12 Shelf Life of Foods

12.1 DEFINITIONS

The term *food quality* has a variety of meanings to professionals in the food industry, but the ultimate arbiters of food quality must be consumers. This notion is embodied in the frequently cited definition of food quality as "the combination of attributes or characteristics of a product that have significance in determining the degree of acceptability of the product to a user." Another definition of food quality is "the acceptance of the perceived characteristics of a product by consumers who are regular users of the product category or those who comprise the market segment." The phrase "perceived characteristics" includes the perception of the food's safety, convenience, cost, value and so on.

The quality of most foods and beverages decreases with storage or holding time. Exceptions include distilled spirits (particularly whiskeys and brandies), which develop desirable flavor components during storage in wooden barrels, some wines, which undergo increases in flavor complexity during storage in glass bottles, and many cheese varieties, where enzymic degradation of proteins and carbohydrates, together with hydrolysis of fat and secondary chemical reactions, leads to desirable flavors and textures in aged cheeses.

For the majority of foods and beverages in which quality decreases with time, it follows that there will be a finite length of time before the product becomes unacceptable. This time from production to unacceptability is referred to as *shelf life*. Although the Wizard of Id (and maybe many consumers) thought that shelf life related to the time until the shelf displaying the food rotted out (see Figure 12.1), shelf life includes the time on the retailer's shelf as well as the consumer's shelf, plus time in warehouses and the distribution chain. Although the shelf lives of foods vary, they are generally determined routinely for each particular product by the manufacturer or processor who attempts to provide the longest practicable shelf life consistent with costs and the pattern of handling and use by distributors, retailers and consumers. Supermarkets will generally not accept product into their distribution centers unless at least 75% of the shelf life remains.

Quality loss during storage may be regarded as a form of processing at relatively low temperatures that goes on for rather a long time. It is, therefore, not surprising that many of the concepts developed in connection with food processing find application in shelf life studies. Such studies are an essential part of food product and package development, which should be carried out in parallel.

Inadequate shelf life will often lead to consumer dissatisfaction and complaints. At best, such dissatisfaction will eventually affect the acceptance and sales of brand-name products, and, at worst, it can lead to illness or even malnutrition. Therefore, food processors pay considerable attention to determining the shelf lives of their products.

Despite its importance, there is no simple, generally accepted definition of shelf life in the food technology literature. The Institute of Food Technologists (IFT) in the United States defined shelf life (Shelf life of foods, 1974) as "the period between the manufacture and the retail purchase of a food product, during which time the product is in a state of satisfactory quality in terms of nutritional value, taste, texture and appearance." This definition overlooks the fact that the consumer may store the product at home for some time before consuming it yet will still want the product to be of acceptable quality.

The Institute of Food Science and Technology (IFST) in the United Kingdom defined shelf life as "the period of time during which the food product will remain safe; be certain to retain desired sensory, chemical, physical, microbiological and functional characteristics; and comply with any label declaration of nutritional data when stored under the recommended conditions" (*Shelf Life of Foods: Guidelines for Its Determination and Prediction*, 1993).

FIGURE 12.1 Shelf life according to the Wizard of Id. (Used with permission of John L. Hart FLP, Creators Syndicate, Inc., Los Angeles, CA.)

ASTM E2454 "Standard Guide for Sensory Evaluation Methods to Determine the Sensory Shelf Life of Consumer Products" defines sensory shelf life (SSL) as "the time period during which the products' sensory characteristics and performance are as intended by the manufacturer." The product is consumable or usable during this period and provides the end user with the intended sensory characteristics, performance and benefits. In this standard, shelf life is described as "the time period that a product may be stored before reaching its end point" and defines the endpoint as "the point at which a product no longer meets predetermined criteria as defined by test data (e.g., discrimination, descriptive or affective, or a combination thereof)."

Another definition is that "shelf life is the duration of that period between the packing of a product and the end of consumer quality as determined by the percentage of consumers who are displeased by the product" (Labuza and Schmidl, 1988). This definition accounts for the variation in consumer perception of quality (i.e., not all consumers will find a product unacceptable at the same time) and has an economic element in that, because it is not possible to please all consumers all of the time, a baseline of consumer dissatisfaction must be established (Labuza and Szybist, 1999).

Until recently, the European Union (EU) had no definition of shelf life or legislation on how shelf life should be determined. The consolidated EU Directive on food labeling (2000/13/EEC) requires prepackaged foods to bear a date of "minimum durability" or, in the case of foods that from the microbiological point of view are highly perishable, the "use by" date. The date of minimum durability is defined as the "date until which a foodstuff retains its specific properties when properly stored" and any special storage conditions (e.g., temperature not to exceed 7°C) must be specified. This concept (essentially equivalent to the "best before" date defined in the following) allows the processor to set the quality standard of the food, because the product would still be acceptable to many consumers after the "best before" date has passed. More recently, shelf life was defined for the first time in EU legislation in Commission Regulation (EC) No. 2073/2005 thus: "Shelf-life means either the period corresponding to the period preceding the 'use by' or the minimum durability date, as defined respectively in Articles 9 and 10 of Directive 2000/13/EC."

According to Cheftel (2005), the date of minimum durability must be indicated by the words "Best before" followed by the date (or a reference to where the date is given on the labeling). Depending on how long the food can keep, the date can be expressed by the day and the month, the month and year, or the year alone. A list of foods and beverages exempted from date marking is given in Article 9(5) of Directive 2000/13/EC. Foods that are highly perishable microbiologically (and therefore likely to be dangerous for health after a short period of time) must indicate the words "Use by" followed by the date (day and month) or a reference to where the date is given on the labeling. Any distribution after this date is forbidden. The "use by" date must be followed by a description of the storage conditions that should be observed.

In many countries a "best before" date is required to appear on the label. However, if the food is highly perishable from a microbiological point of view and, therefore, likely, after a short period, to constitute an immediate danger to human health, then the "best before" date must be replaced by a "use by" date. It is illegal to sell food after the "use by" date; food consumed after the "best before" date will still be edible but its quality will have deteriorated to a level below what the manufacturer considers desirable. Recently, the use of the hybrid term "best by" has become popular. A major U.S. brewer now labels bottles of beer with the "born on" date, that is, the date of bottling, leaving consumers to decide when the beer is no longer acceptable.

Given the variety of definitions, it is not surprising that there is no uniform or universally accepted open dating system for packaged foods. In some countries, mandatory open dating of all perishable (and sometimes semi-perishable) foods is required, while in other countries such requirements are voluntary. Arguments can be advanced both for and against the open dating of foods. However, there is an increasing quantity of open-dated food on sale throughout the world, and this trend is likely to continue.

12.2 SHELF LIFE DETERMINATION

12.2.1 Introduction

There are at least three situations when a shelf life determination might be required:

1. To determine the shelf life of existing products
2. To study the effect of specific factors or combinations of factors such as storage temperature, packaging materials, processing parameters or food additives on product shelf life
3. To determine the shelf life of prototype or newly developed products

Several established approaches are available for estimating the shelf life of foods:

1. *Literature study*: The shelf life of an analogous product is obtained from the published literature or in-house company files. Examples can be found in recent books on the shelf life of foods (e.g., Robertson, 2010; Kilcast and Subramaniam, 2011). The problem is that these data are very limited and generally apply to commodity-type foods.
2. *Turnover time*: The average length of time which a product spends on the retail shelf is found by monitoring sales from retail outlets, and from this the required shelf life is estimated. This does not give the "true" shelf life of the product but rather the "required" shelf life, where it is implicitly assumed that the product is still acceptable for some time after the average period on the retail shelf.
3. *Endpoint study*: Random samples of the product are purchased from retail outlets and then tested in the laboratory to determine their quality. From this, a reasonable estimation of shelf life can be obtained because the product has been exposed to actual environmental stresses encountered during warehousing and retailing.
4. *ASLT*: Laboratory studies are undertaken during which environmental conditions are accelerated by a known factor so that the product deteriorates at a faster than normal rate. This method requires that the effect of environmental conditions on product shelf life can be quantified. This approach is discussed later in this chapter.

Shelf life can be determined from two sides: the product side or the consumer side (van Boekel, 2009). Determining shelf life from the product side implies that the deterioration of the product is investigated as a function of time and may involve measuring the number of microorganisms or the decrease in desired components such as nutrients or texture, or the increase in undesired components such as brown pigments, off-flavors or moisture. Several models are available to assist in the

determination and are discussed later in this chapter. Alternatively, determining shelf life from the consumer side implies asking consumers to accept or reject food that has been stored for various lengths of time without normally specifying the reason. In the branch of statistics known as survival analysis, consumer dissatisfaction can be related to the survival function, defined as "the probability of a consumer accepting a product beyond a certain storage time." Models permitting the application of survival analysis to the sensory shelf life of foods have been published and are discussed later in this chapter.

12.2.2 Critical Descriptors and Indices of Failure

When a food is stored, changes occur that can be defined by one or more descriptors. The critical descriptor is the one that limits shelf life (Hough, 2010). In designing suitable packaging for foods, it is important first to define the critical descriptor(s) or indices of failure (IoFs) of the food, that is, the quality attributes that will indicate that the food is no longer acceptable to the consumer. In shelf life testing, there can be one or more critical descriptors that constitute sample failure. An IoF could be development of rancid flavors in cereals due to oxidation, loss of red color (bloom) in chilled beef due to depletion of O_2, reduction of carbonation in bottled soda due to permeation by CO_2 through the bottle wall, caking of instant coffee due to moisture ingress, development of microbial taint in chilled poultry, loss of crispness in a snack food due to moisture uptake or moisture loss in green vegetables resulting in wilting.

When the shelf life is determined from the product side, sensory evaluation of the food is likely to be used either alone or in combination with instrumental or chemical analyses to determine the quality of the product. Many sensory test methodologies are available and can be classified into either analytical tests or hedonic tests as shown in Figure 12.2. Analytical tests are used to measure the sensory characteristics of foods and answer questions such as "Is there a difference?" "What is the nature of the difference?" and "How big is (are) the difference(s)?" Hedonic or affective tests are used to measure consumer response to the sensory characteristics of foods and answer questions such as "Which food is preferred?" and "How much is it liked?" (Kilcast, 2011). ASTM E2454 describes three types of SSL endpoints: (1) the product's overall sensory profile has changed;

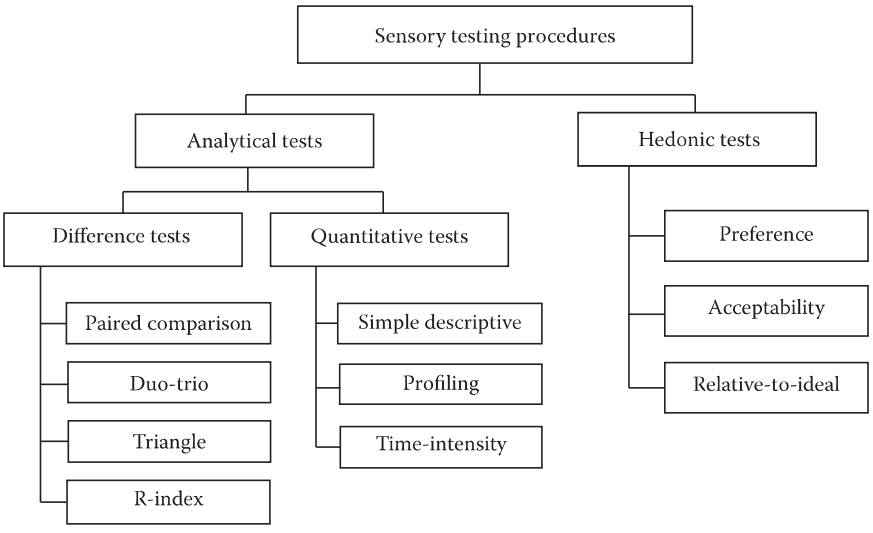

FIGURE 12.2 Main classes of sensory testing procedures. (From Kilcast, D., Sensory evaluation methods for food shelf life assessment, in: *Food and Beverage Stability and Shelf Life*, Kilcast, D. and Subramaniam, P. (Eds), Woodhead Publishing, Cambridge, England, pp. 350–380, 2011.)

(2) a product attribute(s) that is known or suspected to be key to the consumers' perception of the product has changed and (3) the acceptability of the product is too low.

12.2.3 Cutoff Point

Once the critical descriptor or IoF for a particular food has been defined, the next step is to specify the cutoff point (COP) or the endpoint of the particular degradation, for example, how much moisture or O_2 can react with the food, or how much the flavor can deteriorate, before the food becomes unacceptable. The COP indicates the limit on an analytical sensory scale or instrumental measurement beyond which (normally) acceptance by the consumer is significantly decreased (Hough, 2010). A sensory COP could be an increase or decrease by a specified amount in the mean panel score. The determination of a sensory COP is a function of the criteria selected, the test method used and sampling risk.

Three test methods are most commonly used: (1) discrimination, (2) descriptive and (3) affective. Descriptive methods are used to measure quantitative and/or qualitative characteristics of products and require specially trained panelists. Affective methods are used to evaluate preference, acceptance and/or opinions of products and do not require trained panelists. Further details about these tests can be found in standard texts on sensory evaluation (e.g., Meilgaard et al., 2007; Lawless and Heymann, 2010).

