11 Deteriorative Reactions in Foods

11.1 INTRODUCTION

The principal aim of this chapter is to provide a brief overview of the major biochemical, chemical, physical and biological changes that occur in foods during processing and storage and show how these combine to affect food quality. Knowledge of such changes is essential before a sensible choice of packaging materials can be made, because the rate and/or magnitude of such changes can often be minimized by selection of the correct packaging materials.

The deterioration of packaged foods—which includes virtually all foods because very few foods are currently sold without some form of packaging—depends largely on transfers that may occur between the internal environment inside the package and the external environment which is exposed to the hazards of storage and distribution. For example, there may be transfer of moisture vapor from a humid atmosphere into a dried food or transfer of an undesirable odor from the external atmosphere into a high fat food. In addition to the ability of packaging materials to protect and preserve foods by minimizing or preventing such transfers, packaging materials must also protect the product from mechanical damage and prevent or minimize misuse by consumers (including tampering).

Although certain types of deterioration will occur even if there is no transfer of mass (or heat, since some packaging materials can act as efficient insulators against fluctuations in ambient temperatures) between the package and its environment, it is often possible to prolong the shelf life of food through the use of packaging.

It is important that food packaging not be considered in isolation from food processing and preservation, or indeed from food marketing and distribution. All of these factors interact in a complex way, and concentrating on only one aspect at the expense of the others is a surefire recipe for commercial failure.

The development of an analytical approach to food packaging is strongly recommended; and to achieve this successfully, a good understanding of food safety and quality is required. Without question, the more important of these is food safety, which is the freedom from harmful chemical and microbial contaminants at the time of consumption. Packaging is directly related to food safety in two ways.

First, if the packaging material does not provide a suitable barrier around the food, microorganisms can contaminate the food and make it unsafe. However, microbial contamination can also arise if the packaging material permits the transfer of, for example, moisture or O_2 from the atmosphere into the package. In this situation, microorganisms that are present in the food, but present no risk because of the initial absence of moisture or O_2, may subsequently be able to grow and present a risk to the consumer. Second, the migration of potentially toxic compounds from some packaging materials to the food is a possibility in certain situations, which gives rise to food safety concerns. In addition, migration of other components from packaging materials, while not harmful to human health, may adversely affect the quality of the product.

The major quality attributes of foods are texture, flavor, color, appearance and nutritive value, and these attributes can all undergo undesirable changes during processing and storage; a summary of such changes is given in Table 11.1. With the exception of nutritive value, the changes that can occur in these attributes are readily apparent to the consumer, either prior to or during consumption. Packaging can affect the rate and magnitude of many of the quality changes shown in Table 11.1. For example, development of oxidative rancidity can often be minimized if the package is an effective

TABLE 11.1
Classification of Undesirable Changes That Can Occur in Foods

Attribute	Undesirable Change
Texture	a. Loss of solubility
	b. Loss of water-holding capacity
	c. Toughening
	d. Softening
Flavor	Development of
	e. Rancidity (hydrolytic or oxidative)
	f. Cooked or caramel flavors
	g. Other off-flavors
Color	h. Darkening
	i. Bleaching
	j. Development of other off-colors
Appearance	k. Increase in particle size
	l. Decrease in particle size
	m. Nonuniformity of particle size
Nutritive value	Loss, degradation or altered bioavailability of
	n. Vitamins
	o. Minerals
	p. Proteins
	q. Lipids
Safety	Generation of toxic substances

Source: Adapted from Fennema, O.R. et al., Introduction to food chemistry, in: *Fennema's Food Chemistry*, 4th edn., Damodaran, S., Parkin, K.L., and Fennema, O.R. (Eds), CRC Press, Boca Raton, FL, pp. 1–14, 2007.

O_2 barrier; flavor compounds can be absorbed by some types of packaging material and the particle size of many food powders can increase (i.e., clump) if the package is a poor moisture barrier. This chapter outlines the major biochemical, chemical, physical and biological changes that occur in foods during processing and storage and shows how these combine to affect food quality. This chapter addresses the issue of shelf life, which is very clearly related to food quality.

11.2 DETERIORATIVE REACTIONS IN FOODS

Knowledge of the kinds of deteriorative reactions that influence food quality is the first step in developing food packaging that will minimize undesirable changes in quality and maximize the development and maintenance of desirable properties. Once the nature of these reactions is understood, knowledge of the factors that control their rates is necessary, in order to fully control the changes occurring in foods during storage (i.e., while packaged). The nature of the deteriorative reactions in foods is reviewed in this section, and the factors which control the rates of these reactions are discussed in the following section.

11.2.1 Enzymic Reactions

Enzymes are complex globular proteins that can act as catalysts, accelerating the rate of chemical reactions by factors of 10^{12}–10^{20} over that of uncatalyzed reactions. An understanding of the biological

mechanisms for controlling enzymic activities, and the biochemical mechanisms of enzyme action, can provide the food technologist with the means of effectively exploiting enzymes in food processing. From a food packaging point of view, knowledge of enzyme action is fundamental to a fuller understanding of the implications of one form of packaging over another. The importance of enzymes to the food processor is often determined by the conditions prevailing within and outside the food. Control of these conditions is necessary to control enzymic activity during food processing and storage. The major factors useful in controlling enzyme activity are temperature, a_w (water activity), pH, chemicals that can inhibit enzyme action, alteration of substrates, alteration of products and preprocessing control.

Three of these factors are particularly relevant in a packaging context. The first is temperature, where the ability of a package to maintain a low product temperature and thus retard enzyme action will often increase product shelf life. The second important factor is a_w because the rate of enzyme activity is dependent on the amount of water available; low levels of water can severely restrict enzymic activities and even alter their pattern of activity. Finally, alteration of substrate (in particular, the ingress of O_2 into a package) is important in many oxygen-dependent reactions that are catalyzed by enzymes.

11.2.2 Chemical Reactions

Many of the chemical reactions occurring in foods can lead to deterioration in food quality (both nutritional and sensory) or the impairment of food safety. The more important classes of these reactions are listed in Table 11.2 and are discussed fully in standard textbooks on food chemistry. In the present context, it is noteworthy that such reaction classes can involve different reactants or substrates depending on the food and the particular conditions for processing or storage. The rates of these chemical reactions are dependent on a variety of factors amenable to control by packaging including light, O_2 concentration, temperature and a_w. Therefore, in certain circumstances, the package can play a major role in controlling these factors and thus indirectly the rate of the deteriorative chemical reactions.

11.2.2.1 Sensory Quality

The two major chemical changes that occur during the processing and storage of foods, leading to deterioration in sensory quality, are lipid oxidation and nonenzymic browning (NEB). Chemical reactions are also responsible for changes in the color and flavor of foods during processing and storage.

TABLE 11.2
Some Chemical, Biochemical and Physical Reactions That Can Lead to Food Quality Deterioration

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

Source: Adapted from van Boekel, M.A.J.S., *Compr. Rev. Food Sci. Food Safety*, 7, 144, 2008.

11.2.2.1.1 Lipid Oxidation

Autoxidation is the reaction, by a free radical mechanism, of molecular O_2 with hydrocarbons and other compounds. The reaction of free radicals with O_2 is extremely rapid, and many mechanisms for initiation of free radical reactions have been described. Autoxidation is a major cause of food deterioration; the crucial role that this reaction plays in the development of undesirable flavors and aromas in foods is well documented.

As well as being responsible for the development of off-flavors in foods, the products of lipid oxidation may also react with other food constituents such as proteins, resulting in extensive cross-linking of the protein chains through either protein–protein or protein–lipid cross-links.

Factors that influence the rate and course of oxidation of lipids are well known and include light, local O_2 concentration, high temperature, the presence of catalysts (generally transition metals such as iron and copper, but also heme pigments in muscle foods) and a_w. Control of these factors can significantly reduce the extent of lipid oxidation in foods.

11.2.2.1.2 Nonenzymic Browning

NEB is one of the major deteriorative chemical reactions which occur during storage of dried and concentrated foods. The NEB or Maillard reaction can be divided into three stages: (1) early Maillard reactions, which are chemically well-defined steps without browning; (2) advanced Maillard reactions, which lead to the formation of volatile or soluble substances and (3) final Maillard reactions, leading to insoluble brown polymers.

The initial reaction involves a simple condensation between an aldehyde (usually a reducing sugar) and an amine (usually a protein or amino acid) to give a glycosylamine. The glycosylamine then undergoes an Amadori rearrangement to form an Amadori derivative. The formation of Amadori compounds accounts for the observed loss of both reducing sugar and amine during the Maillard reaction. Although the early Maillard reactions forming Amadori compounds do not cause browning, they do reduce nutritive value.

The final step of the advanced Maillard reaction is the formation of many heterocyclic compounds such as pyrazines and pyrroles, as well as brown melanoidin pigments. These pigments are formed by polymerization of the reactive compounds produced during the advanced Maillard reactions. The polymers are relatively inert and have a molecular weight greater than 1000.

11.2.2.1.3 Color Changes

Acceptability of color in a given food is influenced by many diverse factors, including cultural, geographical and sociological aspects of the population. However, regardless of these many factors, certain food groups are only acceptable if they fall within a certain color range. The color of many foods is due to the presence of natural pigments. The major changes that these can undergo are briefly described; a more detailed discussion can be found elsewhere (Schwartz et al., 2007).

11.2.2.1.3.1 Chlorophylls The name *chlorophyll* describes those green pigments involved in the photosynthesis of higher plants. The major change which chlorophylls can undergo is *pheophytinization*—the replacement of the central magnesium atom by hydrogen and the subsequent formation of dull, olive-brown pheophytin. Because this reaction is accelerated by heat and is acid catalyzed, it is unlikely to be influenced by the choice of packaging.

Almost any type of food processing or storage causes some deterioration of the chlorophyll pigments. Although pheophytinization is the major change, other reactions are possible. For example, dehydrated products such as green peas and beans packed in clear glass containers undergo photo-oxidation and loss of desirable color.

11.2.2.1.3.2 Heme Pigments Meat is an important part of many diets, and the color of red meat is due to the presence of the heme pigment *myoglobin*. Myoglobin is a complex muscle protein contained within the cells of the tissues where it acts as a temporary storehouse for

the O_2 brought by the hemoglobin in the blood. The protein moiety is known as *globin* and the nonpeptide portion is called *heme*.

The color cycle in fresh meats is reversible and dynamic, with the three pigments—oxymyoglobin, myoglobin and metmyoglobin—constantly interconverted. In cured meat products, nitrite reacts with these pigments to form additional heme-based compounds. These reactions are discussed in more detail in Chapter 17. At this stage, it is sufficient to note that packaging has an extremely important influence on meat pigments. For example, at low partial pressures of O_2 (i.e., an almost impermeable package), the formation of brown metmyoglobin is favored. If the package is completely impermeable to O_2, the heme pigments are fully reduced to the purple myoglobin.

11.2.2.1.3.3 Anthocyanins Anthocyanins are a group of more than 150 reddish water-soluble pigments that are very widespread in the plant kingdom. An anthocyanin pigment is composed of an aglycone (an anthocyanidin) esterified to one or more of five sugars (in order of relative abundance glucose, rhamnose, galactose, xylose and arabinose). The rate of anthocyanin destruction is pH dependent, being greater at higher pH values.

