Journal of Thermal Analysis, Vol. 9 (1976) 425–434

THE NUMERICAL COMPUTATION OF KINETIC PARAMETERS FOR CONTRACTING INTERFACE REACTIONS

A. C. NORRIS, M. I. POPE and M. SELWOOD

Department of Chemistry, Portsmouth Polytechnic, Portsmouth, U. K.

(Received May 14, 1975)

This paper discusses the performance of a variety of numerical methods applied to the determination of the rate constant and order of contracting interface reactions in the solid state. The methods studied are (a) a direct search method proposed by Várhegyi, (b) a modification of Várhegyi's method which involves a unidimensional search, (c) the direct search procedure of Hooke and Jeeves and (d) the Gauss–Newton technique of non-linear least squares. The results demonstrate that the modified strategy (b) is by far the most efficient of the three direct search methods but that the non-linear least squares technique is superior in performance to any of the direct search methods.

When a solid decomposes under isothermal conditions by a contracting interface mechanism, the fraction of material decomposed, α_i at time, t_i may be expressed by the equation:

$$\alpha_i = 1 - [1 - kt_i(1 - n)]^{1/(1-n)} \qquad i = 1, 2, 3 \ldots p \tag{1}$$

where k is the rate constant for the reaction and n ($\neq 1$) is the reaction order. In this equation only values of $n = 1/2$ and $2/3$, which correspond respectively to the reaction interface moving as a contracting disc or sphere, have theoretical significance [1]. Other values may be expected in practice, however, due to variations in sample geometry etc. [2, 3]. In such cases, the accurate determination of the kinetic parameters is complicated by the non-linear form of Eq. (1).

Several approaches to the evaluation of kinetic parameters have been reviewed by Judd and Norris [4] who showed that the simultaneous determination of k and n is readily achieved by the Gauss–Newton method of non-linear least squares (NLLS). In this method, α_i, is approximated by a first order, differential Taylor series and iterative corrections to initial estimates of k and n are calculated so as to minimize:

$$Q(k, n) = \sum_{i=1}^{p} (\alpha_{i,e} - \alpha_{i,c})^2 W_i \tag{2}$$

in which $\alpha_{i,e}$ is the experimental value of α_i, $\alpha_{i,c}$ is the value predicted from Eq. (1) and each term in the sum is weighted by the factor $W_i = 1/\sigma^2(\alpha_i)$, where $\sigma(\alpha_i)$ is the standard deviation in $\alpha_{i,e}$.*

* If the values of $\alpha_{i,e}$ are equally precise, $\sigma^2(\alpha_i)$ has the same value for all i and W_i can be taken as 1.

More recently Várhegyi [5] has proposed an alternative approach based on a direct search method. The present paper discusses Várhegyi's (V) method in detail and describes an improvement to it. The performance of the *V* and improved methods is then examined and the results are compared with those obtained from the NLLS technique and the standard direct search scheme of Hooke and Jeeves [6, 7].

Mathematical background

In essence, Várhegyi's approach is to replace the quasi-linearization of the NLLS method by a direct linearization which avoids the necessity to calculate derivatives. To do this he minimizes not $Q(k, n)$, but $Q'(k, n)$ defined by:

$$Q'(k, n) = \sum_{i=1}^{p} (Y_{i,e} - Y_{i,c})^2 W'_i \tag{3}$$

where $Y_{i,e} = (1 - \alpha_{i,e})^{1-n}$, $Y_{i,c}$ is calculated from Eq. (1) rewritten as:

$$Y_{i,c} = (1 - \alpha_{i,c})^{1-n} = 1 - kt_i(1 - n) \qquad i = 1, 2, \ldots p \tag{4}$$

and the weighting factor $W'_i = 1/\sigma^2(Y_i) = [(1 - \alpha_{i,e})^n/(n - 1)]^2$,*. The procedure commences by assigning a value of n to calculate a consistent value of k from a linear least squares analysis with $Y_{i,e}$ and t_i as the response and predictor variables respectively. Várhegyi then predicts $Y_{i,c}$, forms $Q'(k, n)$ and repeats the process for a range of (10−15) values of n, taking the optimum values of k and n as the set which produces $Q'(k, n)_{min}$.

