FLOW AND STOP FLOW METHODS WITH COAXIAL INDICATION*

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Relations are derived for dependence of arbitrary quantities which are linear functions of composition on time, position and flow rate for the flow and stop methods with optical indication coaxial to the direction of flow. Determination of the rate constant for reversible second order reaction which requires solution of a transcendent equation is transformed to a simple plot of a straight line in the single nomogram; in another approximation where the error is less than 5%, to the solution of intersection of two straight lines with experimentally determined slopes and intercepts. The apparatus with indication coaxial to the direction of flow is described and its function is verified on a model reaction $Ce(IV) + V(IV) = Ce(III) + V(V)$.

The condition for a satisfactory application of optical indication for studies in reaction kinetics is a sufficiently large absorbance of reaction components. For compounds insufficiently coloured it is then necessary to increase either the initial concentration of reactants or the optical path. The first method cannot be used where, due to increased concentration, the reaction rate increases beyond certain limits sufficient for measurements in the given type of apparatus and its parameters. The second method operating with optical path perpendicular to the direction of flow would increase dimensions of the apparatus above the limits of practical applicability. Thus there only remains to increase the optical path so that absorbance of the whole column of mixture is measured along the reaction tube at flow or after the flow is stopped. Such experiment based on the optical system coaxial with the direction of flow is in the literature described only once — at flow and for the special condition of stoichiometric ratio of reactants for an irreversible second order reaction[1].

Here an attempt has been made to present a solution for the reversible second order reaction with an arbitrary ratio of initial concentrations of reactants both for the flow as well as for the stop flow methods with optical indication coaxial with the direction of flow and to demonstrate their practical application.

THEORETICAL

The age of a selected volume element of reaction mixture τ is given by the time interval from the moment of mixing the reactants to the moment of measurement. This interval is given by the time y/v, which is necessary for the volume element of reaction mixture to reach with the velocity

v the observation point in the distance y from the point of mixing, and by the time t which elapsed from the moment the flow is stopped to the moment of measurement at the point y.

For plug flow all volume elements have the same velocity, under other hydrodynamic conditions the velocity profile forms (for laminar flow parabolic distribution) so that velocity of the volume element is a function of polar coordinates $v(r, \varphi)$ changing in the area given by the cross--section of the reactor.

This means that in integrated forms of kinetic equations in various types there appears as time the variable $\tau = (y/v) + t$. If the indication is performed locally $e.g.$ in the j-th volume element of the reaction mixture at the distance y_j then concentration of the i-th reaction component c_i is given by the initial concentrations $a_1, a_2, \ldots$ of reactants, by the rate constants $k_1, k_2 \ldots$ of individual reaction steps and by the time τ_j in the form

$$c_i = f_i(a, k, \tau_j), \tag{1a}$$

where the form of the function f_i is known from the solution of kinetic equations of the corresponding scheme. If some quantity which is linearly dependent on the composition of the reaction mixture is used for studies of the state of reaction component in the j-th volume element $e.g.$ the absorbance A of the optical path l in the measured element and the extinction coefficients of components ε_i, then it holds

$$A_j = l \sum_i \varepsilon_i f_i(a, k, \tau_j). \tag{1b}$$

But if measurements are performed in all the elements of the reaction mixture simultaneously by the beam passing through the whole length of the tube L, it is necessary to sum all absorbances of individual elements (with the differentially small optical path $l \equiv \mathrm{d}y$) so that

$$A = \sum_j A_j = \int_0^L \sum_i \varepsilon_i f_i(a, k, (y/v) + t)\, \mathrm{d}y. \tag{1c}$$

This relation holds for the plug flow in the whole cross-sectional area of the reactor tube. For the case with the velocity distribution $v(r, \varphi)$ it holds only for the differentially narrow streamline. As the probe of the indicating device reacts to the overall luminous flux, it is necessary in the case of velocity distribution to add the differential luminous fluxes corresponding to individual differential streamlines. By use of these integral flows (inlet $J_0 \pi r_0^2$ and outlet $J_0 \int_{\varphi=0}^{2\pi} \int_{r=0}^{r_0} [\exp(-A)]\, r\, \mathrm{d}r \cdot \mathrm{d}\varphi$) we obtain after arrangement the resulting absorbance A (at the assumption that the outlet slit corresponds to the total cross-sectional area of the reactor).

