FEED REACTOR AND ITS APPLICATION TO OXIDE-REDUCTION AND SECOND ORDER COUPLING REACTIONS*

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The rate constants were measured in the feed reactor on five model oxidation-reduction reactions in the range 10 to $10^3 M^{-1}s^{-1}$. One or both reactants were fed in the stoichiometric or nonstoichiometric ratio and their absorbances were measured. For two coupling reactions, absorbances of products were measured at stoichiometric feed of both reactants. The experimental results are in a very good agreement with the literature data.

In the last study[1] the model of a feed reactor was solved theoretically and simple procedures for determination of rate constants were presented. Here the practical application of the feed reactor on several model reactions is demonstrated and the obtained rate constants are compared with the data given in literature.

EXPERIMENTAL

Chemicals. The compounds forming the basical media (technical grade reagents, products of Lachema, Brno) used as aqueous solutions: 2M hydrochloric acid, 2M sulfuric acid, 0·1M citric acid, 0·2M sodium phosphate dibasic, 0·2M sodium acetate, 0·2M acetic acid. As components of the oxidation-reduction reactions were used 0·5M solution of ceric sulfate in $2N-H_2SO_4$, 0·2M solution of vanadyl sulfate in $2N-H_2SO_4$ (produced from the ammonium *meta*-vanadate[2]), 0·5M solution of titanium tri-chloride in 2M-HCl, 0·75M solution of stannous chloride in 2·5M-HCl, 0·3M solution of stannous sulfate (prepared by precipitation of saturated $SnCl_2$ in acetone by sulfuric acid) in $2N-H_2SO_4$, ferrous ammonium sulfate as the cerimetric standard (mostly t. g., produced by Lachema Brno), ferric chloride (technical grade reagent, Reanal Budapest) as its 0·1M solution in 2M and 2·5M-HCl. Titre of reducible compounds was determined cerimetricaly, of oxidation compounds titanometrically with the potentiometric indication[3].

In diazotizations and coupling reactions the following acids were used: aniline-4-sulfonic acid (pure), 1,8-dihydroxy naphthalene-3,6-disulfonic acid (a.g.), aniline-3-sulfonic acid (Lachema, Brno), and 2-naphthol-6-sulfonic acid (VCHZ Rybitví). The last two were purified by their repeated dissolving in boiling water, by their filtration at higher temperature through active carbon and by cooling. The passive components were used as 0·05M solutions in the chosen buffer solution. Titra of solution of the Schäffer acid was determined by the diazonium salt of sulfanilic acid with

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the external dot reaction, chromotropic acid was exactly weighted. The reactants represented by 0·05M solutions of diazonium salts of the metanilic acid and sulfanilic acid were prepared by mixing at 2°C the accurately calculated volumes of their solutions (dissolved in water; titre by nitrites[3]), the stoichiometric quantity of hydrochloric acid was by 10% greater and 0·1M aqueous solution of sodium nitrite (t. g. by Spolana Neratovice, titre cerimetrically[3]) and were kept before use at 2°C.

As buffer solutions were used: 0·2M acetate, with pH 3·9, 5·0 and 5·6 (for the E reaction) and the 0·2M dibasic phosphate–citric acid with pH 6 (for reaction (F)).

Apparatus. For the experiments the apparatus (Fig. 1) was used, where the curves transparence––time were automatically registered. As the feed reactor a measuring cell 2, made of perspex was used coupled with the spectrophotometer 4. The optical length of the measuring cell was chosen according to the value of the rate constant and the extinction coefficient from 3 to 5 cm with the rectangular front 4 cm wide and 7 cm high. The propeller mixer was situated in the lower end of the cell and in 1/3 of the side wall. Its speed of rotation was fixed so that the forming eddy would not suck the forming bubbles into the solution and the registered curve of transparence would be smooth. The cell was fed by distilled water 17, medium 18, the inert gas (not drawn), both reaction components 19, and the outlet 20. The cell was situated in an empty brass block 16 partially optically transparent, kept at constant temperature by termostat 15. Reactants were fed by the linear doser 1 which was adapted for two syringes. The mouth of capillary tubes 19 introducing the reactants was immersed 1·5 cm beneath the liquid surface as close to the mixer as possible. The capillary tubes had to be very thin so that at the nill motion of the piston the extinction of the solution would not change at least for 5 min by the possible removal of the reactants from the capillaries. The instrument Spekol (Zeiss, Jena) with the stabiliser[7] used was as the monochromator. The current from the photocell 3 was measured by the measuring part of Spekol and was connected in parallel to the divider 5 with the overall resistance $10^6 \Omega$ where it was registered by the register 6. The divider was fitted so that the zero and the hundredth point of the register scale corresponded to the scale of transparence on Spekol. The wave lengths were chosen so that only one reactant was coloured significantly *i.e.* either the reactant or the product. For reactions (A) to (D) these were values λ(Fe) 435 nm, λ(Ce) 390 nm and for reactions (E) and (F) λ 600 nm.