Of interest from a packaging point of view is the ability of some anthocyanins to form complexes with metals such as Al, Fe, Cu and Sn. These complexes generally result in a change in the color of the pigment (e.g., red sour cherries react with tin to form a purple complex) and are, therefore, undesirable. Because metal packaging materials such as cans could be sources of these metals, they are usually coated with special organic linings (enamels) to avoid these undesirable reactions (see Chapter 7).

11.2.2.1.3.4 Carotenoids The *carotenoids* are a group of mainly lipid-soluble compounds responsible for many of the yellow and red colors of plant and animal products. Carotenoids include a class of hydrocarbons called *carotenes* and their oxygenated derivatives called *xanthophylls*. Carotenoids can exist in the free state in plant tissue or in solution in lipid media such as animal fatty tissue.

The main cause of carotenoid degradation in foods is oxidation. The mechanism of oxidation in processed foods is complex and depends on many factors. The pigments may autoxidize by reaction with atmospheric O_2 at rates dependent on light, heat and the presence of pro- and anti-oxidants.

11.2.2.1.3.5 Miscellaneous Natural Pigments There are a number of other groups of compounds which are responsible for some of the colors in foods. These include *flavonoids* (yellow compounds with chemical structures similar to the anthocyanins), *proanthocyanidins* (these are colorless but contribute to enzymic browning reactions in fruits and vegetables) and *tannins* (which contribute to enzymic browning reactions, but their mechanisms of action are not well understood).

11.2.2.1.4 Flavor Changes

The term *flavor* has evolved to a usage that implies an overall integrated perception of the contributing senses of smell and taste at the time of food consumption. Specialized cells of the olfactory epithelium in the nasal cavity are able to detect trace amounts of volatile odorants. Taste buds located on the tongue and back of the oral cavity enable humans to sense sweetness, sourness, saltiness, bitterness and umami, and these sensations contribute to the taste component of flavor.

In fruits and vegetables, enzymically generated compounds derived from long-chain fatty acids play an extremely important role in the formation of characteristic flavors. In addition, these types of reactions can lead to important off-flavors. Enzyme-induced oxidative breakdown of unsaturated fatty acids occurs extensively in plant tissues, and this yields characteristic aromas associated with some ripening fruits and disrupted tissues (Lindsay, 2007).

Fats and oils are notorious for their role in the development of off-flavors through autoxidation. Aldehydes and ketones are the main volatiles from autoxidation, and these compounds can cause painty, fatty, metallic, papery and candle-like flavors in foods when their concentrations are sufficiently high. However, many of the desirable flavors of cooked and processed foods derive from modest concentrations of these compounds (Lindsay, 2007). The permeability of packaging

materials is important in retaining desirable volatile components within packages and for preventing undesirable components permeating through the package from the ambient atmosphere.

Many flavor compounds found in cooked or processed foods occur as the result of reactions common to all types of foods regardless of whether they are of animal, plant or microbial origin. These reactions take place when suitable reactants are present and appropriate conditions such as heat, pH and light exist. Packaging can play an important role in these reactions.

11.2.2.2 Nutritional Quality

As well as the chemical changes described earlier, which may have a deleterious effect on the sensory properties of foods, there are other chemical changes which can affect the nutritive value of foods. As these reactions are discussed fully in standard textbooks, only a brief review of some of these reactions is presented here to illustrate the potential role of packaging in minimizing nutrient degradation in foods.

The four major factors that impact on nutrient degradation and can be controlled to varying extents by packaging are light, O_2 concentration, temperature and a_w. However, because of the diverse nature of the various nutrients, as well as the chemical heterogeneity within each class of compounds and the complex interactions of the aforementioned variables, generalizations about nutrient degradation in foods are necessarily broad.

11.2.2.2.1 Vitamins

The chemical conversion of vitamins to biologically inactive products during storage of foods has been the subject of extensive research. A generalized summary of vitamin stability is presented in Table 11.3, although it is important to note that exceptions exist and invalid conclusions could be reached on the basis of these generalizations.

Ascorbic acid is the most sensitive vitamin in foods; its stability varies markedly as a function of environmental conditions such as pH and the concentration of trace metal ions and O_2. The nature of the packaging material can significantly affect the stability of ascorbic acid in foods. The effectiveness of the material as a barrier to moisture and O_2, as well as the chemical nature of

TABLE 11.3
General Stability of Vitamins to Environmental Effects

Nutrient	Oxygen	Light	Temperature
Vitamin A	U	U	U
Vitamin B_6	S	U	U
Vitamin B_{12}	U	U	S
Biotin	S	S	U
Vitamin C	U	U	U
Carotenes	U	U	U
Choline	U	S	S
Vitamin D	U	U	U
Folic acid	U	U	U
Inositol	S	S	U
Vitamin K	S	U	S
Niacin	S	S	S
Pantothenic acid	S	S	U
Riboflavin B_2	S	U	U
Thiamin B_1	U	S	U
Tocopherols	U	U	U

U, unstable; S, stable.

the surface exposed to the food, are important factors. For example, problems of ascorbic acid instability in aseptically packaged fruit juices have been encountered because of O_2 permeability and the O_2 dependence of the ascorbic acid degradation reaction. In addition, because of the preferential oxidation of metallic tin, citrus juices packaged in cans with a tin contact surface exhibit greater stability of ascorbic acid than those in enameled cans or glass containers. The aerobic and anaerobic degradation reactions of ascorbic acid in reduced-moisture foods are highly sensitive to a_w, with the reaction rate increasing in an exponential fashion over the a_w range of 0.1–0.8.

11.2.2.2.2 Proteins

The nutritive value (and sometimes the wholesomeness) of proteins can be modified by heating and oxidation. Oxidation of proteins results in the formation of degradation products, which are known to detract from protein nutritive value. Proteins can also react with lipids to form complexes that can affect food texture and, to a minor extent, protein nutritive value. In addition, the Maillard reaction can result in loss of nutritional properties, primarily from losses in the amino acid lysine.

11.2.2.2.3 Lipids

Lipids, especially when unsaturated, undergo many kinds of chemical changes during processing, and some of these changes can affect their nutritional value and wholesomeness. Peroxidizing lipids exert negative effects on the nutritive value of foods by their chemical interaction with proteins and vitamins. Oxygen often plays an important role in lipid degradation, and packaging can play an important role in limiting or preventing O_2 ingress.

11.2.3 Physical Changes

The physical properties of foods can be defined as those properties that lend themselves to description and quantification by physical rather than chemical means. Their importance stretches from product handling, through processing, packaging and storage, to consumer acceptance. Physical properties include geometrical, thermal, optical, mechanical, rheological, electrical and hydrodynamic properties (Sahin and Gulum, 2006). Geometrical properties encompass the parameters of size, shape, volume, density and surface area as related to homogeneous food units, as well as geometrical texture characteristics. The latter can be sub-divided into two classes: those referring to particle size and shape (e.g., gritty and grainy) and those referring to particle shape and orientation (e.g., fibrous and cellular).

Although many of these physical properties are important and must be considered in the design and operation of a successful packaging system, the focus here is on undesirable physical changes in packaged foods. The way in which some of these changes can be affected by the nature of the packaging is now outlined.

Food powders are a diverse group and represent a large proportion of the total processed food in the world; they can be categorized in a number of ways (Onwulata, 2005). On the basis of major chemical components, powders may be classified as starchy (e.g., wheat flour), proteinaceous (e.g., soy isolate), crystalline (e.g., sugars, salts and organic acids), amorphous (e.g., dehydrated fruit juices) and fatty (e.g., soup mix). Powders may also be classified according to their particle size, although many food powders exhibit a range of several orders of magnitude in this parameter. They may also be classified according to their moisture sorption pattern, ranging from extremely hygroscopic (in the case of dehydrated fruit juices) through hygroscopic (in the case of spray dried coffee) to moderately hygroscopic (in the case of flours). Finally, powders can be classified as free flowing (e.g., granular sugar), moderately cohesive (e.g., flour) and very cohesive (most food powders after absorbing moisture).

A major undesirable change in food powders is the sorption of moisture as a consequence of an inadequate barrier provided by the package, resulting in caking. This can occur either as a result of a poor selection of packaging material in the first place or failure of the package integrity during storage.

Caking is the uncontrolled agglomeration of food powders (especially those containing soluble components or fats) and occurs when they are exposed to moist atmospheres or elevated storage temperatures. The phenomenon can result in anything from small soft aggregates that break easily to rock hard lumps of variable size or solidification of the whole powder. In most cases, the process is initiated by the formation of liquid bridges between the particles that can later solidify by drying or cooling. The size of such bridges determines the flow properties of the powder. The increase of the sinter bridges during caking has been modeled, and the calculated sinter bridge diameter correlated with the strength of the caked powder bulk (Hartmann and Palzer, 2011).

The agglomeration of amorphous particulate material is a major problem in the food industry. Currently, the glass transition temperature (T_g), which depends on water content, is used as a fundamental parameter to describe and control agglomeration. Although models are available that describe the kinetics of the agglomeration process as a function of the distance of the material from T_g (i.e., $T - T_g$), they are often not applied because they assume that the powder is instantly in equilibrium with the ambient humidity and that solid mobility only occurs at $T > T_g$. Renzetti et al. (2012) showed that the water migration mechanism is controlled by relaxation phenomena when the amorphous material is still far from the glass–rubber transition. The $T - T_g$ at which the relaxation phenomena occur depends on the material and could describe the onset of agglomeration, independently from the material properties. They concluded that matrix relaxation occurring far below T_g did not affect the onset of agglomeration.

Flow conditioners or anticaking agents are very fine powders of an inert chemical substance that are added to powders with much larger particle size at concentrations up to 2% in order to inhibit caking and improve flowability. Most conditioners are insoluble in water, but many of them can absorb a considerable amount of water owing to their very large surface areas. The main food-grade commercial conditioners generally consist of silicon dioxide, silicates, phosphates, salts of stearic acids, talcum starches and modified carbohydrates such as maltodextrins (Intipunya and Bhandari, 2010).

Studies on sucrose and onion powders showed that at ambient temperature, caking does not occur at a_ws of less than about 0.4. However, at higher activities ($a_w > 0.45$), the observed time to caking is inversely proportional to a_w, and at these levels, anticaking agents are completely ineffective. It appears that although they reduce interparticle attraction and interfere with the continuity of liquid bridges, they are unable to cover moisture sorption sites.

For foods containing solid carbohydrates, the largest change in physical properties results from sorption of water, especially for the recrystallization of amorphous carbohydrates. Such changes can occur in boiled sweets (leading to stickiness or graining) and milk powders (leading to caking and lumpiness). In addition, lactose crystallization in milk powders can lead to protein insolubility, increased free fat through rupture of fat globules and accelerated flavor deterioration.

11.2.4 Biological Changes

11.2.4.1 Microbiological

Microorganisms can make both desirable and undesirable changes to the quality of foods, depending on whether or not they are introduced as an essential part of the food preservation process (e.g., as inocula in food fermentations) or arise adventitiously and subsequently grow to produce food spoilage. In the latter case, they only reach readily observable proportions when they are present in the food in large numbers. Because the initial population or microbial load is usually small, observable levels are only reached after extensive multiplication of the microorganism(s) in the food.

