

NONISOCHORIC REACTOR WITH CONSTANT FEED RATE OF ONE COMPONENT

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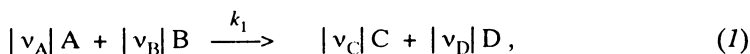
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For a chemical reactor with constant volume feed rate equations have been derived which describe the time dependences of concentration of the reaction components, and their approximation has been suggested. The applicability of the approximation has been verified on a model redox system Ce(IV)/V(IV) in sulfuric acid medium.

The feedback controlled chemical reactor (FCCR) was described in refs¹⁻³. It is an experimental apparatus for monitoring chemical kinetics in homogeneous liquid phase: it is charged with one component and the other component is injected therein by a controlled negative feedback. Before this can take place, the respective chemical reaction must be started. One of the possibilities consists in feeding the reaction component at a constant feed volume rate. The present paper offers the possibility of using the initial phase of experiment to follow the kinetic of chemical reaction.

THEORETICAL

Let us presume an irreversible nonisochoric 2nd order reaction, 1st order in each of the starting components, with the rate constant k_1 :



where the stoichiometric coefficients of the starting components (v_A , v_B) are negative and those of products (v_C , v_D) are positive.

The reaction component A of the concentration a is continuously fed into the other component B (initial volume V_0 , initial concentration b_0) pre-charged in the reactor.

$$\frac{dn_A}{dt} = v_A k_1 \frac{n_A n_B}{V_0 + v t} + \dot{v} a \quad (2)$$

$$\frac{1}{\nu_B} \frac{dn_B}{dt} = \frac{1}{\nu_C} \frac{dn_C}{dt} = \frac{1}{\nu_D} \frac{dn_D}{dt} = k_1 \frac{n_A n_B}{V_0 + \dot{\nu} t} \quad (3)$$

If we introduce the expressions for actual concentrations:

$$[I] = \frac{n_I}{V_0 + \dot{\nu} t}; \quad I = A, B, C, D \quad (4)$$

we can use them to modify Eqs (2) and (3) into the following form:

$$\frac{d[A]}{dt} = \nu_A k_1 [A] [B] + \dot{\nu} \frac{a - [A]}{V_0 + \dot{\nu} t} \quad (5)$$

$$\frac{d[B]}{dt} = \nu_B k_1 [A] [B] - \dot{\nu} \frac{[B]}{V_0 + \dot{\nu} t} \quad (6)$$

$$\frac{d[C]}{dt} = \nu_C k_1 [A] [B] - \dot{\nu} \frac{[C]}{V_0 + \dot{\nu} t} \quad (7)$$

$$\frac{d[D]}{dt} = \nu_D k_1 [A] [B] - \dot{\nu} \frac{[D]}{V_0 + \dot{\nu} t} \quad (8)$$

The subtraction of Eq. (6) from Eqs (5), (7), (8) and subsequent integration for the initial conditions at the time $t = 0$

$$[B]_{t=0} = b_0$$

$$[A]_{t=0} = [C]_{t=0} = [D]_{t=0} = 0$$

gives the following relations:

$$[A] = \frac{a \dot{\nu} t}{V_0 + \dot{\nu} t} + \frac{\nu_A}{\nu_B} \left([B] - \frac{b_0 V_0}{V_0 + \dot{\nu} t} \right) \quad (9)$$

$$[C] = \frac{\nu_C}{\nu_B} \left([B] - \frac{b_0 V_0}{V_0 + \dot{\nu} t} \right) \quad (10)$$

$$[D] = \frac{v_D}{v_B} \left([B] - \frac{b_0 V_0}{V_0 + \dot{v} t} \right) . \quad (11)$$

After introducing the actual concentration of reaction component [A] from Eq. (9) into Eq. (6) we obtain the Bernoulli differential equation:

$$\frac{d \ln[B]}{dt} = k_1 \left(v_A [B] + \frac{v_B a \dot{v} t - v_A b_0 V_0}{V_0 + \dot{v} t} \right) - \frac{\dot{v}}{V_0 + \dot{v} t} , \quad (12)$$

whose solution gives the time dependence of actual concentration of reaction component B in the following form:

$$[B] = \frac{b_0 e^{v_B k_1 a t} \left(1 + \frac{\dot{v} t}{V_0} \right)^{-\frac{k_1 V_0}{\dot{v}} (v_B a + v_A b_0) - 1}}{1 - v_A k_1 b_0 \int_0^t e^{v_B k_1 a t} \left(1 + \frac{\dot{v} t}{V_0} \right)^{-\frac{k_1 V_0}{\dot{v}} (v_B a + v_A b_0) - 1} dt} . \quad (13)$$

