COMPREHENSIVE REVIEWS IN FOOD SCIENCE AND FOOD SAFETY

Kinetic Modeling of Food Quality: A Critical Review

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ABSTRACT: This article discusses the possibilities to study relevant quality aspects of food, such as color, nutrient content, and safety, in a quantitative way via mathematical models. These quality parameters are governed by chemical, biochemical, microbial, and physical changes. It is argued that the modeling of such quality aspects is in fact kinetic modeling. Therefore, attention is paid to chemical kinetics, and its possibilities and limitations are discussed when applied to changes occurring in foods. The discussion is illustrated with examples from the literature. A major difficulty is that principles from chemical kinetics are strictly speaking only valid for simple elementary reactions, and foods are all but simple. Interactions in the food matrix and variability are 2 complicating factors. It is discussed how this difficulty can be tackled, and research priorities are suggested to come to better models in food science, and thereby to a better control of food quality.

Introduction

Food quality is obviously an important issue. Quality in a very broad sense means satisfying the expectation of the consumer; in other words, quality experience delivered by a food should match quality expectations of a consumer. Though not the topic of this article, the link with the consumer should not be forgotten. This aspect is discussed, for instance, by Saguy and Moskowitz (1999), van Boekel (2005), and Linnemann and Van Boekel (2007). Here, we will focus more on the quantitative modeling of indicators for quality. Incorporating quality into product and process design is the big challenge for a food manufacturer. Product and process designs need to be flexible these days for several reasons, and reaching quality by trial and error does not seem the best way anymore. A more systematic way is by use of modeling; in fact, one could think of the design process as being simulated in a virtual lab using quantitative models. Modeling can be done on several levels. This article concentrates on kinetic modeling. Other types of modeling are also important in food design, such as response surface models and multivariate statistical tools. A useful reference for these aspects is Hu (1999); the topic will not be discussed here.

For the purposes of this review, we assume that we have an idea about the desired quality and that we can decompose that into manageable quality indicators, and our task is to see if and how we can model these. That is to say, we are looking for mathematical models that describe the fate of quality indicators as a function of conditions in the food chain. Examples of such indicators could be color, presence or absence of certain flavor compounds, presence or absence of certain microorganisms, texture, vitamins, protein composition, and so on. Building mathematical models with which we can simulate such quality indicators requires knowledge of food science and nutrition, as well as of modeling. First, it is essential to know what to model and for what purpose. It makes a difference whether a model is used to gain scientific insight in food properties, or whether it will be used to predict quality upon manufacturing a food. We will come back to this while discussing some applications.

The first thing a food technologist would tend to do is to relate quality changes to chemical and physical processes taking place in the food. We start, therefore, with a short overview of key reactions that have an effect on quality. After that we give a general description of models and some possible applications. The goal of this article is to critically evaluate food quality models, how good they are, how they can be integrated in engineering models, and to show what the needs are for further work in this area.

Reactions in Foods That Affect Quality

Quality indicators are not constant: the quality of a food changes over time. The most important quality-related changes are:

- Chemical reactions, mainly due to either oxidation or Maillard reactions.
- Microbial reactions: microorganisms can grow in foods; in the case of fermentation this is desired, otherwise microbial growth will lead to spoilage and, in the case of pathogens, to unsafe food.
- Biochemical reactions: many foods contain endogenous enzymes that can potentially catalyze reactions leading to quality

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loss (enzymatic browning, lipolysis, proteolysis, and more). In the case of fermentation, enzymes can be exploited to improve quality.
- Physical reactions: many foods are heterogeneous and contain particles. These particles are unstable, in principle at least, and phenomena such as coalescence, aggregation, and sedimentation lead usually to quality loss. Also, changes in texture can be considered as physical reactions, though the underlying mechanism may be of a chemical nature.

Foods are unstable in the thermodynamic sense. This means that they have the tendency to change from a low-entropy, high enthalpy state to a high-entropy, low enthalpy state. Food technology is in fact a battle against this thermodynamic instability. However, there are barriers to overcome this tendency so that foods can be in a kinetically stable state (without such barriers life would be impossible!). Thermodynamics indicate the direction of change but not the rate at which this occurs, which is why we need kinetics. The models that are used in quality change modeling are therefore kinetic models, describing degradation of compounds (such as vitamins), formation of undesired compounds (such as acrylamide), kinetics of aggregation in texture formation, kinetics of inactivation of enzymes and microorganisms, and kinetics of crystallization and sedimentation. When models are developed to describe quality changes, it must be acknowledged that foods are very complex, and that many interactions may occur. For instance, the growth of microorganisms may lead to pH changes, which in turn may have consequences for chemical reactions if they are acid-catalyzed. Nevertheless, models can help in controlling and predicting food quality attributes and their changes.

Table 1 gives an overview of the most important reactions in foods. General references are Fennema (1996), Owusu-Apenten (2005) for chemical reactions, Whitaker and others (2003) for biochemical reactions, Walstra (2003) for physical reactions, while Jay and others (2005) is a reference for microbial reactions. Some reviews on kinetics of quality changes in food are by Hindra and Baik (2006), van Boekel and Walstra (1995), and van Boekel (2007).

Another way to look at reactivity and consequences for quality is to look at the various ways in which the main components in foods can react (Table 2).

These tables indicate that quality indicators may be affected in many ways. When models are proposed, one should be aware of possible interactions. In many cases, model parameters will in fact embed all kinds of confounding factors. As long as this is realized, that is not a severe problem, but if one wants to draw conclusions in chemical and physical terms, there could be a serious problem when making predictions and extrapolations; some examples will be shown.

Kinetic Modeling of Food Quality Attributes

The previous section suggested that chemical, biochemical, microbial, and physical quality changes can be tackled by kinetics. Kinetic modeling implies that changes can be captured in mathematical models containing characteristic kinetic parameters, such as activation energies and rate constants. Before discussing this, let us take a closer look at the purpose of modeling. Following Haefner (2005), modeling in science can serve 3 goals: understanding, prediction, and control. As for understanding, modeling is a tool in applying the scientific method, and in that sense it can contribute to our understanding of the chemistry and physics taking place in the studied food. If this is the intention of kinetic modeling, it makes sense to make a link to the thermodynamics and chemical kinetics. This will then yield insight in the mechanisms of reactions at the molecular level and results in fundamental kinetic parameters such as activation energies, enthalpies, and entropies. Thus, kinetic modeling of changes in foods can lead to a better understanding at the molecular level of what we observe in foods. There is, however, a pitfall here. Connecting to fundamental reaction mechanisms and associated kinetic parameters yields parameters that are only valid for elementary reactions in simple, usually dilute, ideal systems. Foods are all but dilute, ideal systems, and the observed changes may be due to many interacting, complex reaction mechanisms rather than a single elementary step. One of the ways to get around this problem in food science is that simplified model systems are used rather than real foods. While this indeed can contribute significantly to scientific understanding, it is not straightforward to translate such results to real foods, and it is really necessary to adapt the model systems to specific food properties if one wants to make this translation (Wedzicha and others 1993). As for the prediction and control purposes of modeling, this serves more an engineering goal. The difference between prediction and control is that prediction implies a quantitative prediction of the future state of a food, based upon knowledge of the food and the processing steps that are applied. Control, on the other hand, implies that we set processing conditions and food properties in such a way that a desired outcome (say, a certain desired quality) is realized. If we can use kinetic models based on fundamental scientific insight for prediction and control purposes of changes taking place in real foods, this would be the most ideal situation. However, the question is whether this is possible with our current state of knowledge. Foods are so incredibly complex that there is a real danger in applying models directly to food when these models are based on fundamental reactions studied in model systems. The alternative is, of course, to study kinetics directly in real foods. The price to be paid then is that the derived parameters cannot immediately be interpreted as they would be in well-defined dilute ideal systems. In other words, the derived models are empirical,

Table 1—Overview of reactions in foods affecting quality (adapted from van Boekel 2007).

Example	Type	Consequences
Nonenzymatic browning	Chemical reaction (Maillard reaction)	Color, taste and aroma, nutritive value, formation of toxicologically suspect compounds (acrylamide)
Fat oxidation	Chemical reaction	Loss of essential fatty acids, rancid flavor, formation of toxicologically suspect compounds
Fat oxidation	Biochemical reaction (lipoxygenase)	Off-flavors, mainly due to formation of aldehydes and ketones
Hydrolysis	Chemical reaction	Changes in flavor, vitamin content
Lipolysis	Biochemical reaction (lipase)	Formation of free fatty acids, rancid taste
Proteolysis	Biochemical reaction (proteases)	Formation of amino acids and peptides, bitter taste, flavor compounds, changes in texture
Enzymatic browning	Biochemical reaction of polyphenols	Browning
Separation	Physical reaction	Sedimentation, creaming
Gelation	Combination of chemical and physical reaction	Gel formation, texture changes

Table 2—Reactions of key components in foods (adapted from van Boekel 2007).

Component	Reaction	Consequences
Proteins	Denaturation	Gelation, precipitation, solubility, inactivation of antinutritional factors (ANFs)
	Hydrolysis	Formation of peptides and amino acids, texture changes
	Deamidation	Loss of charge and change in reactivity
	Maillard reaction	Crosslinking, loss of nutritional value, browning
Lipids	Oxidation	Loss of essential fatty acids, rancidity
	Fat hardening	Formation of trans fatty acids
	Hydrolysis (usually enzymatically)	Formation of free fatty acids, leading to a soapy off-flavor
Mono- and disaccharides	Maillard reaction	Nonenzymatic browning.
	Caramelization	Taste and flavor changes
	Hydrolysis	Sugar inversion
Polysaccharides	Hydrolysis (enzymatically during ripening, chemically during cooking)	Softening of tissue, texture changes
	Physical interaction with other components	Gelation, phase separation
	Gelatinization and retrogradation of starch	Staling of bread
Polyphenols	Enzymatic polymerization	Browning
	Interaction with proteins	Crosslinking, gelation
Vitamins	Oxidation	Loss of nutritional value

or at best semi-empirical. As long as one is aware of this, there is not a real problem and one can use such models especially for prediction and control purposes. However, as with all (semi) empirical models, one should be very cautious in applying such models outside the parameter region on which the models are based.

