# Chapter 8

# Kinetics of Chemical Reactions in Foods

Chemical reactions occur in foods during processing and storage. Some reactions result in a quality loss and must be minimized, whereas others result in the formation of a desired flavor or color and must be optimized to obtain the best product quality. Kinetics is a science that involves the study of chemical reaction rates and mechanisms. An understanding of reaction mechanisms coupled with quantification of rate constants will facilitate the selection of the best conditions of a process or storage, in order that the desired characteristics will be present in the product.

## 8.1 THEORY OF REACTION RATES

Two theories have been advanced as a theoretical basis for reaction rates. The collision theory attributes chemical reactions to the collision between molecules that have high enough energy levels to overcome the natural repulsive forces among molecules. In gases, chemical reaction rates between two reactants have been successfully predicted using the equations derived for the kinetic energy of molecules and the statistical probability for collisions between certain molecules that possess an adequate energy level for the reaction to occur at a given temperature. The activation theory assumes that a molecule possesses a labile group within its structure. This labile group may be normally stabilized by oscillating within the molecule or by steric hindrance by another group within the molecule. The energy level of the labile group may be raised by an increase in temperature, to a level that makes the group metastable. Finally, a chemical reaction results that releases the excess energy and reduces the energy level of the molecule to another stable state. The energy level that a molecule must achieve to initiate a chemical reaction is called the activation energy. Both theories for reaction rates will give a reaction rate constant, which is a function of the number of reacting molecules and the temperature.

Reactions may be reversible. Reversible reactions are characterized by an equilibrium constant, which establishes steady-state concentration of product and reactants.

## 8.2 TYPES OF REACTIONS

### 8.2.1 Unimolecular Reactions

One type of chemical reaction that occurs during degradation of food components involves a single compound undergoing change. A part of the molecule may split off, or molecules may interact with each other to form a complex molecule, or internal rearrangement may occur to produce a new compound. These type of reactions are unimolecular and may be represented as:

$$A \xrightarrow{k_1} \text{products} \tag{8.1}$$

The reaction may occur in more than one step, and in some cases the intermediate product may also react with the original compound.

$$A \xrightarrow{k_1} B \xrightarrow{k_2} \text{products} \tag{8.2}$$

$$A \xrightarrow{k_1} B + A \xrightarrow{k_3} \text{products} \tag{8.3}$$

The reaction rate, r, may be considered the rate of disappearance of the reactant A or the rate of appearance of a reaction product. In reactions 8.1 and 8.2, the rate of disappearance of A, dA/dt, is proportional to a function of the concentration of A, while in reaction 8.3, dA/dt will be dependent on a function of the concentration of A and B. In reaction 8.1, the rate of formation of products will equal the rate of disappearance of the reactant, but in reactions 8.2 and 8.3, accumulation of intermediate products will result in a lag between product formation and disappearance of the original reactant. When intermediate reactions are involved, the rate of appearance of the product will depend on the rate constant $k_2$.

The rate constant, k, is the proportionality constant between the reaction rate and the function of the reactant concentration, F(A) or F(B). Thus, for reactions 8.1 and 8.2:

$$\frac{dA}{dt} = kF(A) \tag{8.4}$$

For reaction 3:

$$\frac{dA}{dt} = k_1F(A) + k_3[F(A) + F(B)] \tag{8.5}$$

In Equations (8.4) and (8.5), A and B represent concentrations of reactants A and B, and it becomes obvious that the reaction rate will increase with increasing reactant concentration. The concentration function, which is proportional to the reaction rate, depends on the reactant and could change with the conditions under which the reaction is carried out. When studying reaction rates, it is either the rate of appearance of a product or the rate of disappearance of reactants that will be of interest. On the other hand, if intermediate reactions are involved in the process of transforming compound A into a final reaction product, and the rate constants and $k_2$ and $k_1$ are affected differently by conditions used in a process, it will be necessary to postulate rate mechanisms and evaluate an overall rate constant based on existing conditions in order to effectively optimize the process. Most of the reactions involving degradation of food nutrients are of the type shown in reaction 8.1.

