EVALUATION OF THE PARAMETERS OF THE ELOVITCH EQUATION: A DIFFERENTIAL APPROACH

Part 2. Some Factors Influencing the Accuracy of Estimated Parameters

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1. Introduction

In a previous paper[1], a differential approach was suggested as a possible means of evaluating the parameters of the ELOVITCH equation from experimental data. For the initial exploration, the 'noise' level of simulated experimental data was deliberately chosen to be very low; but, since a differentiation procedure magnifies 'noise' the present paper examines the effect of significant 'noise' in the data on the accuracy of the estimated parameters.

2. Numerical Procedure

In this paper, an attempt has been made to generate simulated experimental data containing a known level of 'noise'. Following the procedure described in the earlier paper[1], values of a and α were chosen in the ELOVITCH equation:

$$R = \frac{dq}{dt} = a \cdot \exp(-\alpha q)\,, \tag{1}$$

where R is the rate of sorption, q the amount sorbed, t the time, and a, α, are parameters.

In the integrated form, using the initial conditions (t_0, q_0), (1) becomes:

$$(q-q_0) = \frac{1}{\alpha} \cdot \ln\left\{1 + \frac{a\alpha}{\exp(\alpha q_0)}(t-t_0)\right\}. \tag{2}$$

From (2), and the chosen values of a and α, values of q can be calculated for a series of values of t, at a given interval h, for a given initial condition (t_0, q_0). The simulated experimental data used in this paper was generated by

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superposing errors of a controlled 'noise', level onto the values of q determined above. The error added was randomly chosen from a Gaussian distribution, the 'noise' level being measured by the standard deviation of the distribution. The result of the addition of an error to a calculated value of q, produced a simulated experimental point. As an example of this procedure, a set of simulated experimental points is given in Table 1.

TABLE 1. A set of simulated experimental data

$a=1$; $\alpha=0.001$; $t_0=q_0=0$; $h=10$; standard deviation of error $=1.0$

t	q theoretical	error	q experimental
0	0	−1. 61	−1.161
10	9.950	0.736	10.686
20	19.803	−0.521	19.282
30	29.559	0.604	30.163
40	39.221	−0.007	39.214
50	48.790	0.694	49.484
60	58.269	−2.028	56.211
70	67.659	−0.964	66.695
80	76.961	0.116	77.077
90	86.178	−0.748	85.430
100	95.310	−0.138	95.172
110	104.360	−1.822	102.538

The parameters were determined from the simulated experimental data using the method described in the previous paper[1]; the 'one neighbour' equation was used throughout this paper to determine the derivatives. All computations, including the random choice of error from a Gaussian distribution, were carried out on the digital computer SILLIAC in the Basser Computing Laboratory, the School of Physics, of the University of Sydney.

3. Results

The estimated parameters from eight sets of simulated data, generated from chosen pairs of (a, α) with various levels of 'noise', are summarised in Table 2.

4. Discussion

Possible factors influencing the accuracy of estimated parameters include: the differentiation procedure used (one, two or three neighbours); the spacing

TABLE 2. Parameters estimated from simulated data

a exact	α exact	% error in data*	a estimated	α estimated
10.0	0.01	0	11.04**	0.0105**
10.0	0.01	0.5	11.03	0.0104
10.0	0.01	1.0	11.79	0.0109
10.0	0.001	0.2	10.01	0.000994
10.0	0.001	0.4	9.97	0.000984
1.0	0.01	2.0	1.113	0.0126
1.0	0.01	4.0	1.049	0.0111
1.0	0.001	2.0	1.011	0.001412
1.0	0.001	4.0	0.921	0.000709

* Average value for whole set.
** Taken from previous paper[1].

of data points; the absolute magnitudes of the parameters; and the 'noise' level of the data. To predict which of these factors predominates in any given sitvation will require much more work than is covered in the present paper. It seems clear, from the results presented in Table 2, that the differential approach by itself cannot be expected to give the 'best values' of the parameters from any given experimental data. It could, however, provide starting values for the other known methods for non-linear parameter estimation[2]. These methods rely on an iterative technique, using successive approximations to the parameters until a minimum is reached in the sum of squares of the errors. An example of this is given by ENOMOTO, HORIUTI and KOBAYASHI[3] in the determination of the stoichiometric number of the ammonia synthesis reaction.

Whatever the method adopted for parameter estimation, the amount of work involved in determining the 'best values' is likely to be great. It remains for some procedure to be found which would minimise the amount of computational work necessary to obtain any desired accuracy; and it may be that some combination of the differential and the iterative methods would achieve this.

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