

# A FEEDBACK REACTOR WITH CONTINUOUS INJECTION OF ONE REACTION COMPONENT USING SPECTROPHOTOMETRIC INDICATION I

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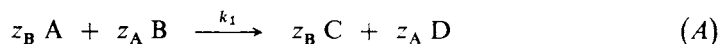
The time dependence of the volume of solution of one reaction component injected continuously to the solution of the other reaction component is derived for the case that the injection is controlled by feedback to hold the absorbance of the reaction mixture constant. An experimental apparatus based on this principle has been set up and its function tested on two 2nd order reactions, whereby the theoretical relations derived for the determination of the rate constants have also been verified.

This paper deals with a measurement procedure where a quantity linearly dependent on the concentrations of the reaction components is held constant by feedback control. In the particular case where this quantity is directly proportional to the concentration of one of the components only, an artificial feedback-controlled stationary state for this component thus establishes.

The principle of the method is demonstrated in Fig. 1. To the solution of one reaction component in reactor 1, solution of the other reaction component is injected continuously by means of injector 4. The value  $Y$  of the quantity dependent on the concentrations of the substances in the reaction mixture in the reactor is monitored by means of indicator device 2 and compared continuously with the reference value  $Y_0$  set on compensator 3. The differences  $U$  between the pairs of values provide feedback control of the injection. The recording device 5 enables recording of the volume injected and/or checking that the value of  $Y$  is held constant. This new method is a limiting case of the discontinuous feedback injection treated previously<sup>1</sup>, where the individual volumes added are differentially small. The experimental procedure suggested can be employed not only for kinetic measurements but also for quantitative analysis purposes.

## THEORETICAL

The irreversible nonisochoric 2nd order reaction



conducted so that a solution of component A is injected to solution of component B, obeys the following system of differential kinetic equations:

$$-\frac{1}{z_B(V_s + V)} \frac{dn_A}{dt} = k_1 \frac{n_A}{V_s + V} \frac{n_B}{V_s + V} - \frac{a}{z_B(V_s + V)} \frac{dV}{dt} \quad (1a)$$

$$-\frac{1}{z_A(V_s + V)} \frac{dn_B}{dt} = \frac{1}{z_B(V_s + V)} \frac{dn_C}{dt} = \frac{1}{z_A(V_s + V)} \frac{dn_D}{dt} = k_1 \frac{n_A}{V_s + V} \frac{n_B}{V_s + V}, \quad (1b)$$

where  $V_s$  is the initial volume of the reaction mixture in  $\text{dm}^3$ ,  $V$  is the actual volume of the injected solution of substance A in  $\text{dm}^3$ ,  $a$  is the concentration of substance A in the solution injected in  $\text{mol dm}^{-3}$  and  $n$ 's are the respective actual amounts of substance in mol.

The indicated value  $Y$  is required to be linearly dependent on the concentrations  $c_i$  ( $c_i = n_i/(V_s + V)$ ) of the substances with proportionality factors  $\alpha_i$ :

$$Y = \sum_i \alpha_i c_i. \quad (2)$$

The feedback control causes  $Y$  to be time constant,  $dY/dt = 0$ , for which we obtain a differential equation in the general form

$$dV/dt = (1/Y) \sum_i \alpha_i (dn_i/dt). \quad (3)$$

Its solution using Eq. (1) then gives the dependence of the injected volume  $V$  on time  $t$ .

The dependences of the quantity  $Y$  (e.g., absorbance) and of the volume  $V$  on time  $t$  are shown schematically in Fig. 2. In the starting segment, up to a time  $t_0$ , the chosen  $Y_0$  value is attained (the reaction is started) by injection of a volume  $\Delta V$  of solution of substance A in an arbitrary manner (e.g., in the linear mode). Since time  $t_0$  the volume injected is controlled by feedback so that  $Y$  is held constant.

