

REACTIONS $\text{Fe(III)} + \text{V(III)} + \text{V(IV)} + \text{Fe(II)}$
AND $\text{V(II)} + \text{V(IV)} = 2 \text{V(III)}$ STUDIED BY THE STOP-FLOW METHOD
WITH A DROPPING MERCURY ELECTRODE*

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The title reactions were studied with a dropping mercury electrode in a static reactor and by the stop-flow method. Systems of $E-t$ curves obtained experimentally are in full agreement with theory, and rate constants derived from them are in accord with values obtained spectrophotometrically. The results for the medium of $2\text{N-H}_2\text{SO}_4$ at 20°C are: $k(\text{Fe(III)} + \text{V(III)}) = 1.5\text{M}^{-1}\text{s}^{-1}$, $E_{\text{act}} = 21.5 \text{ kcal/mol}$; $k(\text{V(II)} + \text{V(IV)}) = 5.6\text{M}^{-1}\text{s}^{-1}$, $E_{\text{act}} = 17 \text{ kcal/mol}$.

Previous studies dealing with potential-time curves at zero current used a platinum indicator electrode and a reactor in a static arrangement. A complicating factor is the variable quality of the platinum surface, *i.e.* the problem of ideality or nonideality of the indicator electrode and its influence on the reproducibility of the $E-t$ curves and the determination of rate constants. These difficulties are overcome by using a dropping mercury electrode, whose surface is automatically renewed, the solution at the electrode being spontaneously stirred. It can be therefore used with advantage not only in a static reactor but also in the stop-flow method, which is useful in the case of reactions that are too rapid to permit a relatively slow mixing of reaction components by the classical method. The application of the dropping mercury electrode in studying the $E-t$ curves at zero current is, however, restricted to such reactions where the oxidation agent, Ox_2 , does not react with mercury or reacts very slowly as compared with oxidation of the Red_1 form. This condition is fulfilled, *e.g.*, by Fe(III) ions in sulphate solutions.

It was the aim of the present work to verify the applicability of the dropping mercury electrode in studying the kinetics of reduction-oxidation reactions by the method of $E-t$ curves both in a static and a flow-through reactor, and at the same time to verify the method of determination of rate constants based on the complete, nonsimplified equation of $E-t$ curves, described previously¹.

EXPERIMENTAL

Chemicals

An approximately 0.4M-VOSO_4 solution in $2\text{N-H}_2\text{SO}_4$ (reagent grade, Lachema, Brno) was prepared by dissolving ammonium tetravanadate (pure, Lachema, Brno), reducing with sulphur

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dioxide and boiling while the solution was bubbled with carbon dioxide², the excess of SO₂ being thus removed. Vanadium(II) sulphate was prepared freshly before every measurement by reduction of a vanadyl sulphate solution with amalgamated zinc in a reactor in argon atmosphere. Approximately 0.1M-V₂(SO₄)₃ in 2N-H₂SO₄ was prepared by mixing equal parts of VOSO₄ and VSO₄ solutions of the same concentration in an atmosphere of argon. The concentration of the vanadium salt solutions was determined by potentiometric titration with cerium(IV) sulphate³. Approximately 0.1N-Fe₂(SO₄)₃ of reagent grade (Lachema, Brno) in 2N-H₂SO₄ was standardized potentiometrically with a V(III) solution of a known concentration³.

Apparatus

Electrochemical measurement. The method of measurement of *E-t* curves and their recording was described previously⁴⁻⁶. Dropping mercury indicator electrodes according to Smoler⁷ had a drop time of 4 s in a quiet solution of 2N-H₂SO₄ on open circuit; this value was maintained by adjusting the height of the mercury level. A mercurous sulphate electrode with a salt bridge filled with saturated potassium sulphate served as reference. The reactor in a static arrangement was of the type previously described⁴ except that the capillary of the dropping electrode after Smoler⁷ was inserted through the opening designed for a platinum electrode. Since the action of the electromagnetic stirrer caused irregular dropping of the indicator electrode,* the solution was stirred only during adding the Ox₂ form to Red₂, and after the abrupt increase of potential the stirring was stopped. Thus, an excellent reproducibility of the *E-t* curves besides stability of the drop time was achieved.