The selection of a particular sensory evaluation procedure for evaluating products undergoing shelf life testing is dependent on the purpose of the test. Acceptability assessments by untrained panelists are essential to an open dating program, while discrimination testing with expert panels might be used to determine the effect of a new packaging material on product stability. However, an expert panel is not necessarily representative of consumers, much less different consumer segments. Even if that assumption can be made, a cutoff level of acceptability has to be decided. The time at which a large (but predetermined) percentage of panelists judge the food to be at or beyond that level is the end of shelf life, but just what that percentage is depends on the company and is a business rather than a technical decision.

Although a consumer panel would seemingly be the most appropriate tool to determine the shelf life and quality of a food product, to repeatedly assemble consumer panels for multiple measurements would be both impractical and expensive. Although a sensory panel is more appropriate for repeated assessments, its results would be more analytical and not necessarily representative of consumer responses. By correlating data from a consumer panel with those obtained from a trained panel, these analytical measures can be used to determine the shelf life or quality of a food product, greatly benefiting sensory quality control programs.

Not surprisingly, many food scientists and technologists in industry attempt to replace human judgment or sensory panels with instrumental or chemical analyses because the latter are neither prone to fatigue nor subject to the physiological and psychological fluctuations that characterize human performance. However, because human judgment is the ultimate arbiter of food acceptability, it is essential that the results obtained from any instrumental or chemical analysis correlate closely with the sensory judgments for which they are to substitute. Correlation of values of individual chemical parameters with sensory data is often not straightforward because overall organoleptic quality is a composite of a number of changing factors (Kilcast, 2011). The relative contribution of each factor to the overall quality may vary at different levels of quality or at different storage conditions. Other problems with sensory evaluation include the high cost of using large testing panels and the ethics of asking panelists to taste spoiled or potentially hazardous samples.

Alternatively, a COP could be microbial deterioration of the sample to an extent that renders it unsuitable or unsafe for human consumption. Other COPs could relate to changes in odor, color, texture, flavor and so on, which render the sample unacceptable to the consumer. Thus, the COP can be defined as the condition when the product exhibits either physical, chemical, microbiological or sensory characteristics that are unacceptable to the consumer, and the time required for the food to

exhibit such conditions is the shelf life of the food. One challenge with shelf life testing is to develop experimental designs that minimize the number of samples required (thus minimizing the cost of the testing), while still providing reliable and statistically valid answers.

12.2.4 Influence of Packaging Material

The final step is to ascertain which (if any) of the critical descriptors or IoFs might be influenced by the packaging material, as packaging cannot prevent all deteriorative reactions or undesirable changes in foods. If, for example, the IoF of a snack food was loss of crispness, then the packaging material could influence this by the extent to which it permitted the ingress of moisture. Different plastic films, for example, have different WVTRs and, thus, the shelf life obtained varies depending on the particular plastic polymer(s) selected for a given pack size.

Similar considerations apply to foods for which the IoF is oxidation, as different packaging materials have different OTRs. However, it is not just the packaging material itself that can influence shelf life; the method of filling the product into the package is also important. For example, with roasted and ground coffee, vacuum filling into metal cans will remove 95% or more of the O_2 from the can compared with inert gas flush packing in plastic foil laminate pouches, which will remove or displace 80%–90% of the O_2 in the package. The residual O_2 in the package at the time of filling will have a major influence on shelf life regardless of the O_2 barrier properties of the package itself.

If the food is sensitive to light, then the packaging material can have a significant influence, depending on how much light and at what wavelengths it is transmitted, as discussed in Section 11.5.3.

12.3 DETERMINING SHELF LIFE FROM THE PRODUCT SIDE

The shelf life of a food is controlled by three factors:

1. The product characteristics including formulation and processing parameters (intrinsic factors)
2. The properties of the package
3. The environment to which the product is exposed during distribution and storage (extrinsic factors)

Intrinsic factors include pH, a_w, enzymes, microorganisms and concentration of reactive compounds. Many of these factors can be controlled by selection of raw materials and ingredients, as well as the choice of processing parameters.

Extrinsic factors include temperature, RH, light, total pressure and partial pressure of different gases, as well as mechanical stresses including consumer handling. Many of these factors can affect the rates of deteriorative reactions that occur during the shelf life of a product.

The properties of the package can have a significant effect on many of the extrinsic factors and, thus, indirectly on the rates of the deteriorative reactions. Thus, the shelf life of a food can be altered by changing its composition and formulation, processing parameters, packaging system or environment to which it is exposed.

12.3.1 Product Characteristics

12.3.1.1 Perishability

Based on the nature of the changes that can occur during storage, foods may be divided into three categories—perishable, semi perishable and nonperishable or shelf stable, which translate into very short shelf life foods, short to medium shelf life foods and medium to long shelf life foods.

Perishable foods are those that must be held at chill or freezer temperatures (i.e., 0°C to 7°C or −12°C to −18°C, respectively) if they are to be kept for more than short periods. Examples of such foods include milk, fresh flesh foods such as meat, poultry and fish, minimally processed foods and many fresh fruits and vegetables.

Semi perishable foods are those that contain natural inhibitors (e.g., some cheeses, root vegetables and eggs) or those that have received some type of mild preservation treatment (e.g., pasteurization of milk, smoking of hams and pickling of vegetables) that produces greater tolerance to environmental conditions and abuse during distribution and handling.

Shelf stable foods are considered *nonperishable* at room temperatures. Many unprocessed foods fall into this category, and are unaffected by microorganisms because of their low moisture content (e.g., cereal grains and nuts, and some confectionery products). Processed food products can be shelf stable if they are preserved by heat sterilization (e.g., canned foods), contain preservatives (e.g., soft drinks), are formulated as dry mixes (e.g., cake mixes) or processed to reduce their water content (e.g., raisins or crackers). However, shelf stable foods only retain this status if the integrity of the packages that contain them remains intact. Even then, their shelf life is finite due to deteriorative chemical reactions that proceed at room temperature independently of the nature of the package, and the permeation through the package of gases, odors and water vapor.

12.3.1.2 Bulk Density

The free space volume of a package (V) is directly related to the bulk density (ρ_b) and the true density (ρ_p) of the food as follows:

$$V = V_t - V_p = \frac{W}{\rho_b} - \frac{W}{\rho_p} \tag{12.1}$$

where

V_t is the total volume of the package
V_p is the volume of the product
W is the weight of the product

Thus, for packages of similar shape, equal weights of foods of different bulk densities will have different free space volumes, and, therefore, package areas and package behavior will differ. This has important implications when changes are made in package size for the same food, or alterations are made to the process, which result in changes to the food bulk density.

While the true density of a food depends largely on its composition and cannot be changed significantly, the bulk density of food powders can be affected by processing and packaging. Some food powders (e.g., milk and coffee) are instantized by treating individual particles so that they form free-flowing agglomerates or aggregates in which there are relatively few points of contact; the surface of each particle is, thus, more easily wetted when the powder is rehydrated. Instantization results in a reduction of bulk density—for example, for skim milk powder, from 0.64 to 0.55 g mL^{-1}. A wide range of bulk densities is encountered in foods, from around 0.056 g mL^{-1} for potato chips to 0.96 for granulated salt.

The free space volume has an important influence on the rate of oxidation of foods: if a food is packaged in air, then a large free space volume is undesirable because it constitutes a large O_2 reservoir. Conversely, if the product is packaged in an inert gas, then a large free space volume acts as a huge "sink" to minimize the effects of O_2 transferring into the package. It follows that a large package surface area and a low food bulk density result in greater O_2 transmission.

12.3.1.3 Concentration Effects

In Chapter 11, the major types of deteriorative reactions that are likely to be encountered in packaged foods were described, with the factors affecting the rates of these reactions quantified with

the aid of simple chemical kinetic expressions. Thus, the progress of a deteriorative reaction can be monitored by following the change in concentration of some key component.

However, in many foods such as those containing whole tissue components, or where the reacting species are partially bound as in membranes, structural proteins or carbohydrates, the concentration varies from one point to another, even at zero time. Furthermore, because most of these compounds will have little opportunity to move, the concentration differences will get greater as the reactions proceed out from isolated initial foci. This has been described as the "brush-fire" effect and is especially important in chain reactions such as oxidation.

In addition, there may be several different stages of the deteriorative reaction proceeding at once, and the different stages may have different dependence on concentration and temperature, giving disguised kinetics. Such a situation is frequently the case for chain reactions and microbial growth, which have both a lag and a log phase with very different rate constants.

The point to be taken from this is that for many foods, it may be difficult to obtain kinetic data of use for predictive purposes. In such situations, use of sensory panels to determine the acceptability of the food is the recommended procedure (provided, of course, that there are no microbial risks).

12.3.2 Package Properties

Foods can be classified according to the degree of protection required, and a very generalized scheme is shown in Table 12.1. The advantage of this sort of analysis is that attention can be focused on the key requirements of the package such as maximum moisture gain or O_2 uptake. This then enables calculations to be made to determine whether or not a particular packaging material would provide the necessary barrier required to give the desired product shelf life. In the case of metal cans and glass containers, these can be regarded as essentially impermeable to the passage of gases, odors and water vapor, while paper-based packaging materials can be regarded as permeable. This then leaves plastics-based packaging materials that provide varying degrees of protection, depending largely on the nature of the polymers used in their manufacture.

In Chapter 4, the permeability of thermoplastic polymers was discussed. The way in which this information can be utilized to select the most appropriate polymer for a particular product is discussed in the following.

The expression for the steady-state permeation of a gas or vapor through a thermoplastic material was derived earlier (see Equation 4.13) and can be written as

$$\frac{\delta w}{\delta t} = \frac{P}{X} A(p_1 - p_2) \tag{12.2}$$

where

P/X is the permeance (the permeability constant P divided by the thickness of the film X)
A is the surface area of the package
p_1 and p_2 are the partial pressures of water vapor outside and inside the package
$\delta w/\delta t$ is the rate of gas or vapor transport across the film, where the latter term corresponds to Q/t in the integrated form of the expression

12.3.2.1 Water Vapor Transfer

The prediction of moisture transfer either to or from a packaged food requires analysis of the preceding equation given certain boundary conditions. The simplest analysis requires the assumptions that P/X is constant, that the external environment is at constant temperature and humidity, and that p_2, the vapor pressure of the water in the food, follows some simple function of the moisture content.

External conditions will not remain constant during storage, distribution and retailing of a packaged food. Therefore, P/X will not be constant. However, using WVTRs determined at 38°C and

TABLE 12.1
Degree of Protection Required by Various Foods and Beverages (Assuming 1 Year Shelf Life at 25°C)

Food/Beverage	Maximum Amount of O_2 Gain (ppm)	Other Gas Protection Needed	Maximum Water Gain or Loss	Requires High Oil Resistance	Requires Good Barrier to Volatile Organics
Canned milk and flesh foods	1–5	No	3% Loss	Yes	No
Baby foods	1–5	No	3% Loss	Yes	Yes
Beers and wine	1–5	<20% CO_2 (or SO_2) loss	3% Loss	No	Yes
Instant coffee	1–5	No	2% Gain	Yes	Yes
Canned soups, vegetables and sauces	1–5	No	3% Loss	No	No
Canned fruits	5–15	No	3% Loss	No	Yes
Nuts, snacks	5–15	No	5% Gain	Yes	No
Dried foods	5–15	No	1% Gain	No	No
Fruit juices and drinks	10–40	No	3% Loss	No	Yes
Carbonated soft drinks	10–40	<20% CO_2 loss	3% Loss	No	Yes
Oils and shortenings	50–200	No	10% Gain	Yes	No
Salad dressings	50–200	No	10% Gain	Yes	Yes
Jams, jellies, syrups, pickles, olives, vinegars	50–200	No	10% Gain	Yes	No
Liquors	50–200	No	3% Loss	No	Yes
Condiments	50–200	No	1% Gain	No	Yes
Peanut butter	50–200	No	10% Gain	Yes	No

Source: Adapted from Salame, M., The use of low permeation thermoplastics in food and beverage packaging, in: *Permeability of Plastic Films and Coatings*, Hopfenberg, H.B. (Ed.), Plenum, New York, p. 275, 1974.

90% RH gives a "worst-case" analysis, but if the food is being sold in markets in temperate climates, use of WVTRs determined at 25°C and75% RH is more appropriate. As noted in Chapter 4, WVTRs can be converted to permeances by dividing by Δp.

A further assumption is that the moisture gradient inside the package is negligible; that is, the package should be the major resistance to water vapor transport. This is the case whenever P/X is less than about 10 g m^{-2} day^{-1} (cm Hg)$^{-1}$, which is the case for most films but not paperboard under high humidity conditions.

The critical point about Equation 12.2 is that the internal vapor pressure is not constant but varies with the moisture content of the food at any time. Thus, the rate of gain or loss of moisture is not constant but falls as Δp gets smaller. Therefore, some function of p_2, (the internal vapor pressure) as a function of the moisture content, must be inserted into the equation to be able to make proper predictions. If a constant rate is assumed, then the food will be overprotected.

In low and intermediate moisture foods, the internal vapor pressure is determined solely by the moisture sorption isotherm of the food (Bell and Labuza, 2000). As discussed in Section 11.4.1.2, several functions can be applied to describe a sorption isotherm, although the preferred one is the

GAB model. If a linear model is used, the result can be integrated directly, but if the GAB model is used, then it must be numerically evaluated.