The goal of fundamental and empirical models alike is to state something quantitatively. Mathematical models consist of equations that provide an output (such as vitamin content) based on a set of input data (for example, time, temperature). It is a concise way to express physical behavior in mathematical terms. Modeling as such is not new in food technology. One of the earliest models was developed in the 1920s to predict the inactivation of microorganisms as a function of heating time and temperature, the so-called Bigelow model, which is effectively a 1st-order model, to be discussed subsequently. This model has been of great help in optimizing processes for the sterilization of foods, especially in the canning industry. Every food technologist is familiar with the *D*- and *Z*-values that are used in this model. Incidentally, this model has been criticized recently and new models have been proposed (van Boekel 2002; Peleg 2006a, 2006b). Also, the incorporation of the Bigelow model in a process model has been updated recently (Simpson and others 2003).

As argued previously, modeling food quality attributes means modeling changes: the quality of a food nearly always changes over time. Food quality modeling is therefore almost synonymous with kinetic modeling. The consequence is that differential equations frequently form the basis for mathematical models; these can sometimes be solved analytically, but if not it is relatively easy nowadays to solve them numerically with the available software, or even using spreadsheets. A few examples of chemical, biochemical, physical, and microbial phenomena are given below.

Modeling chemical reactions

Suppose we have a reaction between 2 molecules A and B, which yield 2 products P and Q:

$$A + B \rightarrow P + Q \tag{1}$$

The rate r is then defined as:

$$r = -\frac{d[A]}{dt} = -\frac{d[B]}{dt} = \frac{d[P]}{dt} = \frac{d[Q]}{dt} = k[A][B] \tag{2}$$

The proportionality constant k is the so-called rate constant. For molecules to react, they must first come together, and this happens via diffusion. If the encounter frequency is rate limiting, a reaction is called diffusion limited, which implies that the reaction itself takes place very rapidly. This is the case for acid-base reactions and radical reactions, for instance. The bimolecular rate constant for such a case is:

$$k_{dif} = \frac{8 \cdot 10^3 RT}{3\eta} \quad (dm^3/mol/s) \tag{3}$$

R is the gas constant (J/mol/K), T absolute temperature (K), η the viscosity of the solution (Pa s). If we take Eq. 3 as the measure for the fastest bimolecular reaction possible, it is found that for $\eta = 1$ mPas (viscosity of water at 20 °C) $k_{dif} = 6.6 \times 10^9$ dm^3/mol/s and at 100 °C $k_{dif} = 3 \times 10^{10}$ dm^3/mol/s. These should be roughly the upper limits for *bimolecular* reaction rate constants in aqueous solutions at the temperature indicated. The effect of temperature on the encounter rate is incorporated via the effect of temperature on the viscosity of the solvent.

In most cases, however, the actual reaction step will be rate limiting rather than the encounter rate. Instead of using Eq. 2 we move to the most simple equation possible, the so-called general rate law, which is for a single reactant at concentration c:

$$r = -\frac{dc}{dt} = kc^n \tag{4}$$

This differential equation is thus in the form of a power law expression, where n is the so-called order of the reaction. The equation reflects the dependence of rate r on concentration for just 1 component; k is again the reaction rate constant. The unit for k for a reaction having order n is (dm^3/mol)$^{n-1}$/s. Equation 4 can be integrated with respect to time to obtain the course of the concentration as a function of time:

$$c^{1-n} = c_0^{1-n} + (n-1)kt \quad \text{for} \quad n \neq 1 \tag{5a}$$

$$c = c_0 \exp(-kt) \quad \text{for} \quad n = 1 \tag{5b}$$

c_0 is the initial concentration at $t = 0$.

Figure 1 shows a decomposition reaction for dimensionless scales and varying order, using Eq. 5a and 5b. It appears that no real distinction can be made between the models if the fractional conversion is less than, say, 20% to 30%. In other words, for a proper estimation of the order, one should conduct the experiment such that a considerable extent of reaction is reached. Proper experimental design is therefore of utmost importance; in this case it is the product $k \cdot t \cdot {c_0}^{n-1}$ that determines the extent of the reaction. If $t > 1/[(1\text{-}n){c_0}^{n-1}k]$ for $n < 1$, $c_t/c_0 = 0$, whereas for $n \geq 1$ c_t/c_0 approaches 0 asymptotically. It should also be noted that in a closed system a reaction order $n = 0$ cannot run indefinitely; the order will have to change at some point in time.

In the food science literature, quality changes are usually modeled by means of a zero-, 1st-, or 2nd-order reaction, as pioneered by Labuza (summarized in Labuza 1984) and Karel (Saguy and Karel 1980). From Eq. 5a it follows that for $n = 0$ for a decomposition reaction:

$$-\frac{dc}{dt} = k \tag{6}$$

Integration leads to:

$$c = c_0 - kt \tag{7}$$

Zero-order reactions are rather frequently reported for changes in foods, especially for formation reactions when the amount of product formed is only a small fraction of the amount of precursors present, or for decomposition reactions where only a small amount of product is formed from a reactant. The reactant is then in such large excess that its concentration remains effectively constant throughout the observation period, and hence the rate appears to be independent of the concentration. A frequently reported example of a zero-order reaction is the formation of brown color in foods as a result of the Maillard reaction: see Figure 2. Color is the quality indicator here.

The kinetics of Maillard-type browning is rather intricate, and it is just fortuitous that a zero-order reaction equation fits. A much more detailed analysis of the kinetics of the Maillard reaction is given by Martins and van Boekel (2004, 2005). However, it depends on the purpose and application of a model which approach is the best. For scientific understanding, the multiresponse approach would give much more insight, whereas for a quick idea of color formation a zero-order model is much more effective and efficient.

First-order reactions are also frequently reported for reactions in foods. The equations for a degradation reaction for $n = 1$ are:

$$-\frac{dc}{dt} = kc \tag{8}$$

Integration leads to:

$$c = c_0 \exp(-kt) \tag{9}$$

(see also Eq. 5b). Frequently, the logarithmic form is used instead of the exponential equation:

$$\ln c = \ln c_0 - kt \tag{10}$$

The nonlinear Eq. 9 is thus transformed into the linear Eq. 10. An example of a food-related 1st-order reaction is shown in Figure 3. It concerns the heat-induced degradation of betanin, a natural color compound from red beets; betanin is thus the quality indicator here. Figure 3A shows the 1st-order plot for untransformed data according to Eq. 9, while Figure 3B shows the plot for logarithmically transformed data according to Eq. 10. A log plot resulting in a straight line is frequently taken as proof of a 1st-order reaction. The plot in Figure 3B indeed looks reasonably straight.

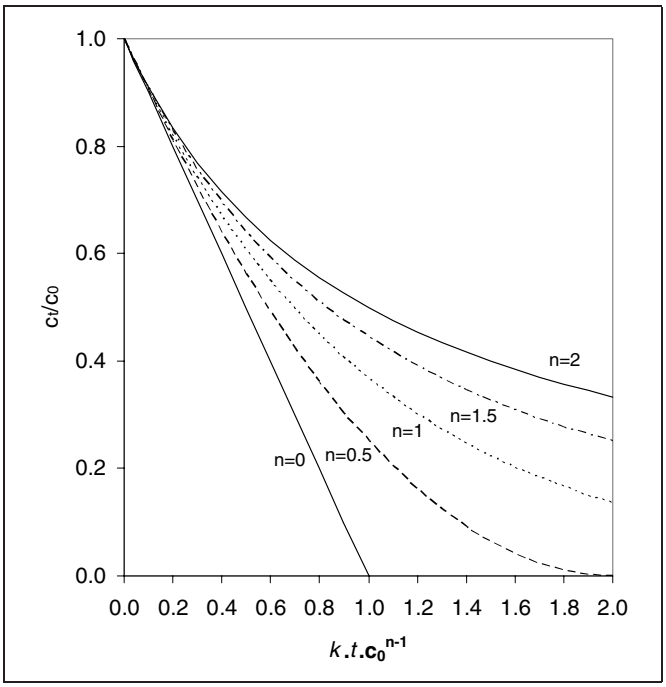

Figure 1—Decomposition of a component for a reaction having the same initial concentration and rate constant but a varying order *n*.

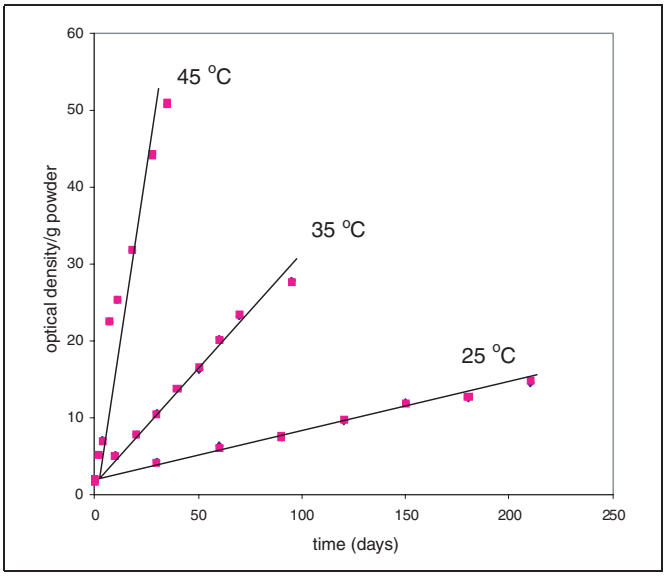

Figure 2—Example of a zero-order reaction reported for the nonenzymatic browning of whey powder (adapted from Labuza 1983).

