THE HANDBOOK OF FOOD ENGINEERING PRACTICE

CRC PRESS

CHAPTER 10

KINETICS OF FOOD DETERIORATION AND SHELF-LIFE PREDICTION

Petros S. Taoukis, Theodore P. Labuza and Israel Sam Saguy

10.1 INTRODUCTION

Quality is an attribute of food, on which understandably a lot of consideration is focused. *Food quality* can be defined as the assemblage of properties which differentiate individual units and influence the degree of acceptability of the food by the consumer or user (Kramer and Twigg, 1968). Due to the nature of foods as a physicochemically and biologically active systems, food quality is a dynamic state continuously moving to reduced levels (with the notable exception of the cases of maturation and aging). Therefore, for each particular food, there is a finite length of time after production it will retain a required level of quality organoleptically and safetywise, under stated conditions of storage. This period of time can be generally defined as the *shelf life* of the food product. There is no established, uniformly applicable definition of shelf life. The definition of shelf life and the criteria for the determination of the end of shelf life are dependent on specific commodities and on the definition's intended use (i.e., for regulatory vs. marketing purposes). Food related authorities have proposed various definitions that can serve as guidelines. The International Institute of Refrigeration (IIR) recommendations for frozen food (IIR, 1972) introduce two different definitions. *High Quality Life* (HQL) is the time from freezing of the product for a just noticeable sensory difference to develop (70-80% correct answers in a triangular sensory test). Another type of shelf life definition that can be extended to other types of food products is the *Practical Storage Life* (PSL). PSL is the period of proper (frozen) storage after processing (freezing) of an initially high quality product during which the organoleptic quality remains suitable for consumption or for the process intended. PSL is usually in the order of two to three times longer than HQL. *Time of minimum durability*, introduced by the EEC directive on food labeling, and defined as the time during which the foodstuff retains its specific properties when properly stored is different in principle from the aforementioned ones, in that it relates to properties of the product itself and not to considerations of its use.

It is a working definition for the food scientist satisfying the often made fundamental assumption that the highest quality product is the freshly processed (or harvested) one. However, since characteristic properties are overlaid, a decision has to be made at what level the change in a certain characteristic or the development of an undesirable one can be detected by the consumer. For example, if having a specific flavor means the absence of off flavors, it has to be decided at what intensity levels are these flavors detectable by the consumer. Thus this definition is closely related to the HQL definition.

For any definition to be used as a working tool it has to be followed by further guidelines i.e. the meaning of organoleptic quality has to be accurately defined and appropriate methods of measuring it and criteria for setting acceptability limits must be discussed.

Sensory evaluation by a trained panel, whereby the food is graded on a "standardized" hedonic scale, usually best approximates the overall quality state of the food (Labuza and Schmidl, 1988). This approach is not without problems. There are considerable difficulties in establishing a meaningful scale for each food product. An expert panel is not necessarily representative of consumers, let alone different consumer segments (Mackie et al., 1985). Even if that assumption can be made, a cut-off level of acceptability has to be decided upon. The time at which a large (but preset) percentage of panelists judge the food as being at or beyond that level is the end of shelf life (PSL). A criterion like that includes an indication of the proportion of the consumers to which the product must be acceptable till the end of shelf life, another variable to which reference or agreement is required. Other problems of the sensory approach are the high cost that is involved with large testing panels and the questions connected with tasting spoiled or potentially hazardous samples. In some cases microbial growth or nutrient degradation could reach unacceptable levels while the food is still judged organoleptically acceptable. Sensory data are not "objective" enough for regulatory purposes and in cases of legal

action or dispute. Sometimes consumers can be "trained" to accept lower standard products by being exposed to products of gradually slipping quality. That makes the need of alternative ways of assessing quality apparent (Herborg, 1985).

Chemical, microbiological and physical tests are being used widely in the study of food quality. Characteristics used by the consumer for evaluation of a product, such as flavor, color and textural properties can be measured instrumentally or chemically. The study of the chemical and biological reactions and physical changes that occur in the food during and after processing allows the recognition of the ones that are most important to its safety, integrity and overall quality. Physicochemical or microbiological parameters can be used to quantitatively assess quality. The values of these parameters can be correlated to sensory results for the same food and a limit that corresponds to the lowest acceptable organoleptic quality can be set. However, caution should be drawn to the fact that correlation of values of individual chemical parameters to sensory data is often not straightforward because overall organoleptic quality is a composite of a number of changing factors (Trant et al., 1981). The relative contribution of each factor to the overall quality may vary at different levels of quality or at different storage conditions.

Despite the discussed difficulties in defining and evaluating quality and determining shelf life of a food, a lot of progress has been made towards a scientific and generally accepted approach. It is an area of continuous and extensive research. An in-depth study of the different deteriorative mechanisms that occur in a food system and systematic analysis and interpretation of the results lead to more meaningful and objectively measurable ways of assessing food quality and determining shelf life. Proper application of chemical kinetic principles to food quality loss is essential for efficiently designing appropriate tests and analyzing the obtained results.

10.2 KINETICS OF FOOD DETERIORATION

10.2.1. Reaction modeling principles

Applying fundamental chemical kinetic principles the rate of food quality change may in general be expressed as a function of composition and environmental factors (Saguy and Karel, 1980):

$$\frac{dQ}{dt} = \boldsymbol{F}\,(C_i, E_j) \qquad (1)$$

where C_i, are composition factors, such as concentration of reactive compounds, inorganic catalysts, enzymes, reaction inhibitors, pH, water activity, as well as microbial populations and E_j environmental factors, such as temperature, relative humidity, total pressure and partial pressure of different gases, light and mechanical stresses. What the food kineticist is thus faced with, is a physicochemical system of high complexity involving numerous physical and chemical variables and coefficients which in most cases are imposible or impractical to quantitatively define. Even if the system could be explicitly expressed in terms of measurable parameters, an analytical solution is usually nonexistent and exact numerical solutions are too complicated and laborious to be useful as working tools.

The established methodology consists of first identifying the chemical and biological reactions that influence the quality and the safety of the food. Then, through a careful study of the food components and the process, the reactions judged to have the most critical impact on the deterioration rate, are deternined (Labuza, 1985). Excluding the effect of the environmental factors, E_j, by assuming them constant, at the most propable level or judging it negligible within their expected variation, a simplified reaction scheme that expresses the effect of the concentration of the reactants, is developed. The ultimate

objective is to model the change of the concentrations of constituents connected to food quality, as functions of time. Molecular, irreversible reactions are typically expressed as

$$\mu_1 A_1 + \mu_2 A_2 + \mu_3 A_3 + ... + \mu_m A_m \xrightarrow{k_f} P \qquad (2)$$

where A_i are the reactant species, μ_j the respective stoichiometric coefficients (j=1,2...m), P the products and k_f the forward reaction rate constant. For such a scheme the reaction rate, r, is given (Hills and Grieger-Block, 1980) by:

$$r = -\frac{1}{\mu_j}\frac{d[A_j]}{dt} = k_f [A_1]^{n_1} [A_2]^{n_2} ..... [A_m]^{n_m} \qquad (3)$$

where n_j is the order of the reaction with respect to species A_j. For a true molecular reaction, it holds that: $n_j = \mu_j$. More often than not, the degradation of important components to undesirable products is a complex, multistep reaction for which the limiting reaction and intermediate products are difficult to identify. A lot of reactions are actually reversible having the form:

$$\alpha A + \beta B \underset{k_b}{\overset{k_f}{\rightleftarrows}} \gamma C + \delta D \qquad (4)$$

In this case A reacts with B to form products C and D which can back react with a rate constant of k_b. The reaction rate in this case would be:

$$r = \frac{-d[A]}{\alpha\, dt} = \frac{-d[B]}{\beta\, dt} = \frac{+d[C]}{\gamma\, dt} = \frac{+d[D]}{\delta\, dt} = k_f [A]^{\alpha} [B]^{\beta} - k_b [C]^{\gamma} [D]^{\delta} \qquad (5)$$

For the majority of food degradation systems either k_b is negligible compared to k_f, or for the time period of practical interest they are distant from equilibrium, i.e.[C] and [D] are

very small, allowing us to treat it as an irreversible reaction. In most cases the concentration of the reactant that primarily affects overall quality is limiting, the concentrations of the other species being relatively in large excess so that their change with time is negligible (Labuza, 1984). That allows the quality loss rate equation to be expressed in terms of specific reactants, as:

$$r = \frac{-d[A]}{dt} = k_f' [A]^{\alpha} \qquad (6)$$

where α is an apparent or pseudo order of the reaction of compoment A and k_f' is the apparent rate constant. Another case that can lead to a rate equation similar to equation (6) is when the reactants in reaction (2) are in stoichiometric ratios (Hills, 1977). Then from equation (3) we have:

$$r = k_f \prod_i^m [A_i]^{n_i} = k_f \left(\prod_i^m \mu_i^{n_i} \right) \left[\frac{A_1}{n_1} \right]^{\sum n_i} \qquad (7)$$

or

$$r = \frac{-d[A]}{dt} = k_f' [A]^{\alpha} \qquad (8)$$

where $A = A_1$ and $\alpha = \Sigma n_i$, an overall reaction order.

Based on the aforementioned analysis and recognizing the complexity of food systems, food degradation and shelf life loss is in practice represented by the loss of desirable quality factors A (e.g. nutrients, characteristic flavors) or the formation of undesirable factors B (e.g. off flavors, discoloration). The rates of loss of A and of formation of B are expressed as in eq. (6), namely:

$$r_A = \frac{-d[A]}{dt} = k\,[A]^m \qquad (9)$$

$$r_B = \frac{d[B]}{dt} = k'\,[B]^{m'} \qquad (10)$$

The quality factors [A] and [B] are usually quantifiable chemical, physical, microbiological or sensory parameters characteristic of the particular food system. Both k and k' are the apparent reaction rate constants and m and m' the reaction orders. It should be again stressed that equations (9) and (10) do not represent true reaction mechanisms and m and m' are not necessarily true reaction orders with respect to the species A and B but rather apparent or pseudo orders. The apparent reaction orders and constants are determined by fitting the change with time of the experimentally measured values of [A] or [B] to equations (9) or (10). The techniques used for the solution can be generally classified into two categories: a) Differential Methods and b) Integral Methods (Hills and Grieger-Block, 1980).

In experimental kinetic studies, it is impossible to measure the reaction rate itself. Instead, the concentration of A or B is measured (directly or indirectly) as a function of time. If these concentrations are plotted against time and smooth curves are fitted either graphically or using a statistical fitting method (e.g., polynomial regression) the reaction rates may be obtained by graphical or numerical differentiation of the curves. By taking the logarithm of both sides of equation (9) and (10), the following linear expressions are obtained:

$$\log r_A = \log k + m \log [A] \qquad (11)$$

$$\log r_B = \log k' + m' \log [B] \qquad (12)$$

Data can be fitted to these equations by the method of least squares to determine values of the constants.

Two differential approaches can be alternatively used. The first involves differentiation of data obtained from a single experimental run. It requires measurement of A or B concentrations with time, to at least 50% conversion. The second is differentiation of data from initial rate measurements. In this approach, measurements of concentrations are carried out to very small conversions (e.g., 5%). This is repeated for a number of initial reactant concentrations. Thus, each estimated rate corresponds to a different initial reactant concentration and involves a separate experimental run. Another difficulty often faced with this method is in fitting data from kinetic experiments in which the rate changes rapidly even within the low conversions that are used (e.g., in case of enzymatic reactions). One has to obtain an initial slope from a set of data points with a rapid change in slope and also inevitable scatter from experimental errors. The usual methods of least square fitting of a polynomial may give erratic estimates of the initial slope. A flexible mathematical method to overcome this problem is the use of spline functions (Wold, 1971). The major advantage of the spline function method is that it uses all the data to estimate the intial rate, but is not unduly influenced by experimental error in individual data points.In general, the differential methods involve two statistical fittings, thus being more sensitive to experimental scattering and requiring a large number of data points for a dependable parameter estimate.

In the integral method, variables in equations (9) and (10) are separated and integration is carried out. For example for equation (9), we have:

$$-\int_{A_o}^{A} \frac{d[A]}{[A]^m} = k\,t \qquad (13)$$

Regardless of the value of m, equation (13) can be expressed in the form:

$$\boldsymbol{Q}(A) = k\,t \qquad (14)$$

where the expression $\boldsymbol{Q}(A)$ is defined as the ***quality function*** of the food.

The form of the quality function of the food for an apparent zero, 1st, 2nd and mth order reaction can be derived from the eq.(14) and is shown in the following Table 1. The half life time of the reaction i.e. the time for the concentration of the quality index A to reduce to half its inital value is also included.

Table 1. Quality function form and half life times for different order reactions.

Apparent Reaction Order	**Quality Function** $\boldsymbol{Q(A)_t}$	**Half Life time** $\boldsymbol{t_{1/2}}$
0	$A_o - A_t$	$A_o/(2k_o)$
1	$\ln(A_o/A_t)$	$\ln 2/k_1$
2	$1/A_o - 1/A_t$	$1/(k_2 A_o)$
$m(m\neq 1)$	$\frac{1}{m-1}(A_t^{1-m} - A_o^{1-m})$	$\frac{2^{m-1}-1}{k_m(m-1)}\,A_o^{1-m}$

To determine the quality function one assumes different values of m (0, 1 or other) and tries out a graphical or a least square linear fit to the corresponding equations (Table 1) of the experimental data. If the experiment has been carried out to at least 50% conversion and preferably 75%, it is usually easy to determine which reaction order and equation gives the best fit, either graphically or by using statistical goodness of fit criteria. The coefficient of determination (R^2) of the linear regression is in most cases a sufficient

criterion. The value of the R^2, for a least square fit in general, is given by the following equation:

$$R^2 = 1 - \left(\sum_{i=1}^{N} (y_i - \hat{y}_i)^2 / \sum_{i=1}^{N} (y_i - \bar{y})^2 \right) \qquad (15)$$

where y_i the experimentally observed values of the measured parameter (i=1 to N), $\hat{y}_i$ the value predicted from the regression equation, $\bar{y}$ the average of the observed values and N the number of measurements (Ott, 1984). The correct apparent order is that for which the R^2 is closer to unity. The overwhelming majority of the food reactions that have been studied have been characterized as pseudo-zero or pseudo-first order (Labuza, 1984). Characteristic examples are listed in Table 2.

Table 2. Important quality loss reactions that follow zero or first order kinetics.

Zero order	• Overall quality of frozen foods
	• Non-enzymatic browning
First order	• Vitamin loss
	• Microbial death / growth
	• Oxidative color loss
	• Texture loss in heat processing

Caution is advised in deciding the appropriate apparent order and quality function, as noted by Labuza (1988). For example when the reaction is not carried far enough (less than 50% conversion) both zero and first order might be indistinguishable from a goodness of fit point of view as is illustrated in Figure 1. On the other hand, if the

end of shelf life is within less than 20% conversion, for practical purposes either model is sufficient.

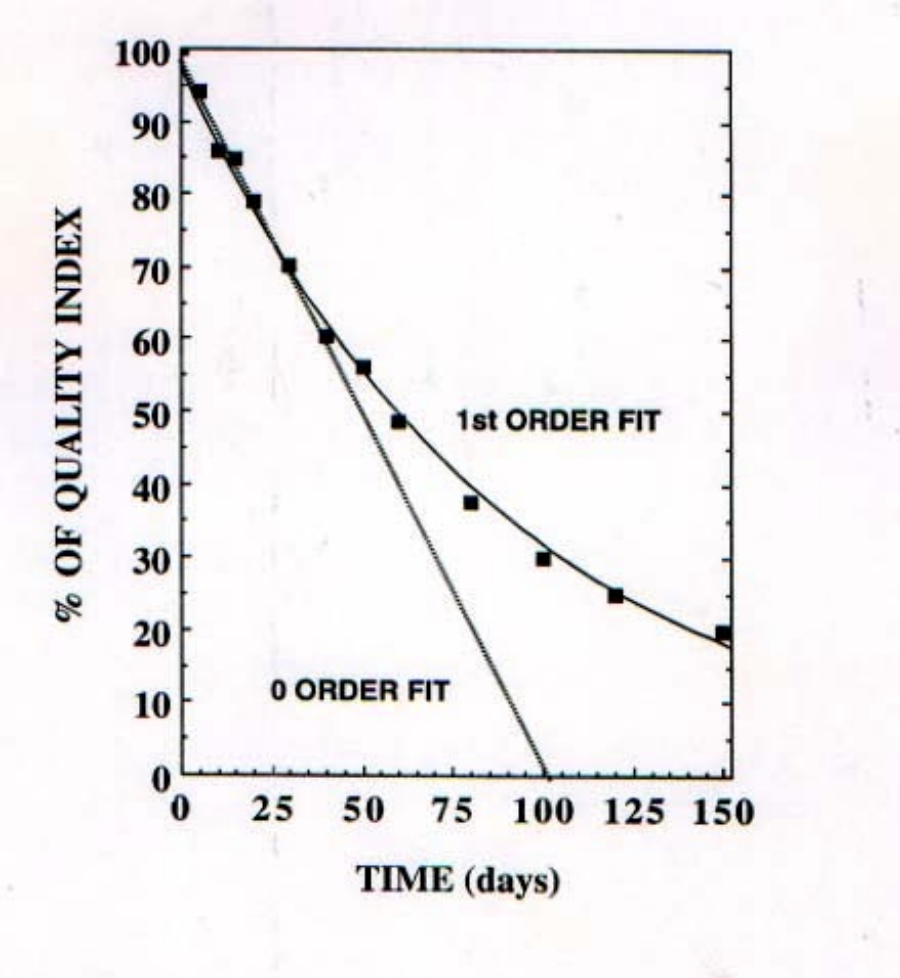

Figure 1. Loss of food quality as a function of time, showing difference between zero and first- order reaction.

