FEEDBACK REACTOR WITH CONTINUOUS INJECTION OF ONE REACTION COMPONENT WITH POTENTIOMETRIC INDICATION

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The time dependence of the volume of one reactant solution injected into the other was derived. The injection is feedback-controlled to hold the reaction mixture potential constant. The theoretical relations were tested in a feedback reactor on two second-order reactions.

This paper deals with an additional application of the feedback reactor to the monitoring of chemical reactions. Previous work[1] was concerned with the feedback reactor with spectrophotometric indication, where the absorbance of the reaction mixture is linearly dependent on the concentrations of the reactants. In the present treatment the indication quantity is the nonequilibrium potential of the reaction mixture, which, however, is no linear function of the reactant concentrations. The feedback reactor with potentiometric indication is based on the principle of the reaction mixture electric potential being held constant through the entire reaction by a suitable injection of one reactant solution to the other; the control system is assumed to suffer from no lag.

THEORETICAL

In the feedback reactor with spectrophotometric indication, the irreversible nonisochoric second-order reaction

$$z_1 \, \text{Ox}_2 + z_2 \, \text{Red}_1 \quad \xrightarrow{\;k_1\;} \quad z_1 \, \text{Red}_2 + z_2 \, \text{Ox}_1 \qquad (A)$$
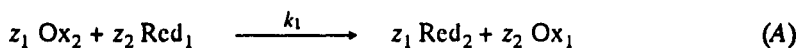
proceeds. The dependence of the volume V of the reactant Ox_2 injected into the solution of the reactant Red_1 on time t has been derived[1] in the form

$$\frac{V_s + V_{\infty \text{Ox}_2}}{V_{\infty \text{Ox}_2} - V_{\infty \text{Red}_1}} \ln \frac{V_{\infty \text{Ox}_2} - V}{V_{\infty \text{Ox}_2} - \Delta V} - \frac{V_s + V_{\infty \text{Red}_1}}{V_{\infty \text{Ox}_2} - V_{\infty \text{Red}_1}} \ln \frac{V_{\infty \text{Red}_1} - V}{V_{\infty \text{Red}_1} - \Delta V} =$$
$$= z_1 \, c_{\text{Ox}_2} k_1 \left[\, (V_s + \Delta V)/(V_{\infty \text{Ox}_2} - \Delta V) \, \right] t \,, \qquad (1)$$

where V_s is the starting volume of the reaction mixture containing the reaction component Red$_2$ in a concentration b_{Red_1}, ΔV is the starting volume of the solution of the reactant Ox$_2$ at an injection concentration a, and

$$V_{\infty Ox_2} = \frac{(V_s + \Delta V)\, c_{Ox_2}\, \kappa}{z_1\,(a\,\kappa_{Ox_2} - Y_0) - a\,\kappa_{Ox_2}} + \Delta V$$

$$V_{\infty Red_1} = \frac{(V_s + \Delta V)\, c_{Red_1}\, \kappa}{z_2\,(a\,\kappa_{Ox_2} - Y_0) - a\,\kappa_{Ox_2}} + \Delta V \tag{2}$$

$$\kappa = z_1\,\kappa_{Ox_2} + z_2\,\kappa_{Red_1} - z_1\,\kappa_{Red_2} - z_2\,\kappa_{Ox_1},$$

c_{Ox_2}, c_{Red_1} are concentrations of the reactants Ox$_2$ and Red$_1$ at the beginning of action of the feedback. Symbol Y_0 denotes a constant value of a quantity Y (e.g. absorbance) which obeys the general equation

$$Y = \sum_i c_i\,\kappa_i, \tag{3}$$

where c_i is the actual concentration of the i-th reactant.

