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

## Part 1. The Choice of a Numerical Differentiation Procedure

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### 1. Introduction

Several graphical and numerical methods for determining the parameters of the ELOVITCH equation, based mainly on the integrated form of the equation, have appeared in the literature[1,2,3]. The ELOVITCH equation is:

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

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

Integrating, using the initial condition $(t_0, q_0)$, (1) becomes:

$$q = \frac{1}{\alpha} \cdot \ln\left[\exp(\alpha q_0) + a\alpha(t - t_0)\right] \qquad \text{(2 a)}$$

or

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

An advantage of the integrated form is that the experimental $(t, q)$ data can be used directly: a disadvantage is the non-linearity of the expression. No established procedure, corresponding to the "least squares" method for linear equations, exists, whereby the parameters for such an expression may be evaluated. One method, of SARMOUSAKIS and LOW[2], uses selected points from the experimental data to yield three simultaneous equations, which are solved for the parameters. The selection process is arbitrary, and the procedure must be followed with several different sets of points to obtain average values of the parameters.

A differential approach has the merit of determining the parameters from

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a linear expression, obtained by taking natural logarithms of both sides of equation (1), using the "least squares" method.

$$\ln(R) = \ln(a) - \alpha q \qquad (3)$$

A disadvantage of this approach is the problem of the errors appearing in the derivatives $R$, due to the magnification of "noise" in the original experimental $(t, q)$ data.

The choice between the two approaches reduces itself to one between, on the one hand, the use of arbitrary procedures to fit the original experimental data; and, on the other hand, the use of the established "least squares" method, using derivatives which may be subject to considerable error.

The purpose of this investigation is to examine some aspects of the differential approach.

## 2. Numerical Procedure

One of the limitations of a numerical differentiation method is the magnification of "noise" in the original data. Any method which first smooths the original data, for example by a polynomial, and then obtains the derivatives by differentiating the function so obtained, may lead to inaccurate derivatives, for reasons which can be found in any text on numerical methods.

LANCZOS[4] recommends the following formula for estimating a derivative in the presence of "noise":

$$f'(x) = \frac{\sum_{\varphi=-k}^{+k} \varphi f(x+\varphi h)}{2\sum_{\varphi=1}^{k} \varphi^2 h} \qquad (4)$$

where $k$ is the number of neighbours on each side of the point where the derivative is required, and $h$ the interval between successive points.

The formula is tested in this paper for the cases of one, two and three neighbours respectively, under the conditions described below.

Values of the parameters a and $\alpha$ were chosen, and the theoretical values of $q$ evaluated for a series of values of $t$ at a given interval $h$, for given initial conditions $(t_0, q_0)$.

TABLE 1. Calculated values of $q$

$a=10.0$; $\alpha=0.01$; $t_0=q_0=0$; $h=10$

| $t$ | $q$ | $t$ | $q$ |
|---|---|---|---|
| 0 | 0 | 130 | 263.906 |
| 10 | 69.315 | 140 | 270.805 |
| 20 | 109.861 | 150 | 277.259 |
| 30 | 138.629 | 160 | 283.321 |
| 40 | 160.944 | 170 | 289.037 |
| 50 | 179,176 | 180 | 294.444 |
| 60 | 194.591 | 190 | 299.573 |
| 70 | 207.944 | 200 | 304.452 |
| 80 | 219.722 | 210 | 309.104 |
| 90 | 230.259 | 220 | 313.549 |
| 100 | 239.790 | 230 | 317.805 |
| 110 | 248.491 | 240 | 321.888 |
| 120 | 256.495 | 250 | 325.810 |

The values are summarised in Table 1.

The derivatives were evaluated from equation (4), for values of $k$ equal to one, two and three respectively, using values of $q$ taken from Table 1. The derivatives are summarised in Table 2.

