

## FEEDBACK CONTROLLED CHEMICAL REACTOR WITH FEED OF TWO REACTION COMPONENTS WITH SPECTROPHOTOMETRIC INDICATION

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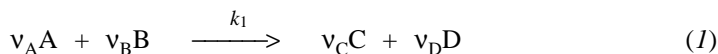
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Theoretical relationships and simplifying conditions have been derived for the feed of two reaction components into a nonisochoric reactor with ideal stirring. The feed of reaction components is controlled by the negative feedback at a constant absorbance of the reaction mixture. The theoretical relationships have been verified using model 2. order oxidation-reduction reactions of Ce(IV)/V(IV) and Fe(III)/V(III) in 1 M sulfuric acid at 20 °C.

In the previous papers<sup>1-5</sup> we described a feedback-controlled chemical reactor (FCCR) with the feed of one component. This feed maintains a constant value of absorbance or potential (the quantities depending linearly or nonlinearly upon the concentrations of reaction components in the reactor, respectively). The papers derived general theoretical relationships for the feed of any number of reaction components inclusive of the reaction products. The present paper deals with the simultaneous feed of two starting reaction components. The feed is controlled by the feedback in such a way as to keep a constant absorbance of the reaction mixture. Also given are the conditions for creating the steady state with respect to one or several reaction components.

### THEORETICAL

Let us presume an irreversible nonisochoric reaction



involving a second order reaction with rate constant  $k_1$  as the slowest step, i.e. a reaction with unit order with respect to each of the starting components. Let a quantity  $Y$  (e.g. absorbance) be linearly dependent on concentrations of the starting components. In a chemical reactor with suitable feed of reaction components A and B controlled by

a feedback the quantity  $Y$  is kept constant for a time interval of any length. For such conditions the paper<sup>3</sup> gave a differential equation (Eq. (2)) in which  $\alpha_i$  is given by Eq. (3).

$$\sum_i \alpha_i \frac{dV_i}{dt} = k_1 \frac{\prod_i (b_i V_0 + c_i V_i + v_i \sum \alpha_i V_i)}{V_0 + \sum_i V_i} \quad i = A, B, \quad (2)$$

$$\alpha_i = \frac{c_i K_i - Y_0}{-v_A K_A - v_B K_B + v_C K_C + v_D K_D}. \quad (3)$$

The actual concentration  $a_i$  [mol dm<sup>-3</sup>] of reaction components A, B is given by Eq. (4).

$$a_i = \frac{b_i V_0 + c_i V_i + v_i \sum_{i=A}^B \alpha_i V_i}{V_0 + \sum_{i=A}^B V_i} \quad (4)$$

As the single differential equation (2) contains two time-dependent variables  $V_A$  and  $V_B$ , the feed of one reaction component (e.g. B) can be chosen arbitrarily.

If the feedback simultaneously controls the feed of both reaction components, then it must be

$$V_A = K_B V_B, \quad (5)$$

where  $K_B$  is the coefficient of proportionality between the volumes.

Introduction of Eq. (5) into Eq. (2) and its solution gives Eq. (6).

$$\left[ 1 - \frac{b_A(1 + K_B)}{c_A + v_A(\alpha_A + K_B \alpha_B)} \right] \ln \left( 1 + \frac{c_A + v_A(\alpha_A + K_B \alpha_B)}{b_A} \frac{V_A}{V_0} \right) -$$

$$\begin{aligned}
 & - \left[ 1 - \frac{b_B(1 + K_B)}{c_B K_B + v_B(\alpha_A + K_B \alpha_B)} \right] \ln \left( 1 + \frac{c_B K_B + v_B(\alpha_A + K_B \alpha_B)}{b_B} \frac{V_A}{V_0} \right) = \\
 & = \left( \frac{c_A b_B - c_B b_A K_B}{\alpha_A + \alpha_B K_B} - v_B b_A + v_A b_B \right) k_1 t \quad (6)
 \end{aligned}$$

From this relatively complex implicit relationship between the  $V_A$  volume feed and time  $t$  it is possible to determine the unknown parameters  $b_A$ ,  $b_B$  and the rate constant  $k_1$  using numerical optimization methods.