$$\bar{A} = -\ln \int_0^1 \exp\left[-\int_0^L \sum_i \varepsilon_i f_i\left(a, k, \frac{y}{v(r/r_0)} + t\right) \mathrm{d}y \right] \cdot \mathrm{d}\left(\frac{r}{r_0}\right)^2. \tag{1d}$$

For such reaction-kinetic systems where the actual concentration of each coloured reactant can be expressed as the difference in the initial concentration and another single mutual parameter

e.g. of the decrease x^*

$$C_i = a_i - v_i x, \qquad (2a)$$

where v_i is the constant coefficient and for isolated reactions the stoichiometric coefficient, x-similarly as c_i-a function of initial concentrations, of rate constants and of time τ, *i.e.* $x = g$ (a, k, τ), the relation $(1c)$ can be arranged in the form

$$A = \int_0^L \sum_i \varepsilon_i \left[a_i - v_i\, g \left(a, k, \frac{y}{v} + t \right) \right] \mathrm{d}y = L \sum_i \varepsilon_i a_i - \sum_i \varepsilon_i v_i \int_0^L x\, \mathrm{d}y . \qquad (2b)$$

By introducing the absorbance A_0 or the zero decrease x in the time $t = 0$ and the final absorbance A_∞ in the time $t = \infty$, which corresponds to the drop x_∞, the relations $L \sum \varepsilon_i a_i = A_0$ and $\sum \varepsilon_i v_i = (A_0 - A_\infty)/x_\infty L$, can be eliminated so that by substitution into $(2b)$ and by an explicitly expressed integral $x\, \mathrm{d}y$ the relation is obtained

$$\frac{A_0 - A}{A_0 - A_\infty} = \int_0^L \frac{x}{x_\infty} \frac{\mathrm{d}y}{L} = \int_0^L \frac{g\,(a, k, \tau)}{g\,(a, h, \tau = \infty)} \frac{\mathrm{d}y}{L}. \qquad (2c)$$

As left hand side of Eq. $(2c)$ can be obtained from the experiments and the right hand side includes for the unknowns the rate constants $k_1, k_2, \ldots$ only, the relation $(2c)$ can be considered to be the key for their determination. A similar arrangement of Eq. $(1d)$ gives the relation

$$\frac{\bar{A}_0 - \bar{A}}{\bar{A}_0 - \bar{A}_\infty} = \frac{1}{\bar{A}_0 - \bar{A}_\infty} \ln \int_0^1 \exp \left[(\bar{A}_0 - \bar{A}_\infty) . \int_0^L \frac{x}{x_\infty} \frac{\mathrm{d}y}{L} \right] . \mathrm{d} \left(\frac{r}{r_0} \right)^2 , \qquad (2d)$$

which by use of the mean value theorem for the velocity $v(r^+)$, where $r^+ \in (0, r_0)$ gives formally the same equation as is the $(2c)$ where only the velocity of plug flow is substituted by the mean velocity $v(r^+)$ the value of which depends on the type of reaction, on the difference in colour during the reaction and on the hydrodynamic character of flow. For illustration is in Table I demonstrated comparison of the plug flow velocity v with the mean velocity $v(r^+)$ for the irreversible second order reaction and the parabolic velocity distribution.

From tabulated ratios $v(r^+)$ in dependence on v is obvious that the mean velocity $v(r^+)$ is the smaller the greater is the velocity v for laminar flow which would lead in Eq. (7) to the correct value of the rate constant in respect to velocity v (calculated from the displacement of syringes at the assumption of plug flow). The time t and thus the reaction extent are of considerable magnitude only if the absorbance increases during the reaction $(i.e.$ for $\Theta > 0)$.

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* *E.g.* for isolated, simple reversible, or side reactions — as long the Wegescheider's principle holds, not for consecutive.

Table I

Ratio $v(r^+)/v$ of Mean Velocity and Plug Flow Velocity

$B = \beta \cdot \exp[\Phi a_1 k_1 z_1 t]$; $\Omega = \Phi a_1 k_1 z_1 l \cdot v_{max}^{-1}$; $v_{max} = \frac{1}{2}v$; $\Theta = (\bar{A}_0 - \bar{A}_\infty)(1 - \beta)$.