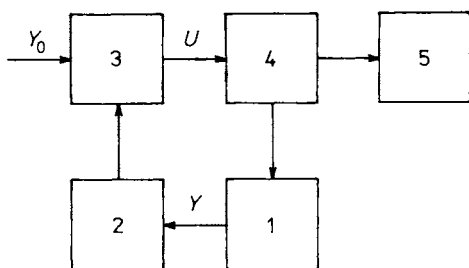


FIG. 1

Schematic of method suggested. 1 Reactor, 2 indication, 3 compensator, 4 injector, 5 recorder;  $Y$  value of quantity measured,  $Y_0$  reference value of quantity,  $U$  voltage applied to injector

The state of the reaction (*A*) in time  $t_0$  can be described by solving the system of equations (1) after elimination of time:

$$-(dn_A/z_B) + a(dV/z_B) = -(dn_B/z_A) = (dn_C/z_B) = (dn_D/z_A), \quad (4)$$

and by integration for volumes within the limits of  $0 - \Delta V$ , the balance relations

$$-(n_{Ak}/z_B) + a(\Delta V/z_B) = (n_{B0} - n_{Bk})/z_A = (n_{Ck}/z_B) = (n_{Dk}/z_A) \quad (5)$$

are obtained; here  $n_{B0}$  is the initial amount of substance B in the volume  $V_s$  and  $n_{Ak}$ ,  $n_{Bk}$ ,  $n_{Ck}$ ,  $n_{Dk}$  are amounts of the respective substances in time  $t_0$ .

Integration of Eq. (4) with feedback (for volumes within the limits of  $\Delta V$  to  $V$ ) gives

$$a(V - \Delta V)/z_B - (n_A - n_{Ak})/z_B = (n_{Bk} - n_B)/z_A = (n_C - n_{Ck})/z_B = (n_D - n_{Dk})/z_A. \quad (6)$$

Combining Eqs (2) and (6) we obtain

$$n_A = n_{Ak}[(V_{\infty A} - V)/(V_{\infty A} - \Delta V)] \quad (7a)$$

$$n_B = n_{Bk}[(V_{\infty B} - V)/(V_{\infty B} - \Delta V)] \quad (7b)$$

$$n_C = (z_B/z_A) [n_{B0} - n_{Bk}(V_{\infty B} - V)/(V_{\infty B} - \Delta V)] \quad (7c)$$

$$n_D = n_{B0} - n_{Bk}(V_{\infty B} - V)/(V_{\infty B} - \Delta V), \quad (7d)$$

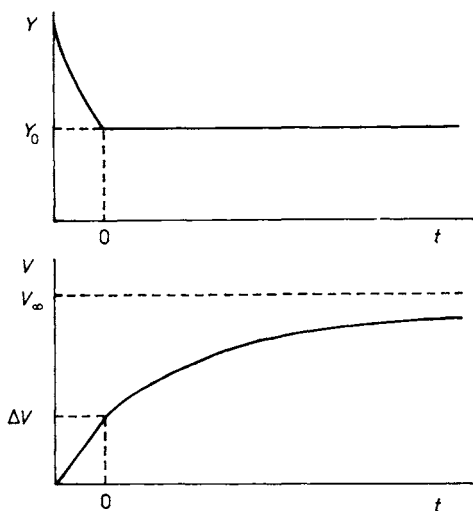


FIG. 2

Typical dependences of transmittance and volume on time.  $Y$  and  $Y_0$  measured and reference transmittances, respectively,  $V$ ,  $\Delta V$ , and  $V_{\infty}$  volume injected, starting volume, and volume in time  $t \rightarrow \infty$ , respectively

where

$$V_{\infty A} = (V_s + \Delta V) c_{Ak} \kappa / [z_B(a\kappa - Y_0) - a\kappa] + \Delta V \quad (8a)$$

$$V_{\infty B} = (V_s + \Delta V) c_{Bk} \kappa / [z_A(a\kappa - Y_0)] + \Delta V \quad (8b)$$

$$c_{Ak} = n_{Ak} / (V_s + \Delta V) \quad (8c)$$

$$c_{Bk} = n_{Bk} / (V_s + \Delta V) \quad (8d)$$

$$\kappa = z_B \kappa_A + z_A \kappa_B - z_B \kappa_C - z_A \kappa_D. \quad (8e)$$