The expression (6) can be simplified by choosing appropriate experimental conditions. If, e.g., starting from the time  $t = 0$  the constant concentration of component A during the feed (i.e.  $a_A$  – steady state with respect to the reaction component A) is equal to  $b_A$ , then according to Eq. (4) we get a condition between  $c_A$  and  $c_B$  with the help of Eq. (5).

$$b_A(1 + K_B) = c_A + v_A(\alpha_A + \alpha_B K_B) \quad (7)$$

The solution of the differential equation (2) gives a much simpler relationship (8).

$$\begin{aligned}
 V_A & = \frac{V_0 b_B}{-v_A c_B K_B + v_B [c_A - b_A(1 + K_B)]} \cdot \\
 & \cdot \left[ \exp \left[ \left( \frac{-v_A c_B K_B}{c_A - b_A(1 + K_B)} + v_B \right) b_A k_1 t \right] - 1 \right] \quad (8)
 \end{aligned}$$

From this expression we can obtain the unknown parameters either by the numeric optimization method or simply by the linear regression after modification.

The form of dependence of  $V_A$  vs  $t$  according to Eq. (8) is affected by the value of exponent

$$p = \frac{-v_A c_B K_B}{c_A - b_A(1 + K_B)} + v_B \quad (9)$$

If the conditions are fulfilled which fit the set of Eqs (7) and (9) for  $p = 0$ , then the relationship (8) changes to a linear time dependence of  $V_A$ :

$$V_A = \frac{V_0 b_A b_B k_1 t}{c_A - b_A(1 + K_B)}. \quad (10)$$

The dependence of  $V_A$  vs  $t$  according to Eq. (8) is concave for the conditions fulfilling the set of Eqs (7) and (8) for  $p > 0$ . If it is  $p < 0$ , then the dependence of  $V_A$  vs  $t$  is convex and asymptotically approaches the value  $V_\infty$  for  $t \rightarrow \infty$ .

$$V_\infty = \frac{V_0 b_B}{-v_B [c_A - b_A(1 + K_B)] + v_A c_B K_B} \quad (11)$$

This value is important for numerical treatment of results or for analytical purposes in the determination of concentrations. The situation is schematically represented in Fig. 1.

The simultaneous feed of both starting reaction components makes it possible to create a steady state even for both the entering reaction components A and B. Thus Eq. (7) changes to a set of two equations for any two unknown parameters. For example, elimination of  $\alpha_A$  and  $\alpha_B$  from the system will give Eq. (12).

$$-v_B c_A + v_A c_B = (-v_B b_A + v_A b_B) (1 + K_B) \quad (12)$$

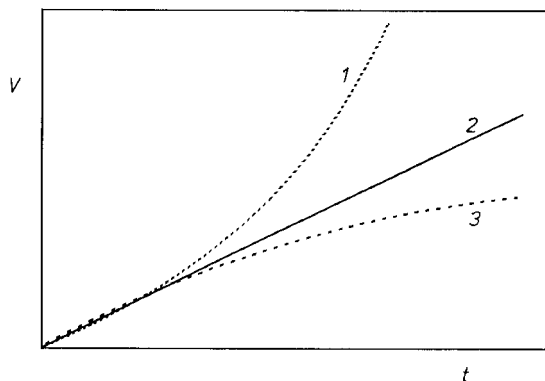


FIG. 1  
Types of dependences of injected volume of reaction component A upon time  $t$  for the reaction component A in steady state. 1 concave dependence, 2 linear dependence, 3 convex dependence

The solution of differential equation (2) with the help of Eqs (5), (7), (12) gives a simpler dependence of the volume fed ( $V_A$ ) upon time  $t$ :

$$V_A = V_0 \left[ \exp \left[ \frac{-v_A(1 + K_B)b_A b_B k_1 t}{c_A - b_A(1 + K_B)} - 1 \right] \right]. \quad (13)$$

For the known concentrations  $b_A$  and  $b_B$  at the steady state the rate constant can be determined by the linear regression.

The procedures of simplifying the differential equation (2) can also be continued by an appropriate choice of  $\kappa_i$ . If e.g. in the steady state for the reaction component A the coefficient  $\kappa_A \neq 0$  and, at the same time,  $\kappa_{B,C,D} = 0$ , then the binding condition (7) is always fulfilled. The concentrations  $c_A$  and  $c_B$  can be chosen arbitrarily, mutually independent, and it is

$$b_A = Y_0/\kappa_A. \quad (14)$$

## EXPERIMENTAL

### Chemicals

Cerium(IV) sulfate p.a. (Lachema Brno), vanadyl sulfate was prepared from ammonium metavanadate<sup>6</sup> (Lachema Brno), vanadium(II) sulfate was prepared by reduction of vanadyl sulfate in a zinc reduction reactor<sup>7</sup>, vanadium(III) sulfate was prepared by mixing a solution of vanadyl sulfate with a solution of vanadium(II) sulfate, ferric sulfate (Lachema Brno), sulfuric acid p.a. (Lachema Brno). The concentrations of solutions were checked potentiometrically<sup>7</sup>.