### 8.2.2 Bimolecular Reactions

Another type of reaction involves more than one molecule. The second step of reaction 8.3 above, is one example of a bimolecular reaction. In general, a bimolecular reaction is as follows:

$$aA + bB \xrightarrow{k_3} cC + dD \tag{8.6}$$

In this type of reaction, the rate may be based on one of the compounds, either the reactant or the product, and the change in concentration of other compounds may be determined using the stoichiometric relationships in the reaction.

$$r_{3c} = \frac{dC}{dt} = -\frac{c}{b}\frac{dB}{dt} = -\frac{c}{a}\frac{dA}{dt} = \frac{c}{d}\frac{dD}{dt} = kF(A)F(B) \tag{8.7}$$

An example of the use of the relationship shown in Equation (8.7) is the expression of productivity of fermentation systems as reduction of substrate concentration, increase in product concentration, or increase in mass of the microorganism involved in the fermentation.

### 8.2.3 Reversible Reactions

Some reactions are reversible.

$$nA \underset{k_2}{\overset{k_1}{\rightleftharpoons}} bB + cC \tag{8.8}$$

Again, F(A), F(B), and F(C) are functions of the concentrations of A, B, and C.

The net reaction rate expressed as a net disappearance of A is

$$r = -\frac{dA}{dt} = k_1F(A) - k_2[F(B) \cdot F(C)] \tag{8.9}$$

Expressing B and C in terms of A: $B = (n/b)(A_0 - A)$ and $C = (n/c)(A_0 - A)$, where $A_0$ = initial concentration of A. Let F(A) = A, F(B) = B, and F(C) = C (i.e. the reaction rate is directly proportional to the concentrations of the reactants).

$$r = -\frac{dA}{dT} = k_1A - k_2\left[\left[\frac{n}{b}(A_0 - A)\right]\left[\frac{n}{c}(A_0 - A)\right]\right] \tag{8.10}$$

At equilibrium, $r_1 = r_2$ and:

$$k_1A = k_2\left[\left[\frac{n}{b}(A_0 - A)\right]\left[\frac{n}{c}(A_0 - A\right]\right]$$

Clearing fractions Equation (8.11) becomes:

$$k_{eq} = \frac{k_1}{k_2} = \left[\frac{\left[\frac{n}{b}(A_0 - A)\right]\left[\frac{n}{c}(A_0 - A)\right]}{A}\right] \tag{8.11}$$

Once a constant of equilibrium is known, it will be possible to determine the concentrations of A, B, and C from the stoichiometric relationships of the reaction. An example of this type of reaction is the dissociation of organic acids and their salts.

**Example 8.1.** Cottage cheese whey containing initially 4.3%(w/w) lactose when treated with β-galactosidase showed maximum hydrolysis of 80% of the lactose. Calculate the equilibrium constant. In one experiment, enzyme was added to the whey and half of the lactose was hydrolyzed in 25 minutes. Calculate the rate constant for the forward and reverse reactions, and the time required to obtain 77% conversion of lactose, under the conditions given.

**Solution:**

The reaction involved in the hydrolysis of lactose is

$$C_{12}H_{22}0_{11} + H_2O \underset{k_2}{\overset{k_1}{\rightleftharpoons}} C_6H_{12}O_6 + C_6H_{12}O_6$$

Lactose Glucose Galactose

Water is not rate limiting in this reaction, therefore its contribution to the reaction rate is ignored. Let L = the concentration of lactose, G = the concentration of glucose, and C = the concentration of galactose. The rate equations are

$$r_1 = -dL/dt = k_1L; \quad r_2 = dL/dt = k_2GC$$

At equilibrium, $r_1 = r_2$, and:

$$k_1L_{eq} = k_2G_{eq}C_{eq}$$

$$k_{eq} = \frac{k_1}{k_2} = \frac{G_{eq}\, C_{eq}}{L_{eq}}$$

Let f = fraction of lactose converted. From the stoichiometry of the reaction, $G_{eq} = C_{eq} = L_o - L_{eq} = L_o(f)$. $L_{eq} = L_o(1 - f)$.

Basis: 1 L of whey. $L_o = 4.3(10)/342 = 0.1257$ moles/L
$L_{eq} = (1 - 0.80)(0.1257) = 0.02514$
$G_{eq} = C_{eq} = 0.80(0.1257) = 0.10056$ moles/L
$k_{eq} = (0.10056)^2/0.02514 = 0.4022$

The rate constants for the reaction will be calculated by first setting up the rate equations and integrating.

