FEEDBACK REACTOR AND NONLINEAR REGRESSION METHODS

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Received February 13, 1992
Accepted April 25, 1992

Linear and nonlinear regression methods are compared with respect to their application to the evaluation of chemico-kinetic measurements of a feedback reactor. Their assets and pitfalls are demonstrated.

The feedback-controlled chemical reactor (FCCR) is an experimental device for examining the kinetics of liquid-phase chemical reactions in an arrangement where one reactant is injected into another reactant, the injection rate being controlled by a negative feedback[1].

THEORETICAL

We shall deal with an irreversible nonisochoric 2nd order reaction with a unit order for the two starting components:

$$\nu_A A + \nu_B B \rightarrow \nu_C C + \nu_D D . \qquad (A)$$

Into the starting volume V_0 of reaction component B is continuously injected volume $V(t)$ of component A whose injection concentration is a. The absorbance of the reaction mixture A is held constant via a negative feedback:

$$A = \frac{\sum_{i=A}^{D} n_i(t)\,\kappa_i}{V_0 + V(t)} = \text{const.} , \qquad (1)$$

where $n_i(t)$ is the amount of substance of the i-th reaction component in time t and κ_i is the molar absorptivity of the i-th component multiplied by the optical pathlength of the absorbing medium.

The implicit dependence of the injected volume V on time t has been derived[2] in the form

$$(V_0 + V_{\infty A}) \ln\frac{V_{\infty A} - V}{V_{\infty A} - \Delta V} - (V_0 + V_{\infty B}) \ln\frac{V_{\infty B} - V}{V_{\infty B} - \Delta V} =$$

$$= -\nu_B k_1 a \left(V_{\infty B} - \frac{\nu_A b_0 V_0}{\nu_B a}\right) t \,, \tag{2}$$

where

$$V_{\infty A} = \frac{-n_{AK}\kappa}{\nu_A(a\kappa_A - A) - a\kappa} + \Delta V \,, \tag{3}$$

$$V_{\infty B} = \frac{-n_{BK}\kappa}{\nu_B(a\kappa_A - A)} + \Delta V \,, \tag{4}$$

$$\kappa = -\nu_A \kappa_A - \nu_B \kappa_B - \nu_C \kappa_C - \nu_D \kappa_D \,. \tag{5}$$

Equation (2) can formally be written as

$$t = a_3 \ln(a_1 - V) + a_4 \ln(a_2 - V) + a_5 \,, \tag{6}$$

where the five independent parameters a_1 through a_5 are

$$a_1 = V_{\infty A} \,, \tag{7}$$

$$a_2 = V_{\infty B} \,, \tag{8}$$

$$a_3 = -(V_0 + V_{\infty A}) / \left\{\nu_B k_1 a \left(V_{\infty B} - \frac{\nu_A b_0 V_0}{\nu_B a}\right)\right\} \,, \tag{9}$$

$$a_4 = -(V_0 + V_{\infty B}) / \left\{\nu_B k_1 a \left(V_{\infty B} - \frac{\nu_A b_0 V_0}{\nu_B a}\right)\right\} \,, \tag{10}$$

$$a_5 = \left\{[(V_0 + V_{\infty A}) \ln(V_{\infty A} - \Delta V) - (V_0 + V_{\infty B}) \ln(V_{\infty B} - \Delta V)]\right\} / \\ / \left\{\nu_B k_1 a \left(V_{\infty B} - \frac{\nu_A b_0 V_0}{\nu_B a}\right)\right\} \,. \tag{11}$$

In general, nonlinear regression methods (both derivation and nonderivation ones) can be employed to determine all the five parameters in Eq. (6) and, in turn, the five experimental parameters in the FCCR equation (2). However, detailed analysis revealed that out of the five equations (7) – (11), only three are independent while the remaining two are their combinations, such as

$$a_4 = a_3 \frac{V_0 + a_2}{V_0 + a_1} \tag{12}$$

$$a_5 = \frac{-a_3}{V_0 + a_1} [(V_0 + a_1) \ln (a_1 - \Delta V) - (V_0 + a_2) \ln (a_2 - \Delta V)] . \tag{13}$$

Thus, nonlinear regression methods can only serve to determine no more than three out of the five parameters a_1 through a_5, and thus, no more than three experimental parameters of the FCCR equation.

If the argument of one or the other logarithm in Eq. (2) approaches unity across the entire region of experimental values, one of the parameters of Eq. (2) becomes poorly conditioned and its determination by nonlinear regression is very uncertain. Only the remaining two parameters can be determined successfully.

Thus, having determined two or three a_i parameters in Eq. (6) by nonlinear regression we can determine experimental parameters of Eq. (2): the rate constant of the chemical reaction k_1, concentrations of the reaction components, their molar absorptivities. The results so obtained, however, must be assessed very critically.

EXPERIMENTAL

The above theoretical conclusions were tested on a model system of Ce(IV)/V(IV) in 1M-H_2SO_4 at 20 °C, for which enough data have been published, e.g. in refs[3,6,7].

The measurements were carried out on the experimental equipment described in ref.[2]; the wavelength was 390 nm. The proportionality factors κ_i of the reaction components in order Ce(IV), Ce(III), V(IV), V(V) were determined at this wavelength to be 2 682, 0, 0, and 29 $cm^2\ mol^{-1}$. The reaction component concentrations were chosen within the regions of 5.3 – 31.6 mmol dm^{-1} for Ce(IV) (injected reactant A) and 50 – 600 μmol dm^{-1} for V(IV) (reactant B). The reaction mixture absorbance was chosen so that the complete dependence of volume injected on time could be obtained with a correct operation of the negative feedback.