Additionally, the worse the precision of the method of measuring the quality factor A the larger the extent of change to which the experiment should be carried out to obtain an acceptably accurate estimate of the reaction rate constant as illustrated in Figure 2. It should be noted here that most measurements in complex foods involve typically an error of 5% or worse.

Erroneous results are often obtained this way, especially if the data are used to extrapolate to longer times. Unfortunately, this has often occurred in the literature. Studies

of reaction systems involved in food quality loss are not followed to sufficient reaction extent, resulting in inaccurate reaction rate constants and undeterminable reaction orders. A lot of valuable data cannot be utilized to their fullest extent and databases of food reaction kinetic parameters contain a lot of uncertainties.

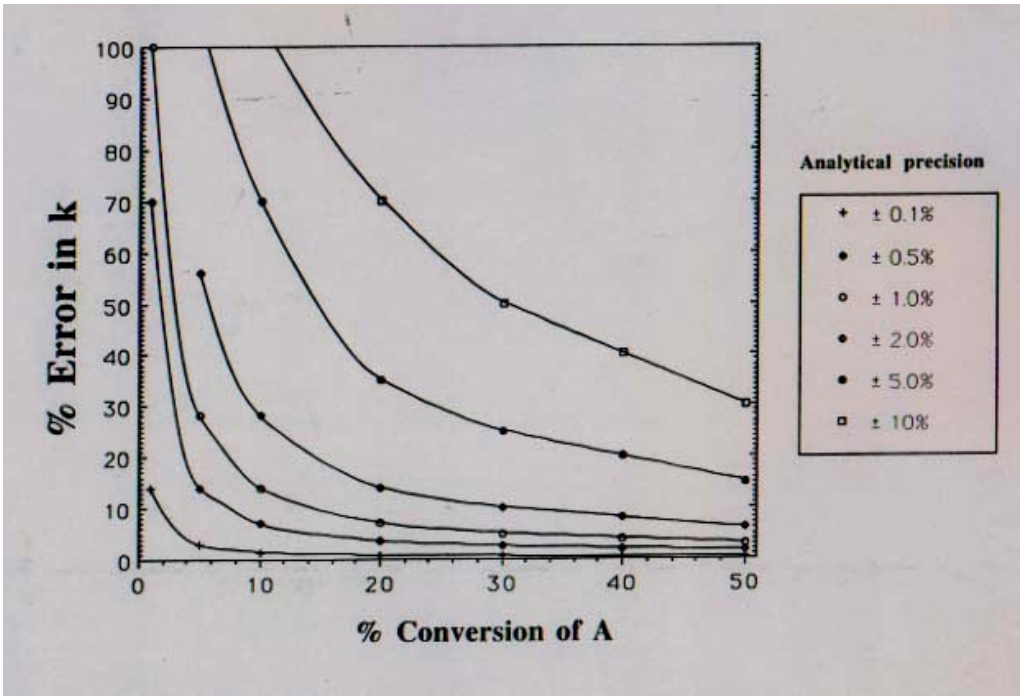

Figure 2. Effect of the Analytical Precision on the Accuracy of the Estimated Reaction Rate Constant.

Another problem that scattered data can cause are values of R^2 obtained by the zero order fit and by the first order fit that are practically indistinguishable. In the case of the first order reaction the logarithms of the measured quanitites are used (semilog plot) thus the R^2 is calculated for $\ln y_i$ and $\ln y$ rather than y_i and y (equation (15)). This in effect tends to give a larger R^2, especially if the larger scatter is at the larger values (Boyle et al., 1974). This bias in the criterion might lead to a skewed preference to the first order model. In these cases it is advisable to use additional criteria for goodness of fit, like

residual plots. Alternatively, instead of the logarithmic equation for the first order reaction (Table 1) the exponential form can be used, where:

$$A = A_o \exp (- k t) \qquad (15)$$

and a nonlinear least square fitting computed, for determination of the k parameter. The R^2 for this fit is given by equation (14) and is directly comparable to the R^2 from the linear regression for the zero-order model.

A final pitfall that should be avoided when determining the apparent order, concerns reactions that exhibit a lag period. During a typical lag period there is a build-up of a critical intermediate concentration. The rate of the reaction during the build-up period is is normally slower. In some cases, the reaction is not detectable due to analytical limitation as in the case of the formation of brown pigments monitored at 420 nm during a nonenzumatic Maillard type reaction. The most common approach to deal with a lag period , is to draw each data point and to look for the time where a distinct change in the reaction rate occured. Obviously, this approach calls for special attrention as a change in the reaction mechanism may also take place. Typical reactions where lag period is observed are nonenzymatic browning (Labuza, 1982; Saguy, et al., 1979) and microbial growth.

Once the apparent order of the quality deterioration reaction has been decided, further statistical analysis and statistical evaluation of the parameter k, the rate constant is required, to get an estimate of the error in the determination of k (Labuza and Kamman, 1983). If a linear regression method is used to estimate the parameters, their 95% confidence limits can be calculated using the Student t distribution. In addition to the confidence limits, a list of standarized residuals and a residual plot is a useful statistical tool that allows evaluation of how well the chosen equation can model the data and also permits the recognition of extreme or outlier values that may be the result of experimental errors or other extraneous effects and should be excluded from the calcualtions (Arabshasi and

Lund, 1985). The standarized residuals should be randomly distributed around zero and usually within -2 and +2. Any data that generate standard residuals outside this range are possible outliers.

An alternative procedure to linear regression for the calculation of k is the point by point or long interval method (Margerison, 1969; Lund, 1983), in which each data point is an independent experiment with respect to zero time. The value of k is calculated as the average of the n individual slopes. Labuza (1984) showed that one gets similar value ranges for k from the two methods. A minimum of 8 data points is recommended by Labuza and Kamman (1983) for reasonably narrow confidence limits in k within the practical and economic limits of most experimentation.

In some cases higher or fractional order models are clearly indicated by the experimental data. To determine the apparent order m, two methods can be alternatively used. As mentioned before, different values for m can be assumed and the fit of the quality function for $m \neq 1$ (Table 1), tested. A second method is to allow m as a parameter and run a nonlinear least square regression on the equation to determine the order that best conforms with the experimental data. For example, it was found that second order kinetics best described the oxidation of extractable color pigments from chili pepper (Chen and Gutmanis, 1968). Autoxidation of fatty acids in presence of excess oxygen is best described with a 1/2 order model with respect to the fatty acid concentration (Labuza, 1971), whereas hexanal production from lipid oxidation is shown to theoretically fit a cubic model (Koelsch and Labuza, 1992).

As has been explained before, the developed food quality loss functions are based on the stated assumptions and do not necessarly reflect true reaction mechanisms. In case for which the assumptions are not applicable or the actual mechanism is very complex due to side reactions or limiting intermediate steps, equations (9) and (10) may not sufficiently model the measured changes. One approach in this case is to develop a

semi-empirical kinetic/mathematical model that effectively represents the experimental data. Preferably the model would still have the general form of the quality function of eq.(14), where Q(A) can obtain any form other than the typical ones of Table 1. The steps for building such a model are described by Saguy and Karel (1980). Multivariable linear models, polynomial equations or nonlinear models can be defined and their fit to the data can be tested with computer aided multiple linear, polynomial or nonlinear regressions. Empirical equations modeling the effect of different composition or process parameters can be derived from statistical experimental designs, like the surface response methods (Thompson, 1983).

A special category of reactions, the enzymatic reactions, important in foods are usually modeled by the Michaelis-Menten equation. This is a reaction rate function based on the steady-state enzyme kinetics approach (Engel, 1981). For an enzymatic system, with no inhibition, the rate equation has the form:

$$r_A = \frac{k\,[A]}{K_m + [A]} \qquad (16)$$

where A is the substrate, $k=k_o[e]$ is proportional to the enzyme (e) concentration (k is usually called v_{max} in biochemical terminology) and K_m is a constant ($r_A = 0.5\ k$ for $[A] = K_m$). When $[A]>>K_m$, the equation reduces to a zero order reaction, $r_A=k$. This is often the case in foods with uniformly distributed substrate in excess and small amounts of enzyme, e.g., lipolysis of milk fat. When $K_m>>[A]$, the equation reduces to first order, $r_A=(k/K_m)\,[A]$. This occurs in foods where the enzymes are highly compartmentalized and have limited access to the substrate or where generally the substrate limits the reaction, e.g., browning of fruit and vegetable tissue due to polyphenolase activity. Thus, a large portion of enzymatic reactions in foods can be handled as zero or first order systems.

When a Michaelis-Menten rate equation has to be used, the Lineweaver-Burk transformation is used that allows the estimation of the parameters by linear regression

$$\frac{1}{r_A} = \frac{K_m}{k}\frac{1}{[A]} + \frac{1}{k} \qquad (17)$$

The described initial rate measurement differential method is usually applied for the kinetic analysis of enzymatic reactions.

When one of the quality deterioration models previously described is used its applicability usually is limited to the particular food system that was studied. Since the model often does not correspond to the true mechanism of the reaction, a compositional change in the system may have an effect in the rate of loss of the quality parameter that cannot be predicted by it. Thus, any extrapolation of kinetic results to similar systems should be done very cautiously. In certain cases, an in depth kinetic study of specific reactions important to food quality is desirable, so that the effect of compositional changes can be studied. In these cases the actual mechanism of the reactions is sought to be revealed if possible. Such studies are usually done in model systems, rather than in actual foods, so that the composition and the relative concentrations of the components are closely controlled and monitored. They are particularly useful in cases where the toxicological or nutritional impact of the accumulation of breakdown products, including intermediate or side step reactions, is examined. Examples of such studies are the multistep breakdown of the sweetener aspartame (Stamp, 1990) and the two step reversible isomerization of β-carotene (Pecek et al, 1990). In the first case a complex statistical analysis using a non-linear multiresponse method was employed where all the reaction steps for the true reaction mechanism are expressed in the form of a linear system of differential equations. With this method, all the experimental data is utilized simultaneously to determine the kinetic parameters for each degradation step by a multidimensional nonlinear regression

analysis of the system of differential equations. These parameters can be used to predict the concentration of each degradation product as a function of time at any temperature.

10.2.2.EFFECT OF ENVIRONMENTAL FACTORS

10.2.2.1 Temperature

The hitherto outlined approaches to kinetically define a food system include the underlying assumption that the environmental conditions are constant. A shelf life loss kinetic model is characteristic not only of the studied food but equally impotantly to the set of environmental conditions of the experiment. These conditions can determine the reaction rates and have to be defined and monitored during kinetic experiments.

Since most enviromental factors do not remain constant the next logical step would be to expand the models to include them as variables, especially the ones that more strongly affect the reaction rates and are more prone to variations during the life of the food. The practical approach is to model the effect into the apparent reaction rate constant, i.e. expressing k of eq. (9) as a function of E_j : $k = k(E_j)$.

Of the aforementioned environmental factors namely temperature, relative humidity, total pressure and partial pressure of different gases, light and mechanical stresses, the factor most often considered and studied is temperature. This is justifiable because temperature not only strongly affects reaction rates but is also directly imposed to the food externally (direct effect of the environment), the other factors being at least to some extent controlled by the food packaging.

The history of the fundamental thermodynamic reasoning in developing models of temperature effect on reactions, going back to the late nineteenth century with Van't Hoff (1884), Hood (1885) and Arrhenius (1889), has been reviewed by Bunher (1974). The most prevalent and widely used model is the Arrhenius relation, derived from thermodynamic laws as well as statistical mechanics principles where:

$$\frac{\partial \ln K_{eq}}{\partial (1/T)} = - \frac{\Delta E^o}{R} \qquad (18)$$

The Arrhenius relation, developed theoretically for reversible molecular chemical reactions, has been experimentally shown to hold empirically for a number of more complex chemical and physical phenomena (e.g., viscosity, diffusion, sorption). Food quality loss reactions described by the aforementioned kinetic models have also been shown to follow an Arrhenius behavior with temperature. For m^{th} order systems shown in Table 1 the reaction rate constant is a function of temperature (with the rest of E_j factors assumed constant) given by the following equation, directly obtainable from equation (18) with k in place of K_{eq}:

$$k = k_A \exp \left(- \frac{E_A}{RT} \right) \qquad (19)$$

with k_A the Arrhenius equation constant and E_A the excess energy barrier that factor A needs to overcome to proceed to degradation products (or B to form), generally referred to as *activation energy* . In practical terms it means that if values of k are available at different temperatures and ln k is plotted against the reciprocal absolute temperature, 1/T, a straight line is obtained with a slope of $-E_A/R$.

$$\ln k = \ln k_A - \frac{E_A}{R} \left(\frac{1}{T}\right) \qquad (20)$$

If the rate constants k_2, k_1 at two temperatures, T_2 and T_1 are known the Arrhenius parameters can be calculated by the equations

$$E_A = \ln \left(\frac{k_2}{k_1}\right) \frac{R\, T_1\, T_2}{T_2 - T_1} \qquad (21)$$

and

$$k_A = k_1^{\left(\frac{T_1}{T_1 - T_2}\right)} \; k_2^{\left(\frac{T_2}{T_1 - T_2}\right)} \qquad (22)$$

In practice, since there is experimental error involved in the determination of the values of k, calculations of E_A from only two points will give a substantial error. The precision of activation energy calculated from equation (21) is examined by Hills and Grieger-Block (1980). Usually, the reaction rate is determined at three or more temperatures and k is plotted vs. 1/T in a semilog graph or a linear regression fit to equation (20) is employed.

It should be pointed out that there is no explicit reference temperature for the Arrhenius function as expressed in Eq. (19), 0 K, the temperature at which k would be equal to k_A, being implied as such. Alternatively to Eq. (19) it is often recommended that a reference temperature is chosen corresponding to an average of the temperature range characteristic of the described process. For most storage applications 300 K is such a typical temperature, whereas for thermal processes 373.15 K (100.0 ° C) is usually the choice. The modified Arrhenius equation would then be written as:

$$k = k_{ref} \exp\left(-\frac{E_A}{R}\left[\frac{1}{T} - \frac{1}{T_{ref}}\right]\right) \qquad (23)$$

where k_{ref} the rate constant at the reference temperature T_{ref}. Respectively Eq. (20) is modified to:

$$\ln k = \ln k_{ref} - \frac{E_A}{R}\left[\frac{1}{T} - \frac{1}{T_{ref}}\right] \qquad (24)$$

The above transformation is critical for enhanced stability during numerical integration and parameter estimation. Aditionally, by using a reference reaction rate constant, besides giving the constant a relevant physical meaning, one signals the applicability of the equation within a finite range of temperatures enclosing the reference temperature and corresponding to the range of interest. Indeed, as it will be discussed further in this section the Arrhenius equation may not be uniformly applicable below or above certain temperatures, usually connected with transition phenomena.

When applying regression techniques statistical analysis is again used to determine the 95% confidence limits of the Arrhenius parameters. If only three k values

are available, the confidence range is usually wide. To obtain meaningfully narrow confidence limits in E_A and k_A estimation, rates at more temperatures are required. An optimization scheme to estimate the number of experiments to get the most accuracy for the least possible amount of work was proposed by Lenz and Lund (1980). They concluded that 5 or 6 experimental temperatures is the practical optimum. If one is limited to 3 experimental temperatures a point by point method or a linear regression with the 95% confidence limit values of the reaction rates included will give narrower confidence limits for the Arrhenius parameters (Kamman and Labuza, 1985)

Alternatively, a multiple linear regression fit to all concentration vs. time data for all tested temperatures, by eliminating the need to estimate a separate A_o for each experiment and thus increasing the degrees of freedom, results in a more accurate estimation of k at each temperature (Haralampu et al., 1985). Since it is also followed by a linear regression of ln k vs. 1/T, it is a two step method as the previous ones.

One step methods require nonlinear regression of the equation that results by substitution of equations (19) or (23) in the equations of Table 1. For example, for the first order model the following equations are derived:

$$A = A_o \exp[-k_A t \exp\left(\frac{-E_A}{RT}\right)] \qquad (25)$$

or

$$A = A_o \exp \{- k_{ref} t \exp (- \frac{E_A}{R} [\frac{1}{T} - \frac{1}{T_{ref}}])\} \qquad (26)$$

These equations have as variables both time and temperature and the nonlinear regression gives simultanously estimates of A_o, k_A (or k_{ref}) and E_A/R (Haralampu et al, 1985; Arabshahi and Lund, 1985). Experimental data of concentration vs. time for all tested temperatures are used, substantially increasing the degrees of freedom and hence giving much narrower confidence intervals for the estimated parameters. The use and the

statistical benefits of employing a one step method were demonstrated for computer simulated food degradation data, following first order kinetics by Haralampu et al. (1985) and for actual data for nonenzymatic browning of whey powder (zero order model) and for thiamin loss in an intermediate moisture model system (first order model), by Cohen and Saguy (1985). In this method , the Arrhenius parameters estimates were judged on the size of the joint confidence region at 90%. The joint confidence region is an ellipsoid in which the true parameters propably exist together at a specified confidence level. The extremes of the 90% confidence ellipsoid region do not correspond to the 95% confidence intervals (derived from a t-test) for the individual parameters. Since experience shows that E_A and $\ln k_{ref}$ are highly correlated, the ellipsoid is thus a more accurate representation of the confidence region (Draper an Smith, 1981; Hunter,1981).