The rate of disappearance of lactose is

$$r = -dL/dt = k_1L - k_2GC$$

$$L = L_0(1 - f); \quad dL/dt = -L_0(df/dt)$$

$$G = f\,L_0; C = f\,L_0; \quad k_1 = k_2k_{eq}$$

$$L_0df/dt = k_2k_{eq}(1 - f)L_0 - k_2f^2L_0^2$$

$$k_2\,dt = \frac{df}{k_{eq}(1 - f) - f^2L_0}$$

The equation is evaluated by graphical integration. Using the trapezoidal rule and using a BASIC program shown in Fig. 8.1. The integral has a value of 1.814.

$$k_2 = 1.814/25 = .0726$$

$$k_1 = k_2k_{eq} = .0726(0.4022) = 0.1805$$

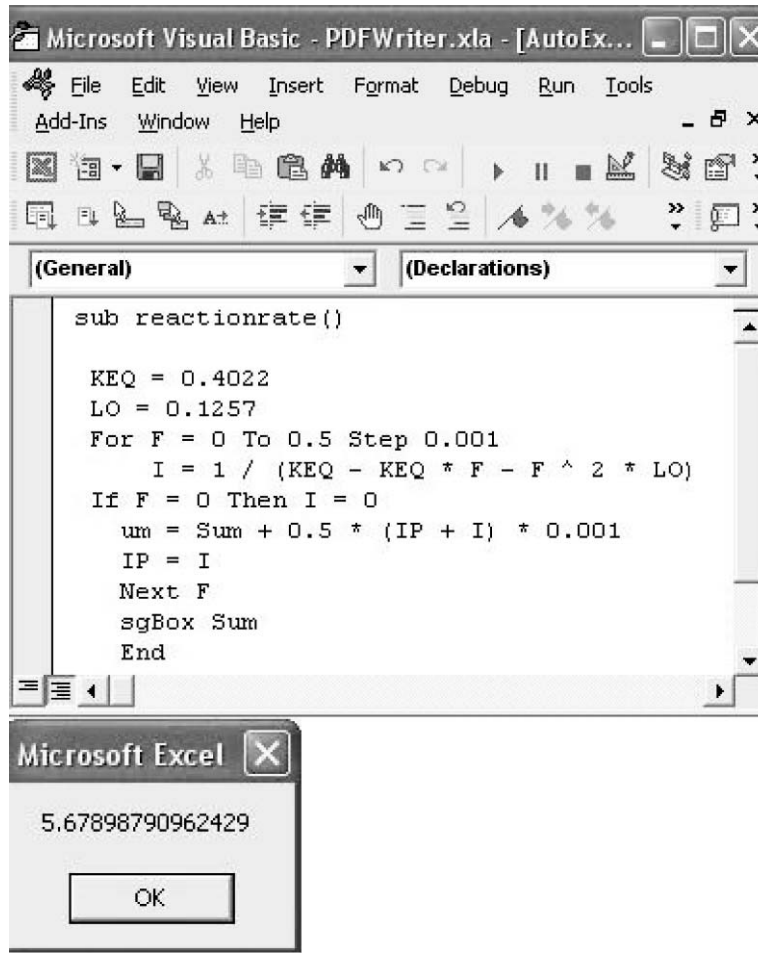


**Figure 8.1** Visual BASIC program to solve kinetic parameters for example 8.1.

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To obtain the time, the integral is evaluated using the limits 0 to 0.77. The same BASIC program will be used except that the second line of the program is changed to go from f = 0 to 0.77.

The value of the integral is 5.679.

$t = 5.679/k2 = 5.679/(0.0726) = 78.2$ minutes

## 8.3 ENZYME REACTIONS

Enzymatic reactions encountered in food processing occur at a rate that is limited by the concentration of enzymes present. There is usually an abundance of the substrate (reactant) so that changes in substrate concentration do not affect the reaction rate. The activity of an enzyme is defined as the rate at which a specified quantity of the enzyme will convert a substrate to product. The reaction is followed by either measuring the loss of reactant or the appearance of product. The specific activity of

an enzyme is expressed as activity/mass of protein. When using an enzyme in a process, the activity of added enzyme must be known in order that the desired rate of substrate conversion will be achieved.

If there is no product inhibition:

$$-\frac{dS}{dt} = a \tag{8.12}$$

where a is the enzyme activity. Thus, an enzymatic reaction without product inhibition suggests a linear change in substrate concentration, at the early stages of the reaction when substrate concentration is so high that enzyme concentration is rate limiting. Most enzymatic reactions however proceed in a curvilinear pattern which approaches a maximum value at infinite time. Consider an enzyme reaction where product inhibition exists. The reaction rate will be

$$-\frac{dS}{dt} = a_0 - B$$

B = enzyme bound to the product.

Assuming that B is proportional to the amount of product formed, and using ki as the constant representing the product inhibitory capacity

$$-\frac{dS}{dt} = a_0 - k_i P$$

P = product concentration.

