Chapter 7

Food Preservation and Shelf Life

Introduction

The problem of preserving food and keeping its nutrients intact for long periods of time is an essential feature of cultures that have to cope with periods, whether seasonal or situational, where crops cannot be continuously produced or foraging cannot be continuously productive. Food preservation methods are as varied as the cultures, climates, and dietary habits that produce them, but most have common features. Indigenous cultures from the poles to the equator have relied on simple drying, smoking, salting, and pickling techniques for millennia, and many of these types of preservation methods have been reincorporated into the palates of various cultures. For other cultures, typically situated in warm climates, the nearly constant availability of fresh foods has shaped their dietary habits, and as those cultures have become more globally dispersed, the demand for high-quality fresh products has increased and created new challenges for fresh-food preservation.

As nations grew and sought global dominance, the saying that "armies (and navies) travel on their stomachs" became a limiting factor in the speed and effectiveness of military units, particularly where armies were large enough and scavenging insufficient enough to cause whole campaigns to fail. The limitations on traditional methods of food preservation were challenged by the requirements of global empires that could no longer depend on indigenous food supplies, particularly when retreating armies learned to destroy any useful materials or food as they traveled.

These needs began to be met by the development of ad hoc methods of bottled food preservation by Nicholas Appert in Napoleonic-era France, and the immediate adoption of the metal-can-based equivalent by their usual adversary, the understandably worried British Navy. With the subsequent understanding of the microbial processes involved in food spoilage by Louis Pasteur and others, food preservation not only allowed small groups of people to survive winters and to travel, but it became possible to merge the industrial revolution, changes in the productivity of the agrarian economy, and a burgeoning world trade into a system that is the ancestor of our current food preservation and distribution system. Much as the primitive preservation methods created distinct lifestyle changes for early people, these new processes allowed not only a continued food supply but the creation of previously unheard-of products.

Thermal processing was the first step, but was not well suited to large products; fitting an entire side of beef into a can would be a daunting task (or a very big can), but Henri Nestlé developed a canned infant formula in 1867 that was being distributed worldwide within five years, and the modern version continues to be sold today, as is James Kraft's thermally pasteurized cheese. Frozen foods, shown to be a viable method of preservation in the 1800s

Food and Package Engineering, First Edition. Scott A. Morris.

as various methods of refrigeration were being experimented with, added another dimension to food distribution, allowing the distribution of frozen and chilled meats and vegetables on a grand scale. The development of vapor-compression refrigeration systems in the 1800s, despite opposition from well-placed natural-ice interests, furthered this process by allowing frozen food to travel great distances. In 1876, the French successfully shipped chilled meat from South America to France using ether-evaporation refrigeration and again in 1878, a shipment of frozen meat was shipped from Argentina to Le Havre using ammonia-based vapor compression refrigeration. By 1881, after several false starts, the dinner tables of Great Britain (and the economy of Australia) were enjoying frozen mutton that had been shipped halfway around the world with shipments exceeding 51,000 tons by 1900. This capacity for storage has been multiplied by the ubiquitous presence of (relatively) small domestic refrigerators in homes in developed countries, allowing chilled and frozen foods to be stored for long periods of time.

The ongoing search for improved preservation methods that are more efficient and cost effective have yielded some newer technologies such as irradiation and HTST/UHT processing, as well as newer combined technologies such as aseptic processing and packaging systems and *sous vide* distribution. As mentioned in the previous chapter, other methods using ultrasound, light, and electrical discharge may show some promise for use in specific processing applications, and will be highly dependent on the barrier properties of packaging to keep products in useable shape. In any event, the intent of all of these is to produce a product that retains as much quality as possible for as little cost as possible in order to survive the very competitive marketplace.

Further, the increased globalization of both people and the food supply have placed demands for fresh products of all types at an all-time high, paradoxically reversing the trend for preserved food and increasing demand on the transportation and logistics systems that can bring fresh flowers halfway around the world and fresh fruit around the calendar. This has resulted in the development of both very highly efficient transportation systems and several methods of extending shelf life, including controlled atmosphere (CA) storage and modified atmosphere packaging (MAP) that, when used in conjunction with (refrigeration-based) temperature controls, can keep produce, seafood, and meats in a very high-quality, near-fresh condition.