The confidence region may be constrtucted by considering both the variance and covariance of the parameters estimates, and by assuming that the estimates are from a bivariate normal distribution. The confidence contours for a nonlinear regression creates a deformed ellipsoid. The complexity of the computation hampers its application as a routine statistical test. However, the appropriate extreme points of the confidence region could be derived using a computer program (Draper and Smith, 1981) which incorporates approximation for a nonlinear regression:

$$S = SS \left\{1+\frac{N_p}{n-Np} \; \mathbf{F}[N_p, n-N_p, (1-q)]\right\} \qquad (27)$$

where f is the fitted nonlinear model, SS is the nonlinear least square estimate of the fitted model, i.e. $SS= \Sigma(A_i-f)^2$ for i=1 to n , n is the number of data points, N_p the number of parameters derived from the nonlinear least squares, 100(1-q)% the confidence level and **F** the F -statistics. This method allows a reliable derivation of the confidence limits of the determined parameters that can affect the application of the kinetic data for shelf life prediction and product design and demonstrates the caution that should be exercised when

kinetic data is compared. Its main disadvantage is the complexity of calculations and the need for special software.

In case there are large differences in the calculated confidence intervals for the reaction rates at the different temperatures, this variability can be incorporated into the linear regression of ln k vs. 1/T by using weighted regression analysis. Arabshahi and Lund (1985) proposed appropriate regression weight factors that can be used in this case. A weighted nonlinear least squares method was developed that involves weighing of all the individual concentration measurements (Cohen and Saguy, 1985). This method requires a large increase in the number of calculations and it was concluded that its use was not justified, except in the case of substantial skewness of the standardized residuals obtained from the unweighted nonlinear least squares method.

Estimation of the Arrhenius parameters as described hitherto, requires isothermal kinetic experiments at least at three temperatures Alternatively, a single nonisothermal experiment can be conducted. During this experiment the temperature is changed according to a predetermined function, T(t) such as a linear function. From equations (9) and (19)

$$r_A = k_A \exp\left[\frac{-E_A}{R}\frac{1}{T(t)}\right] [A]^m \quad \text{or} \quad \ln r_A = \ln k_A + m\,[A] - \frac{E_A}{R}\frac{1}{T(t)} \qquad (28)$$

The rate r_A is determined by the differential method and the parameters k_A, m and E_A through a multiple linear regression . Usually m is set as either zero or one. The second approach uses a nonlinear regression on the integrated form of equation (28), which for a first order reaction is:

$$A = A_o \exp\left[-k_A \int_0^t \exp\left[\frac{-E_A}{R}\frac{1}{T(t)}\right] dt\right] \qquad (29)$$

The integral is calculated numerically (Nelson, 1983). The nonisothermal approach requires very good temperature control and small experimental error in the concentration measurements. Yoshioka et al. (1987) in a statistical evaluation showed that a larger number of samples need to be measured to a higher reactant conversion than the isothermal method. The nonisothermal approach is very sensitive to experimental error in concentration measurements. Even at the precicion level of 2%, the one step isothermal method with experiments at three temperatures gave better accuracy in the estimation of the Arrhenius parameters than the nonisothermal method with a linearly increasing temperature in the same range and for the same total number of data points. Another usually overlooked factor is the nonuniform temperature within the samples due to the unsteady state heat transfer occurring during the nonisothermal experiment (Labuza, 1984). The nonisothermal method also does not allow for recognition of possible deviation of the reaction from an Arrhenius behavior above or below a certain temperature that sometimes occurs in foods.

Temperature dependence has been traditionally expressed in the food industry and the food science and biochemistry literature as Q_{10} the ratio of the reaction rate constants at temperatures differing by 10°C or the change of shelf life θ_s when the food is stored at a temperature higher by 10°C . The majority of the earlier food literature reports end-point data rather than complete kinetic modelling of quality loss. The Q_{10} approach in essence introduces a temperature dependence equation of the form

$$k(T) = k_o\, e^{bT} \qquad \text{or} \qquad \ln k = \ln k_o + bT \tag{30}$$

which implies that if ln k is plotted vs. temperature (instead of 1/T of the Arrhenius equation) a straight line is obtained. Equivalently, ln θ_s can be plotted vs. temperature. Such plots are often called shelf life plots, where b is the slope of the shelf life plot and k_o is the intercept. The *shelf life plots* are true straight lines only for narrow temperature ranges of 10 to 20 °C (Labuza, 1982). For such a narrow interval, data from an Arrhenius

plot will give a relatively straight line in a shelf life plot, i.e. Q_{10} and b are functions of temperature:

$$\ln Q_{10} = 10\ b = \frac{E_A}{R}\ \frac{10}{T\ (T+10)} \qquad (31)$$

The variation of Q_{10} with temperature for reactions of different activation energies is shown in Table 3.

Table 3. Q_{10} dependence on E_A and temperature.

E_A kJ/mol	Q_{10} at 4°C	Q_{10} at 21°C	Q_{10} at 35°C	Reactions in E_A range
50	2.13	1.96	1.85	Enzymic, hydrolytic
100	4.54	3.84	3.41	Nutrient loss, lipid oxidation
150	9.66	7.52	6.30	Non enzymatic browning

Similarly to Q_{10} the term Q_A is sometimes used. The definition of Q_A is the same as Q_{10} with 10 °C replaced by A °C :

$$Q_A = Q_{10}^{A/10} \qquad (32)$$

Another term used for temperature dependence of microbial inactivation kinetics in canning and sometimes of food quality loss (Hayakawa, 1973) is the z-value. The value of z is the temperature change that causes a 10-fold change in the reaction rate constant. As in the case of Q_{10}, z depends on the reference temperature. It is related to b and E_A by the following equation

$$z = \frac{\ln 10}{b} = \frac{(\ln 10)\ R\ T^2}{E_A} \qquad (33)$$

Other forms of the k(T) function have been proposed (Kwolek and Bookwalter, 1971) like linear, power and hyperbolic equations, but over a wide range of temperatures, the Arrhenius equation gave as good or better correlation.

Eyring's equation was utilized in the pharmaceutical industry (Kirkwood,1977):

$$\ln k = \ln(k_B/h) + S/R - H/RT + \ln T \qquad (34)$$

where H is the heat of activation, h is the Planck constant, k_B the Boltzmann constant and S is the entropy. Eyring's equation was applied to calculate the enthalpy/entropy compensation in food reactions (Labuza, 1980a) Theoretical equations based on the collision theory and the activated complex theory that introduce an additional temperature term to the Arrhenius relation were also discussed by Labuza (1980a). An example of such an equation is:

$$k = k' T^n \exp\left(-\frac{E_A}{RT}\right) \qquad (35)$$

where k' the preexponential factor and n a constant with value between 0 and 1.

It was concluded that the contribution of these terms is negligible at the temperatures relevant to food processing and storage.

Nevertheless, there are factors relevant to food and food quality loss reactions that can cause significant deviations from an Arrhenius behavior with temperature. (Labuza and Riboh, 1982). Phase changes are often involved. Fats may change to the liquid state contributing to the mobilization of organic reactants or vice-versa (Templeman et al., 1977). In frozen foods the effect of phase change of the water of the food is very pronounced in the immediate subfreezing temperature range. Generally, as freezing proceeds and the temperature is lowered, the reaction rate in nonenzymatic frozen systems follows a common pattern: (a) just below the initial freezing point the rate increases (in an almost discontinuous fashion) to values well above those obtained in the supercooled state at the same temperature; (b) passes through a maximum; and (c) finally declines at lower

temperatures (Fennema et al., 1973). This behavior is shown schematically in an Arrhenius plot in Figure 3. The rate increase is especially notable for reactants of low initial concentration. The rate enhancement induced by freezing is related basically to the freeze-concentration effect. This enhancement is prominent in the temperature zone of maximum ice formation. The width of this zone will depend on the type of food but generally will be in the range of -1°C to -10°C. Experimental studies showing this negative temperature effect were reviewed by Singh and Wang (1977). A dramatic demonstration of the described pattern was shown by Poulsen and Lindelov (1975) who studied the reaction rate between myosin and malonaldehyde in the range of 45°C to -40°C. Enzymatic reactions also deviate from the Arrhenius behavior in the immediate subfreezing range.

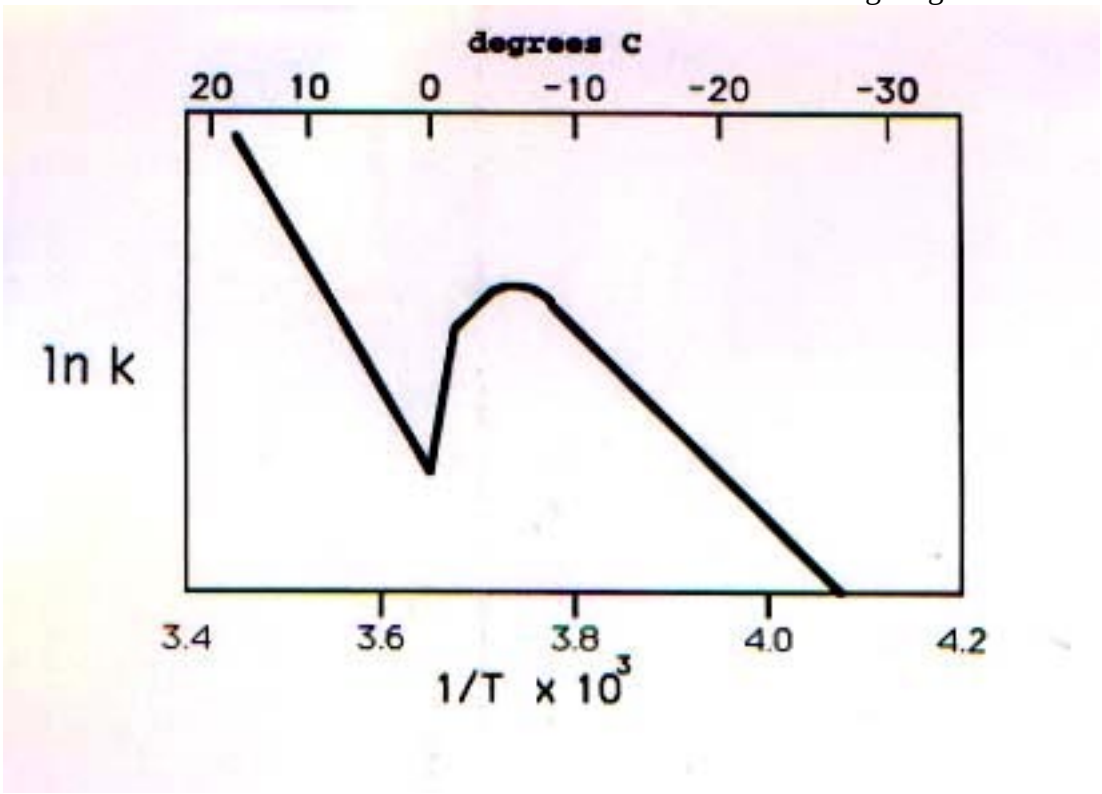

Figure 3. Anomalies in Arrhenius behavior. Typical effect of subfreezing temperatures to reaction rates.

Other phase change phenomena are also important. Carbohydrates in the amorphous state may crystallize at lower temperatures, creating more free water for other reactions but reducing the amount of available sugars for reaction (Kim et al., 1981). A characteristic case is the phenomenon of staling of bread (Zobel, 1973). Retrogradation of the amylopectin and a redistribution of moisture between starch and gluten have been implicated in staling. Staling shows a negative temperature effect between 4°C and 40°C, having the maximum rate at 4°C. A number of studies, using a variety of textural indices, were reviewed by Labuza (1982). A typical bread staling Arrhenius plot is shown in Figure 4 with an average "negative E_A " of - 9 kcal/mol.

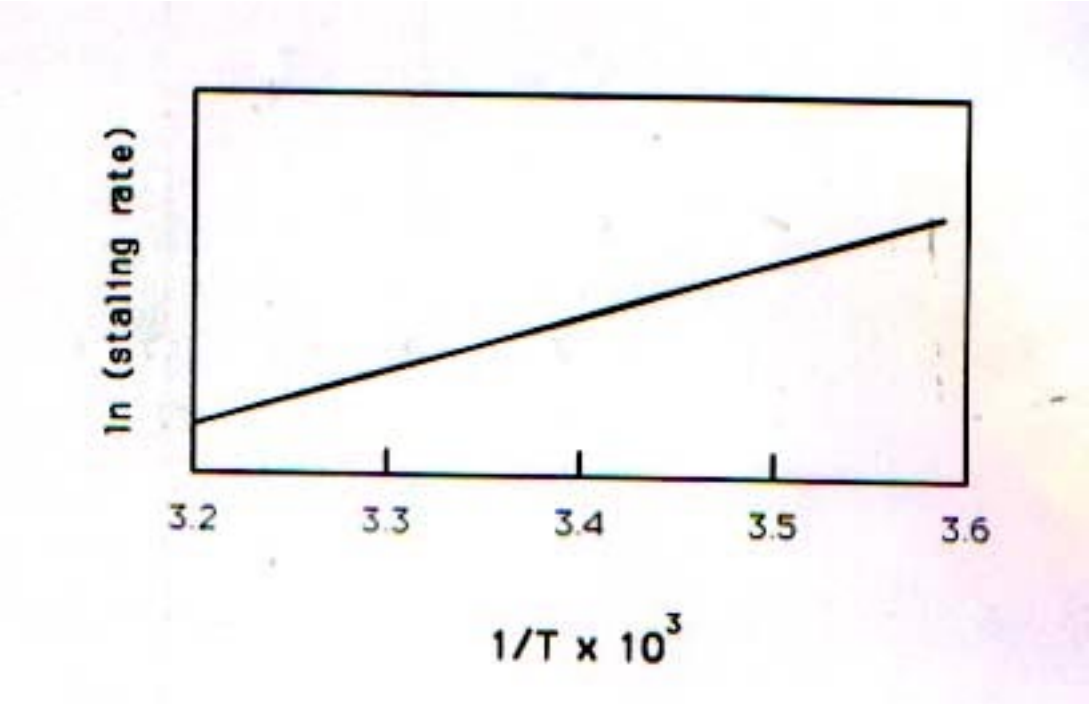

Figure 4. Anomalies in Arrhenius behavior. Effect of temperature on rate of bread staling.

Glass transition phenomena are also implicated in systems that, at certain temperature ranges, deviate significantly from an Arrhenius behavior. Certain processing conditions or drastic changes in storage conditions, such as rapid cooling and solvent removal, result in formation of metastable glasses, especially in carbohydrate containing foods (MacKenzie, 1977; Roos and Karel,1990; Levine and Slade,1988). Examples of such foods include spray dried milk (Bushill,1965), boiled sweets (White and Cakebread, 1969), frozen solutions (MacKennzie, 1977), whey powder and dehydrated vegetables (Buera and Karel, 1993).

Glass transition theory applicable to amorphous polymers has been used for food polymers and compounds of smaller molecular weight. Amorphous glasses undergo a glass to rubber transition at a temperature T_g. Above the glass transition temperature,T_g, there is a drastic decrease in the viscosity (from an order of 10^{12} to 10^3 Pa.sec) (Ferry, 1980) and a substantial increase in the free volume i.e. the space which is not taken by polymer chains themselves. This results in a greater polymer chain mobility and faster reactant diffusion. Often the dependence of the rate of a food reaction on temperature, when Tg is crossed, cannot be described with a single Arrhenius equation. A change of slope (i.e. in activation energy) is observed at Tg. Furthermore, above Tg, in the rubbery state, the activation energy may exhibit a temperature dependency, expressed as a gradually changing slope in the Arrhenius plot. Williams, Landel and Ferry (1955) introduced the WLF equation to empirically model the temperature dependence of mechanical and dielectric relaxations within the rubbery state. It has been proposed (Slade et al, 1989) that the same equation may describe the temperature dependence of of chemical reaction rates within amorphous food matrices, above Tg. In diffusion controlled systems where diffusion is free volume dependent, reaction rate constants can be expressed as function of temperature by the WLF equation (Sapru and Labuza, 1992):

$$\log\left(\frac{k_{ref}}{k}\right) = \frac{C_1(T-T_{ref})}{C_2+(T-T_{ref})} \qquad (36)$$

where k_{ref} the rate constant at the reference temperature T_{ref} ($T_{ref} > T_g$) and C_1, C_2 are system-dependent coefficients. Williams et al (1955), for $T_{ref}=T_g$, using experimental data for different polymers, estimated average values of the coefficients: $C_1=-17.44$ and $C_2=51.6$. In various studies these are used as universal values to establish the applicability of WLF equation for different systems. This approach can be misleading (Ferry,1980; Peleg, 1990; Buera and Karel,1993) and effort should be made to obtain and use system specific values.

Alternative approaches for accessing the applicability of the WLF model and calculating the values of C_1 and C_2 have been evaluated (Nelson, 1993; Buera and Karel, 1993). Eq. (36) can be rearranged into an equation of a straight line. Thus the plot of $\left[\log\frac{k_{ref}}{k}\right]^{-1}$ vs. $\frac{1}{T-T_{ref}}$ is a straight line with a slope equal to C_2/C_1 and an intercept of $1/C_1$. If the glass transition temperature, Tg, is known, the WLF constants at Tg can be calculated (Peleg,1992):

$$C_{1g}=\frac{C_1C_2}{C_2+T_g-T_{ref}} \qquad \text{and} \qquad C_{2g}=C_2+T_g-T_{ref} \qquad (37)$$

These values can be compared to the aforementioned average WLF coefficients.

When Tg and reaction rate data at many higher temperatures are available, k_g, C_1 and C_2 can be estimated from eq.(36) using non linear regression methodology.

