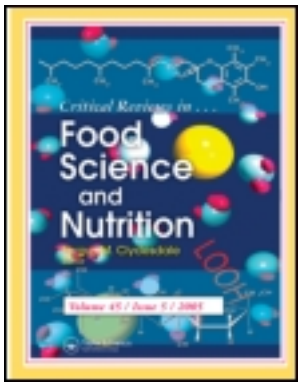

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The Arrhenius Equation Revisited

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The Arrhenius Equation Revisited

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The Arrhenius equation has been widely used as a model of the temperature effect on the rate of chemical reactions and biological processes in foods. Since the model requires that the rate increase monotonically with temperature, its applicability to enzymatic reactions and microbial growth, which have optimal temperature, is obviously limited. This is also true for microbial inactivation and chemical reactions that only start at an elevated temperature, and for complex processes and reactions that do not follow fixed order kinetics, that is, where the isothermal rate constant, however defined, is a function of both temperature and time.

The linearity of the Arrhenius plot, that is, Ln[k(T)] vs. 1/T where T is in °K has been traditionally considered evidence of the model's validity. Consequently, the slope of the plot has been used to calculate the reaction or processes' "energy of activation," usually without independent verification. Many experimental and simulated rate constant vs. temperature relationships that yield linear Arrhenius plots can also be described by the simpler exponential model $Ln[k(T)/k(T_{reference})] = c(T\text{-}T_{reference})$*. The use of the exponential model or similar empirical alternative would eliminate the confusing temperature axis inversion, the unnecessary compression of the temperature scale, and the need for kinetic assumptions that are hard to affirm in food systems. It would also eliminate the reference to the Universal gas constant in systems where a "mole" cannot be clearly identified. Unless proven otherwise by independent experiments, one cannot dismiss the notion that the apparent linearity of the Arrhenius plot in many food systems is due to a mathematical property of the model's equation rather than to the existence of a temperature independent "energy of activation." If T+273.16°C in the Arrhenius model's equation is replaced by T+b, where the numerical value of the arbitrary constant b is substantially larger than T and* $T_{reference}$*, the plot of Ln k(T) vs. 1/(T+b) will always appear almost perfectly linear. Both the modified Arrhenius model version having the arbitrary constant b,* $Ln[k(T)/k(T_{reference}) = a[1/(T_{reference}+b)\text{-}1/(T+b)]$*, and the exponential model can faithfully describe temperature dependencies traditionally described by the Arrhenius equation without the assumption of a temperature independent "energy of activation." This is demonstrated mathematically and with computer simulations, and with reprocessed classical kinetic data and published food results.*

Keywords kinetics, modeling, temperature effects, accelerated storage, shelf life, time-temperature integrators

INTRODUCTION

The effect of temperature on the rate of chemical reactions that had been described by van't Hoff was given physical foundations by Arrhenius resulting in the famous equation that carries his name. This equation can be written in the form:

$$k(T) = k\left(T_{ref}\right) Exp\left[\frac{E_a}{R}\left(\frac{1}{T_{ref}} - \frac{1}{T}\right)\right] \quad (1)$$

or

$$Ln\left[\frac{k(T)}{k\left(T_{ref}\right)}\right] = \frac{E_a}{R}\left(\frac{1}{T_{ref}} - \frac{1}{T}\right) \quad (2)$$

where $k(T)$ is the reaction rate at temperature T in °K, $k(T_{reference})$ the reaction rate at a reference temperature $T_{reference}$ in °K, E_a the energy of activation in J, kJ, cal, or kcal per mole, and R the Universal gas constant in the corresponding units. The model has been applied to many different kinds of chemical reactions and processes and become almost universally accepted. According to the model's equation (Eq. 2), a plot of Ln $k(T)$ vs. $1/T$ (T in °K) should be a straight line, see Fig. 1, whose slope has been used to calculate the reaction or processes' energy of activation. This has led many researchers to define the "energy of activation"

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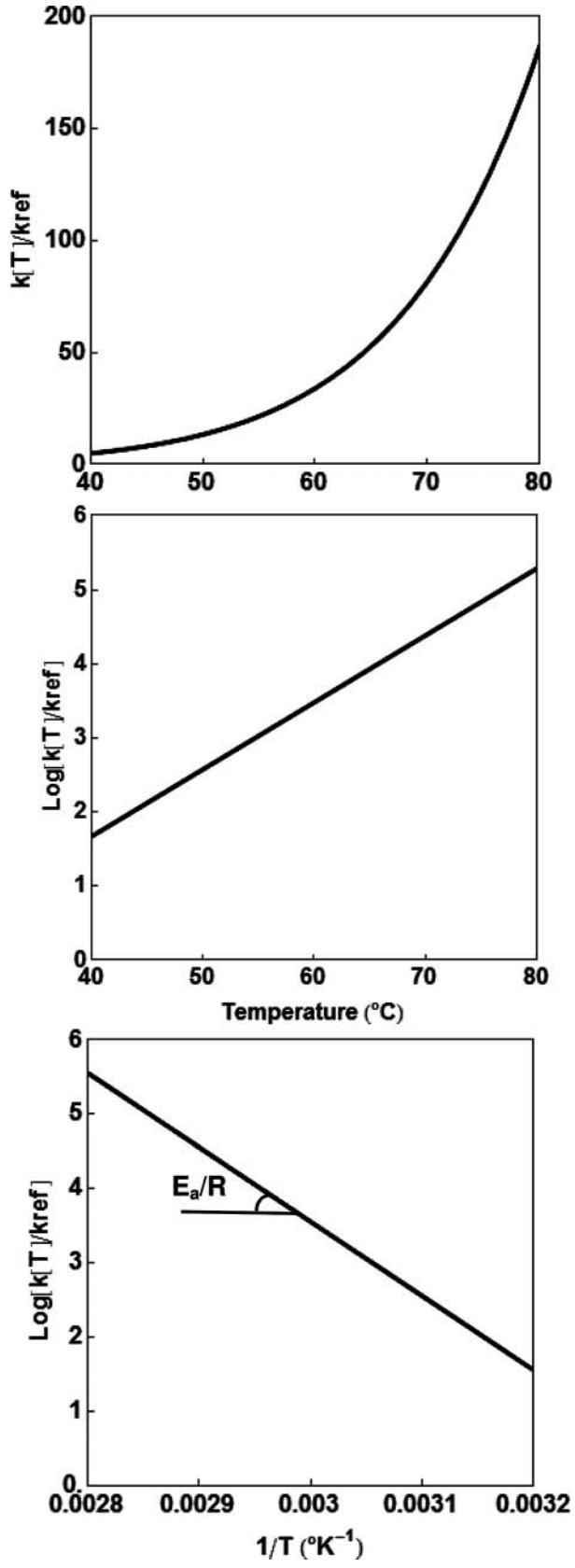

Figure 1 Simulated $k(T)/k(T_{ref})$ vs. T plots on linear and semi-logarithmic coordinates using the traditional Arrhenius equation (Eq.1) as a model. Compare with Fig. 3.

as:

$$E_a = R\frac{dLnk(T)}{d\left(\frac{1}{T}\right)} \tag{3}$$

The Arrhenius equation has also been widely used in food research, technology, and engineering. The reported applications of the model have not been restricted to the rates of simple chemical reactions such as vitamin degradation (Dermesonlouoglou et al., 2007; Dutta et al., 2006; Rekha et al., 2005; Giannakourou and Taoukis, 2004; Martins and Silva, 2003; Uddin et al., 2002; Rojas and Gerschenson, 2001). They also include biochemical (enzymatic) reactions (Goncalves et al., 2009; Domenek et al., 2002; Voegel-Turenne et al., 1999; Pedreschi et al., 2005), enzyme inactivation (Anthon and Barret, 2001; Weemaes et al. 1999; Dogan and Dogan, 2004; Nourian et al., 2003; Ortega et al., 2004), viscosity (Cohen and Weihs, 2010; Hosseini-Parvar et al., 2010; Dutta et al., 2006), and microbial growth and inactivation (Murphy et al., 2000; Lee et al., 2001; Mitchell et al., 2004). The Arrhenius model's concept and its mathematical format have been expanded in food research to describe the rate's dependence on factors such as pH and a_w (Cerf et al., 1996; Koutsoumanis et al., 2006; Fernandez et al., 2002). And, by analogy, the notion of "energy of activation" has been extended to the effect of ultra high pressure on the rate of microbial inactivation (Lee et al., 2001; Fachin et al., 2002).

In the Ross model of peaked microbial growth, the equation has been modified to include thermodynamic considerations associated with a controlling enzymatic reaction (Ross and Dalgaard, 2004). Ross (1993) has rearranged the model to produce a dimensionless version of the equation for the purpose of predicting bacterial spore inactivation using chemical markers, based on the assumption that the marker thermal degradation and spore destruction both follow first order kinetics.

Also, because the applicability of the Arrhenius model has been taken for granted, it has been implemented in time-temperature integrators (Tsironi et al., 2011; Kreyenschmidt et al., 2010; Giannakorou et al., 2005; Mendoza et al., 2004; Shimoni et al., 2001) and used in accelerated storage studies (Karathanos et al., 2006; Gomez-Alonso et al., 2004) as a means for anticipating spoilage and predicting shelf life (van Boekel, 2009). Formulas to estimate shelf life under static conditions also based on the Arrhenius model can be found in both the food and pharmaceutical literatures (e.g., Duyvesteyn et al., 2001; Waterman et al., 2005; 2007). The underlying assumption has been that under constant humidity conditions the time to a product's expiration, t_s, is inversely proportional to the exponential deterioration "rate" and hence that Ln t_s is proportional to the reciprocal of the absolute temperature.

Despite the successful use of the Arrhenius equation in many fields and its derivation from statistical mechanics, the notion that it has universal applicability has not gone unchallenged. Thus according to Wikipedia (http://en.wikipedia.org/wiki/Arrhenius_equation) the equation is

considered an empirical rather than a fundamental physical model. Although clearly less numerous in comparison with reports on the successful application of the Arrhenius model, a web search for "Non-Arrhenius kinetics" still renders thousands of entries providing counter examples. There are many publications that show considerable discrepancy between the expected linearity of the Ln $k(T)$ vs. $1/T$ plot and its actual shape. There are also such reports in the food literature as well, notably those that have led to the attempts to replace the Arrhenius equation by the WLF model (e.g., Slade and Levine, 1991; Sapru and Labuza, 1993), which has already been discussed by Peleg (1992) and Peleg et al. (2002), or by the Eyring-Polanyi model (e.g., Cisse et al., 2009; Huang et al., 2011) (see below).

Perhaps the earliest challenge to the use of the Arrhenius model in food research was based on its incompatibility with the growth rate of microorganisms (see McMeekin et al.,1998). The use of the Arrhenius equation in microbial inactivation modeling has been criticized also (Peleg, 2006), and more recently by Peleg and Corradini (2011) who have offered additional arguments against the use of the equation in microbial growth kinetics modeling. The criticism has been extended to the kinetics of complex chemical reactions such as lipid oxidation and acrylamide formation, which are governed by competing mechanisms of synthesis and degradation and have interactive paths (Peleg et al., 2009).

The importance of kinetics to the successful design of a safe preservation process that maintains the quality of the product while minimizing nutritional losses is obvious. The same can be said about the role of kinetics in choosing a product's storage conditions and setting its commercial shelf life. Therefore, it would be worthwhile to re-examine the properties of the Arrhenius model and critically assess its application in processes and operations involving foods. In this review we will not address the physical chemistry of reactions that occur in foods. They are simply too numerous and their detailed mechanisms, especially those of the more complicated ones, might not be always fully known. The same is true of microbial systems. Direct translation of the kinetics of chemical and biophysical processes within cells or spores and of events at the cellular level to changes at the population level are rarely if ever possible, except perhaps where cells can be individually monitored. Instead, we will focus on the mathematical properties of the Arrhenius equation, explore their potential implications, and evaluate how they can be related to or compared with those of alternative temperature dependence models when applied to the temperature effect on chemical, biochemical, and microbial processes in food systems.

POINTS TO BE CONSIDERED BEFORE USING THE ARRHENIUS EQUATION IN FOOD

Despite the numerous reports on its successful application, the notion that the Arrhenius equation is an effective model of the temperature effect on the rate of chemical reactions and biological processes in foods can be challenged on several grounds. The same can be said about its use to calculate these reactions and processes' "energy of activation." The arguments against the use of the Arrhenius model uncritically are of different kinds, some already mentioned. They will be listed and discussed in no particular order because all of them lead to the conclusion that in most food applications the Arrhenius model has not been a particularly useful.