Mass balance at the start of reaction (A) gives

$$z_1\left(\frac{b_{Red_1}\, V_s}{V_s + \Delta V} - c_{Red_1}\right) = z_2\left(\frac{a\,\Delta V}{V_s + \Delta V} - c_{Ox_2}\right), \tag{4}$$

where b_{Red_1} is the starting concentration of the reactant Red$_1$ in the reactor. If the volume V_e of the reactant Ox$_2$ in the equivalence point of reaction (A) obeys the equation

$$V_e = [(z_1\, b_{Red_1})/(z_2\, a)]\, V_s, \tag{5}$$

then, by eliminating the quantities c_{Red_1}, κ and κ_{Ox_2} from Eqs (2) and (4), the concentration c_{Ox_2} at the beginning of action of the feedback can be calculated as

$$c_{Ox_2} = a\,\frac{(V_{\infty Red_1} - V_e)\,(V_{\infty Ox_2} - \Delta V)}{(V_s + \Delta V)\,(V_{\infty Ox_2} - V_{\infty Red_1})}. \tag{6}$$

Inserting this relation in Eq. (1) we obtain

$$(V_s + V_{\infty Ox_2})\ln[(V_{\infty Ox_2} - V)/(V_{\infty Ox_2} - \Delta V)] - (V_s + V_{\infty Red_1})\ln[(V_{\infty Red_1} - V)/(V_{\infty Red_1} - \Delta V)] =$$

$$= z_2\, a\, k_1\,(V_{\infty Red_1} - V_e)\, t \tag{7}$$

Based on this implicit dependence of the injected volume on time, the rate constant and other unknowns can be determined by an optimization numerical method.

Assume that for the oxidation-reduction reaction (A) the electromotive voltage of the cell is held constant through a feedback by injection of the reactant Ox_2. The cell is formed by an indicator oxidation-reduction electrode (e.g. a platinum electrode) and a reference electrode (e.g. a saturated calomel electrode). Provided that reaction (A) does not occur through the electrodes (no current passes through the measuring circuit) and perfect stirring of the reaction mixture is provided (the reactant concentrations at the electrode surface and in the solution bulk are identical), potential E of the indicator electrode obeys the equation[2]

$$\sum_i k_i z_i q_i (P_{\alpha_i} c_{Ox_i} - P_{1-\alpha_i} c_{Red_i}) = 0, \qquad (8)$$

where k_i is the rate constant of the electrode process of the i-th system, q_i is the electrode surface area for the i-th system, $P_{\alpha_i} = \exp[-\alpha_i (z_i F/RT)(E - E_{0i})]$, $P_{1-\alpha_i} = \exp\{(1 - \alpha_i)(z_i F/RT)(E - E_{0i})]$, α_i is the charge transfer coefficient of the i-th oxidation-reduction system, E_{0i} is the standard oxidation-reduction potential of the i-th system, F is the Faraday constant, R is the gas constant, and T is temperature.

Assuming ideal behaviour of the indicator electrode[3], i.e. independence of k_i and α_i on the actual reactant concentrations, the following coefficients can be defined for the constant potential E:

$$\kappa_{Ox_1} = z_1 k_1 q_1 P_{\alpha_1} \qquad \kappa_{Red_1} = -z_1 k_1 q_1 P_{1-\alpha_1}$$

$$\kappa_{Ox_2} = z_2 k_2 q_2 P_{\alpha_2} \qquad \kappa_{Red_2} = -z_2 k_2 q_2 P_{1-\alpha_2} \qquad (9)$$

By inserting these coefficients in Eq. (8) we obtain

$$\sum_{i=1}^{2} (c_{Ox_i} \kappa_{Ox_i} + c_{Red_i} \kappa_{Red_i}) = 0 \qquad (10)$$

This equation is formally identical with the general definition of quantity Y according to Eq. (3) for $Y = 0$. Thus, all the theoretical relations derived previously[1] can be applied to the feedback reactor with potentiometric indication so that the value of quantity Y will be zero by definition. The experimental data processing, however, will be different. While in the case of spectrophotometric indication the coefficients κ_i are rather readily available, in the case of potentiometric indication they are practically unavailable. Therefore, the determination of all the parameters in the dependence of the injected volume on time (Eqs (1), (7)) must be made by using a numerical optimization method. The chosen constant value of the potential E_k can only lie within the region of the equilibrium potentiometric titration curve of the oxidation-reduction system (A), as shown schematically in Fig. 1.