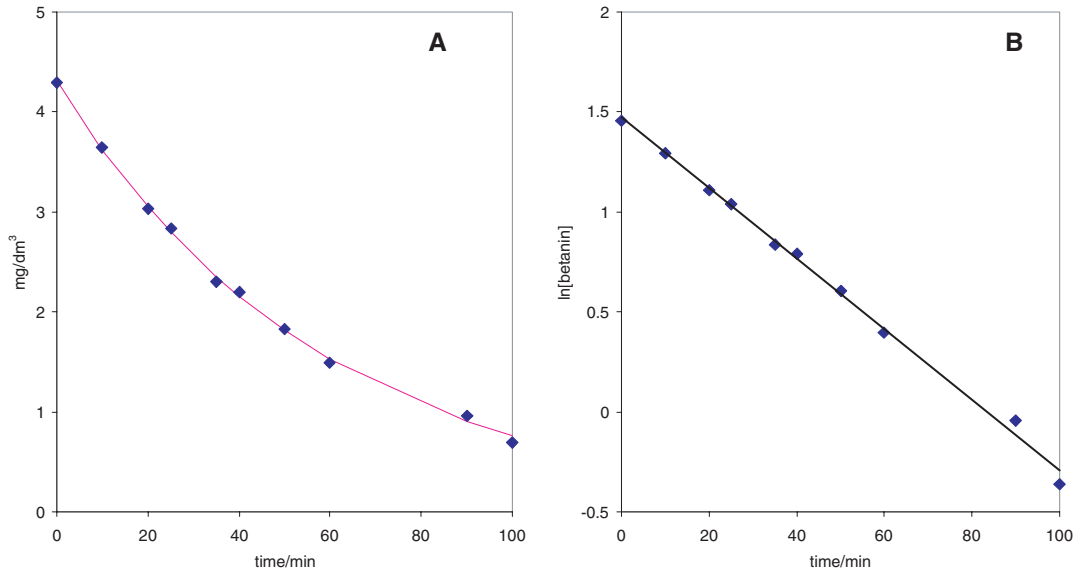

Figure 3—Example of a 1st-order reaction for the degradation of betanin at 75 °C. (A) Untransformed concentration and the fit according to a 1st-order reaction, Eq. 9 and (B) log-transformed data fitted by a linear line according to Eq. 10. Adapted from Saguy and others (1978).

While this may be done for a visual check, such a transformation should not be performed for estimating the rate constant, for statistical reasons. The problem is that upon transformation not only the data are transformed but also the error structure related to the data, and this may lead to bias in estimation because then some assumptions that underlie regression are violated (van Boekel 1995). With the available software nowadays, it is not a problem anymore to perform nonlinear regression. A remaining problem is that sometimes the error estimates resulting from nonlinear regression are nonsymmetric (van Boekel 1996), depending on the nonlinearity of the model and the quality of the data.

The equation for a 2nd-order reaction, $n = 2$, is:

$$-\frac{dc}{dt} = kc^2 \tag{11}$$

Integration leads to:

$$c = \frac{c_0}{1 + c_0 kt} \tag{12}$$

In its linearized form it reads:

$$\frac{1}{c} = \frac{1}{c_0} + kt \tag{13}$$

Second-order reactions are sometimes reported for changes of amino acids involved in the Maillard reaction. A case in point is the loss of lysine (bound in proteins, hence the ε-amino group of lysine) in sterilized milk due to the Maillard reaction; loss of lysine is the quality indicator for loss of quality here. According to the literature this is a 2nd-order reaction in lysine; namely, a plot of the inverse of [lysine] compared with time gives a straight line (Eq. 13): see Figure 4. Here also, there is a statistical caveat in transforming data by taking the inverse; one should use these plots only for visual examination, not for estimation of the parameters (van Boekel 1996). Incidentally, the actual mechanism of lysine loss is much more complicated than a relatively simple bimolecular reaction: apart from the initial condensation with lactose, there is regeneration of lysine (it acts as a catalyst), but subsequent further reaction of lysine residues also occurs with intermediate and advanced Maillard reaction products (Brands and van Boekel 2002). Again, it depends on the purpose or application which model should be used.

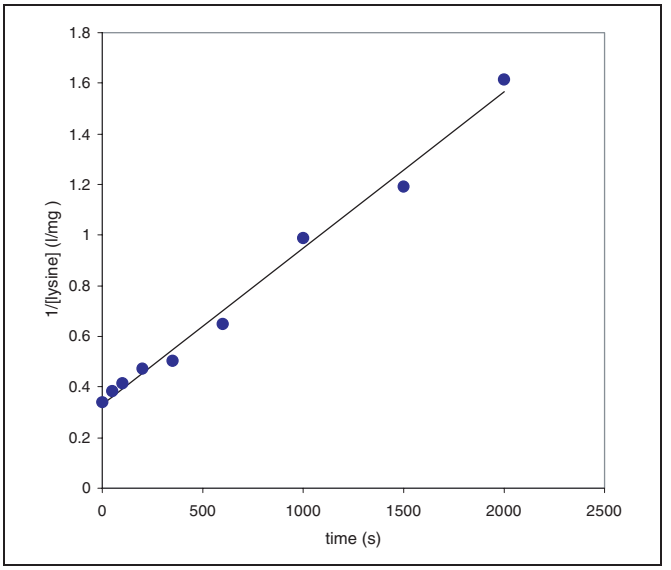

Figure 4—Lysine loss in milk heated at 160 °C plotted as 1/[lysine] compared with time according to a 2nd-order model (drawn line). Adapted from Horak (1980).

Second-order kinetics is reported in the food science literature not as frequently as one might perhaps expect. A likely reason is the following. If we take Eq. 1 and suppose that one of the reactants, say B, is present in excess, it follows that:

$$-\frac{d[A]}{dt} = k[A][B] = k'[A] \tag{14}$$

$$k' = k[B] \tag{15}$$

k' is called a pseudo 1st-order rate constant, which is constant as long as [B] does not change notably. This goes to show that the experimentally observed kinetics of a reaction does not necessarily correspond to the actual mechanism.

Even though simple kinetics are frequently applied in food science, reactions are usually much more complicated. Examples are fat oxidation and the Maillard reaction; they cannot be given in 1 simple equation; a network of linked reaction steps is more appropriate. Unraveling of such a network can be done by so-called multiresponse mechanistic modeling, as explained by Brands and van Boekel (2002), Martins and van Boekel (2004, 2005), and van Boekel (1999, 2000). Such models are very helpful in scientific explanations, probably less so for practical applications. There are also models proposed for color formation in the Maillard reaction that simplify reaction networks to a few critical steps (Leong and Wedzicha 2000; Mundt and Wedzicha 2003, 2007; Wedzicha and Roberts 2006).

Another critical remark is that there is often not a compelling theoretical reason to choose for a certain order of a reaction. In fact, in many cases reported in the literature the order is just a fit parameter. For this reason, it is recently proposed to consider alternative models that are just of an empirical nature (Corradini and Peleg 2006a, 2006b). Such models are not better or worse than the commonly used models of a certain order, and they are certainly worth considering, in the view of this article's author. In some cases, they might provide a better fit.

The previously given models are so-called deterministic models: they give always the same output when given the same input. In a sense, deterministic models are not realistic because the real world is not deterministic; there is always variability and uncertainty. Variability is inherent in the world we live in: biological materials are never completely the same as time progresses. Uncertainty reflects our state of knowledge about the system that we study. Variability is typical for a given system and it cannot be reduced, but uncertainty can be reduced by doing more and better measurements. In any case, it is important to account for variation and uncertainty. Therefore, stochastic models are introduced, such as for a 1st-order model:

$$c = c_0 \exp(-kt) + \varepsilon \tag{16}$$

The symbol ε reflects the error, or uncertainty, involved. In Eq. 16 it is an additive model. In some cases, multiplicative errors may be more appropriate, in which case a log transformation is actually needed (van Boekel 1996). The point to note is that variation can be modeled as well. The numerical value of parameters can be estimated from experimental data by means of regression. However, since experimental data always contain errors, the estimates will also contain error and, consequently, model predictions will be uncertain. It is therefore very important to always state an estimate of the errors involved. It makes no sense to report, for instance, an activation energy of 100 kJ/mol just like that. Such information is really useless if the uncertainty in the estimate is not supplied. We would interpret a value of 100 ± 90 completely different from a value reported as 100 ± 10 kJ/mol. Furthermore, it should be indicated how the error is reported: as standard deviation, standard error, or 95% confidence interval.

When the number of parameters in a model increases, the fit to a data set becomes better. The price to be paid for this is that the uncertainty in the parameter estimates also increases with the number of parameters, which is undesirable. It should be clear that the uncertainty in model *predictions* increases dramatically with increase in parameter uncertainty due to propagation of error (van Boekel 1996). Therefore, one should always strive for a model with the lowest number of parameters that still gives an acceptable fit. This is the so-called principle of parsimony, or Occam's razor. If more models seem to give a reasonable fit, model discrimination is a useful procedure. A useful discrimination tool is the so-called Akaike criterion, which uses the residual sums-of-squares of the various models but adds a penalty for the model that has more parameters (Burnham and Anderson 1998). Other model discrimination tools are the log-likelihood ratio and the Bayesian Information criteria. In relation to discrimination of kinetic models, the articles of Stewart and others (1996, 1998) are relevant. The use of R^2 as a model discrimination tool is discouraged (van Boekel 1995).