Measuring procedure. The required volume of reaction media (usually 47 ml) was sampled by the cell 13 kept at chosen temperature in the vessel 14 and fed into the measuring cell and the mixer[8] was set into motion. After temperation the scale of transparence on Spekol and the register were callibrated and one reactant was filled into the cell (if two have not been fed simultaneously). The register and doser filled through three-way cocks K_1 and K_2 by both (or only one) solns. of reactants 9, 10 were switched on.

The curves transparence–time were registered either up to an obvious maximum at nonstoichiometric feed of both components or up to a clear formation of final branches (horizontal at the stoichiometric feed and with a steep slope for feed of only one component). In this case the maximum volume fed was 1·5 ml. The reaction mixture was removed by the outlet 20, the measuring cell was washed 3 times by distilled water from the storage vessel 11 and the experiment was repeated either with the altered feed rate of one, eventually with different initial concentration of the second component or with the altered feed rates r_A and r_B of both components at the chosen ratio $\gamma = r_B / v r_A$ (for the reaction $A + \nu B \rightarrow P$).

The registered curves transparence–time were evaluated for reactions (A) to (D) as follows: at feeding one component into the initial solution of the second (method 1) simultaneously with the curve obtained at feeding into the empty solution $(a = 0)$ the curves transparance–time were replotted to the curves absorbance–time, the linear branches were extrapolated (Fig. 2) and

from the time coordinate of intersection was then calculated the rate constant from the relation[1] $k = 1/vta$. Advantage of this method is that neither the feed rate nor the extinction coefficient need to be known of the coloured reaction component. At feeding both reaction components into the empty solution (method II) at their stoichiometric ratio was from the horizontal asymptote to the curve transparence–time taken (by use of the calibration curve) the stationary concentration and from it the corresponding horizontal line was drawn up to the intersection with the straight line $r.t$ drawn on basis of the known feed rate r. The rate constant was then determined[1] either from the time coordinate of this intersection according to the relation $k = 1/vr_A t^2$ or from the value of the stationary (asymptotic) concentration [A] according to the relation $k = r_A/v[A]^2$. At the nonstoichiometric ratio of the feed only the coordinates of the extreme on the curve transparence–time were determined and from the calibration curve the corresponding concentration was red off and the rate constant was evaluated according to the relation (15)[1]. For reactions (E) and (F) the reaction products were considered only at the method of stoichiometric feed and the rate constant was determined[1] from the time coordinate of intersection of the linear branch of the curve absorbance–time extrapolated to the x-axis.

The feed rates for the method I were chosen by trial so that the time coordinate of intersection would not depend on the feed rate[1] which at the radius of pistons of the syringe 0·25 cm, linear displacement 0·1 to 1 cm/min, molarity of the feed solution 0·5 to 0·1M and volume of the reaction mixture 50 ml could vary in the range from $3·6 . 10^{-5}$ to $6·6 . 10^{-7}$ mol/l s. The initial concentration of the non-fed component was about 10^{-3}M and is given in Table I similarly as the
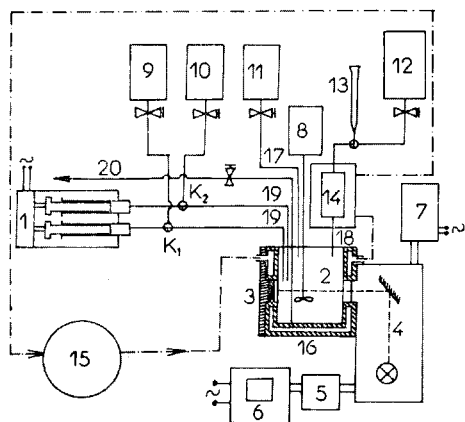