The parameter $n = [\text{Ox}_1(t = 0)]/[\text{Red}_2(t = 0)]$ was changed in the case of the first reaction by adding increasing amounts of Fe³⁺ ions to the solution of V³⁺ ions of always the same initial concentration, and with the second reaction analogously by feeding V²⁺ ions to a solution of vanadyl sulphate. For the reaction of Fe(III) with V(II), the range of initial concentrations of V³⁺ ions was 0.001–0.02M and the initial concentration of Fe³⁺ ions was chosen so that the parameter *n* lay in the range 0.02–0.99 (Fig. 3). With the reaction of V(II) with V(IV), the initial concentration of VO²⁺ ions was 0.001–0.032M and that of V²⁺ ions such that the parameter *n* was in the range 0.09–0.9 (Fig. 4).

The reactor in the flow-through (or, alternatively, stop-flow) arrangement with accessories is shown schematically in Fig. 1; the reaction components were fed into the mixing compartment by means of syringes (this part of the apparatus was the same as in ref.⁵). The outlet of the mixing compartment was connected with a reaction tube provided with an opening for the Smoler capillary, a salt bridge for the reference electrode, and an outlet of the reaction mixture. Stopping of the flow (after an abrupt increase of the potential) was achieved by the stopcock 8 synchronously with switching on the recorder. Afterwards the action of the syringes was stopped. The time necessary to stop the flow was of the order of 50 ms provided that the stopcock was turned by 90° during 0.5 s, the mean radius of its cone was 7.5 mm and the bore diameter 1 mm. The parameter *n* was changed by diluting gradually the stock solution of Fe³⁺ or V²⁺ ions sucked into the syringes. The diameter of the syringes was 10 mm, of the reaction tube 1.5 mm, and the feed rate was about 2.5 mm/s; the indication point was 6.5 cm apart from the mixing point. The measured solutions were deaerated with argon. The rate constant, *k*₁, was determined from the slope of the straight line obtained by transformation of the dependence of $t(1 - n)$ on $\log n$ by the method described previously¹ for an ideal electrode.

* Irregular dropping, however, does not result in a large error in the determination of the rate constant as can be seen from the results obtained during continuous stirring of the reaction mixture.

Spectrophotometry. The flow-through apparatus⁵ was used, but the method of measurement was different. Starting from the kinetic equation in the integrated form for a second-order reaction with a rate constant k , we express the relative concentration of the product, x/b (for $n \leq 1$) or x/a (for $n \geq 1$), as $(A - A_0)/(A_\infty - A_0)$, where A , A_0 and A_∞ denote actual, initial and final absorbances, respectively; further we express the age of the reaction mixture as the sum of the time, τ , necessary to pass the distance, Z , between the mixing and indication points (in a tube of radius r , the radius of the syringes being R and the linear feed velocity S) and the time, t , elapsed from the moment of stopping the flow. Then we can write the kinetic equations in the form

$$\tau = (Z/2S)(r/R)^2, \quad (Ia_1)$$

$$bk(\tau + t) \frac{1-n}{n} \log e = \log \frac{(1-n)A_0 - A_\infty + nA}{A - A_\infty} \equiv \log R_1, \quad n < 1, \quad (Ia_2)$$

$$bk(\tau + t) \frac{n-1}{n} \log e = \log \frac{(n-1)A_0 - nA_\infty + A}{n(A - A_\infty)} \equiv \log R_2, \quad n > 1, \quad (Ia_3)$$

$$bk(\tau + t) = (A_0 - A)/(A - A_\infty) \equiv R_3. \quad (Ia_4)$$

Two different methods were used in connection with these equations. In the first, flow-through method (where t is set equal to zero) the absorbance in a chosen place of the reaction tube was measured in dependence on the shifting rate, S , of the syringe piston. By plotting $\log R_{1,2}$ or R_3 against $1/S$, straight lines passing through the origin of coordinates with a slope σ are obtained, from which the rate constant, k , can be determined, since

$$\sigma_{n \neq 1} = \frac{1}{2}bkZ(r/R)^2 |1 - 1/n| \log e; \quad \sigma_{n=1} = \frac{1}{2}bkZ(r/R)^2. \quad (Ib_{1,2})$$

The initial absorbance, A_0 can be determined by measuring the absorbances (in a chosen place of the tube), A_b and A_a of the pure components, Ox_1 and Red_1 , and taking their arithmetic mean. The value of A_∞ is measured after stopping the flow and after a sufficiently long time when it does not change any more with time.