Ferry (1980) proposed an additional approach for verifying the WLF equation and determining the coefficients. A temperature T_∞ , at which the rate of the reaction is practically zero, is used. T_∞ can be approximated by the difference between the reference temperature and C_2 i.e. $T_\infty=T_{ref}-C_2$. Rearranging eq. (36)

$$\log\left(\frac{k_{ref}}{k}\right) = \frac{C_1(T-T_{ref})}{T-T_\infty} \qquad (38)$$

i.e. if T_∞ is chosen correctly, a plot of $\log(k/k_{ref})$ vs. $(T-T_{ref})/(T-T_\infty)$ is linear through the origin with slope equal to C_1. T_g-50° C was proposed as a good initial estimate of T. Buera and Karel (1993) used this approach to test the applicability of WLF equation in modeling the effect of temperature on the rate of nonenzymatic browning, within several dehydrated foods and carbohydrate model systems. Table 4 gives the calculated values of the coefficients of the WLF equation for the different systems at the used reference temperature as well as at T_g, for different moisture contents.

Table 4. WLF coefficients determined for several foods and model systems reported at a reference temperature (C_1 and C_2) and transformed to correspond to $T_{ref} = T_g$ (C_{1_g} and C_{2_g}) (Buera and Karel, 1993)

System	T_{oo}	Tref (C)	Tg (C)	moisture (g H_20/g solid)	.C_1	C_2	C_{1_g}	C_{2_g}
apple	T_g-50	55	22	0.014	8.79	83	14.59	50
			2	0.022	8.79	103	18.05	50
			-7	0.050	8.79	112	19.69	50
			-13	0.087	8.70	118	20.73	50
			-24	0.011	8.79	129	22.68	50
			-38	0.017	8.79	143	25.14	50
cabbage	T_g-50	45	15	0.014	7.82	80	12.5	50
			5	0.021	7.82	90	14.07	50
			1	0.032	7.82	94	14.7	50
			-8	0.056	7.82	103	16.1	50
			-29	0.089	7.82	115	17.98	50
			-26	0.117	7.82	121	18.92	50
			-58	0.179	7.82	153	23.93	50
carrot	T_g-50	43	-5	0.054	7.44	98	14.58	50
			-20	0.062	7.44	103	15.33	50
			-15	0.080	7.44	108	16.07	50
nonfat	T_g-100	90	101	0.000	8.1	89	7.2	100
dried milk			65	0.012	8.1	125	10.14	100
			44	0.059	8.1	146	11.83	100
nonfat	T_g-100	90	50	0.030	6.8	140	9.52	100
dried milk			45	0.040	6.8	145	9.86	100
			40	0.050	6.8	150	10.2	100
onion	T_g-50	30	-8	0.056	8.8	88	15.9	50
			-20	0.089	8.8	100	18.1	50
			-58	0.189	8.8	138	24.5	50
potato	T_g-65	50	30	0.049	7.92	85	10.4	65
			20	0.094	7.92	95	11.6	65
			-5	0.150	7.92	120	14.6	65
			-15	0.200	7.92	130	15.84	65
whey powder	T_g-100	35	29	0.059	8.4	106	9.0	100
			18	0.080	8.4	117	9.9	100
model sys1*	T_g-90	45	45	0.059	8.3	90	8.3	90
model sys2**	T_g-10	55	40	0.073	6.93	135	7.8	120

* model system 1 composition: 99 % poly(vinyl pyrrolidone), 0.5 % glucose, 0.5 % glycine.
** model system 2 composition: 98 % poly(vinyl pyrrolidone), 1 % xylose, 0.5 % lysine.

A number of recent publications debate the relative validity of the Arrhenius and WLF equations in the rubbery state namely in the range 10 to 100° C above Tg. This dilemma may very well be an oversimplification. (Karel,1993). As mentioned above, processes affecting food quality that depend on viscosity changes (e.g. crystallization, textural changes) fit the WLF model. However chemical reactions may be either kinetically limited, when $k<<\alpha D$ (where D the diffusion coefficient and α a constant independent of T) , diffusion limited when $k>>\alpha D$ or dependent on both when k and αD of the same order of magnitude. In the latter case the effective reaction rate constant can be expressed as $\frac{k}{1+k/\alpha D}$. k in most cases exhibits an Arrhenius type temperature dependence and D has been shown in many studies to either follow the Arrhenius equation with a change in slope at T_g or to follow the WLF equation in the rubbery state and especially in the range 10 to 100° C above T_g. The value of the ratio $k/\alpha D$ defines the relative influence of k and D and determines whether the deteriorative reaction can be successfully modeled by a single Arrhenius equation for the whole temperature range of interest or a break in slope occurs at T_g with a practically constant slope above T_g or with a changing slope in which case the WLF equation will be used for the range 10 to 100° C above T_g. In complex systems where multiple phases and reaction steps can occur, successful fit to either model has to be considered as an empirical formula for practical use and not an equation explaining the mechanism or phenomenon.

When several reactions with different E_A's are important to food quality, it is possible that each of them will predominantly define quality for a different temperature range. Thus, for example, if quality is measured by an overall flavor score, the quality change rate vs. 1/T will have a different slope in each of these regions. This is shown schematically in Figure 5. A typical example of such a behavior is quality loss of

dehydrated potatoes where lipid oxidation and loss of fat soluble vitamins predominates up to 31°C and nonenzymatic browning and lysine loss above 31°C (Labuza, 1982).

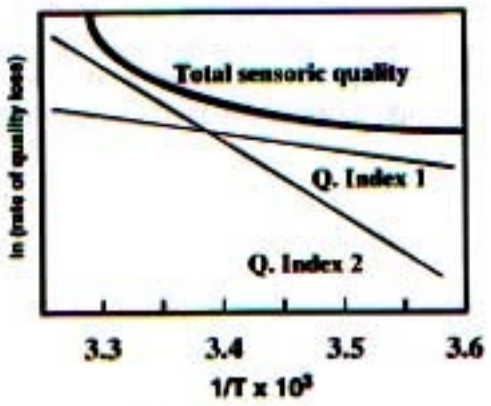

Figure 5. Typical temperature dependence of quality loss when reactions of different E_A affect quality.

The behavior of proteins at high enough temperature whereby they denature and thus increase or decrease their susceptibility to chemical reactions depending upon the stereochemical factors that affect these reactions, is another factor that can cause non-Arrhenius behavior. For reactions that involve enzymatic activity or microbial growth the temperature dependence plot shows a maximum rate at an optimum temperature, below and above which an Arrhenius type behavior is exhibited. This is demonstrated in Figure 6.

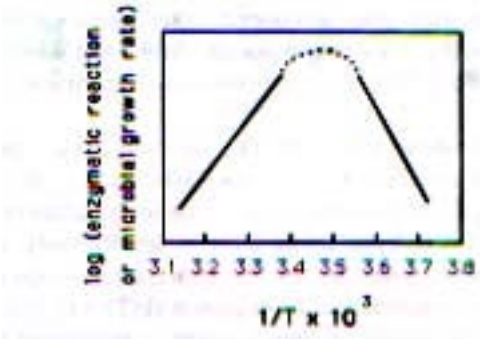

Figure 6. Typical temperature dependence curve of an enzymatic reaction or microbial growth.

The study of the temperature dependence of microbial growth has lately been an area of increased activity. The described kinetic principles are applied to compile the neccessary data for modeling growth behavior, in a multidisciplinary field coded *predictive microbiology* (Buchanan,1993; McClure et al., 1994; McMeekin et al., 1993). For a temperature range below the optimum growth temperature either of the two simple equations, Arrhenius and square root, sufficiently model the dependence for all practical purposes (Labuza et al., 1991). The two-parameter empirical square root model, proposed by Ratkowsky et al.(1982) has the form

$$\sqrt{k} = b\,(T-T_{min}) \qquad (39)$$

where k is growth rate, *b* is slope of the regression line of $\sqrt{k}$ vs temperature, and T_{min} is the hypothetical growth temperature where the regression line cuts the T axis at $\sqrt{k}$ =0. The relation between Q_{10} and this expression is

$$Q_{10}=\left(\frac{T-T_{min}+10}{T-T_{min}}\right)^2 \qquad (40)$$

Equations with more parameters, to model growth (and lag phase) dependence through the whole biokinetic range, were also introduced, either based on the square root model (Ratkowsky et al., 1983) or the Arrhenius equation (Mohr and Krawiek, 1980 ; Scoolfield et al., 1981, Adair et al., 1989). They were reviewed and experimentally evaluated by Zwietering et al. (1991).

Traditionally the mathematical models relating the numbers of microorganisms to temperature have been divide into two main groups (Whiting and Buchanan, 1994): Those describing propagation or growth primarily refer to the lower temperature range, and those describing thermal destruction at lethal temperature range. Recently, a combined approach utilizing a single mathematical formula to describe both the propagation and destruction rate constant over the entire temperature range, from growth (k(T)>0) to lethality was

proposed (Peleg, 1995). The main applicability of such a model is to account for changes that take place at a temperature range where transition from growth to lethality occurs.

Finally, temperature can have an additional indirect effect by affecting other reaction determining factors, which will be discussed in the next section. A temperature increase, increases the water activity at the same moisture level or enhances the moisture exchange with the environment in cases of permeable packaging affecting the reaction rate. Reactions that are pH-dependent can be additionally affected by temperature change, since for many solute systems pH is a function of temperature (Bates, 1973). Solubility of gases, especially of oxygen, changes with temperature (25% decrease with every 10°C increase for O_2 in water) thus affecting oxidation reactions where the oxygen is limiting.

10.2.2.2.Effects of other environmental factors

Moisture content and water activity (a_w) are the most important E_j factors besides temperature that affect the rate of food deterioration reactions. Water activity describes the degree of boundness of the water contained in the food and its availability to act as a solvent and participate in chemical reactions (Labuza, 1977).

Critical levels of a_w can be recognized above which undesirable deterioration of food occurs. Controlling the a_w is the basis for preservation of dry and intermediate moisture foods (IMF). Minimum a_w values for growth can be defined for different microbial species. For example, the most tolerant pathogenic bacterium is *Staphylococcus aureus* , which can grown down to an a_w of 0.85-0.86. This is often used as the critical level of pathogenicity in foods. Beuchat (1981) gives minimum a_w values for a number of commonly encountered microorganisms of public health significance.

Textural quality is also greatly affected by moisture content and water activity. Dry, crisp foods (e.g., potato chips, crackers) become texturally unacceptable upon gaining moisture above the 0.35 to 0.5 a_w range (Katz and Labuza, 1981). IMF like dried fruits

and bakery goods, upon losing moisture below an a_w of 0.5 to 0.7, become unacceptably hard (Kochhar and Rossel, 1982). Recrystallization phenomena of dry amorphous sugars caused by reaching an a_w of 0.35 - 0.4 affect texture and quality loss reaction rates, as already mentioned.

Besides the specific critical a_w limits, water activity has a pronounced effect on chemical reactions. This effect plays a very important role in the preservation of IMF and dry foods. Generally, the ability of water to act as a solvent, reaction medium and as a reactant itself increases with increasing a_w. As a result, many deteriorative reactions increase exponentially in rate with increasing a_w above the value corresponding to the monolayer moisture. This can be represented schematically in a global food stability map (Figure 7) .

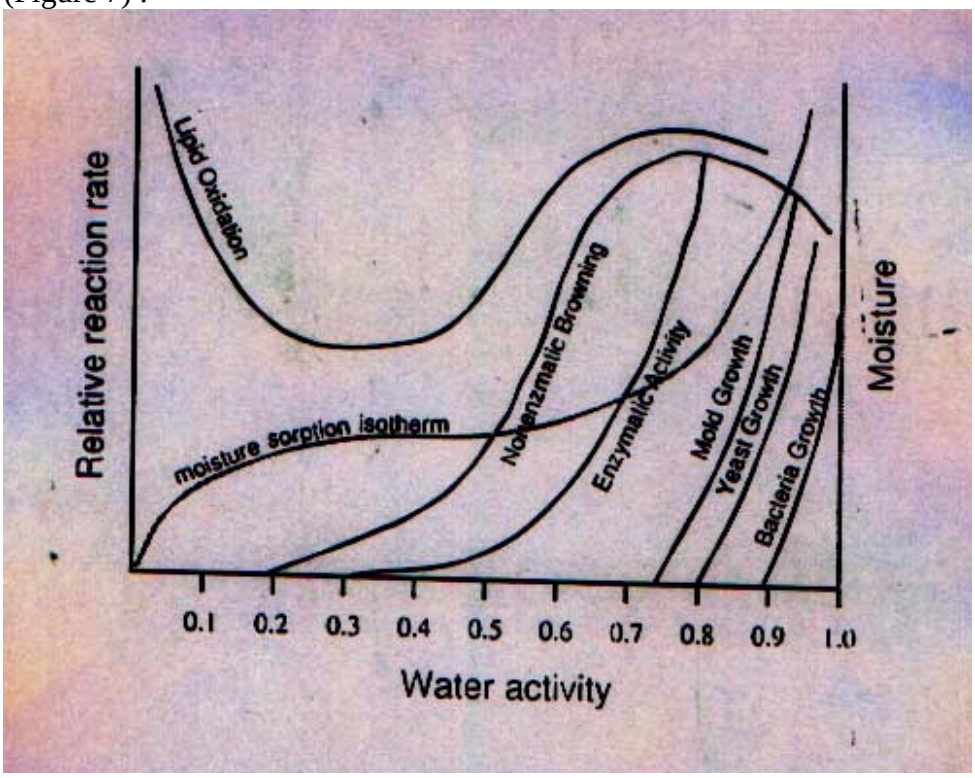

Figure 7. Global Food Stability Map (adapted from Labuza et al., 1969).

The critical a_w limits for microbial growth and the relative rates of reactions important to food preservation such as lipid oxidation and nonenzymatic browning can be seen in this figure (Fig.7). The underlying reasons for this behavior has been the subject of several studies (Taoukis et al., 1988a). Most reactions have minimal rates up to the monolayer value. Lipid oxidation shows the peculiarity of a minimum at the monolayer (m_o) with increased rates below and above it (Labuza, 1975; Quast et al., 1972).

The proposed theories that attempt to explain the effect of a_w on food deterioration reaction as well as ways to systematically approach and model this effect are discussed by Labuza (1980b). The moisture content and water activity can influence the kinetic parameters (k_A, E_A), the concentrations of the reactants and in some cases even the apparent reaction reaction order, n. Most relevant studies have modeled either k_A as a function of a_w (Labuza, 1980b) related to the change of mobility of reactants due to a_w dependent changes of viscosity, or E_A as a function of a_w (Mizrahi, et al., 1970 a; b). The inverse relationship of E_A with a_w (increase in a_w decreases E_A and vice versa) could be theoretically explained by the proposed phenomenon of enthalpy-entropy compensation. The applicability of this theory and data that support it have been discussed by Labuza (1980a).

Additionally moisture content and a_w directly affect the glass transition temperature of the system. With increasing a_w, T_g decreases. As was discussed in the previous section, transverse of T_g and change into the rubbery state, has pronounced effects, especially in texture and viscosity depended phenomena but also in reaction rates and their temperature dependence. It has been proposed for dehydrated systems that a critical mosture content / a_w alternative to the monolayer value of the BET theory, is the value at which the dehydrated system has a T_g of 25° C (Roos,1993). Consideration of these critical values contribute to explain textural changes occuring at distinct a_w and

ambient temperatures (e.g loss of crispness of snack foods above 0.3-0.5 or unacceptable hardness of IMF foods below 0.7-0.5) but their practical significance in a_w dependent chemical reactions is not straightforward and cannot be viewed isolated. Nelson and Labuza (1994) reviewed cases where the fundamental assumption that reaction rates within the ruberry state were dramatically higher than in the "stable" glassy state was not verified. In complex systems, matrix porosity, molecular size, and phenomena such as collapse and crystallization occuring in the rubbery state result in more complicated behavior. Both water activity and glass transition theory contribute to explain the relationship between moisture content and deteriorative reaction rates. It should be stressed though, that in contrast to the well established moisture isotherm determination, i.e the moisture-aw relation, accurate detremination of T_g as a function of moisture in a real food system is a difficult task and an area where much more work is needed. Furthermore, caution should be exercised when extrapolating state of the art knowledge to matters of safety. Water activity, used as mentioned above as an index of microbial stability, is a well established and practical tool in the context of hurdle technology. Additional criteria related to T_g should be considered only after careful challenge and sufficient experimental evidence (Chirife and Buera, 1994).

Mathematical models that incorporate the effect of a_w as an additional parameter can be used for shelf life predictions of moisture sensitive foods (Mizrahi et al.,1970 a; Cardoso and Labuza, 1983, Nakabayashi et al., 1981). Such predictions can be applied to packaged foods in conjunction with moisture transfer models developed based on the properties of the food and the packaging materials (Taoukis et al., 1988b). Also ASLT methods have been used to predict shelf life at normal conditions based on data collected at high temperature and high humidity conditions (Mizrahi et al., 1970b).

The pH of the food system is another determining factor. The effect of pH on different microbial, enzymatic and protein reactions has been studied in model biochemical

or food systems. Enzymatic and microbial activity exhibits an optimum pH range and limits above and below which activity ceases, much like the response to temperature (Figure 6). The functionality and solubility of proteins depend strongly on pH, with the solubility usually being at a minimum near the isoelectric point (Cheftel et al.,1985), having a direct effect on their behavior in reactions.