RESULTS AND DISCUSSION

The experimental dependences of the injected volume on time were treated by nonlinear regression methods (Simplex[4], Rossenbrock[8], Lewenberg–Marquardt). The objective function was formulated as the sum of squares of residuals of the experimental and calculated time according to Eq. (6) with three parameters. The values in Table I (column $k_{1,3}$) demonstrates that some results were inacceptable because the residuals[5] of the experimental and calculated times exhibited trends and the rate constants lacked physical meaning.

Therefore, nonlinear regression with an objective function with two parameters was applied to all experiments. Practice confirmed that the poor conditioning in the model is due to the a_1 or a_2 parameter. The results of evaluation are given in column $k_{1,2}$ in

Table I. It is evident that some results could not be admitted for the same reasons as above.

All the experimental parameters in the FCCR equation except the rate constant were determined for the model reaction chosen. Thereafter, linear regression could be performed with one unknown – the rate constant. The evaluation met with no problems, and the rate constants are given in column $k_{1,\mathrm{lin}}$ in Table I.

TABLE I
Results of evaluation of experimental measurements on the feedback reactor

Experiment No.	a mmol dm^{-3}	b_0 μmol dm^{-3}	A	$k_{1,3}$	$k_{1,2}$ dm^3 mol^{-1} s^{-1}	$k_{1,\mathrm{lim}}$
1	5.3	50	0.077	723.2	813.5	890.8
2	5.3	50	0.047	763.2	790.8	845.9
3	5.3	50	0.028	800.6	840.3	878.5
4	5.3	100	0.072	756.3	829.2	837.0
5	5.3	100	0.051	794.1	840.7	837.1
6	5.3	100	0.023	827.7	936.3	801.2
7	15.8	200	0.071	774.4	844.8	787.6
8	15.8	200	0.047	1 051.5	1 061.5	774.6
9	15.8	400	0.078	932.9	951.2	805.7
10	31.6	200	0.076	952.2	957.3	792.1
11	31.6	400	0.070	710.0	940.1	814.8
12	31.6	400	0.046	671.9	921.1	898.1
13	31.6	600	0.069	843.3	1 095.9	820.0
14	15.8	200	0.017	1 023.5	3 156.2[a]	849.1
15	15.8	400	0.038	1 004.4	1 984.9[a]	746.6
16	15.8	600	0.062	997.9	1 150.9[a]	688.5
17	15.8	600	0.047	1 006.3	1 462.2[a]	750.7
18	31.6	600	0.020	864.8	-1 291.3[b]	932.4
19	31.6	600	0.040	873.5	918.2[a]	821.5
20	31.6	200	0.048	637.4[a]	780.8	927.5
21	31.6	200	0.024	301.9[a]	862.5	846.2
22	15.8	400	0.024	638.9[a]	-358.7[b]	825.2
23	15.8	600	0.024	1 185.4[a]	-124.2[b]	777.8
24	31.6	400	0.021	286.9[a]	1 772.9[a]	1 043.7
	Average value			861.7	897.7	833.0
	Standard deviation			118.3	94.0	72.6

[a] Value rejected based on graphical and statistical analysis of time residuals. [b] Value lacks physical meaning.

All the three approaches applied to the evaluation of FCCR experiments gave rate constants which are in a good agreement with published data, such as the value of k_1 = 833 dm^3 mol^{-1} s^{-1} given in ref.[3]. When assessing results obtained by nonlinear regression, however, one must proceed with circumspection.

It must be borne in mind that a single FCCR experiment cannot provide the maximum information on the chemical reaction. One must be realistic and test the results obtained. If enough objective spectrophotometric and analytical parameters of the FCCR equation are available, the linear regression method can be employed with success. Otherwise, some of the nonlinear regression methods (derivative or nonderivative) must be used. When admitting the results, however, one must be circumspect and treat them critically.

Measurement on a feedback reactor is easy and can be readily automated (by interfacing a computer in the on-line mode, with subsequent data processing), and this novel method is a further contribution to the study of kinetics of homogeneous-phase chemical reactions.

SYMBOLS

A	reaction component (injected reactant)
A	reaction mixture absorbance
a	concentration of injected component A, mol dm^{-3}
$a_1 - a_5$	parameters of the FCCR equation
B	reaction component (reactant)
b_0	concentration of component B in the reactor before the injection of component A, mol dm^{-3}
C	reaction component (product)
D	reaction component (product)
k_1	chemical reaction rate constant, dm^3 mol^{-1} s^{-1}
$n_{i\mathrm{K}}$	amount of substance of the i-th reaction component in time $t = 0$ ($V = \Delta V$), mol
$n_i(t)$	amount of substance of i-th reaction component in time t, mol
t	time, s
$V(t)$	injected volume of reactant A, cm^3
V_0	starting volume of reactant B, cm^3
ΔV	starting volume of reactant A, cm^3 (after its injection, the constant reaction mixture absorbance A is attained in time $t = 0$)
κ_i	molar absorptivity of the i-th reaction component multiplied by the optical pathlength of the absorbing medium, cm^2 mol^{-1}
ν_i	stoichiometric coefficient of the i-th reaction component

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Translated by P. Adámek.