Unfortunately, the computational simplicity gained by avoiding derivatives is offset by the opposing requirements of speed, which is greatest with few widely spaced values for n, and accuracy, which is low unless many closely spaced values of n are selected over the anticipated range. These two requirements can be reconciled, however, using the same basic approach but adopting a more powerful strategy to search for the optimum values of k and n. An efficient method which is particularly suitable in the present circumstances is the unidimensional search (UDS) as implemented by Davies, Swann and Campey [8].

In this routine, the function $Q'(k, n)$ is first evaluated with an initial estimate $n^{(0)} = 0.5$ and $k^{(0)}$, the consistent linear least squares value of the rate constant. An amount Δn is then added to obtain $n^{(1)} = n^{(0)} + \Delta n$, and the consistent rate constant $k^{(1)}$ is calculated. If $Q'(k^{(1)}, n^{(1)}) \leq Q'(k^{(0)}, n^{(0)})$ the step length Δn is doubled and a further move is made in this direction to give $n^{(2)} = n^{(1)} + 2\Delta n$ and $Q'(k^{(2)}, n^{(2)})$. This process is repeated until the function value increases indicating that the minimum has been passed.

* A propagation of error analysis defines $\sigma^2(Y_i) = (\delta Y_{i,c}/\delta \alpha_{i,e})^2 \sigma^2(\alpha_i)$ and the equation for W'_i follows assuming $\sigma(\alpha_i)$ is constant for all i.

At this stage the current step size is halved and the last value of n is reduced by this new step to give four equally spaced points a distance d apart. The point furthest from the point of lowest function value is rejected and the remaining three points are used to fit a parabola, the minimum [7] of which is given by:

$$n_{\min} = n^{(b)} + 0.5d[Q'(k^{(a)}, n^{(a)}) - Q'(k^{(c)}, n^{(c)})]/[Q'(k^{(a)}, n^{(a)}) - 2Q'(k^{(b)}, n^{(b)}) + Q'(k^{(c)}, n^{(c)})] \quad (5)$$

where $n^{(b)}$ is the central point, $n^{(a)} = n^{(b)} - d$ and $n^{(c)} = n^{(b)} + d$. If the first step fails to reduce the function value then the search is reversed by setting $\Delta n = -\Delta n$. An immediate failure on reversal indicates that the minimum has been bracketed and the quadratic interpolation may be performed. If necessary, the accuracy with which the minimum is obtained can be increased by restarting the search from the estimated minimum with a reduced step size.

An alternative direct search approach to the minimization of $Q'(k, n)$ is afforded by the procedure of Hooke and Jeeves (HJ) [6, 7], the application of which, like the NLLS method, has been described in detail elsewhere [9]. In contrast to the UDS approach, the HJ method is multidimensional and k as well as n is changed incrementally. The method seeks the minimum in $Q'(k, n)$ by making exploratory searches to establish a direction in which further minimization is likely and then extrapolating in this direction to accelerate the search.

Experimental

Both simulated and experimental data have been used to test the performance of the numerical methods. The simulated α, t data were generated from Eq. (1) using a value of $k_{\text{sim}} = 0.01$ and values of $n_{\text{sim}} = 0.225$, 0.525 and 0.825 representative of the typical range of n encountered in contracting interface decompositions. The latter values were chosen so that, with the UDS method, a starting estimate of $n = 0.5$ coupled with the optimum initial step size of $\Delta n = 0.027$ did not locate n_{sim} fortuitously. The selection of the optimum value of Δn is described in the appendix. Values chosen for t_i were 0, 5, 10, . . . 100 time units; the highest time producing maximum values for α of 0.85, 0.74 and 0.67 when $n_{\text{sim}} = 0.225$, 0.525 and 0.825 respectively. Initial estimates of k for the HJ and NLLS methods were calculated by a linear least squares analysis of Eq. (4) with $n = 0.5$ and $Y_{i,c} = Y_{i,e}$ $(i = 1, 2, 3 \ldots p)$.

The effect of experimental error was studied by calculating random errors, $\varepsilon_{\alpha,i}$ within a range $\pm E_\alpha$ and adding them to the exact values of α_i. Two ranges of $E_\alpha = \pm 0.002$ and ± 0.005 were used and, since the distribution of the errors was independent of time, $\sigma(\alpha_i)$ was assumed to be constant.

The methods were also used to determine kinetic parameters for the isothermal (298.2 K) dehydration of strontium hydroxide octahydrate under vacuum. Details of the experimental apparatus, procedures and experimental data are given elsewhere [4, 9]. Computer programs were written in ALGOL 60 for the ICL 4130 computer.