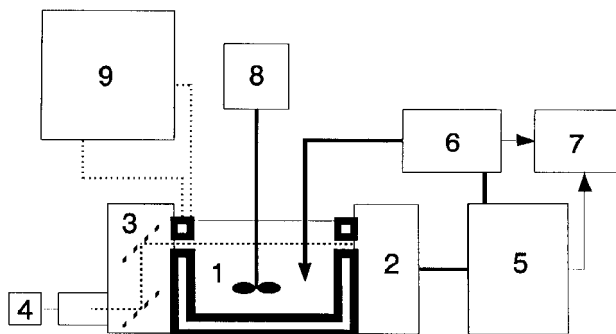


FIG. 2

Scheme of experimental apparatus: 1 reactor, 2 photocell, 3 Spekol, 4 voltage stabilizer, 5 compensator, 6 doser, 7 line recorder and on-line computer, 8 motor and stirrer, 9 thermostat

## Apparatus

The main parts of the feedback-controlled chemical reactor used for obtaining the dependences of feed volume upon time at a constant absorbance are described in refs<sup>1,4</sup> and its schematic representation is in Fig. 2. The linear doser was extended by a second syringe for a simultaneous injection of both reaction components. The measurements were carried out under inert gas (argon) to prevent oxidation of the reaction components by air oxygen.

The procedure was the same as in ref.<sup>5</sup>.

## RESULTS AND DISCUSSION

The theoretical conclusions were verified on two model systems which are sufficiently described in literature. One oxidation-reduction system was Ce(IV)/V(IV) in 1 M H<sub>2</sub>SO<sub>4</sub> at 20 °C and the other was Fe(III)/V(III) at the same conditions.

The measurements were carried out in three phases. At first both the oxidation-reduction systems were measured and the results obtained were evaluated according to Eq. (6) by the methods of nonlinear regression and then by those of linear regression. Finally, such experimental conditions were found for which the presumptions of steady state for the chosen component were fulfilled and these experimental dependences were evaluated by linear regression of Eq. (8).

TABLE I

Rate constants of oxidation-reduction system Ce(IV) + V(IV)  $\longrightarrow$  Ce(III) + V(V) in 1 M sulfuric acid at 20 °C measured at the wavelengths  $\lambda = 380$  and 410 nm

Experiment No.	$\lambda = 380$ nm		$\lambda = 410$ nm		$k_1$ (ref. <sup>9</sup> )
	$k_{1,opt}$	$k_{1,lin}$	$k_{1,opt}$	$k_{1,lin}$	
	$\text{dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$				
1	787.2	824.7	801.2	816.2	
2	767.3	905.4	830.5	851.4	
3	895.4	936.7	865.0	845.7	
4	818.0	992.0	852.1	875.5	
5	985.7	893.0	889.3	865.3	
6	949.7	905.2	764.2	862.4	833.0
7	693.9	913.0	794.3	936.8	
8	830.7	865.8	842.8	888.3	
9	843.3	908.7	902.7	931.8	
10	789.1	971.2	779.8	943.3	
Average	836.0	911.6	832.2	882.0	
Standard deviation	27.6	15.2	14.8	13.6	

Both the model systems were measured at two wavelengths at various concentrations of the reaction components and various constant levels of absorbance of the reaction mixture. The obtained results of evaluation of selected experiments are presented in Tables I – III.

Tables I and II give the results of evaluation of the experiments carried out with the oxidation–reduction systems Ce(IV)/V(IV) and Fe(III)/V(III). For each experiment the rate constant value is given which was obtained by the methods of nonlinear regression (Simplex<sup>8</sup> – the objective function was formulated as a sum of squares of residues of experimental and calculated times) and linear regression. The obtained values of rate constants agree well with literature data<sup>9,10</sup>.