By differentiating Eq. (7) and substituting in Eq. (3) by means of relation (8) we arrive at the differential equation

$$\frac{dV}{dt} = z_A c_{Ak} k_1 \frac{V_s + \Delta V}{V_{\infty A} - \Delta V} \frac{(V_{\infty A} - V)(V_{\infty B} - V)}{V_s + V} \quad (9)$$

whose integration over volume limits from  $\Delta V$  to  $V$  and time limits from zero to  $t$  gives

$$\frac{V_s + V_{\infty A}}{V_{\infty A} - V_{\infty B}} \ln \frac{V_{\infty A} - V}{V_{\infty A} - \Delta V} - \frac{V_s + V_{\infty B}}{V_{\infty A} - V_{\infty B}} \ln \frac{V_{\infty B} - V}{V_{\infty B} - \Delta V} = z_A c_{Ak} k_1 \frac{V_s + \Delta V}{V_{\infty A} - \Delta V} t \quad (10)$$

at  $V_{\infty A} \neq V_{\infty B}$ , and

$$\frac{V_s + V_{\infty}}{V_{\infty} - \Delta V} \frac{V - \Delta V}{V_{\infty} - V} - \ln \frac{V_{\infty} - V}{V_{\infty} - \Delta V} = z_A c_{Ak} k_1 \frac{V_s + \Delta V}{V_{\infty} - \Delta V} t \quad (11)$$

at  $V_{\infty A} = V_{\infty B} = V_{\infty}$ .

These, then, are the final implicit dependences of injected volume of solution of substance A on time; they contain parameters  $c_{Ak}$ ,  $V_{\infty A}$  and  $V_{\infty B}$ , which can be determined from their definitions for the particular experimental conditions used. For  $c_{Ak}$  and  $c_{Bk}$ , Eqs (2) and (5) give

$$c_{Ak} = \{z_B [Y_0 - b_0 \kappa_B V_s / (V_s + \Delta V)] + a[\Delta V / (V_s + \Delta V)] (\kappa - z_B \kappa_A)\} / \kappa \quad (12a)$$

$$c_{Bk} = b_0 [V_s / (V_s + \Delta V)] - (z_A / z_B) \{a[\Delta V / (V_s + \Delta V)] - c_{Ak}\}, \quad (12b)$$

where  $b_0$  is the starting concentration of substance B in volume  $V_s$ . For the determination of the rate constant  $k_1$ , relations (10) and (11) can be linearized by plotting their left sides against time ( $k_1$  is determined by the slope). Far more convenient is the use of a numerical optimization method capable of providing all parameters of Eqs (10) and (11) including the rate constant  $k_1$ .

Eq. (10) is rather complex; it can be simplified by a suitable choice of experimental conditions. At  $V_{\infty A} = -V_s$ , i.e., if

$$z_B b_0 x_B = a(z_B x_C + z_A x_D - z_A x_B), \quad (13)$$

Eq. (10) transforms into

$$-\ln [(V_{\infty B} - V)/(V_{\infty B} - \Delta V)] = k_1 z_A c_{Ak} t, \quad (14a)$$

or in volume terms,

$$V = V_{\infty B} - (V_{\infty B} - \Delta V) \exp(-k_1 z_A c_{Ak} t). \quad (14b)$$

Additional simplification is achieved if  $x_{B,C,D} = 0$ .

The condition  $V_{\infty A} = -V_s$  inserted in Eq. (8) for  $n_A$  implies that during the whole controlled reaction, concentration of substance A is constant and equal to  $c_{Ak}$ . Hence, a steady state is established with respect to substance A and the reaction becomes a pseudomonomolecular one. The reaction rate can be influenced efficiently by a suitable choice of  $Y_0$  and thereby,  $c_{Ak}$ . The dependence of the measured injected volume on time is a simple exponential function whose linearization (14a) or optimization (14b) can serve for verification and determination of the rate constant  $k_1$ .