In the second, stop-flow method, the photocell current corresponding to a chosen place of the reaction tube is automatically recorded by a compensation recorder (such as G_1B_1 , Zeiss, Jena) and the dependence of transmittance on time is measured from the moment of stopping the flow; from this the dependence of absorbance on time is obtained: Plotting the quantities $\log R_{1,2}$ or R_3 against time gives straight lines with a slope s and section U given as

$$U_{(n \neq 1)} = bk\tau |1/n - 1| \log e, \quad U_{(n=1)} = bk\tau, \quad (Ic_{1,2})$$

$$s_{(n \neq 1)} = bk |1/n - 1| \log e, \quad s_{(n=1)} = bk, \quad (Id_{1,2})$$

whence the rate constant, k , can be again calculated. The choice of the beginning of the time scale does not influence the determination of k if the slope s is used; however if use is made of the section U then the instant $t = 0$ must be found by extrapolation of the transmittance-time dependence to the value of transmittance = $10^{-\epsilon_0}$. (Provided that the instant $t = 0$ is known, it is possible to determine the reaction half-time, $(t + \tau)_{1/2}$, and from it the rate constant according to Eqs (Ia₂₋₄), where we set $A = (A_0 + A_\infty)/2$.) The connexion between the shift of the beginning of the transmittance-time curves and the shift rates S (according to equation (Ia₁)) can be seen

from Fig. 2. In the apparatus used, the radius of the reaction tube, r , was 1.5 mm and the radius of the syringes $R = 10$ mm, as already stated. With the reaction of Fe(III) with V(III), all optical measurements were made at a wave length λ 380 nm, a distance $Z = 20$ cm, shift rate $S = 4.3$ mm/s, concentration of Fe(III) $b = 0.05$ and 0.1 M, and concentration of V(IV), a , variable so that the parameter n attained the values of 0.496, 0.605, 1, and 1.188. With the reaction of V(II) with V(IV), all measurements were made at a wave length λ 770 nm, distance $Z = 25$ cm, shift rates $S = 2.5, 3.5, 4.3$ and 5.5 mm/s, initial concentrations of V(IV) 0.03, 0.04 and 0.05856 M and values of $n = 1.333, 1$ and 0.64 .

RESULTS AND DISCUSSION

Both reactions were followed in a medium of 2N-H₂SO₄ at 15 and 40°C electrochemically with the use of $E-t$ curves at zero current in a static reactor and by the stop-flow method, and also spectrophotometrically during the flow as well as after stopping it. The system of $E-t$ curves together with the $t(1-n) - \log n$ dependence and its

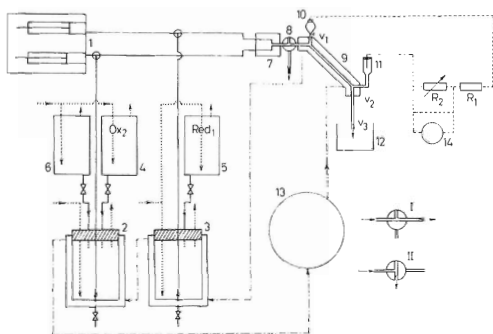


FIG. 1

Apparatus for Recording $E-t$ Curves by the Stop-Flow Method

1 Feeder; 2, 3 vessels for tempering solutions of reaction components before entering into the feeder; 4, 5 stock burettes with reaction components; 6 stock burette for the reaction medium, by the addition of which the initial concentration of a reaction component could be changed, and after mixing with the other component the parameter n could be changed as well; 7 mixing jet compartment; 8 three-way stopcock (position I — stationary flow, II — stopped flow); 9 two-mantle tempered reaction tube with outlet v_1 for inserting mercury electrode 10, v_2 for salt bridge of reference electrode 11 and v_3 for leading the reaction mixture into reservoir 12. — · — · — Flow of tempering liquid from thermostat 13, — — — electrical connections of the measuring circuit with resistances R_1 and R_2 and with the EZ 2 recorder 14, ····· flow of argon.