Table III gives the results of evaluation of the experiments carried out at the conditions corresponding to the steady state with regard to one reaction component [Ce(IV) and Fe(III)]. The experiments were evaluated by the method of linear regression. Again the obtained values of rate constants agree well with literature data<sup>9,10</sup>. The evaluation of these experiments was the easiest and quickest one because it made use of a simple equation describing the dependence of the injected volume upon time.

The derived theoretical conclusions were confirmed by measuring two model oxidation-reduction systems at various conditions. The evaluation of all experiments was without any problems and the results obtained agree well with literature.

TABLE II  
Rate constants of oxidation-reduction system Fe(III) + V(IV)  $\longrightarrow$  Fe(II) + V(IV) in 1 M sulfuric acid at 20 °C measured at the wavelengths  $\lambda = 370$  and 390 nm

Experiment No.	$\lambda = 370$ nm		$\lambda = 390$ nm		$k_1$ (ref. <sup>10</sup> )
	$k_{1,opt}$	$k_{1,lin}$	$k_{1,opt}$	$k_{1,lin}$	
	$\text{dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$				
1	1.34	1.49	1.75	1.51	
2	1.49	1.58	1.62	1.54	
3	1.42	1.51	1.65	1.55	
4	1.48	1.60	1.81	1.61	
5	1.55	1.68	1.82	1.53	
6	1.54	1.48	1.67	1.50	1.55
7	1.45	1.41	1.78	1.55	
8	1.54	1.52	1.45	1.55	
9	1.51	1.55	1.57	1.53	
10	1.51	1.59	1.61	1.46	
Average	1.48	1.54	1.67	1.53	
Standard deviation	0.02	0.02	0.04	0.01	

The application of the feedback controlled chemical reactor was extended by the possibility of feed of additional reaction components. The conclusions obtained can be applied also to industrial practice – the use of feedback makes it possible to create artificial steady states with regard to selected reaction components according to the requirements of the technology.

TABLE III  
Oxidation-reduction systems Ce(IV)/V(IV) and Fe(III)/V(III) in 1 M sulfuric acid at 20 °C at steady states

Experiment No.	$k_1, \text{dm}^3 \text{mol}^{-1} \text{s}^{-1}$			
	Ce(IV)/V(IV)		Fe(III)/V(III)	
	$\lambda = 380 \text{ nm}$	$\lambda = 410 \text{ nm}$	$\lambda = 370 \text{ nm}$	$\lambda = 390 \text{ nm}$
1	792.1	883.2	1.61	1.52
2	845.1	868.7	1.63	1.55
3	865.5	868.4	1.54	1.56
4	987.5	820.9	1.54	1.63
5	843.9	860.1	1.58	1.50
6	873.2	818.3	1.46	1.54
7	881.7	823.8	1.59	1.52
8	848.4	842.4	1.53	1.56
9	863.5	842.4	1.62	1.58
10	856.9	853.1	1.50	1.55
Average	865.8	848.1	1.56	1.55
Standard deviation	15.6	7.1	0.02	0.01

## LIST OF SYMBOLS

A	general reaction component
$a_i$	actual molar concentration of reaction component $i$ , $\text{N L}^{-3}$
B	general reaction component
$b_i$	molar concentration of reaction component $i$ at $t = 0$ , $\text{N L}^{-3}$
C	general reaction component
$c_i$	feed concentrations of reaction components A and B, $\text{N L}^{-3}$
D	general reaction component
$K_B$	coefficient of proportionality between volumes
$k_1$	rate constant of chemical reaction, $\text{L}^3 \text{N}^{-1} \text{T}^{-1}$
$l$	length of absorbing medium, L



$t$	time, T
$Y$	absorbance of reaction mixture
$Y_0$	constant absorbance of reaction mixture
$V_I$	injected volumes of reaction components A and B, L <sup>3</sup>
$V_\infty$	injected volume of reaction component A at $t \rightarrow \infty$ , L <sup>3</sup>
$V_0$	volume of reaction mixture at $t = 0$ , L <sup>3</sup>
$\lambda$	wavelength of monochromatic radiation, L
$\kappa_i$	molar absorption coefficient of $i$ -th reaction component ( $i = A, B, C, D$ ) multiplied by optical length of absorbing medium, L <sup>3</sup> N <sup>-1</sup>
$\nu_i$	stoichiometric coefficient of $i$ -th reaction component ( $i = A, B, C, D$ )

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