Examples of important acid-base catalyzed reactions are nonenzymatic browning and aspartame decomposition. Nonenzymatic browning of proteins shows a minimum near pH=3-4 and high rates in the near neutral-alkaline range (Feeney et al., 1975; Feeney and Whitaker, 1982). Aspartame degradation is reported at a minimum at pH=4.5 (Holmer, 1984), although the buffering capacity of the system and the specific ions present have significant effect (Tsoumbeli and Labuza, 1991). Unfortunately very few studies consider the interaction between pH and other factors e.g temperature. Such studies (Bell and Labuza, 1991and1994; Weismann et al., 1993) show the significance of these interactions and the need for such information for the design and optimization of real systems. Significant progress in elucidating and modeling the combined effect to microbial growth of factors such as T, pH, a_w or salt concentation has been achieved in the field of predictive microbiology (Ross and McMeekin, 1994; Rosso et al., 1995)

Gas composition also affects certain quality loss reactions. Oxygen affects both the rate and apparent order of oxidative reactions, based on its presence in limiting or excess amounts (Labuza, 1971). Exclusion or limitation of O_2 by nitrogen flushing or vacuum packaging reduces redox potential and slows down undesirable reactions. Further, the presence and relative amount of other gases, especially carbon dioxide, and secondly ethylene and CO, strongly affects biological and microbial reactions in fresh meat, fruit and vegetables. The mode of action of CO_2 is partly connected to surface acidification (Parkin and Brown, 1982) but additional mechanisms, not clearly established, are in action . Quantitative modeling of the combined effect on microbial growth of

temperature and is an area of current research (Willocx et al., 1993). Different systems require different O_2 - CO_2 - N_2 ratios to achieve maximum shelf life extension. Often excess CO_2 can be detrimental. Alternatively, hypobaric storage, whereby total pressure is reduced, has been studied. Comprehensive reviews of controlled and modified atmosphere packaging (CAP/MAP) technology are given by Kader (1986); Labuza and Breene (1988) and Farber (1991). Bin et al. (1992) review the efforts that have focused on kinetically modeling the CAP/MAP systems.

Currently experiments with very high pressure technology (1,000 to 10,000 atm) are being conducted. This hydrostatic pressure, applied via a pressure transfering medium, acts without time delay and is independent of product size and geometry. It can be effective at ambient temperatures (Hoover, 1993). Key effects sought from high pressure technology include (Knorr, 1993): a) Inactivation of microorganisms, b) modification of biopolymers (protein denaturation, enzyme inactivation or activation, degradation), c) increased product functionality (e.g. density, freezing temperatures, texture) and d) quality retention (e.g. color, flavor due to the fact that only nonvalent bonds are affected by pressure). Kinetic studies of changes occurring during high pressure processing and their effects on shelf life of the foods are very limited and further research will be needed for this technology to be fully utilized.

To express the above diccussed effect of different factors in a simple mathematical form, the concept of the quality function can be used in a more general approach. Assuming that the quality of the food depends on i different quantifiable deterioration modes (quality factors), A_i, respective quality functions can be defined in analogy to Eq.14.

$$\boldsymbol{Q_i}(A_i) = k_i\, t \qquad (41)$$

The rate constant k_i of each particular deterioration mode is a function of the aforementioned factors, namely

$$k_i = \boldsymbol{f}\,(T, a_w, pH, P_{O_2}, P_{CO_2}...) \quad (42)$$

the values of which are in turn time dependent:

$$T=T(t),\ a_w = a_w(t),\ pH=pH(t),\ P_{O_2}= P_{O_2}(t),\ P_{CO_2}= P_{CO_2}(t) \quad (43)$$

The functions of (32) incorporate the effects of storage conditions, packaging method and materials and biological activity of the system. Thus for variable conditions the rate constant is overall a function of time, i.e. $k_i=k_i(t)$. In that case the quality function value at certain time is given by the expression

$$\boldsymbol{Q_i}(A_i) = \int_0^t k_i\, dt \quad (44)$$

If the lower acceptable value of the quality parameter A_i, noted as A_m is known then at time t the consumed quality fraction, Φ_{c_i} , and the remaining quality fraction, Φ_{r_i} , are defined as:

$$\Phi_{c_i}= \frac{\boldsymbol{Q_i}(A_i)-\boldsymbol{Q_i}(A_o)}{\boldsymbol{Q_i}(A_m)-\boldsymbol{Q_i}(A_i)} \quad (45)$$

$$\Phi_{r_i}= \frac{\boldsymbol{Q_i}(A_m)-\boldsymbol{Q_i}(A_i)}{\boldsymbol{Q_i}(A_m)-\boldsymbol{Q_i}(A_o)} \quad (46)$$

Knoweledge of the value of Φ_{r_i} for the different deterioration modes allows the calculation of the *remaining shelf life* of the food, θ_r, from the expression

$$\theta_r= \min\,[\,\Phi_{r_i}/k_i] \quad (47)$$

where the rate constants k_i are calculated for an assumed set of "remaining" constant conditions.

The above analysis sets the foundations of shelf life prediction of a complex system under variable conditions. The major tasks in a scheme like this, is recognition of the major deterioration modes, determination of the corresponding quality functions and estimation of Eq.(42) i.e. the effects of different factors on the rate constant. The latter is a difficult task for real food systems. Most actual studies concern the effect of temperature

and variable temperature conditions, with the expressed (or implied) assumption that the other factors are constant. Controlled temperature functions like square, sine, and linear (spike) wave temperature fluctuations can be applied to verify the Arrhenius model, developed from several constant-temperature shelf life experiments . Labuza (1984) gives analytical expressions for Eq. (44) for the above temperature functions using the Q_{10} approach. Similarly solutions can be given using the Arrhenius or square root models.

To systematically approach the effect of variable temperature conditions the concept of effective temperature, T_{eff}, can be introduced. T_{eff} is a constant temperature that results in the same quality change as the variable temperature distribution over the same period of time. T_{eff} is characteristic of the temperature distribution and the kinetic temperature dependence of the system. The rate constant at T_{eff} is analogously termed effective rate constant, and $\boldsymbol{Q_i}(A_i)$ of Eq.(44) is equall to k_{eff} t. If T_m and k_m are the mean of the temperature distribution and the corresponding rate constant respectively, the ratio Γ is also characteristic of the temperature distribution and the specific system, where

$$\Gamma=\frac{k_{eff}}{k_m} \qquad (48)$$

For some known characteristic temperature functions shown in Fig.8 analytical expressions for the Q_{10} and Arrhenius models are tabulated in Table 5.

Table 5. Analytical expressions for calculation of Γ for different temperature functions.

Function	Q_{10} Approach	Arrhenius Approach
Sine wave	$\Gamma=I_o(a_o b)$	$\Gamma \approx I_o\left[\frac{E_a a_o}{RT_m\langle T_m+a_o\rangle}\right]$
Square wave	$\Gamma=\frac{1}{2}[e^{a_o b}+e^{-a_o b}]$	$\Gamma=\frac{1}{2}\exp[\frac{E_A a_o}{RT_m(T_m+a_o)}]+\frac{1}{2}\exp[\frac{-E_A a_o}{RT_m(T_m-a_o)}]$
Spike wave	$\Gamma=\frac{e^{a_o b}-e^{-a_o b}}{2a_o b}$	$\Gamma=\frac{\exp[\frac{E_A a_o}{RT_m(T_m+a_o)}]-\exp[\frac{-E_A a_o}{RT_m(T_m-a_o)}]}{2\frac{E_A a_o}{RT_m(T_m+a_o)}}$
Random	$\Gamma=\frac{\sum_{j=0}^{n} e^{bT_j}\Delta t_j}{e^{bT_m}}$	$\Gamma=\frac{\sum_{j=0}^{n}\exp(\frac{-E_A}{RT_j})\Delta t_j}{\exp(\frac{-E_A}{RT_m})}$

$I_o(x)$ is a modified Bessel function of zero order. Its values can be calculated from an infinite series expansion, $I_o(x)=1+\frac{x^2}{2^2}+\frac{x^4}{2^2 4^2}+\frac{x^6}{2^2 4^2 6^2}+...$, or found in Mathematical Handbooks (Tuma, 1988).

From Γ of a variable temperature distribution the effective reaction rate and temperatures k_{eff} andT_{eff} and the value of the quality function for the particular deterioration mode are calculated. Comparison of this value to the experimentally obtained quality value, for variable temperature functions covering the range of practical interest is the ultimate validation of the developed kinetic models. This methodology was applied by Labuza and coworkers for various food reaction systems and agreement or deviation from predicted kinetic behavior was assessed (Berquist and Labuza, 1983; Kamman and Labuza,1981; Labuza et al. 1982; Riboh and Labuza, 1982; Saltmarch and Labuza,1982; Taoukis and Labuza,1989).

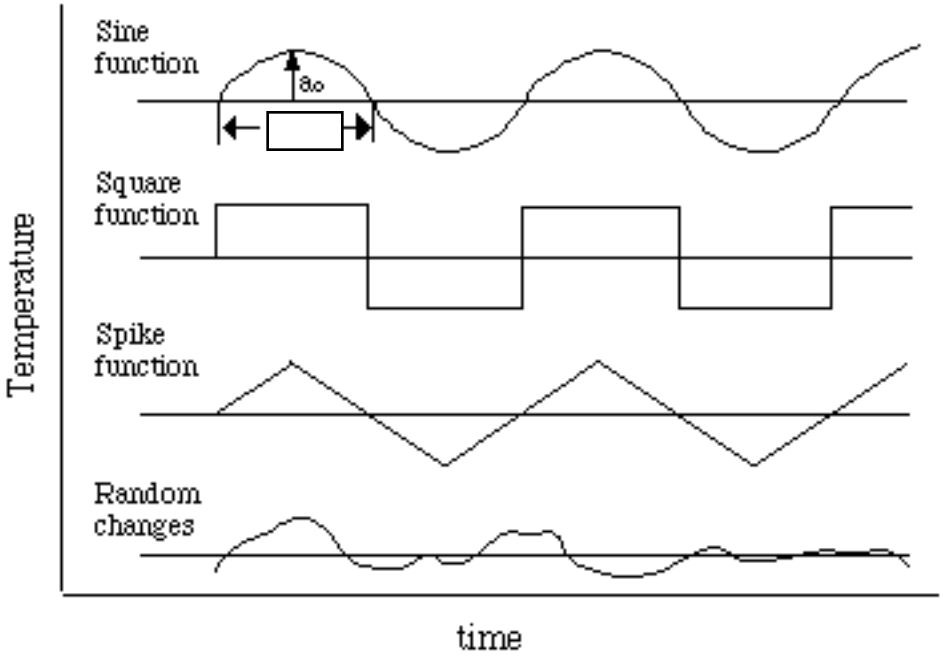

Figure 8. Characteristic fluctuating temperature distributions used to verify validity of kinetic models. a_o is the amplitude of the sine, square and spike wave functions.

Alternatively the effect of variable temperature distribution can be expressed through an equivalent time (t_{eq}), defined as the time at a reference temperature (is) resulting in the same quality change (i.e. same value of quality function) as the variable temperature. The practicality of t_{eq} is that if the chosen T_{ref} is the suggested keeping temperature e.g. 4°C for chilled products, it will directly give the remaining shelf life at that temperature. Note that if the mean temperature is chosen as the reference temperature, $T_{ref}=T_m$, then $t_{eq}/t=\Gamma$.

Further a short mention of the Equivalent point method is relevant. This approach has been used for evaluation and modelling of thermal processes (Nunes and Swartzel, 1990) and the response of Time Temperature Indicators (TTI) (Fu and Labuza, 1993). The same methodology would apply for quality loss during the shelf life of foods. Using the expression of the quality function

$$\boldsymbol{Q}(A) = k_A \exp\left(-\frac{E_A}{RT}\right) t \qquad (49)$$

and if $Y = \boldsymbol{Q}(A)/k_A$ then the above equation can be written as

$$\ln Y = \frac{-1}{RT} E_A + \ln t \qquad (50)$$

i.e a plot of lnY vs E_A of different food systems gives a straight line. For a particular variable time-temperature distribution it is proposed that a unique point (T_e,t_e) is defined from the slope and intercept of Eq.(50). This would allow calculation of the quality change in a food system of known E_A from the measured change of two (at least) other food systems (or TTI) subjected to the same time -temperature conditions. It has been recently argued that this approach is only valid for isothermal conditions (Maesmans et al., 1995).

10.3 APPLICATION OF FOOD KINETICS IN SHELF LIFE PREDICTION AND CONTROL

10.3.1.Accelerated Shelf Life Testing

Taking into account the described limitations and the possible sources of deviation, the Arrhenius equation can be used to model food degradation for a range of temperatures. This model can be used to predict reaction rates and shelf life of the food at any temperature within the range, without actual testing. Equally important it allows the use of the concept of accelerated shelf life testing (ASLT).

ASLT involves the use of higher testing temperatures in food quality loss and shelf life experiments and extrapolation of the results to regular storage conditions through the use of the Arrhenius equation. That cuts down very substantially the testing time. A reaction of an average E_A of 90 kJ/mol may be accelerated by 9 to 13 times with a 20°C increase in the testing temperature, depending on the temperature zone. Thus an experiment that would take a year can be completed in about a month. This principle and the methodology in conducting effective ASLT are described by Labuza (1985), Labuza and Schmidl (1985), and in a publication by the Institute of Food Science and Technology, UK (IFST,1993).

Designing a shelf life test is a synthetic approach that requires sufficient understanding of all food related disciplines, namely food engineering food chemistry, food microbiology, analytical chemistry, physical chemistry, polymer science and food regulations. The following steps outline the ASLT procedure:

1. Evaluate the microbiological safety factors for the proposed food product and process. Use of the Hazard Analysis Critical Control Point (HACCP) principles is a good approach to be followed from the design stage. If major potential problems exist at this

stage (i.e .CCP's exist that are difficult to control) , the formula or process should be changed.

2. Determine from a thorough analysis of the food constituents, the process and the intended storage conditions, which biological and physicochemical reactions will significantly affect shelf life and hence can be used as quality loss indices. A good knowledge of the system, previous experience and a thorough literature search are the tools to fulfill this step. If from this analysis it seems likely, without actual testing, that required shelf life is not likely to be achieved because of serious quality loss potential, product design improvement must be considered.

3. Select the package to be used for the shelf life test. Frozen, chilled and canned foods can be packaged in the actual product packaging. Dry products should be stored in sealed glass containers or impermeable pouches at the product's specified moisture and a_w.

4. Define the test's storage temperatures. The following Table can be used a quldeline.

Product type	Test temperatures (°C)	Control (°C)
Canned	25, 30, 35, 40	4
Dehydrated	25, 30, 35, 40, 45	-18
Chilled	5, 10, 15, 20	0
Frozen	-5, -10, -15	< -40

5. From the desired shelf life at the expected storage and handling temperatures, and based on available information on the most likely Q_{10}, calculate testing

time at each selected temperature. If no information is available on the expected Q_{10} value, minimum three testing temperatures should be used.

6. Decide the type and frequency of tests to be conducted at each temperature. A useful formula to determine the minimum frequency of testing at all temperatures based on the testing protocol at the highest temperature

$$f_2=f_1\, Q_{10}^{\Delta T/10} \qquad (51)$$

where f_1 is the time between tests (e.g., days, weeks) at highest test temperature T_1; f_2 is the time between tests at any lower temperature T_2; and ΔT is the difference in degrees Celsius between T_1 and T_2. Thus, if a canned product is held at 40°C and tested once a month, then at 30°C (i.e $\Delta T=5$) and a Q_{10} of 3, the product should be tested at least every 1.73 months. Usually, more frequent testing is recommended, especially if the Q_{10} is not accurately known. Use of too long intervals may result in an inaccurate determination of shelf life and invalidate the experiment. At each storage condition, at least six data points are required to minimize statistical errors; otherwise, the statistical confidence in the obtained shelf life value is significantly reduced.

7. Plot the data as it is collected to determine the reaction order and to decide whether test frequency should be altered. It is a common practice for the data not to be analyzed until the experiment is over and then it is recognized that changes in the testing protocol, affected early on, would have added significantly to the reliability of the results.

8. From each test storage condition, determine reaction order and rate, make the appropriate Arrhenius plot, and predict the shelf life at the desired actual storage condition. Product can also be stored at the final condition, to determine its shelf life and test the validity of the prediction. However, in industry this is uncommon because of time and cost constraints. It is a much more effective and realistic practice to test the obtained

predictive shelf life model by conducting an additional test at a controlled variable temperature. The results will be compared to the predicted values according to Table 5.

Mathematical models that incorporate the effect of a_w as an additional parameter can be used for shelf life predictions of moisture sensitive foods. Such predictions can be applied to packaged foods in conjunction with moisture transfer models developed based on the properties of the food and the packaging materials (Taoukis et al., 1988b). Also ASLT methods have been used to predict shelf life at normal conditions based on data collected at high temperature and high humidity conditions (Mizrahi et al., 1970b). Weissman et al. (1993) propose a novel approach for ASLT whereby not only external conditions but concentration of selected reactants or catalysts are used to accelerate the storage test. When this is feasible high acceleration ratios can be achieved and testing times can be reduced significantly.

10.3.2 Use of Time Temperature Indicators as shelf life monitors

Generally a *Time-Temperature Indicator* (TTI) can be defined as a simple, inexpensive device that can show an easily measurable, time-temperature dependent change that reflects the full or partial temperature history of a (food) product to which it is attached. TTI operation is based on mechanical, chemical, enzymatic or microbiological systems that change irreversibly from the time of their activation. The rate of change is temperature dependent, increasing at higher temperatures in a manner similar to most physicochemical reactions. The change is usually expressed as a visible response, in the form of a mechanical deformation, colour development or colour movement. The visible reading thus obtained gives some information on the storage conditions that have preceded it. The ability of TTI to function as cumulative recorders of temperature history from their activation time to the time each response measurement is taken, make them useful for two types of applications.

TTI can be used to monitor the temperature exposure of individual food packages, cartons or pallet loads during distribution up to the time they are displayed at the supermarket. By being attached to individual cases or pallets they can give a measure of the preceding temperature conditions at each receiving point. These points would serve as information gathering and decision making centres. The information gathered from all stations could be used for overall monitoring of the distribution system, thus allowing for recognition and possible correction of the more problematic links.