FIG. 1

Block Diagram of the Apparatus
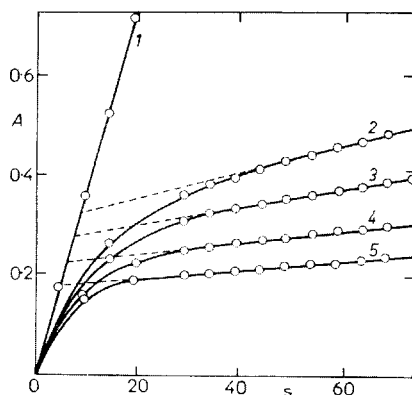   Individual symbols are given in the paper.

FIG. 2

Curves Absorbance–Time at the Feed of One Component

   The component fed is Fe^{3+}, the component in solution Sn^{2+} with the initial concentration in mmol/litre: *1* 0·00, *2* 8·11, *3* 9·44, *4* 11·42, *5* 13·38. Temperature 20°C, solution 2M-HCl.

TABLE I

Rate Constants k [$M^{-1} \cdot s^{-1}$] and their Standard Deviation σ for Reactions (A) to (D)

Reactions and feed conditions	Temperature	Method I		Method II, $\gamma = 1$			Method II, $\gamma \neq 1$		References or independent method
		$k_1 \pm \sigma$	n	$k_2 \pm \sigma$	$k_3 \pm \sigma$	n	$k_4 \pm \sigma$	n	
(A) $a \cdot 10^3$ 13—5; $10^6 r_{Fe}(\gamma=1)$ 41—2; $10^5 r_{Fe'}(\gamma=0.5)$ 11—1;	20	14.3 ± 1.7	30	15.0 ± 1.3	16.8 ± 1.3	10	13.4 ± 0.4	10	14.1; 15.9; 16.1[5]
	30	34.7 ± 2.8	22	32.1 ± 2.1	31.9 ± 1.9	16	29.6 ± 0.8	10	—
	40	76.0 ± 5.2	12	82.4 ± 5.5	82.3 ± 5.8	14	80.3 ± 6.4	10	—
	50	184 ± 10	8	190 ± 15	187 ± 12	14	174 ± 15	10	—
E_{akt} (kcal/mol)		15.1		15.2	14.5		14.9		16.1[5]
(B) $a \cdot 10^3$ 20—2; $10^5 \cdot r_{Fe}(\gamma=1)$ 47—2; $10^5 \cdot r_{Fe}(\gamma=0.18)$ 47—2;	15	14.6 ± 1.1	20	16.4 ± 1.5	16.3 ± 1.7	10	15.4 ± 0.6	8	14.6[6]
	20	21.4 ± 1.5	40	20.5 ± 1	20.7 ± 1.2	10	21.9 ± 1.1	10	23.5[6]; 23[7]
	25	36.9 ± 1.9	20	32.9 ± 2.4	32.9 ± 2.4	12	35.3 ± 3.9	10	35.3[6]
	35	79.2 ± 6.1	30	72.2 ± 7.6	71.4 ± 6.2	12	78.0 ± 4.4	10	—
E_{akt}		15.3		13.0	13.0		15.2		15.4[6]
(C) $a \cdot 10^3$ 22—3; $10^6 \cdot r_{Ce}(\gamma=1)$ 16—1; $10^6 \cdot r_{Ce}(\gamma=0.25)$ 41—1;	15	12.1 ± 0.7	27	12.4 ± 0.5	12.8 ± 0.6	12	11.3 ± 0.6	18	11.3[6]; 12.2
	20	18.5 ± 1.4	34	17.6 ± 0.8	18.4 ± 0.6	12	19.1 ± 0.9	18	18.3[6]; 18.5; 18[7]
	25	23.2 ± 1.8	30	21.8 ± 1.5	22.3 ± 1.5	10	25.2 ± 1.0	18	26[6]; 26.4
	30	30.5 ± 1.9	20	32.3 ± 1.9	34.4 ± 1.8	10	35.3 ± 1.9	17	37.2[6]; 36.7
	35	44.6 ± 4.6	20	43.5 ± 3.9	44.4 ± 2.2	10	45.8 ± 3.5	15	—
E_{akt}		11.1		11.0	11.2		12.1		14.4[6]; 12.9
(D) $a \cdot 10^4$ 12—2; $10^6 \cdot r_{Ce}(\gamma=1)$ 17—1; $10^6 \cdot r_{Ce}(\gamma=0.5)$ 41—13;	15	628 ± 80	19	619 ± 74	588 ± 51	10	630 ± 38	11	—
	20	882 ± 105	36	923 ± 71	884 ± 28	10	848 ± 47	21	833[4]
	25	1 151 ± 165	17	1 338 ± 61	1 349 ± 25	10	1 280 ± 194	21	957[7]
	30	1 614 ± 170	16	2 079 ± 322	1 988 ± 342	10	1 925 ± 133	16	1 350[8]
E_{akt}		10.8		13.6	14.5		13.1		13[8]