In the simplest case when the isotherm is treated as a linear function

$$m = ba_w + c \tag{12.3}$$

where

m is the moisture content in g H_2O g^{-1} solids
a_w is the water activity
b is the slope of the isotherm
c is the constant

The moisture content can be substituted for water gain using the relationship

$$m = \frac{W\ (\text{weight of water transported})}{W_s\ (\text{weight of dry solids enclosed})} \tag{12.4}$$

$$\therefore W = mW_s \tag{12.5}$$

and

$$\delta W = \delta m W_s \tag{12.6}$$

By substitution

$$\frac{\delta W}{\delta t} = \frac{\delta m W_s}{\delta t} = \frac{P}{X} A \left[\frac{p_0 m_e}{b} - \frac{p_0 m}{b} \right] \tag{12.7}$$

which on rearranging, gives

$$\frac{\delta m}{m_e - m} = \frac{P}{X} \frac{A}{W_s} \frac{p_0}{b} \delta t \tag{12.8}$$

and on integrating

$$\ln \frac{m_e - m_i}{m_e - m} = \left[\frac{P}{X} \frac{A}{W_s} \frac{p_0}{b} \right] t \tag{12.9}$$

where

m_e is the equilibrium moisture content of the food if exposed to external package RH
m_i is the initial moisture content of the food
m is the moisture content of the food at time t
p_0 is the vapor pressure of pure water at the storage temperature (*not* the actual vapor pressure outside the package)

A plot of the log of the unaccomplished moisture change—the term on the left-hand side of Equation 12.9—versus time is a straight line with a slope equivalent to the bracketed term on the right-hand side of the equation.

The end of product shelf life is reached when $m = m_c$, the critical moisture content, at which time $t = \theta_s$, the shelf life. Thus, Equation 12.9 can be rewritten as

$$\ln \frac{m_e - m_i}{m_e - m_c} = \frac{P}{X} \frac{A}{W_s} \frac{p_0}{b} \theta_s \tag{12.10}$$

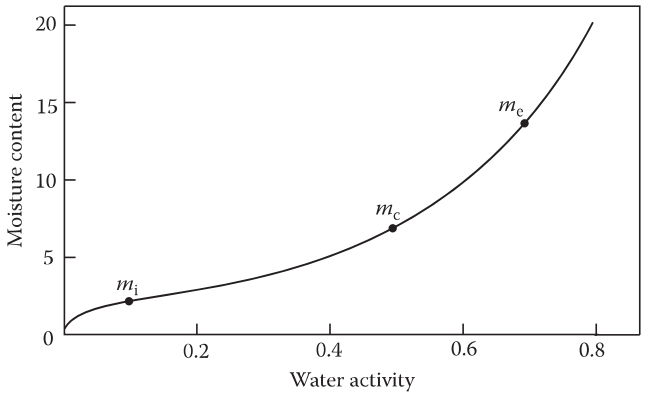

FIGURE 12.3 Typical moisture sorption isotherm for a snack bar, where m_i is the initial moisture content; m_c is the critical moisture content of product; and m_e is the equilibrium moisture content.

The relationship between the initial, critical and equilibrium moisture contents is illustrated in Figure 12.3.

Equation 12.10 and the corresponding one for moisture loss

$$\ln \frac{m_i - m_e}{m - m_e} = \frac{P}{X}\frac{A}{W_s}\frac{p_0}{b}\theta_s \tag{12.11}$$

have been extensively tested for foods and found to give excellent predictions of actual weight gain or loss. These equations are also useful when calculating the effect of changes in the external conditions (e.g., temperature and humidity), the surface area:volume ratio of the package and variations in the initial moisture content of the product.

Example 12.1

A breakfast cereal has an initial moisture content m_i of 2.5%. The COP is the critical moisture content m_c of 8% due to loss of crispness (Robertson, 2011a). The equilibrium moisture content m_e at 25°C is 14.8% and the pseudo-equilibrium moisture content m_e' obtained by extension of the linear portion of the isotherm is 11%; the slope of the line (b) is 0.147 g H_2O/g solids/unit a_w (see Figure 12.4).

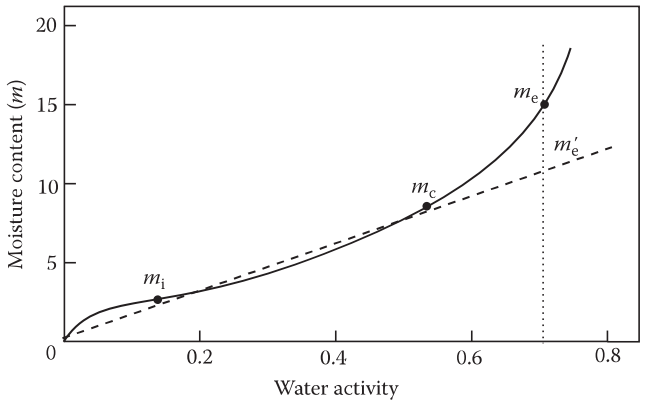

FIGURE 12.4 Schematic of a typical moisture sorption isotherm for breakfast cereal with a superimposed straight line of slope b. Initial (m_i), critical (m_c) and equilibrium (m_e) moisture contents are indicated together with the pseudo-equilibrium (m_e') moisture content used for package shelf life calculations.

Calculate the shelf life of the cereal if it is packaged in a bag of 50 µm LDPE or 50 µm OPP. The weight of dry cereal in the package is 400 g and the dimensions of the bags are 20 cm × 30 cm. The packed product is to be stored at 25°C and 75% RH.

$$\text{Surface area of the bags is } 20 \times 30 = 600 \text{ cm}^2 = 0.06 \text{ m}^2$$

$$\text{Vapour pressure of pure water at } 25°\text{C} = 2.3756 \text{ cm Hg}$$

Data from a plastic film supplier indicated that WVTRs determined at 25°C/75% RH were

$$50 \text{ µm LDPE} = 8.0 \text{ g m}^{-2} \text{ day}^{-1}$$

$$50 \text{ µm OPP} = 1.35 \text{ g m}^{-2} \text{ day}^{-1}$$

These WVTRs must be converted into water vapor permeances P/X by dividing by the driving force for water vapor transfer. The saturated water vapor pressure at 25°C is (from Table 4.10) 2.376. Thus, the driving force at 25°C/75% RH is

$$2.376 \times 0.75 = 1.782 \text{ cm Hg}$$

For LDPE film,

$$\frac{P}{X} = \frac{8.0 \text{ g}}{\text{m}^2 \text{ day}} \times \frac{1}{1.782 (\text{cmHg})}$$

$$= 4.489 \text{ g} H_2O \text{ m}^{-2} \text{ day}^{-1} (\text{cmHg})^{-1}$$

For OPP film,

$$\frac{P}{X} = \frac{1.35 \text{ g}}{\text{m}^2 \text{ day}} \times \frac{1}{1.782 (\text{cmHg})}$$

$$= 0.758 \text{ g} H_2O \text{ m}^{-2} \text{ day}^{-1} (\text{cmHg})^{-1}$$

Substituting into Equation 12.10 for cereal packed in LDPE film,

$$\ln \frac{11 - 2.5}{11 - 8} = 4.489 \cdot \frac{0.06}{400} \cdot \frac{2.3756}{0.147} \cdot \theta_s \tag{12.12}$$

Solving for shelf life θ_s,

$$\theta_s = \frac{[\ln 2.833]}{1.088 \times 10^{-2}}$$

$$= \frac{1.0413}{1.088 \times 10^{-2}}$$

$$= 96 \text{ days}$$

If the cereal were packed in OPP film instead,

$$\theta_s = \frac{[\ln 2.833]}{1.837 \times 10^{-3}}$$

$$= 567 \text{ days}$$

The shelf life is inversely related to the water vapor permeances of the film; since P/X for LDPE is 5.9 times that for OPP, the shelf life in the latter film is 5.9 times that in the former. If the required

shelf life were, say, 300 days, then Equation 12.10 could be recalculated using $t_s = 300$ and solved for P/X. From this, the corresponding WVTR could be calculated and the film supplier requested to supply a film that met this specification at 25°C and 75% RH.

As noted earlier, the shelf lives calculated earlier will be longer than what would be achieved in practice because the pseudo-equilibrium moisture content m'_e used in the calculations is less than the actual equilibrium moisture content, which is the real driving force for water vapor transport. Because of the simplifying assumptions made in the earlier calculations, the calculated shelf lives should be verified by actual shelf life testing.

12.3.2.2 Gas and Odor Transfer

The gas of major importance in packaged foods is O_2 because it plays a crucial role in many reactions that affect the shelf life of foods (e.g., microbial growth, color changes in fresh and cured meats, oxidation of lipids and consequent rancidity and senescence of fruits and vegetables).

The transfer of gases and odors through packaging materials can be analyzed in an analogous manner to that described for water vapor transfer, provided that values are known for the permeance of the packaging material to the appropriate gas, and the partial pressure of the gas inside and outside the package. Regrettably, the latter data are scarce for all but the common gases.

Packaging can control two variables with respect to O_2, and these can have different effects on the rates of oxidation reactions in foods:

1. *Total amount of O_2 present*: This influences the extent of the reaction, and in impermeable packages (e.g., hermetically sealed metal and glass containers), where the total amount of O_2 available to react with the food is finite, the extent of the reaction cannot exceed the amount corresponding to the complete exhaustion of the O_2 present inside the package at the time of sealing. This may or may not be sufficient to result in an unacceptable product quality after a certain period of time dependent on the rate of the oxidation reaction. Of course, such a rate will be temperature dependent. With permeable packages (e.g., plastic packages), where ingress of O_2 will occur during storage, two factors are important: there may be sufficient O_2 inside the package to cause product unacceptability when it has all reacted with the food, or there may be sufficient transfer of O_2 through the package over time to result in product unacceptability through oxidation.
2. *Concentration of O_2 in the food:* In many cases, relationships between the O_2 partial pressure in the space surrounding the food and the rates of oxidation reactions can be established. If the food itself is very resistant to diffusion of O_2 (e.g., very dense products such as butter), then it will likely be very difficult to establish a relationship between the O_2 partial pressure in the space surrounding the food and the concentration of O_2 in the food.

The principal difference between predominantly water-vapor-sensitive and O_2-sensitive foods is that the latter are generally more sensitive by 2–4 orders of magnitude. Thus, the amount of O_2 present in the air-filled headspace of O_2-sensitive foods must not be neglected when predicting their shelf life. This amount is actually 32 times higher per unit volume of air than per unit volume of O_2-saturated water. A further complicating factor with O_2-sensitive foods is that, in these foods, a concentration gradient occurs much more frequently than in moisture-sensitive foods. In the latter, it is practically limited to hard-boiled candies and freezer burn in frozen foods.

Example 12.2

Suppose that the feasibility of packaging fine wine in an oriented PET bottle with O_2 and SO_2 permeabilities of 0.03 and 0.3 *barrer*, respectively (all permeabilities calculated in air at 25°C and 50% RH on one side and 100% RH on the other) is to be investigated. If each bottle has a surface area of 720 cm^2, a thickness of 0.046 cm and holds 1 L of wine, calculate the shelf life of the wine in the bottle, assuming that the bottles are perfectly sealed with gas-impermeable, screwcap closures. The COP for the wine is when 5 ppm O_2 and half of the free SO_2 (25 ppm) has permeated through the bottle wall.

(a) Oxygen Ingress:

Because the atmosphere has an O_2 concentration of 21%, the O_2 vapor pressure outside the bottle will be $0.21 \times 76 = 16.0$ cm Hg. Assume that the O_2 vapor pressure inside the bottle is zero.

The maximum quantity of O_2 able to be absorbed by the wine and still retain acceptable quality is 5 ppm = 5 mg L^{-1} = 5×10^{-3} g L^{-1}, and because the bottle holds 1 L, 5×10^{-3} g of O_2 can be absorbed.

Using a value for the density of oxygen of 1.43×10^{-3} g mL^{-1}, the maximum quantity of oxygen (Q) permissible = $(5 \times 10^{-3})/(1.43 \times 10^{-3}) = 3.5$ mL.

Equation 4.13 can then be used:

$$\frac{Q}{t} = \frac{P}{X} A(p_1 - p_2) \tag{12.13}$$

which, on rearrangement and letting $t = \theta_s$ (the shelf life), is

$$\theta_s = \frac{QX}{PA\Delta p} \tag{12.14}$$

$$\theta_s = \frac{3.5 \times 0.046}{0.03 \times 10^{-10} \times 720 \times 16} = 4.654 \times 10^6 \text{ s} = 54 \text{ days}$$

(b) Sulfur Dioxide Egress:

Assume that the initial concentration of SO_2 in the wine is 100 ppm and that 50% of this is in the free form. The vapor pressure of 50 ppm SO_2 in the wine has been estimated to be 1.73×10^{-3} cm Hg.