Consider a reaction where S is converted to P. If f = the fraction of substrate converted to product: $S = S_0(1 - f)$ and $P = S_0 f$. Substituting into the rate equation, and letting $S_0$ = initial substrate level and $a_0$ = initial enzyme activity:

$$S_0\left[\frac{df}{dt}\right] = a_0 - k_i S_0 f \tag{8.13}$$

$$\frac{df}{dt} = \frac{a_0}{S_0} - k_i f \tag{8.14}$$

The differential equation can be easily integrated by separation of variables if the transformation $f = a_0/S_0 - k_i f$ is used.

$$\frac{df}{dt} = -\frac{1}{k_i}\frac{df'}{dt}; \quad \frac{df'}{dt} = k_i f'$$

Integrating, substituting f′ for f and using the boundary condition f = 0 at t = 0:

$$\ln\left(1 - \frac{k_i f S_0}{a_0}\right) = -k_i t; \quad f = \frac{a_0}{k_i S_0}\left(1 - e^{-k_i t}\right) \tag{8.15}$$

A plot of the fraction of substrate converted against time, will show a curvilinear plot that will level off at a certain value of f at infinite time. The maximum conversion will be $f_{max}$.

$$f_{max} = \frac{a_0}{k_i S_0}; \quad \ln\left(1 - \frac{f}{f_{max}}\right) = k_i t$$

Depending on the enzyme and substrate concentration, the conversion may not immediately follow the exponential expression. For example, if the initial enzyme activity is quite high relative to substrate concentration, the fraction converted may initially be a linear function of time. However, once product accumulates and substrate concentration drops, the influence of product inhibition becomes significant and substrate conversion occurs exponentially as derived above. With product inhibition, the product

**Table 8.1** Kinetic constants of reactions occurring in foods.

| *Factor* | *$D_o$ (min)* | *Z (EC)* | *Reference* |
|---|---|---|---|
| Ascorbic acid (peas) | 246 | 50.5 | Rao et al. (1981) |
| Browning reaction (milk) | 12.5 | 26 | Burton (1954) |
| Carotene (beef liver paste) | 43.6 | 25.5 | Wilkinson et al. (1981) |
| Chlorophyll (peas) | 13.2 | 38.8 | Rao et al. (1981) |
| Overall sensory | 12.5 | 26 | Lund (1977) |
| Thiamin | 158 | 21 | Holdsworth (1985) |
| Pectin methyl esterase (citrus) | 0.053 | 14 | Williams et al. (1986) |

competes for active sites on the enzyme making these sites unavailable for making a complex with the substrate. Eventually, all enzyme active sites are occupied by the product and the reaction stops. Enzyme activities are determined as the slope of the substrate conversion vs. time curves at time zero (initial reaction velocity) to avoid the effect of product inhibition.

## 8.4 REACTION ORDER

Reaction order is the sum of the exponents of reactant concentration terms in the rate equation. Table 8.1 lists various deteriorative reactions in foods, and the order of the reaction.

### 8.4.1 Zero-Order Reactions

$$r = \frac{dA}{dt} = k \tag{8.16}$$
$$A = A_0 + kt$$

A characteristic of a zero-order reaction is a linear relationship between the concentration of reactant or product with time of the reaction, t.

### 8.4.2 First-Order Reactions

$$r = -\frac{dA}{dt} = kA \tag{8.17}$$
$$\ln\left(\frac{A}{A_0}\right) = kt$$

$A_0$ is the concentration of A at time $= 0$. A first-order reaction is characterized by a logarithmic change in the concentration of a reactant with time. Most of the reactions involved in the processing of foods as shown in Table 8.1 are first order reactions.

### 8.4.3 Second-Order Reactions

$$r = -\frac{dA}{dt} = kA^2 \tag{8.18}$$

$$\frac{1}{A} - \frac{1}{A_0} = kt$$

Second-order unimolecular reaction is characterized by a hyperbolic relationship between concentration of the reactant or product, and time. A linear plot will be obtained if 1/A is plotted against time. Second-order bimolecular reactions may also follow the following rate equation:

$$r = -\frac{dA}{dt} = kAB$$

where A and B are the reactants. The differential equation may be integrated by holding B constant to give:

$$\ln\left(\frac{A}{A_0}\right) = -k't \tag{8.19}$$

$k'$ is a pseudo–first-order rate constant: $k' = kB$.

