

STATISTICAL EVALUATION OF ARRHENIUS MODEL AND ITS APPLICABILITY IN PREDICTION OF FOOD QUALITY LOSSES

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Received for Publication September 13, 1985

ABSTRACT

To minimize quality losses occurring during processing and storage and to predict shelf-life, quantitative kinetic models, expressing the functional relationship between composition and environmental factors on food quality, are required. The applicability of these models is based on the accuracy of the model and its parameters. In this paper, the calculation of the Arrhenius parameters and the accuracy of the derived model were compared, using three statistical methods, namely: linear least squares, nonlinear least squares and weighted nonlinear least squares. Results indicated that the traditional two-step linear method, was the least accurate and the derived energy of activation and the pre-exponential factor had the largest confidence interval. The latter was shown to have a profound effect on the precision of the calculated rate constant and the predicted shelf life. Based on previous reports that indexes of deterioration

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are log-normal distributed, the unweighted nonlinear least squares method was applied in a single-step on all the data points, following a logarithmic transformation. The overall better accuracy and superior performance of the nonlinear least squares method, suggests that this method should be utilized for routine kinetic data analysis.

INTRODUCTION

Foods are very sensitive and susceptible to quality losses due to chemical instability which depends both on compositional and environmental factors. To minimize quality losses occurring in processing and storage, to have a better understanding and an insight in these deleterious reactions, and to predict shelf life, kinetic models are utilized. The models express in a functional form the rate of the quality loss and its dependency on factors such as temperature, moisture content, water activity, concentration and others.

Compositional and/or environmental effects can be expressed by a functional relationship which applies only occasionally to several food systems and reactions. More often, food quality reactions are more complex and unique in their behavior, and the appropriate model must be derived for each product and food system individually.

Temperature is one of the main environmental factors which has a major impact and influence on quality loss rate. The most common and generally valid assumption is that temperature-dependency of food quality deterioration rate follows the Arrhenius model:

$$k = k_0 \exp(-E_a/RT) \quad (1)$$

where: k is the rate constant; k_0 is a constant, independent of temperature (also known as pre-exponential or frequency factor); E_a is the activation energy; R is the gas constant; and T is the absolute temperature.

The Arrhenius equation is frequently used as a theoretical basis for the development of a mathematical model which describes the temperature sensitivity of a food product and for shelf-life prediction. However, such prediction has limited practical use if the large statistical confidence interval and error of the predicted shelf life is considered (Labuza and Kamman 1983). Furthermore, the activation energy generally depends on composition factors such as water activity, moisture content, solid concentration, pH and others (Cohen and Saguy 1983; Connor *et al.* 1981; Goldman *et al.* 1983; Labuza 1972; Saguy 1979; Saguy *et al.* 1979; 1980).

Other models describing temperature effect were discussed (Labuza and Riboh 1982; Kirkwood 1977). However, the Arrhenius model provides the soundest approach for predicting the reaction rate and shelf life at temperatures different from those used in establishing the model. Table 1 summarizes a literature search which indicates the wide spread of the Arrhenius model.

Table 1. Literature Search (Key words and Abstracts) FSTA Files (1969-1984).

Topic	No. of citation
Arrhenius	172
Kinetic(s)	2037
Arrhenius & Kinetic(s)	66
Prediction(s)	3366
Arrhenius & Prediction(s)	36
Simulation(s)	2562
Arrhenius & Simulation(s)	15
Arrhenius & Kinetic(s) & Simulation(s)	12

The most common method to estimate the Arrhenius parameters is the "classic" successive ordinary linear least squares fit (Lund 1983). In this method the first regression is used to derive the rate constant which is then regressed versus the absolute of the 1/temperature to obtain the estimates for E_a and k_0 . The large confidence interval derived for E_a and k_0 (Arabshahi and Lund 1985; Labuza and Kamman 1983; Haralampu *et al.* 1985) is explained by the low number of temperatures (i.e., degrees of freedom), and unnecessary parameters estimated. The derived wide confidence interval reduces the applicability of the model and hampers its utilization. To avoid some of the aforementioned drawbacks nonlinear

least squares regression was suggested (Arabshahi 1982; Davies and Hudson 1981; Haralampu *et al.* 1985; Lund 1983; Nelson 1983). This approach increased the accuracy of the estimated Arrhenius parameters and ultimately improved the confidence interval of the predicted quality attribute.

