l⁻¹ solution of V(III), injection amount 0·103 cm³ of 0·311 mol.l⁻¹ solution of Fe(III), total number of injections 24, the constant transparence level $T = 0·5$, $n = 0·0474$; $y = t_{i0exp}[1 - (i + + 1)\Delta n]$
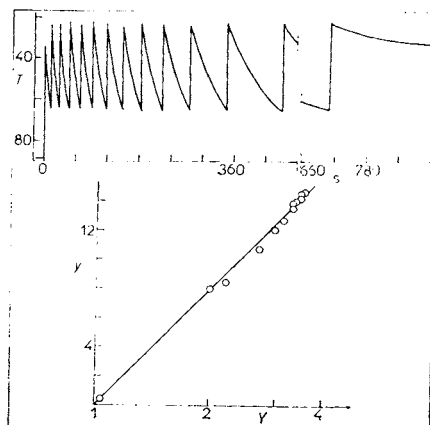
FIG. 5

Experimental record of the course of the reaction $Ce(IV) + Sn(II) \rightarrow Ce(III) + + Sn(IV)$. Temperature 25°C, wavelength 420 nm, optical path length 4 cm, the first component charge 38·5 cm³ of 0·00176 mol.l⁻¹ solution of Sn(II), injection amount 0·104 cm³ of 0·1 mol.l⁻¹ solution of Ce(IV), total number of injections 14, the constant transparence level $T = 0·65$, $n = 0·0768$; $y = t_{i0exp} . [1 - (i + 1)\Delta n]$

injections was within the range from 0·1 to 0·01 cm^3, which corresponded to the total injections number from 10 to 100.

The relation (*10*) was verified by linear regression for the wavelength of 420 nm: Fig. 5 gives an example of the experimental record and linearization. For the wavelength of 390 nm the experiments were evaluated both by the linear regression and by the optimization procedure by Rosenbrock and Storey[11] using a digital computer Robotron EC 1040. Table II gives the values of the rate constant and of the P parameter for the two wavelength values given and for various initial Sn(II) concentrations.

The correlation coefficient values obtained from the evaluation of this system were in the interval 0·98 − 0·99, *i.e.* lower than in the previous system. The value of the P parameter close to zero shows that practically only Ce(IV) absorbs at the wavelengths mentioned. The rate constant values were practically independent of the evaluation method, they were, however, dependent on initial Sn(II) concentration, which indicates a more complicated reaction mechanism[12−15].

In conclusion it can be stated that the two systems investigated confirmed correctness of the relations derived. The measurements of reaction kinetics are simple and rapid, their numerical evaluation presents no serious difficulties. The fact that the concentration of the first reaction starting component decreases to zero during the measurement by the method of discontinuous injections has a practical consequence: if the same result had to be obtained in a study using a normal discontinuous reactor (*i.e.*, one addition followed by investigation of the whole reaction course), the individual measurements would have to be repeated separately many times. Therefrom there follows saving of time and chemicals. Last but not least, it is also possible to affect the reaction rate by the magnitude of injection and choice of the absorbance level, which enables to study kinetics of the IInd order reactions within a broad range of reaction velocities.

TABLE II

Values of the rate constants of the reaction Ce(IV) + Sn(II) $\xrightarrow{k_1}$ Ce(III) + Sn(IV)

T, °C	λ, nm	b_p, M	P	k_1, M^{-1} s^{-1} lin. regression	k_1, M^{-1} s^{-1} optimization	k_1, M^{-1} s^{-1} reference
20	390	0·0027	−0·00276 ± 0·00125	28·22 ± 2·90	28·20 ± 3·65	53·7[13]
25	420	0·00045	−0·00095 ± 0·00094	44·16 ± 6·87	—	27·05[14]
25	420	0·00105	−0·00116 ± 0·00125	31·60 ± 1·72	—	23·2[15]
25	420	0·00165	−0·00038 ± 0·00025	26·86 ± 0·79	—	—
25	420	0·0021	−0·00093 ± 0·0061	26·91 ± 1·61	—	—

REFERENCES

1. Tockstein A., Tocksteinová D.: This Journal *34*, 1625 (1969).
2. Tocksteinová D., Tockstein A.: This Journal *34*, 2169 (1969).
3. Tocksteinová D., Tockstein A.: This Journal *36*, 1111 (1971).
4. Cover R. E., Meites L.: J. Phys. Chem. *67*, 1528 (1963).
5. Cover R. E., Meites L.: J. Phys. Chem. *67*, 2311 (1963).
6. Carr P. W., Jordan J.: Anal. Chem. *45*, 634 (1973).
7. Rehm R. G., Bright D. S.: Anal. Chem. *54*, 398 (1982).
8. Fresno del C., Mairlot E.: Z. Anorg. Chem. *214*, 73 (1933).
9. Čihalík J.: *Potenciometrie*. Published by SNTL, Prague 1961.
10. Tockstein A., Skopal F.: This Journal *39*, 3430 (1974).
11. Čoupek L.: Automatizace *XV*, 38 (1972).
12. Brübacker Ch., Court A. J.: J. Amer. Chem. Soc. *78*, 5530 (1956).
13. Remick A. E.: J. Amer. Chem. Soc. *69*, 94 (1947).
14. Tockstein A., Jaroš F.: This Journal *35*, 2523 (1970).
15. Tockstein A., Ludvík B.: This Journal *40*, 2287 (1975).

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