A second-order bimolecular reaction will yield a similar plot of the concentration of the reactant against time as a first-order unimolecular reaction, but the reaction rate constant will vary with different concentrations of the second reactant. An example of a second-order bimolecular reaction is the aerobic degradation of ascorbic acid. Oxygen is a reactant and a family of pseudo-first order plots will be obtained when ascorbic acid degradation is studied at different levels of oxygen availability.

### 8.4.4 *n*th-Order Reactions

$$r = -\frac{dA}{dt} = kA^n; \quad n > 1 \tag{8.20}$$

The integrated equation (8.20) is:

$$A^{1-n} - A_0^{1-n} = -(1-n)kt$$

Evaluation of reaction order is a trial and error process that involves assuming various values for n and determining which value would result in the best fit with the nth order equation above.

## 8.5 REACTIONS WHERE PRODUCT CONCENTRATION IS RATE LIMITING

These type of reactions are usually followed not in terms of the concentration of the reactant but by some manifestation of the completion of the reaction in terms of a physical property change. Examples are protein gelation measured as an increase of the strength of the gel, nonenzymatic browning reaction in solid foods, textural changes during cooking, sensory flavor scores during storage, and so forth. The magnitude of the attribute measured usually levels off not because of depletion of the reactants, but because the measuring technique could no longer detect any further increase in intensity. Reactions of this type could be fitted to the following:

$$\ln\left(1-\frac{C}{C^*}\right)=\pm kt \tag{8.21}$$

where C* is the value of the measured attribute when it remained constant at long reaction times, and C is the value at any time during the transient stage of the process.

**Example 8.2.** The following data shows the firmness of a protein gel as a function of time of heating. Derive an appropriate equation to fit this data and determine the rate constant for the reaction.

| Time (min) | 0 | 1 | 2 | 3 | 4 | 5 | 10 | 20 |
|---|---|---|---|---|---|---|---|---|
| Firmness (g) | 0 | 6.01 | 8.41 | 9.36 | 9.75 | 9.90 | 10.2 | 10.2 |

**Solution:**

The data shows firmness to reach a constant value at 10 minutes of heating. The data will be fitted to the equation:

$$\ln\left(1-\frac{F}{F^*}\right)=-kt$$

F = firmness value and F* = the final firmness value.

The following are the transformed data that will be analyzed by linear regression to obtain the slope, which will be the value of k.

| *x (time)* | *y [ln (1 − F/F*)]* |
|---|---|
| 0 | 0 |
| 1 | −0.889 |
| 2 | −1.74 |
| 3 | −2.497 |
| 4 | −3.121 |
| 5 | −3.526 |

Linear regression of x and y using Microsoft Excel gives a slope of −1.3743. k = 1.3743 $min^{-1}$.

A plot of the data will show a linear fit except for the last point, which deviated slightly from linearity.

## 8.6 THE REACTION RATE CONSTANT

The reaction rate constant defines the reaction rate. There are several ways in which the speed of a chemical reaction can be reported for first order reactions which predominate in food systems.

*Rate constant, k, for an exponential model of concentration change:* This rate constant has units of reciprocal time and is the slope of a plot of ln(c) against time. This rate constant is defined for the various types of reactions in section "Reaction Order."

*The D value:* This method of representing the rate constant for a reaction had its origins in thermobacteriology, where the inactivation rate of microorganisms during heating is expressed as a decimal reduction time. This approach was later applied to chemical reactions, in order that the same computational

scheme can be used for determining microbial inactivation and nutrient degradation during a thermal process for sterilization of foods.

The D value is defined as:

$$\log \frac{C}{C_0} = -\frac{t}{D} \tag{8.22}$$

Thus, the D value is the negative reciprocal of the slope of a plot of log(C) against t. C in the above equation is the concentration of a reactant. D is based on common logarithms, in contrast with k, which is based on natural logarithms. D and k are related as follows:

$$\ln\left(\frac{C}{C_0}\right) = \ln(10)\log\left(\frac{C}{C_0}\right) = -kt$$

Thus:

$$\frac{1}{D} = \frac{k}{\ln(10)}; \quad D = \frac{\ln(10)}{k} \tag{8.23}$$

*The half-life:* This method of expressing the rate of a reaction is commonly used in radioisotope decay. It is easier to visualize the rate of the reaction when expressed as a half-life rather than a rate constant based on natural logarithms. The half life is the time required for the reactant to lose half of its original concentration. The half life is related to k and D as follows:

$$\ln(10.5) = -k(t_{0.5}); \quad t_{0.5} = -\frac{\ln(0.5)}{k} \tag{8.24}$$

$$\log(0.5) = -\frac{t_{0.5}}{D}; \quad t_{0.5} = -D\log(0.5)$$

## 8.7 TEMPERATURE DEPENDENCE OF REACTION RATES

### 8.7.1 The Arrhenius Equation

The activated complex theory for chemical reaction rates is the basis for the Arrhenius equation which relates reaction rate constants to the absolute temperature. The Arrhenius equation is

$$k = A_0[e]^{-E_a/RT} \tag{8.25}$$

$E_a$ is the activation energy, and $A_0$ is the rate constant as T approaches infinity. Another form of the Arrhenius equation involves the reaction rate constant at a reference temperature.

Let $T_0$ = the reference temperature at which $k = k_0$.

$$k_0 = A_0[e]^{-E_a/RT_0}; \quad k = A_0[e]^{-E_a/RT}$$

Taking the ratio of the two equations:

$$\frac{k}{k_0} = [e]^{(-E_a/R)(1/T-1/T_0)} \tag{8.26}$$

The negative sign is placed on the exponent of the Arrhenius equation in order that a positive activation energy will indicate an increasing reaction rate constant with increasing temperature. Using Equation (8.26), the rate constant at any temperature can be determined from the activation energy and the rate constant ko at a reference temperature, $T_0$.

### 8.7.2 The $Q_{10}$ Value

The $Q_{10}$ value of a reaction is often used for reporting temperature dependence of biological reactions. It is defined as the number of times a reaction rate changes with a 10°C change in temperature. If a reaction rate doubles with a 10°C change in temperature, the $Q_{10} = 2$. For reactions such as enzymatically induced color or flavor change in foods, degradation of natural pigments, nonenzymatic browning, and microbial growth rate, the $Q_{10}$ is usually around 2. Thus the general rule of thumb in food storage is that a 10°C reduction in storage temperature will increase shelf life by a factor of 2. The relationship between the $Q_{10}$ value and the activation energy is derived as follows:

Let $k_1$ = rate constant at $T_1$ and $k_2$ − rate constant at $T_2$

From the definition of the $Q_{10}$:

$$k_2 = k_1[Q_{10}]^{(T_2-T_1)/10} \tag{8.27}$$

Taking the logarithm of Equation (8.27):

$$\ln\left(\frac{k_2}{k_1}\right) = \frac{T_2 - T_1}{10}\ln Q_{10} \tag{8.28}$$

Substituting $k_2$ for k, $k_1$ for $k_0$, $T_2$ for T, and $T_1$ for $T_0$ in equation 26:

$$\frac{k}{k_1} = [e]^{(-E_a/R)(1/T_2-1/T_1)} \tag{8.29}$$

Taking the logarithm of Equation (8.29):

$$\ln\left[\frac{k_2}{k_1}\right] = \frac{-E_a}{R}\left[\frac{1}{T_2} - \frac{1}{T_1}\right] \tag{8.30}$$

$$\ln\left[\frac{k_2}{k_1}\right] = \frac{-E_a}{R}\left[\frac{T_1 - T_2}{T_2T_1}\right] \tag{8.31}$$

The negative sign on $E_a$ in Equation (8.31) drops out when the signs on $T_1$ and $T_2$ in the numerator are reversed. Equating Equations (8.28) and (8.31) and solving for $E_a/R$:

$$\frac{E_a}{R} = \frac{\ln(Q_{10})}{10}T_2T_1 \tag{8.32}$$

$$Q_{10} = [e]^{(E_a/R)(10/T_2T_1)} \tag{8.33}$$

The $Q_{10}$ is temperature dependent and should not be used over a very wide range of temperature.

### 8.7.3 The z Value

The z value had its origins in thermobacteriology and was used to represent the temperature dependence of microbial inactivation rate. z was defined as the temperature change needed to change microbial inactivation rate by a factor of 10. The z value has also been used to express the temperature dependence of degradative reactions occurring in foods during processing and storage. The z value expressed in terms of the reaction rate constant is as follows:

$$k_2 = k_1[10]^{(T_2-T_1)/z} \tag{8.34}$$

Taking the logarithm:

$$\ln\left[\frac{k_2}{k_1}\right] = \frac{T_2 - T_1}{z}\ln(10) \tag{8.35}$$

Equating the right hand side of Equations (8.31) and (8.35):

$$\frac{\ln(10)}{z} = \left[\frac{E_a}{R}\right]\left[\frac{1}{T_2T_1}\right] \tag{8.36}$$