The Meaning of k(T)

For a reaction following fixed order kinetics, zero, first, or second order kinetics for example, the rate constants $k(T)$ and $k(T_{ref})$ are clearly defined, and hence can be incorporated into the Arrhenius model's equation. A problem arises when the reaction or process in question does not follow fixed order kinetics. Perhaps the best examples are microbial growth and inactivation. To start with, growth and survival curves describe the evolution or demise of cell or spore populations and not the synthesis or disintegration of molecules (see below). Also, before the onset of the mortality phase, most isothermal microbial growth curves have a sigmoid shape. This is an indication that the momentary growth rate is governed by different mechanisms or the interplay of different processes in the "lag," "exponential," and "stationary" phases. The absolute and relative rates of the cells physical growth, of their division and mortality, and of the intra- and extracellular exchanges that affect them continuously vary in a manner that cannot be deduced from the shape of the growth curve alone (Peleg and Corradini, 2011). It is known that a change of temperature can affect the lag phase duration, the overall growth level, and the steepness of the curve at the exponential phase. Thus, the treatment of the "specific maximum growth rate" (the growth rate at the inflection point of the growth curve) as the sole representative of the growth kinetics, and linking it to the "energy of activation" of the growth processes not only needs theoretical justification but also independent experimental verification (Peleg and Corradini, 2011). Moreover, the "specific maximum growth rate" itself becomes a problematic measure when the growth curve is grossly asymmetric around the inflection point or when the effect of temperature and/or other ambient factors is mainly expressed in the time taken to reach the exponential phase (ibid). The explanation offered by the proponents of the use of the Arrhenius equation is that the "energy of activation" calculated with this model is of a "limiting enzymatic reaction." This explanation will be difficult to accept until this limiting reaction is identified and proven to be the same at all pertinent temperatures, and until its energy of activation is determined independently (Peleg and Corradini, 2011), an issue to which we will return. But suppose that such a reaction did exist. Will its identification enable to predict the lag phase duration and the asymptotic growth level? Notice that the application of the Arrhenius model hinges on the assumption that the reaction or process at hand follows fixed order kinetics and hence that its rate constant ambient conditions is a

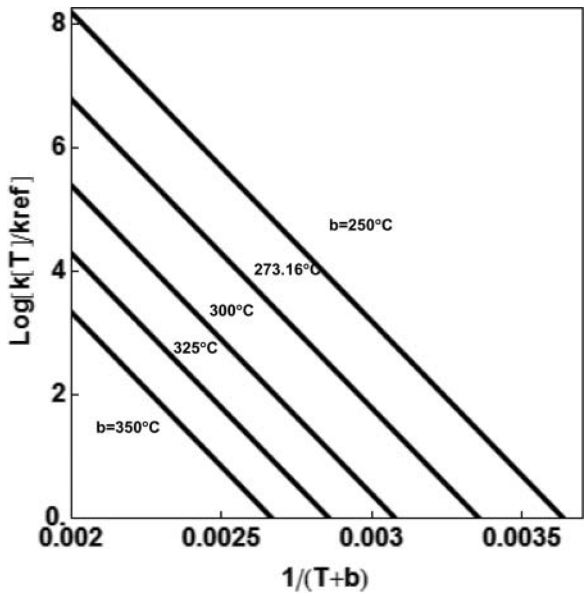

Figure 2 Ln[$k(T)/k(T_{ref})$] vs. $1/(T+b)$ plots generated with the 'generalized' Arrhenius equation (Eq. 11) as a model with b having different values. Notice that b need not be 273.16° for the plots to be linear.

function of temperature but not of time. As will be repeatedly mentioned, this is certainly not the case in several important processes in foods besides microbial growth, notably in microbial inactivation and complex peaked reactions where synthesis and degradation occur simultaneously at changing rates.

Processes having Optimal or Onset Temperature

The mathematical construction of the Arrhenius equation entails that a process's rate increases monotonically with temperature and approaches, asymptotically, a constant value (see below). Obviously, a monotonic rate rise with temperature cannot be the case in microbial growth. This is because all microorganisms have an optimal growth temperature and because at either end of the pertinent temperature range growth can turn into mortality. A similar and not unrelated phenomenon can be observed in enzymatic reactions where the enzyme can be denatured at elevated temperatures. Users of the Arrhenius equation are aware of these facts, of course, and their claim is that the model is only applicable within the "pertinent temperature range." This range's limits, however, are rarely specified although they ought to. This could be done either by an explicit statement or by including the limits in the model, which would add two adjustable parameters to its equation. But one can also claim that the processes, which lead to a cell's death, a spore's destruction, or an enzyme inactivation, need not start abruptly at a particular temperature. In other words, there can be a continuous mechanistic shift as the temperature increases or decreases, which the model equation should have to account for. To do this will require a more intensive modification of the model equation and further

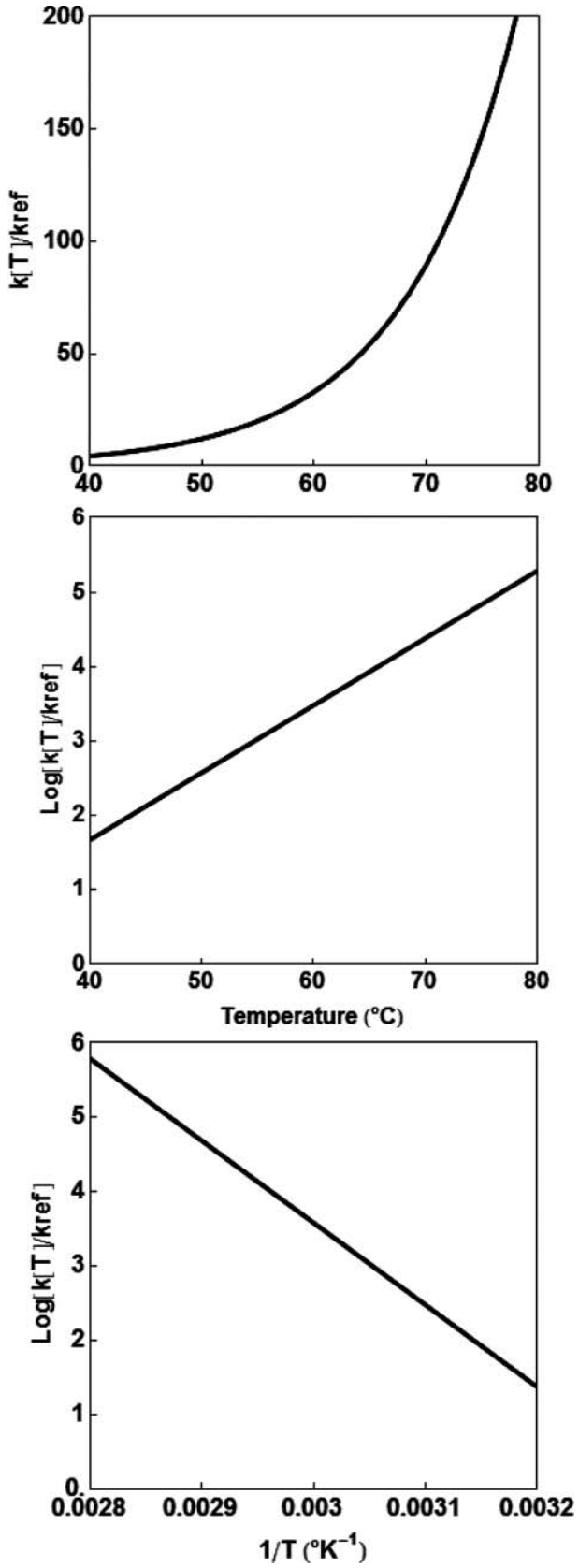

Figure 3 Simulated $k(T)/k(T_{ref})$ vs. T plots on linear and semi-logarithmic coordinates using the exponential model (Eq. 13). Compare with Fig. 1.

increase the number of adjustable parameters. All this raises new questions concerning the utility of the idea that there is always a single limiting reaction with a time independent rate constant having a temperature independent "energy of activation." Also, notice that the burden of proof of the existence of a limiting reaction is on the model's proponents and not on its critics. Therefore, it is the user of the Arrhenius equations who should come up with convincing evidence that microbial growth and inactivation are always controlled by a single biochemical reaction.

Most of the arguments against the use of the Arrhenius equations are not new, and criticism of its use in food systems is not difficult to find. One of the earliest resulted in Belerádek's model of microbial growth (see McMeekin et al., 1998), which gave rise to the original and expanded versions of the square root model. The former only accounts for the rise or fall of the rate constant above a threshold temperature, and the latter has markers for both the lowest and highest temperatures between which growth is observed (see Ratkowsky et al., 1982; 1983). Expressed mathematically:

$$\sqrt{\mu_{max}} = b\,(T - T_{min}) \tag{4}$$

and

$$\sqrt{\mu_{max}} = b\,(T - T_{min})\,\{1 - Exp\,[c\,(T - T_{max})]\} \tag{5}$$

where $\mu_{\max}$ is the "maximum specific growth rate," b and c are constants and T_{min} and T_{max} mark the temperature range of the organism's growth. [It has also been shown that experimental $\mu_{\max}$ vs. T data, which have been successfully fitted with the square root model, can also be described by a model where the square root is replaced by different powers (Huang, 2009; Ross et al., 2011; Huang, 2011)]. Equation (5) with its two growth limit markers, T_{min} and T_{max}, is qualitatively consistent with the actual response of microbial populations to heat, albeit at the cost of having four adjustable parameters instead of the traditional Arrhenius model's two. But Eq. (5) achieves what the original Arrhenius equation, which has no markers, cannot. Enzymes are heat inactivated, usually at temperatures only slightly above their optimal. Thus, a kinetic model of at least certain industrial biochemical reactions would have a practical advantage if it included $T_{optimal}$ and/or T_{max} as parameters. When it comes to microbial inactivation, a marker of its onset temperature, or of the sub-lethal range, would be helpful too. The inclusion of a temperature marker concept has already been implemented in the Weibull-log logistic (WeLL) inactivation model (see Peleg, 2003; 2006). The Weibullian model of isothermal inactivation can be written in the form:

$$Log\,S(t) = -b(T)t^{n(T)} \tag{6}$$

where $S(t)$ is the survival ratio at time t, that is, $N(t)/N_0$ where $N(t)$ and N_0 are the momentary an initial number of viable cells or spores, respectively, $b(T)$ a rate or scale parameter, primarily representing the steepness of the survival curve, and $n(T)$ a measure of the concavity degree and direction of the isothermal survival curve. The temperature dependence of the rate parameter has been shown to follow the log-logistic model:

$$b(T) = Ln\{1 + Exp[k(T - T_c)]\} \tag{7}$$

where T_c marks the temperature range where inactivation starts and k the slope of the $b(T)$ vs. T relationship at temperatures well above T_c. According to this model, when $T \ll T_c$, $b(T) \to 0$ and when $T \gg T_c$, $b(T) \to k\ (T - T_c)$. The WeLL model is most probably also applicable to enzymes where, again, heat inactivation only starts at a certain temperature and possibly to other degradation processes were thermal instability is only noticeable beyond a certain temperature. Notice that in cases where microbial or enzyme's inactivation follows first order kinetics, $n(T) = 1$ at all pertinent temperatures and Eq. (6) becomes:

$$Log\,S(t) = -K(T)t \tag{8}$$

$$K(T) = Ln\{1 + Exp[k(T - T_c)]\} \tag{9}$$

where K is the exponential survival rate, the reciprocal of the traditional "D value."

Either way, the temperature effect on the inactivation rate is expressed here by two parameters, k and T_c, the minimum needed number, and not by one as in the log-linear model (the 'z-value'), Arrhenius equation (E_a), or Eyring-Ploanyi model ($\Delta G'‡$). This enables the WeLL model to account for the qualitative difference between lethal and non-lethal temperatures, which neither of the traditional models does.