The E_k value not only affects that overall reaction rate but also, in particular, the quality of the results, as will be demonstrated later. In Eq. (7), one of the V_∞ parameters has physical meaning; this is usually $V_{\infty Red_1}$, the injected volume of the reactant

Ox_2 at time $t \to \infty$. For the chosen potential $E_k = E_e$ (the equivalence potential) the V_∞ value will be V_e, and applying the l'Hospital rule to Eq. (7) we obtain

$$\frac{(V_s + V_e)(V - \Delta V)}{(V_e - \Delta V)(V_e - V)} = z_2 \, a \, k_1 \, t \, . \tag{11}$$

EXPERIMENTAL

Chemicals

Cerium(IV) sulfate and iron(III) sulfate were chemicals of reagent grade purity (Lachema, Brno). Vanadyl sulfate was prepared from ammonium metavanadate[4] (Lachema, Brno), vanadium(III) sulfate was prepared by reacting vanadyl sulfate with vanadium(II) sulfate[5] obtained by reducing ammonium metavanadate with zinc. All concentrations were checked potentiometrically[6].

Apparatus

The basic setup of the feedback reactor for obtaining the experimental dependence of the injected volume on time has been described in ref.[1] and is shown schematically in Scheme 1. The input indication part of the equipment with a current follower was supplemented with a voltage follower. For a more objective and rapid obtaining of the results, the equipment was interfaced to a computer; through an analog/digital converter (A/D), a Sinclair computer with a printer was connected for sampling the analog voltage. Thus the time dependence of the volume was digitized, facilitating the data processing by an optimization method. The printer can serve to archive the results. The A/D converter followed the data at a thousand levels and the total voltage of 1 V corresponded to the volume of 1 cm^3, the reading resolution was 1 mm^3. This is the limiting factor because the injection accuracy was better than 0.1%.

The measuring procedure was as in ref.[1].
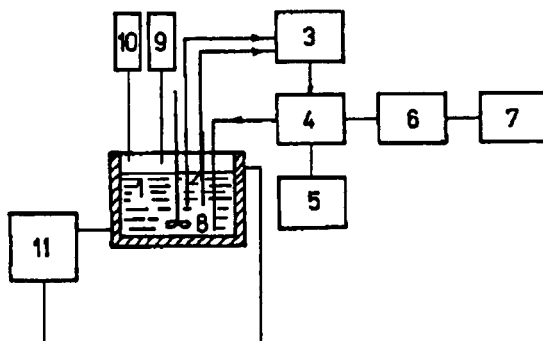
Block diagram of the apparatus. 1 reactor, 2 indicator and reference electrodes, 3 compensator with current and voltage followers, 4 linear dispenser with injected volume–voltage conversion, 5 X–t recorder, 6 A/D converter, 7 Sinclair computer, 8 coil stirrer, 9 B reactant tank, 10 reaction medium tank, 11 thermostat

SCHEME 1

RESULTS AND DISCUSSION

For testing the function of the apparatus and verification of the theoretical relations, two oxidation-reduction reactions in sulfuric acid solutions were chosen (concentrations 1 mol dm^{-3}):

$$Ce(IV) + V(IV) \longrightarrow Ce(III) + V(V)$$

$$Fe(III) + V(III) \longrightarrow Fe(II) + V(IV)$$
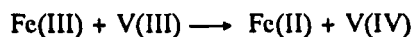
The experimental dependences of the injected volume on time were evaluated based on Eqs (1) and/or (7) on a PC/AT; software set up by us for this contained three selectable optimization methods for nonlinear models: the Rosenbrock–Storey, the Simplex and the Levenberg–Marquardt models[7].

Even preliminary measurement gave evidence that the parameter values obtained by the Simplex method do not correspond to the true values or lack physical meaning. With the object function for n experimental points

$$F_t = \sum_{i=1}^{n} (t_{i,exp} - t_i)^2 \qquad (12a)$$

or

$$F_V = \sum_{i=1}^{n} (V_{i,exp} - V_i)^2 \qquad (12b)$$

the likelihood of the results was dependent on the chosen level of potentials within the titration curve. Therefore, the dependences of volumes on time according to Eqs (1) or (7) were first simulated with chosen parameters k_i and α_i by means of Eq. (9). The volume values were rounded from 0.01 to 1 mm^3. From these results, the rate constants
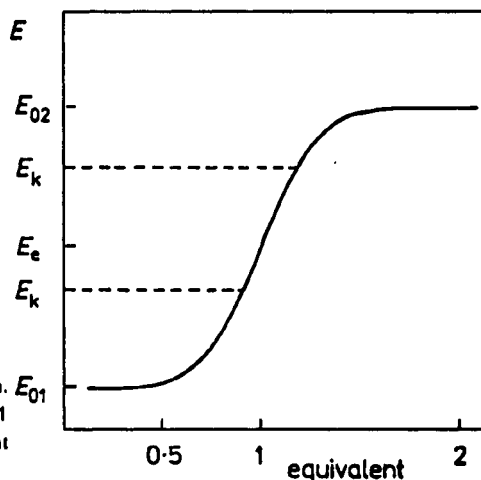