Results and discussion

To facilitate comparison with Várhegyi's approach the calculations carried out with the direct search methods have minimized $Q'(k, n)$ using the functional relationship of Eq. (3). This relationship cannot be used for the NLLS method, however, since the assignment of a value of n to calculate the response variable $(1 - \alpha_{i,e})^{1-n}$ produces a linear least squares problem and any attempt to optimize simultaneously the values of k and n gives linearly dependent normal equations and a singular coefficient matrix. The function $Q(k, n)$ has therefore been minimized for the NLLS technique. Tests with the direct search methods confirm that the reductions of $Q(k, n)$ and $Q'(k, n)$ give identical values for k and n.

Geometrical interpretation of the least squares function $Q'(k, n)$

It is instructive to examine the shape of the response surface of the function $Q'(k, n)$ since it gives information on the results to be expected from optimization procedures. For this purpose, values of $k = 0.01$ and $n = 0.5$ were used to generate error-free α-t data, and values of $Q'(k, n)$ were calculated from combinations of k and n within the ranges $k = 0.0 - 0.05$ and $n = 0.0 - 1.0$.

Figure 1 shows a three-dimensional representation, drawn by computer, of the response surface near the minimum in $Q'(k, n)$. The flat, cross-hatched area is obtained by assigning a constant arbitrary value C to all values of $Q'(k, n)$ greater than C; a device which greatly facilitates the visualization of the response surface. The orientation has been chosen to show that the minimum lies in an elongated valley and, when due consideration is given to the scales of the axes, the floor of this valley is found to make an angle of $<1°$ with the n-axis. Representations of

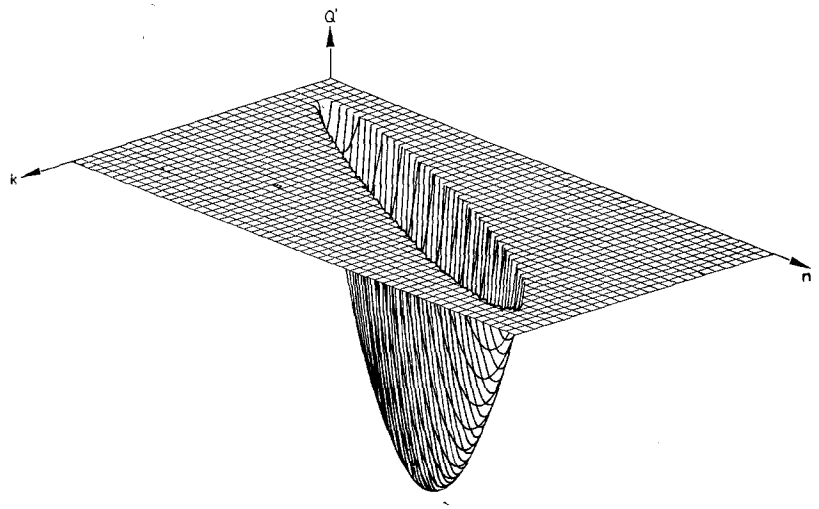

Fig. 1. Three-dimensional representation of the response surface near the minimum of the $Q'(k, n)$ function ($0.008 \leq k \leq 0.0125$, $0.1 \leq n < 1.0$).

the response surface over greater ranges of k and n confirm that the valley is almost straight and very much flatter in the n- than in the k-direction. The alignment demonstrates that the value of k will be determined more accurately than the value of n [10] whilst the steep sides and comparative flatness of the ravine suggest that k will also be found more reproducibly than n. Finally, representations over the full ranges of k and n show the presence of a single, well defined minimum. Thus, $Q'(k, n)$ is unimodal and all optimization procedures locating the minimum will produce approximations to the same unique values of k and n.

Simulated data

The results of applying the V and UDS methods to the estimation of k and n are shown in Table 1 and the results of the HJ and NLLS techniques are given in Table 2. Data in both tables confirm the above conclusion that k is determined more accurately than n. The relative accuracies of the direct search methods, which specify an interval in which the minimum in $Q'(k, n)$ lies, are assessed by comparing the predictions for k and n with the (NLLS) least squares values shown in Table 2.

