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Estimating thermal degradation kinetics parameters from the endpoints of non-isothermal heat processes or storage

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ABSTRACT

Where specimen retrieval for chemical analysis is not an option, as during a UHT process, or impeded by logistic considerations as in storage studies, a thermal degradation reaction's kinetic parameters can be estimated from the nutrient's or other compound's final concentrations after three or more known but different non-isothermal temperature histories. Provided the reaction follows fixed yet unknown order kinetics and its rate constant's temperature dependence follows a two-parameter algebraic model, the kinetic parameter estimation can be done by solving three simultaneous equations, themselves being the numerical solutions of three corresponding differential rate equations. In computer simulations of heat sterilization processes and storage under oscillating temperatures that include small experimental scatter, the reaction's kinetic order, its rate at a reference temperature, and the rate's temperature dependence were estimated from the final concentrations and correctly predicted dynamic degradation curves not used in their determination. The method's predictive ability was also tested with published experimental isothermal degradation data on ascorbic acid, patulin, sulforaphane, and thiamine, where the final concentrations at temperatures not used in the parameters determination were estimated from three endpoints. The described method only works where the above mentioned conditions are fully satisfied. Where applicable, it eliminates the need to experimentally determine sets of complete isothermal degradation curves, which might be impractical or too costly.

1. Introduction

Many chemical degradation reactions in foods, notably vitamin loss during thermal processing or long storage, probably follow fixed order kinetics. The same can be said about certain other biochemical reactions and biological processes, if the medium does not undergo substantial chemical and/or physical changes as well.

A degradation reaction's kinetic order is defined by the power, n, in the isothermal degradation rate equation:

$$\frac{dC(t)}{dt} = -k(T)C(t)^n \tag{1}$$

where $C(t)$ is the momentary concentration of the degrading compound at time t, and $k(T)$ a temperature-dependent rate constant specific to the particular medium and its conditions, such as the pH or water activity.

In what follows the discussion will focus on ideal or close to ideal scenarios where heat and mass transfer considerations can be ignored, i.e., where the measured $T(t)$ and $C(t)$ can be assumed uniform throughout the analyzed sample. In principle at least, once the reaction's kinetic order and $k(T)$ have been determined, one can predict or estimate the concentration profile in a body when the temperature is a function of both time and location, as in the contents of a food can or pouch undergoing a heat treatment, but this will not concern us here.

For isothermal conditions, where $k(T)$ = constant, Eq. 1 can be integrated to yield the familiar decay functions (e.g., van Boekel, 2008, 2009):

For zero order kinetics ($n = 0$):

$$C(t) = C_0 - k(T)t. \tag{2}$$

For first order kinetics ($n = 1$):

$$C(t) = C_0 \operatorname{Exp}\left[-k(T)t\right]. \tag{3}$$

For nth order kinetics ($n \neq 1$):

$$C(t) = \left(C_0{}^{(1-n)} + k(T)(n-1)t\right)^{1/(1-n)} \tag{4}$$

where C_0 is the initial concentration, $C(0)$.

Notice that Eq. 2 is a special case of Eq. 4, but it will be treated separately following the traditional classification. Also note that

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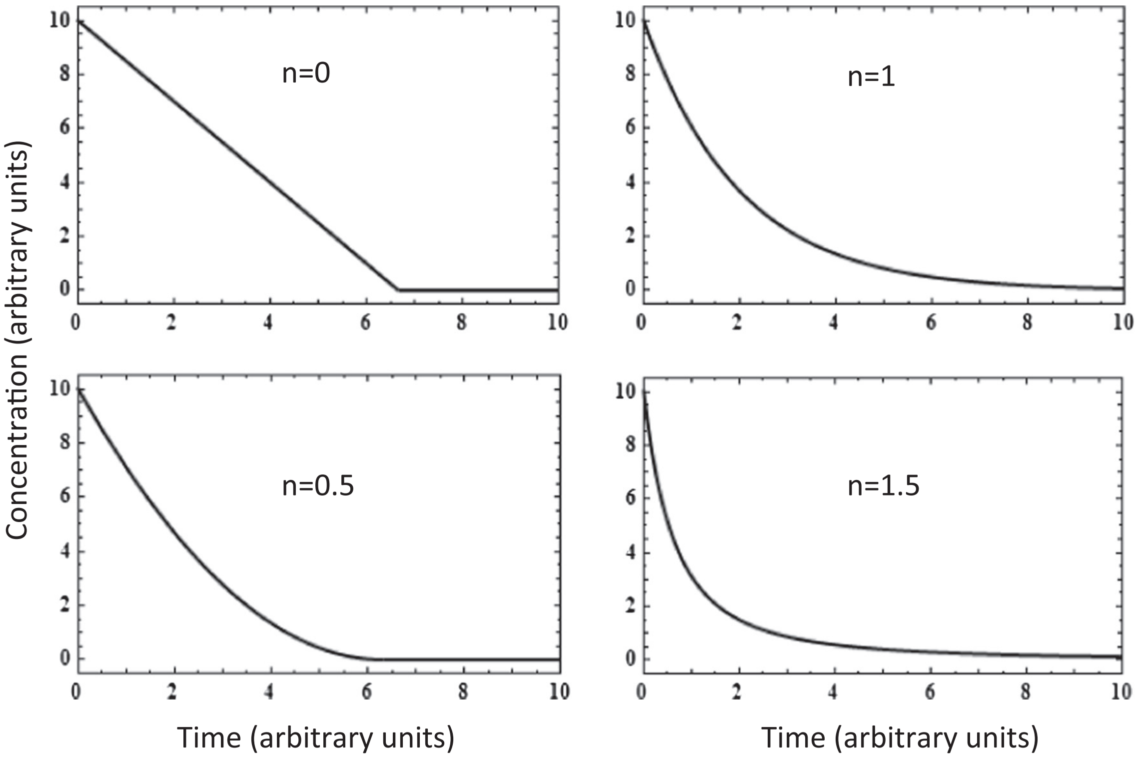