FIG. 1
Titration curve of the oxidation-reduction reaction. E_{01}, E_{02} standard potentials of the redox systems 1 and 2, respectively; E_k arbitrarily chosen constant potential value

k_1 and volumes V_∞ were back-determined by the optimization method and compared with the true values. Simulation was performed for various combinations of common parameters, some of which were as follows for the redox systems 1 and 2, respectively: E_{0i} (V): 0, 0.4; α_i: 0.99, 0.01; $k_i q_i$: 0.01, 1; z_i: 1, 1; a (mol dm^{-3}): –, 0.02; b_{Red_1} (mol dm^{-3}): 0.0008, –; V_s (cm^3): 25, –; ΔV (cm^3): –, 0.2; k_1 (dm^3 mol^{-1} s^{-1}): 1 000. The relative errors of the rate constant k_1 and of the volume V_∞, in dependence on the rounding are given in Table I for the two object functions F_t and F_V.

Considering satisfactory those parameters whose relative error is lower than 5%, Table I demonstrates that for the sub-equivalent dependences ($E_k < E_e$) the experimental volumes must be read with a high precision. The reason for this demand is in the difference ($V_{\infty Red_1} - V_e$) on the right-hand side of Eq. (7). Simulations gave evidence that for the sub-equivalent dependences, $V_{\infty Red_1} \approx V_e$, so that in these cases the $V_{\infty Red_1}$ parameter must be determined with a very high precision. For the above-equivalence dependences ($E_k > E_e$), this requirement is not so stringent. The kind of the object function applied has nearly no effect on the calculation results but the use of the function F_V is more time consuming because the volume must be first calculated explicitly by some other numerical method (Newton's iterative method[9]).

For the Ce(IV)/V(IV) redox system, the measurements were performed with the injection of Ce(IV) solution at a concentration $a = 0.155$ mol dm^{-3} into a solution of V(IV) at a concentration within the region of 0.001 to 0.006 mol dm^{-3} at 20 °C. The indicator electrode was a platinum wire 1 mm in diameter. Of the three electrodes manufactured, only one responded immediately to changes in the reaction mixture. In none case could the dependence of the injected volume V on time t be obtained in the above-equivalence region. The results of optimization of the sub-equivalence dependences confirmed the assumptions and conclusions from the simulation. The determined rate constants often lacked physical meaning or were entirely different from published data[1,5].

TABLE I
Relative errors (%) of the rate constant k_1 and of the final volume V_∞ in the sub-equivalence region ($E_k = 0.025$ V) (a) and in the above-equivalence region ($E_k = 0.275$ V) (b) for various precisions of volume reading

Volume reading precision mm^3	F_V				F_t			
	δ_{V_∞}		δ_{k_1}		δ_{V_∞}		δ_{k_1}	
	a	b	a	b	a	b	a	b
0.01	0.00	0.00	5.05	0.02	0.00	0.00	7.35	0.04
0.10	0.00	0.00	8.47	0.51	0.01	0.00	4.87	0.32
1.00	0.02	0.03	70.94	3.89	0.09	0.02	473.43	4.18

For the $Fe(III)/V(III)$ redox system, the measurements were performed with the injection of a $Fe(III)$ solution at a concentration $a = 0.3087$ mol dm^{-3} into a solution of $V(IV)$ at a concentration b_0 within the region of 0.001 to 0.011 mol dm^{-3} at 20 °C. All the experimentally obtained dependences were from the above-equivalence region. Curves from the sub-equivalence region could not be obtained because the technical parameters of the feedback reactor failed to satisfy. The rate constants obtained by optimization were subjected to the Dean–Dixon test[9] to eliminate outliers; none of the 50 values in the set was so eliminated. An example of experimental dependence of the injected volume on time is shown in Fig. 2. The experimental rate constant, 1.52 ± 0.11 $dm^3 \, mol^{-1} \, s^{-1}$, is in a good agreement with the literature[5].

