Estimating the Parameters of the Arrhenius Equation

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Abstract—Estimation of the parameters of the Arrhenius equation often leads to multicollinearity, or, in other words, a degenerate set of equations in the least-squares procedure. This circumstance makes it difficult to estimate the unknown parameters. Simple expedients for model modification are suggested that reduce multicollinearity, thus allowing the parameters to be determined. Simulated and real examples are considered.

The same physical law can be represented in different ways. It is assumed that the kind of model and the degree of detailing for each particular process are chosen by the researcher. At the same time, in processing experimental data to obtain a quantitative estimate, the mathematical representation is also significant. Obviously, the way the equation is written cannot modify the law, but it can strongly influence the estimation of the model parameters. Here, we consider this methodological issue for the Arrhenius equation

$$k = k_0 \exp\left(-\frac{E}{RT}\right), \tag{1}$$

which is widely used in chemical kinetics to describe the dependence of the reaction rate constant k on temperature T. This equation contains one constant (the universal gas constant R) and two unknown parameters, namely, a preexponential factor k_0 and an activation energy E, which are to be derived from experimental data, for example, by the least-squares method. This is the so-called inverse problem of chemical kinetics.

It is well known that the Arrhenius equation in the form of Eq. (1) often leads to strongly correlated estimates of k_0 and E. The probability ellipse of these estimates is very strongly elongated: the ratio of its principal axes is of the order of 10^{20}. Therefore, the surface of the objective function (sum of squares) is degenerate, making the inverse problem difficult to solve. The minimum point is indeterminate, and it is impossible to estimate the parameters. In the general case, the degree of this degeneracy, which is called multicollinearity [1], can be characterized by the spread

$$N(\mathbf{A}) = \log\lambda_{\max} - \log\lambda_{\min},$$

where $\mathbf{A}$ is the matrix of the second derivatives of the objective function with respect to the parameters and $\lambda_{\max}$ and $\lambda_{\min}$ are the maximum and minimum eigenvalues of this matrix. The larger $N(\mathbf{A})$, the worse conditioned the matrix $\mathbf{A}$ and the more difficult it is to invert.

The problem of multicollinearity can be viewed from different standpoints. In linear modeling, it shows itself as a very large number of unknown parameters [2]. Therefore, we will use methods reducing the dimensionality of the problem, specifically, principal component regression and projection on latent structures. In nonlinear regression analysis, one usually has insufficient experimental data rather than excess parameters [3]. As regards the Arrhenius equation, this insufficiency arises from the narrow range of measured temperatures: in solid-phase kinetic measurements, this range is generally 300–500 K. In terms of reciprocal temperature, this range is as narrow as 0.0013. Obviously, this value depends on the temperature unit chosen, the way Eq. (1) is written, and other circumstances. We will focus on these circumstances, suggesting special methods for solving the problem of multicollinearity in nonlinear regression.

The problem of multicollinearity has a computational aspect associated with the precision of number representation in the computer. A number is represented as a sequence of zeros and unities (bits) in a computer word. Although this word can be rather long, its length may nevertheless be insufficient and some significant digits may be lost in the course of calculations. This is the case when a very small number is added to a very large number, as in the following example: $10^{+20} + 10^{-20} + \ldots + 10^{-20} = 10^{+20}$. This very situation takes place when a matrix with a large spread of eigenvalues is inverted. There are special expedients to modify the original problem so that the spread $N(\mathbf{A})$ is substantially reduced. They do not alter the essence of the problem to be solved, but they allow the problem to be reformulated so as to facilitate computer calculations.

Let us return to the Arrhenius equation. The simplest model temperature dependence of the rate constant is plotted in Fig. 1. With Eq. (1), the inverse kinetic problem is very stiff: the spread of eigenvalues is as wide as
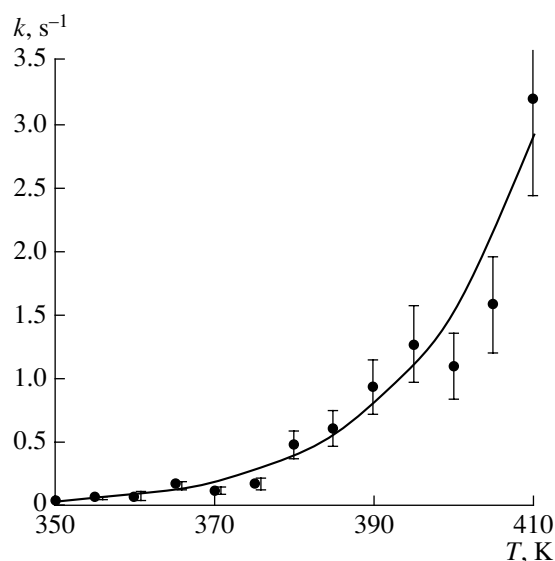
Fig. 1. Simulated example of the temperature dependence of the rate constant.

Fig. 2. Elongation at break for aged rubber and fitting curves at (*1*) 110, (*2*) 125, and (*3*) 140°C.