Table 1

Comparison of V and UDS methods for the optimization of k and n ($k_{sim} = 0.01$)

Method		V			UDS		
n_{sim}	E_α	k	n	$N_{Q'}$	k	n	$N_{Q'}$
0.225	0.000	0.0102	0.25	14	0.0100	0.232	8
	0.002	0.0102	0.25	14	0.0100	0.232	8
	0.005	0.0102	0.25	14	0.0101	0.233	8
0.525	0.000	0.0101	0.55	14	0.0100	0.525	5
	0.002	0.0101	0.55	14	0.0100	0.526	5
	0.005	0.0101	0.55	14	0.0100	0.527	5
0.825	0.000	0.0101	0.85	14	0.0100	0.828	7
	0.002	0.0101	0.85	14	0.0100	0.829	7
	0.005	0.0101	0.85	14	0.0100	0.830	7

When the data are error-free, the least squares estimates naturally correspond to the simulated values but, when error is assigned, the least squares values are perturbed slightly.

Várhegyi's original scheme has been tested using 14 values of n starting from 0.2 and increasing in steps of 0.05 to 0.85, that is, the number of evaluations of the function $Q'(k, n)$ is $N_{Q'} = 14$. The results in Table 1 demonstrate that, whatever the value of E_α, the V method estimates k to within $1-2\%$ of k_{sim} at all levels of n_{sim}, whilst n is predicted to be from 11% ($n_{sim} = 0.225$, no error) to 2% ($n_{sim} = 0.825$, $E_\alpha = \pm 0.005$), higher than the least squares values.

Table 2*

Comparison of HJ and NLLS methods for the optimization of k and n ($k_{sim} = 0.01$)

Method		HJ			NLLS		
n_{sim}	E_α	k	n	$N_{Q'}$	k	n	$N_{Q'}$
0.225	0.000	0.0100	0.227	93	0.0100(0)	0.225(0)	4
	0.002	0.0100	0.210	71	0.0100(0)	0.227(3)	4
	0.005	0.0100	0.229	90	0.0100(0)	0.230(9)	4
0.525	0.000	0.0100	0.527	57	0.0100(0)	0.525(0)	3
	0.002	0.0100	0.527	50	0.0100(0)	0.528(5)	3
	0.005	0.0100	0.533	54	0.0100(0)	0.532(13)	3
0.825	0.000	0.0100	0.823	95	0.0100(0)	0.825(0)	4
	0.002	0.0100	0.829	94	0.0100(0)	0.829(7)	4
	0.005	0.0100	0.834	97	0.0100(0)	0.834(18)	4

* In Tables 2 and 3, numbers in parentheses indicate standard deviations e.g. 0.0101(1) $= 0.0101 \pm 0.0001$, $0.834(18) = 0.834 \pm 0.018$ etc.

Now, with the UDS procedure it is convenient to start the minimization with $n = 0.5$ since the search reverses automatically if $Q'(k, n)$ increases at the first step. Hence, only half the possible range of n is searched and the resulting increase in efficiency, together with the improved search strategy, reduce $N_{Q'}$ by a factor of two. Here $N_{Q'}$ includes the evaluation of $Q'(k, n)$ at the interpolated value of n. In addition, whilst both V and UDS methods predict k_{sim} to similar accuracy, the UDS strategy decreases significantly the error in the estimation of n to between 3% and <0.5%, at the lowest (no error) and highest ($E_\alpha = \pm 0.005$) values of n_{sim} respectively. Clearly, the accuracy can be increased further by restarting the search from the interpolated minimum with a reduced step size. Thus, for exact data, when $n_{sim} = 0.825$ and the search is restarted from $n = 0.828$ with a step size of 0.0027 the least squares estimate of 0.825 is reached when $N_{Q'} = 12$; similar gains are found at other levels of n_{sim} and with assigned error. The results demonstrate clearly the improvement that the UDS modification makes to Várhegyi's method.

In contrast, the values of $N_{Q'}$ in Table 2 show that the HJ search performs very inefficiently on the present problem. In all cases the search commences from $n = 0.5$ and the consistent linear least squares value of k. Initial fractional steps Δn and Δk of 0.2 are reduced to 0.02 when no further reduction in the value of $Q'(k, n)$ is obtained and the search is terminated when $Q'(k, n)$ is a minimum with the smaller step sizes. The estimates of k and n are generally comparable in accuracy with those obtained from the UDS routine but $N_{Q'}$ is very much higher. The inefficiency of the HJ search in the present case arises from the fixed incremental changes made to k for a given value of n. This practice contrasts with the

V and UDS schemes which both produce a minimizing least squares estimate of k for a particular value of n. The linear minimization, or accurate line search, is very effective in optimization methods [11] but it can be time-consuming when the number of parameters is large. The HJ technique is obviously more appropriate for multidimensional problems (see below).