B	$\Omega = 0\cdot01$	$0\cdot03$	$0\cdot05$	$0\cdot1$	$0\cdot5$	1	2	Θ
2	0·424	0·546	0·604	0·686	0·874	0·942	0·992	+1
	0·302	0·438	0·494	0·568	0·771	0·862	0·942	−1
2·5	0·386	0·504	0·566	0·646	0·844	0·922	0·982	+1
	0·300	0·436	0·492	0·566	0·770	0·866	0·946	−1
3	0·364	0·490	0·544	0·624	0·828	0·912	0·976	+1
	0·298	0·434	0·490	0·564	0·769	0·868	0·948	−1
5	0·326	0·456	0·512	0·588	0·798	0·892	0·966	+1
	0·292	0·428	0·484	0·558	0·768	0·868	0·950	−1
9	0·306	0·438	0·492	0·568	0·780	0·880	0·960	+1
	0·290	0·424	0·478	0·554	0·766	0·868	0·952	−1
15	0·298	0·430	0·484	0·558	0·772	0·874	0·958	+1
	0·290	0·422	0·476	0·550	0·764	0·868	0·954	−1
30	0·300	0·424	0·478	0·552	0·768	0·870	0·956	+1
	0·290	0·420	0·476	0·548	0·762	0·866	0·954	−1

This means that for other than plug flow conditions there must be a strong dependence of rate constants on changes in the velocity of flow v and *vice versa*. This fact is a useful indication for considerations on the hydrodynamics of flow in practical applications of the reactor.

Eq $(2c)$ includes both experimental alternatives: For the flow method is t identically equal to zero and the change in the absorbance A is obtained at the constant length of the tube L by selection of variour flow velocities v. In the stop flow method L/v is a constant and the absorbance A is changing with time t.

In the following we will consider the relation $(2c)$ for the case which is of great importance in practice — the reversible second order reaction with a general stoichiometry $z_1 : z_2$

$$z_2 \text{ Red}_1 + z_1 \text{ Ox}_2 \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} z_2 \text{ Ox}_1 + z_1 \text{ Red}_2 \tag{3a}$$
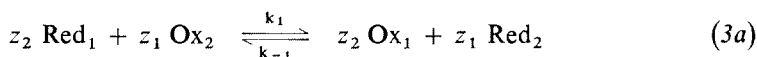
with the non-zero initial concentrations $[\text{Red}_1(t = 0)] = a_1$, $[\text{Ox}_2(t = 0)] = a_2$.

For the decrease x holds

$$\frac{[\text{Ox}_1]}{a_1} = \frac{z_2 x}{a_1} = \frac{\omega(n') \left[\exp\left[\Phi(n')\,\bar{\tau}\right] - 1\right]}{\beta(n') \exp\left[\Phi(n')\,\bar{\tau}\right] - 1}, \tag{3b}$$

where

$$n' = \frac{a_2 z_2}{a_1 z_1}; \quad \Phi = \left[(1 + n')^2 - 4n'(1 - k_{-1}/k_1)\right]^{1/2}; \quad \omega = \frac{1 + n' + \Phi}{2(1 - k_{-1}/k_1)}, \tag{3c,d,e}$$

and

$$\beta = \frac{1 + n' + \Phi}{1 + n' - \Phi}; \quad \bar{\tau} = a_1 k_1 z_1 \left(\frac{y}{v} + t\right), \tag{3f,g}$$

so that

$$\frac{z_2 x_\infty}{a_1} = \frac{\omega(n')}{\beta(n')} \tag{3h}$$

and by substitution into $(2c)$ and on integration the relation is obtained

$$\frac{A_0 - A}{A_0 - A_\infty} = \beta + \frac{v(1 - \beta)}{L \Phi a_1 k_1 z_1} \ln \frac{\beta \exp\left[\Phi a_1 k_1 z_1 \left(\frac{L}{v} + t\right)\right] - 1}{\beta \exp\left[\Phi a_1 k_1 z_1 t\right] - 1} \tag{4a}$$

with the limit for $v \to \infty$

$$\frac{A_0 - A}{A_0 - A_\infty} = \beta + (1 - \beta) \frac{\beta \exp \left[\Phi a_1 k_1 z_1 t\right]}{\beta \exp \left[\Phi a_1 k_1 z_1 t\right] - 1} , \qquad (4b)$$

which is identical with the relation valid for static reactor as the concentration changes along the tube are negligible for large flow rates.

For laminar flow the velocity v in $(4a)$ would mean the mean velocity $v(r^+)$ in the sense of Eq. $(2d)$.