Fig. 1. Simulated concentration vs. time curves in isothermal degradation reactions following different kinetic orders produced with Eq. 5 as a model. Notice that where $n = 0$ or $0 < n < 1$, negative or complex values are avoided by assigning a zero value to the concentration.

Eq. 1 implies that for $t > C_0 / k(T)$ the concentration becomes negative, which is obviously physically impossible. Therefore, $C(t)$ at this range will be assigned a zero value as demonstrated in Fig. 1. A less familiar troublesome situation can theoretically arise with the use of Eq. 4 where $0 < n < 1$. This model implies that at and beyond time $t = (C_0 / k(T))^{1 - n}$, $C(t)$ becomes a complex number, which again has no physical meaning in our context. In this case too $C(t)$ is assigned zero value (or the real part of the last point where the imaginary part is still zero) — see Fig. 1.

Combining these considerations in a single expression yields the general model for any kinetic order ($n \geq 0$):

$$\begin{aligned} C(t) = {} & \mathrm{If}\left[n = 0, \mathrm{If}\left[C_0 - k(T)t > 0, C_0 - k(T)t, 0\right], \mathrm{If}\left[n = 1, C_0\,\mathrm{Exp}\left[-k(T)t\right],\right.\right. \\ & \mathrm{If}\left[\mathrm{n}<1, \mathrm{If}\left[\mathrm{t}<{C_0}^{(1-n)/(k(T)(1-n))}, \left({C_0}^{(1-n)} + k(T)(n-1)t\right)^{1/(1-n)}, 0\right],\right. \\ & \left.\left.\left.\left({C_0}^{(1-n)} + k(T)\;(n-1)\mathrm{t}\right)^{1/(1-n)}\right]\right]\right]. \end{aligned} \tag{5}$$

What Eq. 5 says is that if $n = 0$, the concentration drop follows Eq. 2 until its calculated value becomes zero. From this point onward the concentration continues to be recorded as zero. If $n = 1$, the concentration follows Eq. 3. If $0 < n < 1$ the degradation follows Eq. 4 until the calculated concentration becomes a complex number, at which point it becomes and continues to be zero. If $n > 1$, the concentration follows Eq. 4 all the way.

In Mathematica® (Wolfram Research, Champaign, IL), the program used in this work, the "If" statement and "Piecewise" function can be used interchangeably in the model. Also, once $C(t)$ as defined by Eq. 5 is written in the syntax of Mathematica®, it is treated by the program as any analytical function such as the familiar x^m, $\mathrm{Exp}(x)$, and $\mathrm{Log}(x)$. This includes not only plotting the $C(t)$ vs. t curve but also operations such as calculating the momentary derivative and extracting the time t^* which corresponds to a given concentration $C(t)$, see below. Additional benefit of Mathematica® is its function 'Manipulate' which allows one to examine the properties of elaborate functions by varying their parameters with sliders on the screen. For viewing isothermal degradation curves with any chosen value of n in the range of $0 \leq n \leq 2.5$, an interactive freely downloadable Wolfram Demonstration entitled "Kinetic Order of Degradation Reactions" (http://demonstrations.wolfram.com/KineticOrderOfDegradationReactions/) has been written and posted on the Internet. Its screen display is shown in Fig. 2. [Once the free "Wolfram CDF Player" is downloaded following instructions on the screen, the user gets free access to over 9800 interactive Demonstrations to date covering a large variety of scientific disciplines and many other areas of interest.]

2. Experimental determination of the kinetic order and the rate constant's temperature dependence

A degradation reaction's kinetic order has been traditionally determined by recording a set of $C(t)$ vs. t curves at various constant temperatures and testing the linearity of the $C(t)$, $\mathrm{Ln}C(t)$ or $1 / C(t)^{n - 1}$ vs. time relationship. The linear plots' slopes have been used to determine the rate constant, $k(T)$, at the temperatures examined. In principle at least, both n and $k(T)$ can also be extracted directly from the untransformed data by nonlinear regression, when $n = 1$ or $n \neq 0$ is suspected. With modern mathematical software such as Mathematica®, Eq. 5 can be used directly as a single model, see below. Its use as a single model would eliminate the need to guess the reaction's order or test the linearity of several plots where n is in doubt. It is well known, of course, that logarithmic or power transformation of the experimental data points alters their relative weight. Also, in scattered data, the linear plot method might not reveal slight deviations form the determined integer n value, e.g., 0.96 or 1.04 instead of the 'ideal' 1.0. These issues, although important, will not concern us here. Either way, once the reaction's kinetic order has been established by Eq. 5 and the corresponding rate constant