19 decimal orders of magnitude. Changing to the conventional coordinates ($\ln k$, $1/T$) diminishes the spread of eigenvalues to nine orders of magnitude. Note that this change means a $k_0 \longrightarrow q = \ln k_0$ change of variables and reduces model (1) to $k = \exp(q - E/RT)$. The purpose of this transformation is very clear: while the initial parameter is as large as $k_0 = 2.80 \times 10^{11}$, the new parameter is $q = 26.36$. However, the second parameter, E, is still much different from the first. This situation can be remedied by scaling the temperature: $T \longrightarrow X = E_0/RT$. The scaling factor is taken to be $E_0 = 6.13 \times 10^4$, so that the variation of the new predictor X is unity. The Arrhenius model will then take the form $k = \exp(q - bX)$, where the new parameter b is related to the original parameter E by the formula $b = E/E_0 = 1.41$. The spread of eigenvalues with this model is five orders of magnitude. Although it can be regarded as very good, it can be further decreased. To do this, we will apply the predictor centering $X \longrightarrow X' = X - X_0$, setting $X_0 = 19.62$, so that the mean value of the new parameter X' is zero. After that, the Arrhenius model appears as

$$k = \exp(a - bX'), \qquad (2)$$

where the new parameter a is related to the initial parameters k_0 and E by the formula $a = q - bX_0 = \ln(k_0) - (E/E_0)X_0 = -1.00$. With this model, the spread of eigenvalues is equal to unity, the minimum possible value. The inverse transformations appear as $k_0 = \exp(a + bX_0)$ and $E = bE_0$. A similar expedient was used by Chen [4].

This example demonstrates that, using simple transformations, one can bring the original, "physical" model (1) to a new mathematical form (Eq. (2)),
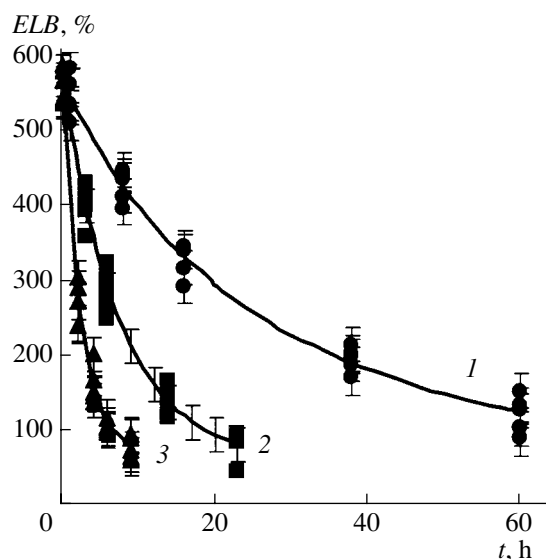
thereby circumventing all of the difficulties arising from multicollinearity. It is important that the transformation of the initial data and model in no way affects the estimation accuracy. The standard deviations for the estimates of a and b in model (2) are 0.070 (7%) and 0.072 (5%), respectively, the correlation coefficient being 0.005. Converting these deviations into the standard deviation for the initial parameter k_0 gives a value of 3.95×10^{11}, which is 141% of the initial value 2.80×10^{11}. The same standard deviation is obtained by direct calculations using model (1).

Now consider processing of real data for accelerated thermal aging of tire rubber [5]. Figure 2 shows how elongation at break (*ELB*) varies with time at three temperatures. The *ELB* curves are described by the model

$$ELB = c_0 + c_1 e^{-k_1 t} + c_2 e^{-k_2 t},$$

where t is time and the constants k_1 and k_2 depend on temperature in the Arrhenius way. Here, solving the inverse problem implies determining seven unknowns, namely, three shape parameters and four Arrhenius parameters. With Eq. (1), the problem will be multicollinear, with a spread of $N(\mathbf{A}) = 27$, and it will be impossible to estimate the parameters. Note that passing to the conventional coordinates ($\ln k$, $1/T$) is impossible here. With Eq. (2), the spread is much smaller, $N(\mathbf{A}) = 9$, and all of the estimates can be found.

The same approach can be taken in modeling nonisothermal processes. For example, the following model is used to determine the oxidation onset temper-
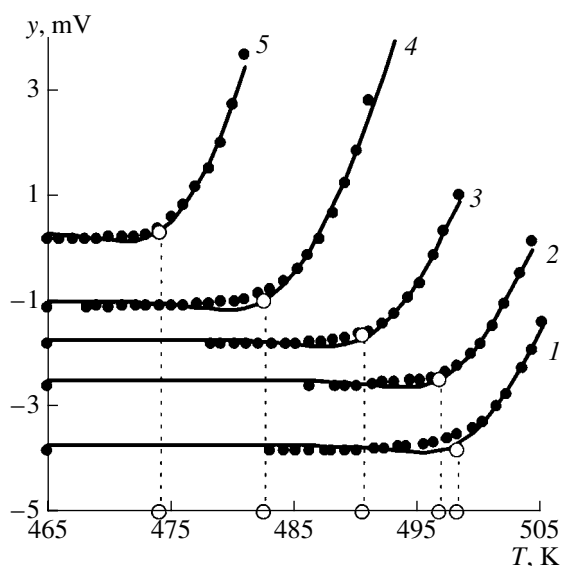
Fig. 3. DSC data for polypropylene and regression curves corresponding to heating rates (v) of (1) 20, (2) 15, (3) 10, (4) 5, and (5) 2 K/min.