For the purposes of quantitative analysis, it is convenient to combine Eqs (8) and (12) to obtain

$$b_0 = \frac{z_B Y_0 (V_s + V_{\infty A}) + a V_{\infty A} (z_A x_B - z_B x_C - z_A x_D)}{z_B x_B (V_s + \Delta V)} \quad (15a)$$

or

$$b_0 = \frac{z_A a x_A V_{\infty B} - z_A Y_0 (V_s + V_{\infty B})}{V_s (z_B x_A - z_B x_C - z_A x_D) - z_A x_B \Delta V}. \quad (15b)$$

The  $V_{\infty A}$  or  $V_{\infty B}$  values can be usually determined experimentally as the maximum, no more variable injected volume of solution of substance A (see Fig. 2). Which of the expressions (15a), (15b) to use is determined by which of the substances A, B is depleted at the end of the operation of the feedback: if substance A is absent, Eq. (15a) applies, whereas if substance B has reacted completely (which is the usual case), Eq. (15b) should be used.

## EXPERIMENTAL

### Chemicals

Cerium(IV) sulphate was a commercial chemical of reagent grade purity (Lachema, Brno). Tin(II) sulphate was prepared by precipitation of a saturated solution of tin dichloride pure (Lachema, Brno) in sulphuric acid with acetone<sup>2</sup>. Vanadyl sulphate was prepared from ammo-

nium metavanadate pure (Lachema, Brno) by reduction with sulphur dioxide<sup>3</sup> and flushing with carbon dioxide and argon. All factors were determined potentiometrically<sup>4</sup>.

### Apparatus

An apparatus whose layout is shown in Fig. 3 was set up for obtaining the time dependences of transmittance and volume injected. It consists of a monochromator with a reactor, a compensator, linear injector and recorder. Reactor 1 with a photocell 2 is accommodated on a Spekol 6 single-beam monochromator 3 (Carl Zeiss, Jena, G.D.R.) with a tungsten lamp fed from a stabilizer 4. The reactor is a double-jacketed thermostated brass block, accommodating a 30 cm<sup>3</sup> glass cell with a coil stirrer 10. The light beam intensity is indicated by the photocell whose signal is amplified and compared with the value set on the compensator 5; the deviations are amplified and transmitted via a power amplifier to the injector.

The injector comprises a driving unit, a 1 cm<sup>3</sup> syringe and an Aripot precise multiturn potentiometer (Aritma, Prague), all interconnected by a mechanical gear. A constant voltage is applied to the potentiometer, and the voltage at the slider controls the position of the syringe plunger. The time dependence of the volume and transmittance are recorded on a TZ 4 200 two-line recorder 7 (Laboratorní přístroje, Prague).

Auxiliary components include solution storage tanks 8, 9, burettes and argon manifold. A U 1 thermostat 11 (Prüfgeräte-Werk Medingen, G.D.R.) was employed.

### Procedure

Reaction medium, previously argon purged, is placed in the cell and at a constant slight argon feed above the level, solution of substance B is added; the total volume of the reaction mixture then is  $V_s$  and the concentration of substance B in it is  $b_0$ . After thermostating the reaction mixture, the feedback is activated for an arbitrary time. The measurement is usually performed until no change in the volume added takes place.