Deterioration of Food Products

To understand improved preservation processes, it is helpful to understand something of the nature of the processes that cause foods to spoil or deteriorate. Generally speaking, these can be broken down into several broad classes: microbial degradation, chemical degradation, and mechanical or rheological changes, the latter often brought on by effects of the distribution system.

Microbial degradation of food is typically prevented with preservatives, by reducing the temperature or moisture availability of the food to a point where the organisms cannot grow, or by enclosing them in a hermetically sealed package and inactivating the organisms to the point of commercial sterility as described in the previous chapter.

Chemical degradation is most often dealt with either by preventing the deleterious reactant (oxygen, for example) from contacting the product, formulating the product so that the reactions do not occur readily, or by adding a chemical preservative such as an antioxidant.

Mechanical and physical changes can be difficult to trace, often appearing as a mysterious change in viscosity or separation of ingredients in a product, as well as outright breakage, but

when they occur, they may be dealt with by changes in the product formulation or by changes in the packaging or distribution system. This will be discussed more fully in Chapter 9.

Chemical Degradation Reactions in Foods

Since foods are complex chemical mixtures, the reactions and processes that can change their quality and safety are complex as well, and there is a huge and growing base of literature on the subject. This chapter (and this book) cannot consider every degradation mechanism in great detail, but several of the most common ones will be discussed.

What is more important from the food engineering and packaging perspective is the ability to remediate and control these reactions in a product in a manner similar to the *critical element analysis* discussed in Chapter 9. To do this, one must have a basic notion of several factors:

– What is the nature of the degradation reaction?
– What endogenous and exogenous factors accelerate or retard it?
– What is the final effect on the product?
– How can the reaction be controlled or utilized to advantage?

To understand the prevention or remediation of degradation reactions in food and biological materials, it is first necessary to understand the basic processes that cause degradation to occur. In general terms, the processes may be arbitrarily divided into chemical, biological, and environmental degradation, although these are not entirely clear-cut. Chemical degradation may include processes such as browning and oxidation reactions as well as many biochemical processes within the complex chemistry of the product. Biological processes may include things such as biotic degradation, but will also include fermentation, which is a preservation or even food-forming process for some products such as coffee, cocoa, yogurt, bread, and alcoholic beverages. Environmental changes may include thermal or photocatalytic reactions that are considered to be chemical changes in some instances, even though the remedial step is to keep the product from the extreme light or temperature exposure that will promote the reaction.

Sometimes, the results of these reactions can be hard to measure and it may be that the only practical solution when tracking degradation is to examine an easily assayed component that is a good indicator of the degradation reaction of interest. For example, the destruction of phosphatase that is used in the pasteurization reactions described in the subsequent chapter will give an idea of the thermal input and is easily measured.

Reaction Rates and Quality Degradation

For an engineer, the consideration of a particular chemical reaction will concentrate on a measureable reaction step, and the rate at which it occurs in response to a controllable stimulus. Reaction rates have been observed to approach several orders of curves, and variation of these will be correlated to changes in the inputs to the reaction. These are often referred to as reaction rate curves and may be the source of some error if the observed data is assumed to be applicable to conditions beyond those measured. An additional source of error is often found in data sets that are obviously non-linear but have been fitted to a linear or low-order curve because it is inconvenient to do otherwise, or because current experts have published results that only consider low-order effects. This may cause the results of calculation to be easier, and occasionally quite wrong.

Zero-Order Reactions

Zero-order reactions appear to act independently of exogenous factors or the concentration of reactants and obey a simple time relationship:

$$r = \frac{-\mathrm{d}A}{\mathrm{d}t} = c \tag{7.1}$$

r: reaction rate
c: constant
A: concentration of reactant
t: time

A_t, the concentration at time (t) can be found through integration to be

$$A_t = A_0 - kt$$

Where
A_0: initial concentration of reactant

$$k = r$$

First-Order Reactions

First-order reactions are simple, linear reactions based on a single reactant that follow the general equation:

$$r = k\left(\frac{-\mathrm{d}A}{\mathrm{d}t}\right) = k\,(A) \tag{7.2}$$

k: first order, rate dependent constant that can be integrated to produce

$$A_t = A_0 \mathrm{e}^{-kt}$$

Although these are often easy to calculate, the risk of *over-smoothing* the results is considerable and higher-order results should be checked when possible.