Modeling temperature dependence of chemical reactions

Arrhenius' law was empirically derived to describe the temperature dependence of simple chemical reactions. It has proven to be very worthwhile in chemical kinetics. It relates the rate constant k of a reaction to absolute temperature T:

$$k = A \exp\left(-\frac{E_a}{RT}\right) \tag{17}$$

The linearized form is:

$$\ln k = \ln A - \frac{E_a}{RT} \tag{18}$$

in which A is a so-called "pre-exponential factor" (sometimes called the frequency factor), E_a the activation energy, and R and T the gas constant and absolute temperature, respectively. The dimension of A should be the same as that of the rate constant k; it therefore does have units of frequency only in the case of a 1st-order reaction. The activation energy can be seen as the energy barrier that molecules need to cross in order to be able to react. The proportion of molecules able to do that increases with temperature, which qualitatively explains the effect of temperature on rates. Arrhenius' equation gives a quantitative account. The physical meaning of A is that it represents the rate constant at which all molecules have sufficient energy to react ($E_a = 0$). Incidentally, it is not a good idea to derive the activation energy parameters from linear regression of $\ln k$ compared with $1/T$ because of the transformation of data points with their errors by taking logarithms; rather, nonlinear regression should be used, as discussed previously. Another remark in this respect is that the 2-step procedure of first deriving rate constants and then regressing them versus temperature usually results in very wide confidence intervals if only 3 to 4 temperatures have been studied, as is frequently the case. As argued previously, the imprecision in parameters results in very imprecise predictions. A better approach is, therefore, to substitute the rate constant in the appropriate rate equations and perform a nonlinear regression (van Boekel 1996). For instance, for a 1st-order reaction this would be:

$$c = c_0 \exp\left[-A \exp\left(-\frac{E_a}{RT}\right) \cdot t\right] \tag{19}$$

In this way, all data are used at once to estimate the activation parameters and a much more precise estimate of these parameters is obtained. It probably remains a good idea to present Arrhenius' expression in the form of a plot of $\ln k$ or $\ln(k/T)$ compared with $1/T$ because any deviation of the data from these expressions becomes immediately apparent. In doing so, however, the values of the parameters estimated by nonlinear regression should be used to construct the plot. The 1st step should always be to check the validity of the law of Arrhenius, and only if it appears to be correct should the next step be the estimation of the activation parameters. Obvious as this may seem, this rule is not always

obeyed. It is essential to realize that the concept of activation energies is strictly speaking only valid for elementary reactions.

It is possible to reparameterize the Arrhenius equation; and it is actually desired from a statistical point of view because of the strong correlation between A and E_a (van Boekel 1996). A very simple reparameterization is to introduce a reference temperature T_{ref}. The basis for this arises from the application of Eq. 17 at 2 temperatures T_1 and T_2:

$$k_1 = A \exp\left(-\frac{E_a}{RT_1}\right)$$

$$k_2 = A \exp\left(-\frac{E_a}{RT_2}\right)$$

If one arbitrarily chooses a reference temperature, say $T_2 = T_{ref}$, one can combine these 2 equations, assuming that the pre-exponential factor and E_a do not depend on temperature:

$$\frac{k}{k_{ref}} = \exp\left[-\frac{E_a}{R}\left(\frac{1}{T} - \frac{1}{T_{ref}}\right)\right] \quad (20)$$

The actual result of this is that the pre-exponential factor A is replaced by a rate constant at some reference temperature k_{ref}. The reference temperature should preferably be chosen in the middle of the studied temperature regime.

It is perhaps instructive to consider the range of values that rate constants can take. Table 3 shows orders of magnitude for rate constants, depending on conditions. The very large effect of activation energy on the rate of a reaction is apparent. In fact, without activation barriers, reactions would be so fast that foods would spoil immediately.

There are also other Arrhenius-like equations proposed in the literature (Laidler 1987) that could be used just as well, but which are not commonly used. The following equation would do equally well as the Arrhenius equation:

$$k = A \exp\left(-\frac{B}{T}\right) \quad (21)$$

with A and B as fit parameters without a physical meaning. Although this seems undesirable, one has to realize that sometimes parameters do not really have a physical meaning. For instance, if one determines an activation energy for microbial inactivation, what does it mean if an activation energy of, say 300 kJ/mol, has been derived? A mole of bacteria is somewhat hard to envisage. It would actually be better to use Eq. 21 for phenomena that do show Arrhenius-like behavior but do not really reflect a defined chemical reaction. For instance, the effect of temperature on diffusivity can often be described using the Arrhenius equation, but there is no activation energy for molecular mobility (though there may be barriers), and therefore it does not make much sense to report an activation energy for diffusion; temperature coefficients A and B like in Eq. 21 seem more appropriate. Another way to model temperature dependencies is via purely empirical models (Peleg and others 2002). The rationale behind this is that, in most cases described in the food science literature, the temperature dependence is studied for complicated reactions, not for simple reactions for which the Arrhenius equation was developed. Hence, the activation energies derived seem to be of a fundamental nature but they are in fact empirical and in that sense comparable to the alternative models suggested by Peleg and coworkers. Therefore, it is an interesting approach to investigate the performance of these purely empirical models and compare them with the (semi-empirical) Arrhenius parameters.

Table 3—Orders of magnitude for rate constants of bimolecular reactions in aqueous solutions at 25 °C.

Conditions	Order of magnitude of k (dm^3/mol/s)
No diffusion limit and no barrier[a]	10^{14}
Diffusion limit, no activation energy[b]	10^{10}
No diffusion limit:	
activation energy 25 kJ/mol	10^{10}
activation energy 50 kJ/mol	10^{5}
activation energy 100 kJ/mol	10^{-4}

[a]This is in fact the value of the pre-exponential factor in the Arrhenius equation, corresponding to the hypothetical situation that $T \to \infty$.
[b]As given by Eq. 3.

The parameters that have been discussed so far, orders, rate constants, activation parameters, are actually all that is needed in (chemical) kinetics. It has become the habit to use several other kinetic parameters in food science. They originate from days gone by when it was necessary to derive parameters and models to describe (mainly microbial) changes in foods during processing and storage when no use was made yet of modern reaction kinetics. We give a brief overview of these parameters so that the reader can see how they relate to the fundamental parameters discussed previously.

The parameter Q_{10} describes the temperature dependence of a reaction as the factor by which the reaction rate is changed when the temperature is increased by 10 °C:

$$Q_{10} = \frac{k_{T+5}}{k_{T-5}} \approx \frac{k_{T+10}}{k_T} \quad (22)$$

If the Arrhenius equation holds, it can be shown that:

$$Q_{10} = \exp\left(\frac{10E_a}{RT^2}\right) \quad (23)$$

The parameter Q_{10} is thus seen to depend strongly on temperature, which is a drawback and so if it is reported the temperature range for which it applies should be mentioned.

Another parameter to describe temperature dependence is Z, which expresses the increase in temperature that would produce an increase in rate by a factor of 10. Z is defined as:

$$Z = \frac{2.303RT^2}{E_a} = \frac{10}{\log Q_{10}} \quad (24)$$

Like the parameter Q_{10}, Z is temperature dependent which restricts its use. Z is frequently used in bacteriology to describe inactivation of cells.

Also used is the parameter D, especially in thermobacteriology. It is the decimal reduction value, the time needed to reduce a concentration by a factor of 10. D is nothing other than an inverse rate constant. For a 1st-order reaction:

$$D = \frac{\ln 10}{k} = \frac{2.303}{k} \quad (25)$$

and for a 2nd-order reaction:

$$D = \frac{9}{c_0 k} \quad (26)$$

A plot of log D compared with T' (in °C) is usually taken to be a straight line (for a limited temperature range); see Figure 5. D relates to the Z-value, as k is related to E_a,:

$$\log D = \log D_R - \frac{T' - T'_R}{Z} \tag{27}$$

D_R is the reference value of D at the reference temperature T'_R (often chosen as 250 °F for historical reasons, which is equal to 121.1 °C). Equation 27 is referred to as the TDT curve (thermal death time curve) or the Bigelow model.

As shown, all these parameters can be linked to the more fundamental kinetic parameters. They still serve a purpose. On one hand, they are usually estimated in real foods and as such reflect a time–temperature dependence characteristic (not pretending it is something like an activation energy) that can be used for engineering purposes; less so, however, for understanding behavior at the molecular level. On the other hand, the parameters are used commonly by regulatory agents in food safety programs in relation to thermal treatments. While this is as such not a reason to maintain these parameters, it is a fact that they helped in ensuring food safety, and if better models are coming up they will have to prove in practice that they are indeed performing better also in food safety aspects.

Modeling enzyme reactions

Biochemical reactions are important for food quality, as mentioned previously in "Reactions in Foods That Affect Quality," because many foods, being biological materials, contain enzymes. Sometimes these enzymes are desired (for instance, in cheese ripening) but mostly enzymes need to be deactivated because otherwise their action will lead to deterioration of food quality. Examples are the enzymatic browning of apples, potatoes, and cauliflower due to polyphenoloxidase, or formation of a soapy or rancid taste in raw milk due to the action of lipases. If one wants to exploit enzymes, enzyme kinetics is useful. In most cases reported in the literature, Michaelis–Menten kinetics is applied, although one should check whether or not Michaelis–Menten kinetics is actually applicable. The Michaelis–Menten equation reads:

$$v = v_{max}\frac{[S]}{[S] + K_M} \tag{28}$$

in which v is the *initial* rate of the reaction, v_{max} the maximum rate of the enzyme under the conditions studied, [S] is the substrate concentration, and K_M the Michaelis constant. v_{max} and K_M are the parameters of the equation. With knowledge of these parameters the rate of the enzymatic reaction can be predicted. Frequently, Lineweaver–Burke plots are made to estimate the kinetic parameters, but this should not be done because of transformation of errors, thereby violating some critical assumptions underlying regression, as discussed previously. Nonlinear regression estimation is preferable. Figure 6 gives a simple example of Michaelis–Menten kinetics.