The test reactions of Ce(IV) with Sn(II) and V(IV), respectively, were conducted in 1M-H<sub>2</sub>SO<sub>4</sub> at 20°C. The reactor contained a solution of Sn(II) or V(IV) at initial concentrations of 1.4 to 2.0 mmol dm<sup>-3</sup> or 0.4–0.7 mmol dm<sup>-3</sup>, respectively, and the solution injected contained

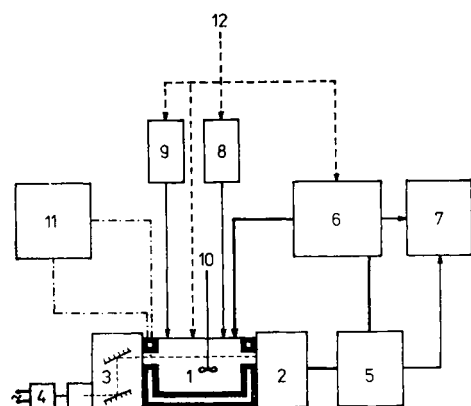


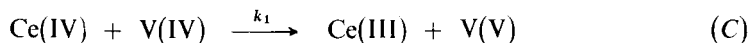
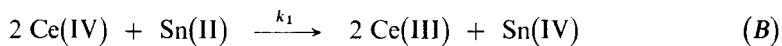
FIG. 3

Layout of apparatus used. 1 Reactor, 2 photocell, 3 SPEKOL 6 monochromator, 4 stabilizer, 5 compensator, 6 injector, 7 recorder, 8 tank for substance in reactor, 9 tank for medium, 10 coil stirrer, 11 thermostat, 12 inert gas manifold

Ce(IV) in concentrations of 94.6 and 20.0 mmol dm<sup>-3</sup>, respectively. The analytical wavelength was 390 nm.

## RESULTS AND DISCUSSION

The function of the apparatus was tested and the validity of the theoretical relations verified on two 2nd order redox reactions, viz.



The molar absorptivities at 390 nm were determined for the components of the two systems. For Ce(III), Sn(IV), and V(IV) the absorptivities are virtually zero, for Ce(IV), Sn(II), and V(V) the values are  $1.08 \cdot 10^6$ ,  $2.25 \cdot 10^3$ , and  $1.45 \cdot 10^4$  cm<sup>2</sup> · mol<sup>-1</sup>, respectively.

For the Ce-Sn system, constant transmittances were chosen within the region of 0.2–0.85, and the precise absorbance values were determined for them from the experimental record. Since the absorptivities of Sn(II), Sn(IV), and Ce(III) are negligibly low against that of Ce(IV), an artificially steady state with respect to the starting Ce(IV) component was established during the measurement, owing to which Eq. (14b) was applicable to the time dependence of the volume injected and Eq. (14a) could be used for its verification. The left side of Eq. (14a) was plotted against time, and the rate constant  $k_1$  was calculated from the slope of this linear dependence. Illustrative dependences of transmittance and injected volume on time are shown in Fig. 4 and the results of the measurements are summarized in Table I. The rate

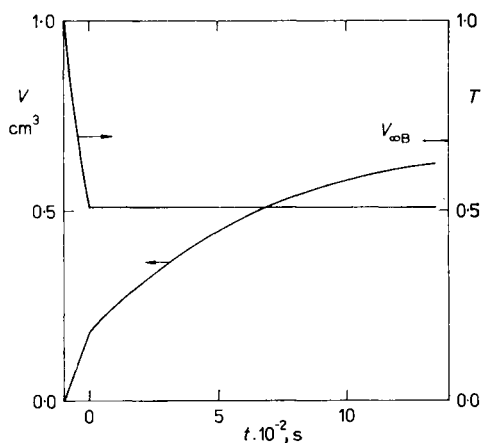


FIG. 4

Dependences of transmittance  $Y$  and injected volume  $V$  on time  $t$  for the Ce-Sn system. Cell (pathlength 4 cm) contained 40 cm<sup>3</sup> of solution at  $c_{\text{Sn(II)}} = 1.59$  mmol · dm<sup>-3</sup>, solution injected contained Ce(IV) in a concentration of 94.6 mmol dm<sup>-3</sup>; reference transmittance 0.513