This investigation was carried out with the overall goal of suggesting the most favorable method for deriving the Arrhenius parameters. Also, to compare the methods commonly utilized in the derivation of E_a and k_0 , and to establish their statistical confidence, limitation, drawbacks, implication, and applicability.

MATERIALS AND METHODS

The statistical analysis is illustrated on the kinetic data of nonenzymatic browning of nonhygroscopic whey (Labuza and Kamman 1983; Table 2), and thiamine retention in an intermediate moisture model system (Arabshahi and Lund 1985; Table 3). These data represent typical zero and first-order reaction kinetics, respectively. The original data (Labuza and Kamman 1983; Arabshahi and Lund 1985) which included duplicate determinations was randomly divided into two groups and named I and II. The first group was utilized to generate the kinetic model, the second group was used for checking the "goodness" of fit. Also, based on previous experience (Arabshahi and Lund 1985; Haralampu *et al.* 1985), to avoid time lags normally accounted at initial equilibration of the samples, zero time observations were omitted.

The methods to be discussed herewith, were used to estimate the activation energy (E_a), the pre-exponential factor (k_0), to evaluate the accuracy and precision of the parameter estimates and to draw conclusions on the statistical accuracy and applicability of these methods.

Kinetics of nonenzymatic browning of nonhygroscopic whey and thiamine retention in an intermediate moisture model system containing propylene glycol can be described by a zero and first-order model (Labuza and Kamman 1983 and Arabshahi and Lund 1985), respectively:

$$dC/dt = k \quad (2a)$$

$$dC/dt = -kC \quad (2b)$$

where:

C is the browning index or the thiamine concentration at time t;

k is the rate constant; and

a, b denotes zero or first-order reaction.

Table 2. Browning data¹ for nonhygroscopic whey ($a_w=0.44$) as a function of storage temperature

TEMP. (*C)	TIME (days)	Browning value (OD/g solid) X 10 ²	
		Group I	Group II
25	30	4.3	4.1
	60	6.1	6.3
	90	7.4	7.6
	120	9.6	9.8
	150	11.8	12.0
	180	12.7	12.5
	210	14.5	14.8
35	10	5.0	5.2
	20	7.9	7.9
	30	10.5	10.6
	40	13.7	13.8
	50	16.3	16.5
	60	20.2	20.1
	70	23.2	23.4
	95	27.7	27.8
45	2	5.2	5.2
	4	7.1	7.0
	7	22.4	22.4
	11	25.2	25.3
	18	31.7	31.7
	28	44.4	44.2
	35	50.9	50.7

¹Adopted from Labuza and Kamman (1983).

Integration of Eq. (2) yields:

$$C = C_0 + kt \quad (3a)$$

$$C = C_0 \exp(-kt) \quad (3b)$$

where C_0 is the initial browning index or thiamine concentration.

Table 3. Thiamin data¹ for an intermediate-moisture model system containing propylene glycol ($a_w = 0.75$ @ 20°C) as a function of storage temperature

TEMP. (°C)	TIME (days)	Thiamin concentration (µg/g solid)	
		Group I	Group II
25	31	61.6	61.1
	62	60.2	60.3
	91	56.7	53.9
	122	47.9	46.9
	152	48.1	47.1
	197	42.7	39.8
	257	32.2	34.4
35	31	50.5	48.9
	62	43.8	42.7
	91	39.2	38.7
	122	33.0	32.4
	152	24.1	23.5
45	31	31.1	32.9
	62	17.2	19.0
	91	7.0	7.1
55	3	55.5	56.2
	7.25	35.2	33.8
	11.1	24.7	25.3
	19	9.1	9.9

¹Adopted from Arabshahi and Lund (1985).