An extensive overview of enzyme kinetics can be found in Marangoni (2003).

If one wants to prevent the action of enzymes, inactivation kinetics is needed. Enzymes are proteins and inactivation is due to unfolding of the protein. A general model for that is:

$$N \underset{k_2}{\overset{k_1}{\rightleftharpoons}} D \xrightarrow{k_3} I \tag{29}$$

in which N represents the native protein, D the denatured protein, I the inactivated protein, and k_1, k_2, k_3 the rate constants for each step. The importance of the equilibrium between N and D is that proteins can refold after denaturation and, hence, enzyme activity may be restored upon removing the cause of denaturation. In most cases in foods, the cause of denaturation is heating. In any case, if the denatured protein is subject to further reactions leading to the inactive form I, the enzyme cannot return to its active form and, consequently, enzyme activity is lost. In most cases, a 1st-order model as given in Eq. 9 appears to be applicable to describe enzyme inactivation. This implies that the 3rd step in Eq. 29 is rate-determining. Many examples of inactivation curves can be found in the food science literature. Figure 7 shows an example in which 1st-order behavior is apparent. Figure 8 on the other hand shows an example of biphasic behavior, which can also be

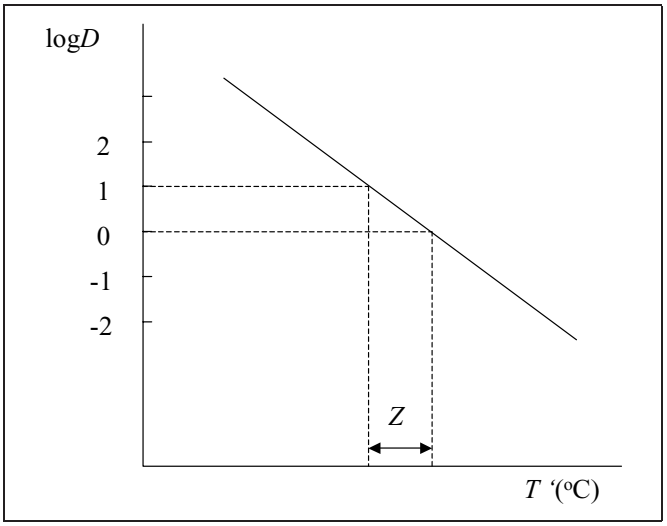

Figure 5—Schematic example of a TDT curve and interpretation of the *Z*-value.

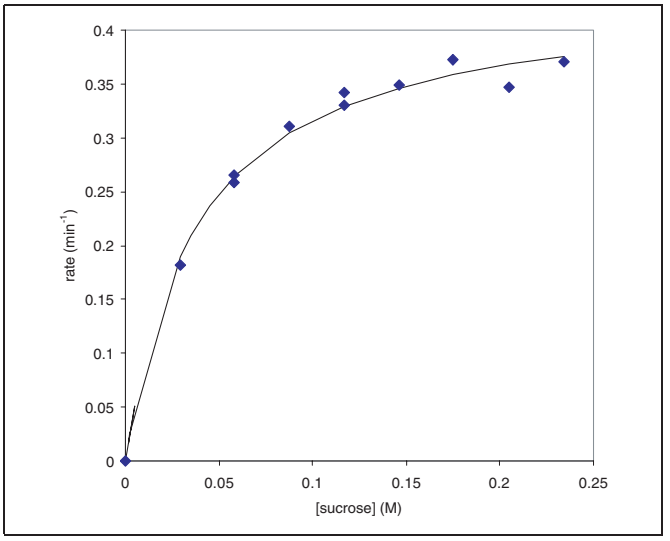

Figure 6—Nonlinear regression fit (solid line) of the Michaelis–Menten equation to initial rates of sucrose hydrolysis by yeast invertase as a function of substrate concentration. Adapted from Chase and others (1962).

frequently observed, so one should not automatically assume that enzyme inactivation is by definition 1st-order behavior.

Modeling physical reactions

Physical processes frequently lead to quality change. Examples are creaming or sedimentation, fracture phenomena, viscosity changes, gelation of biopolymers, crystallization, and moisture migration. Modeling these phenomena is not easy because the changes are rather complex and may be accompanied by chemical changes. As an example, 2 models are presented for predicting viscosity of dispersions. The first one is an equation derived by Einstein for dilute dispersions:

$$\frac{\eta}{\eta_s} = 1 + 2.5\varphi \tag{30}$$

in which η represents the viscosity of the dispersion, η_s the viscosity of the solvent, and φ the volume fraction of the dispersed

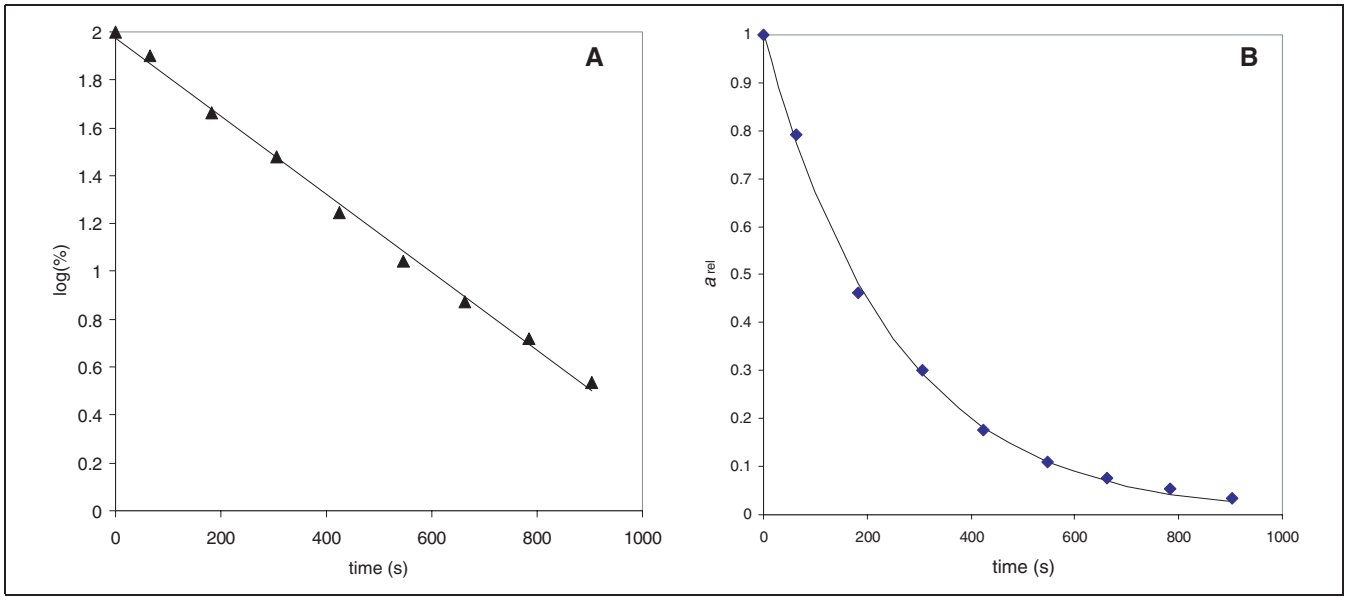

Figure 7—An example of apparent 1st-order heat-induced inactivation kinetics of pectin-methylesterase from tomato at 69.8 °C, presented as a logarithmic plot (A) and as relative activity plot (B). The lines represent a 1st-order model. Adapted from Anthon and others (2002).