Unlike the procedures described above the NLLS technique will converge iteratively to the true least squares solution.* The results in Table 2 demonstrate clearly the superiority of the NLLS method not only with respect to accuracy but also with regard to the small number of function evaluations, although it should be recalled that a matrix inversion is carried out at each step to solve the normal equations and to generate the inverse coefficient matrix [13]. The evaluation of the inverse matrix has an added benefit, however, since it can be used to estimate the standard deviations in the parameters; information which is not readily obtainable from direct search strategies.

The standard deviations obtained for k and n confirm the deductions made from an examination of the response surface.

Experimental data

When the numerical methods described above are applied to the determination of kinetic parameters for the dehydration of strontium hydroxide octahydrate they lead to the data shown in Table 3. The results support entirely the conclusions

Table 3

Prediction of k and n for isothermal (298.2K) dehydration of strontium hydroxide octahydrate under vacuum

	Method			
Parameter	(V)	(UDS)	(HJ)	(NLLS)
k	0.0576	0.0567	0.0563	0.0567(0)
n	0.40	0.383	0.369	0.382(3)
$N_{Q'}$	14	7	64	4*

* The function $Q(k, n)$ was used for the NLLS method.

drawn from the tests with simulated data. Thus, the NLLS approach is found to perform better than any of the three direct search methods. Of the latter schemes, the UDS strategy is a considerable improvement to Várhegyi's method whereas the HJ search is less efficient if comparable accuracy is required.

* Gorbachev et al. [12] state that the NLLS method can lead to (unspecified) difficulties. However, if the minimizing function is weighted correctly, n and k can be located accurately over the whole range of interest, $0.05 < n < 0.95$, even when $E_\alpha = \pm 0.01$.

Extension of the numerical methods

The determination of k and n from Eq. (1) is a two-dimensional non-linear problem, the solution to which can be obtained, with varying efficiency, by any of the methods discussed in this paper. However, the extent of reaction, α, is not a directly observable quantity and it is calculated by measuring the value of a property which is directly proportional to the amount of reactive material in the system. Thus, in gravimetric work, α is expressed in terms of the total mass, m, of the reactant using the relationship:

$$\alpha_t = (m_0 - m_t)/(m_0 - m_\infty)$$

where the suffices o, t and ∞ refer to the initial, intermediate and final values of the sample mass.

Frequently, m_0 and m_∞ are known with high accuracy, and are regarded as constants. With overlapping decompositions, however, the measurement of m_∞ may be inaccurate, whilst, less frequently, the value of m_0 may also be unreliable. In these circumstances it is obviously desirable to optimize k, n, m_∞ and possibly m_0. Clearly, the V and UDS methods, which are both strictly unidimensional strategies are unsuitable for this purpose and the problem can only be solved effectively by a multidimensional technique such as the HJ and NLLS methods. The detailed solution will be considered in a subsequent paper [14].

The authors would like to thank Messrs. B. A. Collins and M. J. J. Holt for helpful discussions and for writing the perspective plotting program.

Appendix

Calculation of optimum step size for the UDS strategy

Let the function $f(x)$ be unimodal within the interval (a, b), the minimum value occurring at $x = x$.* Then, if the search begins from the mid-point of the interval, $x_m = (a + b)/2$ with a step Δx, comparison of the function values $f(x_m)$ and $f(x_m + \Delta x)$ will determine if the search is moving in the correct direction. If it is not, the search is reversed and so, in either case, only the half-interval $| b - a |/2$ needs to be investigated.

Now, if the initial step is doubled at each move then the total distance travelled after one, two, three etc. steps is $| \Delta x |$, $3 | \Delta x |$, $7 | \Delta x |$ etc. After s steps, the total distance moved is therefore $(2^s - 1) | \Delta x |$, and if the user specifies that the half-interval must be covered in no more than this number of moves then

$$|b - a|/2 = (2^S - 1)\,|\Delta x|$$

or

$$|\Delta x| = |b - a|/[2(2^S - 1)]$$

In the present work a value of $s = 4$ is a suitable compromise between speed and accuracy so that, for the full search interval of $n = 0.1 - 0.9$, the optimum initial step size is given by

$$|\Delta x| = |0.9 - 0.1|/(2 \times 15) = 0.027$$

Clearly the search will be more accurate but slower for larger values of s.