$$z = \frac{\ln(10)}{(E_a/R)}T_1T_2$$

Solving for $E_a/R$ in Equations (8.32) and (8.36) and equating:

$$z = \frac{10\ln(10)}{\ln(Q_{10})} \tag{8.37}$$

**Example 8.3.** McCord and Kilara (J. Food Sci. 48:1479, 1983) reported the kinetics of inactivation of polyphenol oxidase in mushrooms to be first order and the rate constants at 50°C, 55°C, and 60°C were 0.019, 0.054, and 0.134 $min^{-1}$, respectively. Calculate the activation energy, the z value and $Q_{10}$ value for the inactivation of polyphenol oxidase in mushrooms.

**Solution:**

The absolute temperatures corresponding to 50°C, 55°C, and 60°C are 323, 328, and 333 K respectively. A regression of ln(k) against 1/T gives a slope of $-21009.6$, thus; $-E_a/R = -21009.6$ $Ea/R = 21009\,K^{-1}$; $R = 1.987$ Cal/(gmole$K); and Ea = 41.746 kcal/gmole.

$$\ln(Q_{10}) = 10\left(\frac{E_a}{R}\right)\left(\frac{1}{T_1T_2}\right) = \frac{10(21,009)}{323(333)} = 1.95$$

$$Q_{10} = 7.028$$

$$z = \frac{\ln(10)}{E_a/R}T_1T_2 = \frac{323(333)\ln(10)}{21,009} = 11.8°C$$

## 8.8 DETERMINATION OF REACTION KINETIC PARAMETERS

The reaction rate constant is usually determined at constant temperature by measuring changes in the concentration of reactant or concentration of reaction product with time. Because reaction rate can be affected by the presence of interfering compounds, pH, and water activity, kinetic parameters are determined with the reacting compound contained in a specific substrate. Model systems may be used to ensure that the substrate composition is constant during the determination of the kinetic parameters. However, literature data indicate variations in the value of the kinetic parameters for the same reaction in different food products.

The temperature dependence of the reaction rate constant is determined by conducting the kinetic studies at several constant temperatures and determining the z value or activation energy for the reaction.

A typical technique for determination of the kinetic parameters is to derive a linear form of the reaction rate equation and applying regression analysis on the transformed data. This approach however, has been shown to have limitations because of the smoothing out effect of the transformation used to linearize the data. One method that can be used is nonlinear curve fitting. The use of statistical software packages for determining the reaction rate constant has been shown in the section on "Nonlinear Curve Fitting" in Chapter 1.

Another approach is the use of the Solver feature in Microsoft Excel. Although Solver only allows the manipulation of one variable to minimize the least-square error, an iteration method may be employed to fit two-parameter equations to the data.

**Example 8.4.** Data on softening of carrots at 90°C from Paulus and Saguy (J. Food Sci. 45:239, 1980) given as (x, y) where y = rupture stress in kg/cm$^2$ and x = time in min are as follows: (30, 0.85), (40, 0.60), (50, 0.40), (60, 0.29), (70, 0.24). Determine the rate constant k, defined as: ln(y) = kt + b.

**Solution:**

Transformation of y to ln(y) and conducting a linear regression on Excel gives a slope of −0.03256 and an intercept of 0.7772. Thus, linear regression finds a k value of −0.03256.

To use the Solver feature in Microsoft Excel, enter the data in the spreadsheet. Designate two cells to contain values of k and b. For example time values are in cells A2 to A6 and force values are in B2 to B6. Designate B7 to hold the value of k and B8 to hold the value of b. Calculate y in column C as: y = exp (kt + b). Then calculate the error square in column D as the difference between the calculated and experimental value squared. For example in column D2, enter (C2 − B2)^2. Calculate the sum of squares error, e.g. in D7 enter Sum(D2.D6).

Go to Tools and choose Solver on the menu. Assume a value for k and b, e.g enter in B7 the value −.03, and in B8 the value 0.7772.

Solver asks to set target cell (in this case the sum of squares, error in D7) to a minimum by changing the value of k in B7. Then click solve. The sum of squares and the value of k is displayed. Repeat the process this time designating the value of b in B8 as the designated cell to change. Then click solve and Solver will find a value of b that minimizes the sum of squares of error. Results of Solver gives k = −0.3248 and b = 0.7868. Plotting the calculated y and experimental y shows better agreement with the Solver solution compared to that obtained by linear regression after data transformation.

