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COMPARISON OF METHODS OF DETERMINING ARRHENIUS EQUATION PARAMETERS BY THE LEAST SQUARES METHOD

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The parameters of the Arrhenius equation determined by the linear, weighted linear and non-linear least squares methods and by the simplex method are compared. Since the non-linear least squares method permits the consideration of statistical weights of both the dependent (k) and independent (T) variables and does not involve logarithmic transformation, it is advisable to calculate the parameters of the Arrhenius equation by means of the non-linear least squares method.

The parameters of the Arrhenius equation are usually determined by the linear least squares method, by the weighted linear and non-linear least squares methods, or by the simplex method. For a given set of experimental data, different results are obtained depending on the calculation method employed.

The parameters of the Arrhenius equation may be determined by either graphical or calculation methods. In the graphical method it is not possible to determine the error in the parameters read out from the plot. The obtained values also include a subjective error connected with the plotting of the line by the experimenter. The subjective error does not appear when calculation methods are applied.

The parameters of the Arrhenius equation

$$k = b_0 \cdot e^{-\frac{b_1}{T}} \tag{1}$$

are determined from the experimentally found rate constants k for different temperatures T. The values of the parameters are calculated by means of the above-given numerical methods.

In the most frequently applied linear least squares method, Eq. (1) is used in the logarithmic form

$$\ln k = \ln b_0 + \left(-\frac{b_1}{T}\right) \tag{2}$$

and the values of b_0 and b_1 fulfilling the following condition

$$\sum_{i=1}^{n} \left(\ln k_i - \ln b - \left(-\frac{b_1}{T_i}\right)\right)^2 = \min \qquad (3)$$

are calculated, according to a described algorithm [1], for n pairs of k and T values.

In this method the assumption is made that the variance of k is constant and independent of T. It follows from the literature data [2, 3] that the assumption is not true. Disregarding the often accessible information on the variance of k may lead to the calculation of incorrect values of the parameters and their errors.

In the case of the weighted least squares method, the values of b_0 and b_1 are calculated as fulfilling the following condition

$$\sum_{i=1}^{n} w_i \left(\ln k_i - \ln b_0 - \left(-\frac{b_1}{T_i}\right)\right)^2 = \min \qquad (4)$$

where w_i is the weight calculated from the known variances of k_i. The weight w_i is calculated [4] from the formula

$$w_i = \frac{1}{s^2_{\ln k_i}} \qquad (5)$$

and $s^2_{\ln k_i}$ is calculated from the formula

$$s^2_{\ln k_i} = k_i^{-2} \cdot s^2_{k_i} \qquad (6)$$

The algorithm of calculations by the weighted least squares method has been given by Pattengill and Sands [5].

In both methods described above, the calculations should be performed with the use of transformed data: $\ln k_i$, $1/T$, and $s^2_{\ln k_i}$ (Eq. (6)). As a result of the calculations, one obtains the values of $\ln b_0$ and b_1, and their variances $s^2_{\ln b_0}$ and $s^2_{b_1}$. The variance of b_0 is calculated from the formula

$$s^2_{b_0} = s^2_{\ln b_0} \cdot (e^{\ln b_0})^2 \qquad (7)$$

The non-linear least squares method has been described by Wentworth [3]. In this method the parameters of the equation

$$k_i - b_0 \cdot e^{-\frac{b_1}{T_i}} = 0 \qquad (8)$$

are calculated from properly formulated minimalization conditions taking account of the weights proportional to $1/s^2_k$ and/or $1/s^2_T$. The calculations are started by assuming initial values of parameters b_0 and b_1 and by replacing Eq. (8) by its form converted to the Taylor series limited to first terms. After suitable transformations, it is possible to find the corrections for b_0 and b_1 from the condition of the minimum of the weighted difference between the calculated and experimental values. The calculations are ended when the newly found parameters differ only slightly from the previous ones.

The parameters of the function are sometimes calculated by means of the simplex method [6]. After assuming three sets of pairs of the values b_0 and b_1, one calculates the value of the following expression for each pair:

$$\sum_{i=1}^{n} \frac{1}{s_{k_i}^2} (k_i - b_0 \cdot e^{-\frac{b_1}{T_i}})^2 \qquad (9)$$

The b_0 and b_1 pair for which the value of expression (9) is highest is then rejected, and a new b_0 and b_1 pair are calculated according to appropriate rules of geometry. The procedure is continued until values of b_0 and b_1 are found for which the value of expression (9) is sufficiently small, or the differences between the values of the parameters for individual simplex vertices are negligible. In the simplex method no variance of the calculated parameters is determined. It should also be pointed out that the values of the determined parameters depend to a certain degree on the initial values assumed in the calculations.