By introducing the substitution $(4c,d)$

$$\frac{v}{L} \cdot t = \xi ; \quad \mathfrak{z} = \Phi a_1 k_1 z_1 \frac{L}{v} . \qquad (4c,d)$$

Eq. $(4a)$ can be arranged into the form

$$U \equiv \frac{A_\infty - A}{A_0 - A_\infty} \cdot \frac{1}{1 - \beta} + 1 = \mathfrak{z}^{-1} \cdot \ln \frac{\beta \exp \left[\mathfrak{z}(1 + \xi)\right] - 1}{\beta \exp \left[\mathfrak{z} \cdot \xi\right] - 1} \qquad (5a)$$

If the equilibrium constant k_{-1}/k_1 is considerably smaller than 1 and if we choose $n' \neq 1$, then β has a very simple form: $\beta = 1/n'$ for $n' < 1$; $\beta = n'$ for $n' > 1$ as $\Theta = |(1 - n')|$.

For $n' = 1$ it is then necessary to use the limit $(3b)$ for $k_{-1} \to 0$, which equals to $z_2 x/a_1 = \bar{\tau}/(\bar{\tau} + 1)$ and which leads to the Eq. similar to Eq. $(5a)$ in the form

$$Q \equiv \frac{A - A_\infty}{A_0 - A_\infty} = \frac{1}{\varkappa} \ln \left(1 + \frac{\varkappa}{1 + \varkappa \cdot \xi}\right) , \qquad (5b)$$

where $\varkappa = a_1 \cdot k_1 z_1 L/v$ i.e. formally $\varkappa = \mathfrak{z} (\phi = 1)$.

The same result can be obtained directly by the limiting transfer $\beta \to 1$ in Eq. $(5a)$ if $\mathfrak{z}$ is expressed by use of β. Use of Eq. $(5b)$ is similar as use of Eq. $(5a)$ as is demonstrated in the following part.

Eqs $(5a,b)$ are including both experimental alternatives: for flow measurements $\xi = 0$, at the stop flow is $\mathfrak{z} = \text{const}$. In the first case changes in the quantity U are reached by changes in the ratio L/v which in practical application means by changes in flow rates. In the second case U is changing with time (Fig. 1).

The root $\mathfrak{z}$ is determined from Eq. $(5a)$ or $(5b)$ or numerically[+] (for the first approximation can be for $\mathfrak{z}$ chosen the value resulting from Eqs $(8a,b)$ or graphically.

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* As long as the computer with a standard procedure is not available for calculation of the roots of equations, the simple iteration procedure can be used:

$$\mathfrak{z}_{i+1} = \frac{1}{U} \cdot \ln \frac{\beta \exp \left[\mathfrak{z}_i(1 + \xi)\right] - 1}{\beta \exp \left[\mathfrak{z}_i \xi\right] - 1} .$$

A simple graphical procedure is based on the following considerations: Equation $(5a)$ can be considered to be the dependence of variables ξ, $\mathfrak{z}$ and with the parameter U *i.e.* like in the system $U(\log \xi)$ of curves the intersection is chosen $U = $ const and the corresponding relation between ξ and $\mathfrak{z}$ is observed. The explicit expression of quantity ξ from Eq. $(5a)$ and by introducing the substitution $(6a)$ the dependence can be brought into the form

$$\exp \left(\mathfrak{z}\right) = Y \tag{6a}$$

$$\xi \ln Y + \ln \beta = \ln \frac{Y^U - 1}{Y^U - Y}, \tag{6b}$$

which can be understood as the relation for the intersection of the curve $F(\ln Y, U) = \ln . \, . \, (Y^U - 1)/(Y^U - Y)$, in which the parameter U has an experimental value, with the straight line $P(\ln Y) = \xi \ln Y + \ln \beta$ (Fig. 2) whose slope ξ and intercept $\ln \beta$ are known from the experiment. The chosen values U and ξ represent one experimental point on the $U(\xi)$ curve at the given n, *i.e.* at the corresponding value of β and at the selected time of flow L/v.