TABLE I

Parameters and results of experiments with the Ce(IV)/Sn(II) system;  $V_{\infty A} = -40 \text{ cm}^3$ ,  $b_0 = = 1.59 \text{ mmol dm}^{-3}$  (No. 1–10), 2.00 (No. 11–20)

No.	$Y_0 \equiv A_0$	$c_{Ak} \text{ } \mu\text{mol dm}^{-3}$	$c_{Bk} \text{ mmol dm}^{-3}$	$V_{\infty B} \text{ cm}^3$	$\frac{k_1}{\text{dm}^3 \text{ mol}^{-1} \cdot \text{s}^{-1}}$
1	0.663	153.5	1.25	1.412	24.75
2	0.664	153.8	1.25	1.412	24.72
3	0.292	67.7	1.2	1.374	24.19
4	0.292	67.7	1.2	1.374	22.66
5	0.215	49.8	1.19	1.366	22.79
6	0.212	49.1	1.19	1.366	23.12
7	0.151	34.9	1.19	1.360	25.71
8	0.153	35.4	1.19	1.360	24.64
9	0.097	22.4	1.18	1.350	25.00
10	0.096	22.2	1.18	1.350	24.22
11	0.669	154.9	1.65	1.760	24.84
12	0.667	154.4	1.65	1.760	25.00
13	0.290	67.1	1.61	1.721	22.22
14	0.288	66.7	1.61	1.721	22.34
15	0.210	48.6	1.60	1.713	22.64
16	0.217	50.2	1.60	1.713	24.88
17	0.151	34.9	1.59	1.707	20.88
18	0.144	33.3	1.59	1.706	23.10
19	0.094	21.7	1.59	1.701	26.73
20	0.092	21.3	1.59	1.701	23.01

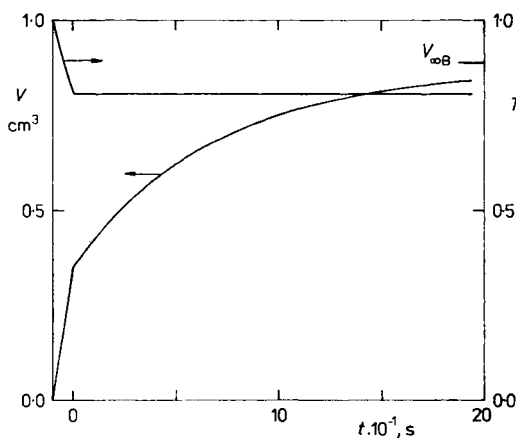


FIG. 5

Dependences of transmittance  $Y$  and injected volume  $V$  on time  $t$  for the Ce-V system. Cell (pathlength 4 cm) contained  $40 \text{ cm}^3$  of solution at  $c_{V(IV)} = 0.431 \text{ mmol dm}^{-3}$ , solution injected contained Ce(IV) in a concentration of  $20 \text{ mmol dm}^{-3}$ ; reference transmittance 0.815



constants obtained do not exhibit any trend and are in a good agreement with published data<sup>5-7</sup>.

For the Ce-V system, constant transmittances were chosen within the region of 0.75–0.95. The contribution from  $V(V)$  being significant, the unsimplified Eq. (10) had to be used for the determination of the rate constant; its parameters were obtained by graphical linearization, i.e. by plotting its left side against time. The rate