If the units for ρ are g mL^{-1} and for V_w g, then the units for Q (the quantity of SO_2 permeating through the bottle wall) will be g SO_2 g^{-1} of wine. The initial level of free SO_2 is 50 ppm or 50 mg L^{-1}; this corresponds to 50 mg kg^{-1} of wine (assuming that the wine has the same density as water) or 5×10^{-5} g g^{-1}. In this example, the shelf life of the wine can be considered to be over when half of the free SO_2 has permeated through the bottle (i.e., when 2.5×10^{-5} g g^{-1} has been lost). Using a value for the density of SO_2 of 2.93×10^{-3} g mL^{-1}, the maximum quantity of SO_2 that can be lost is $(2.5 \times 10^{-5})/(2.93 \times 10^{-3}) = 8.5 \times 10^{-3}$ mL g^{-1} = 8.5 mL for a 1 L bottle.

Substituting into Equation 12.13 and solving gives

$$\theta_s = \frac{8.5 \times 0.046}{0.03 \times 10^{-10} \times 720 \times 1.73 \times 10^{-3}} = 1.05 \times 10^{10} \text{ s} = 333 \text{ years}$$

(c) Conclusion:

Ingress of O_2 from the atmosphere into the wine is likely to be the major mode of failure for wine packaged in a PET bottle. The calculated shelf life of 54 days is probably too short, and, therefore, the bottle would have to be laminated or coated with a barrier material. Permeation of SO_2 through the bottle walls is not going to be a limiting factor in the shelf life of wine in PET bottles.

Example 12.3

This example involves oxidation of biscuits containing 25% fat (Robertson, 2011b). Sensory testing has revealed that they become unacceptable to 50% of consumers due to rancidity when the peroxide value (PV) reaches 15.6 milliequivalents (meq) of O_2 per kg (Calligaris et al., 2007). Assume that the surface area of the package is 440 cm^2 (0.044 m^2) and each pack contains 250 g of biscuits.

Calculate the shelf life of the biscuits if they were packaged in (a) a laminate film consisting of two 25 μm layers of coextruded OPP with an overall OTR of 650 mL m^{-2} day^{-1}, and (b) a laminate film consisting of 15 μm biaxially oriented nylon-6 (BON-6) and 80 μm LDPE with an overall OTR of 2 mL m^{-2} day^{-1}, both OTR measurements being performed at 23°C and 0% RH. Assume that

there is zero O_2 inside the packs immediately after sealing and that all the O_2 that enters the packs reacts with the fat in the biscuits.

Fat content of biscuits is 25%. Therefore, weight of fat in each pack is

$$25\% \times 250\,\text{g} = 62.5\,\text{g}$$

The maximum level of peroxide value (PV) for rejection by 50% of consumers is 15.6 meq O_2 per kg biscuits. Therefore, the maximum quantity of O_2 that can enter each pack is

$$\frac{(15.6 \times 62.5)}{1000} = 0.975\ \text{meq}\ O_2$$

The value expressed in millimoles of O_2 per kg is equal to half that expressed in milliequivalents of O_2 per kg. Thus, since 1 meq O_2 = 0.5 mmol,

$$0.975\ \text{meq}\ O_2 = 0.4875\ \text{mmol} = 4.875 \times 10^{-4}\ \text{mol}$$

The Ideal Gas Law can be used to convert this quantity of O_2 to mL at 23°C:

$$V = \frac{nRT}{P} = (4.875 \times 10^{-4}) \times 82.06 \times \frac{296}{1} = 11.8\ \text{mL}$$

where

R = 82.06 mL atm mol^{-1} K^{-1}

P is the atmospheric pressure = 1 atm

The OTR of laminate film (a) = 650 mL m^{-2} day^{-1}, which for a pack of surface area 0.044 m^2 means that 650 × 0.044 = 28.6 mL O_2 will permeate through per day.

Therefore, the predicted shelf life for the biscuits packed in laminate film (a) is 11.8/28.6 = 0.412 days = 9.9 h at 23°C.

The predicted shelf life for the biscuits packed in laminate film (b) with an OTR of 2 mL m^{-2} day^{-1} is 11.8/(0.044 × 2) = 134 days at 23°C.

Because various simplifying assumptions were made in the preceding calculations, the calculated shelf lives would need to be verified by actual shelf life testing.

12.3.2.3 Light Transmission

Light is known to have a damaging effect on several foods such as milk and other dairy products, and their sensitivity is attributed to the presence of light-sensitive vitamins like vitamins A and B_2, and the action of vitamin B_2 as a photosensitizer, which is able to induce a cascade of oxidative reactions leading to significant losses in other vitamins (e.g., vitamin D) and changes in sensory quality. Saffert et al. (2009) stored UHT low-fat milk under light with an intensity of 700 lx in PET bottles with varying light transmittance. PET bottle variant 1 allowed almost complete light transmittance from 700 to around 310 nm. In the critical wavelength range below 500 nm, the pigmented PET bottle variant 2 showed a light transmittance of around 25%, variant 3 of 12%–15% and variant 4 of 5%–10%. Changes in the vitamin A, B_2 and D_3 concentrations were monitored over 12 weeks at 23°C.

Milk packed in pigmented PET bottles with the lowest light transmittance were stored in the dark under the same experimental conditions and served as the control sample. In clear PET bottles, a reduction of 93% in the initial content was observed for vitamin A and 66% for vitamin D_3, while the vitamin B_2 content was completely degraded. In all pigmented PET bottles, the vitamin retention was only slightly higher; the losses ranged between 70% and 90% for vitamin A, between 63% and 95% for vitamin B_2 and between 35% and 65% for vitamin D_3 depending on the pigmentation

level. In the control stored in the dark, a 16% loss was observed for vitamin A, while the level of vitamins B_2 and D_3 remained essentially stable. It was concluded that light-induced sensory changes in UHT milk under commercially relevant storage conditions can only be excluded in packages that provide an almost total barrier to light.

12.3.2.4 Package Dimensions

The dimensions of the package for a given weight of food can have a significant influence on shelf life. Although a spherical shape will minimize the surface area of the package (and thus the quantity of moisture or O_2 that will permeate the package wall), it is not a practical shape for commercial use, and in practice most packages tend to be rectangular or cylindrical. Table 12.2 gives the surface areas for a range of different shapes with the same volume (~450 mL). Compared with the surface area of a sphere, the surface area of a cylinder is 16% greater; a cube 24% greater; a tetrahedron 49% greater; a rectangular shape 58% greater and a thin rectangular shape 246% greater. Extremely thin packages have a much greater surface area:volume ratio and thus require a plastic with better barrier properties to get the same shelf life than if the same quantity of product were packaged in a thicker format.

Because the surface area:volume ratio decreases as a package size gets smaller by a factor equivalent to the characteristic thickness of the package, the shelf life using the same film will decrease directly by this thickness. In other words, when different quantities of the same product are packaged in different-sized packages using the same plastic material, the smallest package will have the shortest shelf life as it inevitably has a greater surface area per unit volume. Many food companies still seem unaware of this fact as they continue to launch smaller packages without changing the packaging material and then wonder why the shelf life is shorter for the smaller package. To ensure adequate shelf life for a food in multiple-sized packages, shelf life tests should be based on the smallest package.

12.3.2.5 Package/Product Interactions

With certain products packaged with certain materials, the end of shelf life arises when an unacceptable degree of interaction between the package and the product has occurred. The COP in these cases is normally the legal limit for a contaminant in a food, but it can be based on a sensory criterion such as flavor or color. Several examples will be given to illustrate the nature of this phenomenon.

The first example is that of a tomato product processed under typical conditions and packaged in a three-piece can with a plain tinplate body and enameled ECCS ends. Over a storage period of 24 months

TABLE 12.2
Surface Areas of Different Package Shapes, All with a Volume of ~450 mL

Shape	Dimensions cm	Surface Area cm²	Surface Area m²	Increase %	Surface Area: Volume Ratio
Sphere	Diameter 9.52	285	0.0285	0	0.63
Cylinder	Diameter 7.3 Height 10.8	331	0.0331	16	0.73
Cube	Sides 7.67	353	0.0353	24	0.78
Tetrahedron	Sides 15.65	424	0.0424	49	0.94
Rectangular pack	Height 3 Length 15 Width 10	450	0.0450	58	1.0
Thin rectangular pack	Height 1 Length 20 Width 22.5	985	0.0985	246	2.18

at ambient temperature, several deteriorative reactions occur. The concentration of tin ions in the product increases rapidly during the first 3 months from ~20 to about 160 ppm, reaching 280 ppm after 24 months. Iron also dissolves, increasing slowly from 8 ppm initially to 10 ppm after 18 months to reach 14 ppm after 24 months. The flavor score declines due to the increasing quantities of dissolved tin and iron; the color value shows a decrease due to an increase in brown pigments, but remains acceptable.

While high concentrations of tin in food may cause stomach upsets in some individuals, this is unlikely to be the case where tin concentrations remain below the legal limit of 200 mg kg^{-1} (100 mg kg^{-1} in canned beverages and 50 mg kg^{-1} in canned baby foods).

There are two factors that limit the shelf life for this tomato product. One is the deterioration in flavor resulting from the dissolution of tin and iron from the package into the product, giving an acceptable shelf life of 24–30 months. The other is the legal limit for tin in canned foods of 200 mg kg^{-1}, which is reached within 4 months. If a longer shelf life was required, it would be necessary to use a full enamel-lined can. Alternatively, the product could be stored at chill temperatures to reduce the rate of the degradative reactions.

Grassino et al. (2009) reported maximum values of tin in cans of tomato purée up to 301 mg kg^{-1} after 180 days at so-called elevated storage temperatures (36°C), which in countries near the equator is the ambient temperature. Based on the legal limit for tin, the shelf life of these canned foods would be less than 5 months.

The second example concerns foods sold in glass jars with metal lids. To ensure tight closure and fairly easy opening, the lids contain a gasket of PVC with 40%–45% plasticizer, usually epoxidized soy bean oil (ESBO) that can migrate into the food in amounts sometimes exceeding the tolerable daily intake (TDI). Fankhauser-Noti et al. (2005) reported that the migration of ESBO into food products with some free oil far exceeded the specific migration limit (SML) of 60 mg kg^{-1}. When the gasket was tightened against the rim of the jar, 60–250 mg (average 165 mg) was in contact with food and on average 70 mg ESBO was in food contact. After exposure to olive oil for 4 weeks at ambient temperature, all the ESBO was transferred; 70 mg ESBO in a 250 g jar resulted in a concentration of 280 mg kg^{-1} food; in a 100 g jar it was 700 mg kg^{-1} food. In oily foods such as garlic, chilli or olives in oil, these predicted concentrations are approached, and, therefore, the end of shelf life for these products is when the legal limit for ESBO in the food is exceeded. ESBO migration into food containing free oil in contact with the gasket has been reported with a mean of 166 mg kg^{-1} in 86 samples and a maximum of 580 mg kg^{-1} (Fankhauser-Noti et al., 2005).

A third example involves an orange juice packaged aseptically in LDPE–alufoil–paper laminate cartons and glass containers. After 2.5 months storage at 25°C, an experienced taste panel detected a significant ($p \leq 0.05$) difference between the orange juices in cartons and glass containers. Analysis of the *d*-limonene (one of the major components of the essential oils in citrus juices) content showed that it had decreased from 70 to 40 ppm in the cartons within 35 days. The limonene had been absorbed (scalped) by the LDPE surface in contact with the orange juice. As well, ascorbic acid degradation and consequent browning was accelerated due to contact with the LDPE film.

Thus, the shelf life of aseptically packaged citrus juices in cartons is limited (largely as a result of package/product interaction) to about 9 months, the end of shelf life being determined by flavor changes to the juices as a result of "scalping" of the flavor components by the package.

12.3.3 Distribution Environment

12.3.3.1 Climatic

The deterioration in product quality of packaged foods is often closely related to the transfer of mass and heat through the package. Packaged foods may lose or gain moisture; they will also reflect the temperature of their environment, because very few food packages are good insulators. Thus, the climatic conditions (i.e., temperature and humidity) of the distribution environment (warehouses; trucks and rail cars; supermarkets; consumer pantries) have an important influence on the rate of deterioration of packaged foods.

12.3.3.1.1 Mass Transfer

With mass transfer, the exchange of vapors and gases with the surrounding atmosphere is of primary concern. Water vapor and O_2 are generally of most importance, although the exchange of volatile aromas from the product, or to the product from the surroundings, can be important. As well as O_2, transmission of N_2 and CO_2 may have to be taken into account in packages where the concentration of these gases inside the package has been modified from ambient to inhibit or slow down deteriorative reactions in the food.

Generally, the difference in partial pressure of the vapor or gas across the package barrier will control the rate and extent of permeation, although transfer can also occur due to the presence of pinholes in the material, imperfect seals and closures, or cracks that result from flexing of the packaging material during filling and subsequent handling. In contrast to the common gases, the partial pressure of water vapor in the atmosphere varies continuously, although the variation is generally much less in controlled climate stores.

To summarize, mass transfer depends on the partial pressure difference across the package barrier of gases and water vapor, and on the nature of the barrier itself. These factors were discussed in Section 12.3.2.

12.3.3.1.2 Heat Transfer

One of the major determinants of food shelf life is the temperature to which the food is exposed during the time from production to consumption. Without exception, foods are exposed to fluctuating temperature environments during this time, and to accurately estimate shelf life, the nature and extent of these temperature fluctuations need to be known. There is little point in carefully controlling the processing conditions inside the factory and then releasing the product into the distribution and retail system without knowledge of the conditions that it will experience in that system. Such knowledge is essential in the case of products containing a "best before" or "use by" date.