The combination of Eq. (13) with Eq. (9) gives the time dependence of actual concentration of reaction component A:

$$[A] = \frac{\frac{v_A}{v_B} b_0 e^{v_B k_1 a t} \left(1 + \frac{\dot{v} t}{V_0} \right)^{-\frac{k_1 V_0}{\dot{v}} (v_B a + v_A b_0) - 1}}{1 - v_A k_1 b_0 \int_0^t e^{v_B k_1 a t} \left(1 + \frac{\dot{v} t}{V_0} \right)^{-\frac{k_1 V_0}{\dot{v}} (v_B a + v_A b_0) - 1} dt} - \frac{v_A b_0 V_0 - v_B a \dot{v} t}{v_B (V_0 + \dot{v} t)} . \quad (14)$$

The relations (13) and (14) are relatively complex. Their application is possible after the numerical evaluation of the integral and therefore they are not much useful in routine applications.

That is why we will describe a derivation of their possible approximation. At the beginning of feeding, the second term at the right-hand side of Eq. (12) is insignificant, and $V_0 \gg \dot{v} t$. Hence Eq. (12) is simplified to give Eq. (15):

$$\frac{d \ln[B]}{dt} = k_1 \left[v_A ([B] - b_0) + \frac{v_B a \dot{v} t}{V_0} \right] . \quad (15)$$

If it is presumed that the concentration of reaction component B decreases linearly with time according to the relation:

$$[B] = b_0 - \alpha t , \quad (16)$$

in which the parameter α is positive and time-independent, Eq. (15) can be transformed into Eq. (17):

$$\frac{d \ln[B]}{dt} = k_1 \left(-v_A \alpha + \frac{v_B a \dot{v}}{V_0} \right) t . \quad (17)$$

The integration in the limits $\langle b_0, [B] \rangle$ and $\langle 0, t \rangle$ for the concentration of reaction component B and time, respectively, and the elimination of parameter α with the help of Eq. (16) gives the implicit time dependence of concentration of reaction component B:

$$\ln \frac{[B]}{b_0} = \frac{k_1 t^2}{2} \left(\frac{v_A ([B] - b_0)}{t} + \frac{v_B a \dot{v}}{V_0} \right) . \quad (18)$$

The approximation derived is valid at the beginning of feed when the concentration of reaction component B is close to b_0 and if the condition (16) is fulfilled. Developing the logarithm at the left-hand side of Eq. (18) into the Taylor series in the neighbourhood of the point $[B]/b_0 = 1$ and taking its first two members will result in Eq. (19):

$$\ln \frac{[B]}{b_0} \approx \frac{[B]}{b_0} - 1 . \quad (19)$$

Modifying Eq. (18) with the help of Eq. (19) gives the explicit time dependence of concentration of reaction component B at the beginning of the reaction in the following form:

$$[B]_{\text{approx}} = b_0 + \frac{k_1 v_B a b_0 \dot{v} t^2}{V_0 (2 - k_1 v_A b_0 t)} . \quad (20)$$

The introduction of Eq. (20) into Eq. (9) gives the time dependence of concentration of reaction component A at the beginning of the reaction:

$$[A]_{\text{aprox}} = \frac{2 a \dot{v} t}{V_0 (2 - k_1 v_A b_0 t)} \quad (21)$$

The introduction of the dimensionless parameters n and σ :

$$n = \frac{v_B a}{v_A b_0} \quad (22)$$

$$\sigma = - \frac{v_A b_0 k_1 V_0}{\dot{v}} \quad (23)$$

makes it possible to rewrite the exact relations (13), (14) and their approximations (20), (21) into the following dimensionless forms:

$$\varphi_A = \frac{1}{n} \left[\frac{e^{-n\tau} \left(1 + \frac{\tau}{\sigma}\right)^{\sigma(n+1)-1}}{1 + \int_0^\tau e^{-n\tau} \left(1 + \frac{\tau}{\sigma}\right)^{\sigma(n+1)-1} d\tau} + \frac{n\tau - \sigma}{\tau + \sigma} \right] \quad (24)$$