The two major groups of microorganisms found in foods are bacteria and fungi, the latter consisting of yeasts and molds. Bacteria are generally the fastest growing, so that in conditions favorable to both, bacteria will usually outgrow fungi. The phases through which the two groups pass are broadly similar: a period of adjustment or adaptation (known as the *lag* phase) is followed by accelerating growth until a steady, rapid rate (known as the *logarithmic* phase since growth is

exponential) is achieved. After a time, the growth rate slows until growth and death are balanced and the population remains constant (known as the *stationary* phase). Eventually, death exceeds growth and the organisms enter the phase of decline.

Foods are frequently classified on the basis of their stability as nonperishable, semiperishable and perishable. An example of the first classification is sugar; provided it is kept dry, at ambient temperature and free from contamination, it should have a very long shelf life. However, few foods are truly nonperishable, and an important factor in determining their perishability is packaging.

For example, hermetically sealed and heat processed (e.g., canned) foods are generally regarded as nonperishable. However, they may become perishable under certain circumstances when an opportunity for recontamination is afforded following processing. Such an opportunity may arise if the can seams are faulty, or if there is excessive corrosion resulting in internal gas formation and eventual bursting of the can. Spoilage may also take place when the canned food is stored at unusually high temperatures where thermophilic spore-forming bacteria may multiply, causing undesirable changes such as flat sour spoilage.

Low moisture content foods such as flour, dried fruits and vegetables and baked goods are classified as semiperishable. Frozen foods, though basically perishable, may be classified as semiperishable provided that they are properly stored at freezer temperatures.

The majority of foods (e.g., flesh foods such as meat and fish; milk, eggs and most fruits and vegetables) are classified as perishable unless they have been processed in some way. Often, the only form of processing, which such foods receive, is to be packaged and kept under controlled temperature conditions.

The species of microorganisms which cause the spoilage of particular foods are influenced by two factors: the nature of the foods and their surroundings. These factors are referred to as intrinsic (compositional) and extrinsic (environmental) parameters and are listed in Table 11.4 and discussed further in Sections 11.4 and 11.5. The intrinsic parameters are an inherent part of the food with most microorganisms growing best at pH values around 7.0, while few grow below pH 4.0. Bacteria tend to be more fastidious in their relationships to pH than molds and yeasts, with the pathogenic bacteria being the most fastidious. The minimum a_w values reported for growth of some microorganisms in foods are presented in Table 11.5. It is noteworthy that yeasts and molds grow over a wider a_w range than bacteria.

In order to grow and function normally, microorganisms require several nutrients including water, a source of energy, a source of nitrogen, vitamins and related growth factors and minerals. The availability of water is related directly to the a_w of the food. The primary source of nitrogen utilized by microorganisms is amino acids. Growth factor and vitamin requirements tend to be specific to individual groups of microorganisms. Some foods contain certain naturally occurring substances that have been shown to have antimicrobial activities, thus preventing or retarding the growth of specific microorganisms in those foods.

TABLE 11.4
Intrinsic and Extrinsic Parameters Influencing Microbial Growth in Foods

Intrinsic Factors	Extrinsic Factors
pH	Storage temperature
a_w	Relative humidity of environment
E_h	Presence and concentration of gases in the environment
Nutrient content	
Antimicrobial constituents	
Biological structures	

TABLE 11.5
Approximate Minimum a_w Values for the Growth of Microorganisms of Importance in Foods

Organism	Minimum a_w
Most spoilage bacteria	0.90
Most spoilage yeasts	0.88
Most spoilage molds	0.80
Halophilic bacteria	0.75
Xerophilic molds	0.61
Osmophilic yeasts	0.61

The extrinsic parameters of foods are those properties of the storage environment that affect both the foods and their microorganisms. The growth rate of the microorganisms responsible for spoilage primarily depends on such extrinsic parameters as storage temperature, RH and gas composition of the surrounding atmosphere. The temperature of storage is particularly important, and several food preservation techniques (e.g., chilling and freezing) rely on reducing the temperature of the food to extend its shelf life.

Although there is a very wide range of temperatures over which the growth of microorganisms has been reported (–34°C to 90°C), specific microorganisms have relatively narrow temperature ranges over which growth is possible. Those that have an optimal temperature for growth at about 15°C or lower, a maximal temperature for growth at about 20°C and a minimal temperature for growth at 0°C or lower are referred to as *psychrophiles* or *psychrotrophs*. Those that grow well between 20°C and 45°C with optima between 30°C and 40°C are referred to as *mesophiles*, and those that grow well at and above 45°C with optima between 55°C and 65°C are referred to as *thermophiles*. Molds are able to grow over a wider range of temperature than bacteria, with many molds being capable of growth at refrigerator temperature. Yeasts grow over the psychrophilic and mesophilic temperature ranges but generally not within the thermophilic range. The approximate lowest limits of a_w, pH and temperature for growth of some microorganisms of importance in foods are shown in Table 11.6.

The RH of the ambient environment is important and can influence the a_w of the food unless the package provides a barrier. Many flexible plastic packaging materials provide good moisture barriers, but none are completely impermeable, thus limiting the shelf life of low a_w foods.

The presence and concentration of gases in the environment has a considerable influence on the growth of microorganisms. Increased concentrations of gases such as CO_2 are used to retard microbial growth and thus extend the shelf life of foods (see, in particular, Chapters 16 and 17 for a full discussion of this topic). Moreover, vacuum packaging (i.e., removal of air, and thus O_2, from a package prior to sealing) can also have a beneficial effect by preventing the growth of aerobic microorganisms. This type of packaging (known as *modified atmosphere packaging* [MAP]) raises certain safety issues, which are discussed in Chapter 16. Most food pathogens do not grow at refrigeration temperatures, and CO_2 is not highly effective at nonrefrigeration temperatures. Therefore, most MAP food is usually held under refrigeration. Temperature abuse of the product (i.e., holding at nonrefrigerated temperatures) could allow the growth of organisms (including pathogens), which had been inhibited by CO_2 during storage at lower temperatures. For these reasons, it is difficult to evaluate MAP safety solely on the growth of certain pathogens at abusive temperatures.

Microbial growth in perishable foods can typically be represented as a function of time as shown in Figure 11.1 with the curve usually divided into lag, exponential and stationary phases. The four

TABLE 11.6
Approximate Lowest Limits[a] of a_w, pH and Temperature for Growth of Some Microorganisms

Organism	Lowest a_w Limit	Lowest pH Limit	Lowest Temperature Limit (°C)
Bacteria			
Bacillus cereus (mesophilic)	0.93	4.9	10
B. cereus (psychrotrophic)	0.93	4.9	5
Brochothrix thermosphacta	0.94	4.6	0
Campylobacter spp.	0.98	4.9	30
Clostridium botulinum (nonproteolytic)	0.97	5.0	3.3
Clostridium botulinum (proteolytic)	0.94	4.6	10
Clostridium perfringens	0.96	4.5	5
Escherichia coli	0.95	4.4	7
Lactobacillus spp.	0.93	3.0	4
Most lactic acid bacteria	0.95	3.5	5
Listeria monocytogenes	0.92	4.3	0
Pseudomonas spp.	0.97	5.0	−2
Salmonella spp.	0.95	4.0	5
Staphylococcus aureus	0.86	4.0	7
Molds			
Aspergillus flavus	0.78	2.0	3
Most molds	0.80	1.5	<0
Yeasts			
Most yeasts	0.87	1.5	−5
Saccharomyces cerevisiae	0.90	2.3	0

Source: 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.

[a] Values may vary with food type and microbial strain.

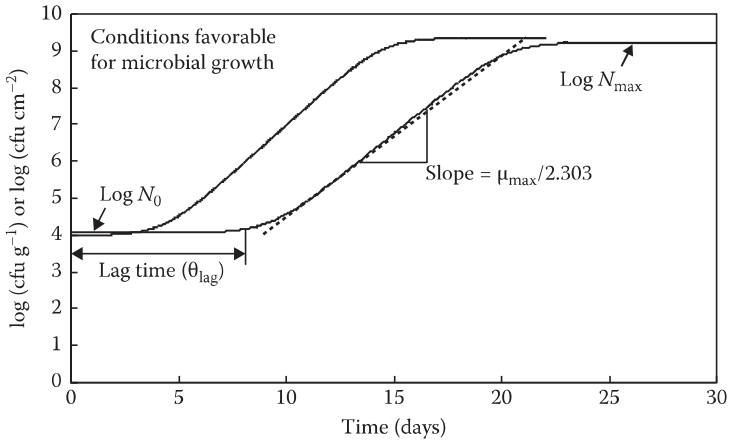

FIGURE 11.1 Typical pattern of bacterial growth on perishable food stored under constant environmental conditions. (Lee D.S., Packaging and the microbial shelf life of food, in: *Food Packaging and Shelf Life*. Robertson G.L. (Ed). CRC Press, Boca Raton, FL, pp. 55–79, 2010.)

key parameters log N_o, θ_{lag}, μ_{max} and log N_{max} describe the progress of microbial growth with time under certain defined conditions. 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_{max} represents the maximum cell density attainable under given conditions and is usually beyond the acceptable limit of quality (Lee, 2010). 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. The maximum specific growth rate, μ_{max}, can be assumed to represent the main part of the exponential growth. With this simplified treatment, the time (θ_s) to reach a critical limit cell density of N_c located on the exponential growth phase is the shelf life and can be calculated by

$$\theta_s = \theta_{lag} + \frac{1}{\mu_{max}} \ln \frac{N_c}{N_o} \tag{11.1}$$

The protection of packaged food from contamination or attack by microorganisms depends on the mechanical integrity of the package (e.g., the absence of pinholes and seal imperfections) and on the resistance of the package to penetration by microorganisms. Metal and glass packaging cannot be penetrated by microorganisms, and extensive studies on a variety of plastic films and metal foils have shown that molds, yeasts and bacteria cannot penetrate these materials in the absence of pinholes. In practice, thin sheets of packaging materials such as aluminum and plastic do contain pinholes. However, because of surface tension effects, microorganisms cannot pass through very small pinholes, unless the microorganisms are suspended in solutions containing wetting agents and the pressure outside the package is greater than that within.

11.2.4.2 Macrobiological

11.2.4.2.1 Insect Pests

The common insect pests of fresh (unpackaged) food are flies (from the order Diptera), and cockroaches. They are attracted by food odors regardless of whether the food is fresh or beginning to decay. Any insect in food is a pest since not only does the food become contaminated with their bodies and excreta, but they are also capable of transmitting pathogens, including food poisoning organisms.

In contrast, the main insect species important as pests of stored (packaged) foods are entirely from the orders Lepidoptera (moths) and Coleoptera (beetles). They regularly damage and destroy large quantities of stored foods around the world every year. The number of species involved is not large and includes weevils, various other beetles and the larvae of several moths. Most stored product insects are cosmopolitan in that any given species is, for the most part, found worldwide in areas with similar climatic conditions. Warm humid environments promote insect growth, although most insects will not breed if the temperature exceeds about 35°C or falls below 10°C. Also, many insects cannot reproduce satisfactorily unless the moisture content of their food is greater than about 11%.

Moths and beetles are generally found in dry storage areas. They are able to survive on very small amounts of food, and thus can persist on food residues in improperly cleaned premises or equipment. Good ventilation, the use of cool storage areas and rotation of stock assists in keeping these pests at bay. Basic to effective control of insect pests is an understanding of their life cycles and feeding habits.