linearization by means of the quantity \mathfrak{z} (defined in ref.¹) for the reaction of Fe^{3+} with V^{3+} ions is shown in Fig. 3, and for the reaction of V^{2+} with VO^{2+} in Fig. 4.

These systems were obtained either by injecting 0.0208M solution of V(III) (Fig. 3) or 0.01632M V(IV) (Fig. 4) into the mixing compartment filled with 2N- H_2SO_4 at 20°C, and the other component of variable concentration to make the parameter $n = [\text{Fe}^{3+}(t=0)]/[\text{V}^{3+}(t=0)]$ or $[\text{V}^{2+}(t=0)]/[\text{VO}^{2+}(t=0)]$ attain the values indicated in Fig. 3 or 4. The instant of stopping the flow is denoted by a perpendicular

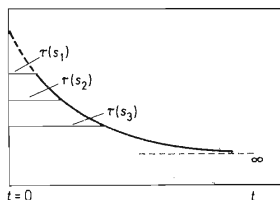


FIG. 2

Transmittance-Time Curve During Combination of Flow-Through and Stop-Flow Methods

The positions of the horizontal lines correspond to different rates of flow given by the shifting rates S , their lengths give the time τ (s). The extrapolation to determine the instant $t = 0$ is denoted by a broken line.

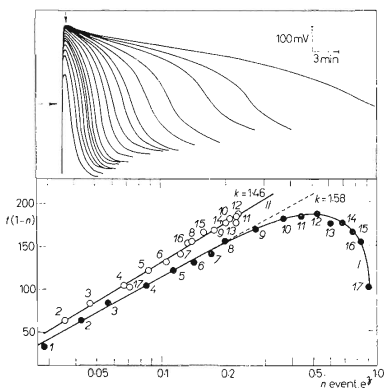


FIG. 3

System of $E-t$ Curves and its Evaluation for Reaction (A) Followed by the Stop-Flow Method

Parameter n for each curve beginning from below: 0.0288; 0.0431; 0.0575; 0.0860; 0.115; 0.143; 0.171; 0.199; 0.277; 0.366; 0.450; 0.533; 0.616; 0.695; 0.773; 0.847; 0.921; 0.994. Dropping mercury electrode according to Smoler, $t_1 = 0.7$ s.

TABLE I

Values of Rate Constants, $k(M^{-1} s^{-1})$

Spectrophotometric data refer to the stop-flow method except for reaction (B) at 35 and 40°C (flow-through method) and 30°C (both methods).

Reaction	t °C	Potential-time curves		Spectrophotometric
		static reactor	stop-flow	
(A)	15	0.78 ± 0.1^d	$0.85 \pm 0.11_a$	0.82 ± 0.02^c
	20	1.58 ± 0.17^d	1.50 ± 0.12^a	1.55 ± 0.01^c
	25	2.88 ± 0.16^c	2.70 ± 0.28^a	2.92 ± 0.18^c
	30	5.30 ± 0.18^c	5.71 ± 0.54^a	5.15 ± 0.24^c
	35	9.91 ± 0.59^c	10.00 ± 1.73^d	8.91 ± 0.38^c
	40	15.60 ± 0.65^d	17.96 ± 2.29^d	16.62 ± 0.64^c
(B)	15	3.47 ± 0.45^b	2.98 ± 0.35^b	3.61 ± 0.24^e
	20	5.38 ± 0.77^b	6.21 ± 1.58^a	5.18 ± 0.51^e
	25	8.56 ± 0.72^b	9.18 ± 1.42^a	8.15 ± 0.83^e
	30	13.18 ± 1.97^b	12.94 ± 1.04^a	16.26 ± 0.59^d
	35	22.92 ± 2.27^b	24.67 ± 0.24^e	23.24 ± 2.41^d
	40	33.72 ± 2.52^d	36.49 ± 1.65^e	34.86 ± 3.43^d