Substituting the Arrhenius model in Eq. (3) results:

$$C = C_0 + k_0 t \exp(-E_a/RT) \quad (4a)$$

$$C = C_0 \exp[-k_0 t \exp(-E_a/RT)] \quad (4b)$$

Three least squares methods were considered for deriving the Arrhenius model parameters. The following methods were utilized:

Method 1: Two-step Linear Least Squares

The most common method to estimate the Arrhenius parameters is the "classic" successive two-steps ordinary linear least squares fit. In this method the first regression of C vs. t , is done at each temperature, to estimate the rate constant k . The second step is to regress $\ln(k)$ vs. $1/T$ to obtain the estimates of $\ln(k_0)$ and E_a/R .

Method 2: Nonlinear Least Squares

The nonlinear regression performs a single regression on all of the data points ($i = 1, \dots, n$), to estimate E_a/R and $\ln(k_0)$ without calculating the rates at each temperature.

It was shown previously that most measured indexes of deterioration are log-normal distributed (Davies and Hudson 1981; Haralampu 1984; Nelson 1983). Hence, for the deterioration of a single reactant following a zero or a first-order model (Eq. 4), may be rewritten (Nelson 1983):

$$\ln(C) = \ln(C_0) + \ln\{1 + t \exp[\alpha - (E_a/R)(1/T - \beta)]\} \quad (5a)$$

$$\ln(C) = \ln(C_0) - t \exp[\delta - (E_a/R)(1/T - \beta)] \quad (5b)$$

where:

$$\alpha = \ln(k_0/C_0) - \beta (E_a/R)$$

$$\beta = [\sum(1/T) w_i] / (\sum w_i) \quad i = 1, \dots, n$$

and

$$\delta = \ln(k_0) - \beta (E_a/R)$$

For clarity of the presentation, the temperature subscript, i (i.e., $i = 1, \dots, m$; $m =$ number of temperatures tested) was omitted throughout the manuscript.

For unweighted regression $w_i = 1$ and for weighted nonlinear least squares (see method 3 below) w_i is the inverse of the variance estimated by Eq. (7) (Nelson 1983).

It is worth noting that for the unweighted least squares ($w_i = 1$) the origin of $1/T$ was moved to the unweighted mean, β . This was required since the parameters are highly colinear and are not easily regressed

directly (Haralampu *et al.* 1985; Nelson 1983). The latter transformation obviates in most cases the severe numerical difficulties in some nonlinear softwares.

Finally, to avoid bias in the determination, C_0 was derived as a parameter (Haralampu *et al.* 1985). The COMPLEX method (Saguy 1983) was used to derive C_0 , Ea/R and k_0 .

Method 3: Weighted Nonlinear Least Squares

Davies and Budget (1980) postulated that the errors in the index of deterioration originate from three sources. The variance of the errors can therefore be described as:

$$\text{Variance of } \log(C) = \sigma_0^2 + (C_0/C - 1) \sigma_1^2 + (C_0/C) \sigma_2^2 \quad (6)$$

where: σ_0 is the standard error that is proportional to the concentration (e.g., dilution error); σ_1 is the standard error proportional to the amount of deterioration (e.g., temperature variations); and σ_2 is the standard error which is proportional to the measurement method.

The overall error in the measurement of the index of deterioration has a log normal distribution (Davies and Hudson 1981) with a zero mean and variance of σ_t^2 .

Based on the above assumptions, Nelson (1983) developed the following relationship:

$$\sigma_t^2 = \ln[(1 + \frac{1}{2}\sqrt{(1 + 4\epsilon)}] \quad (7)$$

where: ϵ is the right-hand-side of Eq. (6).

A FORTRAN program which initially fit the data using unweighted least squares (Eq. 5), and then refits the model using weighted least squares where the appropriate weights are derived from eq. (7) was developed by Nelson (1983). This program was adopted for an IBM PC and utilized to carry out the calculations

As in the previous method, to avoid bias in the determination, C_0 was derived as a parameter.

It is worth noting that all the methods used for the nonlinear least squares (BMDPAR, Dixon 1983; Nelson 1983) are derivative free codes, thus the need for the parameter derivatives normally required was obviated. However, if these computer programs are not available, the appropriate parameters derivatives may be found in the literature (Arabshahi and Lund 1985).