In common with many insects, moths pass through four stages during their development: the egg, the larva (caterpillar), the pupa (chrysalis) and the adult moth. Food is consumed only in the larval stage. The presence of larvae can be recognized by a characteristic mixture of silken

threads and frass (droppings) that they produce. Beetles have the same four life stages as moths, but they differ in that the adult beetle is a considerably harder-bodied insect than the moth and may live and feed for months or even years. Cockroaches are larger, more robust insects, which are highly mobile. Their young are like small versions of the adult and, unlike beetles and moths, cockroaches do not inhabit packaged foods. Ants are a highly specialized group of insects, which form nests, normally outside buildings. Worker ants may travel considerable distances and collect almost any type of food (especially sweet or high-protein foods) and take it back to the nest.

Mites, which sometimes occur in stored foods, are not insects but are closely related to spiders, having eight legs. They are minute in size, requiring a lens to see them, and are primarily pests of cereals and other foods with a moisture content of at least 12%. Mites are so small that the presence of a few would pass unnoticed; they produce a sour odor in the food. Typically eggs and some other life stages are cold tolerant and development can proceed at lower temperatures than required by insect stored product pests, but low humidities prevent development (Bell, 2011).

The main categories of foods subject to pest attack are cereal grains and products derived from cereal grains, other seeds used as food (especially legumes), dairy products such as cheese and milk powders, dried fruits, dried and smoked meats and nuts. As well as their possible health significance, the presence of insects and insect excreta in packaged foods may render products unsalable, causing considerable economic loss, as well as reduction in nutritional quality, production of off-flavors and acceleration of decay processes due to the creation of higher temperatures and moisture levels.

Unlike microorganisms, some insect species (penetrators) have the ability to bore through one or more of the flexible packaging materials in use today and take up residence inside. Other species (invaders) usually do not enter packages unless there is an existing opening. However, such openings need not be very large; for example, the adult saw-toothed grain beetle can enter an opening less than 1 mm in diameter (Highland, 1991). Newly hatched larvae can enter much smaller openings; holes only 0.1 mm in diameter are sufficient to admit immature mites and the larvae of some insects. Thus, package seal quality is critical in protecting foods from insect infestations.

Unless plastic films are laminated with foil or paper, insects are able to penetrate most of them quite easily, where the rate of penetration is usually directly related to film thickness. In general, thicker films are more resistant than thinner films, and oriented films tend to be more effective than cast films. The looseness of the film has also been reported to be an important factor, with loose films being more easily penetrated than tightly fitted films.

Generally, the penetration varies depending on the basic resin from which the film is made, on the combination of materials, on the package structure, and on the species and stage of insects involved. The relative resistance to insect penetration of common flexible packaging materials is given in Table 11.7; where no thicknesses are given, the estimations are based on thicknesses commonly used in food packaging. Absolute values are difficult to determine because resistance to penetration is influenced by factors such as package configuration and the presence or absence of folds, tucks and other harborage sites. Therefore, after appropriate packaging materials have been selected, they must be evaluated in situ for insect resistance (Highland, 1991).

AACC (2001) has approved a method to determine the characteristics of insects chewing on food packaging materials to differentiate between exit and entrance holes. However, in mature infestations with multiple stages, insects often enlarge entry holes for exit and reentry. The method is applicable to various types of packaging materials. Typically, different types of commercially prepared packages are exposed to five species of insects (the red flour beetle, the saw-toothed grain beetle, the Indianmeal moth, the cigarette beetle and the warehouse beetle). These species represent a good cross section of both penetrators and invaders and are generally representative of the most common insect pests associated with packaged foods. At periodic intervals, packages are checked for infestation. Penetration holes (entry or exit) and obvious flaws in the seams and closures are noted. After the outside is examined, the commodity inside the package is examined,

TABLE 11.7
Resistance of Various Materials to Insect Penetration

	Excellent	Good	Fair	Poor
Polycarbonate	x			
Poly(ethylene terephthalate)	x			
Cellulose acetate		x		
Polyamide		x		
Polyethylene (0.254 mm)		x		
Polypropylene (biaxially oriented)		x		
Poly(vinyl chloride) (unplasticized)		x		
Acrylonitrile			x	
Poly(tetrafluoroethylene)			x	
Polyethylene (0.123 mm)			x	
Regenerated cellulose film				x
Corrugated paperboard				x
Ethylene vinyl acetate copolymer				x
Ionomer				x
Kraft paper				x
Paper/foil/polyethylene laminate pouch				x
Polyethylene (0.0254–0.100 mm)				x
Poly(vinyl chloride) (plasticized)				x
Poly(vinylidene chloride) copolymer				x

Source: Adapted from Highland, H.A., Protecting packages against insects, in: *Ecology and Management of Food-Industry Pests*, Gorham, J.R. (Ed.), Association of Official Analytical Chemists, Arlington, VA, pp. 345–350, 1991.

the insects of each species are identified and counted, and the numbers are recorded. After each test, a report is prepared and suggestions are made. The manufacturer can use this information to improve the performance of future package designs. Packaging studies have been conducted on a variety of commodities, including dry pet foods, breakfast cereals, baby foods, rice products, military rations and raisins (Mullen and Mowery, 2006).

A study by Wong et al. (2005) discussed the development of a bioassay for the evaluation of insect-repellent packaging, the use of paperboard coatings as carriers of insect repellents and the persistence with which citronella-treated cartons deter beetle infestation. Of five commercial plant extracts (citronella, garlic oil, neem extract, pine oil and pyrethrum), it was found that citronella was effective in deterring the infestation by red flour beetles of cartons containing muesli and wheat germ. The chemical components were applied as part of a coating on the carton board and reduced beetle infestation to approximately 50% of the level observed in control cartons. The insect-repellent effect persisted for at least 16 weeks. Navarro et al. (2007) reviewed the use of turmeric oil, neem and pyrethrum incorporated into packaging materials to repel insects.

The development of alternative treatments for pest control in foods is an increasing plea from the food industry, as consumers demand reduced use or elimination of pesticides. The use of CO_2 at high pressure is one of the most rapid options for pest control among current commercial treatments, offering complete control within hours. Riudavets et al. (2010) established the efficacy of this option against different stages of several insect and mite pests, and achieved a high level of control for most species and development stages when treated with CO_2 at 2000 kPa for 60 min.

11.2.4.2.2 Rodents

The rodents rats and mice are among humanity's most cunning and capable enemies. They have highly developed senses of touch, smell and hearing, and can identify new or unfamiliar objects in their environment. Rats can wriggle through openings the size of a quarter; a mouse needs a hole only as large as a nickel to gain access. Rats and mice carry disease-producing organisms on their feet and/or in their intestinal tracts and are known to harbor salmonellae of serotypes frequently associated with foodborne infections in humans. In addition to the public health consequences of rodent populations in close proximity to humans, these animals also compete intensively with humans for food.

Rats and mice gnaw to reach sources of food and drink and to keep their teeth short. Their incisor teeth are so strong that rats have been known to gnaw through lead pipes and unhardened concrete, as well as sacks, wood and flexible packaging materials. Obviously, proper sanitation in food processing and storage areas is the most effective weapon in the fight against rodents, because all packaging materials apart from metal and glass containers can be attacked by rats and mice.

11.3 RATES OF DETERIORATIVE REACTIONS

As discussed in the preceding section, a number of deteriorative chemical, biochemical and microbiological reactions can occur in foods. The rates of these reactions depend on both intrinsic and extrinsic factors. As well as understanding the nature of these reactions, it is also important to have an appreciation of their rates, so that they can be controlled. Control of deteriorative reactions requires a quantitative analysis based on knowledge of the kinetics of food deterioration. Fortunately, simple chemical kinetics can be applied to such reactions (van Boekel, 2009).

Quantitative analysis of the deteriorative reactions which occur in a food during processing and storage requires the existence of a measurable index of deterioration; that is, a chemical, physical or sensory measurement or set of measurements that may be used reproducibly to assess the changes occurring. An increase or decrease in the index of deterioration must correlate with changes in food quality. For quantitative analysis of quality changes, the index must be expressed as a function of the conditions existing during processing and storage so that the changes can be predicted or simulated. Thus, calculation of quality losses requires a mathematical model that expresses the effect of intrinsic and extrinsic factors on the deterioration index.

The general equation describing quality loss may be written as

$$\frac{-dC}{d\theta} = f(I_i, E_j) \tag{11.2}$$

where

$-dC/d\theta$ is the rate of change of some index of deterioration C with time θ; a negative sign is used if the concentration of C decreases with time

I_i are the intrinsic factors ($i = 1, \ldots, m$)

E_j are the extrinsic factors ($j = 1, \ldots, n$)

Because the quality of foods and the rate of quality changes during processing and storage depend on intrinsic and extrinsic factors, it is possible in many cases to correlate quality losses with the loss of a particular component such as a vitamin or pigment. The conversion of a single component or quality factor A to an end product B (e.g., conversion of chlorophyll to pheophytin, or conversion of ascorbic acid to brown pigments) may be written as

$$A \rightarrow \text{intermediate products} \rightarrow B \tag{11.3}$$

The absolute concentrations of A or B need not be measured. For example, the production of brown pigments in foods is often measured as the increase in absorbance at 420 nm of an alcoholic extract of the food, and the change in absorbance used as an indicator of the extent of the reaction. Such quality loss can be represented as being proportional to the power of the concentration of the reactant or product:

$$\frac{-dA}{d\theta} = kA^n \tag{11.4}$$

or

$$\frac{dB}{d\theta} = kB^n \tag{11.5}$$

where

A and B are the concentrations of quality factor measured
θ is the time
k is the rate constant (dependent on extrinsic factors)
n is a power factor called the order of the reaction, which defines whether or not the rate is dependent on the concentration of A. The value of n can be a fraction or a whole number
$dA/d\theta$ and $dB/d\theta$ is the change in concentration of A or B with time

Equation 11.5 implies that extrinsic parameters such as temperature, a_w and light intensity are held constant; if they are not, then their influence on the rate constant k must be taken into account in evaluating the equation. For most quality changes in foods, the reaction order n has generally been shown to be either 0 or 1.

From a packaging point of view, it is often useful to know the concentration of A or B at which the product is no longer acceptable, for example, when the concentration of a vitamin or pigment has fallen below some level (e.g., 50% reduction in concentration), or the concentration of some undesirable brown color has risen above some level. In these situations, the shelf life of the food (θ_s) is the time for the concentration of A (or B) to reach an undesirable level (A_c or B_c).