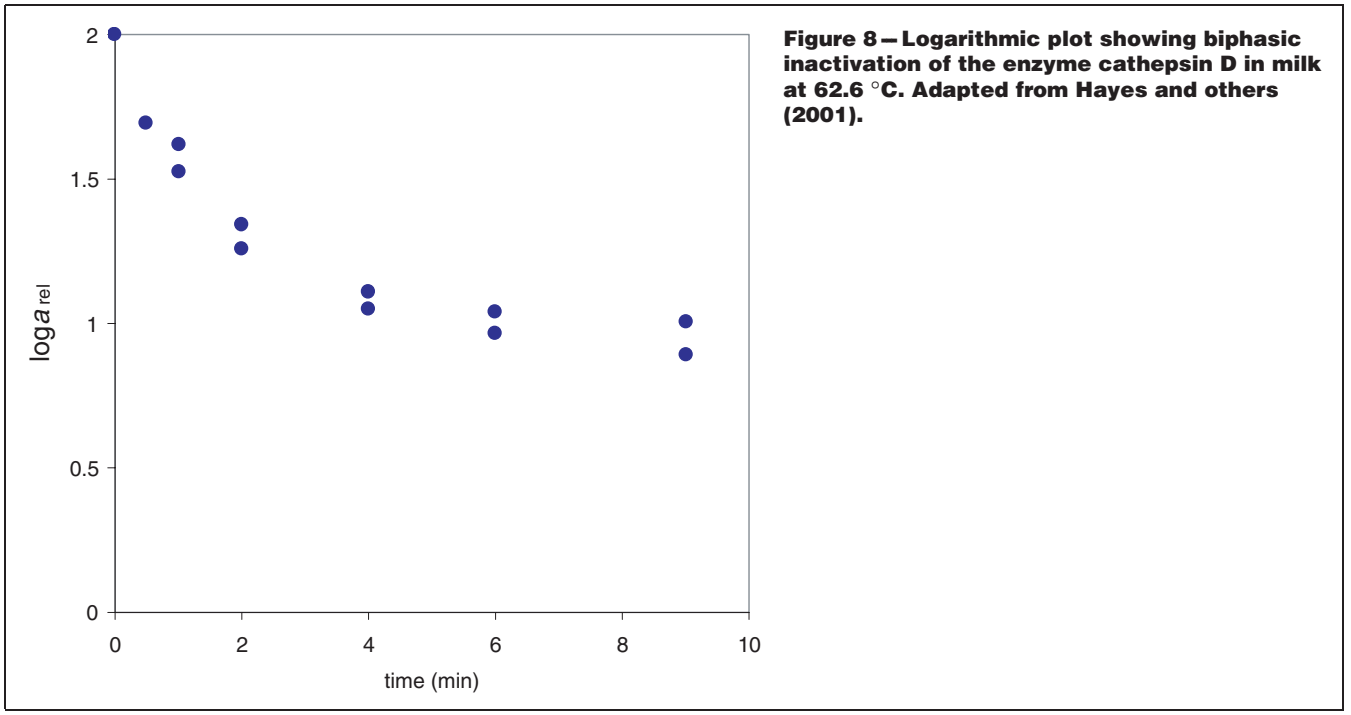

Figure 8—Logarithmic plot showing biphasic inactivation of the enzyme cathepsin D in milk at 62.6 °C. Adapted from Hayes and others (2001).

particles (Einstein 1906, 1911). The interesting aspect of this equation is that only the volume fraction, but not the size of the dispersed particles, is of importance in determining the viscosity. However, this equation is only valid for very dilute dispersions ($\varphi < 0.01$) and, therefore, not very suitable for foods. For more concentrated dispersions, an empirical relation has been derived, which is the so-called Eilers equation:

$$\frac{\eta}{\eta_s} = \left[1 + \left(\frac{1.25\varphi}{1 - \frac{\varphi}{\varphi_{max}}}\right)\right]^2 \quad (31)$$

This equation works quite well for foods. Anema and others (2004) applied this model to skimmed milk samples with varying volume fraction of casein micelles. Manski and others (2007) used such a model to describe the influence of dispersed particles on deformation properties of concentrated caseinate composites. Such equations can thus be used to predict the rheological properties of a food if one knows the volume fraction of dispersed particles. As indicated previously, there are numerous models describing physical phenomena, such as aggregation and flocculation, crystallization kinetics, drying and dehydration. A useful reference for all kinds of physical models can be found in Walstra (2003).

A critical remark here is that physical quality indicators are frequently modeled as if they concern a simple chemical reaction. A case in point is texture changes, for instance, during cooking of potatoes. The reason why there is softening of tissue is the result of very complicated processes, among which is the degradation of pectin. However, this is not what is measured; one uses a physical device to measure texture. This can, for instance, be modeled as a 1st-order reaction, and the resulting rate constant is then further evaluated in the Arrhenius equation. Subsequently, an activation energy is reported in kJ/mol. Now the question is of course what that actually means: a mole of potatoes is hard to get by. In such cases, empirical models such as that reported in Eq. 21 or suggested by Peleg and others (2002) are probably better.

Modeling microbial changes

Microbiological changes are due to the growth of microorganisms. This is usually desirable in a fermentation, but mostly undesirable in other environments because microbial growth may lead to spoilage and even health-threatening situations when pathogens come into play. Regardless of this fact, the ability to predict growth of bacteria in foods is of the utmost importance for food design and predicting shelf life. A frequently used growth model is the modified Gompertz model:

$$\ln\frac{N}{N_0} = A_s \exp\left\{-\exp\left[\frac{\mu_{max} e}{A_s}(\lambda - t) + 1\right]\right\} \quad (32)$$

in which N is the number of microorganisms, N_0 the number of microorganisms at time zero, A_s is the asymptotic value of the maximum number of microorganisms, μ_{max} the maximum growth rate, λ the lag phase, and e is the number 2.718 (= exp(1)). Figure 9 shows an example of the modified Gompertz model applied to the growth of *Salmonellae* in a laboratory medium.

It should be noted that there are many more growth models published. A quick scan of the *International Journal of Food Microbiology, Journal of Food Protection*, and *Food Microbiology* will overwhelm the reader with the many variations on a theme. However, a useful overview of the state of the art is McKellar and Lu (2004) and Brul and others (2007).

Another important aspect related to microbiology is the ability to inactivate microorganisms in foods, and for that we need inactivation kinetics. As mentioned previously, the 1st model published in food science was on this topic in the 1920s; it is actually a 1st-order model as displayed in Eq. 9:

$$S(t) = \exp\left(-\frac{t}{D}\right) \quad (33)$$

or

$$\log S(t) = -\frac{t}{D} \quad (34)$$

in which

$$S(t) = \frac{N}{N_0} \quad (35)$$

Equation 34 is the so-called Bigelow model, which is still used today, with D the decimal reduction time already displayed in Eq. 25. This model is widely applied in food science, probably because it is so simple. Nevertheless, there are problems with it. Equation 34 shows that a plot of log$S(t)$ compared with time should be linear, but if one screens the literature it is found that most plots are surprisingly nonlinear. This fact is simply ignored by many authors. In order to account for this nonlinearity, a new model has come up (Peleg and Cole 1998), which has been tested for a number of cases by van Boekel (2002). The model is a so-called Weibull model:

$$S(t) = \exp\left[-\left(\frac{t}{\alpha}\right)^{\beta}\right] \quad (36)$$

and

$$\log S(t) = -\frac{1}{2.303}\left(\frac{t}{\alpha}\right)^{\beta} \quad (37)$$

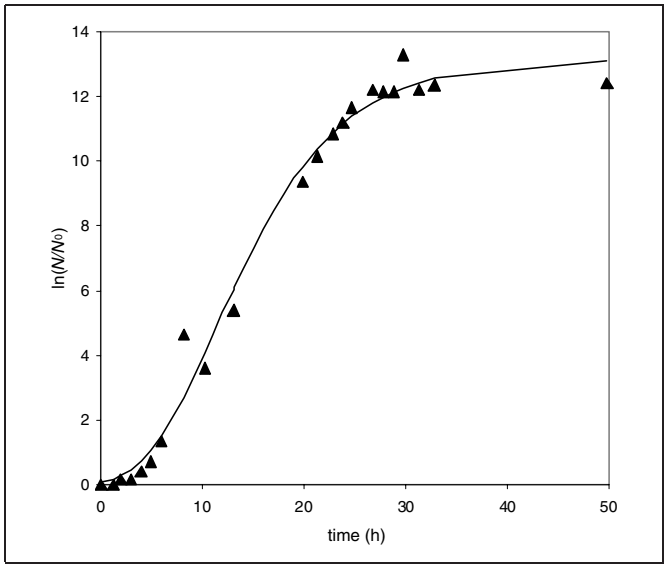

Figure 9—Example of the fit of the modified Gompertz equation to the growth of *Salmonellae* in a laboratory medium. Fit parameters: $A_s = 13.1 \pm 0.3$, $\lambda = 4.4 \pm 0.5$ h, $\mu_{max} = 0.70 \pm 0.04$/h (± 95% standard deviation). Adapted from Gibson and others (1988).

In comparison with Eq. 33 and 34 one extra parameter is added, namely, β. This is the so-called shape factor because its value determines the shape of the inactivation curve (2 examples are given below). The parameter α has units of time and could be considered as the alternative for the *D*-value. The interesting aspect is that if $\beta = 1$, then the Weibull model reduces to the Bigelow model; it is thus a rather flexible model. However, there are only a few cases in which $\beta = 1$ (van Boekel 2002). Both Figure 10 and 11 show an example of the fit of the Weibull model to the inactivation of microorganisms.

Applications of Models to Reactions in Foods

When the effect of temperature on reactions in foods has been established, the value of the parameters needs some discussion. For instance, if a high activation energy is found, the conclusion is sometimes drawn that the reaction will proceed slowly or will be difficult. This is not necessarily true, because the reaction may proceed quite fast at very high temperature. Furthermore, if a high value of activation energy goes along with a high value of the pre-exponential factor, the reaction may indeed proceed at a noticeable rate; this is the case, for instance, for protein denaturation. The point is that a high activation energy indicates a strong temperature dependence; that is to say, it will run very slowly at low temperature, but relatively fast at high temperature. What is relevant for foods is that chemical reactions (such as the Maillard reaction) have a "normal" activation energy of about 100 kJ/mol, whereas the inactivation of microorganisms can be characterized by a high activation energy, say, 300 kJ/mol (even though, as already mentioned, it is incorrect to express it in this way because the killing of microorganisms is not a simple elementary reaction). Figure 12 illustrates this difference in temperature sensitivity. These phenomena are exploited in processes such as HTST (high-temperature short-time heating) and UHT (ultra-high-temperature treatment). These processes are designed by choosing time–temperature combinations such that desired changes are achieved (microbial inactivation), while undesired changes (chemical reactions leading to quality loss) are minimized. Another important consequence for foods is that reactions with relatively low activation energy will continue at a measurable rate at low temperatures, for instance, during storage, leading to a limited shelf life.

