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Review

Multiplicative algorithm for discriminating between Arrhenius and non-Arrhenius behaviour

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ABSTRACT

The Arrhenius equation $k_A = Ae^{-E/Rt}$ has found numerous applications throughout chemical kinetics for diverse rate processes. This equation involves the assumption that the pre-exponential factor, *A*, does not vary with temperature. For simple reactions, deviations from this equation are usually quite small, and in only a few instances are they at all readily detectable. However kinetic measurements over wide ranges of temperature show up the inadequacy of the Arrhenius expression (Smith, 2008 [1]). The temperature dependence of the linear parameter is widely used as an alternative model. Consequently, a correct selection of the model and a correct estimation of the parameters are crucial tasks.

The focus of this paper is the construction of a new procedure based on the multiplicative algorithm in order to determining optimal experimental conditions for discriminating between two rival models. Even for moderate examples the calculation of *T*-optimal designs is not straightforward. There are no known specific iterative numerical techniques for constructing *T*-optimum designs; there is just the classical adaptation of the Wynn–Fedorov scheme (Atkinson and Fedorov, 1975 ; Fedorov and Hackl, 1997), which is far from being satisfactory to solve these computational problems.

The results are illustrated by numerical examples for different deviations of the Arrhenius equation. On the other hand we demonstrate in several examples that the new algorithm is more efficient than those existing in the literature.

Contents

1. Introduction

The Arrhenius equation was initially developed in 1884 by Svante August Arrhenius through his studies of dissociation of electrolytes. Currently it is widely accepted to describe the influence of temperature on the rates of chemical and biological processes such as abstraction reaction, bimolecular reactions in gaseous hydrocarbon chemistry, solid–solid reactions, crystallizations, desorption gases adsorbed on solid surface and sintering, and metabolism, growth, development and fitness, respectively. This model expresses the rate of a process *k* in terms of temperature *t*,

$$E(k_A) = Ae^{-B/t},\ \text{var}\,(k_A) = \sigma^2, t \in \mathcal{T} = [T_1, T_2], T_1 \geq 0. \quad (1)$$

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The parameter A is known as the Arrhenius A-factor or frequency factor and B expresses the activation temperature through the relationship, $B = \mathfrak{E}/R$, $\mathfrak{E}$, being the difference of energy between the activated and the inert states and R being the gas constant. When this is so, the theory of absolute reaction rates can be used to evaluate the entropy and the enthalpy of activation for the process. The Arrhenius equation thus predicts a linear relationship between $\ln(k_A)$ and t^{-1}. The observation errors are assumed to be independent and have mean zero and constant variance.

For the analysis of more precise rate-temperature data, particularly in studies covering a wide temperature range, it is evident that the Arrhenius equation fails to express fully the temperature dependence of reaction velocity (see for example [1,4]). In biological processes, a critical assumption of the Arrhenius model is that the probability that the rate-limiting enzyme is in this active conformation is 100% and that this does not vary within the physiological temperature range [5,6]. If the probability that the rate-limiting reaction is in active form declines at high or low temperatures within the physiological temperature range, then this will make the relationship between $\ln(k_A)$ and t^{-1} concave rather than linear.

The Arrhenius equation assumes that the pre-exponential factor A is temperature independent, but for some kinetic systems it has been observed that the enthalpy, or heat content change of the activation process, is temperature dependent. Quite substantial errors can be introduced if a linear Arrhenius extrapolation of low and high temperature date is made. The simplest way to express this dependence is as a power series in t [7,8]. They proposed that the pre-exponential factor is connected with the temperature through the following relationship $A = A_0 t^m$,

$$E(k_{MA}) = A_0 \cdot t^m e^{-B/t},\ \text{var}\,(k_{MA}) = \sigma^2, \tag{2}$$

where A_0 is a constant and values of m ranging from -2 to 5. The original Arrhenius expression above corresponds to $m = 0$. Thus m is equal either to 1 in the case of the thermal decomposition of a single solid reactive or to 1/2 for reactions between a gas and the surface of a solid. Segal [9], Varghegyi [10] and Dollimore [11] have considered other positive values for this exponent. On the other hand, values of m from 0 to 2.5 have been proposed for the case of reactions of desorption of gases from surface of solids. Moreover, values of m from $-3/2$ to 0 have been proposed for shrinkage processes depending on the sintering mechanism (see [12]). In that work the importance of the dependence of the pre-exponential factor on the temperature is shown. They proved that the error introduced by omitting the dependence of A on t is considerably larger than the error due to the Arrhenius integral approach used for carrying out the kinetic analysis of data.