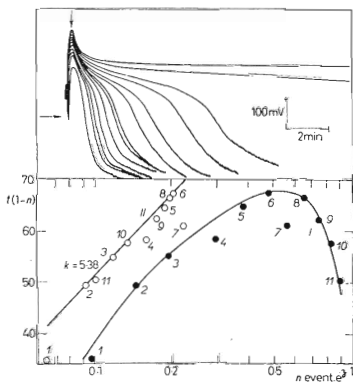
The standard deviation was calculated from ^a 7, ^b 6, ^c 5, ^d 4, ^e 3 measurements.

FIG. 4

System of $E-t$ Curves and its Evaluation for Reaction (B) Followed by the Stop-Flow MethodParameter n for each curve beginning from below: 0.0972; 0.145; 0.193; 0.287; 0.380; 0.471; 0.561; 0.650; 0.737; 0.823; 0.880; 0.991; 1.073. Dropping mercury electrode, $t_1 = 2.4$ s, $2N-H_2SO_4$, $20^\circ C$.

arrow, the time readings refer to the potential level denoted by a horizontal arrow. The corresponding values of the term $t(1 - n)$ were plotted both against $\log n$ (curve system I) and against $3 \log e$ (curve system II) with $n_{\max} = 0.52$ (Fig. 3) or 0.54 (Fig. 4); a logarithmic scale on the abscissa was used. The point numbers correspond to the order of chosen n values. The numerical data at the straight lines give the values of the rate constant k (in $\text{M}^{-1} \text{s}^{-1}$ units) found from the slope.

Both figures show the linear correlation between $t(1 - n)$ and 3 to be well fulfilled, an evidence for the correctness of the complete equation of the $E-t$ curves as well as for the method of determining the rate constant¹.

In the case of spectrophotometry, accurate straight lines were obtained by plotting $\log R_{1,2}$ and R_3 against t and $1/S$. With the reaction (A), $\text{Fe(III)} + \text{V(III)}$, the stop-flow method was used. The reaction (B), $\text{V(II)} + \text{V(IV)}$, at 15–30°C was followed in the same way but at 30–40°C the flow-through method was used since the low absorptivity of the reaction components makes it necessary to use higher concentrations (of the order of 0.01–0.1M), and at higher temperatures the reaction rate becomes too high for the stop-flow method. The results for both reactions, (A) and (B), are summarized in Table I. The experimental values of the rate constants obtained by the different methods fulfill the Arrhenius equation with activation energies 21.54 and 17.0 kcal/mol for the reactions (A) and (B), respectively. The rate constants determined by the method of $E-t$ curves at zero current are in good agreement with those found spectrophotometrically with both reactions.

In the medium of sulphuric acid and sodium sulphate (pH 0 and 2), the reaction (B) was followed polarographically⁸ at 18–43°C and the results are in a satisfactory agreement with our data. In the medium of perchloric acid and sodium perchlorate, this reaction was measured in the temperature range 0.4–34.5°C spectrophotometrically^{9–11} and found to be slower by a factor of about 0.1. The literature data for the reaction (A) in the medium of perchloric acid^{12,13} show it to be slower by a factor as small as 0.01.

Both spectrophotometry and $E-t$ curves make it possible to determine the rate constant with an accuracy of about 10%. The agreement between the mean values of the rate constants obtained by different methods shows that these values do not depend on the type of the indicator electrode (in analysis of the systems of $E-t$ curves, the transfer coefficient α and the rate constant \mathfrak{R} of the electrode process are separated from the rate constant k of the homogeneous red-ox reaction) and on the type of the reactor. Thus, the correctness of the theoretical equations derived for the $E-t$ curves, obtained either by the classical method of mixing the reaction components or by the stop-flow method, is demonstrated. At the same time it is obvious that the dropping mercury indicator electrode is suitable for obtaining the $E-t$ curves as long as any of the reaction components does not oxidize mercury.

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