Several types of reaction can occur in foods, as discussed previously in "Reactions in Foods That Affect Quality." Chemical

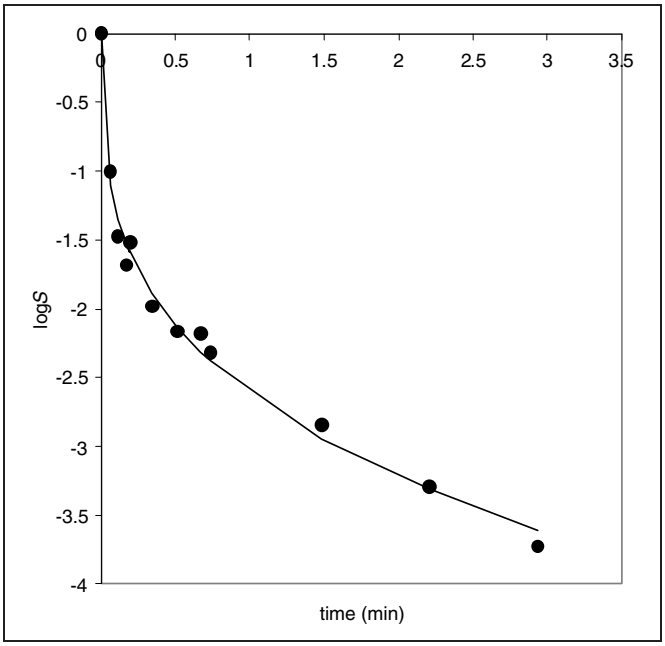

Figure 11—Fit of the Weibull model to the inactivation of *Salmonella enteriditis* in egg yolk. Weibull parameters $\alpha = 0.002 \pm 0.001$ min and $\beta = 0.3 \pm 0.03$ ($\pm$ 95% confidence intervals). After Michalski and others (1999).

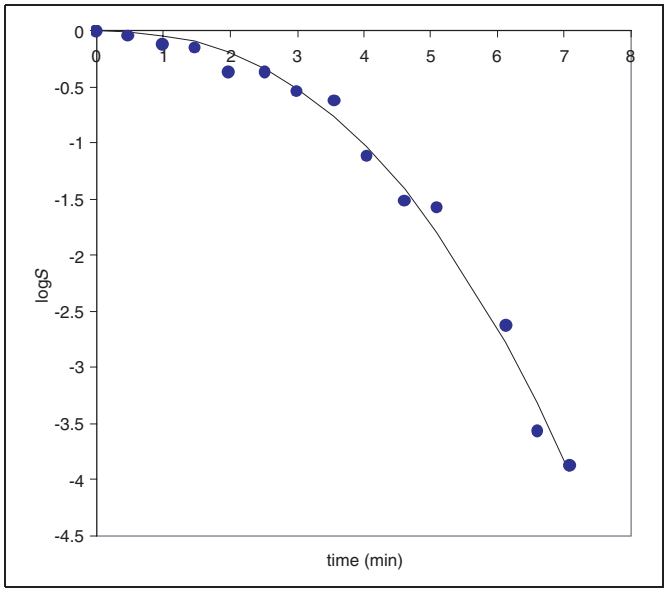

Figure 10—Fit of the Weibull model to the inactivation of *Salmonella Typhimurium*. Weibull parameters $\alpha = 2.8 \pm 0.3$ min and $\beta = 2.4 \pm 0.3$ ($\pm$ 95% confidence intervals). Adapted from Mackey and Derrick (1986).

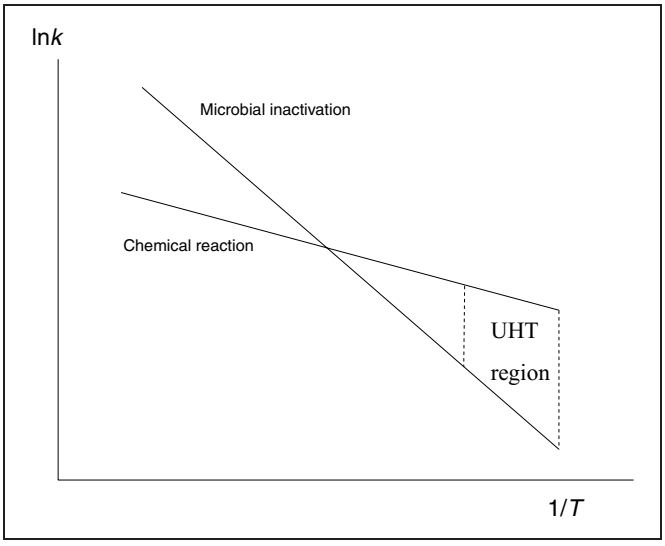

Figure 12—Schematic presentation of the temperature dependence of a chemical reaction and microbial inactivation. The UHT region is characterized by time–temperature combinations that induce enough microbial inactivation and limited chemical reactions.

reactions more or less obey the Arrhenius equation as would be expected.

Several physical reactions are less temperature dependent and often diffusion controlled. The concept of activation energy does not actually apply to physical reactions (such as coalescence, aggregation) because there are no molecular rearrangements. However, physical phenomena do usually have an energy barrier (due to, for instance, electrostatic repulsion), which provide stability to colloidal systems. Hence, the concept of a kind of activation energy does apply but not with a temperature dependence as in the case of chemical reactions. The effect of temperature will be mainly on the rate of encounters. Sometimes, activation energies are reported for physical phenomena such as the temperature dependence of diffusion or viscosity. This would seem to be impossible, since there is nothing to activate and there is no reaction. As discussed previously, the point is that the temperature dependence of diffusion, for example, apparently obeys Arrhenius' law in several systems, but the parameter that comes out of it does not have the physical meaning of an activation energy!

Quite different results are obtained with protein denaturation and microbial inactivation. (Microbial inactivation is, according to some researchers, due to an enzyme's protein denaturation. It is questionable whether this is the sole cause of inactivation.) Protein denaturation is characterized usually by a high activation energy, but the reaction rate is still noticeable because of a high pre-exponential factor. As a result, the temperature dependence of such reactions is very high, much higher than that of chemical reactions.

With biochemical reactions, such as enzyme-catalyzed reactions, there is moderate temperature dependence, as is to be expected for catalyzed reactions. It is of interest to note that the rate enhancement by enzymes, as compared to the uncatalyzed reaction, is much higher at lower temperatures than at higher temperatures: Figure 13 gives a schematic impression. Enzymes lower the activation energy considerably (as compared to the uncatalyzed reaction), whereas the pre-exponential factor is only changed a little. However, with enzyme-catalyzed reactions, enzymes become inactivated above a certain temperature, and the catalyzed reaction effectively comes to an end. Most enzymes relevant in food tend to become inactivated between 50 and 80 °C, though some notably heat-resistant enzymes are known. The same goes for microbial growth: first there is an increase with temperature but eventually microbes start to die. A highly schematic picture of the effect of temperature on microbial growth and enzyme action alike is shown in Figure 14; it should be noted that the actual response to temperature can be time dependent. In the case of microorganisms, there is also a minimum temperature below which there is no growth. For that reason, empirical relations have been derived to describe temperature dependence of microbial growth, for instance, the square root model that describes the effect of temperature on the maximum growth rate:

$$\sqrt{\mu_{max}} = b_1[T - T_{min}][1 - \exp(c_1(T - T_{max}))] \qquad (39)$$

In this equation, b_1 and c_1 are fit constants, and $T_{min,max}$ are the minimum and maximum temperatures for growth of the microorganism under study. In the same way, empirical relations are described for temperature dependencies of lag time λ (the lag time represents the time before a microorganism starts off in its exponential phase). See McKellar and Lu (2004) and Brul and others (2007) for more details.

Photochemical reactions and radical reactions are not or are only slightly temperature dependent because the changes at the molecular level hardly depend on thermal energy. Both types of reactions are of importance in foods. Photochemical reactions cause, for instance, oxidation of vitamins, they may activate certain enzymes, and they may cause flavor defects. Radical reactions are most notable for oxidation reactions (of unsaturated fats or of vitamins).

The role of water activity in food stability has long been recognized in food science. Two recent reviews discuss water activity: one on a fundamental level (Blandamer and others 2005) and another more applied to food (Schmidt 2004). In the past decade, research has shifted to the effects of glass transitions on food stability (Roos and others 1996). Different models are needed to describe temperature dependence of viscosity in foods undergoing a glass transition. In general, a glass is an amorphous solid characterized by a very high viscosity. The phenomenon has been described first for synthetic polymers. Polymer science principles applied to foods appeared to describe also glassy phenomena in foods (Slade and Levine 1991). Examples are low moisture foods, such as milk powder and dried pasta, but also frozen foods where

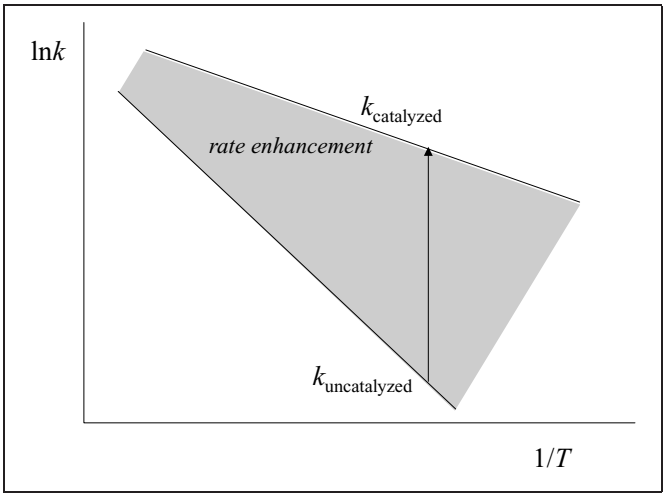

Figure 13—Schematic drawing of rate enhancement accomplished by enzymes as compared to the uncatalyzed reaction.