The detailed climatic statistics of global maximum and mean temperatures, which are available in many countries, are of great assistance. Despite meteorological and secular trends, the daily (and even the annual) cycle of temperatures can be normalized to a standard cycle with a standard frequency distribution derived from the mean and range at many places. This is because of the sinusoidal trend of diurnal (Earth's rotation) and seasonal (Earth's revolution) solar radiation intensity.

The storage climates inside buildings such as warehouses and supermarkets are only broadly related to the external climate as reported by weather stations; climatic variations in temperature and humidity can differ as much between different building constructions as between seasons on one site. Unfortunately, there is no publicly available data on daily temperature and humidity variations in warehouses and supermarkets.

If the major deteriorative reaction causing the end of shelf life is known, simple expressions can be derived to predict the extent of deterioration as a function of available time–temperature storage conditions. The basic types of deteriorative reactions that foods undergo were discussed in Chapter 11, together with the rates of these reactions and the factors controlling these rates. These reactions and their rates will now be analyzed in relation to food shelf life.

Fundamental to such an analysis is that the particular food under consideration follows the laws of additivity and commutativity. *Additivity* implies that the total extent of the degradation reaction in the food produced by a succession of exposures at various temperatures is the simple sum of the separate amounts of degradation, regardless of the number or spacing of each time–temperature combination. *Commutativity* means that the total extent of the degradation reaction in the food is independent of the order of presentation of the various time–temperature experiences.

12.3.3.1.2.1 Shelf Life Plots A useful approach to quantifying the effect of temperature on food quality (especially when little data are available to get rate constants, or when only the time to reach a certain level of quality change has been determined) is to construct shelf life plots. As discussed

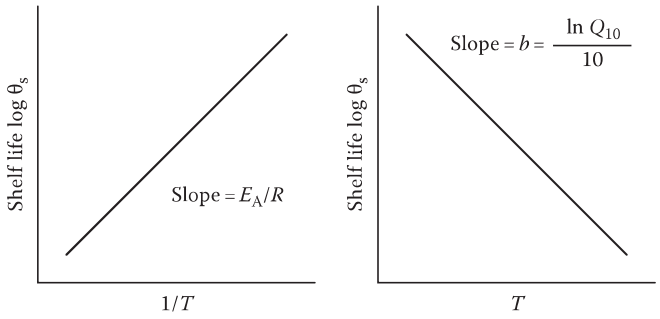

FIGURE 12.5 (a) Arrhenius plot of log shelf life (θ_s) versus reciprocal of the absolute temperature (K) showing a slope of E_A/R, and (b) linear plot of log shelf life versus temperature (°C) showing a slope of $-b$.

in Section 11.5.1, several models are in use to represent the relationship between the rate of a reaction (or the reciprocal of rate, which can be time for a specified loss in quality or shelf life) and temperature. The two most common models are the Arrhenius and linear, and these are shown in Figure 12.5.

The equations for these two plots are

$$\theta_s = \theta_0 \exp \frac{E_A}{R}\left[\frac{1}{T_s} - \frac{1}{T_0}\right] \tag{12.15}$$

and

$$\theta_s = \theta_0 e^{-b(T_s - T_0)} \tag{12.16}$$

where

θ_s is the shelf life at temperature T_s
θ_0 is the shelf life at temperature T_0

If only a small temperature range is used (less than ±20°C), there is little error in using the simpler linear plot rather than the Arrhenius plot.

Most deteriorative reactions in foods can be classified as either zero or first order, and the way in which these two reaction orders can be used to predict the extent of deterioration as a function of temperature is now outlined.

12.3.3.1.2.2 Zero-Order Reaction Prediction Equation 11.10 was derived for the change in a quality factor A when all extrinsic factors are held constant:

$$A_e = A_0 - k_z\theta_s \tag{12.17}$$

and

$$A_0 - A_e = k_z\theta_s \tag{12.18}$$

where

A_e is the value of A at the end of shelf life
A_0 is the value of A initially
k_z is the zero-order rate constant (time^{-1})
θ_s is the shelf life in days, months, years and so on

For variable time–temperature storage conditions, Equation 12.17 can be modified as follows:

$$A_e = A_0 - \Sigma(k_i\theta_i) \tag{12.19}$$

where $\Sigma k_i\theta_i$ is the sum of the product of the rate constant, k_i, at each temperature, T_i, multiplied by the time interval, θ_i, at the average temperature, T_i, for the given time period, $\Delta\theta$.

To apply this method, the time–temperature history is broken up into suitable time periods and the average temperature in that time period determined. The rate constant for that period is then calculated from the shelf life plot using a zero-order reaction. The rate constant is multiplied by the time interval, θ_i, and the sum of the increments of $k_i\theta_i$ gives the total amount lost at any time.

Alternatively, instead of calculating actual rate constants, the time for the product to become unacceptable (i.e., for A to become A_e) can be measured, and Equation 12.19 modified to give

f_c = fraction of shelf life consumed = change in A divided by total possible change in A

$$= \frac{A_0 - A}{A_0 - A_e} \tag{12.20}$$

$$= \frac{\Sigma(k_i\theta_i)}{\Sigma(k_i\theta_s)} \tag{12.21}$$

$$= \Sigma\left[\frac{\theta_i}{\theta_s}\right]T_i \tag{12.22}$$

A similar approach to that described earlier is employed. The temperature history is divided into suitable time periods and the average temperature, T_i, at each time period evaluated. The time held at that temperature, θ_i, is then divided by the shelf life, θ_s, for that particular temperature, and the fractional values summed up to give the fraction of shelf life consumed. Astute readers will recognize the similarity between this method and the graphical method used to determine the lethality of a thermal process. This is not surprising because both are concerned with summing the effects of various temperatures on the rates of reactions (in thermal processes such as canning, it is the rate of microbial destruction that is the focus).

The shelf life can also be expressed in terms of the fraction of shelf life remaining, f_r:

$$f_r = 1 - f_c \tag{12.23}$$

Thus, for any temperature T_s

$$f_r\theta_s = (1 - f_c)\theta_s = \text{shelf life left at temperature } T_s \tag{12.24}$$

In other words, the shelf life left at any temperature is the fraction of shelf life remaining times the shelf life at that temperature.

This method was initially developed by the U.S. Department of Agriculture in California during the1950s for the determination of the shelf life of frozen foods and is referred to as the *time–temperature–tolerance* (TTT) approach (Van Arsdel, 1969). In these and related studies, the period of time (designated as the *high quality life* [HQL]) for 70%–80% of a trained taste panel to correctly identify the control samples (held at −29°C) from samples stored at various subzero temperatures using the triangle or duo-trio test was determined. The change in quality at this stage has been designated the *just noticeable difference* (JND) or *first noticeable difference* (FND). The HQL has no real commercial significance and is quite different from the *practical storage life* (PSL), which is of

interest to food processors and consumers. The ratio between PSL and HQL is often referred to as the *acceptability factor* and can range from 2:1 up to 6:1.

The TTT work on frozen foods demonstrated that the HQL varied exponentially with temperature. However, it has been subsequently shown that when overall quality is measured (rather than just one single quality factor), a semilogarithmic plot results in curved rather than straight lines. It was suggested that a semilogarithmic plot was convenient for products with very long shelf lives, but for other products, a plot utilizing two linear scales was more convenient.

TTT relationships are not strict mathematical functions but empirical data subject to large variability, particularly because of variations in product, processing methods and packaging (the PPP factors). Therefore, any shelf life prediction made will be specific for a particular product (e.g., specific breed of animal slaughtered at a certain age or weight) that is processed, packaged and stored under specific conditions. Failure to specify PPP factors leads to the vast plethora of seemingly contradictory shelf lives for frozen foods reported in the literature. For example, the frozen shelf life of cod stored at −18°C has been reported by various authors to be anywhere from 15 to 45 weeks, and it has been calculated that, on the basis of data in the literature, the 95% confidence interval for the HQL of frozen lean meat ranges from 8 months to 3 years. Thus, predictions cannot be made with any precision on the quality or quality change in a frozen food from knowledge of its time–temperature history and TTT literature data only. Therefore, in determining the shelf life of frozen foods, the PPP factors must be taken into account in addition to the TTT relationships.

Example 12.4

A frozen food (ground beef packaged in LDPE film) has a PSL at various temperatures as follows:

Temperature (°C)	PSL (Days)
−8	120
−12	180
−15	230
−18	300
−20	350
−23	420
−25	480

Calculate the total loss of PSL along the freezer chain from processor to consumer given the time and temperature history shown in the following.

Links in the Freezer Chain	Average Temperature (°C)	Storage Time (Days)	PSL (Days)	PSL Loss (% per Day)	Loss (%)
Processor	−23	40	420	0.238	9.5
Transport	−20	2	350	0.286	0.6
Cold store	−25	190	480	0.208	39.9
Transport	−18	1	300	0.333	0.3
Wholesale	−23	30	420	0.238	7.2
Transport	−15	1	230	0.435	0.2
Display cabinet					
Center	−20	20	350	0.286	5.8
Upper layer	−12	6	180	0.556	3.4
Transport	−8	1/6	120	0.833	0.1
Consumer	−18	50	300	0.333	16.5
Total loss of PSL			340		83.6%

By dividing the PSL into 100, the product life loss per day as a percentage at that temperature is determined (e.g., at −23°C, 100/420 = 0.238% loss per day). When the storage time in column 3 is multiplied by product life loss per day in column 5, the product life loss expressed as a percentage of the PSL can be calculated.

The total loss of PSL for the ground beef at the end of the freezer chain (340 days) is 84%. Thus, 16% of its PSL is left; that is, the product could be kept by the consumer at −18°C for another 16 × 300/100 = 49 days before it exceeds its PSL.

More recently, the TTT approach has also been applied to nonfrozen foods, for example, to determine the PSL of sweet whey powder as a result of temperature abuse (Dattatreya et al., 2007).

12.3.3.1.2.3 First-Order Reaction Prediction The equivalent expression to Equation 12.16 for a first-order reaction was derived as Equation 11.15 for the case where all extrinsic factors are held constant:

$$A_e = A_0 \exp(-k\theta_s) \tag{12.25}$$

From this, an expression can be developed to predict the amount of shelf life used up as a function of variable temperature storage for a first-order reaction in the following form:

$$A = A_0 \exp\left(-\Sigma k_i \theta_i\right) \tag{12.26}$$

where

A is the amount of some quality factor remaining at the end of the time–temperature distribution

$\Sigma k_i\theta_i$ has the same meaning as in Equation 12.18

If the shelf life is based simply on some time to reach unacceptability as defined by a COP, then Equation 12.25 can be modified to give an analogous expression to that derived for the TTT method. Note that because of the exponential loss of quality, A_e will never be zero. Thus,

$$\ln \frac{A}{A_0} = -\sum k_i \theta_i \tag{12.27}$$

and

$$k_i = \frac{\ln A_e / A_0}{\theta_s} \tag{12.28}$$

where

$\ln A/A_0$ is the fraction of shelf life consumed at time θ

$\ln A_e/A_0$ is the fraction of shelf life consumed at time θ_s

The fraction of shelf life remaining, f_r is

$$f_r = 1 - \frac{\ln A_0/A}{\ln A_0/A_e} = 1 - \sum \left[\frac{\theta_i}{\theta_s}\right]_{T_i} \tag{12.29}$$

12.3.3.1.3 Simultaneous Mass and Heat Transfer

In the majority of distribution environments, many packaged foods undergo changes in both moisture content and temperature during storage as a result of variable temperature and humidity conditions in the environment. This has the effect of complicating the calculations for prediction of the

shelf life of packaged foods. An additional challenge is that data on the humidity distribution of environments where foods are stored are scarce and not as easily predicted as the external temperature distribution. Therefore, prediction of the actual shelf life loss of packaged foods will only be approximate. More complete data about the humidity distribution of food storage environments are required so that shelf life predictions can be further refined.

12.3.3.2 Physical

After processing and manufacture, the food leaves the factory and usually moves into the company's warehouse. It is then transported by rail or truck to a distribution center. From here, the food may be taken to the retail outlet by truck or rail or maybe to a port to be transported by sea or air to another distribution warehouse. Further transport by rail or truck then follows to the retail outlet.

Regardless of the distribution pattern, transportation damage may be incurred by the food. The extent of such damage will be a function of not only the packaging (primary, secondary and tertiary), but also the nature of the distribution environment and the method of transportation.

Most secondary packages are stacked on pallets that may or may not be shrink or stretch wrapped. Pallets are usually stacked two high in rail cars and one or two high in trucks; in warehouses, pallets may be stacked four high. Thus, the forces acting on the top tier of a four pallet stack will be quite different from those acting on the bottom tier of the same stack. The longer the time that the product spends in the distribution chain (this is usually directly related to the shelf life of the product), the more significant are the effects arising from pallet stacking height.

Ultimately, knowledge of the distribution environment (both climatic and physical) is essential before meaningful shelf life tests can be designed. Taking a product from the production line and conducting a shelf life test on it while ignoring possible distribution environment hazards will almost certainly lead to an overestimation of shelf life.