11.3.1 Zero-Order Reactions

When $n = 0$, the reaction is said to be pseudo zero-order with respect to A. Equation 11.5 can then be simplified to:

$$\frac{-dA}{d\theta} = k \tag{11.6}$$

Equation 11.6 implies that the rate of loss of A is constant with time and independent of the concentration of A. Rearranging and integrating Equation 11.6 between A_o, the concentration of A at $\theta = 0$, and A, the concentration of A at time θ:

$$\int_{A_o}^{A} dA = -k\int_{0}^{\theta} d\theta \tag{11.7}$$

yields

$$A = A_o - k\theta \tag{11.8}$$

or

$$A_o - A = k\theta \tag{11.9}$$

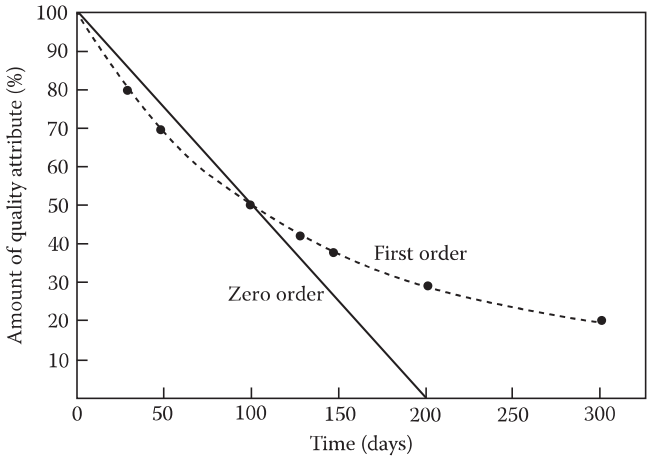

FIGURE 11.2 Change in quality versus time showing the effect of order of the reaction on extent of change.

or

$$A_c = A_o - k\theta_s \tag{11.10}$$

where

A_c is the value of A at end of shelf life

θ_s is the shelf life in days, months, years and so on

For a zero-order reaction, a plot of the amount of A remaining versus time yields a straight line (Figure 11.2) with the slope equal to the rate constant k in units of [concentration] [time^{-1}]. In other words, the loss of quality per day is constant when all extrinsic factors are held constant.

Typical pseudo zero-order deteriorative reactions include NEB (e.g., in dry cereals and powdered dairy products), lipid oxidation (e.g., development of rancidity in snacks foods, dry foods and frozen foods) and enzymic degradation (e.g., in fresh fruits and vegetables, some frozen foods and some refrigerated doughs).

It is important to appreciate that the order of the reaction (i.e., n) is strictly an empirical concept. Thus, a pseudo zero-order reaction does not imply that the mechanism is a monomolecular breakdown independent of the concentration of the reacting species. On the contrary, pseudo zero-order reactions are always an indication that a complex reaction is occurring involving a number of steps. All that a pseudo zero-order reaction suggests is that there is a high correlation between A and time.

Example 11.1

Orange juice was aseptically filled into hermetically sealed glass jars and laminated plastic/alufoil/paperboard cartons and held at 25°C. The extent of browning (expressed as optical density [OD] at 420 nm) measured over a period of weeks gave the following results:

	Browning (OD at 420 nm)	
Time (Days)	Carton	Jar
0	0.100	0.100
10	0.123	0.114
20	0.147	0.127
30	0.171	0.141
40	0.195	0.155

Analyze the data to see if the browning reaction follows a pseudo zero-order reaction, and calculate the shelf life of juice in the two containers if the juice is unacceptable when browning exceeded 0.250 OD.

This problem involves an increase in product (browning) with time, so Equation 11.5 is appropriate; this can be integrated for $n = 0$ to give

$$k = \frac{B - B_o}{\theta}$$

Carton	Jar
At $\theta = 40$ days,	
$k = \frac{(0.195 - 0.100)}{40}$	$k = \frac{(0.155 - 0.100)}{40}$
$= 2.38 \times 10^{-3}$ OD days^{-1}	$= 1.38 \times 10^{-3}$ OD days^{-1}
At $\theta = 20$ days,	
$k = \frac{(0.147 - 0.100)}{20}$	$k = \frac{(0.127 - 0.100)}{20}$
$= 2.38 \times 10^{-3}$ OD days^{-1}	$= 1.35 \times 10^{-3}$ OD days^{-1}

Because the rate constants for juice in each type of container agree closely after two time periods, there is some justification in treating the reaction as pseudo zero-order.

To calculate the shelf life of the juice, the following form of the aforementioned equation is appropriate:

$$\theta = \frac{B - B_o}{k}$$

Carton	Jar
$\theta = \frac{(0.25 - 0.10)}{2.365 \times 10^{-3}}$	$\theta = \frac{(0.25 - 0.10)}{1.365 \times 10^{-3}}$
$= 63$ days	$= 109$ days

Thus using these data, the shelf life of the orange juice packaged in a glass jar is 46 days longer than juice packaged in a laminated carton.

11.3.2 First-Order Reactions

In general, foods that do not follow a pseudo zero-order reaction deteriorate according to a pseudo first-order ($n = 1$) reaction in which the rate of loss is dependent on the amount left. In this case, the solution of Equation 11.4 for $n = 1$ is

$$\int_{A_0}^{A} \frac{dA}{A} = -k \int_{0}^{\theta} d\theta \tag{11.11}$$

and

$$\ln \frac{A}{A_o} = -k\theta \tag{11.12}$$

(where ln = natural logarithm) or

$$\ln A = \ln A_o - k\theta \tag{11.13}$$

or

$$A = A_o e^{-k\theta} \tag{11.14}$$

or

$$A_e = A_o e^{-k\theta s} \tag{11.15}$$

A plot of first-order data as the concentration of A versus time gives a curved line as shown in Figure 11.2. However, if the data are plotted as the base 10 logarithm of A versus time, a straight line is obtained, the slope of which is equal to $-k/2.303$. The unit of k for a first-order reaction is [time^{-1}].

Typical pseudo first-order deteriorative reactions include NEB (e.g., loss of protein quality in dry foods), lipid oxidation (e.g., development of rancidity in salad oils and dry vegetables), vitamin loss in canned and dry foods and microbial production of off-flavors and slime in flesh foods.

Example 11.2

Lemon juice at a concentration of 9° Brix is stored at 10°C and the concentration of ascorbic acid measured over a period of weeks to give the following results:

Time (Weeks)	Ascorbic Acid (mg 100 mL^{-1})
0	52.9
4	45.1
8	38.3
12	32.9
16	26.7

Determine the rate constant for the loss of ascorbic acid assuming that the reaction is pseudo first-order and calculate the time for the ascorbic acid concentration in the juice to reach 20 mg 100 mL^{-1}.

From Equation 11.13,

$$k = \frac{(\ln A_o - \ln A)}{\theta}$$

After 16 weeks,

$$k = \frac{(\ln 52.9 - \ln 26.7)}{16} = 0.043 \text{ weeks}^{-1}$$

After 8 weeks,

$$k = \frac{(\ln 52.9 - \ln 38.3)}{8} = 0.040 \text{ weeks}^{-1}$$

To calculate the shelf life of the lemon juice,

$$\theta_s = \frac{(\ln A_o - \ln A_e)}{k} = \frac{(\ln 52.9 - \ln 20)}{0.0415} = 23 \text{ weeks}$$

Thus, the concentration of ascorbic acid will have fallen to 20 mg 100 mL^{-1} after 23 weeks at 10°C.

11.3.3 Microbial Growth and Destruction

11.3.3.1 Microbial Growth

Microbial growth has been described by a variety of mathematical models. Their properties and how well they fit and predict experimental growth data are discussed in numerous research articles, reviews and book chapters (e.g., van Boekel, 2009; Peleg and Corradini, 2011).

During the exponential (or logarithmic) growth phase, a microbial culture mimics a first-order chemical reaction, i.e., the rate of increase in cells is proportional to the number of microbes present at that time. Therefore, Equation 11.12 can be rewritten in the form

$$\ln \frac{A}{A_o} = \mu_{max}\theta_{doub} \tag{11.16}$$

where

A_o is the initial number of microorganisms when $\theta = 0$
$A = 2A_o$ (i.e., the number of organisms has doubled)
μ_{max} is the maximum specific growth rate constant (analogous to k in chemical reactions)
θ_{doub} is the time for number of organisms to double (i.e. the generation or doubling time)

On substituting $2A_o$ for A,

$$\ln 2 = \mu_{max}\theta_{doub} \tag{11.17}$$

and

$$\mu_{max} = \frac{0.693}{\theta_{doub}} \tag{11.18}$$

or

$$\theta_{doub} = \frac{0.693}{\mu_{max}} \tag{11.19}$$

This enables calculation of the generation or doubling time if μ_{max} is known, or vice versa. In shelf life studies, it is of interest to know the time to reach a critical upper limit of cells. In this case, Equation 11.16 can be rewritten to include a lag time θ_{lag} as

$$\theta_s = \theta_{lag} + \frac{1}{\mu_{max}} \ln \frac{N_c}{N_o} \tag{11.20}$$

where

N_o is the initial number of microorganisms when $\theta = 0$
N_c is the critical or maximum permitted number of microorganisms
θ_s is the time for number of microorganisms to reach critical level (i.e., microbial shelf life)

Example 11.3

Beef is to be packaged in plastic film and stored at chill temperatures. The initial level of contamination of the beef immediately after packaging is 10^3 microorganisms per cm^2, and the maximum permitted level of microorganisms is 10^8. Assuming that the microorganisms are solely *Pseudomonas fluorescens*, which has a generation or doubling time of 8.5 h at 5°C, calculate the time for which the beef can be stored before the maximum permissible level of microorganisms is reached assuming no lag time.

From Equation 11.18:

$$\mu_{max} = \frac{0.693}{8.5} = 0.0815\,h^{-1}$$

Substituting into Equation 11.20,

$$\theta_s = \frac{1}{\mu_{max}} \ln \frac{N_c}{N_o} = \frac{1}{0.0815} \ln \frac{10^8}{10^3} = 141.5\,h$$

If this shelf life were insufficient, the storage temperature could be lowered. Given that the generation time at –2°C is 19 h, calculate the shelf life of the beef:

$$\mu_{max} = \frac{0.693}{19} = 0.0365\,h^{-1}$$

and

$$\theta_s = \frac{1}{0.0365} \ln \frac{10^8}{10^3} = 315.4\,h$$

If further extension of the shelf life were required, the package could be flushed with CO_2 and the new shelf life calculated, provided of course that the generation time for *Pseudomonas fluorescens* at –2°C in a CO_2 atmosphere was known.

11.3.3.2 Microbial Destruction

For the kinetics of microbial destruction by heat and irradiation, the food industry uses a modified time term—the decimal reduction time or D value. This is defined as the time at constant temperature to reduce the population of microorganisms by 90%. Mathematically, at time $\theta = D$, $A = 0.1A_o$.

Substituting into Equation 11.12,

$$\ln \frac{A_o}{0.1A_o} = kD$$

Because ln 10 = 2.303,

$$D = \frac{2.303}{k}$$

If the logarithm of the D value is plotted against the corresponding temperature, a straight line is obtained, the slope of which is designated by the term z. This can be defined as the temperature change necessary for a 10-fold change in the D value or reaction rate. Mathematically,

$$\frac{k_T}{k_{T-z}} = 10 \tag{11.21}$$

11.4 INTRINSIC FACTORS CONTROLLING THE RATES OF DETERIORATIVE REACTIONS

11.4.1 Water Activity

11.4.1.1 Definitions

Water activity (a_w) is defined as the ratio of the water vapor pressure of a material to the vapor pressure of pure water at the same temperature. Mathematically,

$$a_w = \frac{p}{p_o} \tag{11.22}$$

where

p is the vapor pressure of water exerted by the food

p_o is the saturated vapor pressure of pure water at the same temperature

This concept is related to equilibrium relative humidity (ERH) in that ERH = 100 × a_w. However, while a_w is an intrinsic property of the food, ERH is a property of the atmosphere in equilibrium with the food. As Reid and Fennema (2007) have stressed, the equality in Equation 11.22 is based on the assumption of thermodynamic equilibrium, which is generally violated with foods, and therefore the equality should be replaced with an approximation.