$$\varphi_B = \frac{e^{-n\tau} \left(1 + \frac{\tau}{\sigma}\right)^{\sigma(n+1)-1}}{1 + \int_0^\tau e^{-n\tau} \left(1 + \frac{\tau}{\sigma}\right)^{\sigma(n+1)-1} d\tau} \quad (25)$$

$$\varphi_{A \text{ aprox}} = \frac{2\tau}{\sigma(2+\tau)} \quad (26)$$

$$\varphi_{B \text{ aprox}} = 1 - n \frac{\tau^2}{\sigma(2+\tau)}, \quad (27)$$

where τ means the dimensionless time, and φ_A and φ_B stand for relative concentrations of reaction components A and B, respectively:

$$\tau = -v_A b_0 k_1 t \quad (28)$$

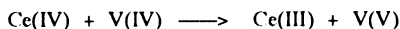
$$\varphi_A = \frac{[A]}{a} \quad \varphi_B = \frac{[B]}{b_0} \quad (29)$$

For the chosen parameters n and σ we calculated the theoretical time dependences of relative concentration of reaction component A from Eqs (24) and (26). Figure 1 presents the dependence of relative concentrations φ_A and $\varphi_{A, \text{approx}}$ on time τ for the chosen parameters $n = 235$ and $\sigma = 200$ ($v_A = v_B = -1$, $a = 0.0235 \text{ mol dm}^{-3}$, $b_0 = 10^{-4} \text{ mol dm}^{-3}$, $V_0 = 25 \text{ cm}^3$, $k_1 = 800 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$, $\dot{v} = 0.01 \text{ cm}^3 \text{ s}^{-1}$). From the dependence it can be seen that the approximation function for these parameters at the beginning of reaction substitutes the exact dependence excellently.

EXPERIMENTAL

The experimental measurements were carried out on an apparatus called Feedback Controlled Chemical Reactor (FCCR)¹⁻³. Among others, this apparatus makes it possible to inject one reaction component at a constant volume feed rate into the other pre-charged component. Only the linear doser was connected to a stabilized power supply unit; the feed rate \dot{v} was controlled by the chosen voltage value at the motor of linear doser.

The following model redox reaction was used to verify the theoretical relations.



The reaction was carried in 1 M H_2SO_4 at 20 °C and measured by both independent methods⁴⁻⁶ and in FCCR (refs^{1,3}).

The reaction course was monitored spectrophotometrically at the wavelength of 380 nm. At the same wavelength and in the same apparatus we also determined the molar absorption coefficients ϵ_1 of the reaction components Ce(IV), Ce(III), V(IV), and V(V), viz. 20 700, 0, 0, and $530 \text{ dm}^2 \text{ mol}^{-1}$, respectively.

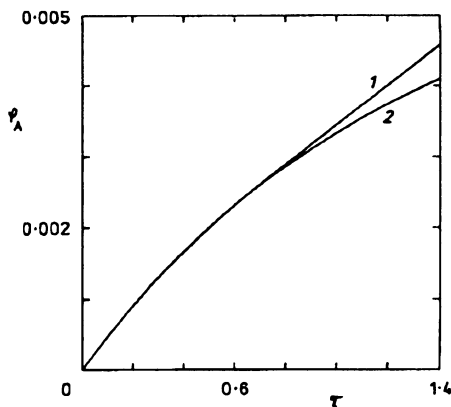


FIG. 1

Dependence of relative concentrations on dimensionless time for $n = 235$ and $\sigma = 200$; 1 dependence φ_A - τ , 2 dependence $\varphi_{A, \text{approx}}$ - τ

On the basis of the Lambert–Beer law, the absorbance of the reaction mixture obeys the relation:

$$A = \sum_{i=A}^D \epsilon_i [I] l. \quad (30)$$

Using the balance equations (9), (11) and relation (30), we calculated the actual concentrations of the reaction component A, i.e. Ce(IV), from the experimental absorbance-time dependence. The rate constant was then determined from Eq. (21) which was transformed into the following form suitable for linear regression:

$$y = Kt + Q, \quad (31)$$

where

$$y = \frac{t}{[A]}$$

$$K = -k_1 \frac{v_A b_0 V_0}{2 \dot{v} a} \quad (32)$$

$$Q = \frac{V_0}{\dot{v} a}.$$

Thereafter, the rate constant k_1 was calculated from the slope value K of the straight line (31). The linear regression was carried out numerically using a personal computer. The estimates of parameters of the regression model were analyzed statistically (test of significance of parameters by means of the Student t -test, estimation of the coefficient of determination, identification of effective points, and verification of presumptions of the least squares treatment)⁷.