Statistical Evaluation

Statistical software BMDP1R and BMDPAR (Dixon 1983) were used for the linear and the nonlinear least squares, respectively. The joint confidence region of the parameters (E_a/R and $\ln k_0$) was established following well documented methods (Draper and Smith 1981; Hunter 1981). The statistical tests may be performed on SAS (SAS, 1982).

RESULTS AND DISCUSSION

To evaluate the accuracy of the regression methods used in this study, two basic criteria were used, namely: the accuracy and precision of the parameters estimates, and the accuracy and precision of the quality losses expressed by their half-lives.

The Arrhenius parameters and the initial concentration derived using the three regression methods are summarized in Tables 4 and 5 for a zero and first-order kinetics, respectively. The results showed no substantial differences among the derived values of E_a and $\ln(k_0)$ when Methods 1 and 2 were applied. Nevertheless, the error mean squares (EMS) was significantly larger in method 1 for all the cases tested. The relatively high EMS values of method 1 is however not surprising, as the number of

Table 4. Effect of the regression method on the Arrhenius parameters derived for browning of nonhygroscopic whey

Regression method	a				b		
	df	E_a/R (K)	$\ln(k_0)$	C_0 ODX100/g	β X1000	EMS	
						Group I	Group II
Method 1	1	14,885	47.08	1.75	-	1.12	1.92
Method 2	19	15,244	48.39	1.79	3.249	1.19	1.19
Method 3	19	17,115	54.18	4.80	3.259	1.30	1.22

a - Degrees of freedom

b - Error mean squares

c - Calculated by applying the individual rates derived for each temperature

d - Calculated by applying the Arrhenius model to derive the appropriate rates

Table 5. Effect of the regression method on the Arrhenius parameters derived for thiamin retention in an intermediate-moisture model system containing propylene glycol

Regression method	a			Co µg/g	β X1000	b	
	df	Ea/R (K)	ln(ko)			EMS	
						Group I	Group II
Method 1	2	12,162	34.68	71.00	-	1.48	1.80
Method 2	16	13,141	37.67	68.01	3.249	1.15	1.16
Method 3	16	13,543	38.86	61.89	3.233	1.15	1.14

^a - Degrees of freedom

^b - Error mean squares

^c - Calculated by applying the individual rates derived for each temperature

^d - Calculated by applying the Arrhenius model to derive the appropriate rates

data points is quite limited for each temperature, thus any discrepancy from the theoretical regression model would have a vast impact on the EMS. The latter can be demonstrated in the case of the nonenzymatic browning tested. The individual EMS at 25, 35 and 45°C were 0.39, 0.78 and 8.86, respectively. Obviously, the extremely high EMS value corresponding to 45°C would have required testing for outliers, and discarding the data points that carry either experimental errors or others extraneous effects. The decision when to discard and omit data should follow proven statistical procedures (e.g., Arabshahi and Lund 1985; Draper and Smith 1981). Yet, in this particular case, to demonstrate the differences between the different regression methods, all the data was included.

The values of the Arrhenius parameters derived for group I and II were very close, for all the methods tested. This verification indicated that the values derived were representing the actual reaction kinetics, and therefore may be used for prediction.

When method 3 was applied the values derived for the initial concentration was completely different from those obtained with Methods 1 and 2. Also, the derived value was in disagreement with the experimental values reported (Arabshahi and Lund 1985; Labuza and Kamman 1983). Yet, the appropriate EMS values for method 3 were very close to those derived by method 2 (Tables 4 and 5), hence a rigorous analysis was required to justify a clear choice between these two methods.

As method 3 is much more complicated than method 2 for computation, its application should be further weighed by the distribution of the residuals. If method 2 yields a randomly unskewed distribution of the residuals about zero and no pattern may be observed, this indicates that method 2 is appropriate and that method 3 may not be needed. When this approach was implemented for both zero and first-order kinetics analyzed, the distribution of the residuals (Fig. 1 and 2) fulfilled all the aforementioned requirements. Although one data point in Fig. 1 was far from the expected mean of the error (i.e., zero), this data was not discarded and justified by the explanation given above.