The a_w of most fresh foods is above 0.99. At subfreezing temperatures, a_w is defined as the vapor pressure of ice divided by the vapor pressure of supercooled water at the same temperature. Thus, the a_w of frozen foods depends only on their temperature and not their composition; at –20°C, a_w = 0.825; at –10°C, 0.905; and at –5°C, 0.953 (Reid and Fennema, 2007).

As mentioned earlier in the definition of a_w, the temperature must be specified, since a_w values are temperature dependent. The temperature dependence of a_w can be described by a modified form of the Clausius–Clapeyron equation:

$$\frac{d \ln a_w}{d(1/T)} = \frac{-\Delta H}{R} \tag{11.23}$$

or

$$\ln \frac{a_{w2}}{a_{w1}} = \frac{\Delta H}{R}\left[\frac{1}{T_1} - \frac{1}{T_2}\right] \tag{11.24}$$

where

a_{w1} is the water activity at temperature T_1 (K)

a_{w2} is the water activity at temperature T_2 (K)

ΔH is the isosteric net heat of sorption at the moisture content of the food (J mol^{-1})

R is the gas constant (8.314 J mol^{-1} K^{-1})

Thus, from Equation 11.23, a plot of ln a_w versus 1/T at constant moisture content should be linear. Such plots are not always linear over wide temperature ranges, and they exhibit sharp breaks with the onset of ice formation (Reid and Fennema, 2007).

11.4.1.2 Isotherms

When a food is placed in an environment at a constant temperature and RH, it will eventually come to equilibrium with that environment. The corresponding moisture content at steady-state is referred to as the equilibrium moisture content. When this moisture content (expressed as mass of water per unit mass of dry matter) is plotted against the corresponding RH or a_w at constant

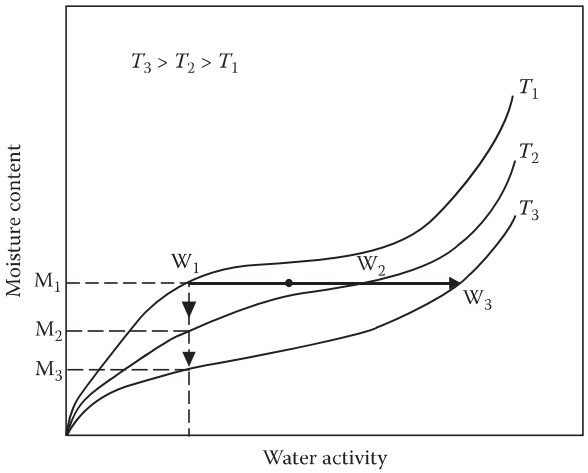

FIGURE 11.3 Schematic of a typical moisture sorption isotherm showing the effect of temperature.

temperature, a moisture sorption isotherm (MSI) is obtained (see Figure 11.3). Such plots are very useful in assessing the stability of foods and selecting effective packaging.

One complication is that a MSI prepared by the addition of water to a dry sample (resorption) will not necessarily be superimposable on an isotherm prepared by removal of water from a wet sample (desorption). This lack of superimposability is referred to as *hysteresis*. Typically, at any given a_w, the water content of the food will be greater during desorption than during resorption. This has important implications with respect to food stability, in that foods adjusted to the desired a_w by desorption rather than resorption may deteriorate more rapidly because of their higher moisture content.

Another complication occurs with some sugars. Crystalline sugars generally have completely different MSIs from those for amorphous sugars, where the equilibrium moisture content is much lower for the crystalline form at any particular a_w. The amorphous form is often present when the food has been dried quickly (e.g., spray drying of milk often results in the formation of amorphous lactose); during storage, it may slowly revert to the crystalline form. This results in a distinct break in the MSI, because the sugar releases moisture at constant a_w (see Figure 19.5).

Because a_w is temperature dependent, it follows that MSIs must also exhibit temperature dependence. Thus, at any given moisture content, a_w increases with increasing temperature, in agreement with the Clausius–Clapeyron equation (Equation 11.23) and shown in exaggerated form for illustrative purposes in Figure 11.3. This can have large consequences for the stability of the food when it is subjected to temperature fluctuations.

Many relationships have been derived relating the a_w of a food to its moisture content and a comprehensive review of the most widely used models has been presented by Basu et al. (2006). For many years, the most used relationship for food was the Brunauer–Emmett–Teller (BET) Type 2 sigmoid isotherm which took the form

$$\frac{m}{m_o} = \frac{C_b a_w}{(1-a_w)(1+C_b a_w - a_w)} \tag{11.25}$$

or

$$\frac{a_w}{m(1-a_w)} = \frac{1}{m_o C_b} + \frac{C_b - 1}{m_o C_b} a_w \tag{11.26}$$

where

m is the moisture content (dry weight basis) at water activity a_w

m_o is the moisture content of the monolayer (dry weight basis)

C_b is a dimensionless parameter related to the heat of sorption of the monolayer region

The BET equation gives a good fit for a variety of foods over the region $0.05 < a_w < 0.45$. It has also been used to estimate the monolayer value, which is equivalent to the amount of water held adsorbed on specific sites. For many foods, the monolayer value corresponds to an a_w of 0.2–0.4. A monolayer does not mean coverage of all dry matter with a closely packed, single layer of water molecules. Rather, the monolayer value should be regarded as the maximum amount of water that can be strongly bound to the dry matter. Recently, Caurie (2011) identified three types of bound water at room temperature and suggested that a food is more stable the smaller the ratio of its type III to type II bound water molecules.

The Guggenheim-Anderson-de Boer (GAB) model has been widely used by European food researchers since the late 1970s, and has now gained worldwide acceptance. It is a three-parameter model with physically meaningful coefficients, which usually fits data very well up to 0.9 a_w. The model is

$$\frac{m}{m_o} = \frac{C_g K a_w}{(1 - K a_w)(1 + C_g K a_w - K a_w)} \tag{11.27}$$

where

m is the moisture content (dry weight basis) at water activity a_w
m_o is the moisture content corresponding to saturation of all primary adsorption sites by one water molecule (equivalent to the BET monolayer)
C_g is the dimensionless GAB parameter related to the heat of sorption of the monolayer region and often referred to as the Guggenheim constant
K is the dimensionless GAB parameter related to the heat of sorption of the multilayer region

Parameters C and K can be represented by Arrhenius-type equations:

$$C = \frac{C_0 \exp(H_m - H_q)}{RT} \tag{11.28}$$

where

H_m is the total heat of sorption of the monolayer
H_q is the total heat of sorption of the multilayer covering the monolayer

and

$$K = \frac{K_0 \exp(H_1 - H_q)}{RT} \tag{11.29}$$

where

H_1 is the heat of condensation of water vapor at the given temperature
C_0 and K_0 are adjusted constants for the temperature effect

This model can be considered as an extension of the BET model, taking into account the modified properties of the sorbed water in the multilayer region; when $K = 1$, the GAB model reverts to the BET model. The real advantage of the GAB model is that it offers an objective method for fitting sorption isotherm data for a majority of foods up to 0.9 a_w. To fit data, the GAB model can be transformed into a quadratic equation to obtain coefficients α, β and γ, from which the

GAB constants (m_o, C_g and K) can be calculated by direct nonlinear regression (Samaniego-Esguerra et al., 1991):

$$\frac{a_w}{m} = \alpha a_w^2 + \beta a_w + \gamma \tag{11.30}$$

where

$\alpha = (K/m_o)(1/C_g - 1)$
$\beta = (1 - 2/C_g)/m_o$
$\gamma = 1/(m_o C_g K)$

and the solution is

$$K = \frac{\sqrt{\beta^2 - 4\alpha\gamma} - \beta}{2\gamma}$$

$$C_g = \frac{\beta}{\gamma K} + 2$$

$$m_o = \frac{1}{\gamma K C_g}$$

The final choice of model will depend on a compromise between the desired closeness of fit and convenience with regard to the number of parameters involved and their calculation.

11.4.1.3 Water Activity and Food Stability

Water may influence chemical reactivity in different ways. It may act as a reactant (e.g., in the case of sucrose hydrolysis) or as a solvent, where it may exert a dilution effect on the substrates, thus decreasing the reaction rate. Water may also change the mobility of the reactants by affecting the viscosity of the food systems and form hydrogen bonds or complexes with the reacting species. Thus, a very important practical aspect of a_w is to control undesirable chemical, enzymic and microbial reactions that reduce the shelf life of foods. It is a well-known generality that rates of changes in food properties can be minimized or accelerated over widely different values of a_w, as the so-called food stability map shown in Figure 11.4 demonstrates. Small changes in a_w can result in large changes in reaction rates.

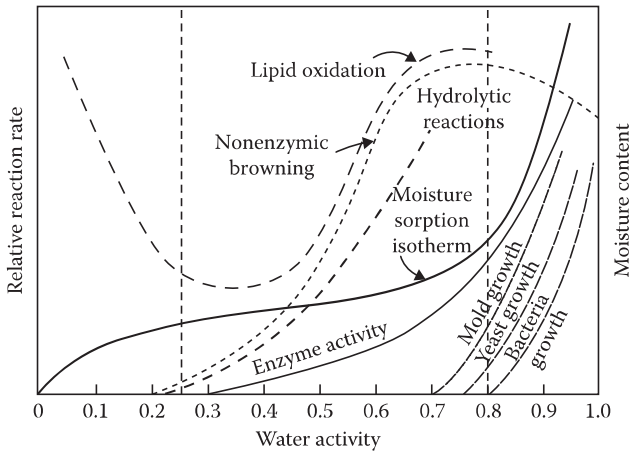

FIGURE 11.4 Relative rates of reactions and microbial growth as a function of water activity. (From Rockland, L.B. and Beuchat, L.R. (Eds), *Water Activity: Theory and Applications to Food*, Marcel Dekker, New York, 1987.)

11.4.1.3.1 Lipids

The influence of a_w on lipid oxidation has been studied extensively, mainly with the use of model systems. The general effect of a_w on lipid oxidation is shown in Figure 11.4. At very low a_w levels, foods containing unsaturated fats and exposed to atmospheric O_2 are highly susceptible to the development of oxidative rancidity. This high oxidative activity occurs at a_w levels below the monolayer level, and as a_w increases, both the rate and the extent of autoxidation decrease until an a_w in the range of 0.3–0.5 is reached. Above this point, the rate of oxidation increases until a steady-state is reached, normally at a_w levels in excess of 0.75. At a_w*s* below the monolayer value, the oxidation rate decreases with increasing a_w. The rate reaches a minimum around the monolayer value and increases with further increases in a_w. Water may influence lipid oxidation by influencing the concentrations of initiating radicals present, the degree of contact and mobility of reactants and the relative importance of radical transfer versus recombination reactions.

11.4.1.3.2 Browning

Water may accelerate browning by imparting mobility to the substrates, or it may decrease the browning rate by diluting the reactive species. In the low a_w range, the mobility factor predominates, whereas the dilution factor predominates in the high a_w range. As a consequence, browning rate generally increases with increasing a_w at low moisture content, reaches a maximum at a_ws of 0.7–0.8, and decreases with further increase in a_w (see Figure 11.4).