Fig. 4. (1) Logarithm of the rate constant and (2) effective activation energy for low-temperature methyl methacrylate polymerization as a function of reciprocal temperature $1/T$ [6].

ature (OOT) from differential scanning calorimetry (DSC) data [3]:

$$y = f_v + \begin{cases} 0, & T < T_v \\ mc\exp\left(-\dfrac{E}{RT}\right), & T > T_v, \end{cases}$$

$$\text{where } \begin{cases} \dfrac{dc}{dT} = \dfrac{k_0}{v}\exp\left(-\dfrac{E}{RT}\right) \\ c(T_v) = 0. \end{cases} \quad (3)$$

Here, y is the observed DSC signal. This model includes three independent variables. They are heating rate v, sample weight m, and temperature T. Furthermore, it includes four unknown parameters: preexponential factor k, activation energy E, OOT value T_v, and baseline parameter f_v. The last two parameters depend on the heating rate v.

Figure 3 presents DSC data for polypropylene heated at different rates, including OOT points for each v. If these data are described in terms of Eq. (3), it is impossible to estimate the unknown parameters because the spread of eigenvalues is very large: $N(\mathbf{A}) > 30$. The transformation $k_0 \longrightarrow q = \ln(k_0)$ reduces the spread to 11; subsequent scaling further reduces the spread to 8; and, finally, centering results in a spread of 4.

Deviations from the Arrhenius law are observed in some cases. From the theoretical standpoint, they are due to the fact that Eq. (1) neglects the temperature dependence of the preexponential factor k_0. However, this dependence must take place, as is made clear by
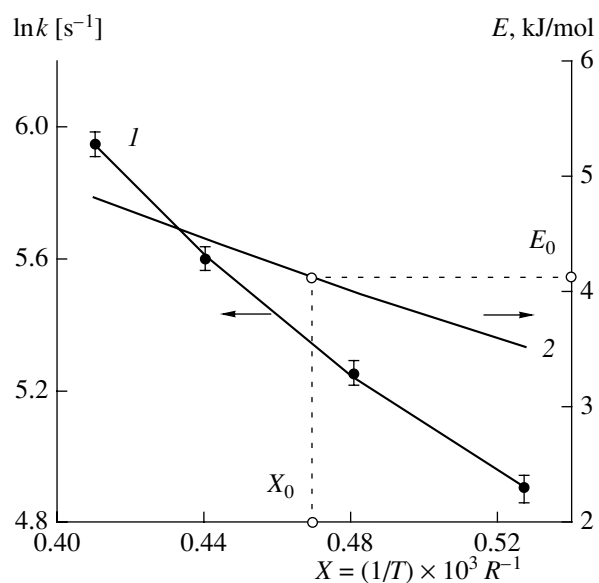
taking into account the partition functions for the activated complex and the initial reactants. Moreover, it is likely that the activation energy E will also depend on temperature. By way of example, we present the temperature dependence of the rate constant for low-temperature methyl methacrylate polymerization (Fig. 4) [6]. This dependence is not linear: the slope of the curve increases with increasing temperature; that is, the activation energy grows with increasing temperature. To take into account this circumstance, it is necessary to modify the Arrhenius equation by introducing an $E(T)$ function. Using the above expedients, we can write the equation for $k(T)$ as

$$\ln k = a - EX', \quad E = b + c\ln(1 + X'), \quad (4)$$

where $X' = X/X_0 - 1$ and $X = 10^3/RT$. Again, X_0 is set so that the mean value of the predictor X' is zero. The model formulated as Eq. (4) is characterized by an eigenvalue spread as small as $N(\mathbf{A}) = 4$, and all of its parameters—a, b, and c—are easy to estimate. Figure 4 plots $\ln k$ (left axis of ordinates) and E (right axis of ordinates) as functions of X. Here, E_0 is the activation energy determined using the "classical" Arrhenius equation (1). Note that it is equal to the E value at the middle point of the X axis; that is, $E(X_0) \approx E_0$.

Modeling using the Arrhenius equation suffers from multicollinearity or degeneracy. As a consequence, it is impossible to estimate the parameters of the model. There are three basic sources of multicollinearity: the representation of the model, the accuracy of calculations, and the quality of experimental data. The expedients suggested here for model and data modification

allow the degeneracy to be markedly reduced and the parameters to be estimated. The calculations were carried out using the Fitter system [7]. All necessary data and computational details can be found in [8].

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