The second type of TTI application involves their use as quality monitors. With quality loss being a function of temperature history and with TTI giving a measure of that history, their response can presumably be correlated to the quality level of the food. If that can be achieved, TTI can be used in either (or both) of two ways. The first would be as an inventory management and stock rotation tool at the retail level. The approach used presently is the First In First Out (FIFO) system according to which, products received first and/or with the closest expiration date on the label are displayed and sold first. This approach aims in establishing a "steady state" with all products being sold at the same quality level. The assumption is that all products have gone through uniform handling, thus quality is basically a function of time. The use of the indicators can help establish a system that does not depend on this unrealistic assumption. The objective will again be the reaching of a "steady state" situation with the least remaining shelf life products being sold first. This approach could be coded LSFO (Least Shelf-life First Out). The LSFO system could theoretically (although not proven) reduce rejected products and eliminate consumer dissatisfaction since the fraction of product with unacceptable quality sent into the distribution system will be eliminated. Secondly, TTI attached on individual packaged products, can serve as dynamic or active shelf life labeling instead of (or in conjunction with) open date labeling. The TTI would assure the consumers that the products were

properly handled and would indicate remaining shelf life. Use of TTI as "consumer indicators" is the ultimate goal of these systems.

A variety of TTI based on different physicochemical principles have been described by Byrne (1976) and Taoukis et al.(1991). Statistical correlations of TTI performance and product quality characteristics have been reported for a variety of perishable and frozen foods (Tnker et al.,1985; Chen and Zall,1987; Wells and Singh,1988). A general approach that allows the correlation of the response of a TTI to the quality changes of a food product of known deterioration modes, without actual simultaneous testing of the indicator and the food, was developed by Taoukis and Labuza (1989a). Three types of TTI commercially available were mathematically modeled using Arrhenius kinetics. One type is based on a time-temperature depended diffusion of a dye along a wick , the second on a change of color due to a controlled enzymatic reaction and the third on development of color based on a solid state polymerization . A scheme was introduced that allows the correlation of the TTI response, X, to the quality index A of the food. X can be expressed as a function of time:

$$F(X)_t = k\,t = k_I \exp(-E_A / RT)\,t \qquad (52)$$

where F(X) is the response function of the TTI, t is the time and k the response rate constant; the constant k_I and the activation energy E_A are the Arrhenius parameters. For a TTI going through the same temperature distribution, T(t) as the monitored food, the value of $F(X)_t$ is known from the response X ; T_{eff} can then be calculated from equation (14) for $T=T_{eff}$. T_{eff} and knowledge of the kinetic parameters of deterioration of the food allows the evaluation of $\boldsymbol{Q}(A)$ and hence the quality loss of the product. The reliability of the TTI under variable temperature conditions was also assessed(Taoukis and Labuza, 1989b), using the relations of Table 5, and in general was judged satisfactory.

10.4 EXAMPLES OF APPLICATION OF KINETIC MODELING

10.4.1. Kinetic calculations

Two examples highlighted, are based on simulated model systems (Saguy and Cohen, 1990) describing a nonenzymatic browning reaction (Table 6; Figure 9) and thiamin retention (Table 7; Figure 10). The data was generated assuming the values of the energy of activation, E_A/R, the rate constant defined at a reference temperature, k_{ref} and the initial concentration A_o. A random error of +/- 5% was introduced to account for realistic experimental conditions and error. It is worth noting that in both examples, the reference temperature, T_{ref}, was chosen as 300 K. As pointed out previously, this transformtaion is important for improving the stability during numerical integration and for nonlinear parameter estimation. The transformation is also recommended since the parameters are highly co-linear and are not easily regressed directly (Cohen and Saguy, 1985; Haralampu et al., 1985; Nelson, 1983).

Linear and nonlinear subroutines were utilized to derive the regression coefficients and analyses (BMDP1R and BMDPAR; Dixon, 1989).

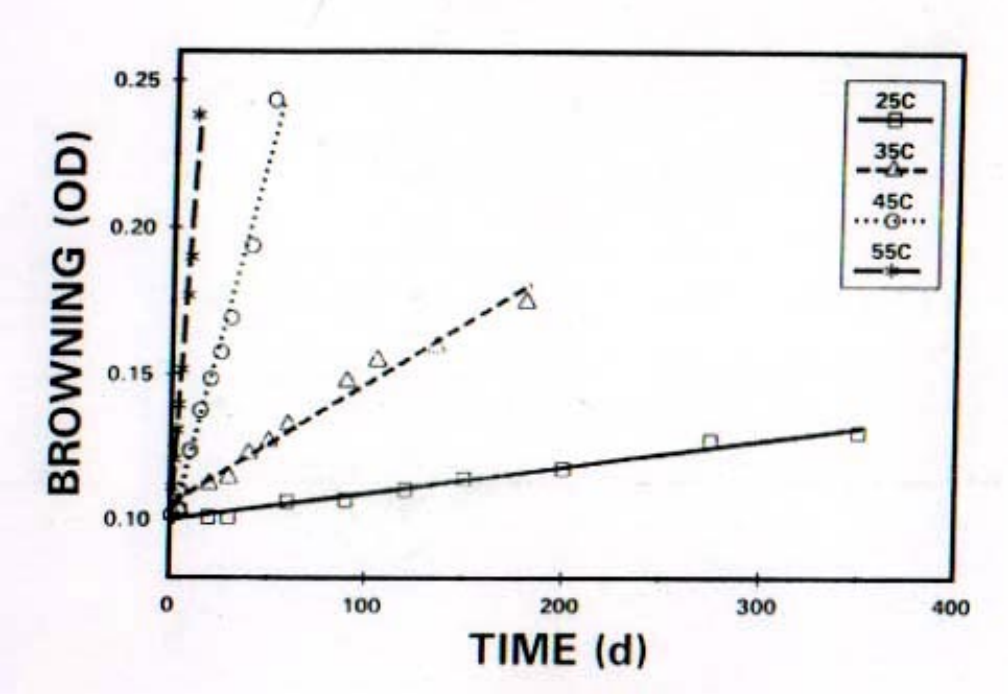

Figure 9. Nonenzymatic browning of a model system as a function of storage temperature (zero order reaction).

Table 6 Simulated nonenzymatic browning data [1] as a function of storage temperature for Figure 9

Time	Nonenzymatic browning (OD/g solid) for temperatures			
(days)	25 °C	35 °C	45 °C	55 °C
1			0.102	0.111
2				0.121
3				0.131
4				0.139
5	0.103	0.104	0.110	0.152
8				0.177
9				0.190
10			0.124	
11				0.238
15			0.137	
20	0.101	0.112	0.148	
25			0.158	
30	0.101	0.114	0.169	
40		0.123	0.194	
50		0.127	0.244	
60	0.106	0.133		
90	0.107	0.148		
105		0.155		
120	0.110			
135		0.160		
150	0.114			
180		0.175		
200	0.117			
275	0.127			
350	0.130			

(1) Adopted from Saguy and Cohen (1990).

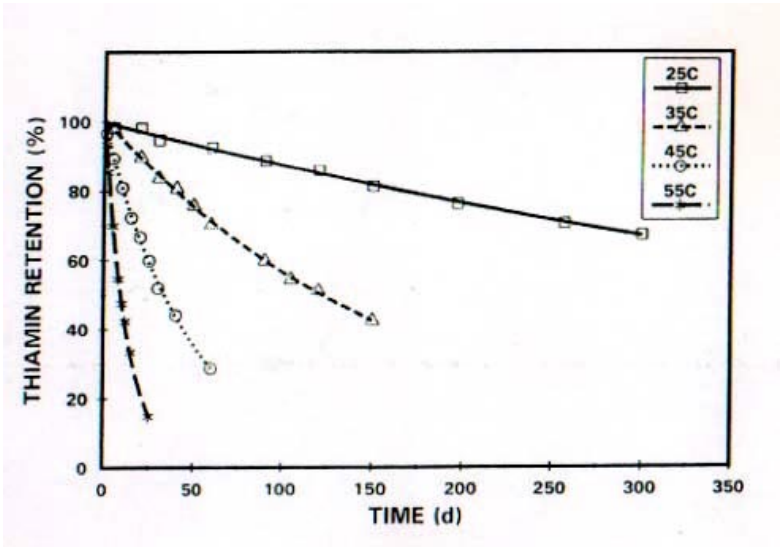

Figure 10. Thiamin retention of a model system as function of storage temperature (first-order reaction).

Table 7 Simulated thiamin retention (1) for a model system as a function of storage temperature (first - order reaction) for Figure 10

Time	Thiamin concentration (mg/g solid) for temperatures			
(days)	25 °C	35 °C	45 °C	55 °C
1			96.70	93.40
2				85.47
5	98.22	0.104	89.44	69.92
8				54.60
10			80.98	47.50
12				42.29
15			72.36	33.43
20	98.16	0.112	66.72	
25			59.91	14.80
30	94.80	0.114	51.93	
40		0.123	44.11	
50		0.127		
60	92.56	0.133	28.62	
90	88.61	0.148		
105		0.155		
120	85.84			
135		0.160		
150	81.27			
180		0.175		
197	76.29			
257	70.55			
300	67.15			

(1) Adopted from Saguy and Cohen (1990).

A. Two-step method

The most common method to estimate the Arrhenius' parameters is the classic succesive two-steps ordinary linear least squares fit. The first step is the regression of the quality function (Table 1; i.e., A_o for zero-order, or ln (A_t/A_o) for a first-order reaction) vs. time, at each temperature, to estimate the rate constant k, and the initial concentration A_o. The estimation of A_o avoids bias in the determination, and provides an additional croiterion of the adequacy of the model to describe the experimental data. A significant descrepancy between the estimated and experimental Ao suggests that a problem exists. The problem may be due to an inadequate kinetic model, large experimental error, insufficient number of data, etc. The second step is regression of ln(k) vs. [1/T - 1/Tref] to obtain the estimated of k_{ref} and E_A/R.

B. Non-linear Least Squares (one step method)

The nonlinear regression performs a single regression an all of the data points (i= 1, ...,n), to estimate E_A/R, k_{ref} and A_o, without calculating the rates for each temperature.

C. Results

The Arrhenius' parameters and the initial concentration derived using the two regression methods are summarized in Table 8 for nonenzymatic browning (zero-order) and thiamin (first-order) kinetics.

The results show no substantial differences among the derived values of E_A/R and k_{ref} when Methods 1 and 2 were applied. Nevertheless, the values derived by method 2 are closer to the actual values used for the simulation.

D. Confidence contour

As mentioned before the confidence contour for Ea/R and kref can be derived using a computer program (Draper and Smith, 1981) which incorporates approximation for a nonlinear regression of Eq.(27):

$$S = SS\ \{1+\frac{N_p}{n-Np}\ \ \mathbf{F}[N_p, n-N_p, (1-q)]\} \qquad (27)$$

where f is the fitted nonlinear model, SS is the nonlinear least square estimate of the fitted model, i.e. $SS= \Sigma[\ln(A_i-f)]^2$ for i=1 to n , n is the number of data points, N_p the number of parameters derived from the nonlinear least squares, 100(1-q)% the confidence level and **F** the F -statistics.

The values used for deriving the confidence contour for the nonlinear regression of the nonenzymatic browning data were as follows (Table 8):
SS=1.331 E-3; E_A/R=15,796; A_o=99.32 and F(3,34,90%)=2.27.
The fitted model, f, is replaced with the appropriate model based on the reaction order:

zero-order

$$f = A_o \pm t \exp\left[-\frac{E_A}{R}\left(\frac{1}{T}-\frac{1}{T_{ref}}\right)\right]$$

first order

$$f = \exp\left\{\ln(A_o) \pm t \exp\left[-\frac{E_A}{R}\left(\frac{1}{T}-\frac{1}{T_{ref}}\right)\right]\right\}$$

n - order (n not equal to 1)

$$f = \left\{A_o^{(n-1)} \pm (1-n)\, t \exp\left[-\frac{E_A}{R}\left(\frac{1}{T}-\frac{1}{T_{ref}}\right)\right]\right\}^{(1/(1-n))}$$

The appropriate sign +/- in the above equations should be chosen. For a reaction where concentration increases a positive should be used. For a depletion reactrion the negative sign should be utilized.

The algorithm implemented to derive the confidence region is as follows:

a. Initial concentration is assumed constant and the estimated value derived by the nonlinear regression is utilized.

b. The confidence contour is derived by choosing values of E_A/R and k_{ref} which fulfill the equality expressed in Eq. (27). Obviously, the value of E_A/R and k_{ref} are varied within the range of values that satisfies the inequality listed in Eq. (27). This trial and error procedure is normally carried out on a computer.

The derived confidence contour is depicted in Fig. 11. It shows the span in the calculated values of E_A/R and k_{ref}. When comparing the confidence regions derived by the

two regression methods. The nonlinear regression yields typically a smaller confidence region. This means that a better estimation of shelf-life prediction and simulation is possible (Cohen and Saguy, 1985; Haralampu et al., 1985).

Table 8 Effect of the regression method on the Arrhenius parameters derived for nonenzymatic browning (zero-order) and thiamin retention (first - order reaction)

Regression method	df[a]	k x 100 [b] 25 °C	35°C	45°C	55°C	E_A/R	k_{ref}[c] 25 °C	Ao[d] 25 °C	35°C	45°C	55°C	Aoavr[e]
Nonenzymatic Browning												
Simulated values						15000	13.5					0.100
Two steps	1	9.1	41.6	270.2	1157.9	16067	11.7	0.100	0.105	0.095	0.098	0.098
Non-linear	19	-	-	-	-	15796	12.2	-	-	-	-	0.099
Thiamin retention												
Simulated values						13000	0.178					100.0
Two steps	2	0.133	0.580	2.065	7.588	13125	0.175	99.7	100.4	99.2	101.5	100.2
Non-linear	16	-	-	-	-	12985	0.182	-	-	-	-	99.8

(a) Degrees of freedom
(b) Reaction rate constant: OD/g/day or day^{-1} for a zero and first order reaction, respectively
(c) Units of kref at 300 K as in b above
(d) Derived initial concentration: OD/g or mg/g thiamin for a zero and first order reaction respectively
(e) Average of the derived initial concentration. Units as in d above

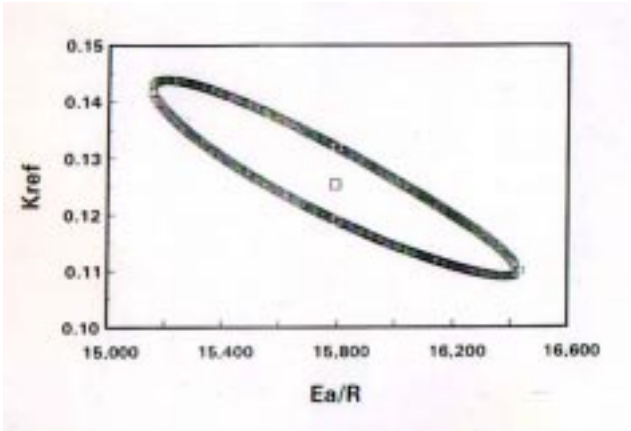

Figure 11. Joint confidence contour (90%) for E_A/R and kref derived by one-step nonlinear least squares method, for nonenzymatic browning.

10.4.2. Examples of shelf life modeling of food products

The preceeding kinetic calculation cases show how judiciously we should use the kinetic parameters we obtain from shelf life experiments. In most practical cases the two step method is used due to its simplicity and convenience. The results should be understood as mean values with possibly large confidence limits, and treated as such. Nevertheless, the information obtained from carefully designed shelf life testing, at three or more temperatures, is usually sufficient to allow derivation of satisfactory shelf life predicive models. Further two examples that illustrate the use of ASLT principles and kinetic modeling. The first, a commercially sterilized, flavored dairy beverage, sweetened with the sweetener aspartame, is a case of straightforward use of these principles, as the quality function of the food is defined by a dominant , quantifiable quality index, aspartame. In contrast, the second example, of a complex food system of many antagonizing quality deterioration modes illustrates the multidisciplinary approach and the deep knowledge of the system required for effective shelf life testing.

10.4.2.1 Aspartame sweetened chocolate drink.

This practical example is based on experimental data generated in studies by Bell and Labuza (1994) and Bell et al. (1994). These studies were intended to evaluate the aspartame stability in commercially sterilized skim milk beverages of various compositions. There is a steadily growing market for nutritious, low calorie dairy products, and aspartame as a high intensity sweetener, without the controversy surrounding saccharin, can be a very desirable ingredient. However, at the inherent pH of milk (6.6) the rate of aspartame degradation is very high, reducing significantly the sensory shelf life of the product Quantifying and modeling the behavior of this dominant quality index would allow optimization of the product formulation and extension of shelf life, possibly by slight alteration of the pH. For that purpose different commercially sterilized skim milks, sweetened with 200 ppm of aspartame and slightly buffered with citrates or phosphates to pH ranging from 6.38 to 6.67 were studied with regards to the aspartame degradation. Samples were stored at 5 temperatures from 0 to 30° C and triplicate samples were analyzed by HPLC, at appropriately spaced time intervals (based on Eq.(51) and an average Q_{10} value of 4 from the literature). Results of these experiments (at pH 6.67 with .008 M citrate) are listed in Table 9.