In an experimental series, Ce(IV) solution was injected at a constant volume rate into the pre-charged V(IV) solution in 1 M H₂SO₄ at 20 °C. The feed concentration was $a = 0.0235 \text{ mol dm}^{-3}$. The concentration of the pre-charged V(IV) solution was chosen in the interval from $0.47 \cdot 10^{-4}$ to $1.82 \cdot 10^{-4} \text{ mol dm}^{-3}$. The volume feed rate of Ce(IV) solution was chosen in the interval from $6 \cdot 10^{-3}$ to $14 \cdot 10^{-3} \text{ cm}^3 \text{ s}^{-1}$. All the experiments were reproduced.

RESULTS AND DISCUSSION

The results of selected experiments with constant volume feed rate of Ce(IV) into the pre-charged V(IV) solution are presented in Table I. The values of rate constants obtained by linear regression from Eq. (31) are presented for various concentrations b_0 of the pre-charged reaction component B, i.e. V(IV), and various volume feed rates \dot{v} .

The obtained average value of rate constant, $836.4 \pm 3.7 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$, agrees well with the values obtained by other, independent methods (e.g. the value of $830 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ given in ref.²).

The dependences (13), (14) are much too complex for a treatment. Therefore, as early as in planning the experiments one should try to suggest such experimental conditions as to be able to use simplifying presumptions in the evaluation – e.g. the approximation solution suggested by us.

The modification of FCCR for measurements with constant volume feed rate is easy and rapid. It only consists in connecting the linear doser to a stabilized power supply unit. If one succeeds in finding such experimental conditions which fulfil the presumptions of approximation of concentrations of reaction components, then the evaluation of experiments by the methods of linear regression is easy and quick and the chemical-kinetical data obtained are of high quality. This new method represents a helpful addition to the methodology of studies of chemical kinetics in homogeneous liquid phase by means of FCCR.

TABLE I

Selected results of experimental series of Ce(IV) feed of concentration $a = 0.0235 \text{ mol dm}^{-3}$ at constant volume rate into pre-charged V(IV) in $1 \text{ M H}_2\text{SO}_4$ at 20°C

No. of measurement	$b_0 \cdot 10^4, \text{ mol dm}^{-3}$	$\dot{v} \cdot 10^3, \text{ cm}^3 \text{ s}^{-1}$	$k_1, \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$
1	5.58	6.58	835.4
2	5.11	9.04	837.0
3	5.11	11.20	806.8
4	5.11	13.16	838.2
5	2.36	6.69	812.6
6	2.36	8.75	856.3
7	1.82	10.87	823.7
8	1.82	13.16	839.8
9	1.82	21.05	820.4
10	1.13	11.11	845.8
11	1.13	13.16	820.9
12	0.91	6.58	851.8
13	0.91	8.82	848.4
14	0.57	11.11	853.2
15	0.57	13.03	834.4
16	0.47	6.64	859.1
17	0.47	9.04	834.9
Average value			836.4
Standard deviation			15.4
Error of arithmetic mean			± 3.7

SYMBOLS

a	molar concentration of injected reaction component A, N L^{-3}
b_0	molar concentration of pre-charged component B before adding component A therein, N L^{-3}
k_1	reaction rate constant, $\text{L}^3 \text{N}^{-1} \text{T}^{-1}$
l	length of absorbing medium, L
n_i	amount of reaction component I ($I = \text{A, B, C, D}$), N
t	time, T
\dot{v}	volume feed rate, $\text{L}^3 \text{T}^{-1}$
A	absorbance of reaction mixture
$[I]$	actual concentration of reaction component I at time t ($I = \text{A, B, C, D}$), N L^{-3}
V_0	initial volume of pre-charged reaction component B, L^3
ϵ_I	molar absorption coefficient of reaction component I ($I = \text{A, B, C, D}$), $\text{L}^2 \text{N}^{-1}$
ν_I	stoichiometric coefficient of reaction component I ($I = \text{A, B, C, D}$)

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