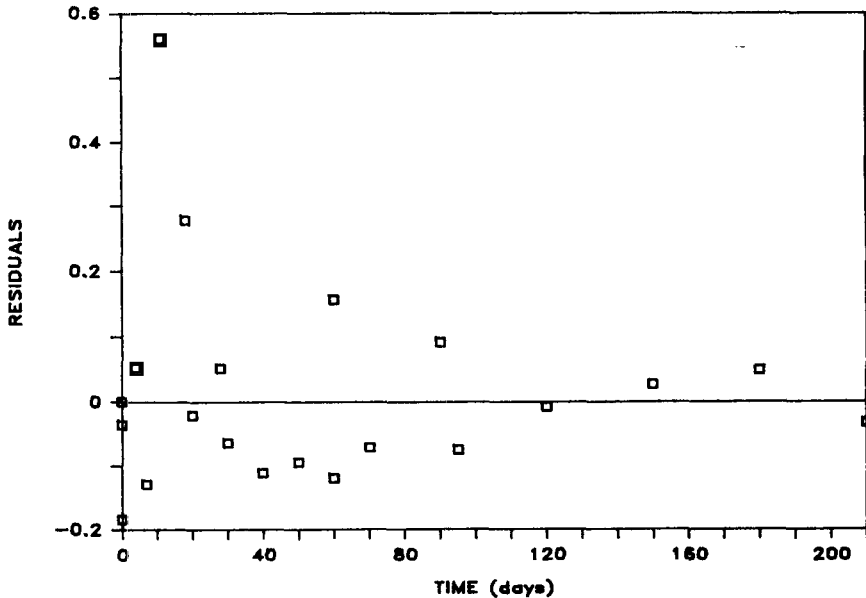


FIG. 1. PLOT OF THE RESIDUALS OF NONENZYMATIC BROWNING DERIVED FROM UTILIZING NONLINEAR LEAST SQUARES REGRESSION (METHOD 2)

Similar normal distribution of the residuals was reported for other cases (Haralampu et al. 1985). Therefore, it was concluded that weighted regression (although has its own merits; e.g., Arabshahi and Lund 1985), may be avoided due to the fact that the logarithmic transformation incorporated in method 2 obviates the need for further variance stabilization. The latter effect of the logarithmic transformation was discussed in detail elsewhere (Haralampu et al. 1985).

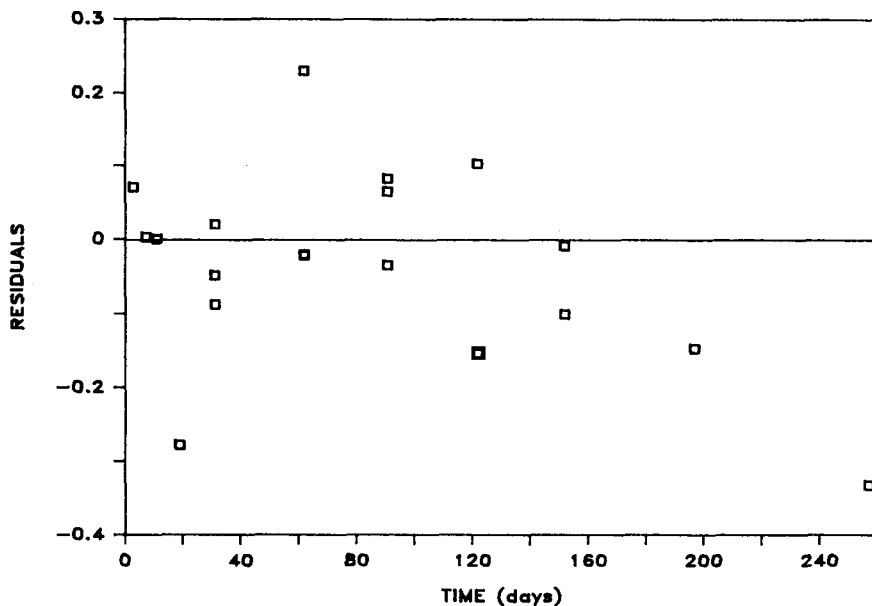


FIG. 2. PLOT OF THE RESIDUALS OF THIAMIN RETENTION DATA DERIVED FROM UTILIZING NONLINEAR LEAST SQUARES REGRESSION (METHOD 2)