TABLE II  
Parameters and results of experiments with the Ce(IV)/V(IV) system

No.	$b_0$ $\mu\text{mol dm}^{-3}$	$Y_0 \equiv A_0$	$c_{Ak}$ $\mu\text{mol dm}^{-3}$	$c_{Bk}$ $\mu\text{mol dm}^{-3}$	$V_{\infty A}$ $\text{cm}^3$	$V_{\infty B}$ $\text{cm}^3$	$k_1$ $\text{dm}^3 \text{mol}^{-1} \text{s}^{-1}$
1	640	0.117	26.01	557	4.487	1.319	809.5
2	620	0.116	25.77	536	4.444	1.279	788.7
3	630	0.115	25.54	546	4.402	1.298	870.0
4	617	0.092	20.14	528	3.445	1.261	781.2
5	613	0.088	19.20	523	3.283	1.251	766.7
6	624	0.092	20.14	535	3.446	1.275	761.6
7	600	0.061	12.87	513	2.220	1.231	895.0
8	648	0.064	13.57	552	2.336	1.309	879.6
9	643	0.064	13.57	547	2.336	1.299	947.0
10	586	0.039	7.71	485	1.392	1.175	1 034.0
11	522	0.041	8.18	521	1.465	1.247	1 041.0
12	510	0.116	24.88	359	4.444	1.061	792.1
13	510	0.117	25.12	359	4.487	1.062	792.1
14	510	0.115	24.65	359	4.402	1.061	792.1
15	510	0.090	18.78	353	3.364	1.049	784.2
16	510	0.090	18.78	353	3.364	1.049	784.2
17	510	0.091	19.02	353	3.405	1.049	784.2
18	510	0.063	12.45	346	2.297	1.036	815.4
19	510	0.063	12.45	346	2.297	1.036	815.4
20	510	0.063	12.45	346	2.297	1.036	815.4
21	442	0.118	25.43	298	4.530	0.928	704.2
22	442	0.119	25.66	298	4.572	0.928	760.0
23	442	0.122	26.36	298	4.701	0.930	738.6
24	431	0.091	19.09	280	3.405	0.893	773.0
25	431	0.089	18.50	280	3.296	0.892	804.4
26	431	0.088	18.39	280	3.283	0.892	828.0
27	416	0.066	13.22	260	2.413	0.852	846.8
28	402	0.066	13.22	246	2.413	0.824	880.6
29	403	0.066	13.22	247	2.413	0.826	780.5
30	405	0.036	6.19	242	1.281	0.816	939.4
31	405	0.036	6.19	242	1.281	0.816	939.4

constant  $k_1$  was determined from the slope of this plot. Illustrative dependences of transmittance and injected volume on time are shown in Fig. 5, the results of measurement are summarized in Table II. The average  $k_1$  value with its standard deviation  $k_1 = 830 \pm 79 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ , agrees well with the published value<sup>8</sup>.

It can be concluded that the study of the two systems confirmed the correct function of the feedback reactor and validated the theoretical expressions derived. Although the demands placed on the instrumentation and preparation of the measurement are rather high, the feedback measurements themselves proceed then automatically and the reproducibility of the experimental data is outstanding. The reaction rate can be controlled very simply by choice of the constant absorbance level; the total time of measurement is thereby also affected. Provided that this absorbance level is only affected by the substance injected, then, for a 2nd order reaction, an artificially steady state establishes with respect to this substance, and this steady state can be adjusted via the constant absorbance level. Such experimental approach is advised for kinetic studies of 2nd order reactions because the data handling then is very simple, the rate constant  $k_1$  can be determined reliably either graphically or numerically.

Since in the actual measurements the  $V_{\infty B}$  value was available (substance B reacted completely), the initial concentration  $b_0$  was controlled. The error of its calculation by means of Eq. (15b) nearly never exceeded 3%.

#### REFERENCES

1. Skopal F.: Collect. Czech. Chem. Commun. 50, 1022 (1985).
2. Donaldson J. D.: J. Chem. Soc. 1960, 789, 4000.
3. Fresno del C., Mairlot E.: Z. Anorg. Chem. 73, 214 (1933).
4. Číhalík J.: *Potenciometrie*. Nakladatelství ČSAV, Prague 1961.
5. Et Tankawy Y. A., Abr-Shady A. I.: Z. Phys. Chem. 76, 3 (1971).
6. Remick A. E.: J. Am. Chem. Soc. 69, 94 (1947).
7. Brubacker C. H., Court A. J.: J. Am. Chem. Soc. 78, 5530 (1956).
8. Tockstein A., Skopal F.: Collect. Czech. Chem. Commun. 39, 3430 (1974).

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