First of all, interesting is the Y-th coordinate Y^+ of the intercept as according to Eqs $(6a)$ and $(4d)$ holds
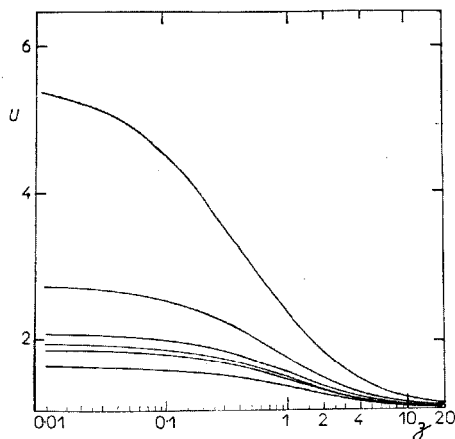

FIG. 1

Curves $U(\mathfrak{z}, \beta)$

The corresponding values of parameters n and k_1/k_{-1} beginning with the upper curve are: $1 - 100$, $1 \cdot 5 - 100$, $1 - 10$, $0 \cdot 5 - 100$, $1 \cdot 5 - 10$, $0 \cdot 5 - 10$.
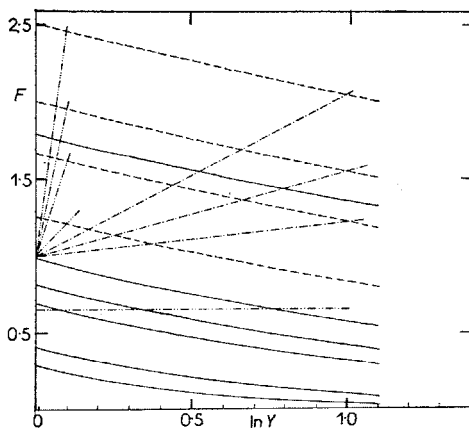
FIG. 2

Nomogram of Functions $F(\ln Y, U)$ and $F(\ln Y, Q)$

Solid lines are related to functions $F(\ln Y, U)$, dashed to functions $F(\ln Y, Q)$. Parameter U, beginning by the solid upper curve: $1 \cdot 2$; $1 \cdot 6$; $1 \cdot 8$; $2 \cdot 0$; $3 \cdot 0$; $4 \cdot 0$. Parameter Q beginning by the dashed upper curve: $0 \cdot 4$; $0 \cdot 5$; $0 \cdot 6$; $0 \cdot 8$.

$$\ln Y^* = \Phi a_1 k_1 z_1 \, L/v \quad \text{or} \quad k_1 = \frac{\ln Y^*}{\Phi a_1 z_1 \, L/v} \tag{7}$$

from which the rate constant k_1 can be calculated.

This procedure can be used in all cases for which $\beta \neq 1$, *i.e.* with the exception of irreversible reactions at the equivalent ratio of initial concentrations $n' = 1$. In this case it is necessary in an analogous method (*i.e.* by an explicit expression of ξ) start with the Eq. (5b) and to solve the intersection of the curve $F(\ln Y, Q) \equiv \ln Y/(Y^Q - 1)$ with the straight line $P(\ln Y) \equiv \xi \ln Y + 1$, while Y is now defined as exp $[\mathfrak{z}(\phi = 1)]$ and $Q = (A - A_\infty)/(A_0 - A_\infty)$.

This means that a single nomogram suffices of the function $\ln (Y^U - 1)/(Y^U - Y)$ or of the function $\ln Y/(Y^Q - 1)$ with the parameter U or Q into which the straight line $P(\ln Y)$ is drawn, the slope and intercept of which are known from the experiments (Fig. 2). It is advantageous to choose such parameters U and ξ so that the straight line P would intersect the curve F under the angle $\pi/2$ if possible. For various selected-mutually corresponding pairs of values U and ξ or Q and ξ from the same experiment *i.e.* at the same n' and L/v the Y-th coordinates of the intersection must be the same as results from Eq. (7). This is a method by which the correctness of the method is done in practice. In Fig. 2 are for illustration plotted
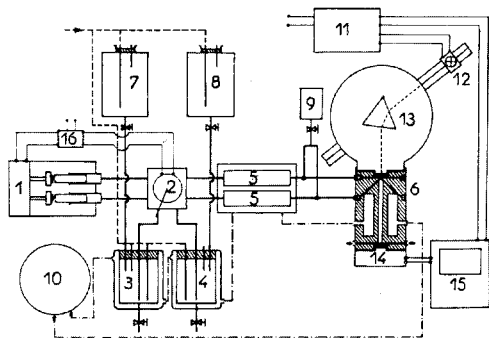