It is worth noting that method 3 yielded completely different values, not only for the energy of activation and the pre-exponential factor, but also for the initial concentration. Also, the values of the latter were substantially different from the reported experimental data (Arabshahi and Lund 1985; Labuza and Kamman 1983). Hence, it was concluded that method 3 should be used only for those cases where the plot of the residuals shows some nonnormal distribution and/or skewness. No further analyses were carried out for method 3.

In this work, C_0 was considered to be a parameter that was estimated by the nonlinear regression methods. This approach was found to be more accurate than defining the initial concentration as 100% (Davies and Hudson 1981; Nelson 1983). Also, by adopting this approach, actual concentration data was used rather than the retention (or percent). The latter avoids the uncertainty introduced by dividing all concentration values by the initial concentration. The uncertainty associated with the initial concentration is at least the same order of magnitude as the uncertainty in any other concentration (Arabshahi and Lund 1985).

The Arrhenius parameters estimates should be judged on the size of the joint confidence region at 90% (i.e., $0.95^2 = \sim 90\%$). The latter is the

ellipsoid in which the true parameters probably exist together at a specified confidence level. The extremes of the 90% confidence ellipsoid region are not corresponding to the ends of the 95% confidence intervals (derived from a t-test) for the individual parameters. Since E_a and $\ln(k_0)$ are so highly correlated, the ellipsoid is by far more accurate representation of the confidence region (Draper and Smith 1981; Hunter 1981). The region is constructed by considering both the variance and covariance of the parameters estimates, and by assuming that the estimates are from a bivariate normal distribution. Figures 3 and 4 depict the joint confidence region for the parameter estimates derived from method 1.

It is important to emphasize that the joint confidence region should be used rather than the individual confidence interval due to the high correlation observed between E_a/R and $\ln(k_0)$.

The confidence contours for the nonlinear regression (method 2) would create some sort of a deformed ellipsoid. However, the complexity of the computation hampers its application as a routine statistical test. Furthermore, based on our knowledge, only one statistical package (i.e., TROLL; Haralampu *et al.* 1985) provides this test as a standard routine.

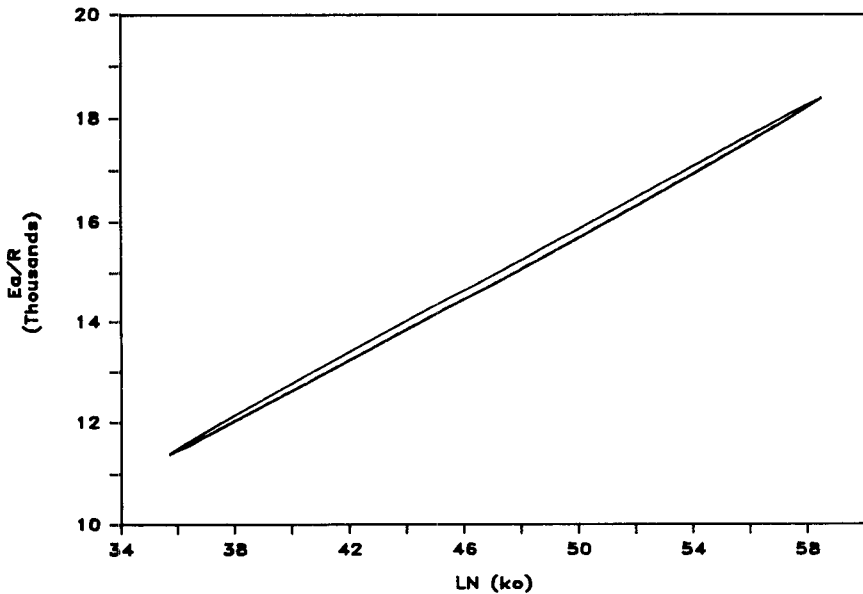


FIG. 3. JOINT CONFIDENCE REGION (90%) FOR E_a AND k_0 DERIVED BY TWO-STEPS LINEAR LEAST SQUARES (METHOD 1), FOR NONENZYMATIC BROWNING