TABLE 2. Derivatives calculated from Table 1

| $t$ | $R$ exact, from (1) | $R$ estimated, from (4) | | |
|---|---|---|---|---|
| | | $k=1$ | $k=2$ | $k=3$ |
| 0 | 10.0000 | — | — | — |
| 10 | 5.0000 | 5.4931 | — | — |
| 20 | 2.3333 | 3.4657 | 3.9120 | — |
| 30 | 2.5000 | 2.5541 | 2.7081 | 3.0521 |
| 40 | 2.0000 | 2.0273 | 2.1001 | 2.2353 |
| 50 | 1.6667 | 1.6824 | 1.7228 | 1.7824 |
| 60 | 1.4286 | 1.4384 | 1.4633 | 1.5043 |
| 70 | 1.2500 | 1.2566 | 1.2730 | 1.2994 |
| 80 | 1.1111 | 1.1157 | 1.1271 | 1.1452 |
| 90 | 0.9999 | 1.0034 | 1.0116 | 1.0245 |
| 100 | 0.9091 | 1.9116 | 0.8178 | 0.9274 |
| 110 | 0.8333 | 0.8353 | 0.8400 | 0.8473 |
| 120 | 0.7692 | 0.7708 | 0.7745 | 0.7802 |
| 130 | 0.7143 | 0.7155 | 0.7185 | 0.7230 |
| 140 | 0.6667 | 0.6677 | 0.6701 | 0.6737 |
| 150 | 0.6250 | 0.6258 | 0.6278 | 0.6308 |
| 160 | 0.6250 | 0.5889 | 0.5906 | 0.5931 |
| 170 | 0.5882 | 0.5561 | 0.5575 | 0.5596 |
| 180 | 0.5556 | 0.5268 | 0.5280 | 0.5298 |
| 190 | 0.5263 | 0.5004 | 0.5014 | — |
| 200 | 0.5000 | 0.4766 | — | — |
| 210 | 0.4762 | — | — | — |

Finally, the values of $a$ and $\alpha$ were found, by substituting corresponding values of $q$ and $R$ from Tables 1 and 2 into the matrix equation:

$$M \cdot x = b \tag{5}$$

where $M$ is the matrix of the coefficients of $\ln(a)$ and $\alpha$ in equation (3), and $b$ the vector given by the values of $\ln(R)$.

The computational work was carried out on the digital computer SILLIAC in the Basser Computing Laboratory, the School of Physics, of the University

TABLE 3. Calculated values of a and $\alpha$

Exact Values: $a = 10.0$; $\alpha = 0.01$

| Method | Range Considered | $a$ | $\alpha$ |
|---|---|---|---|
| One Neighbour | $t = 10$ to $100$ | 11.04 | 0.0105 |
| Two Neighbours | $t = 20$ to $110$ | 12.50 | 0.0109 |
| Three Neighbours | $t = 30$ to $120$ | 14.09 | 0.0114 |
| One Neighbour | $t = 10$ to $200$ | 10.73 | 0.0103 |
| Two Neighbours | $t = 20$ to $190$ | 11.65 | 0.0105 |
| Three Neighbours | $t = 30$ to $180$ | 12.59 | 0.0108 |

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## 3. Discussion

A comparison of the exact derivatives calculated from equation (1) with those estimated by numerical methods (Table 2), shows that for the case considered the "one neighbour" method is more precise than the "two neighbour" method, which in turn is more precise than the "three neighbour" method. This is fortunate, because the "one neighbour" method allows more of the initial and final derivatives to be estimated: in fact, only the first and last derivatives are omitted, compared with the first two and three and the last two and three for the "two" and "three" neighbour methods respectively.

For each method, the accuracies of the estimated derivatives are inversely proportional to the absolute magnitudes of the rates. In the "one neighbour" case, for rates above about 2.0, the estimated derivatives are more than 2% too high: for rates less than 1.0, the errors are 1% or less. Each method overestimates the derivatives.

The influence of the errors in the estimated derivatives is shown in Table 3 by the effect on the calculated values of the parameters of the range of data selected to calculate them. A noticeable feature is that the calculated values of a are subject to much greater errors than the corresponding values of $\alpha$.

In this treatment, two important influences have not been considered. The first of these is the question of "weighting" of the derivatives. Each derivative has been assumed to have identical "weight" with regard to its influence in determining the values of the parameters. Furthermore, the initial and final derivatives were not included in the matrix equation, although formulae are available to estimate them. Since each derivative is in fact estimated with varying degrees of precision, "weighting" of them is indicated in order to obtain a better estimate of the parameters. The second influence is that of "noise". The $q$

values were calculated to the sixth decimal place, although for convenience they are given in Table 1 to the third place only. The data considered in this paper can thus be assumed to be virtually free from "noise".

In spite of the limitations discussed above, this preliminary work shows the differential approach to be sufficiently promising to warrant further study. The work is being extended to include a wider range of parameters, the introduction of "noise" of various levels into the data and the problem of "weighting" of the derivatives.

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