Table 9. Aspartame degradation in a pH 6.67 aseptic dairy system

Time	Aspartame concentration (ppm) for temperatures				
(hr)	30 °C	20 °C	10 °C	4 °C	0 C
10	181				
10	175				
10	182				
23	168	186			
23	166	172			
23	171	181			
38	130				
38	127				
38	141				
48	120	152			
48	101	160			
48	108	162			
78		172			
78		154			
78		153			
95			175		
95			173		
95			175		
121			168	189	198
121			168	180	195
121			167	186	194
143		146			
143		129			
143		150			
262		63	140	165	
262		73	134	165	
262		94	160	167	
455			114	132	159
455			96	117	152
455			118	121	155
599			93	110	136
599			87	104	136
599			91	88	134
694				80	130
694				95	119
694				86	113
767					115
767					109
767					103

In Fig. 12a aspartame concentration (APM or A) is plotted vs. time at the 5 temperatures. The best linear fit of the form $\boldsymbol{Q}(A)=kt$ was achieved for $\boldsymbol{Q}(A)=\ln(A/A_o)$, i.e. first order kinetics (Fig.12b). All measurements were included in the statistical analysis (no averaging of the 3 samples per time) to increase the degrees of freedom and include the measurement spread in the model. Calculated rate constants and 95% C.I. are given in Table 10.

Table 10. Aspartame degradation reaction rate constants with confidence intervals at 5 temperatures.

Rate constant	30° C	20° C	10° C	4° C	0° C
-k (hr^{-1})	0.0125	0.00356	0.00138	0.00121	0.000790
± 95% C.I.	± 0.0013	± 0.00046	± 0.00010	± 0.00009	± 0.000062

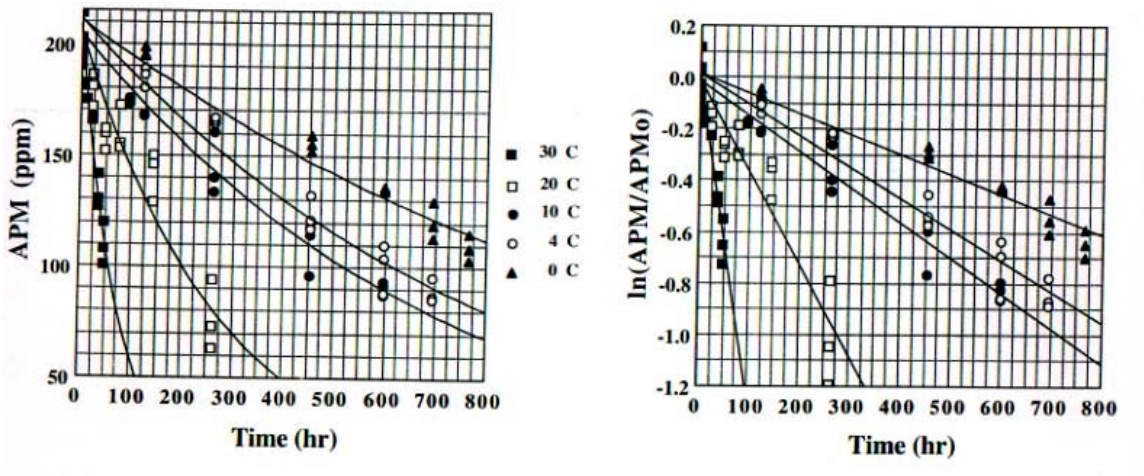

Figure 12. Aspartame degradation kinetics at five temperatures plot as function of time and as semi-log plot

To determine the Arrhenius parameters, -k is plotted in a semilogarithmic scale vs.the inverse of absolute temperature (or ln(-k) vs. 1/T). To increase the degrees of freedom and get a narrower confidence interval for the calculated parameters, the 95% C.I. for k are included (Fig. 13). The Arrhenius plot gives by linear regression the values of k_o=3.163 108 hr^{-1} and activation energy E_A= 14560 cal/mol. The coefficient of determination, R^2, is 0.952 and the 95% confidence interval 1830 cal/mol.

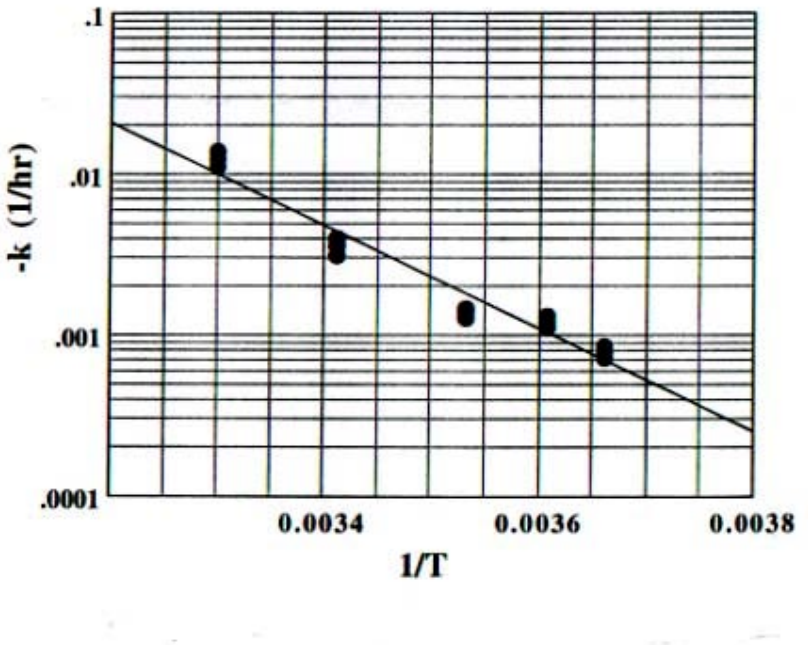

Figure 13. Aspartame degradation kinetics plotted as Arrhenius relation

The obtained kinetic information allows the prediction of aspartame degradation and thus the shelf life of the product for any keeping temperature. Thus, if one assumes that the product is overcompensated with aspartame at 0 time to allow for acceptable product sweetness up to the point that half of the sweetener is degraded, the shelf life at 4° C is approximately 4 weeks (670 hr). Remaining shelf life can also be calculated after exposure at any known temperature conditions. As an example, it is assumed that the aseptic milk product is exposed for ten days the temperature conditions shown in Figure 14. It is a non specific variable distribution with a mean temperature, T_m, of 7.1° C. The total aspartame degradation at the end of the 10 days can be calculated by integration. The value of ratio Γ (Eq.48 and Table 5) is determined as 1.0437. At T_m after 10 days, the remaining aspartame is 71.7%. Thus the actual aspartame level is calculated as 68.7%. This can further be translated to remaining shelf life at constant 4° C of 307 hr (12.8 days). Note that if the product was assumed to have remained at 4° C at the first 10 days, the remaining shelf life would be 18 days.

The practical value of the described approach is that it allows a systematic approach to shelf life prediction and optimization. Indeed similar results at the other studied pHs showed activation energies in the range of 14 to 18 kcal/mol and shelf lifes that reached 60 days at the lower end of pH range of 6.38. This is a valuable indication of

the approach to follow to increase shelf life of a product under development. Note also that although the experiments were conducted also at low temperatures, the satisfactory Arrhenius fit indicate that the alternative formulations can be studied only at the high temperatures, according to ASLT principles reducing the needed test time down to 200 hr.

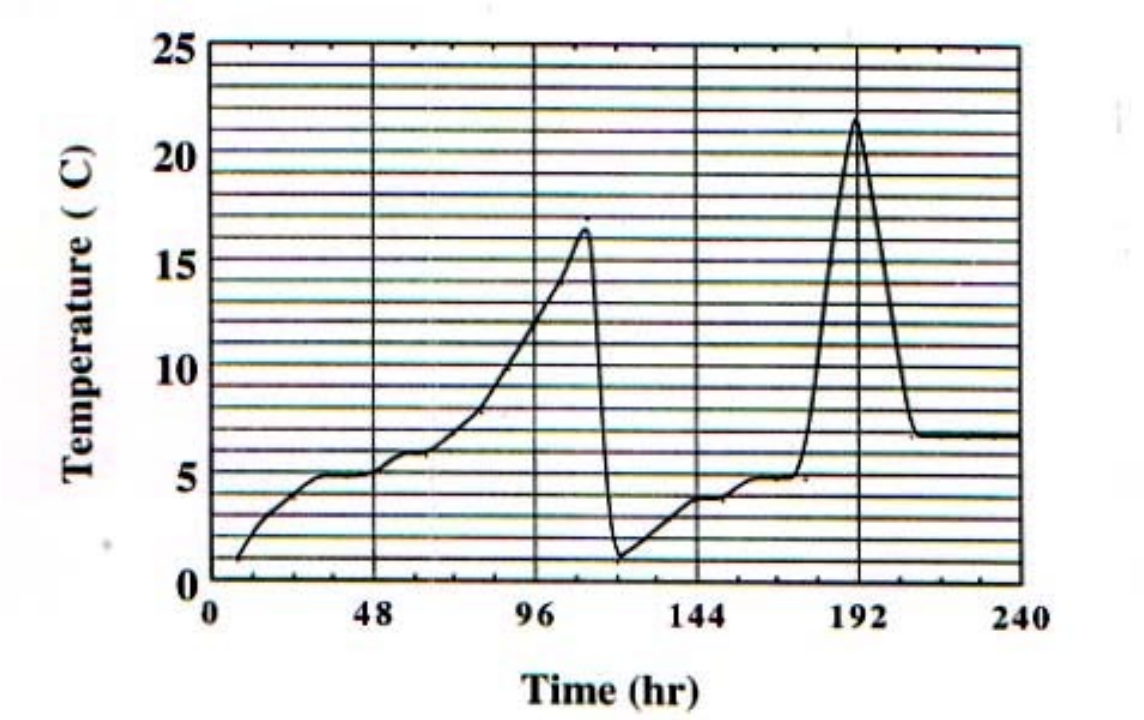

Figure 14. Time temperature sequence for the aspartame sweetened drink over 10 days

10.4.2.2. CASE OF COMPLEX FOOD SYSTEM

The preceeding example is very helpful in illustrating the systematic approach for shelf life life prediction in foods were dominant and easily quantifiable quality indices can be recognized. In multicomponent complex food products the situation might be more difficult to put in quantifiable terms. Nevertheless, a carefull approach of evaluating all the possible modes of deterioration, estimating the importance of their contribution under the expected conditions and the availability of methodology for measuring them, and finally

using a judiciously developed testing protocol based on the principles developed in this chapter. The "ultimate" example of food were such an approach is neededis fozen pizza. All the aspects affecting the quality of this product were detailed by Labuza and Schmidl, 1985 and Labuza, 1985. Systems to be considered for monitoring chemical changes in pizza during frozen storage include: Total free fatty acids, specific volatile free fatty acids by GLC, peroxides, oxidative volatiles (e.g., hexanal) by GLC, spice volatiles by GLC, lysine, color (decrease in red color or increase in brown), sensory properties: taste and flavor, and nutrient loss such as vit. A and C. Physical changes such as loss of crust crispness, loss of cheese functionality and meltability and development of in- package ice must also be considered. Finally, microbiological changes cannot be neglected especillay uder abuse senarios.

Detailed analysis of the relative contribution of the above factors and a proposed testing protocol can be found in the referenced sources.

REFERENCES

Arabshashi, A. (1982). Effect and interaction of environmental and composition variables on the stability of thiamin inintermediate moisture model systems.Ph.D. Thesis, University of Wisconsin, Madison, Wisconsin.

Arabshashi, A. and D.B. Lund (1985). Considerations in calculating kinetic parameters from experimental data. J. Food Proc. Engi. 7: 239-251.

Bates, R. G. (1973) "Determination of pH: Theory and Practice", 2nd ed. John Wiley and Sons, New York, NY.

Bell, L.N. and T.P.Labuza (1991) Aspartame degradation kinetics as affected by pH in intermediate and low moisture food systems. J. Food Sci. 56: 17-20.

Bell, L.N. and T.P.Labuza (1994). Influence of the low-moisture state on pH and its implications for reaction kinetics. J.Food Eng. 22: 291-312.

Bell, L.N. and T.P.Labuza (1994). Aspartame stability in commercially sterilized flavored dairy beverages. J.Dairy Sci. 77: 34-38.

Bell, L.N., Shoeman, D., Tsoubeli, M. and T.P.Labuza (1994). Kinetics of aspartame degradation in liquid dairy beverages. In: Developments in Food Engineering: Proceedings of the 6th Int. Congress on Engineering and Food. (Yano, T. Matsuno, R., Nakamura K. eds.) pp.489-491.

Benson, S.W. (1960). Foundations of Chemical Kinetics, McGraw-Hill, New York.

Bergquist, S., and T.P. Labuza (1983). Kinetics of peroxide formation in potato chips undergoing a sine wave temperature fluctuation. J. Food Sci. 43:712.

Beuchat, L. R. (1981) Microbial stability as affected by water activity. *Cereal Foods World* **26**, 345-349.

Boyle, W. C., Berthouex, P. M. and Rooney, T. C. (1974) Pitfalls in parameter estimation for oxygen transfer data. J. Environ. Engrg. Div., ASCE, 100(EE2), 391-408.

Buchanan, R.L. (1993). Predictive food microbiology. Trends Food Sci. Technol. 4: 6-11.

Bunher, D. (1974) Simple kinetic models from Arrhenius to computer. *Accts. Chem. Res.* **7**, 195.

Bushill, J. H., Wright, W.B., Fuller, C.H.F. and Bell, A.V. (1965). The crystallization of lactose with particular reference to its occurence in milk powders, J. Sci. Food Agr. 16, 622.

Buera, P. and M. Karel (1993). Application of the WLF equation to describe the combined effects of moisture, temperature and physical changes on non-enzymatic browning rates in food systems. J. Food Proc. Preserv. 17: 31-47.

Byrne, C. H. (1976) Temperature indicators - the state of the art. Food Technol. 30(6): 66-68.

Cardoso, G., and T.P. Labuza (1983). Effect of temperature and humidity on moisture transport for pasta packaging material. Br. J. Food Technol. 18: 587.

Cheftel, J. C., Cuq, J. and Lorient, D. (1985) "Aminoacids, peptides and proteins" in *Food Chemistry* , O.R. Fennema (ed), Marcel Dekker, New York.

Chen, SL. L. and Gutmanis, F. (1968) Auto-oxidation of extractable color pigments in chili pepper with special reference to ethoxyquin treatment. J. Food Sci., 33, 274-280.

Chen J. H. and R. R. Zall. (1987b). Packaged milk, cream and cottage cheese can be monitored for freshness using polymer indicator labels. Dairy Food Sanitation 7(8): 402.

Chirife, J. and Buera P. (1994). Water activity, glass transition and microbial stability in concentrated/semimoist food systems. J. Food Sci. 59: 921-927.

Cohen, E. and I. Saguy (1982) The effect of water activity and moisture content on the stability of beet powder pigments. J. Food Sci. 48: 703-707.

Cohen, E. and I. Saguy (1985) Statistical evaluation of Arrhenius model and its applicability in prediction of food quality losses. J. Food Proc. Pres. 9: 273-290.

Davey, K.R. (1989). A predictive model for combined temperature and water activity on microbial growth during the growth phase. J.Appl. Bacteriol. 67:483-488.

Dixon, W.J. (Ed.) (1989). "BMDP - Statistical Software", University of California Press, Berkley, CA.

Draper, N. and Smith, H. (1981). "Applied Regression Analysis", 2nd ed., Wiley, New York, NY.

Engel, (1981) "Enzyme Kinetics. The steady - State approach". 2nd Ed. Chapman and Hall, New York.

Feeney, R. E., Blackenhorn, G., Dixon, H. B. F. (1975) Carbohydrate-Amine reactions in protein chemistry. *Adv. Protein Chem.* **29**, 135-203.

Feeney, R. E., Whitaker, J.R. (1982) The Maillard reaction and its preservation. In Cerry, J. P. (ed) "Food Protein Deterioration, Mechanisms and Functionality". ACS Symposium series 206, ACS, Washington, D.C., 201-229.

Fennema, O., Powrie, W. D., Marth, E. H. (1973) "Low-Temperature Preservation of Foods and Living Matter", Marcel-Dekker, New York.

Ferry, J.D. (1980). Viscoelastic properties of Polymers, 3rd ed., Wiley , New York.

Fogler, H.S. (1986). Elements of Chemical Reaction Engineering, p. 63, Prentice Hall, Englewood Cliffs, NJ.

Fu B.and T.P.Labuza (1993). Shelf -life prediction : theory and application. Food Control 4: 125-133.

Fu, B., P.S. Taoukis, and T.P. Labuza (1991). Predictive Microbiology for monitoring spoilage of dairy products with time temperature indicators. J. Food Sci. 56:1209-1215.

Guadagni, D.G. (1968). Cold storage life of frozen fruits and vegetables as a unction of temperature and time, in Low Temperature Biology of Foodstuffs (J. Hawthorne and E.J. Rolfe, eds.), Pergamon Press, New York.

Haralampu, S. G., Saguy, I. and Karel, M. (1985) Estimation of Arrhenius model parameters using three least squares methods. *J.* Food Proc. Pres. 9: 129-143.

Hayakawa, K. (1973) New procedure for calculating parametric values for evaluating cooling treatments applied to fresh foods. Can. Inst. Food Sci. Technol. 6(3): 197.

Hendel, C.E., Silveira, V.G. and Harrington, W.O. (1955). Rates of nonenzymatic browning of white potato during dehydration, Food Tecnol. 9, 433.

Herborg, L. (1985) Shelf- Life - Quality: A question of relativity. I.I.F. - I.I.R. - (Commisions C2, D3) 1985-4, p. 39-43.

Hills, C. G. Jr. (1977) "An Introduction to Chemical Engineering Kinetics and Reactor Design" John Wiley and son, New York.

Hills, C. G. Jr., Grieger-Block, R. A. (1980) Kinetic data: Generation, interpretation, and use. Food Technol 34 : 56-66.

Holmer, B. (1984) Properties and Stability of Aspartame. Food Technol. 38: 50.

Hong Y.C., C.M. Koelsch, and T.P.Labuza (1991). Using the L number to predict the efficacy of moisture barrier properties of edible food coating materials. J. Food Proc. Pres. 15: 45-62.