12.4 PREDICTING MICROBIAL SHELF LIFE

Microbial spoilage of foods is an economically significant problem for food manufacturers, retailers and consumers. Depending on the food, process and storage conditions, the microbiological shelf life can be determined by the growth of either spoilage or pathogenic microorganisms. In the case of spoilage microorganisms, the traditional method for determining microbiological shelf life involved storing the food at different temperatures and determining spoilage by sensory evaluation or microbial count. Where the microbiological shelf life is determined by the growth of pathogenic microorganisms, the traditional approach has been challenge testing of the food with the organism of concern, followed by storage at different temperatures and microbial analysis at intervals. For processes such as heat treatments, where the elimination of particular microorganisms is required (e.g., canning), the use of inoculated packs is common.

The primary step in the microbial shelf life determination of food is to identify the specific spoilage organisms (SSOs), defined as the fraction of the total microflora that are responsible for spoilage under the particular range of environmental conditions.

The end of shelf life is when a certain level of deterioration is reached because of the SSOs, the microbial metabolic product(s) or both (Jay et al., 2007). After determining the SSOs and the range of environmental conditions over which a particular SSO is responsible for spoilage, the next step is to decide the population level of the SSO at which unacceptable spoilage occurs and, thus, shelf life ends.

The limit of microbial growth determining shelf life differs with food type, packaging and storage conditions (Lee, 2010). SSO counts of 10^6–10^8 organisms g^{-1} or cm^{-2} are commonly used as a convenient upper limit of quality. When dealing with pathogenic bacteria such as *Bacillus cereus* and *Staphylococcus aureus*, a limit of 10^5 organisms g^{-1} has been used for risk management of the food supply system for prepared foods. The time to reach the limit based on pathogen growth should be clearly understood as the minimum requirement for shelf life control. There should always be a safety margin that results in a shorter actual shelf life, this time greatly depending on the initial

contamination level. Hygienic control of food preparation and processing is required so that the end of shelf life is determined by the growth of spoilage organisms rather than of pathogens.

The four key parameters log N_o, θ_{lag}, μ_{max} and log N_c that describe the progress of microbial growth with time under certain defined conditions were presented in Section 11.3.3.1. The parameter log N_o is determined by the initial contamination level of the food, which is dictated by raw materials and food manufacturing conditions, whereas log N_c represents the critical or maximum cell density attainable under given conditions. Lag time (θ_{lag}) and maximum specific growth rate (μ_{max}), depending on environmental conditions, directly affect the time to reach a certain critical level of microbial density corresponding to acceptable quality. Therefore, in dealing with the effect of packaging conditions on microbial shelf life, these two parameters are most often employed (Lee, 2010). The time (θ_s) to reach a critical limit cell density of N_c is the shelf life and can be calculated using

$$\theta_s = \theta_{lag} + \frac{1}{\mu_{max}} \ln \frac{N_c}{N_o} \tag{12.30}$$

Example 12.5

The use of MAP to extend the shelf life of chilled, perishable foods is well established commercially. Recently, very high O_2 concentrations have been applied (mainly for fresh produce packaging) to inhibit microbial growth without the creation of anoxic conditions. Lee (2010) used Equation 12.30 to calculate the time for *Pseudomonas fluorescens* to increase $10^{3.5}$-fold based on the microbial growth parameters reported by Geysen et al. (2006). The dependence of microbial shelf life on superatmospheric O_2 and moderate CO_2 concentrations for fresh-cut lettuce is presented in Figure 12.6. The maximum extended shelf life at 100% O_2 and 20% CO_2 (hypothetical concentrations corresponding to respective partial pressures of 1.0 and 0.2 atm for O_2 and CO_2) was about six times that in a normal atmosphere (20% O_2 and 0% CO_2). Use of higher levels of CO_2 for fresh fruits and vegetables is limited because of the physiological tolerance limit of the commodity (mostly below 20%). Given the microbial inhibitory effect of superatmospheric O_2, its use eliminates the risk of O_2 depletion inside the fresh produce package because of respiration activity, particularly under temperature abuse conditions.

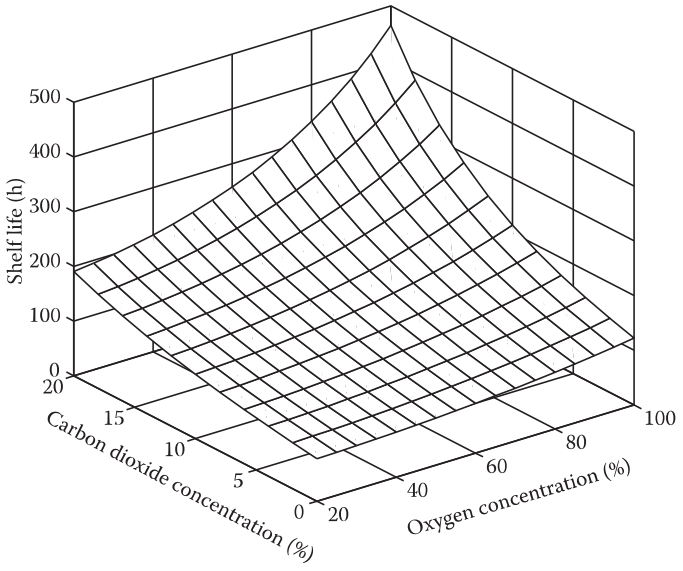

FIGURE 12.6 Estimated shelf life under MA conditions of superatmospheric O_2 and moderate CO_2 concentrations when packaging fresh-cut lettuce at 7°C based on growth of *Pseudomonas fluorescens*. (From Lee, D.S., Packaging and the microbial shelf life of food, in: *Food Packaging and Shelf Life*, Robertson, G.L. (Ed.), CRC Press, Boca Raton, FL, pp. 55–79, 2010.)

Chotyakul et al. (in press) used Monte Carlo procedures to evaluate the uncertainty of food safety and quality estimations caused by the variability in model parameters. Their shelf life predictions were based on the growth of *Lactobacillus sakei* in meat using an equation similar to Equation 12.30 with three variables: temperature, a_w and gas atmosphere. The predicted shelf life when parameter variability was not considered was 7.0 h for a temperature-only model (Case 1, $T = 4°C$), 184.6 h for a temperature and a_w model (Case 2, $T = 4°C$, $a_w = 0.98$), 6.4 h for a temperature and CO_2 model (Case 3, $T = 4°C$, $CO_2 = 2650$ ppm) and 241.6 h for a temperature, a_w and CO_2 model (Case 4.1, $T = 4°C$, $a_w = 0.98$, $CO_2 = 2650$ ppm). The shelf life values estimated considering parameter variability were 7.4 ± 3.5, 190.4 ± 34.8, 7.5 ± 2.0 and 266.1 ± 65.8 h, respectively.

Examining the frequency distribution of the predicted shelf life, as well as imposing a 95% confidence that meat would not spoil before its expiration date, lead to a recommended shelf life of 4, 141, 6 and 176 h for Cases 1–4.1, respectively. If the standard deviation (SD) of all model parameters in Case 4.1 could be lowered by 10%, 50% and 90%, the recommended shelf life time would increase from 176 to 189, 198 and 202 h, respectively. The analysis of the impact of lowering the individual SD of the model parameters showed an even lower impact. This suggested that lowering the uncertainty of microbial shelf life predictions is very difficult when multiple factors are considered in the microbial model used for this estimation.

Predictive microbiology combines mathematical modeling with experimental data on combinations of factors that influence the growth of food spoilage and/or food-borne pathogenic microorganisms. Predictive microbiology is based on the premise that the responses of microorganisms to environmental factors are reproducible, and that it is possible, taking into account past observations, to predict the responses of microorganisms in particular environments. The huge amount of data generated over the past 30 years to predict the behavior of microorganisms under different environmental conditions have allowed for the development of mathematical models, which have enabled prediction of the behavior of microorganisms under certain conditions.

The development and commercialization of predictive models have now become relatively widespread. The use of such models can reduce the need for shelf life trials, challenge tests, product reformulations and process modifications, thus saving both time and money. Although there are both mechanistic and empirical predictive models, the latter predominate. Empirical predictive models can be subdivided into probabilistic and kinetic models. The ultimate test for predictive models is whether they can be used to predict reliable outcomes in real situations.

To model food safety aspects, the predictive microbiology capability provided by the ComBase Modeling Toolbox is very useful. With this toolbox, it is possible to judge more easily the effect of production and storage regimes and changing product formulations on the possible growth of pathogens or spoilage organisms. The ComBase Modeling Toolbox consists of a set of free online applications for predicting the growth or inactivation of microorganisms (see www.combase.cc). The ComBase Initiative is a collaboration between the Food Standards Agency and the Institute of Food Research from the United Kingdom, the USDA Agricultural Research Service and its Eastern Regional Research Center and the Australian Food Safety Centre of Excellence. Its purpose is to make data and predictive tools on microbial responses to food environments freely available via web-based software.

The ComBase Database (accessible via the ComBase Browser) consists of thousands of microbial growth and survival curves that have been collated in research establishments and from publications. They form the basis for numerous microbial models presented in ComBase Predictor that can be used in assessing the microbial risk in foods and ultimately shelf life. The user identifies relevant criteria including a type or species of organism, a type or class of food, pH, temperature, a_w (or NaCl concentration) and specific food conditions. The latest version of ComBase Predictor can simultaneously produce predictions for up to four microorganisms, thereby facilitating comparisons among several scenarios (Amézqita et al., 2011).

Other software packages include the Pathogen Modeling Program (see www.ars.usda.gov/Services/docs.htm?docid=6796), which is a stand-alone software package of 38 microbial models for 11 bacterial pathogens that can be used to predict the growth and inactivation of food-borne pathogens under

various environmental conditions. The Seafood Spoilage & Safety Predictor® software (see http://sssp.dtuaqua.dk/) predicts the shelf life and growth of bacteria in different fresh and lightly preserved seafood. Some of the predictive models in SSSP are equally useful for other types of food.

Despite their increasing sophistication and widespread availability, models should not be relied on completely. Rather, models are best employed as tools to assist decision making. Models do not completely negate the need for microbial testing, and do not replace the judgment of trained and experienced food microbiologists.

12.5 ACCELERATED SHELF LIFE TESTING

12.5.1 Basic Principles

The basic assumption underlying accelerated shelf life testing (ASLT) is that the principles of chemical kinetics can be applied to quantify the effects which extrinsic factors such as temperature, humidity, gas atmosphere and light have on the rate of deteriorative reactions (Corradini and Peleg, 2006). These basic principles and the way in which they can be applied to foods have been described in Chapter 11. By subjecting the food to controlled environments in which one or more of the extrinsic factors is maintained at a higher than normal level, the rates of deterioration will be accelerated, resulting in a shorter than normal time to product failure (Saguy and Peleg, 2009). Because the effects of extrinsic factors on deterioration can be quantified, the magnitude of the acceleration can be calculated and the "true" shelf life of the product under normal conditions calculated (Mizrahi, 2011). Thus, a shelf life test that would normally take a year can be completed in about a 1–2 months if the storage temperature is raised from 20°C to 40°C.

The need for ASLT of food products is simple—because many foods have shelf lives of at least 1 year, evaluating the effect on shelf life of a change in product formulation (e.g., a new antioxidant or thickener), the process (e.g., a different time/temperature sterilization regime) or the packaging (e.g., a new polymeric film) would require shelf life trials lasting at least as long as the required shelf life of the product. Companies cannot afford to wait for such long periods before knowing whether or not the new product/process/packaging will provide an adequate shelf life, because other decisions (e.g., to construct a new factory, order new equipment or arrange contracts for the supply of new packaging material) have lead times of months or years. Some way of speeding up the time required to determine the shelf life of a product is necessary, and ASLT has been developed for that reason. Such procedures have long been used in the pharmaceutical industry where shelf life and efficacy of drugs are closely related. However, the use of ASLT in the food industry is not as widespread as it might be, due in part to the lack of basic data on the effect of extrinsic factors on the rates of deteriorative reactions, in part to ignorance of the methodology required, and in part to skepticism of the advantages to be gained from using ASLT procedures.

As discussed in Chapter 11, quality loss for most foods follows either a zero- or first-order reaction. Figure 12.5 showed the logarithm of shelf life versus temperature and the inverse of absolute temperature. If only a small range of temperature is considered, then the former shelf life plot generally fits the data for food products.

For a given extent of deterioration and reaction order, the rate constant is inversely proportional to the time to reach some degree of quality loss. Thus, by taking the ratio of the shelf life between any two temperatures 10°C apart, the Q_{10} of the reaction can be found. This can be expressed by the extension of Equation 11.36, assuming a linear shelf life plot:

$$Q_{10} = \frac{k_{T+10}}{k_T} = \frac{\theta_{s_T}}{\theta_{s_{T+10}}} \tag{12.31}$$

where

θ_{s_T} is the shelf life at temperature T°C

$\theta_{s_{T+10}}$ is the shelf life at temperature $(T+10)$°C

TABLE 12.3
Effect of Q_{10} on Shelf Life

	Shelf Life (Weeks)			
Temperature (°C)	**Q_{10} = 2**	**Q_{10} = 2.5**	**Q_{10} = 3**	**Q_{10} = 5**
50	2[a]	2[a]	2[a]	2[a]
40	4	5	6	10
30	8	12.5	18	50
20	16	31.3	54	4.8 years

Source: Labuza, T.P. and Kamman, J.F., Reaction kinetics and accelerated tests simulation as a function of temperature, in: *Computer-Aided Techniques in Food Technology*, Saguy, I. (Ed.), Marcel Dekker, New York, pp. 71–115, 1983.