11.4.1.3.3 Vitamins

The rate of degradation of vitamins A, B_1, B_2 and C increases as a_w increases over the range 0.24–0.65. Generally, the rate of ascorbic acid degradation increases exponentially with increase in a_w. The photodegradation of riboflavin has been shown to increase with increasing a_w.

11.4.1.3.4 Enzymes

Near or below the monolayer a_w value, enzyme activities are generally minimized or cease. Above the monolayer value, enzyme activity increases with increasing a_w or increased substrate mobility, as illustrated in Figure 11.4. Substrates of high molecular weight (MW) such as protein and starch are less mobile than low MW substrates such as glucose, and generally the latter have a lower a_w threshold for enzyme activity. At subfreezing temperatures, the reaction rate generally decreases with decreasing temperature and a_w, owing partly to the lower temperature, partly to the increase in viscosity of the partially frozen system, and partly to enzyme denaturation.

11.4.1.3.5 Pigments

Carotenoids are subject to changes due to heating and both enzymic and nonenzymic oxidation, all of which are influenced by water. Water appears to have a protective effect on oxidative degradation, apparently by reducing the free radical content. Values of a_w above the monolayer (up to a_w of 0.41) give almost complete protection against oxidative degradation.

Water activity has a definite influence on the rate of chlorophyll degradation, with the rate decreasing with a decrease in a_w. The color of anthocyanins increases in intensity as a_w is lowered.

11.4.1.3.6 Texture

In the case of sugars, changes in a_w may either inhibit or promote a physical change in the nature of the sugar, which, in turn, affects the texture. A low a_w maintains the sugar in the form of a glassy, amorphous, free-flowing powder, whereas an increase in a_w promotes crystallization resulting in a sticky, caking powder, which has a much lower moisture content than the amorphous sugar.

The sensory crispness of starch-based dried foods decreases with increasing a_w and become unacceptable when $a_w > 0.35–0.50$ for crisp snack foods such as chips, saltine crackers and pop corn, $a_w > 0.44$ for puffed rice cakes and $a_w > 0.28–0.55$ for breakfast cereals.

11.4.1.3.7 Microbial

Every microorganism has a limiting a_w value below which it will not grow, form spores or produce toxic metabolites. Table 11.8 lists the range of a_ws that permit the growth of various common microorganisms, together with common foods categorized according to their a_w. Certain relationships have been shown to exist between a_w, temperature and nutrition (Jay et al., 2007). First, at any temperature, the ability of microorganisms to grow is reduced as a_w is lowered. Second, the range of a_w over which growth occurs is greatest at the optimum temperature for growth; third, the presence of nutrients increases the range of a_w over which the organisms can survive. Therefore, the values given in Table 11.8 should be taken only as a guide.

Water activity can influence each of the four main growth cycle phases by its effect on the germination time, the length of the lag phase, the growth rate phase, the size of the stationary population and the subsequent death rate. Generally, reducing the a_w of a given food increases the lag period and decreases the growth rate during the logarithmic phase, the maximum of which becomes lower.

TABLE 11.8
Water Activity and Growth of Microorganisms in Food at Different Water Activities (a_w)

Range	Microorganisms Generally Inhibited by Lowest a_w of the Range	Foods Generally within This Range of a_w
1.00–0.95	*Pseudomonas*, *Escherichia*, *Proteus*, *Shigella*, *Klebsiella*, *Bacillus*, *Clostrium perfringens*, some yeasts	Highly perishable (fresh) foods and canned fruits, vegetables, meat, fish and milk; cooked sausages and breads; foods containing up to approximately 40% (w/w) sucrose or 7% sodium chloride
0.95–0.91	*Salmonella, Vibrio parahaemolyticus*, *C. botulinum, Serratia, Lactobacillus Pediococcus*, some molds, yeasts	Some cheeses (Cheddar, Swiss, Muenster, Provolone), cured meats (ham), some fruit juice concentrates; foods containing 55% (w/w) sucrose or 12% sodium chloride
0.91–0.87	Many yeasts (*Candida*, *Torulopsis*, *Hansenula*), *Micrococcus*	Fermented sausages (salami), sponge cakes, dry cheeses, margarine; foods containing up to 65% (w/w) sucrose (saturated) or 15% sodium chloride
0.87–0.80	Most molds (mycotoxigenic penicillia), *Staphylococcus aureus*, most *Saccharomyces* (*bailii*) spp., *Debaryomyces*	Most fruit juice concentrates, sweetened condensed milk, chocolate, syrup, maple and fruit syrups; flour, rice, pulses of 15%–17% moisture content; fruit cake, country-style ham, fondants, high-ratio cakes
0.80–0.75	Most halophilic bacteria, mycotoxigenic aspergilli	Jam, marmalade, marzipan, glacéd fruits, some marsh mellows
0.75–0.65	Xerophilic molds (*Aspergillus chevalieri*, *A. candidus*, *Wallemia sebi*), *Saccharomyces bisporus*	Rolled oats of 10% moisture content, grained nougats, fudge, marshmallows, jelly, molasses, raw cane sugar, some dried fruits, nuts
0.65–0.60	Osmophilic yeasts (*Saccharomyces rouxii*), few molds (*Aspergillus echinulatus*, *Monascus bisporus*)	Dried fruits containing 15–20% moisture content, some toffees and caramels; honey
0.60–0.50	No microbial proliferation	Pasta of 12% moisture content; spices of 10% moisture content
0.50–0.40	No microbial proliferation	Whole egg powder of 5% moisture content
0.40–0.30	No microbial proliferation	Cookies, crackers, bread crusts, and so forth of 3%–5% moisture content
0.30–0.20	No microbial proliferation	Whole milk powder of 2%–3% moisture content, dried vegetables of 5% moisture content; corn flakes of 5% moisture content

Source: Adapted from Beuchat, L., *Cereal Foods World*, 26, 345, 1981.

Sporulation may occur at slightly below the minimum a_w for growth. In contrast, germination of spores of some microorganisms may occur at a_w values below that required for growth. The minimum a_w for growth of microorganisms is, without exception, less than or equal to the minimum a_w for toxin production. Optimal conditions of temperature, pH, O_2 tension and nutrient availability are necessary to permit sporulation, germination and toxin production at reduced a_w.

Whether a microorganism survives or dies in a low a_w environment is influenced by intrinsic factors that are also responsible for its growth at a higher a_w. These factors include water-binding properties, nutritive potential, pH, E_h and the presence of antimicrobial compounds. The influences exerted by these factors interact with a_w both singularly and in combination. Microbial growth and survival are not entirely ascribed to reduced a_w, but also to the nature of the solute. However, the exact nature of the role that water plays in the mechanism of cell survival is not clearly understood.

Key extrinsic factors relative to a_w that influence microbial deterioration in foods include temperature, O_2 and chemical treatments. These factors can all combine in a complex way to either encourage or discourage microbial growth.

11.4.2 Oxidation-Reduction Potential

The oxidation-reduction potential (also referred to as the redox potential and abbreviated E_h or ORP) of a substrate may be defined as the ease with which the substrate loses or gains electrons. The more highly oxidized a substance, the more positive will be its electrical potential. It is a physicochemical parameter that determines the oxidizing or reducing properties of the food and depends on the composition of the food, pH, temperature, and for a large part, the concentration of dissolved O_2 (DO). Among the substances in foods that help to maintain reducing conditions are the sulfhydryl groups on proteins, and ascorbic acid and reducing sugars in fruits and vegetables. Deteriorative chemical reactions can alter the E_h value of foods during storage.

E_h plays an important role in the cellular physiology of microorganisms such as growth capacity, enzyme expression and thermal resistance. Aerobic microorganisms require positive E_h values (oxidized) for growth while anaerobes require negative E_h values (Jay et al., 2007). Alwazeer et al. (2003) demonstrated that reducing the E_h of orange juice by gas (N_2 and H_2) immediately after heat treatment maximized microbial destruction during pasteurization, prevented the development of microorganisms and stabilized color and ascorbic acid during storage at 15°C.

The relationship between E_h and DO levels in milk is not well-understood. Several modifications that occur in milk during its processing and storage are driven by different oxidation-reduction reactions. Electrolysis treatments have been applied to milk to produce milk powder with better flavor quality. E_h and DO levels in enriched milk are mainly responsible for the oxidation of unsaturated fatty acids and the loss of viability of probiotic strains such as bifidobacteria. Decreasing the E_h in milk could allow an improvement in the quality of these products. Recent studies on electroreduction of milk by membrane electrolysis have shown that this electrochemical process decreased the E_h of milk without changing the organoleptic and nutritive values (Schreyer et al., 2008).

11.5 EXTRINSIC FACTORS CONTROLLING THE RATES OF DETERIORATIVE REACTIONS

11.5.1 Temperature

Temperature is a key factor in determining the rate of deteriorative reactions, and in certain situations, the packaging material can affect the temperature of the food. This is particularly so with packaging materials which have insulating properties, and these types of packages are typically used for chilled and frozen foods. For packages that are stored in refrigerated display cabinets, most of the cooling takes place by conduction and convection. Simultaneously, there is a heat input by radiation from the fluorescent lamps used for lighting. Under these conditions, aluminum foil offers

real advantages because of its high reflectivity (low emissivity) and high conductivity. However, such advantages are seldom used in the packaging of frozen and chilled foods. Recently, Davies et al. (2012) reported the potential of modern, low emissivity food packaging materials to improve the energy efficiency of open display refrigeration cabinets by up to 30% as a result of operating up to 10°C higher with no loss in food quality.

11.5.1.1 Linear Model

Early studies on the thermal processing of foods obtained a straight line when the thermal death times (now D values or the time for a 90% reduction in numbers) of microorganisms were plotted against temperature on a linear scale. The equation of such a curve is

$$\log\left(\frac{D_1}{D_2}\right) = \frac{(T_1 - T_2)}{z} \tag{11.31}$$

where z is the temperature change required to change the D value by a factor of 10.

For many microorganisms of interest in food canning, z = 10°C, whereas for degradation of quality factors during thermal processing, z = 32°C. Reactions that have small z values are highly temperature dependent, whereas reactions with large z values are less influenced by temperature. This model has been found to be satisfactory for thermal processes and is still in use today. In its more general form it can be written as shown below because $k \propto D$:

$$k = k_r 10^{(T - T_r)/z} \tag{11.32}$$

A similar expression relating the rate of reactions and temperature has also been used for many years, especially in relation to shelf life plots (see Chapter 12):

$$k = k_o e^{b(T - T_o)} \tag{11.33}$$

where

k_o is the rate at temperature T_o (°C)
k is the rate at temperature T (°C)
b is a constant characteristic of the reaction
e = 2.7183

11.5.1.2 Arrhenius Relationship

The most common and generally valid relationship for the effect of temperature on the rate of deterioration is that of Arrhenius. The relationship is correctly expressed in the differential form:

$$\frac{d(\ln k)}{dT} = \frac{E_A}{RT^2} \tag{11.34}$$

For practical reasons the integrated form is used:

$$k = k_o e^{-E_A/RT} \tag{11.35}$$

where

k is the rate constant for deteriorative reaction
k_o is a constant, independent of temperature (also known as the Arrhenius, pre-exponential, collision or frequency factor)
E_A is the activation energy (J mol^{-1})
R is the ideal gas constant (8.314 J K^{-1} mol^{-1} = 1.987 cal K^{-1} mol^{-1})
T is the absolute temperature (K)

TABLE 11.9
Typical Activation Energies for Reactions Important in Food Deterioration

Reaction	Activation Energy (E_A) (kJ mol^{-1})
Diffusion-controlled reaction	8–40
Lipid oxidation	40–105
Flavor degradation in dry vegetables	40–105
Enzymic reactions	40–130
Hydrolysis	60–110
Vitamin degradation	85–130
Color degradation in dry vegetables	65–150
Nonenzymic browning	105–210
Microbial growth	85–250
Protein denaturation	350–700

The integrated relationship contains the inherent assumption that the activation energy and the pre-exponential factor do not change with temperature. This assumption is generally, but not universally, true. Therefore, predictions based on this model sometimes fail when applied over a temperature range of greater than about 40°C. Furthermore, when the reaction mechanism changes with temperature, the activation energy may vary substantially. The value of E_A is a measure of the temperature sensitivity of the reaction; that is, how much faster the reaction will proceed if the temperature is raised. Typical activation energies for reactions important in food deterioration are listed in Table 11.9.