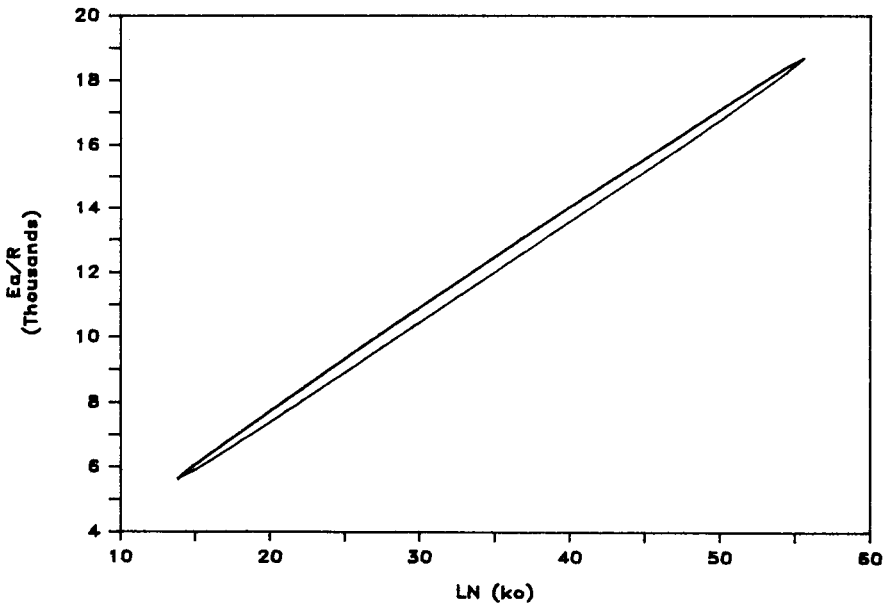


FIG. 4. JOINT CONFIDENCE REGION (90%) FOR E_a AND k_o DERIVED BY TWO-STEPS LINEAR LEAST SQUARES (METHOD 1), FOR THIAMIN RETENTION

Yet, for this case, the appropriate extreme points on the confidence region were derived by a FORTRAN program which was written following the technique recommended by Draper and Smith (1981). The confidence contour, S , was approximated as follows:

$$S = SS[Co, \ln(k_o), Ea/R] [1 + n F(p, n - p, 1 - q)/(n - p)] \quad (8)$$

and

$$SS[Co, \ln(k_o), Ea/R] = \sum [\ln(C_i) - f_i]^2 \quad i = 1, \dots, n \quad (9)$$

where:

f is the fitted nonlinear model defined in Eq. (5);

$SS[Co, \ln(k_o), Ea/R]$ is the nonlinear least squares estimate of the fitted model;

n is the number of data points;

p is the number of parameters derived from the nonlinear least squares (i.e., $p = 3$);

100(1 - q)% is the confidence contour (i.e., $q = 0.1$); and

F is the F-statistics from the F-distribution.

The extreme values of E_a/R and $\ln(k_0)$ were derived using the COMPLEX method (i.e., nonlinear optimization; Saguy 1983). The appropriate values derived are summarized in Table 6. For most practical purposes the confidence region may be evaluated by linearization of the model. The latter is a standard option of most statistical software (Dixon 1983; SAS 1982).

The accuracy of a rate constant for the prediction was estimated by first locating the extremes associated with the boundary of the confidence ellipsoid (Fig. 3 and 4) for E_a and $\ln(k_0)$. In method 2 the appropriate values were derived by the procedure outlined previously. The extreme values (denoted as low and high), and the average of E_a and $\ln(k_0)$ as derived from the regression procedure (denoted mid.) were used to calculate the appropriate half-life and the rate constant. These values are summarized in Table 6. For a first-order reaction, the half-life time is independent of the concentration (i.e., $t_{1/2} = \ln(2)/k$). In the case of a zero-order reaction, the half-life time was defined as the time required to reach an optical density of 0.2/g solids. This definition is obviously arbitrarily, and should be redefined for each case and system studied. Nevertheless, for comparison purposes, this value was quite appropriate.