Although not always explicitly admitted, quite a few reported experimental Arrhenius plots in the food literature are not really linear, as has been assumed. Larger consistent deviations from log-linearity, which could not be overlooked, have led to the proposal to adopt what has been dubbed a "Polymer Science Approach" in food kinetics, that is, to replace the Arrhenius model by the empirical WLF equation (Slade and Levine, 1991). The WLF equation was originally proposed for the temperature effect on the viscosity of rubbery polymers that undergo glass transition. It had the form:

$$Log(a_T) = \frac{-C_1(T - T_{ref})}{C_2 + (T - T_{ref})} \tag{10}$$

where a_T is the shift factor, the ratio between the shear moduli at a temperature T and at a reference temperature T_{ref}, for example and C_1 and C_2 are characteristic constants of the polymer. In both Polymer Science and Food Science research, the "glass transition temperature," "T_g," has frequently served as the reference temperature, and it has been assumed that the rate of both physical and chemical processes in foods primarily depends on

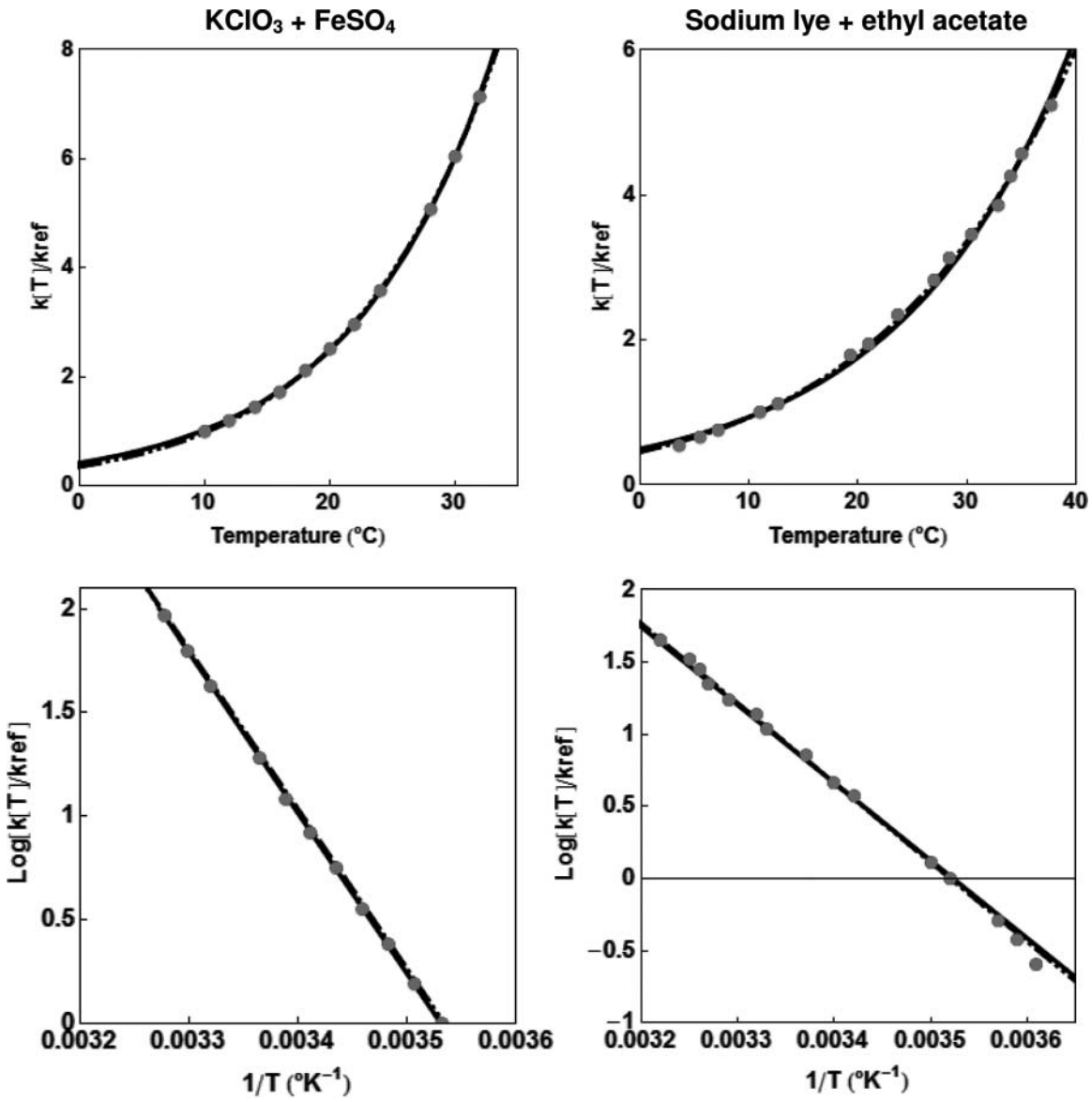

Figure 4 The fit of the traditional Arrhenius, generalized Arrhenius, with $b = 250$ and 300°C, and exponential models to kinetic data of the reactions between $KClO_3$ and $FeSO_4$ and sodium lye and ethyl acetate reaction. The original data are of Hood (1885) and Warder (1881), respectively. They were downloaded with permission from http://web.lemoyne.edu/~giunta/classicalcs/arrkin.html. Notice that for all practical purposes the three models could be used interchangeably. The regression parameters are listed in Table 1.

how far the temperature is above or below their "T_g." It is now well established that most, if not all synthetic polymers, do not have a clearly defined "T_g" (see Seyler, 1994; Donth, 2001; and Langer, 2007, for example) and the same is true for biopolymers, foods, and biological materials in general. Consequently, different methods of glass transition temperature determination render different "T_g" values for the same material. The same is true for the heating rate, that is, a slower or a faster rate of heating during the test will also result in a different "T_g." The implication is that a food can be very stable or unstable at the same temperature depending on how its "T_g" has been determined and at what heating rate. The notion that C_1 and C_2 can be assigned the "universal values" of 17.44 and 51.6°C^{-1}, respectively, should have also been dismissed long ago (Peleg, 1992). This, however, is not the issue here. Even with adjustable C_1 and C_2, the WLF model has the same major deficiencies as the Arrhenius equation, which it was intended to replace. This is because the WLF model also implies that the rate constant, however defined, must increase monotonically with temperature and be independent of the system's thermal history. The ability of the WLF model to fit data that the Arrhenius model cannot should also not come as a surprise since it has two adjustable parameters and not one. Much of the above also pertains to the D and z values. Despite growing evidence that microbial inactivation frequently does not follow first order kinetics, this log linear model is still widely used in food research, and by the

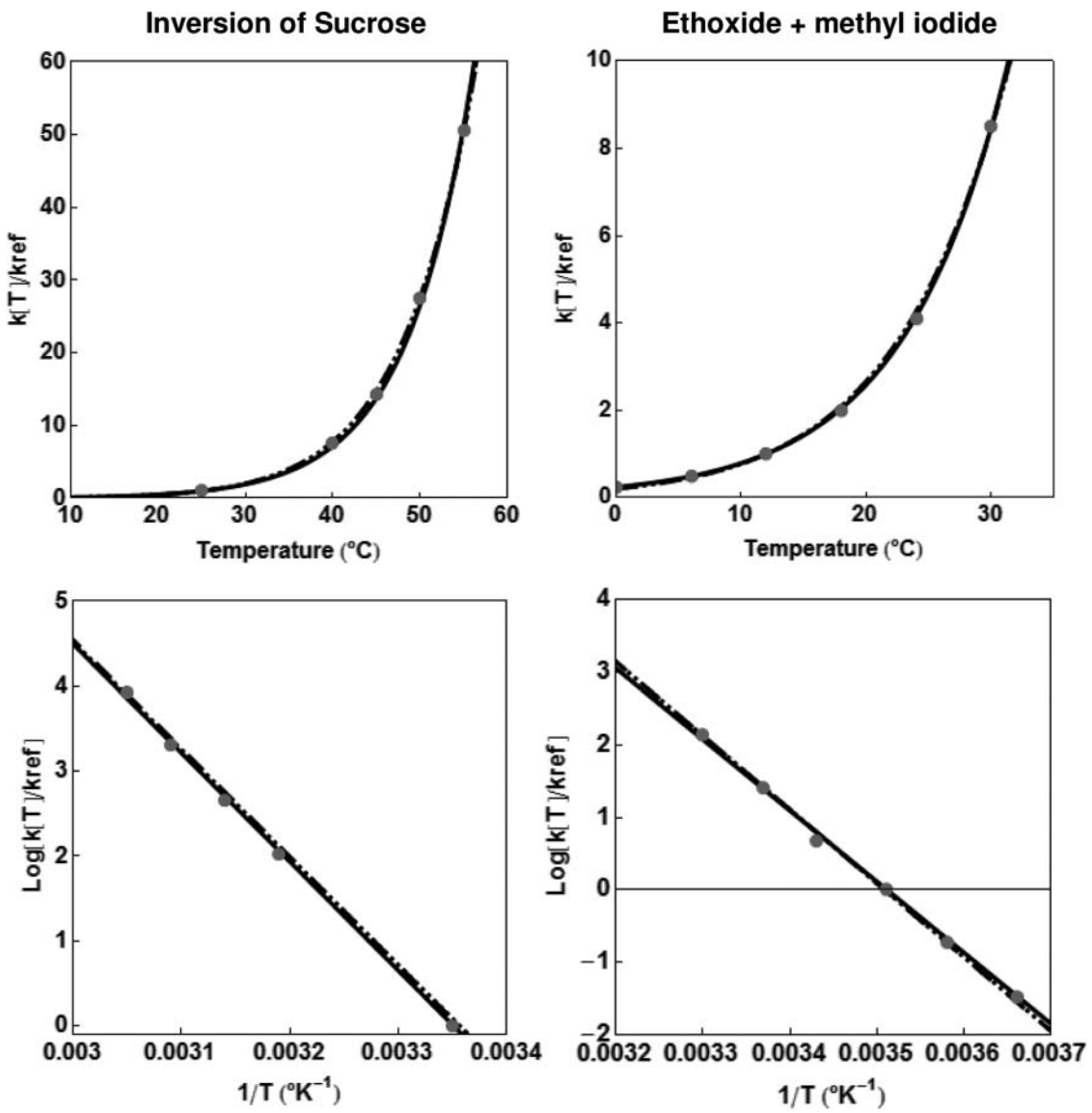

Figure 5 The fit of the traditional Arrhenius, generalized Arrhenius, with $b = 250$ and 300°C, and exponential model to kinetic data of sucrose inversion and the reaction between sodium lye and ethyl acetate. The original data are of Spohr (1888) and Hecht and Konrad (1889), respectively. They were downloaded with permission from http://web.lemoyne.edu/~giunta/classicalcs/arrkin.html. Notice that for all practical purposes the three models could be used interchangeably. The regression parameters are listed in Table 1.

food industry and regulating government agencies to establish the safety of thermally processed foods. In other words, at least where microbial inactivation is concerned, the three models: the older log-linear model, which produced the D and z values, the Arrhenius model that has replaced it, and the WLF model that has been proposed to replace them both, can only be applicable if the kinetics follows first or other fixed order.

Experimental Arrhenius Plots

For years in food research, the validity of the Arrhenius equation has been taken for granted. Consequently, many published linear Ln $k(T)$ vs. $1/T$ (T in °K) plots or relationships from which E_a have been determined are based on 3 or 4 experimental temperatures only, rarely a sufficient number to establish or affirm the linearity of the relationship. The statistical aspects of calculating the $k(T)$ of processes following first and other order kinetics and subsequently computing E_a have been thoroughly discussed by van Boekel (1996; 2009) and others. Suffice it to reiterate here that a high r^2 value by itself does not establish linearity, and in many cases the existence of curvature in the data is clearly evident (see the discussion of the WLF model in the previous section).

According to the theory underlying the use of the Arrhenius model, the existence of curvature implies that the process or

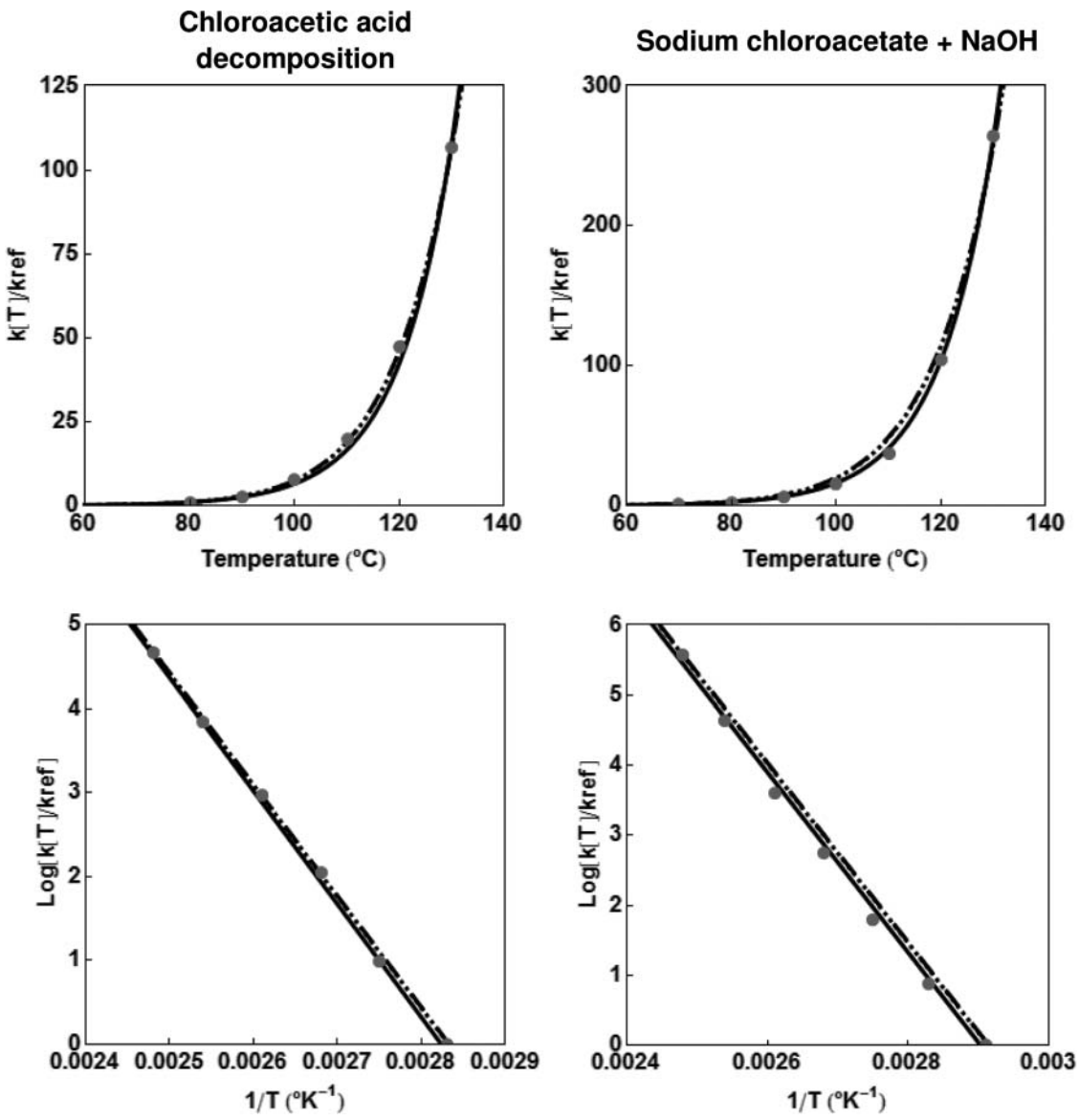

Figure 6 The fit of the traditional Arrhenius, generalized Arrhenius, with $b = 250$ and 300°C, and exponential model to kinetic data of chloroacetic acid decomposition and the reaction between sodium chloroacetate and sodium hydroxide. The original data are of van't Hoff (1884), downloaded with permission from http://web.lemoyne.edu/~giunta/classicalcs/arrkin.html. Notice that for all practical purposes the three models could be used interchangeably. The regression parameters are listed in Table 1.