[a] Arbitrarily set at 2 weeks at 50°C. Shelf lives at lower temperatures are calculated on this arbitrary assumption.

The effect of Q_{10} on shelf life is shown in Table 12.3, which illustrates the importance of accurate estimates of Q_{10} when making shelf life estimations. For example, if a product has a shelf life of 2 weeks at 50°C and a Q_{10} of 2, then it will have a shelf life of 16 weeks at 20°C. However, if Q_{10} were 2.5 rather than 2, the shelf life at 20°C would be almost twice as long (31 weeks). Thus, a small error in Q_{10} can lead to huge differences in the estimated shelf life of the product. Typical Q_{10} values for foods are 1.1–4 for canned products, 1.5–10 for dehydrated products and 3–40 for frozen products.

A further use for Q_{10} values is illustrated in Figure 12.7, which depicts a shelf life plot for a product that has at least 18 months shelf life at 23°C. To determine the probable shelf life of the product at 40°C, lines are drawn from the point corresponding to 18 months at 23°C to intersect

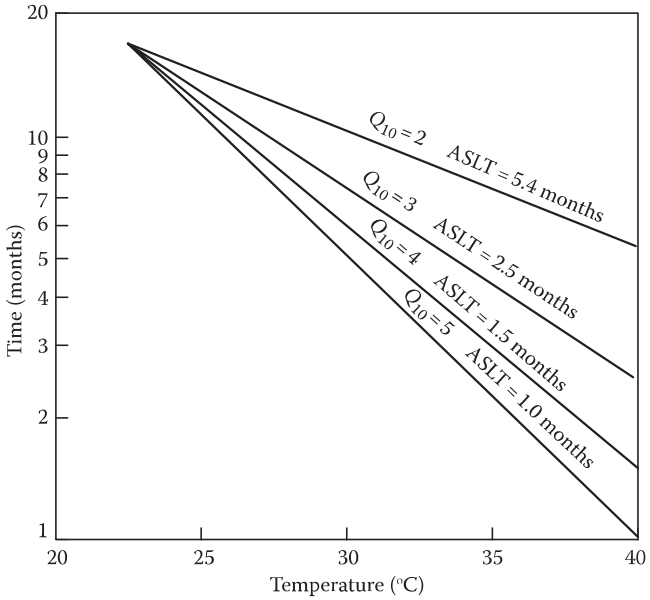

FIGURE 12.7 Hypothetical shelf life plot for various Q_{10}'s passing through a shelf life of 18 months at 23°C. Accelerated shelf life times (ASLT) are those required at 40°C for various Q_{10}'s. (From Labuza, T.P. and Kamman, J.F., Reaction kinetics and accelerated tests simulation as a function of temperature, in: *Computer-Aided Techniques in Food Technology*, Saguy, I. (Ed.), Marcel Dekker, New York, pp. 71–115, 1983.)

TABLE 12.4
Effect of E_A of the Key Deteriorative Reaction on the Time to Complete an ASLT for a Low Moisture Food Product with a Targeted Shelf Life of 2 Years at Ambient Storage

E_A (kJ mol^{-1})	Testing Time at 40°C	Testing Time at 45°C
45	224 days	171 days
85	78 days	47 days
125	28 days	13 days

Source: Taoukis, P.S. and Giannakourou, M.C., Temperature and food stability: Analysis and control, in: *Understanding and Measuring the Shelf-Life of Food*, Steele, R. (Ed.), CRC Press, Boca Raton, FL, pp. 42–68, 2004.

a vertical line drawn at 40°C; the slope of each of the straight lines so drawn is dictated by the Q_{10} value. Thus, if the Q_{10} of the product were 5, then its shelf life at 40°C would be 1 month, increasing to 5.4 months if the Q_{10} was 2. Such a plot is helpful in deciding how long an ASLT is likely to run.

Instead of Q_{10} values, the E_A can be used to determine the duration of an ASLT. An example of the effect of E_A on the time to complete an ASLT is given in Table 12.4.

12.5.2 ASLT Procedures

The following procedure should be adopted in designing a shelf life test for a food product (Taoukis et al., 1997):

1. Determine the microbiological safety and quality parameters for the product.
2. Select the key critical descriptor(s) or IoFs that will cause quality loss and, thus, consumer unacceptability in the food, and decide what tests (sensory and/or instrumental) should be performed on the product during the trial.
3. Select the package to be used. Often, a range of packaging materials will be tested so that the most cost-effective material can be selected.
4. Select the extrinsic factors that are to be accelerated. Typical storage temperatures used for

Product	Test Temperatures (°C)	Control (°C)
Frozen	−7, −11, −15	<−40
Chilled	5, 10, 15, 20	0
Dry and IMF	25, 30, 35, 40, 45	−18
Canned	25, 30, 35, 40	4

   ASLT procedures are shown in the following, and it is usually necessary to select at least two.
5. Using a plot similar to that shown in Figure 12.7, determine how long the product must be held at each test temperature. If no Q_{10} values are known, then an open-ended ASLT will have to be conducted using a minimum of three test temperatures.
6. Determine the frequency of the tests. A good rule of thumb is that the time interval between tests at any temperature below the highest temperature should be no longer than

$$f_2 = f_1 Q_{10}^{\Delta T/10} \tag{12.32}$$

where
f_1 is the time between tests (e.g., days, weeks) at the highest test temperature T_1
f_2 is the time between tests at any lower temperature T_2
ΔT is the difference in degrees Celsius between T_1 and T_2

Thus, if a product is held at 40°C and tested once a month, then at 30°C with a Q_{10} of 3, the product should be tested at least every

$$f_2 = 1 \times 3^{(10/10)} = 3 \text{ months}$$

More frequent testing is desirable, especially if the Q_{10} is not accurately known, because at least six data points are needed to minimize statistical errors, otherwise the confidence in θ_s is significantly diminished.

7. Calculate the number of samples that must be stored at each test condition, including those samples that will be held as controls.
8. Begin the ASLTs, plotting the data as they come to hand so that, if necessary, the frequency of sampling can be increased or decreased as appropriate.
9. From each test storage condition, estimate k or θ_s and construct appropriate shelf life plots from which to estimate the potential shelf life of the product under normal storage conditions. Provided that the shelf life plots indicate that the product shelf life is at least as long as that desired by the company, then the product has a chance of performing satisfactorily in the marketplace.

12.5.3 Examples of ASLT Procedures

12.5.3.1 Dehydrated Products

In dehydrated vegetables, lipid and hydrolytic oxidation, together with nonenzymic browning and (in the case of green vegetables) chlorophyll degradation, are the major modes of deterioration. In dehydrated fruit, the major mode of deterioration is nonenzymic browning. Samaniego et al. (1991) used temperatures of 30°C and 40°C to accelerate deterioration in sliced green beans and onion flakes and found that, for example, at 40°C, the shelf life of onions was 11 times shorter, and at 30°C, 3.5 times shorter than at 20°C when the a_w was 0.56.

12.5.3.2 Frozen Foods

Plots of HQL or PSL versus time were discussed in Section 12.3.3.1.2.2; such curves suggest that accelerated tests could be used for predicting the shelf life of frozen foods with a considerable degree of accuracy. The shape of TTT curves for a wide range of products has been determined, and for any specific set of conditions (e.g., a particular product, process or package), a more detailed TTT curve could be determined. Then, accelerated tests could be carried out at temperatures as warm as −10 or even −8°C. As a result, the shelf life of a frozen food that would normally be stored at −18°C could be predicted in a few weeks or months at these higher temperatures.

Although mold growth has been recorded down to −17°C, no evidence of microbiological growth on meat products has been found at or below −8°C, and therefore −8°C is generally recommended as the warmest temperature for ASLT of meat. Due cognizance must be taken of those frozen products such as frozen bacon, which exhibit so-called reverse stability where the keeping quality is poorer at −25°C than at −5°C.

In ASLT of frozen foods, the formation of ice has to be considered. As ice forms, the concentration of the unfrozen aqueous phase increases and influences reaction rates because they depend on both temperature and concentration. Below about –7°C, the relative change in concentration of the unfrozen aqueous phase is small, but storage at temperatures above –7°C should be avoided. In the temperature range between 0°C and –7°C, the overall observed rate of reaction may increase, stay relatively constant or decrease depending on the specific system. Consequently, there is no generally applicable method to estimate low temperature shelf life from measurements made above –7°C (Reid, 2003).

12.5.3.3 Canned Foods

It is generally assumed that if good manufacturing practices are followed, microbial deterioration of canned foods will not be a problem. If there is thermophilic spoilage when canned foods are stored at elevated temperatures, then this is more than likely due to inadequate cooling of the cans following thermal processing. Microbial spoilage at ambient temperatures is generally the result of "leaker" spoilage, so-called because the microorganisms are drawn into the can during cooling; chlorination of cooling water according to good manufacturing practice will avoid this problem. Thus, deteriorative reactions in canned foods will normally be limited to organoleptic changes such as loss of color, development of undesirable flavors and nutrient degradation.

Labuza (1982) quotes a producer of canned meat products as stating that the major mode of deterioration is H_2 production resulting from internal corrosion of the can. Samples were stored at 37.8°C to accelerate this deterioration; the shelf life at 37.8°C was 40% of the shelf life at 4.4°C, corresponding to a Q_{10} of 1.3.

12.5.3.4 Oxygen-Sensitive Products

In all the classical ASLT methods, temperature is the dominant acceleration factor used, and its effect on the rate of lipid oxidation is best analyzed in terms of the overall activation energy E_A for lipid oxidation. An inherent assumption in these tests is that E_A is the same in both the presence and absence of antioxidants, although indications are that it is in fact considerably lower in the latter case.

Although high O_2 pressures can be used to accelerate reactions involving oxidation, it is not used very often since oxidation reactions typically become independent of the O_2 concentration above a certain level which varies with temperature and other conditions. However, Cardelli and Labuza (2001) reported that increasing O_2 concentrations from 0.5 to 21.3 kPa accelerated the deterioration of roast and ground coffee 20-fold. If both temperature and O_2 concentration are accelerated, then the decreased solubility of O_2 at higher temperatures must be factored into any calculations of shelf life.

12.5.3.5 Oxygen-Absorbing Package

Gomes et al. (2009) investigated the ability of a laminate plastic–alufoil pouch containing a novel iron-based O_2 absorber (Figure 12.8) to maintain and/or extend the shelf life of a hot-filled cheese-spread MRE (meal-ready-to-eat) item. ASLT of filled pouches with and without the O_2 absorber were conducted for 3 months at 51.7°C and 6 months at 37.8°C, with pouches stored for 12 months

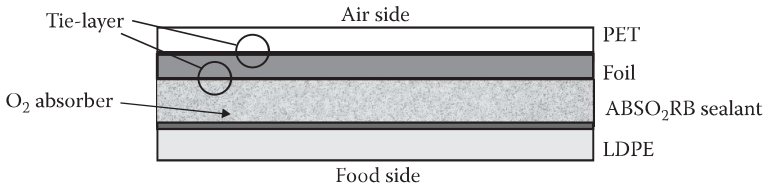

FIGURE 12.8 Schematic of the laminate structure of the oxygen-absorbing packaging material. (From Gomes, C. et al., *J. Food Sci.*, 74, E167, 2009.)

at 26.7°C serving as controls; RH was kept constant at 65%–75%. Sampling intervals consisted of 1, 2, 3, 4 and 6 weeks at 51.7°C; 1, 3 and 6 months at 37.8°C and 1, 6 and 12 months at 26.7°C.

Results showed that the proposed O_2-absorbing laminate was efficient in reducing headspace O_2 concentration from 20.4% to 6.82% within 24 h and to <0.5% in 11 days, with a significant reduction in rancidity of the cheese spread. In addition, the laminate helped delay loss of ascorbic acid. Samples also met the U.S. military shelf life requirement of 6 months at 37.8°C. They concluded that pouches containing an O_2 scavenger in the laminate can help retain nutrition and extend shelf life of high-fat, liquid-like products.

12.5.3.6 Long-Duration Spaceflight

The Advanced Food Technology (AFT) Project of the National Aeronautics and Space Administration (NASA) Human Research Program (HRP) is currently working to design a stable, palatable and nutritious food supply to support long-duration spaceflight. A large part of this food supply is expected to be positioned, unrefrigerated, at relevant destination sites prior to crew arrival. Therefore, AFT anticipates that the food products used on these missions must maintain acceptable quality for a minimum of 3–5 years at ambient conditions.

To determine the suitability of retort processed foods to support long-duration spaceflight, a series of 36 month ASLTs were performed on 13 representative retort pouch products (Catauro and Perchonok, 2012). Combined sensory evaluations, assessment of physical properties and nutritional analyses were employed to determine shelf life endpoints for these foods, which were either observed during the analysis or extrapolated via mathematical projections based on Q_{10} values. Data obtained through analysis of these 13 products were later used to estimate the shelf life values of all retort-processed spaceflight foods.