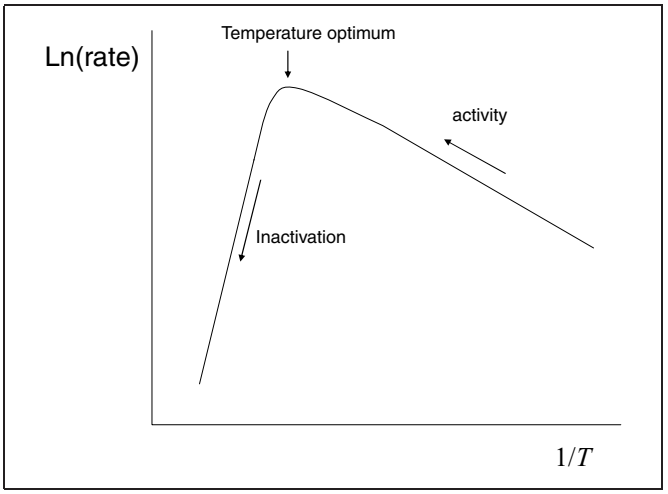

Figure 14—Schematic presentation of the effect of temperature on growth and activity of enzymes and microorganisms and their inactivation.

liquid water has been transformed into ice. Processes that can lead to the glassy state are baking, concentration, drying, extrusion, and freezing, so long as water is removed quickly. Foods in the glassy state usually have a high stability and a long shelf life because of the fact that the molecular mobility is so low. Glass transition is characterized by an enormous increase in viscosity when an amorphous matrix is formed. As a rule of thumb, the viscosity η_g at the glass transition temperature T_g is around 10^{12} Pa s. The molecular mobility depends strongly on $T–T_g$, so how much the actual temperature is away from the glass transition temperature. It should be realized though that glassy foods are in a nonequilibrium state, and therefore there is an inherent tendency to change, albeit at an infinitely slow rate, at least in principle. The effective diffusion coefficient is almost zero for the compounds forming the glass. However, small molecules such as water and oxygen are still able to diffuse, be it slowly. The glass transition temperature is strongly dependent on composition and especially the water content. Water can act as a plasticizer, or in other words, the viscosity may increase drastically at a certain water content, changing from the amorphous glassy state to a supercooled, viscous or rubbery state. Or stated in another way, when the water content increases, the glass transition temperature decreases. When water acts as a plasticizer, it leads to drastic changes in mechanical properties and stability of the food, sometimes referred to as collapse of the matrix, and causing stickiness.

Arrhenius-like dependence is not obeyed in the rubbery state (that occurs at temperatures above the glass transition). When it comes to kinetic models describing the changes in the glassy and rubbery state, the temperature dependence of mechanical properties is mostly described by the so-called WLF (Williams–Landel–Ferry) model, derived for synthetic polymers. It is reported that the Arrhenius model does not function well for such cases. The WLF model was developed for polymers but is nowadays also applied to foods that undergo glass transitions. The WLF model is actually not comparable to the Arrhenius equation, because it does not consider activation energies; it can be derived from fundamental assumptions (Nelson and Labuza 1994) and attempts to model viscosity as a function of temperature and the glass transition temperature T'_g. The WLF model is:

$$\ln\left(\frac{\eta_v}{\eta_{v,g}}\right) = \frac{-C_1(T' - T'_g)}{C_2 + (T' - T'_g)} \tag{38}$$

The parameters C_1 and C_2 are empirical constants, the numerical values of which are sometimes called universal: $C_1 = 17.4$ (dimensionless), $C_2 = 51.6$ °C, but these values may not be universal for foods. A critical appraisal on the importance of glass transitions in foods can be found in Le Meste and others (2002).

The question now arises what happens to the rate of chemical reactions in the glass transition range. The WLF equation allows us to calculate the viscosity in the glass transition range, and therefore we can calculate the diffusion coefficient. It is then possible to see whether the reaction is diffusion limited or reaction limited. It seems that there is no absolute stability in terms of chemical and biochemical reactions when foods are in the glassy state. Molecular mobility is decreased very much, but it does not cease completely, which is not strange because also in a crystal molecular diffusion can take place. As a result, reactions do take place when a food is in a glassy stare, but at a very low rate, so in practical terms foods may be stable for quite a long time when they can be kept in the glassy state. It also appears that the WLF equation is suitable to describe mechanical changes in the glass transition range but less so for chemical reactions.

Shelf life prediction is an important topic, especially with respect to microbial shelf life. However, the models should be capable of dealing with varying temperatures, a situation that will often occur in a food chain, and not all models are able to deal with that. A nice illustration of the use of kinetic models in shelf life is the design of time–temperature integrators, devices that respond to temperature changes as a function of time so that the user can read information on the state of the food from these devices. Some useful references are Taoukis and Labuza (1989a, 1989b), Fu and Labuza (1993), Labuza and Fu (1995), Shimoni and others (2001), and Smolander and others (2002).

Conclusions and Outlook

Several types of models have been described that are currently used in food science to model quality indicators. We seem to be able to model several relevant quality indicators. Some important remaining challenges in quality modeling are as follows.

1. *How to account for effects of the food matrix and the complexity of foods in general?*

It can be concluded that most of the work is done on model systems rather than on foods. This is quite understandable in view of the complexity of foods. Nevertheless, there is a pitfall here, namely, that large mistakes can be made if we translate the outcomes for model systems directly to foods. There could be synergistic and antagonistic factors present in foods that completely change the kinetics of a reaction, or even the reaction mechanism. Also, many reactions occur simultaneously and they interfere with each other. This is an area that requires more attention in the future. We anticipate that this is one of the big challenges for food science in the near future.

2. *How to progress from specific models to more generic models?*

Ideally, it would be best to have general models for, for example, the Maillard reaction, that can be applied to all kinds of foods; but due to very specific effects of foods, this is not yet possible and we are stuck with models that are food specific. While this is not an overwhelming problem it would be helpful if our models were as general as possible. As argued in the previous remark, if we knew the effect of the food matrix better, we could make a move in this direction.

3. *How to deal with parameter uncertainty and variability?*

In view of the biological variability of foods, it is time to study the effect of variability in more detail, certainly if we want to make real model predictions. We can do much better in terms of parameter uncertainty. There has been little attention in the food science literature, so far, for the statistical quality of parameter estimates. Frequently, imprecision is not even mentioned, and that is really unacceptable and a waste of time to report such results. The use of techniques such as Monte Carlo simulations is very promising and should be used much more often. A good example of this has recently been published (Halder and others 2007).

Making better use of statistical design is urgently needed. There is abundant literature on the statistical technique of design of experiments (see, for instance, Box and others 1978; Dean and Vos 1999; Montgomery 1999; Tiao and others 2000). More specific applications tailored to kinetic modeling are harder to find, but they do exist. A good general introduction is given by Atkinson and Donev (1992) and specific applications in kinetic modeling by Atkinson and others (1997, 1998, 2002) and Xu and others (2000). Optimal designs for the Arrhenius equation are discussed by Rodriguez-Aragón and López-Fidalgo (2005). Some more specific food applications can be found in Balsa-Canto and others (2007), Poschet and others (2005), Cunha and others (1997, 1998, 2000), and Nahor and others (2001). Hence, the scene is set and the principles are clear but it is not practiced much yet in food science, probably because many people experience statistics as

difficult. Nevertheless, there is much to be gained if experiments are designed according to sound statistical principles. This is especially so when models are to be used for prediction. A simple calculation using principles from the propagation of errors shows that predictions can become very imprecise with the imprecision reported (if reported at all) in the literature (van Boekel 1996).

4. *How to integrate product and process modeling?*

There is as yet not much work published on how quality changes are related to aspects such as heat and mass transfer, and this is clearly needed for a better product and process design. As regards food processing, modeling techniques are very promising with respect to computational fluid dynamics (CFD). Although this is an application area that requires heavy computing, it allows the engineer to do calculations that were not hitherto possible. Applications are in the area of heat and mass transfer. It allows a fine-tuning of processing in terms of heating, for instance. An overview can be found in Nicolaï and others (2001) and Norton and Da-Wen-Sun (2006). An aspect that receives more attention nowadays is the use of nonisothermal kinetics (Maeder and others 1997; Dolan 2003; Peleg 2003, 2006b; Corradini and Peleg 2004; Corradini and others 2005, 2006). This is of importance because most processes are in practice nonisothermal because of heating-up and cooling-down times.

5. *How to integrate quality attributes into overall quality?*

The ultimate judgment of a consumer about a food product is not on a quality attribute but of the quality of a food as a whole. This is a major challenge for food technologists. It may be that we need to resort to new types of modeling techniques based on artificial intelligence, such as neural networks, fuzzy logic, and Bayesian belief networks (Corney 2000). These modeling techniques come from the area of artificial intelligence and do not yet have many food applications, but they will probably become more important in the future. The characteristics of neural networks and fuzzy logic are that such models can learn when they process data. Bayesian belief networks can deal with uncertainty (via probability distributions) and they allow the use of expert knowledge (van Boekel and others 2004). Hence, they are useful for decision support systems.

6. *How to tailor the need for models to their application?*

Most models published do not really specify the possible application. It is left to readers whether they would like to use it for better insight or to predict or control quality in a real food application. It would perhaps help if we were clearer in this matter.

In conclusion, if we compare the present state of the art with earlier reviews (for example, Saguy and Karel 1980; Labuza 1984), it seems that on one hand we still struggle with the same type of problems, but on the other hand, it is also clear that the computational possibilities have increased enormously in recent years, while insights in the opportunities and limitations of models have become much more apparent. It is hoped that the food science community will profit from these increased insights and opportunities in terms of modeling food quality.

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