range of feed rates for the method II. For reactions (E) and (F) the obtained rate constants were checked spectrophotometrically in a batch reactor or in a flow reactor[4]. For other reactions they were compared with literature.

RESULTS AND DISCUSSIONS

As model reactions were selected:

Solution	Temp., °C	Reaction	
2M-HCl	20 — 50	Fe(III) + Ti(III) = Fe(II) + Ti(IV)	(A)
2,5M-HCl	15 — 35	2 Fe(III) + Sn(II) = 2 Fe(II) + Sn(IV)	(B)
2N-H$_2$SO$_4$	15 — 35	2 Ce(IV) + Sn(II) = 2 Ce(III) + Sn(IV)	(C)
2N-H$_2$SO$_4$	15 — 30	Ce(IV) + V(IV) = Ce(III) + V(V)	(D)
Puffer pH 3·9 — 5·6	15		(E)

Puffer pH 7   20   (F)
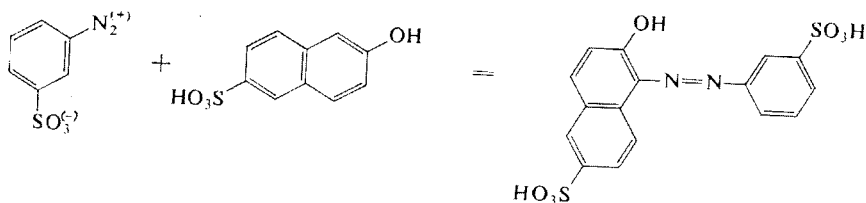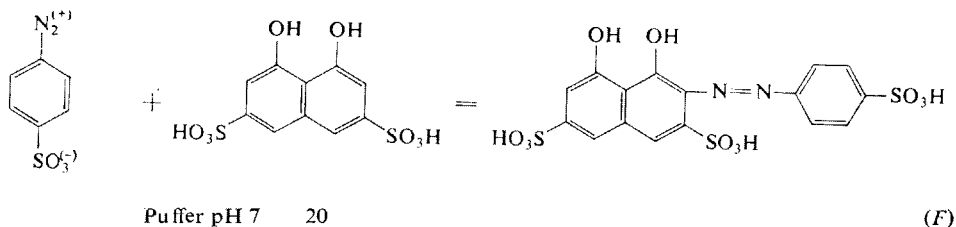
For reactions (A) to (D) were verified both forms of the feed reactor. At feeding only one component (method I) this were for the reaction (A), (B) the ferric ions, for reactions (C) and (D) ceric ions. At constant feed rate were chosen different initial concentrations of the non-fed component. The typical curves absorbance–time obtained at such a procedure are given for illustration in Fig. 2.

At feeding two components (method II) both the stoichiometric ($\gamma = 1$) as well as nonstoichiometric ($\gamma \neq 1$) feed were studied at various feed rates and at their constant ratio γ. The obtained results are summarized in Table I in which the values k_1 and k_2 are determined from the time coordinate of intersection, values of k_3 from the

time and concentration coordinates of intersection, values of k_4 from the time and concentration coordinates of the extreme. Symbol n denotes the number of samples.

As in reactions (E) and (F) the products were analysed, method I could have been used, while method II could have been used for stoichiometric feed[1] only. But only the second method proved to be suitable. The obtained results are given in Table II.