All the presented methods have been applied in processing different series of experimental results. Table 1 shows the data taken from the literature [3], and Table 2 presents the results of calculation of parameters b_0 and b_1 by means of different algorithms.

Table 1 Experimental data [3]

T, K	k	s_k^2
891	$1.16 \cdot 10^{-6}$	$2.49 \cdot 10^{-15}$
903	$3.47 \cdot 10^{-6}$	$8.91 \cdot 10^{-16}$
943	$2.09 \cdot 10^{-5}$	$1.02 \cdot 10^{-13}$
1008	$8.401 \cdot 10^{-5}$	$1.02 \cdot 10^{-12}$
1093	$1.967 \cdot 10^{-4}$	$1.08 \cdot 10^{-11}$
1143	$4.387 \cdot 10^{-4}$	$3.61 \cdot 10^{-11}$
1208	$7.931 \cdot 10^{-4}$	$7.75 \cdot 10^{-11}$

The presented results show that the obtained values of the parameters are different and dependent on the calculation method involved. In the weighted and the non-linear least squares methods, account is taken of the errors in determining the variables, and thus better use is made of the information contained in the experimental results.

The differences in the results of calculations are due both to the different ways of utilizing the information (use of the weights of experimental data) and to the different methods of calculation. To be able to take into account the errors made in determining the values of variables k and T, it is advisable to use the non-linear least squares method for calculation of the parameters of the Arrhenius equation.

Table 2 Results of calculations

Method	Reference	b_0	$s^2_{b_0}$	b_1	$s^2_{b_1}$	Fitting (Eq. 10)
Linear least squares**	1	30547.22	$4.558 \cdot 10^9$	20593.553	$4.968 \cdot 10^6$	$1.73 \cdot 10^{-7}$
Weighted linear least squares*	5	10094.679	$2.674 \cdot 10^8$	19404.206	2672675.5	$7.66 \cdot 10^{-8}$
Non-linear least squares*	3	14004.213	310512.7	19944.517	1620.925	$3.15 \cdot 10^{-8}$
Simplex*	6	10675.094	–	19675.094	–	$2.21 \cdot 10^{-8}$

* Variance s_k^2 taken into account; ** Variance s_k^2 not taken into account.

Calculations were performed for different series of experimental data and for simulated results on the basis of k values and variance s_k^2 divided by 10^l (where l is an integer) taken from Table 1. The obtained results show that the differences between the results of calculations by the different methods are the lower, the smaller the variances of the calculated parameters.

In cases where the criterion for selection of the calculation method is the manner of utilization of the experimental information and the calculated value of

$$L = \sum_{i=1}^{n} (k_i - b_0 \cdot e^{-\frac{b_1}{T_i}})^2 \tag{10}$$

the non-linear least squares method is to be advised for calculation of the parameters of the Arrhenius equation.

Conclusions

In cases where significant experimental errors arise, the results of calculation of the parameters of the Arrhenius equation depend on the calculation method involved. The differences in the results of calculation that are due to the method applied may be a cause of trouble in comparing and drawing conclusions from the results obtained by different authors. Since the non-linear least squares method permits the consideration of the statistical weights of both the dependent (k) and independent (T) variables, and does not involve logarithmic transformations, it is advisable to calculate the parameters of the Arrhenius equation by means of the non-linear least squares method.

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Zusammenfassung — Arrhenius-Parameter bestimmt nach der linearen, mit Gewichten operierenden linearen und nicht-linearen Methode der kleinsten Fehlerquadrate oder nach der Simplex-Methode werden miteinander verglichen. Da bei der nicht-linearen Methode der kleinsten Fehlerquadrate sowohl die abhängige (k) als auch die unabhängige (T) Variable mit statistischen Gewichten versehen werden kann und keine logarithmische Transformation vorgenommen wird, ist es zweckmäßig, die Berechnung der Parameter der Arrhenius-Gleichung nach der nicht-linearen Methode der kleinsten Fehlerquadrate auszuführen.

Резюме — Сопоставлены параметры уравнения Аррениуса, вычисленные методом линейных, весовых линейных и нелинейных наименьших квадратов или же симплексным методом. Поскольку метод нелинейных наименьших квадратов позволяет рассматривать статистический вклад обоих переменных, как зависимого фактора k, так и независимой T, и не включает логарифмического преобразования, он является приемлемым для вычисления параметров уравнения Аррениуса.