FIG. 3

Apparatus for Measurement with the Beam Coaxial to the Direction of Flow

The significance of individual numbers is given in the paper. Dashed is the pipeline of inert gas, dashed-dot the pipeline of tempered liquid, solid narrow lines the electric wires.
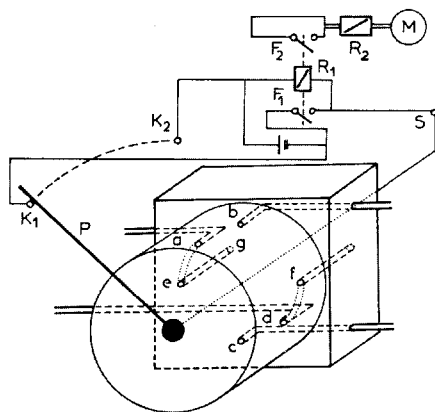
Fig. 4

Switch Valve with the Relay Device

a to g exit of channels, P rotating lever, K_1, K_2, S contacts, R_1 low-voltage relay,, R_2 relay 220 V, F_1, F_2 contacts of the relay, M motor of the doser.

straight lines P for the case $n' = 1$ with the slopes corresponding to values of the parameter Q which is given in the list of symbols and which would correspond to experimental values of the simplex $\mathfrak{z} = 1$ or $\mathfrak{z} = 0.1$.

In this procedure for determination of the rate constant is included also the case of the flow method when $\xi = 0$ and straight lines $P(\ln Y)$ are thus horizontal with the intercept $\ln \beta$ or 1.

Beside this the pairs of values $\mathfrak{z}$ and L/v for selected values of U (which are only functions of L/v as $\xi = 0$) according to Eq. (4d) are giving straight line passing through the origin with the slope $\Phi a_1 k_1 z_1$ on the basis of which the rate constant can be determined.

For illustration, in Fig. 2 is plotted the horizontal corresponding to the value $\beta = 1.925$ *i.e.* $n' = 1$, $k_{-1}/k_1 = 10^{-1}$. Its individual intersections with $F(\ln Y, U)$ curves correspond then to the experiments with the same parameter n' but with a differing residence time L/v.

All procedures for determination of the rate constant by the flow or by the stop flow method are in the described way unified.

Another simplification of the whole procedure for determination of k_1 rests in the fact that in the range $\ln Y(0, 0.5)$ and $\ln \beta \geqq 1$ the curves $F(\ln Y)$ are practically linear with the equation

$$
\begin{array}{cc}
n' \neq 1 & n' = 1 \\
\bar{F}(\ln Y, U) = -\dfrac{1}{2} \ln Y + \ln \dfrac{U}{U - 1} \; ; & \bar{F}(\ln Y, Q) = -\tfrac{1}{2} \ln Y + Q^{-1} \, , \qquad (8a,b)
\end{array}
$$

so that it is not necessary to plot the whole nomogram but the problem is reduced to the plot of the intersection of straight lines F and P. This approximation gives the coordinate of the intersection $\ln Y^+$ with the error smaller than 5%. The approximation $(8a,b)$ are equations of the tangent line to the curve $F(\ln Y)$ in the point $\ln Y = 0$. For the intercepts there holds $\lim\limits_{Y \to 1} \ln (Y^U - 1)/(Y^U - Y) = \ln U/(U - 1)$ and similarly $\lim\limits_{Y \to 1} \ln Y/(Y^Q - 1) = 1/Q$ and for the slope $d[F(\ln Y)]/d \ln Y$ in the point $\ln Y = 0$ for $n' \neq 1$ as well as for $n' = 1$ the value $-1/2$ is obtained.

EXPERIMENTAL

The apparatus for the flow and stop flow method with the spectrophotometric indication coaxial to the direction of flow is schematically drawn in Fig. 3. From the storage vessel of reactants 7, 8 the component are discharged into vessels kept at constant temperature 3, 4. From there they are sucked through a multi way valve 2 into syringes of the doser 1 and from there after turning the valve 2 through tempered cylinders 5 they are sprayed through four nozzles into the reactor 6 whose hollow jacket is also tempered by a thermostat 10. The reactor is directly

mounted on the exit 13 of the Zeiss monochromater VSU 1 with a source of light 12 supplied from the stabilizer 11. At the exit from the reactor is located a photo-cell EG and EGS 14 from which the current proportional to the transparence of the reaction mixture is recorded by a recorder G1B1 Zeiss 15. The switching device numbers 16.