## 8.9 USE OF CHEMICAL REACTION KINETIC DATA FOR THERMAL PROCESS OPTIMIZATION

Data on temperature dependence of chemical degradation reactions in foods are valuable in determining the loss or gain in product quality that might result with an elevation in processing temperature. When microbial inactivation is a major objective of the heating process, the accompanying chemical reactions become an unwanted consequence of the heating process. An acceptable process must satisfy the microbial inactivation constraint, and processing temperature and time must be selected to minimize the extent of unwanted chemical reactions. The application of kinetic data in optimizing quality factors during thermal processing is discussed further in the section "Quality Factor Degradation" in Chapter 9.

D and z values of some chemical reactions that degrade food quality and of enzyme inactivation are shown in Table 8.1. The z value of most chemical reactions associated with loss in food quality is at least two times higher than those for microbial inactivation (generally z = 10°C). Thus, it is a well-known

**Table 8.2** Z values for quality degrading chemical reactions in foods.

| **Texture** | Z(Celsius) | **Overall Sensory** | Z(Celsius) |
|---|---|---|---|
| Apples | 21 | Beans, green | 29 |
| Apples | 28 | Beets | 19 |
| Beans, black | 35 | Broccoli | 44 |
| Beans, Navy | 37 | Carrots | 17 |
| Beans, Soy | 42 | Corn kernels | 32 |
| Beef | 4 | Peas | 32 |
| Beets | 40 | Potatoes | 26 |
| Brussel sprouts | 21 | Squash | 26 |
| Carrots | 18 | | |
| Potatoes | 11 | **Color Loss** | |
| Shrimp | 23 | Green pigment | 30 |
| | | Red pigment | 31 |
| | | Browning | 32 |
| **Nutrients** | | **Enzymes** | |
| Carotene | 25 | Peroxidase | 28 |
| Thaimin | 27 | Catalase | 8 |
| Pyridoxine | 29 | Lipozgenase | 9 |
| Folic acid | 20 | polyphenol oxidase | 8 |
| Ascorbic acid | 27 | Pectin esterase | 16 |

practice in the food industry to increase the processing temperature to shorten the processing time for microbial inactivation and minimize the extent of quality factor degradation.

When only relative quality indices are needed to optimize the temperature required for a process, the actual rate of reaction may not be needed in the calculations and only the temperature dependence of that reaction will be required. Z values for different quality factor degradation reactions are given in Table 8.2.

## PROBLEMS

8.1. Nagy and Smoot (J. Agr. Food Chem 25:135, 1977) reported the degradation of ascorbic acid in canned orange juice to be first order, and the following first-order rate constants can be calculated from their data. At T = 29.4°C, 37.8°C, and 46.1°C , k in $day^{-1}$ was 0.00112, 0.0026, 0.0087, respectively. Calculate the activation energy, $Q_{10}$, D value and half life at 30°C.

8.2. The following data were collected for the sensory change in beef stored while exposed directly to air at −23°C (From: Gokalp et. al. J. Food Sci. 44:146, 1979). Sensory scores were 8.4, 6.2, 5.5, 5.1 at 0, 3, 6, and 9 months in storage. Plot the data and determine an appropriate form of an equation to which the data can be fitted to obtain the reaction rate constant.

8.3. Accelerated shelf life testing is often done to predict how food products would behave in the retail network. If a food product is expected to maintain acceptable quality in the retail network for 6 months at 30°C, how long should this product be stored at 40°C prior to testing in order that the results will be equivalent to 6 months at 30°C. Assume that the temperature

dependence of the sensory changes in the product is similar to that for the nonenzymatic browning reaction in Table 8.1.

8.4. Ascorbic acid degradation in sweet potatoes at a water activity of 0.11 is first order with a rate constant of 0.001500 $h^{-1}$ at 25°C. If the $Q_{10}$ for this reaction is 1.8, calculate the amount of ascorbic acid remaining in dried sweet potato stored at 30°C after 3 months in storage if the initial ascorbic acid content was 33 mg/100 g.

8.5. In the example problem on B-galactosidase action on lactose in acid whey, calculate the lactose conversion that can be expected using the same level of enzyme addition as in the example, if the whey is preconcentrated prior to treatment to have a lactose content of 12.5%, after a treatment time of 60 min.

8.6. Pectin methyl esterase in orange juice has a D value at 85°C of 8.3 min. and the z value is 14°C. Calculate the target juice temperature for pasteurization such that at least 99% of the enzyme will be inactivated after a 1-minute hold time followed by immediate cooling.

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**SUGGESTED READING**

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