the reaction's "energy of activation," E_a, *is* actually temperature dependent. In certain reactions or processes, E_a's temperature dependence might be weak in the reported temperature range. In such cases, the slight curvature could perhaps be ignored if the results are only used for interpolation. But before reporting E_a values as a reaction or process's characteristic, one has to confirm that the calculated "energy of activation" is indeed temperature independent, at least by statistical analysis aimed at proving or disproving the existence of curvature in the data. This can be done by examining the residuals distribution or through comparison of the performance and fit of the linear vis-à-vis nonlinear models, for example. When extrapolation is concerned, the issue becomes even more serious. Provided that the rate constant is well defined, using the parameters of the fitted linear model when the relationship is curvilinear might result in considerable discrepancy between the actual and assumed rates, a mismatch to which the logarithmic scale of the ordinate also contributes. Nonlinear regression might be an improvement, but it would not rid the model of its other problems. Thus, regardless of how E_a is calculated, reporting its magnitude with three or more digits on the basis of 3-4 experimental temperatures gives a misleading impression of the analysis accuracy and the theoretical strength of the model (see below).

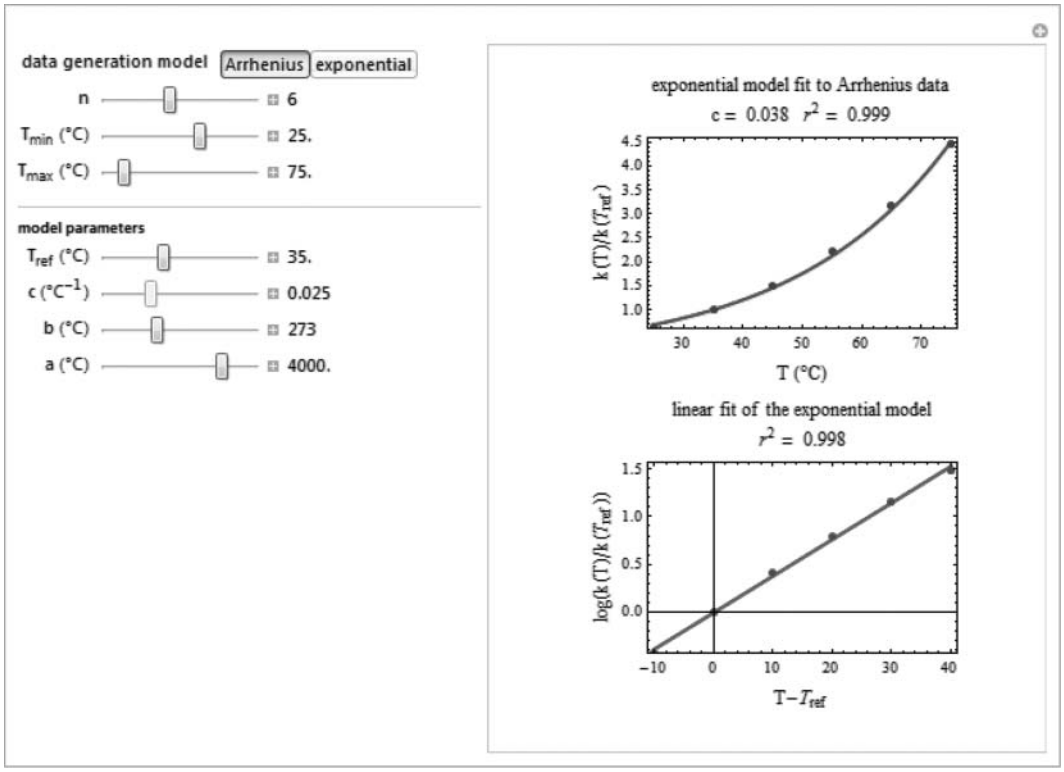

Figure 7 Screen display from the Wolfram Demonstration (http://demonstrations.wolfram.com/ArrheniusVersusExponentialModelForChemicalReactions/) that shows data generated with the generalized Arrhenius equation and fitted with the exponential model. Notice that the models and generation parameters can be entered numerically or by moving sliders on the screen.

Independent Verification

Many, perhaps most chemical reactions or biological processes in foods, occur in a chemically and physically changing environment. Consequently, the notion that the slope of the Ln $k(T)$ vs. $1/T$ (T in °K) plot can be used to determine their "energy of activation" is an assumption that needs independent verification. The magnitude of E_a, calculated from the Arrhenius plot can and should be confirmed experimentally, by calorimetry, for example. Unfortunately, reports on independent determination of E_a in foods and food systems are very difficult to find, and one might suspect that they do not exist. Consequently, any unconfirmed value of E_a in foods should be considered as tentative at best, and where the process or reaction has multiple steps and several alternative pathways, treated with caution. The already discussed microbial heat inactivation is a good example of why. The death of a cell exposed to heat can have several different biochemical and biophysical causes whose roles, unless proven otherwise, need not be the same at all temperatures. Another example is food deterioration caused by reactions involving free radicals such as in lipid oxidation. It is very unlikely that the absolute and relative abundance and the stability of these radicals remain unchanged as the temperature of the food rises or falls and there is no reason to assume that they should. Therefore, the notion that a single temperature independent "energy of activation" can always characterize the entire oxidation process still requires independent confirmation. The attempt to avoid the issue by defining the "energy of activation" by Eq. (3) cannot be a solution because it is based on circular reasoning. The same problem is encountered where a curvilinear Arrhenius plot is divided into two straight-line segments. The frequently accompanying suggestion that the underlying reaction has two regimes must also be viewed with caution, unless their existence is independently confirmed and there is a mechanistic explanation of the transition between them. This is because the alternative explanations, that there might be three or more stages, or that the whole concept of "energy of activation" does not apply, cannot be dismissed out of hand. Another danger in such data interpretation is that experiments covering different temperature ranges might reveal a different sequence of "regimes" or "stages" where the predominant processes or reactions have different "energies of activation." Again, the correct way to establish the existence of the assumed stages and affirm their corresponding energies of activation is through increasing the number of temperatures examined within the pertinent range and independent verification of the proposed mechanism by tests especially designed for the purpose.

The Structure of the Arrhenius Equation and its Kinetic Implications

The Arrhenius equation (Eq. 1) is based on the assumption of first or other fixed order kinetics, which defines the isothermal

Table 1 The fit of the exponential model (Eq. 13), the traditional and generalized versions of the Arrhenius model (Eq. 11 with $b = 273.16^\circ$ and $b \neq 273.16^\circ$) to chemical data

System	Temp. range (°C)	T_{ref} (°C)	Model	Equation	r^2	MSE	Figure	Data Source*
$KClO_3 + FeSO_4$	10-32	10	Exponential	13	0.9999	0.0020	4	Hood (1885)
			Arrhenius	1	0.9999	0.0007		
			Generalized Arrhenius ($b = 250$°C)	11	0.9999	0.0010		
			Generalized Arrhenius ($b = 300$°C)	11	0.9999	0.0005		
Sodium lye + ethyl acetate	3.6-37.7	11	Exponential	13	0.9991	0.008	4	Warder (1881)
			Arrhenius	1	0.9997	0.003		
			Generalized Arrhenius ($b = 250$°C)	11	0.9997	0.003		
			Generalized Arrhenius ($b = 300$°C)	11	0.9996	0.003		
Inversion of sucrose	25-55	25	Exponential	13	0.9995	0.481	5	Sporh (1888)
			Arrhenius	1	0.9999	0.081		
			Generalized Arrhenius ($b = 250$°C)	11	0.9999	0.117		
			Generalized Arrhenius ($b = 300$°C)	11	0.9999	0.055		
Ethoxide + methyl iodide	0-30	12	Exponential	13	0.9999	0.0014	5	Hecht and Konrad (1889)
			Arrhenius	1	0.9995	0.0091		
			Generalized Arrhenius ($b = 250$°C)	11	0.9995	0.0101		
			Generalized Arrhenius ($b = 300$°C)	11	0.9996	0.0081		
Chloroacetic acid decomposition	80-130	80	Exponential	13	0.9974	7.34	6	Van't Hoff (1884)
			Arrhenius	1	0.9999	0.31		
			Generalized Arrhenius ($b = 250$°C)	11	0.9999	0.17		
			Generalized Arrhenius ($b = 300$°C)	11	0.9998	0.49		
Sodium chloroacetate + NaOH	70-130	70	Exponential	13	0.9998	2.8	6	Van't Hoff (1884)
			Arrhenius	1	0.9961	53.5		
			Generalized Arrhenius ($b = 250$ °C)	11	0.9956	59.7		
			Generalized Arrhenius ($b = 300$ °C)	11	0.9965	47.6		

*Compiled and posted by Giunta (2003), http://web.lemoyne.edu/~giunta/classicalcs/arrkin.html

temperature dependent rate constant $k(T)$. Consequently, the equation does not have time as an independent variable. This implies that $k(T)$, however defined, is unaffected by the reaction or the thermal history of the process. Accepting this assumption might give rise to peculiar scenarios. Consider the traditional and still commonly held view that microbial inactivation follows first order kinetics and that the exponential rate constant follows the Arrhenius equation (or the log-linear or WLF model for that matter). If true, then a bacterial spore population reaching 110°C after 1 min of heating in a certain medium must have exactly the same momentary exponential inactivation rate as the same spore population just being cooled to this temperature after being held at 125°C for 30 min in the same medium (Peleg, 2006). In other words, the number of surviving spores will be very different, of course, but not the predicted inactivation rate of the model.

Similarly, if a chemical deterioration process in a food follows fixed order kinetics with a rate constant $k(T)$ obeying the Arrhenius equation, then the deterioration rate constant would have to be exactly the same if the food had been stored for a month at 5°C and then reached 25°C in one day, held at 25°C for a month or cooled to 25°C in one day after being stored for a month at 35°C. Here too, according to the Arrhenius model, the extent of the deterioration in the three scenarios will be very different, this is true. But the prediction that the deterioration rate constant of the food after the three temperature histories must be exactly the same can and should be verified experimentally.