References

1. S. J. GREGG, The Surface Chemistry of Solids, 2nd Ed., Chapman and Hall, London, 1965, p. 361.
2. P. BARRETT, Proc. IV Int. Symp. on Reactivity of Solids, Elsevier, Amsterdam, 1961, p. 178.
3. H. T. S. BRITTON, S. J. GREGG and G. W. WINSOR, Trans. Faraday Soc., 48 (1952) 63.
4. M. D. JUDD nad A. C. NORRIS, J. Thermal Anal., 5 (1973) 179.
5. G. VÁRHEGYI, J. Thermal Anal., 5 (1973) 503.
6. R. HOOKE and T. A. JEEVES, J. Ass. Comp. Mach., 8 (1961) 212.
7. D. M. HIMMELBLAU, Applied Non-linear Programming, McGraw-Hill, New York, 1970, p. 142.
8. M. J. BOX, D. DAVIES and W. H. SWANN, Non-linear Optimisation Techniques, Oliver and Boyd, Edinburgh, 1969, p. 14.
9. A. C. NORRIS, M. I. POPE, M. D. JUDD and M. SELWOOD, Proc. IV I. C. T. A. Conference, Budapest, Hungary, 1974.
10. N. R. DRAPER and H. SMITH, Applied Regression Analysis, Wiley, New York, 1966, p. 292.
11. Ref. 8, p. 38.
12. V. M. GORBACHEV, V. E. FEDEROV and V. A. SHESTAKOV, J. Thermal Anal., 7 (1975) 159.
13. T. R. MCCALLA, Introduction to Numerical Methods and Fortran Programming, Wiley, New York, 1967, p. 148.
14. A. C. NORRIS, M. SELWOOD and M. J. J. HOLT, To be published.

RÉSUMÉ — L'article examine les caractéristiques de plusieurs méthodes numériques appliquées à la détermination de la constante de vitesse et de l'ordre des réactions d'interface contractantes dans l'état solide. Les méthodes étudiées sont (a) une méthode de recherche directe, proposée par Várhegyi, (b) la méthode de Várhegyi modifiée qui met en jeu une recherche uni-dimensionnelle, (c) la méthode de recherche directe suivant Hooke et Jeeves et (d) la méthode des moindres carrés non-linéaires suivant Gauss et Newton. Les résultats montrent que la méthode modifiée (b) est la plus efficace parmi les trois méthodes directes mais que la technique des moindres carrés non-linéaires est supérieure à toutes les méthodes de recherche directe.

ZUSAMMENFASSUNG — Es wird die Eignung einer Anzahl numerischer Methoden, welche zur Bestimmung der Geschwindigkeitskonstante und der Ordnung kontrahierender Zwischenflächenreaktionen im festen Zustand eingesetzt werden, erörtert. Diese Methoden sind a) die von Várhegyi vorgeschlagene direkte Suchmethode, b) eine Abänderung der Methode von Várhegyi, welche eine eindimensionale Suche umfasst, c) das direkte Suchverfahren von Hooke und Jeeves und d) die Gauss—Newton Technik der nicht-linearen kleinsten Quadrate. Die Ergebnisse zeigen, dass von den drei direkten Suchmethoden die modifizierte Strategie b) bei weitem die wirksamste ist, jedoch ist die Technik der nicht-linearen kleinsten Quadrate in dieser Hinsicht allen direkten Suchmethoden überlegen.

Резюме — Обсуждено выполнение ряда числовых методов, применяемых при определении констант скорости и порядка сжимающихся межповерхностных реакций в твердом состоянии. Изучены следующие методы: (а) прямой поисковый метод, предложенный Вархеди, (б) измененный метод Вархеди, включающий безразмерный поиск, (с) прямой поисковый метод Хоки—Джеви, а также метод нелинейных наименьших квадратов Гаусса—Пьютона. Результаты свидетельствуют, что измененный метод (б) является несомненно наиболее эффективным из трех прямых поисковых методов, но метод нелинейных наименьших квадратов является наилучшим по сравнению с прямыми посиковыми методами.