In general, the major determinants of end of shelf life appeared to be the development of off-flavor and off-color. These changes were assumed to be the result of Maillard and oxidation reactions, which can be initiated or accelerated as a result of the retort process and product formulation. Meat products and other vegetable entrées were projected to maintain their quality the longest (between 2 and 8 years) without refrigeration, followed by fruit and dessert products (1.5–5 years); dairy products (2.5–3.25 years) and starches, vegetable and soup products (1–4 years). Aside from considerable losses in vitamins B and C, nutritional value of most products was maintained throughout their shelf life. Fortification of storage-labile vitamins was proposed as a countermeasure to ensure long-term nutritive value of these products. The use of nonthermal sterilization technologies was also recommended, as a means to improve initial quality of these products and extend their shelf life for use in long-duration missions. Data obtained also emphasized the importance of low temperature storage in maintaining product quality.

12.5.4 Problems in the Use of ASLT Conditions

The potential problems and theoretical errors that can arise in the use of ASLT conditions have been described (Labuza and Schmidl, 1985, 1988) as follows:

1. Errors in analytical or sensory evaluation. Generally, any analytical measure should be done with a variability of less than ±10% to minimize prediction errors.
2. As temperature rises, phase changes may occur (e.g., solid fat becomes liquid), which can accelerate certain reactions, with the result that at the lower temperature the actual shelf life will be longer than estimated.
3. Carbohydrates in the amorphous state may crystallize out at higher temperatures, with the result that the estimated shelf life is shorter than the actual shelf life at ambient conditions.
4. Freezing "control" samples can result in reactants being concentrated in the unfrozen liquid, creating a higher rate at the reduced temperature and, thus, confounding estimates.

5. If two reactions with different Q_{10} values cause quality loss in a food, the reaction with the higher Q_{10} may predominate at higher temperatures while at normal storage temperatures the reaction with the lower Q_{10} may predominate, thus confounding the estimation.
6. The a_w of dry foods can increase with temperature, causing an increase in reaction rate for products of low a_w in sealed packages. This results in overprediction of "true" shelf life at the lower temperature.
7. The solubility of gases (especially O_2 in fat or water) decreases by almost 25% for each 10°C rise in temperature. Thus, an oxidative reaction such as loss of vitamin C or linoleic acid can decrease in rate if O_2 availability is the limiting factor. Therefore, at the higher temperature, the rate will be less than theoretical, which in turn will result in an underprediction of "true" shelf life at the normal storage temperature.
8. If the product is not placed in a totally impermeable pouch, then storage in high temperature/low humidity cabinets will generally enhance moisture loss, and this should decrease the rate of quality loss compared to no moisture change. This will result in a shorter estimated shelf life at the lower temperature.
9. If high enough temperatures are used, proteins may become denatured, resulting in both increases or decreases in the reaction of certain amino acid side chains, leading to either under- or overprediction of "true" shelf life.

Therefore, in light of the preceding points, the use of ASLT to estimate actual shelf life can be severely limited except in the case of very simple chemical reactions. Consequently, food technologists should always confirm the ASLT results for a particular food by conducting shelf life tests under actual environmental conditions. Once a relationship between ASLT and actual shelf life has been established for a particular food, then ASLT can be used for that food when process or package variables are to be evaluated.

Another point worth stressing is that ASLT where temperature is the accelerating factor, is really only applicable for foods marketed in temperate climates. In tropical climates, the ambient temperature is typically 30°C–40°C and even higher in warehouses, trucks, and so on. These temperatures correspond to those suggested for ASLTs in Section 12.5.2 and higher temperatures than these cannot be used for ASLT because this would lead to reactions that were not representative of how the foods would deteriorate under actual tropical conditions.

12.6 DETERMINING SHELF LIFE FROM THE CONSUMER SIDE

Acceptance or rejection of foods by consumers is based on sensory evaluation involving a complex interaction of flavor, color, texture and so on. Because quality changes in foods are very complex, it is not always possible to make accurate predictions of shelf life based on a mechanistic insight (van Boekel, 2009). In such situations, it is necessary to resort to a statistical description so that the mean time to failure and its standard deviation can be accurately estimated, and the probability of future failures predicted.

Shelf life in relation to consumer acceptance or rejection is commonly defined as the time for 50% of consumers to find the food unacceptable. Other percentages such as 25% or 75% can be used, the choice being a business decision. Although a 50% rejection rate may sound risky, it should be remembered that the consumers taste the product at the end of its shelf life. Distribution times usually guarantee that the proportion of consumers who taste the product close to the end of its shelf life is small, and of this small proportion, 50% will reject it and 50% will accept it (Hough, 2010).

Shelf life models based on consumer responses are of a probabilistic nature and lead to the prediction of the probability that a certain percentage of consumers will not accept the food anymore. The failure times collected and analyzed in shelf life studies are referred to as "time to event data," "failure time data," "survival data" or more generally "life data." The statistical techniques used to

handle this type of data are referred to as "survival analysis methods" in medicine and "reliability methods" in engineering.

Shelf life data possess properties that make them different from other data collected in research and development. Among the two most important features are the non-normality of these data and the common occurrence of censored observations. The phenomenon technically referred to as "censoring" is the impossibility of systematically observing the failure times for all samples. Three censoring situations are found: left, right and interval censoring (Guillet and Rodrigue, 2010). Censored observations are incomplete or partial data, but they do contain relevant information to determine shelf life and must not be discarded from the statistical analysis of the data. However, they must not be treated as if the exact failure time were observed. Specific statistical methods exist to account for censoring. If censoring is ignored in the data analysis, a biased estimate of shelf life will be obtained (Gacula et al., 2009).

A fundamental concept in shelf life studies is that samples do not all fail at the exact same time. Therefore, to compute an estimate of shelf life, the statistical distribution of the failure times needs to be determined. Stated another way, a curve that depicts the probability of the product survival as a function of time needs to be generated. Such a curve is called a *survival curve*. In simple shelf life experiments, estimating the survival curve corresponds to the ultimate goal of the statistical analysis of the data. Once estimated, survival curves can be used for prediction, for example, to determine the percentage of samples that have failed after a given length of time, or for inverse prediction, for example, to determine the time when a given proportion of the samples have failed (Guillet and Rodrigue, 2010).

The hazard rate at a given time is defined as the risk of failure at that time knowing that the product has survived until that time. The hazard function defines the relationship between time and the hazard rate at that time. In reliability testing, the hazard function is referred to as the failure rate. A statistical relationship exists between the hazard function and the survival curve, so that knowing one gives perfect knowledge of the other.

A classical representation of the risk of failure over time is commonly represented by a "bathtub" curve, which has many applications in the actuarial and engineering sciences; an example for a refrigerated food is shown in Figure 12.9. At time x_0, the finished product leaves the processing plant and begins its journey to the many distribution outlets. During the time between x_0 and x_1, early failures may occur due to faulty packaging (e.g., pinholes or poor seals) and product abuse. However, the early failures should not be taken as true failures relative to the

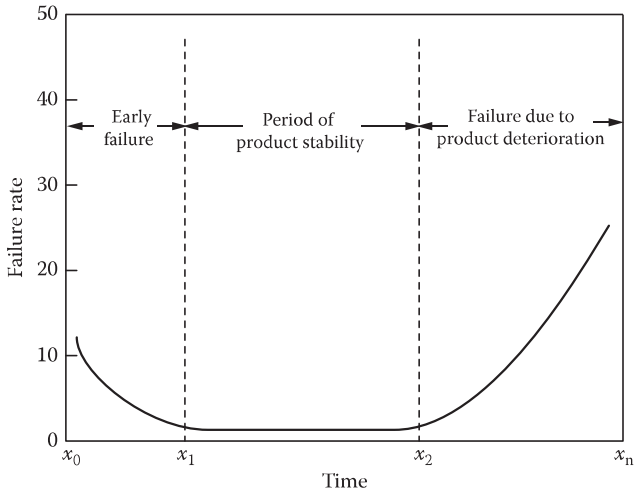

FIGURE 12.9 Bathtub curve showing failure rate as a function of time.

shelf life of the product. From x_1 to x_2, no product failures (barring random fluctuations) would be expected. From the time x_2 to the termination time x_n, the hazard (failure) rate increases, and this time represents the true failure due to deteriorative changes within the product. The length of shelf life is determined between the times x_2 and x_n, and the hazard function plays a central role in the analysis of failure data. It is important to note that the bathtub curve does *not* depict the failure rate of a single item, but describes the relative failure rate of an entire population of products over time.

Given a series of failure times observed for different samples, the goal of the data analysis is to estimate a mathematical function generalizing the distribution of the series to a specific population of products (Guillet and Rodrigue, 2010). This distribution replaces the usual normal distribution, and the way the data are used in the computations should allow for censored data. There are two classical ways of estimating such distributions. If no assumption is made on the mathematical form of the distribution of the failure times, a nonparametric technique may be used. The other, more common, approach consists of assuming a specific statistical distribution to model the failure times, and is known as the parametric modeling approach. With both approaches, survival curves can be estimated and predictions of the failure time for different survival rates can be obtained, along with uncertainty measures.

Three statistical models—lognormal, exponential and Weibull distributions—have been fitted to failure data using the method of hazard plotting that provides information about the adequacy of fit of the observed data to the proposed model, the mean or median time to failure and the probability of future failures. The Weibull distribution (defined by two parameters—shape and scale) has become the most popular model to predict the end of shelf life for foods (e.g., Cardelli and Labuza, 2001; Duyvesteyn et al., 2001). For a detailed discussion of the technique, the reader is referred to Guillet and Rodrigue (2010), Hough (2010) and Gacula et al. (2009). There is also a very useful website for self-paced learning (www.weibull.com) from which it is also possible to download software tools.

Larsen et al. (2010) investigated and compared the statistical properties of various popular estimators of shelf life, and developed a genetic algorithm for finding near-optimal staggered designs for the estimation of shelf life. For almost all of the staggered sampling parameters, the generated designs were very different from the commonly used staggered designs.

12.7 SHELF LIFE DEVICES

As mentioned at the outset of this chapter, the quality of most foods and beverages decreases over time. In other words, there is a continual loss of quality from the time they leave the food processor until they are consumed, even under ideal handling conditions. The goal of modern food distribution techniques is to minimize the extent of quality degradation so that the foods will reach the consumer's table as close to their original state as possible.

Of all the extrinsic factors that accelerate quality degradation, the one which has the greatest influence is temperature. This is well known by food technologists, and most countries have codes of practice that specify optimum storage temperatures for many foods, particularly those classed as perishable. Despite these specifications, problems of storage temperature abuse arise all too frequently. One difficulty when storage temperature abuse is suspected lies in detecting the extent of the quality degradation without sampling the food (i.e., disturbing the integrity of the package). An associated difficulty is that many of those involved in the distribution chain are not trained to make reliable judgments about the quality of the food.

Thus, food processors require a simple way of indicating whether their products have been stored at undesirable temperatures, or better still, a means of indicating how much shelf life remains. Devices that provide the first category of information are time–temperature recorders; devices for the second category are time–temperature indicators (TTIs), and these are discussed further in Chapter 15 (Section 15.4.1.2).

12.8 SOME CAUTIONARY ADVICE

Despite the hundreds of scientific publications on the shelf life of foods and the influence of various packaging materials on shelf life, caution must be emphasized in drawing conclusions from the published data. The packaging of olive oil will be used as an example. Cecchi et al. (2009) critically reviewed the literature results concerning the packaging of olive oil in glass or PET bottles (both of which are used commercially for this purpose). The influence of storage conditions (particularly light) and the initial O_2 concentration were also evaluated. Their conclusions provide a salutary message to researchers (and journal referees) in the shelf life area.

From the analysis of the cited literature, it was clear that the reliability of PET bottles as olive oil containers still needs to be demonstrated, primarily because of inconsistent results. However, the performance of glass still seems to be unsurpassed, even if PET bottles can also provide adequate shelf life. Since the initial O_2 concentration in the oil was demonstrated to play a crucial role in determining oil quality during storage, aside from the bottle material, the influence of this variable should be experimentally evaluated.

Their major criticisms of the published studies concerned the fact that important properties of the PET bottle (O_2 permeability, thickness and brand) were very seldom declared, and most experimental designs were performed using drinking water PET bottles from different commercial brands, with variable thickness and composition. In their view, the low self-consistency of literature results was also probably related to the use of different oxidation markers, and dissimilar methods to predict the shelf life by different research groups. Since olive oil is not a standardized reference material, they suggested that future experimental designs should make use of the same olive oil for all experiments or should carefully declare the initial O_2, antioxidant and pro-oxidant contents, which are widely known to influence olive oil oxidation during storage. They concluded that detailed, comprehensive and standardized experimental studies on the shelf life of olive oil packed in PET bottles should be encouraged.

A further example of the difficulties of accounting for all the variables that affect the shelf life of foods was provided by Lu and Xu (2009). They reported on the effect of the light-barrier properties of three different packaging films on the photooxidation and shelf life of commercial cookies containing 23.5% fat stored at 40°C under UV light. The end of shelf life was determined as the time to reach a critical peroxide value. However, there were large differences in the OTRs of the three films (the OTR of the best was 25 times that of the poorest) which would have had a significant influence on shelf life, in addition to the effect of the different light transmission properties of the three films that varied by a factor of 12. Therefore, it is not possible to draw any conclusions from their results.

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