The Coordinates Compression in the Arrhenius Plot

The presentation of kinetic data in the form of a Ln $k(T)$ vs. $1/T$ (T in °K) plot makes perfect sense in reactions between gases where the covered temperature range is very large, in which case the $1/T$ (T in °K) rises or falls several fold, and the corresponding rates might vary by several orders of magnitude. However, this is rarely the case in foods and biological systems (Peleg, 2006). In food storage, for example, it makes a big difference if the temperature is 5 or 40°C. Yet, this huge temperature range as far as the quality or safety of the food is concerned is transformed into the meager 0.0036 to 0.0032°K^{-1} range for no apparent reason. Another example is the inactivation of bacterial spores. Many bacterial spores survive exposure to a temperature of around 75°C, for example. [This is exploited in the preparation of spore suspensions free of vegetative cells, which almost invariably are killed by the treatment.] But at 120°C, the same spores could be destroyed on the time scale of minutes. Thus the rationale of compressing the temperature range of 75 to 120°C, huge as far the fate of the spore is concerned, to the minute 0.0029 to 0.025°K^{-1}, is not at all clear. Moreover, the temperature conversion from T in °C to $1/T$ (where T is in °K) also reverse the direction of the plot, a higher temperature is on the left of a lower one, which makes intuitive comprehension of the relationship unnecessarily difficult. Suppose now, for the sake of the argument, that a quality loss of a food at 15 to 25°C (0.00335 to 0.00347°K^{-1}) and a spore inactivation in the lethal temperature range of 110 to 120°C (0.00254 to 0.00261°K^{-1})

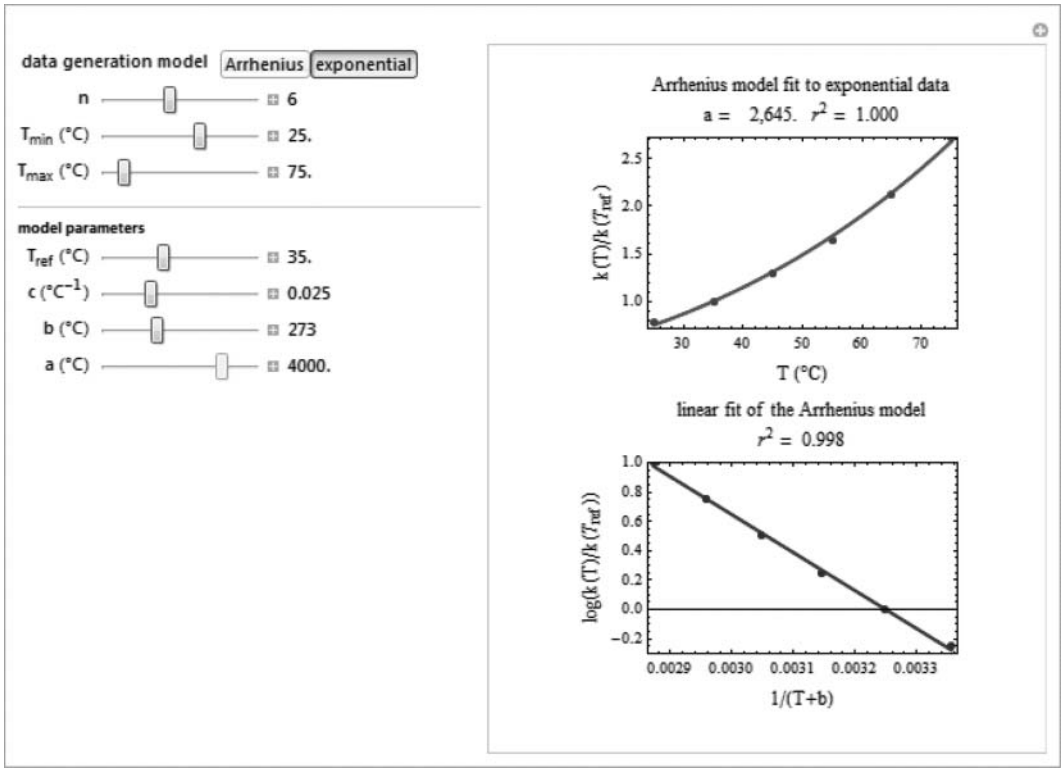

Figure 8 Screen display from the Wolfram Demonstration (http://demonstrations.wolfram.com/ArrheniusVersusExponentialModelForChemicalReactions/) that shows data generated with the exponential model and fitted with the generalized Arrhenius. Notice that the models and generation parameters can be entered numerically or by moving sliders on the screen.

indeed follow first order kinetics. If so, does the exponential rate constant of these processes (not the concentration of a component or the count) always vary by the several orders of magnitude needed to justify its presentation on a logarithmic scale?

The "Energy of Activation" and Universal Gas Constant

The concept of "energy of activation" was originally developed for stoichiometric chemical reactions where the quantities of the reactants are expressed in "moles." Obviously, many complex chemical and biological processes that occur in foods do not fit this description although their individual steps probably do. However, identifying all these steps and quantifying their kinetics might not be easy because of the potential and actual existence of several interacting pathways. Consequently, different literature sources sometimes suggest alternative mechanisms and pathways, which are not necessarily the same or at the same level of detail (Corradini and Peleg, 2006; 2009). Whether all the steps indeed follow first order kinetics as is usually assumed is also not clear but this is not the main issue here. Let us consider the previously mentioned commonly accepted notion that microbial thermal inactivation follows first order kinetics and has a temperature independent "energy of activation" on the order of 100-500 kJ "per mole" (see http://www.fda.gov/Food/ScienceResearch/ResearchAreas/SafePracticesforFoodProcesses/ucm100198.htm.) What is a "mole" of bacterial cells or spores? Well, since what is counted to determine the exponential rate constant is the number of surviving cells or viable spores, trivial calculations will show that a "mole" of these has a mass on the order of 10^5 metric tons, hardly a convenient unit for comparisons (Peleg, 2006). A mole of an inactivated enzyme has a smaller mass, of course, but still huge when compared to that of small inorganic or even organic molecules. As already mentioned, the argument that the energy of activation refers to an underlying "limiting reaction" is unsatisfactory since this reaction has yet to be identified. But even if such a reaction exists, which has yet to be proven, it is doubtful that it will be the same at different temperatures (Peleg and Corradini, 2011). All of the above also pertain to the food applications of the Eyring-Polyani model as a substitute to the Arrhenius model. It too has the Universal gas constant in its mathematical expression and the free energy of activation has J or kJ per "mole" units.

Similar confusion exists in the application of the Arrhenius model to the temperature effect on the viscosity or apparent viscosity of liquid and semi-liquid foods. What is a "mole" of mayonnaise, orange juice concentrate, or ketchup? How does the Universal gas constant enter the relationship between the flowability and temperature of these foods? In light of the numerous reports in the food literature on the Arrhenius model

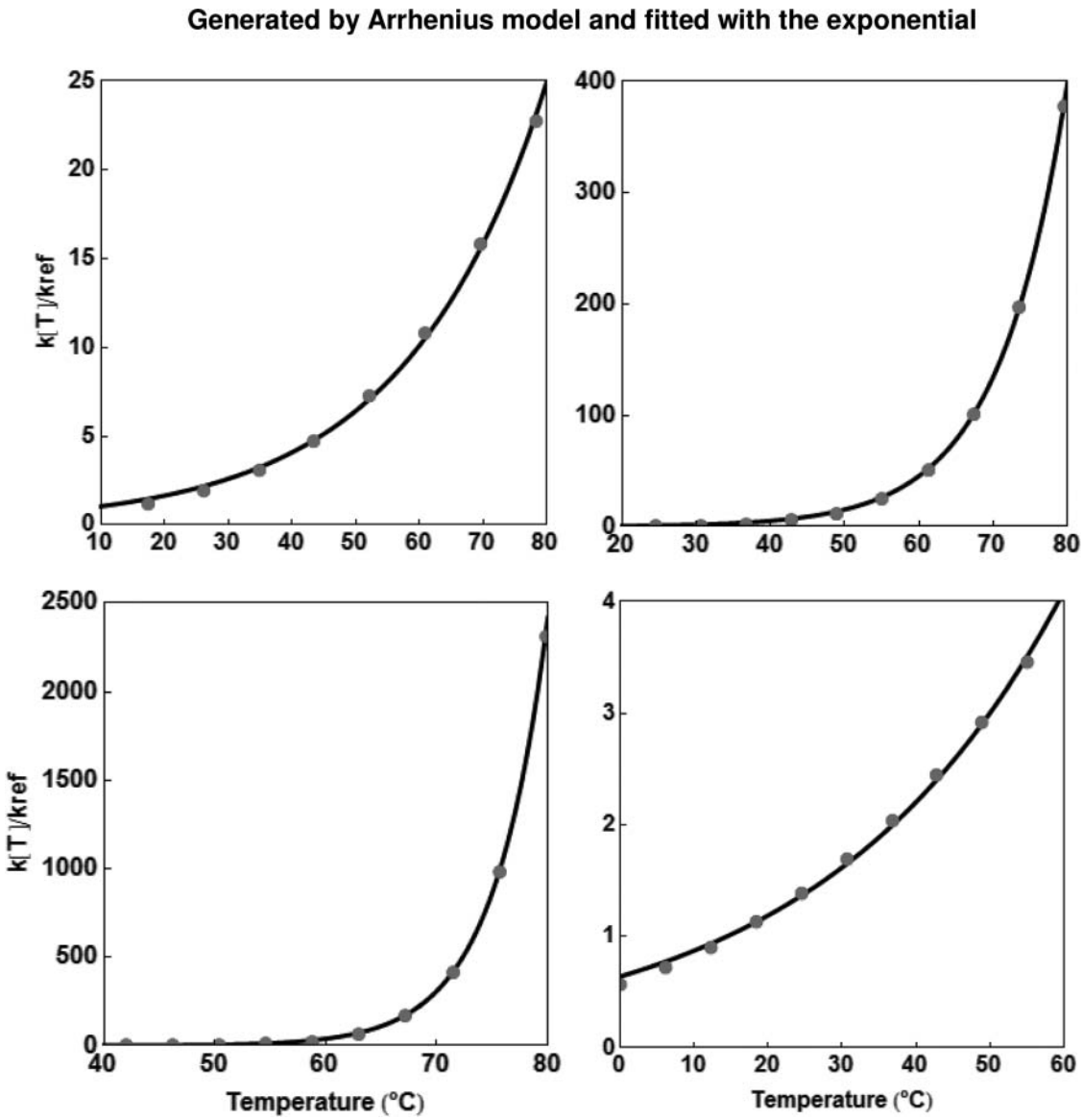

Figure 9 Examples of the exponential model's fit (Eq. 13) to k vs. T data generated with the traditional and "generalized" Arrhenius equations (Eq. 11). For the regression parameters see Table 2.

Table 2 The fit of the exponential model (Eq. 13) to data generated with the traditional and generalized versions of the Arrhenius model (Eq. (11) with $b = 273.16^\circ$ and $b \neq 273.16^\circ$) and vice versa[1)]

Arrhenius equation's parameters				Exponential model's parameters		
Number of points	T_{ref}	a	b	r^2	c by regression	c calculated by Eq. (16)
10	15	5000	273.16	0.999	0.05	0.06
10	45	25000	273.16	0.999	0.21	0.25
10	30	15000	300	0.999	0.11	0.14
10	15	2500	250	0.999	0.031	0.036
Exponential models's parameters				Arrhenius model's parameters		
Number of points	T_{ref}	c	r^2	b (fixed)	a by regression	a calculated by Eq. (17)
10	15	0.05	0.997	273.16	5000	4200
10	15	0.10	0.998	273.16	10800	9500
10	45	0.20	0.998	300	26800	23800
10	5	0.30	0.998	250	22025	19500

[1)] T_{ref} and a are in °C and c is in $^\circ C^{-1}$.

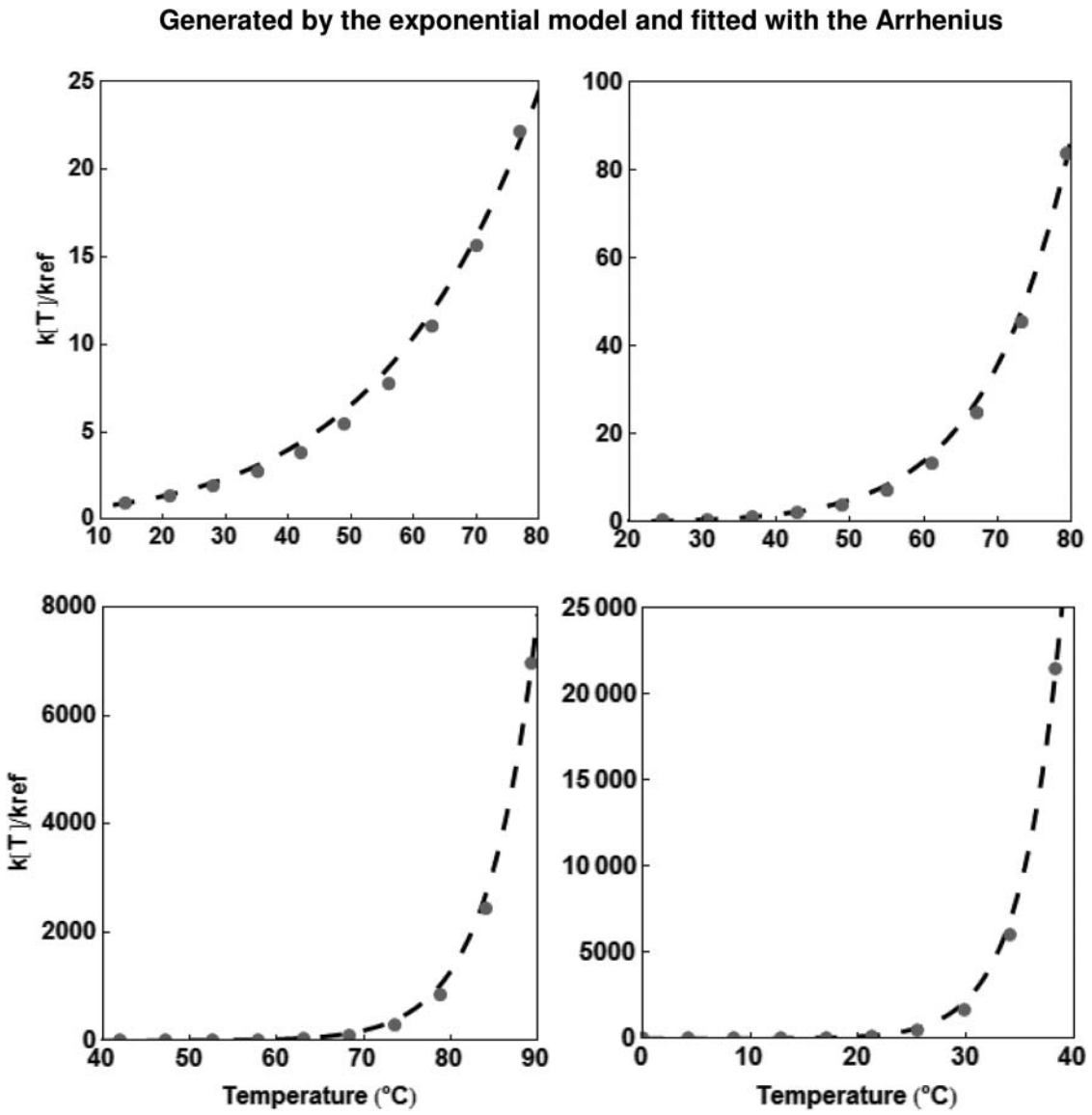

Figure 10 Examples of the traditional and "generalized" Arrhenius models' (Eq. 11) fit to data generated with the exponential model (Eq. 13). For the regression parameters see Table 2.

application, it is most surprising that these questions have not been asked until very recently.