TABLE II

Rate Constant $k[\text{M}^{-1}\text{s}^{-1}]$ and their Standard Deviation for Reaction (E) and (F)

Reaction and feed conditions	pH	Method II stoichiometric feed		Classical method static reactor	
		$k \pm \sigma$	n	$k \pm \sigma$	n
(E) 15°C					
$r \cdot 10^6$ 45—1	3·9	$31 + 2$	16	$25·7 \pm 5$	22
10—1	5·0	331 ± 25	24	302 ± 21	18
10—1	5·6	626 ± 78	16	645 ± 75	12
(F), 20°C					
$r \cdot 10^5$ 6—1	7·0	$14·2 \pm 1$	6	$15 \pm 1·4$	18

For comparison of individual methods the mean values were tested for reactions (A) to (D) by the t-test and the standard deviations by the F-test on the 5% level of significance. It resulted that both forms of feeds are mutually substitutive. The deviations have appeared only in two cases: for reaction (B) at the stoichiometric feed at 35°C when the calculated stationary (assymptotic) concentrations of ferric ions were slightly greater and thus the rate constant was smaller than corresponds to the methods where the initial branches were considered. The reason is probably the under--stoichiometric content of stannous ions at the end of the reaction which is the result of the ten imperfect inert atmosphere in the reactor in this series of experiments. In reaction (D) at feeding the ceric ions into the solution of vanadyl sulfate at 25 and 30°C the calculated rate constants are smaller than in other methods. This is the result of too large rate constants so that the product ak is about equal to one while the concentration of vanadyl ions a cannot be further decreased because the condition[1] $\sigma \approx 0·06$, at the relatively large feed rate of ceric ions (necessary for obtaining the sufficiently obvious stationary concentration) just requires the sufficiently large initial concentration of vanadyl. This shifts the time of intersection $t = 1/ak$ to too small values where it cannot be reliably measured.

The sufficiently large value of the time coordinate of intersection has a specia meaning for reactions where the products are studied as by the intersection of the

coordinate axis shorter times are obtained than those obtained by intersection of the higher situated horizontal lines in cases where the reactants are considered. Here therefore the IInd method is advantageous (stoichiometric feed) in which the time coordinate of intersection can be extended since the product $k \, [A] \, [B]$ is negligible $[A(t) \approx 0)]$ and $[B(t) \approx 0)]$ at the beginning of the reaction. The rate constants for reactions (E) and (F) obtained in this manner are statistically equivalent with the values obtained in another independent way.

Summarily, it can be said that for isolated second order reactions the feed of the component into the solution of the second is suitable for cases where for the satisfied condition $\sigma \leqq 0.06$ the condition $ak \ll 1$ could be arranged for. The reaction can be then studied also by considering the products. Method I is advantageous as neither the concentration of the fed component need to be known nor its feed rate nor the extinction coefficients of the components.

The method of continuous feed of both components into an empty solution in stoichiometric or nonstoichiometric ratio has proved to be suitable for isolated second order reactions with the rate constant up to $10^3 M^{-1} s^{-1}$. This limitation is not a general one but it is given by the experimental arrangement employed, by the sensitivity of the analytical method used and by the intensity of mixing.

A great advantage of both methods in comparison with the flow arrangement is in the small amount of reactants needed and in simplicity of the apparatus employed. Their accuracy is comparable or even greater than of the methods usually used. The advantage of the presented feed reactor as compared to the static (batch) reactor is first of all in the possibility to study even relatively fast reactions without being necessary to use very diluted solutions which can cause a number of problems. So *e.g.* measurement with the reaction (D) performed in the static reactor[8] required the order of magnitude of initial concentrations $10^{-5} M$ while in our arrangement at feeding both components solutions 0·5 and 0·1M were employed and at feeding one component the initial concentration of the non-fed component was $10^{-3} M$. At the same time the experimental arrangement of the feed reactor is not too complicated so that the given advantages would not loose on importance.

In comparison with the backmix flow reactor where the complexity of the used experimental arrangement is at about the same level the advantage of the feed reactor is first of all in the simple method with which the rate constant is determined from the easily to be found time coordinate. Moreover, the nonstationary arrangement is important for more complex mechanisms where on one curve absorbance–time individual steps can be observed, while in the backmix flow reactor operated in the stationary regime this becomes impossible.

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