Method 1 gave a much larger confidence region for E_a/R and k_0 . This large region resulted in a very wide span in the calculated values of E_a/R and k . Method 2 resulted in a much smaller confidence region and a better estimation of the half-life and the rate constant. The comparison also indicated that the traditional method for deriving the Arrhenius parameters agreed only partially with the values derived from method 2. Also, the half-life and k values were quite similar only for 35°C (i.e., the mid of the temperature range studied). This discrepancy not only projects the need for special attention when kinetics data is compared but also depicts the confidence of the determination. Hence, it may be difficult to connect energy of activation and entropy or any other thermodynamic quantities.

The confidence region of method 2 is much narrower when compared to the one derived from method 1. Yet, even in this improved case, prediction at temperature far from the average range used for deriving the kinetic model requires special caution. Since small errors in conducting the tests may be magnified if extrapolation is utilized. Hence, in this case, precaution should be reemphasized.

It is worth noting that method 2 is highly sensitive to the computation method. As the derivation of the parameters is based on nonlinear least squares, the procedures applied in the minimization of the sum of squares of the residuals, are very sensitive to the initial guess of the parameters and the criteria used for convergence. It is therefore strongly recommended that the computation should start at different initial

Table 6. Effect of the regression method on the half-life time and reaction rate constant for different reactions and temperatures (units of the zero and first-order rate constants are given in the text).

	k ₀	E _a /R	Half-life (days)			Reaction rate constant		
			25 C	35 C	45 C	25 C	35 C	45 C
Zero-order reaction								
Method 1								
Low	35.70	11384	223.7	64.7	20.2	0.082	0.282	0.902
Mid.	47.09	14888	322.4	63.7	13.9	0.057	0.287	1.311
High	58.46	18387	464.9	62.7	9.6	0.039	0.291	1.902
Method 2								
Low	45.97	14509	275.9	56.8	12.9	0.066	0.321	1.411
Mid.	48.39	15244	289.0	54.9	11.6	0.063	0.332	1.573
High	50.79	15969	298.6	52.4	10.3	0.061	0.347	1.774
First-order reaction								
Method 1								
Low	13.79	5637	117.2	63.4	35.7	0.006	0.011	0.019
Mid.	34.68	12162	318.2	84.6	24.4	0.002	0.008	0.028
High	55.59	18688	862.2	112.5	16.7	0.001	0.006	0.041
Method 2								
Low	34.95	12255	332.8	87.6	25.1	0.002	0.008	0.028
Mid.	37.67	13141	428.7	102.4	26.8	0.002	0.007	0.026
High	40.39	14032	561.6	121.7	29.1	0.001	0.006	0.024

guesses before any conclusion on the derived value is to be made. Also, the high correlation between the Arrhenius parameters (e.g., Fig. 3 and 4), may indicate the need for reparameterization. The latter may project the inadequacy of the Arrhenius model. Nevertheless, until a better model which is backed by kinetic theory is established, applying empirical models is not recommended.

In conclusion, the traditional analysis (method 1) gave the least accurate estimates for the Arrhenius parameters. This inaccuracy is due probably to the need to estimate many intermediate values and by not considering the data as a whole set. Also, method 1 estimates unnecessary parameters and carry out regressions on regression parameters. Method 2 (i.e., nonlinear least squares) proved to be superior, as it gave unbiased and precise estimation of the parameters. It is undoubtedly the method of choice, and should be applied in kinetic studies. Yet, even this method has limitations mainly due to the computation complexity. Method 3 was much more difficult to apply and the values derived were different from those of methods 1 and 2, and thus should be used only for cases which do not fulfill the assumption of normality.

ACKNOWLEDGMENT

We wish to thank Dr. Peter R. Nelson, Searle, Research and Development for the FORTRAN program of weighted nonlinear least squares. Also, we would like to thank Mr. Steve Fahrenholtz, The Pillsbury Company for the useful statistical discussions.

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