Hoover D.G. (1993). Pressure effects on biological systems. Food Technol. 47(6):150-155.

Institute of Food Science and Technology (UK) (1993). Shelf Life of Foods-Guidelines for its Determination and Prediction. IFST, London.

Kader, A. A. (1986) Biochemical and physiological basis for effects of controlled and modified atmosperes on fruits and vegetables. Food Technol., 40(5):, 99.

Kamman J.F., Labuza T.P. and J.J. Warthesen. 1981. Kinetics of thiamin loss in pasta as a function of constant and variable storage conditions. J. Food Sci., 46(5):,1457.

Karel, M. (1985). Effects of water activity and water content on mobility of food components, and their effects on phase transitions in food systems. In "Properties of water in foods (Simatos, D. and Multon, J.L., eds), pp. 153-169. Martinusm, Nijhoff, Dordrecht.

Karel, M. (1993). Temperature-Dependence of Food Deterioration Processes. (Letter to the editor) J.Food Sci. 58(6): ii.

Karel, M. and Saguy, I. (1993). Effect of water on diffusion in food systems. In: "Water relation in Foods" (Levine, H. and Slade, L., eds), pp. 157-181. Plenum Press, NY.

Katz, E. E. and Labuza, T. P. (1981) Effect of water activity on the sensory crispness and mechanical deformation of snack food products. J. Food Sci., 46, 403.

Kim, M. N., Saltmarch, M. and Labuza, T.P. (1981) Nonenzymatic browning of hygroscopic whey powders inopen versus sealed pouches. J. Food Proc. Preserv. 5: 49.

Kirkwood, T.B.L. (1977). Predicting the stability of biological standards and products, Biometrics 33, 736.

Knorr D.(1993). Effects of high-hydrostatic -pressure processes on food safety and quality. Food Technol. 47(6):155-161.

Kochhar, S. P., Rossel, J. B. (1982). A vegetable oiling agent for dried fruits. J. Food Technol. 17, 661.

Kramer, A. (1974). Storage retention of nutrients. Food Technol. 28:5.

Kramer, A., Twigg, B. (1968) Measure of frozen food quality and quality changes. In "The freezing preservation of foods" 4th Ed., Vol. 2, D. K. Tressler(ed), AVI pub. Co., Westport, Conn.

Kwolek, W. F., Bookwalter, G. N. (1971). Predicting storage stability from time-temperature data. Food Technol. 25(10):51.

Labuza, T.P. (1971). Kinetics of lipid oxidation of foods. C.R.C. Rev. Food Technol. 2:355.

Labuza, T. P. (1975) Oxidative changes in foods at low and intermediate moisture levels. In "Water Relations of Foods", R. Duckworth (ed), Academic Press, New York, p. 455.

Labuza, T.P. (1979). A theoretical comparison of losses in foods under fluctuating temperature sequences. J. Food Sci. 44:1162.

Labuza, T.P. (1980a). Temperature/enthalpy/entropy compensation in food reactions. Food Technol. 34(2):67.

Labuza, T.P. (1980b). The effect of water activity on reaction kinetics of food deterioration. Food Technol. 34:36.

Labuza, T. P. (1982). Shelf-life dating of foods. Food & Nutr. Press, Westport, CT.

Labuza, T. P. (1984). Application of chemical kinetics to deterioration of foods. J. Chem. Educ. 61: 348-358.

Labuza, T. P., Breene, W. M. (1989) Applications of "active packaging" for improvement of shelf life and nutritional quality of fresh and extended shelf life refrigerated foods. J. Food Proc. Pres. 13: 1-69.

Labuza, T.P., and R. Contreras-Medellin (1981). Prediction of moisture protection requirements for foods. Cereal Foods World 26:335-343.

Labuza, T.P., and J. Kamman (1983). Reaction kinetics and accelerated tests simulation as a function of temperature, in Applications of Computers in Food Research (I. Saguy, ed.), Marcel Dekker, New York, Ch. 4.

Labuza,T.P. and J.O. Ragnarsson. (1985). Kinetic history effect on lipid oxidation of methyl linoleate in model system. J. Food Sci. 50(1): 145.

Labuza, T. P.and D. Riboh (1982). Theory and application of Arrhenius kinetics to the prediction of nutrient losses in food. Food Technol. 36: 66-74.

Labuza, T. P. and M.K.Schmidl (1985). Accelerated shelf-life testing of foods. Food Technol., 39(9): 57-62, 64.

Labuza, T. P. and M.K. Schmidl (1988) Use of sensory data in the shelf life testing of foods: Principles and graphical methods for evaluation. Cereal Foods World 33(2): 193-206.

Labuza, T. P. and P. S. Taoukis (1990), The Relationship between Processing and Shelf Life, in Foods for the 90's (G.G.Birch, G.Campbell-Platt,and M.G. Lindley,eds.). Developments Series. Elsevier Applied Science, London and NY pp.73-105

Labuza, T.P., K. Bohnsack, and M.N. Kim (1982). Kinetics of protein quality loss stored under constant and square wave temperature distributions. Cereal Chem. 59:142.

Labuza, T.P., B. Fu, and P.S. Taoukis (1992) Prediction for shelf life and safety minimally processed CAP/MAP chilled foods. J. Food Prot. 55: 741-750.

Labuza, T.P., S. Mizrahi, and M. Karel (1972). Mathematical models for optimization of flexible film packaging of foods for storage. Trans. Amer. Soc. Agr. Eng. 15:150.

Lenz, M. K. and D.B. Lund (1980) Experimental procedures for determining destruction kinetics of food components. Food Technol. 34(2): 51.

Levine, H. and L. Slade (1988) "Collapse" phenomena - A unifying concept for interpreting the behavior of low moisture foods, in Food Structure- Its Creation and Evaluation (J.M.V. Blanshard and J.R.Mitchell, eds.), Butterworths, London, pp.149-180.

Lund, D. B. (1983) Considerations in modeling food processes. Food Technol. 37(1), p. 92.

MacKenzie, A.P. (1977). Non-equilibrium freezing behavior of aqueous systems. Phil. Trans. R. Soc. Lond. B. 278:167-189.

Mackie, I. M., Howgate, P., Laird, W. M., Ritchie, A. H. (1985) Acceptability of frozen stored consumer fish products. I.I.F. - I.I.R. - (Commisions C2, D3) 1985-4, p. 161-167.

Maesmans G., Hendrickx M., De Cordt S., Tobback P. (1995). Theoretical consideration of the general validity of the equivalent point method in thermal process evaluation. J. Food Eng. 24 : 225-248.

Margerison, D. (1969) The treatment of experimental data. In "The practice of Kinetics", Vol I od "Comprehensive Chemical Kinetics", C. H. Banford, C. F. H. Tipper (eds), Elsevier, New York.

McClure, P.J., C. de W. Blackburn, M.B. Cole, P.S. Curtis, J.E. Jones, J.d. Legan, I.D. Ogden, M.W. Peck, T.A. Roberts, J.P.Sutherland, S.J. Walker, 1994. Modeling the growth, survival and death of microorganisms in foods: The UK Foodmodel approach. Int. J. of Food Micro. 23: 265-275.

Mizrahi, S., T.P. Labuza, and M. Karel (1970). Computer aided predictions of food storage stability. *J*. Food Sci. 35:799-803.

Mizrahi, S., Labuza, T. P., Karel, M. (1970) Feasibility of accelerated tests for browning in dehydrated cabbage. J. Food Sci. 35: 804-807.

Mohr, P. W., Krawiec, S. (1980) Temperature characteristics and Arrhenius plots for nominal psychrophiles, mesophiles and thermophiles. *J. Gen. Microbiol.,* **121**, 311-317.

Nakabayashi, K., T. Shimamoto, and H. Mina (1981). Stability of package solid dosage forms. Chem. Pharm. 28(4):1090; 29(7):2027; 2051; 2057.

Nelson, R. R. (1983) Stability prediction using the Arrhenius model. Computer Prog. in Biomed. 16: 55-60.

Nelson, K. (1993). Reaction Kinetics of Food Stability: Comparison of Glass transition and Classical Models for Temperature and Moisture Dependence. Ph.D. Thesis. Univ. of Minnesota.

Nelson,K. and T.P. Labuza (1994). Water activity and food polymer science: Implications of state on Arrhenius and WLF models in predicting shelf life. J.Food Eng. 22: 271-290.

Norwig, J.F. and D.R. Thompson (1986). Microbial population, enzyme and protein changes during processing, in Physical and Chemical Properties of Foods (M. R.Okos, ed.) Am. Soc. Agric. Eng., St. Joseph, MI.

Ott, L. (1984) "An introduction to statistical methods and data analysis" 2nd Ed., PWS Publishers, Boston, MA.

Parkin, K. L., Brown, W. D. (1982) Preservation of seafood with modified atmospheres, in Chemistry and Biochemistry of Marine Food Products (Martin, E. et al.,eds.), AVI , Westport, CT, pp. 453-465.

Pecek C., Warthesen J. and Taoukis P. (1990). "A Kinetic Model for the Equilibration of Isomeric β - carotenes", J. Food Agric. Chem.38:41-45.

Peleg, M. (1990). On the use of WLF model in polymers and foods. Crit. Rev. Food Sci. Nutr. 32 : 59-66.

Peleg, M. (1995). A model of temperature effects on microbial populations from growth to lethality. J. Sci. Food Agri. 68: 83-89.

Poulsen, K. P., Lindelov, F. (1975) Stability of frozen systems and frozen foods. Food Technology Laboratory, DtH, DK 2800 Lyngby, Denmark.

Quast, D.G., and M. Karel (1972). Computer simulation of storage life of foods undergoing spoilage by two interactive mechanisms. J. Food Sci. 37:679.

Quast, D. G., Karel, M., Rand, W. (1972) Development of a mathematical model for oxidation of potato chips as a function of oxygen pressure, extent of oxidation and equilibrium relative humidity. J. Food Sci., 37:679.

Ramaswamy, H.S., F.R. Van de Voort, and S. Ghazala (1989). An analysis of TDT and Arrhenius methods for handling process and kinetic data. J. Food Sci. 54:1322-1326.

Ratkowsky, D.A., J.Olley, T.A. McMeekin, and A.Ball (1982). Relationship between temperature and growth rate of bacterial cultures. J. Bacteriol. 149: 1-5.

Ratkowsky, D.A.,R.K. Lowry, T.A.McMeekin, A.N. Stokes and R.E. Chandler (1983). Model for bacterial culture growth rate throughout the entire biokinetic temperature range. J. Bacteriol. 154:1222- 1226.

Riboh, D.K., and T.P. Labuza (1982). Kinetics of thiamine loss in pasta stored in a sine wave temperature condition. J. Food Proc. Pres. 6(4):253.

Roos Y.H. (1993). Water activity and physical state effects on amorphous food stability. J. Food Proc. Pres. 16: 433-452.

Roos, Y. H. and M. Karel (1990). Differential scanning calorimetry study of phase transitions affecting quality of dehydrated materials. Biotechnol. Prog. 6:159-163.

Roos, Y. and M. Karel (1991). Plastisizing effect of water on thermal behavior and crystallization of amorphous food models. J. Food Sci 56:38-43.

Ross, T. and T.A. McMeekin (1994). Predictive microbiology. Int. J. Food Micro. 23: 242-264.

Rosso, L., J.R. Lobry, S. Bajard and J.P. Flandrois (1995). Convenient model to describe the combined effects of temperature and pH on microbial growth. Appl. Envir. Micro. 61: 610-616.

Saguy, I.S. and Cohen, E. (1990) Shelf-life prediction Course Notes. Course #71917. The Hebrew University of Jerusalem, Faculty of Agriculture.

Saguy, I., Karel, M. (1980) Modeling of quality deterioration during food processing and storage. *Food Technol.* **34(2)**, 78-85.

Saguy, I., Kopelman, I.J. and Mizrahi, S. (1979). Extent of nonenzymatic browning in grapefruit juice during thermal and concentration processes: Kinetics and Prediction. J. Food Processing and Preservation 2: 175.

Saltmarch, M., and T.P. Labuza (1982). Kinetics of browning and protein quality loss in sweet whey powders under steady and non-steady state storage conditions. J. Food Sci. 47:92.

Sapers, G.M. (1970). Flavor quality in explosion puffed dehydrated potato. J. Food Sci. 35:731.

Sapru, V., and T.P. Labuza (1992) Glassy state in bacterial spores predicted by glass transition theory. J.Food Sci. 58 : 445-448.

Simon, I., T.P. Labuza, and M. Karel (1971). Computer aided prediction of food storage stability: Oxidation of a shrimp food product. J. Food Sci. 36:280.

Singh, R. P., Wang, C. Y. (1977) Quality of frozen foods -- A review. J. Food Proc. Eng.(1): 97-127.

Singh, R. P. and Wells, J. H. (1986) Keeping track of time and temperature: new improved indicators may become industry standards. Meat processing, 25(5), 41-42, 46-47.

Shoolfield, R.M., P.J.H. Sharpe, and C.E. Magnuson, C.E. (1981). Non-linear regression of biological temperature-dependent rate models based on absolute reaction -rate theory. J. Theor. Biol. 88, 719-731.

Slade, L., H. Levine, and J. Finey (1989). Protein-water interactions: Water as a plasticizer of gluten and other protein polymers, in Protein quality and the effects of processing (R.D. Phillips and J.W. Finlay eds.), Marcel Dekker, New York, pp.9-123.

Stamp, J.A. (1990). Kinetics and Analysis of Aspartame Decomposition Mechanisms in Aqueous Solutions using Multiresponse Methods. Ph.D. Thesis. Univ. of Minnesota.

Stamp, J.A. and T.P. Labuza (1989). An ion-pair high performance liquid chromatographic method for the determination of aspartame and its decomposition products. J.Food Sci. 54 : 1043.

Taoukis P.S., W. M. Breene, and T. P. Labuza (1988a), "Intermediate-Moisture Foods", in *Advances in Cereal Science and Technology*, **Vol. IX**, Y. Pomeranz (ed), Chapter 4, pp.91-128.

Taoukis, P. S., A. El Meskine, and T. P. Labuza (1988b). Moisture Transfer and Shelf Life of Packaged Foods, in Food and Packaging Interactions, (J. H. Hotchkiss, ed.) ACS Symposium Series No. 365, pp.243-261.

Taoukis, P. S. and T. P. Labuza (1989a), Applicability of Time-Temperature indicators as shelf-life monitors of food products, J.Food Sci. 54 : 783-788.

Taoukis, P. S. and T. P. Labuza (1989b), Reliability of Time-Temperature indicators as food quality monitors under non isothermal conditions. *J. Food Sci.* 54 : 789-792.

Taoukis, P. S., G. A. Reineccius and T. P. Labuza (1990). Application of Time-Temperature Indicators to Monitor Quality of Flavors and Flavored Products in

Flavors and Off-Flavors '89 (G. Charalambus ed.), Developments in Food Science Series, Elsevier Applied Science Publishers. London and New York., pp.385-398.

Taoukis, P.S., B. Fu and T.P. Labuza (1991). Time-Temperature Indicators. Food Technol. 45(10): 70-82.

Templeman, G., Sholl, J. J., Labuza, T. P. (1977). Evaluation of several pulsed NMR techniques for solids in fat determination in commercial fats. J. Food Sci. 42, 432.

Thompson, D. (1983). Response surface experimentation. J. Food Proc. Preserv., 6, 155-188.

Tinker, J. H., Slavin, J. W., Learson, R. J. and V. G. Empola. (1985). Evaluation of automated time-temperature monitoring system in measuring the freshness of chilled fish. IIF-IIR Commissions C2, D3 4 (1985), 286.

Trant, A. S., Pangborn, R. M., Little, A. C. (1981) Potential fallacy of correlating hedonic responses with physical and chemical measurements. J. Food Sci., 41, 583.

Tsoumbeli, M.N. and T.P.Labuza (1991) Accelerated kinetic study of aspartame degradation inthe neutral pH range. J. Food Sci. 56: 1671-1675.

Tuma, J.J. 1988. Engineering Mathematics Handbook. 3rd Ed. McGraw Hill Book Co. New York.

Weissman, I., O.Ramon, I.J. Kopelman and S. Mizrahi (1993). A kinetic model for accelerated tests of Maillard browning in a liquid model system. J. Food Proc. Pres. 17: 455-470.

Wells, J. H., and Singh, R. P. (1988) Application of time-temperature indicators in monitoring changes in quality attributes of perishable and semi-perishable foods. J. Food Sci., 53(1), 148.

White G.W. , and S.H. Cakebread (1966). The glassy state in certain sugar containing food products. J. Food Tech., 1 , 73.

Whiting, R.C. and R. L. Buchanan (1994). Microbial modeling. Food Tech. 48: 113-120.

Williams, M.L.,R.F. Landel and J.D. Ferry (1955).The temperature dependence of relaxation mechanisms in amorphous polymers and other glass-forming liquids. J. Chem. Eng. 77:3701-3707.

Willocx, F., M. Mercier, M. Hendrickx, and P. Tobback (1993). Modelling the influence of temperature and carbon dioxide upon the growth of *Pseudomonas fluorescens*. Food Micro. 10: 159-173.

Wold, S. (1971) Analysis of kinetic data by means of spline functions. *Chem. Scripta*, **1**, 97.

Yoshioka, S., Aso, Y., Uchiyama, M. (1987) Statistical evaluation of nonisothermal prediction of drug stability. J. Pharmaceutical Sci., 76(10): 794-798.

Zobel, H. F. (1973) A review of bread staling. Baker's Dig., 47(5): 52.

Zwietering, M.H., J. De Koos, B.E. Hasenack, J.C. DeWilt and K. Van't Riet (1991). Modeling of bacterial growth as a function of temperature. Appl. Environ. Microbiol. 57: 1094-1101.