Estimation issues for these models have been extensively discussed in the literature in recent years (see [13,3] among others). However, the design problem for discrimination between models has had much less attention and has been developed for simple models only.

The aim of this paper is to obtain an efficient algorithm in order to determining optimal experimental conditions for discriminating between the competing models. Atkinson and Fedorov [2,14] introduced the so called T-optimality criterion which has an interesting statistical interpretation as the power of a test for the fit of a second model when the other is considered as the true model. Usually there is no closed form for the T-optimum design and it must be constructed through an iterative procedure. In this work, we study a new algorithm to determining T-optimal designs based on the approach of the multiplicative algorithm proposed by Torsney and Martín-Martín [15]. This algorithm will be used to provide researchers optimum designs to discriminate between the Arrhenius equation and non-Arrhenius behaviors. These designs have not been computed, while D-optimal designs to perform the best estimation of the parameters following D- and C-optimality criteria can be founded in Dette and Sperlich [16] and Rodríguez-Díaz and Santos-Martín [17].

1.1. Optimum design background for non-linear models

Consider the general non-linear regression model

$$y = k(t;\theta) + \varepsilon, \quad t \in \mathcal{T},$$

where the random variables ε are independent and normally distributed with zero mean and constant variance σ^2 and θ is the unknown parameter vector.

Suppose an experiment is to be designed subject to the constraint that the design variable, t, be in a compact set of a Euclidian space, $\mathcal{T}$, called design space. Let Ξ be the set of probability distributions on the Borel sets of $\mathcal{T}$, then any $\xi \in \Xi$ satisfying

$$\int_{\mathcal{T}} \xi(dt) = 1, \quad \xi(t_i) \geq 0, \quad t \in \mathcal{T},$$

is called a design measure, or an approximate design. Kiefer [18] pioneered this approach, and its many advantages are well documented in design monographs, e.g. [19].

For convenience, the design will be described using a two row matrix with the different support points displayed in the first row, of $t_1, \ldots, t_N$, and their corresponding proportion of observations, $\xi(t_i) = p_i$, in the second,

$$\xi = \begin{Bmatrix} t_1 & t_2 & \ldots & t_N \\ p_1 & p_2 & \ldots & p_N \end{Bmatrix},$$

being $p_1, \ldots, p_N$ non-negative real numbers which sum up to one.

The paper is organized as follows. In Section 2, the main concepts on discrimination between two-rival models are presented. The new approach based on multiplicative algorithms to discriminate between two rival models is provided in Section 3. The aim of Section 4 is to solve the problem of discriminating between both Arrhenius model and the modified-Arrhenius model. Also a robustness study is presented in this section. Conclusions and some final remarks are stated in the last section.

2. Design of experiments to discriminate between two-rival models

The formulation of an adequate model is a crucial step in successfully answering a query about the behavior of an experimental system. The experimenter is frequently faced with the situations that existing data, experimental or theoretical, satisfy two or more mathematical models. Before proceeding to further investigations (for example, the precise estimation of several parameters) it is necessary to set up an experiment that would permit discrimination between the models. The design of a suitable experiment consist in finding those points at which the resulting observations are far from being invariant with respect to a change from one mathematical model to another. The experiment that best discriminates between the models, the optimal discriminatory experiment, is not generally known. In fact, the only way to determine this would be to perform all possible experiments, something we obviously want to avoid. This leads to the question of how to select an appropriate sampling strategy. The most popular design criterion for model discrimination is T-optimality which was proposed by Atkinson and Fedorov [2].

The main goal of this work is to provide an efficient numerical method to construct a good design to discriminate between models, in particular, the T-optimum design to discriminate between Arrhenius equation and modified-Arrhenius model is obtained. It will be used to say whether it is adequate to apply the simpler Arrhenius model or not.

In the following, consider a basic scheme when two models are of interest. This corresponds to the situation in which y_{il} are given by

$$y_{il} = k(t_i,\theta) + \varepsilon_{il} \quad (i = 1\ \ldots, N; l = 1, \ldots, r_i)$$