COMPARISON OF THE ARRHENIUS EQUATION TO THE SIMPLER EXPONENTIAL MODEL

One of the appeals of applying the Arrhenius model to reactions and processes for which it has not been derived can perhaps be attributed to the frequently observed linearity or apparent linearity of the Ln $k(T)$ vs. $1/T$ (T in °K) plot. The slope of this plot can be easily calculated by linear regression (or in the very old days graphically) to render the putative "energy of activation." It is a fact that most chemical reactions and biological processes are accelerated by temperature at least within a certain practical range and that the rise of the rate is exponential rather than linear. The question that should be asked is why so many reactions and processes, which have little or nothing in common, so frequently produce a log-linear or close to log-linear Arrhenius plot. To explain this observation, let us investigate the mathematical properties of the Arrhenius equation and compare them to those of a much simpler exponential model.

The Arrhenius model (Eq. 1) can be written in the generalized form:

$$Ln\left[\frac{k(T)}{k\left(T_{ref}\right)}\right] = a\left(\frac{1}{T_{ref}+b} - \frac{1}{T+b}\right) \tag{11}$$

where T and T_{ref} are in °C and a and b are constants having temperature units. Traditionally, a in this equation is presented as E_a/R and b is assigned the value of 273.16°, to make the

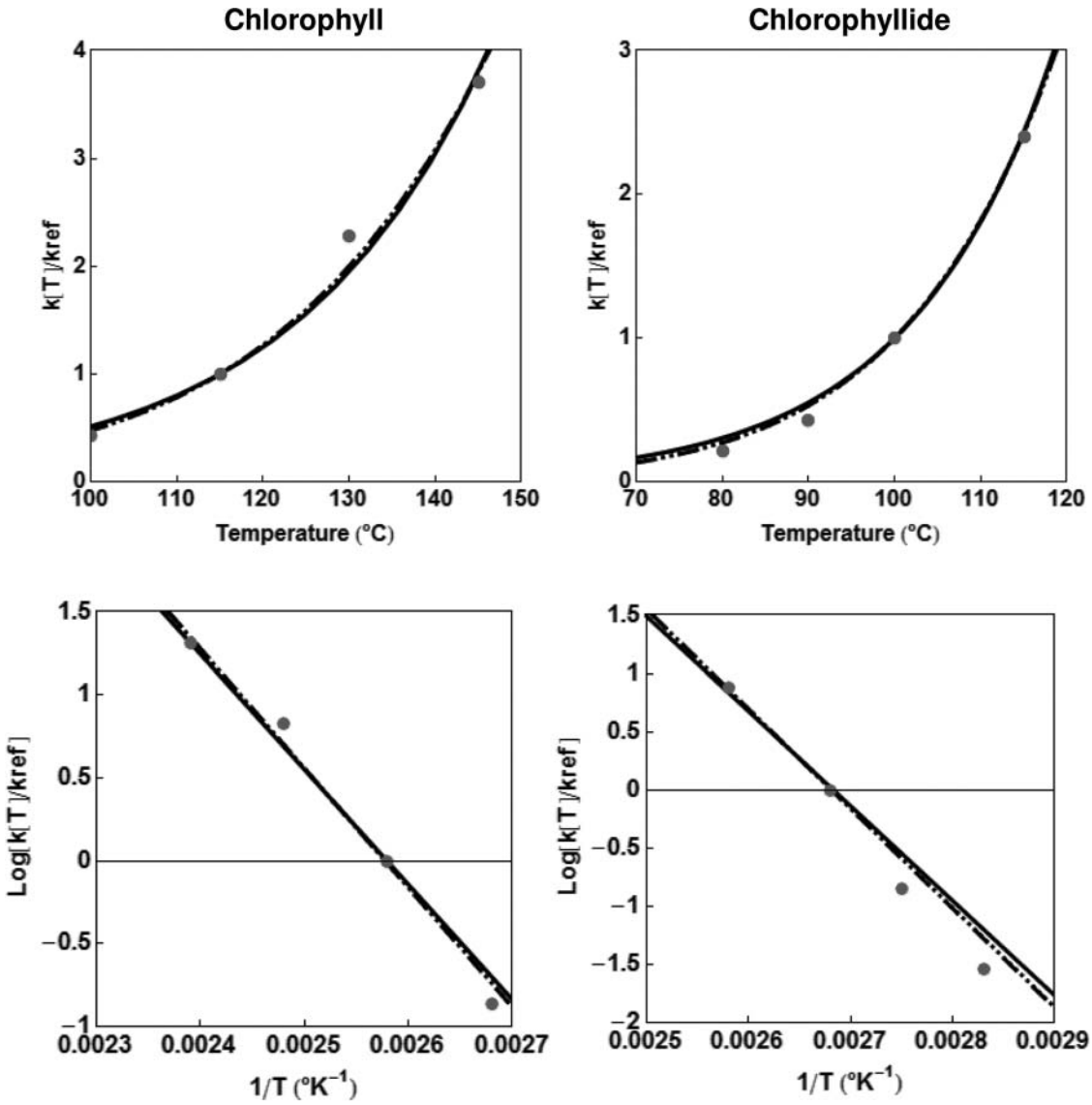

Figure 11 The fit of the traditional Arrhenius, "generalized" Arrhenius, with $b = 250$ and 300°C, and exponential model to kinetic data of chlorophyll and chlorophyllides degradation. The original data are from Canjura et al. (1991). Notice that for all practical purposes the three models could be used interchangeably. The regression parameters are listed in Table 3.

temperature absolute, that is, in °K. The reason for writing the model in the form of Eq. (11) instead of the traditional will soon become clear.

According to this equation, when $T \rightarrow \infty$, $\mathrm{Ln}[k(T)/k(T_{ref})] \rightarrow a/(T_{ref} + b)$, not to infinity. In other words, the rate cannot rise indefinitely, even theoretically, because the $\mathrm{Ln}[k(T)/k(T_{ref})]$ vs. T relationship has an inflection point at $T = (a\text{-}2b)/2$. Also, according to the traditional Arrhenius equation, as $T \rightarrow$-273.16°C or 0°K, $\mathrm{Ln}[k(T)/k(T_{ref})] \rightarrow$-$\infty$, that is, the rate approaches zero, which is consistent with physical considerations. By definition, the model implies that at $T = T_{ref}$, $k(T)/k(T_{ref}) = 1$ and hence $\mathrm{Ln}[k(T)/k(T_{ref})] = 0$. Also, according to both the traditional and general version of the model, if $T > T_{ref}$, $\mathrm{Ln}[k(T)/k(T_{ref})] > 0$, and if $T < T_{ref}$, $\mathrm{Ln}[k(T)/k(T_{ref})] < 0$. Plots of $k(T)/k(T_{ref})$ vs. T and $\mathrm{Ln}[k(T)/k(T_{ref})]$ vs. $1/T$ relationships generated with Eq. (11) as a model are shown in Fig. 2. Consider now a simpler exponential model of the $k(T)$ vs. T relationship at temperatures well below the inflection point of the Arrhenius model, that is,where the curve has upper concavity. Mathematically the exponential model can be written in the form:

$$k(T) = k(T_{ref})Exp[c(T - T_{ref})] \tag{12}$$

or

$$Ln\left[\frac{k(T)}{k\left(T_{ref}\right)}\right] = c(T - T_{ref}) \tag{13}$$

where T and T_{ref} are in °C and c is a constant having $^{\circ}\mathrm{C}^{-1}$ units.

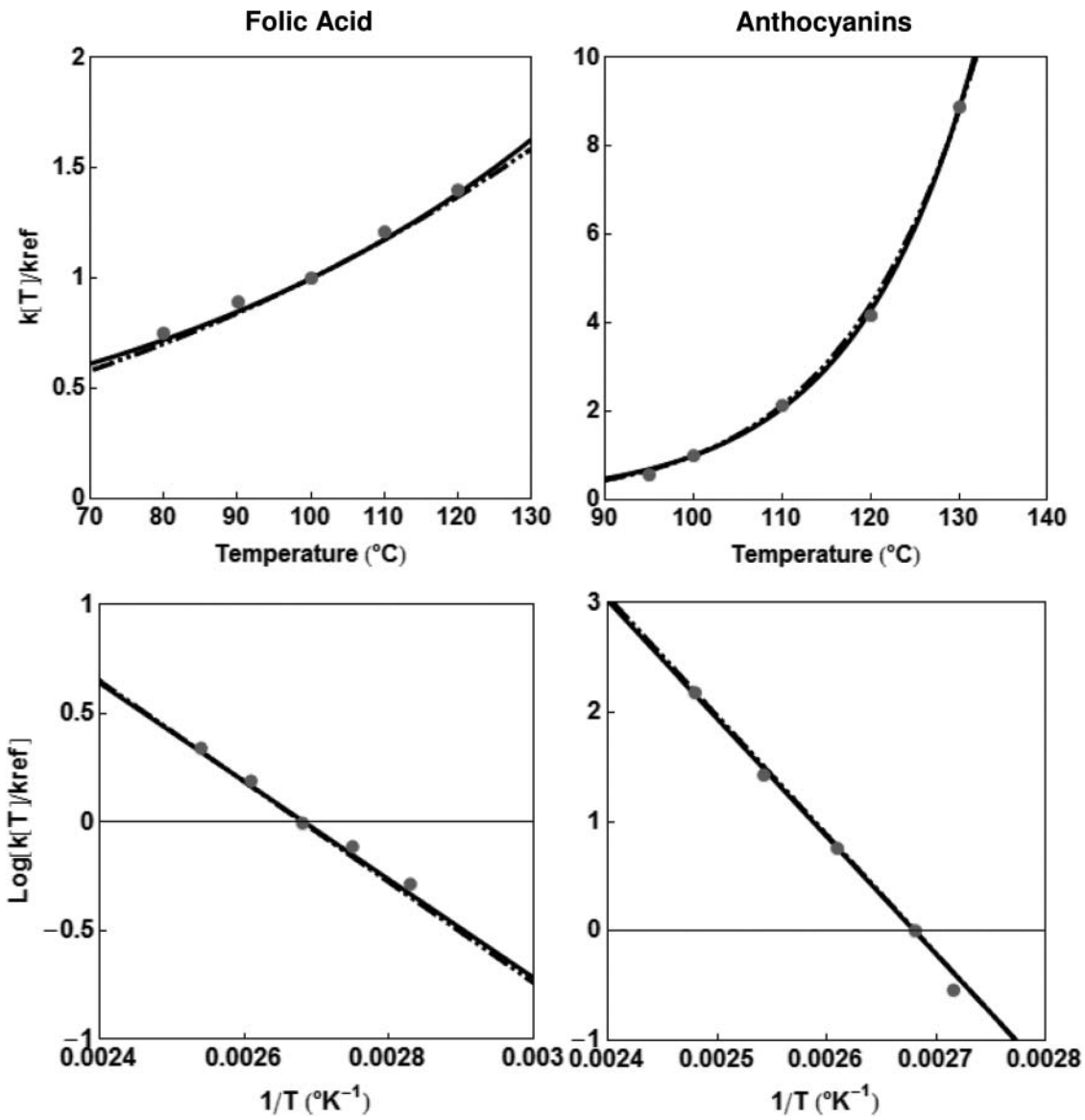

Figure 12 The fit of the traditional Arrhenius, "generalized" Arrhenius, with $b = 250$ and 300°C, and exponential model to kinetic data of folic acid and anthocyanin thermal degradation. The original data are from Nisha et al. (2005) and Verbeyst et al. (2010), respectively. Notice that for all practical purposes the three models could be used interchangeably. The regression parameters are listed in Table 2.