The activation energy is generally derived from the slope of the plot of ln k versus $1/T$ and depends on factors such as a_w, moisture content, solids concentration and pH.

11.5.1.3 Temperature Quotient

Another term used to describe the response of biological systems to temperature change is the Q value, a quotient indicating how much more rapidly the reaction proceeds at temperature T_2 than at a lower temperature T_1. If Q reflects the change in rate for a 10°C rise in temperature, it is then called Q_{10}. Mathematically,

$$Q_{10} = \frac{k_{T+10}}{k_T} \tag{11.36}$$

When the Fahrenheit temperature scale is used instead of the Celsius scale, the symbol q_{10} is used. The relationship between Q_{10} and q_{10} is

$$Q_{10} = (q_{10})^{1.8} \tag{11.37}$$

It can be shown that the rate of a deteriorative reaction at two temperatures is related to the shelf life at those two temperatures:

$$k_T \theta_{s_T} = k_{T+10} \theta_{s_{T+10}} \tag{11.38}$$

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

Therefore,

$$Q_{10} = \frac{\theta_{s_T}}{\theta_{s_{T+10}}} \tag{11.39}$$

For any temperature difference Δ which is not 10°C:

$$Q_{10}^{\Delta/10} = \frac{\theta_{s_{T1}}}{\theta_{s_{T2}}} \tag{11.40}$$

It can be shown when the Arrhenius model is used that

$$\ln Q_{10} = \frac{10E_A}{RT(T+10)} \approx \frac{10E_A}{RT^2} \tag{11.41}$$

or

$$Q_{10} \approx \exp\frac{10E_A}{RT^2} \tag{11.42}$$

and when the linear model is used:

$$\ln Q_{10} = 10b \tag{11.43}$$

or

$$Q_{10} = e^{10b} \tag{11.44}$$

Note that Q_{10} is not constant but depends on both the E_A and the temperature, whereas E_A is assumed to be independent of temperature.

It can also be shown that

$$\frac{E_A}{RT^2} = \frac{\ln 10}{z} = \frac{2.3}{z} \tag{11.45}$$

By combining Equation 11.41 and Equation 11.45, it can be shown that

$$z = \frac{10}{\ln Q_{10}} \tag{11.46}$$

Example 11.4

The pseudo zero-order rate constant for the degradation of ascorbic acid in dried vegetables packaged in a PET-LDPE laminate pouch is 0.0745 mg 100 g^{-1} $week^{-1}$ when stored at 30°C, and 0.0255 mg 100 g^{-1} $week^{-1}$ when stored at 20°C. What is the Q_{10} and activation energy for the reaction?

From Equation 11.36,

$$Q_{10} = \frac{k_{T+10}}{k_r} = \frac{0.0745}{0.0255} = 2.92$$

From Equation 11.41,

$$\ln 2.92 = \frac{10E_A}{8.314 \times 293 \times 303}$$

$$\therefore E_A = 79.1 \text{ kJ mol}^{-1}\text{K}^{-1}$$

11.5.1.4 Bělerádek Function

Because it is not a simple chemical reaction, the temperature dependence of microbial growth cannot be described by the Arrhenius relationship. If an Arrhenius plot of microbial growth is made, it is frequently nonlinear (van Boekel, 2009). Therefore, empirical models are used. A function which has been employed to predict the rate of microbial growth in a range of chilled flesh foods (particularly fresh fish) was first suggested by Bělerádek in the form:

$$k = a(T - \alpha)^d \tag{11.47}$$

where

k is the reciprocal of the time required to reach a specified amount of a metabolite or the specific growth rate constant of a bacterial population
T is the absolute temperature
a, α and d are constants fitted to the particular system under study

In some applications, the constant α is referred to as the "biological zero," a hypothetical temperature at which the growth rate is zero or the reaction time infinite. The exponent d has been found to be two for bacterial growth.

A particular case of the Bělerádek function was developed to describe the growth of bacteria at a fixed pH and a_w; the relationship is usually expressed in the form:

$$\sqrt{k} = b_1(T - T_{\min}) \tag{11.48}$$

or

$$\mu_{\max} = [b_1(T - T_{\min})]^2 \tag{11.49}$$

where

$\mu_{\max}$ is the maximum specific growth rate constant (time^{-1})
$T_{\min}$ is the temperature at which growth ceases
b is a regression coefficient

Equation 11.49 (also referred to as the Ratkowsky square root model) has been widely accepted in predictive microbiology and was later expanded to account for the maximum temperature at which the growth rate peaks:

$$\mu_{\max} = \left\{b_2(T - T_{\min})(1 - \exp[c_2(T - T_{\max})])\right\}^2 \tag{11.50}$$

where

$T_{\min}$ and $T_{\max}$ are minimum and maximum temperatures for growth
b_2 and c_2 are constants

11.5.2 Gas Atmosphere

Atmospheric O_2 generally has a detrimental effect on the nutritive quality of foods, and it is therefore desirable to maintain many types of foods at a low O_2 tension, or at least prevent a continuous supply of O_2 into the package. Lipid oxidation causes the formation of hydroperoxides, peroxides and epoxides, which, in turn, will oxidize or otherwise react with carotenoids, tocopherols and ascorbic acid to cause loss of vitamin activity. The decomposition of hydroperoxides to reactive

carbonyl compounds could lead to losses of other vitamins, particularly thiamine, some forms of B_6 and pantothenic acid (Gregory, 2007). The destruction of other oxidizable vitamins such as folic acid, B_{12}, biotin and vitamin D is also likely.

Changes in the gas atmosphere of packaged foods depend largely on the nature of the package. Correctly sealed metal and glass containers effectively prevent the interchange of gases between the food and the atmosphere. With plastic packaging, however, the diffusion of gases depends not only on the effectiveness of the closure but also on the permeability of the packaging material, which is a function of the physicochemical structure of the barrier. The gas permeabilities of the common thermoplastic packaging materials were given in Table 4.3.

The gas atmosphere inside food packages is often modified prior to closing by pulling a vacuum and removing most of the gases present, or by flushing the headspace area inside the package with an inert gas such as N_2 or CO_2. These procedures are generally referred to as MAP and are becoming increasing important, especially with the packaging of fresh fruits and vegetables, flesh foods and bakery products. Details of the actual procedures used and their effect on product shelf lives are discussed later in Chapter 16.

11.5.3 Light

Many of the deteriorative changes in the quality of foods are initiated or accelerated by light (Andersen and Skibsted, 2010). Light is essentially an electromagnetic vibration in the range between 400 and 700 nm. Each color is represented by a specific wavelength: violet is in the area of 400 nm, blue and green are in the middle of the visible spectrum, and red is in the area of 700 nm. The wavelength of UV light ranges between 200 and 400 nm. The catalytic effects of light are most pronounced in the lower wavelengths of the visible spectrum and in the UV spectrum. The intensity of light and the length of exposure are significant factors in the production of discoloration and flavor defects in packaged foods.

The total amount of light absorbed by a packaged food can be calculated using the following formula (Fellows, 2009):

$$I_a = I_i T_p \frac{1 - R_f}{(1 - R_f) R_p} \tag{11.51}$$

where

I_a is the intensity of light absorbed by the food
I_i is the intensity of incident light
T_p is the fractional transmission by the packaging material
R_p is the fraction reflected by the packaging material
R_f is the fraction reflected by the food

The fraction of the incident light transmitted by any given material can be considered to follow the Beer–Lambert law:

$$I_t = I_i e^{-\alpha x} \tag{11.52}$$

where

I_t is the intensity of light transmitted by the packaging material
α is the characteristic absorbance of the packaging material
x is the thickness of the packaging material

The absorbance α varies not only with the nature of the packaging material but also with the wavelength. Thus, the amount of light transmitted through a given package will be dependent on the incident light and the properties of the packaging material. Some materials (e.g., LDPE) transmit both

visible and UV light to a similar extent, whereas others (e.g., PVC) transmit visible light but absorb UV light. Not all of the light that strikes the surface of a food is absorbed and available to induce chemical reactions in the food. The surface absorption spectrum determines which wavelengths are absorbed and how efficiently they are absorbed. The remaining light is reflected by the surface, and the spectral distribution of the reflected light determines the color of the food as perceived by the human eye (Andersen and Skibsted, 2010).

Modification of plastic materials may be achieved by incorporation of dyes or application of coatings, which absorb light at specific wavelengths. A new coating containing nanoparticles of TiO_2 that is applied to the outside of plastic packaging protects products from both UVA (320–400 nm) and UVB (290–320 nm) radiation. Although it provides over 50% more total integrated UV absorbance than commonly used organic UV absorbers on an equal weight basis, it does impart a translucent appearance to the plastic. Glasses are frequently modified by inclusion of color-producing agents or by application of coatings. In this way, a wide range of light transmission characteristics can be achieved in packages made of the same basic material.

The catalytic effect of light on the free radical reactions involved in fat oxidation is well established; such oxidation is effective not only in lowering the nutritional value of the fat, but also in producing toxic compounds from the fats and oils and destroying fat-soluble vitamins, in particular vitamins A and E.

There have been many studies demonstrating the effect of packaging materials with different light screening properties on the rate of deteriorative reactions in foods. One of the most commonly studied foods has been fluid milk, and the extent of off-flavor development is related to the exposure interval, strength of light and surface area of milk exposed. Many researchers have shown that exposure to visible light between 365 and 500 nm causes a significant increase in light-induced oxidation in milk. All wavelengths below 620 nm must be blocked to prevent "sunlight" flavor in milk.

Smet et al. (2009) reported that for light-induced oxidation in milk, riboflavin was the key factor since it is an excellent photosensitizer, resulting in the production of reactive oxygen species that can catalyze oxidation reactions. The presence of light was strongly detrimental to the oxidative stability of stored milk, observed by degradation of riboflavin. During the first days of illuminated storage, hydrophilic antioxidants present in the milk serum were consumed, followed by degradation of α-tocopherol. When all these antioxidants were depleted, lipid and protein oxidation products were formed.

In summary, light plays an important role in the deterioration of nutrients. Suitable packaging can offer direct protection by absorption or reflection of all or part of the incident light, depending on the light transmission characteristics of the packaging materials. Several plastic packaging materials, while transmitting similar amounts of light in the visible range, give varying degrees of protection against damaging UV wavelengths. These materials are often characterized by a cut-off wavelength below which transmission of light becomes negligible.

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