The switching valve 2 was made of perplex prism $7 \times 5 \times 2$ cm^3. In this body were drilled channels of ID 3 mm (Fig. 4). By rotation of a teflon plate with milled channels it was possible to connect points a, b and c, d, to close e, f (position at the flow) or, on the contrary, to connect locations a, e, and d, f and to close locations c, b (flow stopped) at the simultaneous disengaging of the doser by the switching device which is in detail drawn in Fig. 4. This position has made possible the discharge of the dosed liquids by use of holes g, h into vessels 3, 4 with some delay of the doser after the stoppage of the flow and sucking of the reactants from the space 3, 4 at filling of the dosing syringes. The relay R_1 was handled by a contact of the laver P (forming the inlet S) and by the contacts K_1 and K_2. The body of the reactor is made of a special polyvinylchloride cylindrical block in the axis of which is drilled the observing tube ($\varnothing = 3$ mm, length 100 mm) on both ends fitted by glass windows attached by screws. On one end of the observing tube are mounted twice into its sides four nozzles ($\varnothing = 0.8$ mm) for mixing of both reactants. The first four nozzles are perpendicular to each other as well as to the surface of the observing tube, second fourth nozzles are situated tetraedrically. This arrangement ensures quick and perfect mixing. Inlet of each reaction component into the corresponding four nozzles is through circular channels at the circumference of the tube. Both individual circular channels are milled in the body of the reactor and are covered by case with inlet pipes. At the end of the pipe are perpendicularly to the surface drilled two outlet nozzles ($\varnothing = 1.5$ mm) which are connected with the outlet pipes. Inlet and outlet pipes are passing through the heating jacket and are sealed. The head of the reactor is fitted with a socket for fitting on the head of the monochromator. The cross section through the described device is drawn in Fig. 3 part 14. The linear doser has been operated at velocities 2.5; 3.5; 4.5; 5.5; and 6.6 mm/s with syringes 20 mm in diameter with the diameter of the tube 3 mm and length 100 mm. To make any considerations concerning the character of flow at these dosing velocities and geometry according to the simple Reynolds number (its values are here Re = 660 and 1700 as the lower and upper limit) is not possible as this criterion holds only at the distance from the point of mixing at least 100 times the diameter of the pipe[2]. Moreover the mixing nozzles are bringing the liquid into an intensive whirling. Thus only an experimental criterion is justified which is the independence of the determined rate constants on feeding rates. This was verified for the reactor having the same dimensions for the range of feed velocities in our last study[3] at indication perpendicular to the direction

TABLE II

Rate Constants k dm^3 s^{-1} mol^{-1}

n	Method		n	Method	
	flow	stop flow		flow	stop flow
	15°C			20°C	
0.5	570 ± 68	546 ± 50	0.5	820 ± 77	866 ± 85
1	580 ± 58	552 ± 44	1	860 ± 90	—
2	560 ± 41	530 ± 14	2	830 ± 68	850 ± 75

of flow and this was again confirmed in this study up to velocities 2·5 mm/s. The value of 100% transparence on the register was determined by filling the reactor by the medium from the vessel 9, zero transparence by switching off the light source, initial transparence as the geometric mean of transparencies obtained at feeding each individual reactant. Transparence in time $t = \infty$ was red on the horizontal asymptote to the curve transparence–time if the steadying was sufficiently quick, or the given mixture of reactants was fed into the reactor after a sufficiently long time in which the reactants were reacting outside the reactor.

RESULTS

The described procedures were tested on the reaction $Ce(IV) + V(IV) = Ce(III) + V(V)^*$ in the medium $2N-H_2SO_4$. At the flow method the initial concentrations of ions $V(IV)$ 0·01M at the stop flow method $5 . 10^{-4}M$. The experiments were performed at various wave lengths 750, 680, 500, 490, 480, 440, 430, 420 nm and at two temperatures 15°C and 20°C at the ratio of initial concentrations $Ce/V = 0·5; 1; 2$. The mean experimental rate constants and their standard deviations at the frequency of the system equal to 8 are given in Table II.

Experimental results obtained by the method of coaxial indication with the direction of flow are in a good agreement[3,4] with the results obtained earlier.

REFERENCES

1. Gerischer H., Heim W.: Z. Phys. Chem. (Frankfurt am Main) *46*, 345 (1965).
2. Bauer F., Brůha O., Jaňour Z.: *Základy proudění.* Vědecko-technické nakladatelství, Prague 1950.
3. Tockstein A., Matušek M.: This Journal *34*, 27 (1969).
4. Tockstein A., Skopal F.: This Journal *39*, 3024 (1974).

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* 　　The used chemicals see[4].