In addition to not having an inflection point, the exponential model also implies, by definition, that at $T = T_{ref}$, $\mathrm{Ln}[k(T)/k(T_{ref})] = 0$. And, as in the Arrhenius equation, if $T > T_{ref}$, $\mathrm{Ln}[k(T)/k(T_{ref})] > 0$, and if $T < T_{ref}$, $\mathrm{Ln}[k(T)/k(T_{ref})] < 0$. Unlike in the Arrhenius model, Eq. (12) entails that $k(T) \rightarrow 0$ when $T \rightarrow -\infty$, which has no physical meaning. In contrast with the Arrhenius equation, the exponential model, having no inflection point, implies that as $T \rightarrow \infty$, $k(T) \rightarrow \infty$, that is, that the rate can rise indefinitely. According to Eq. (13), the plot of $\mathrm{Ln}[k(T)/\ k(T_{ref})]$ vs. T- T_{ref} should be a straight line passing through the origin and having a slope c. As shown in Fig. 3, the plot of $\mathrm{Ln}[k(T)/\ k(T_{ref})]$ vs. T will have the same slope but will cross the T-axis at $T = T_{ref}$.

From a purely formalistic viewpoint, the use of the Arrhenius model can become problematic at very high temperatures while the exponential model at very low ones. However, the temperatures at the extreme ends of the scale, are either well above those to which foods are exposed even during heat processing or well below those to which foods are exposed during cold storage and freezing. Hence, this theoretical issue need not be of concern when either model is used to describe the kinetics of food processes at temperatures around the reference temperature. Also, notice that the traditional log-linear (D & z) model used in microbial and enzymes inactivation can be viewed as a special case of the exponential model for first order kinetics, in which case $c = \mathrm{Ln}[10^{(T - Tref)/z}]/(T - T_{ref})$.

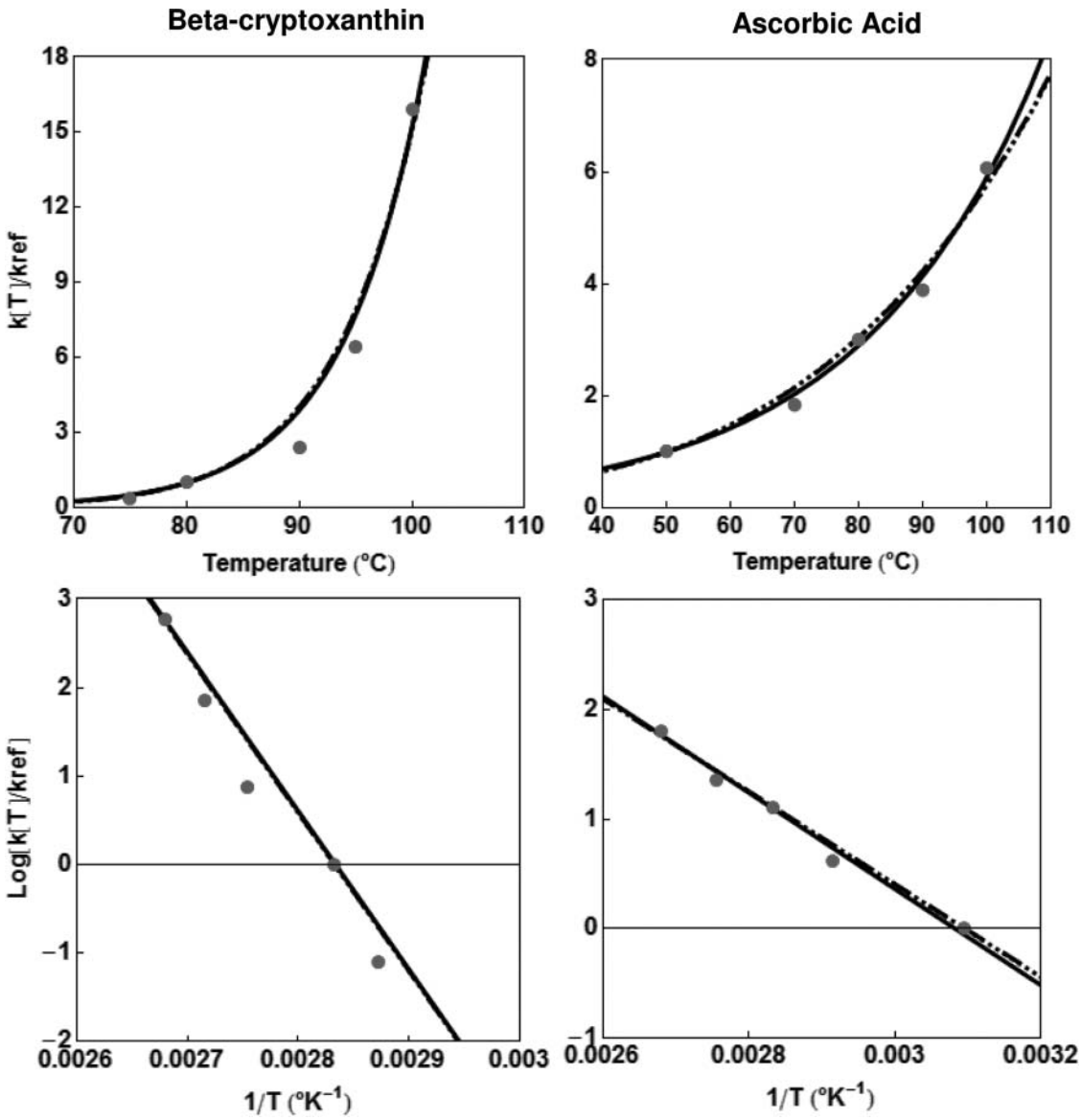

Figure 13 The fit of the traditional Arrhenius, "generalized" Arrhenius, with $b = 250$ and 300°C, and exponential model to kinetic data of betacryptoxanthin and ascorbic acid. The original data are from Dhuique-Mayer et al. (2007). Notice that for all practical purposes the three models could be used interchangeably. The regression parameters are listed in Table 3.

Comparison of the Arrhenius and Exponential Models' Fit to Classical Kinetic Data

Examples of the two model's fit to classical rate vs. temperature data are shown in Figs. 4 to 7, with the regression parameters listed in Table 1. The data have been retrieved from a compiled collection posted on the Internet by Professor Carmen Giunta of Le Moyne College in Syracuse, NY (see http://web.lemoyne.edu/~giunta/classicalcs/arrkin.html). The data are used with Professor Giunta's permission, which is gratefully acknowledged. The figures and other plots not included clearly show that the fit of both the Arrhenius (Eq. 11) and exponential (Eq. 12) models to the data is almost perfect, regardless of the reaction type, the temperature range covered, and the chosen reference temperature. In other words, the two models, despite their different mathematical construction could be used interchangeably for all the data sets examined. The figures show that a similar excellent fit and linear Arrhenius-Type Plot could also be obtained whenever the parameter b in Eq. (10) has been assigned a value other than 273.16°C, as long as it was larger than about 200°C. In light of the very small scatter in the classical experimental data, the excellent fit of the two models cannot be explained as being a statistical fluke. To demonstrate the truth of this statement we have written a program in Mathematica® (Wolfram Research, Champaign IL) that generates data with the "generalized Arrhenius equation" (Eq. 11) and fits them with the exponential model (Eqs. 12 or 13) and vice versa. The program has been posted on the

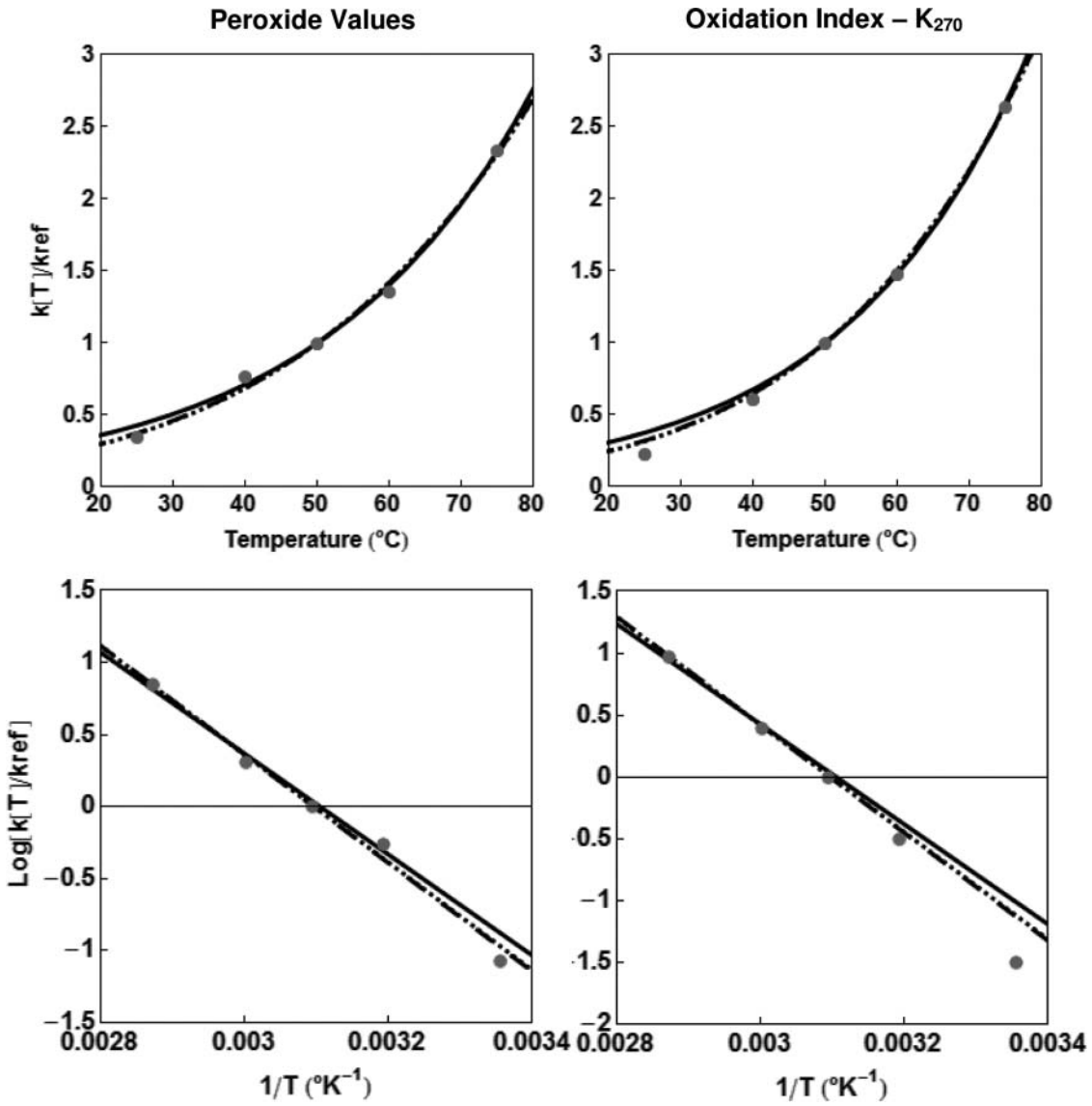

Figure 14 The fit of the traditional Arrhenius, "generalized" Arrhenius, with $b = 250$ and 300°C, and the exponential model to kinetic data of lipid oxidation. The original data are from Gomez-Alonso et al. (2004). Notice that for all practical purposes the three models could be used interchangeably. The regression parameters are listed in Table 3.

Web as a freely downloadable Wolfram Demonstration (http://demonstrations.wolfram.com/ArrheniusVersusExponentialModelForChemicalReactions/). It allows the user to choose and modify the parameters of the two models, the number of generated points, the reference temperature, and the temperature range by moving sliders on the screen. Examples of screen displays of the Demonstration in its two modes, Arrhenius equation vs. the exponential model and the exponential model vs. the Arrhenius equation, are shown in Figs. 8 and 9. The simulations, which the reader can repeat, have shown that there is a wide range of parameter and temperature combinations where the fit, had it been solely judged by statistical criteria, would be considered excellent. Since the generated data had no scatter at all, the agreement between the models ought to be attributed to their mathematical properties. One can surmise that had the analyzed records had scatter, the distinction between the fit of the two models would have been even more difficult (see below). The source of the agreement between the two models is revealed in the series expansion of the generalized Arrhenius equation around T_{ref}:

$$Ln\left[\frac{k(T)}{k\left(T_{ref}\right)}\right]=a\left[\frac{T-T_{ref}}{(T_{ref}+b)^2}-\frac{(T-T_{ref})^2}{(T_{ref}+b)^3}+\frac{(T-T_{ref})^3}{(T_{ref}+b)^4}-\frac{(T-T_{ref})^4}{(T_{ref}+b)^5}+\frac{(T-T_{ref})^5}{(T_{ref}+b)^6}-\ldots\right] \quad (14)$$