CONCLUSIONS

Measurement on a feedback reactor with potentiometric indication is affected appreciably by the precision of input data reading. This fact was confirmed in simulations as well as in the experiments. Whether the measurement affords dependences of V on t in the sub-equivalence region or in the above-equivalence region is governed by the technical parameters of the equipment, by the electrochemical parameters of the oxidation-reduction system, and by the properties of the solid electrode[8]. Attempts to obtain the true rate constant values in the cases of sub-equivalence rates invariably failed. The single parameter applicable to analytical purposes was V_∞. This does not mean that the method should be turned down; only one should strive to meet the high demands placed
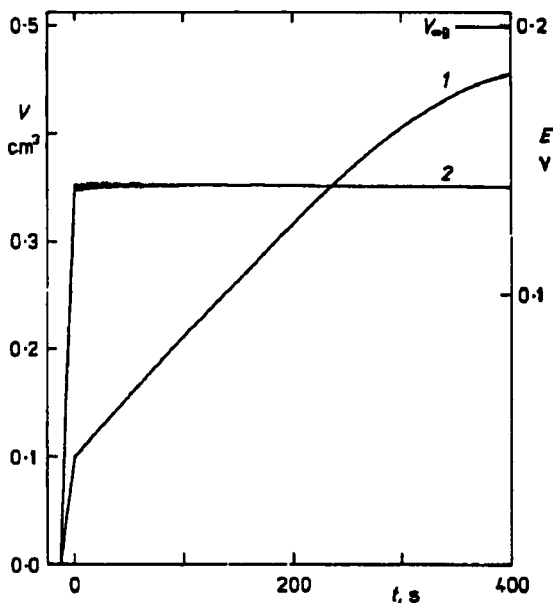

FIG. 2
Experimental record from the measurement of the $Fe(III)/V(III)$ redox system. Temperature 20 °C, chosen constant cell voltage $\Delta E_k = 0.015$ V, concentration of $V(III)$, $b_{Red_1} = 0.0037$ mol dm^{-3}, $V_s = 15$ cm^3, $a = 0.3087$ mol dm^{-3}, $\Delta V = 0.099$ cm^3, $c_{Ox_2} = 0.00135$ mol dm^{-3}, $c_{Red_1} = 0.003$ mol dm^{-3}, $V_{\infty Red_1} = 0.4979$ cm^3, $V_{\infty Ox_2} = -0.0056$ dm^3, $k_1 = 1.46$ $dm^3 \, mol^{-1} \, s^{-1}$, $F_1 = 20.86$ s^2. Curves: 1 volume, 2 potential

on the precision of measurement. Numerical processing of the above-equivalence dependences met with no problems. Therefore, it is convenient to secure conditions of measurement such that the constant potential chosen can lie above the equivalence value.

With respect to the use of the voltage follower, the properties of the solid-phase electrodes are among the limiting factors; they should not vary during the measurement. Instantaneous response of the indicator electrode is a matter of course. Hence, the electrode must exhibit ideal behaviour[8].

The feedback principle with a voltage follower can also be employed during the control of chemical reactions, e.g. during the keeping a constant pH, a constant ligand concentration, etc. The indicator electrodes can be various kinds (the redox electrode mentioned, an ion selective electrode) according to the requirements of the industrial practice.

REFERENCES

1. Skopal F.: Collect. Czech. Chem. Commun. 53, 929 (1988).
2. Tockstein A., Matušek M.: Collect. Czech. Chem. Commun. 31, 316 (1966).
3. Tockstein A., Skopal F.: Collect. Czech. Chem. Commun. 39, 3024 (1974).
4. Fresno del C., Mairlot E.: Z. Anorg. Chem. 73, 214 (1933).
5. Tockstein A., Skopal F.: Collect. Czech. Chem. Commun. 39, 3430 (1977).
6. Číhalík J.: *Potenciometrie*. Nakladatelství ČSAV, Praha 1961.
7. Himmelblau D. M.: *Process Analysis by Statistical Methods*. Wiley, New York 1970.
8. Tockstein A., Skopal F.: Collect. Czech. Chem. Commun. 39, 3016 (1974).
9. Olehla J.: *Basic u mikropočítačů*. NADAS, Praha 1988.

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