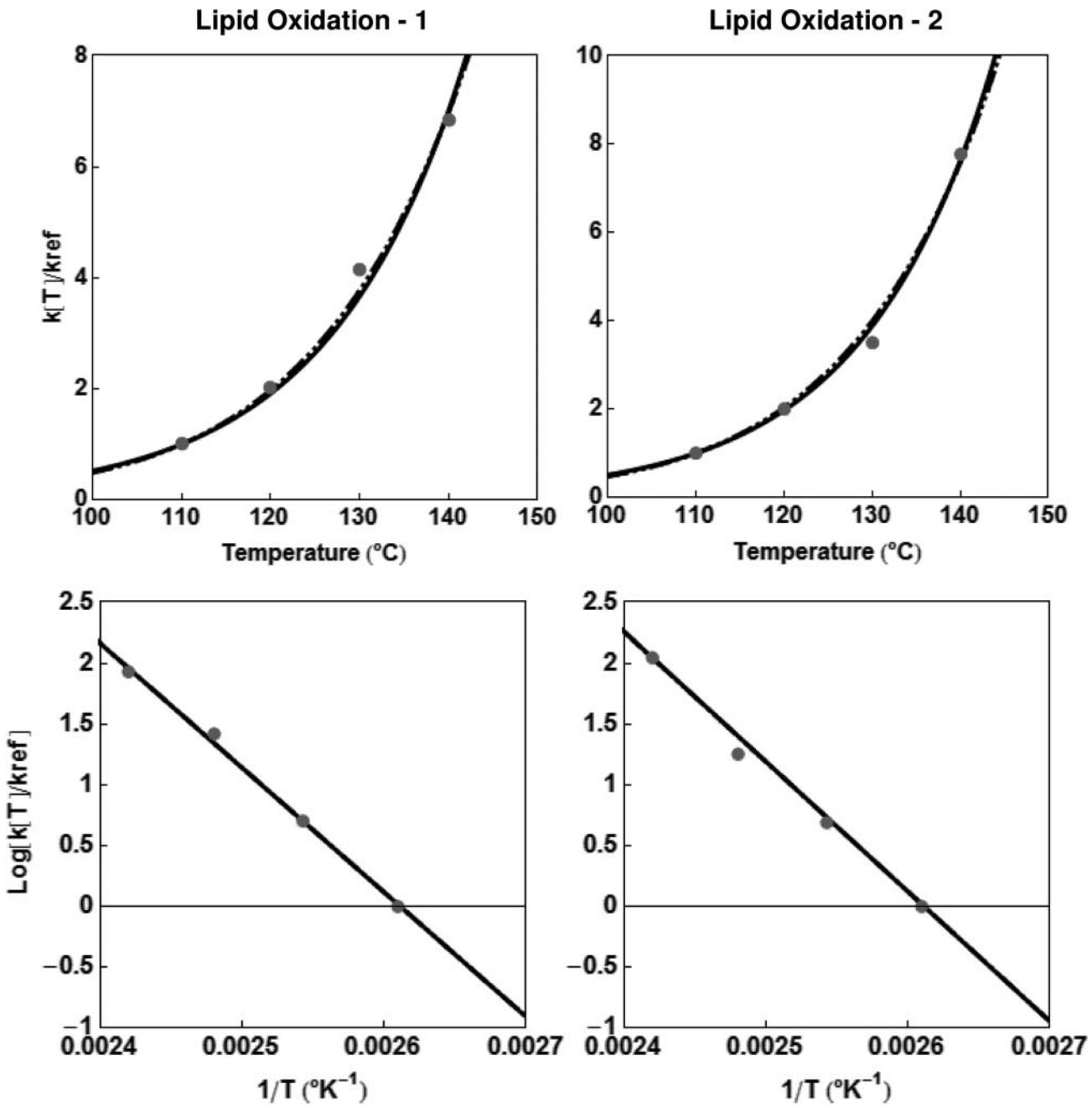

Figure 15 The fit of the traditional Arrhenius, "generalized" Arrhenius, with $b = 250$ and 300°C, and exponential model to kinetic data of lipid oxidation. The original data are from Tan et al. (2001). Notice that for all practical purposes the three models could be used interchangeably. The regression parameters are listed in Table 3.

Since the sum of the terms on the right side of the equation starting with the second is in many cases considerably smaller than the value of the first term, especially where b is much larger than T_{ref}, Eq. (14) can be written as the rough approximation:

$$Ln\left[\frac{k(T)}{k\left(T_{ref}\right)}\right] \approx a\left[\frac{T - T_{ref}}{(T_{ref} + b)^2}\right] \tag{15}$$

But this approximation is the exponential model's equation (Eq. 13) where

$$c \approx \frac{a}{(T_{ref} + b)^2} \tag{16}$$

or

$$a \approx c(T_{ref} + b)^2 \tag{17}$$

Table 3 The fit of the exponential model (Eq. 13), the traditional and generalized versions of the Arrhenius model (Eq. (11) with $b = 273.16^\circ$ and $b \neq 273.16^\circ$) to food systems

System	Temp. range (°C)	T_{ref} (°C)	Model	Equation	r^2	MSE	Figure	Data Source*
Chlorophyll	100–145	115	Exponential	13	0.9914	0.043	11	Canjura
			Arrhenius	1	0.9938	0.031		et al. (1991)
			Generalized Arrhenius ($b = 250^\circ$C)	11	0.9939	0.031		
			Generalized Arrhenius ($b = 300^\circ$C)	11	0.9938	0.032		
Chlorophyllide	80–115	100	Exponential	13	0.9953	0.008	11	Canjura
			Arrhenius	1	0.9972	0.005		et al. (1991)
			Generalized Arrhenius ($b = 250^\circ$C)	11	0.9971	0.005		
			Generalized Arrhenius ($b = 300^\circ$C)	11	0.9973	0.005		
Folic acid	80–120	100	Exponential	13	0.9999	0.001	12	Nisha et al. (2005)
			Arrhenius	1	0.9981	0.002		
			Generalized Arrhenius ($b = 250^\circ$C)	11	0.9982	0.002		
			Generalized Arrhenius ($b = 300^\circ$C)	11	0.9986	0.002		
Anthocyanins	95–130	100	Exponential	13	0.9997	0.007	12	Verbeyst
			Arrhenius	1	0.9992	0.017		et al. (2010)
			Generalized Arrhenius ($b = 250^\circ$C)	11	0.9991	0.018		
			Generalized Arrhenius ($b = 300^\circ$C)	11	0.9994	0.016		
betacryptoxanthin	75–100	80	Exponential	13	0.9818	1.10	13	Dhuique-Mayer
			Arrhenius	1	0.9775	1.36		et al. (2007)
			Generalized Arrhenius ($b = 250^\circ$C)	11	0.9771	1.38		
			Generalized Arrhenius ($b = 300^\circ$C)	11	0.9778	1.34		
Ascorbic Acid	50–100	50	Exponential	13	0.9973	0.035	13	Dhuique-Mayer
			Arrhenius	1	0.9944	0.073		et al. (2007)
			Generalized Arrhenius ($b = 250^\circ$C)	11	0.9947	0.069		
			Generalized Arrhenius ($b = 300^\circ$C)	11	0.9941	0.077		
Peroxide Value	25–75	50	Exponential	13	0.9983	0.003	14	Gomez Alonso
			Arrhenius	1	0.9984	0.003		et al. (2004)
			Generalized Arrhenius ($b = 250^\circ$C)	11	0.9984	0.003		
			Generalized Arrhenius ($b = 300^\circ$C)	11	0.9985	0.003		
Oxidation Index K_{270}	25–75	50	Exponential	13	0.9965	0.007	14	Gomez Alonso
			Arrhenius	1	0.9985	0.003		et al. (2004)
			Generalized Arrhenius ($b = 250^\circ$C)	11	0.9986	0.003		
			Generalized Arrhenius ($b = 300^\circ$C)	11	0.9984	0.003		
Peroxide value 1	110–140	110	Exponential	13	0.9946	0.093	15	Tan et al.(2001)
			Arrhenius	1	0.9968	0.056		
			Generalized Arrhenius ($b = 250^\circ$C)	11	0.9969	0.054		
			Generalized Arrhenius ($b = 300^\circ$C)	11	0.9967	0.058		
Peroxide value 2	110–140	110	Exponential	13	0.9972	0.054	15	Tan et al.(2001)
			Arrhenius	1	0.9952	0.092		
			Generalized Arrhenius ($b = 250^\circ$C)	11	0.9951	0.095		
			Generalized Arrhenius ($b = 300^\circ$C)	11	0.9952	0.089		

Therefore, it is no wonder that the Arrhenius and exponential models can be used interchangeably at temperatures around T_{ref}. It can also be shown that the larger the value of b, the closer is the value of c estimated with Eq. (16), or the value of a estimated with Eq. (17), to the value calculated by nonlinear regression. Examples are given in Figs. 9 and 10 and in Table 2. All this suggests that the common observation of the Arrhenius model's fit to kinetic data in foods and biological systems might have more to do with the high b value (273.16°) used in the °C to °K conversion than to the existence of a temperature independent "energy of activation" as has been traditionally assumed. This issue, as has been repeatedly stated in this work, can only be resolved by direct determination of the "energy of activation" and its comparison with that inferred from the Arrhenius plot. Until this is done, one cannot dismiss the alternative explanation that the rise of a reaction or process's rate with temperature merely follows an exponential model, and that the Arrhenius model's fit stems from the fact that 0°C happens to be 273.16°K, a relatively large number when compared with commonly chosen reference temperatures. If this hypothetical alternative is correct, then at least in foods and biological systems, the relationship between the Arrhenius plot's slope and the "energy of activation" would be unclear.

Comparison of the Arrhenius and exponential Models' Fit to Kinetic Data In Foods

Figures 11–15 show the fit of the Arrhenius equation and exponential model to kinetic data published in the food literature. The regression parameters are listed in Table 3. The figures and table demonstrate that whenever the Arrhenius equation

fits the data, so does the simpler exponential model and with a comparable degree of fit as judged by the regression coefficient r^2 and mean square error (MSE). The figures and table also demonstrate that inserting a sufficiently large b value into Eq. (11), 250, or 350°C in the examples given, results in an Arrhenius plot that is almost perfectly linear and creates excellent agreement between the exponential and generalized Arrhenius models. This observation raises a fundamental theoretical question: Can the reactivity and stability of molecules and enzymes in a food medium, especially solid, or the heat resistance of microbial cells and spores, be affected by the absolute temperature in the same manner as free simple molecules in a gas under low pressure or a dilute solution? If not, and this might well be the case, the reason for the frequently observed fit of the Arrhenius model to experimental temperature-rate data might be the incidental value of absolute zero being -273.16°C. If so, the much simpler exponential model is by far, more convenient and its use will eliminate the need to assume the existence of a temperature-independent "energy of activation" and the invocation of the "mole" unit and Universal Gas Constant in systems where their relevance is not at all obvious.

CONCLUDING REMARKS

The Arrhenius Equation has been widely used in food research as a means to quantify the temperature effect on the rates of a variety of chemical and biochemical reactions and of the growth and inactivation of microorganisms. It has also been used to create a linear Arrhenius Plot in order to extract the process's "energy of activation," E_a, from its slope. This "energy of activation" has found a wide range of uses in food technology. Examples are calibration of time-temperature integrators (TTI's), extrapolation of accelerated storage data, shelf life assessment, and sterility calculations in thermal processing.

The validity of the Arrhenius equation as a temperature dependence model has been so trusted that the "energy of activation" has been frequently calculated from plots based on only 3-4 temperatures, and without any attempt to confirm the value by an independent test. Upon scrutiny, however, the applicability of the Arrhenius model to food systems kinetics has several serious problems, conceptual and practical. Examples of the first kind are: What is a "mole of bacterial cells"? How can the Universal gas constant be linked to a multi-step chemical or biochemical reactions in a solid? Can E_a be temperature independent in a complex process occurring in a continuously changing physical and chemical environment? Examples of practical issues are: How can one identify the applicable temperature range where the reaction or process has optimal or threshold temperature? Can the Arrhenius model be used for extrapolation in order to predict the shelf life of foods and if so, how accurate will the predictions be if the kinetics is nonlinear?

In light of the Arrhenius model's conceptual problems and practical deficiencies when applied to biological systems, one wonders why it has survived for so long. It is also very surprising that the Arrhenius model continues to be taught in food science, food microbiology, and food engineering courses, and to appear in textbooks without expressed reservation or cautionary notes.

The initial appeal of the Arrhenius model can be well understood. In "pre-computer times," there was a premium on mathematical models that could be written in a linear form. This allowed the coefficients of such models to be determined graphically or by linear regression using mechanical desk calculators. But this advantage is hardly relevant today when non-linear regression is a standard option in commercial mathematical and statistical software. Moreover, it has been demonstrated in this work, that many $k(T)$ vs. T relationships, which were originally used to establish the traditional Arrhenius model can also be described by the simpler exponential model (Eqs. 12 and 13) without sacrificing the goodness of fit. The same has been observed in reported $k(T)$ vs. T relationships determined in foods. The use of this alternative model, where applicable, or of similar more elaborate models if needed, will eliminate the unnecessary compression and inversion of the temperature scale that the Arrhenius model requires. They will also eliminate the need to assume the existence of a temperature-independent energy of activation in cases where its physical reality is questionable or where its value as determined by the Arrhenius model has never been confirmed independently. The comparable fit of the simpler exponential model to experimental data raises the specter that the widely reported "success" of the Arrhenius equation might be primarily due to its mathematical construction rather than to the validity of the assumptions on which it is based. Consequently, the mere fit of the Arrhenius model, which was originally derived for reactions between gas molecules or molecules in solution, should not be used in lieu of its independent validation, especially in complex foods and biological systems.

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