Second- and Higher-Order Curves

These have a general form:

$$-\mathrm{d}A/\mathrm{d}t = kA^n \tag{7.3}$$

that gives a concentration A at time t of

$$1/(A^{n-1}) = \left[1/\left(A_0^{n-1}\right)\right] + (n-1)\,kt$$

$$for\ n > 1$$

Arrhenius Curves

Arrhenius curves are first-order, temperature-dependent correlations resulting from the integration of the first-order reaction that is often an accurate correlation of temperature-dependent

processes, and correspond with many biological and physical processes. These follow the general form:

$$k_T = Ae^{-E_a/RT} \tag{7.4}$$

k_T: rate constant of reaction at temperature T, s^{-1}

A: experimentally determined prefactor.

E_a: activation energy, kJ/mol

R: ideal gas constant, $\frac{kJ}{^\circ K \cdot mol}$

T: absolute temperature, $^\circ K$

Activation energy – the energy threshold to be overcome in order to initiate a reaction and produce reactants – is often calculated via rearrangement of terms as:

$$E_a = -RT \ln\left(\frac{k}{A}\right) \tag{7.5}$$

The temperature dependence of the prefactor (A), although often measurable, is frequently considered to be insignificant relative to the exponential components. Both first-order curves and Arrhenius curves are usually plotted on semi-log scales to better visualize the relationships of the reactant to time or temperature, and to understand the underlying chemical thermodynamics more completely.

Shelf Life Testing

Given the previously mentioned models and an understanding of the nature of the degradation of the product that may occur, a reasonable estimate of the shelf life of the product can be made. Unfortunately, there is too often no agreement about how the end of the products' shelf life may be defined. The first task is to quantitatively define what a "bad" product is, whether spoilage, expiration, broken, unsaleable, or some other criteria. Although some things, such as an insect infestation would be self-evident, sometimes a "bad" product is defined in a haphazard or offhand way, causing disagreement among suppliers, manufacturers, and retailers. It may also be useful to understand the distribution system in which the product is dispersed to the customer because a rapidly distributed product that is only on the shelf for a few days before being consumed will have very different considerations from ones that will sit for months.

A good starting point for deciding where the product's shelf life has expired is making the distinction between the product's being no longer saleable and being no longer useable. These factors are not necessarily coincident – a perfectly safe and wholesome product may be unsaleable because of surface oxidation and discoloration of the layer closest to the wall of a clear plastic container, as happened with initial trials of plastic ketchup bottles, or it may appear to be safe, but is actually spoiled, have off-flavors, or be legally unsalable because of the loss of a component so that it no longer meets its label claim. In any case, the specific criteria for acceptability must be quantitatively defined in terms of color loss, microbial count, or other factor that may be objectively measured.

The next step is to decide the specific (and measurable) changes that constitute failure in the product. This does not necessarily have to involve an elaborate and involved laboratory analysis, but the criteria for failure must be related to a reliable (and preferably standardized) measurement method. Additionally, shelf-life testing may involve subjecting the product to

extremes of temperature, humidity, and transportation damage, as well as organoleptic evaluation and test marketing in order to determine what the worst possible case scenario is and how to remedy or avoid it.

Once the kinetics of the deterioration reaction are understood, it is possible to shorten the testing period for shelf-life evaluation by artificially increasing the factors that may cause the product to fail in order to shorten the testing period. This is most often done with temperature, although it might also be oxygen, partial pressure across a package membrane, or some other factor.

Q_{10} Estimation

One of the simplest considerations of quality loss is the Temperature Coefficient, or Q_{10} curve, in which quality change is considered as a function of a ten-degree temperature change. The concept of quality loss is an extension of standard formulations for microbial death at increased temperatures that has been extended to include the loss of a particular temperature-dependent quality factor [1]. This concept can be used for small-level determination of quality changes, and may be used to a certain extent to determine accelerated shelf-life results, but has many pitfalls if the results are extrapolated beyond measured data. Q_{10} is an approximation tool used for the assessment of how much a given quality parameter will change with an incremental (often 10°C) change in temperature calculations, and is based on the assumption of linearity of processes and the presumption that those processes are based on Arrhenius reaction kinetics.

From the previously described Arrhenius curve, one can see that a ratio can be established with a temperature change:

$$
\begin{aligned}
k &= A\mathrm{e}^{-E_\mathrm{a}/RT} \\
\text{For } \mathrm{Q} &= \frac{k_2}{k_1}, \\
\textit{and } \mathrm{Q}_{10} &= \frac{k_2}{k_1} \quad \text{where } k_2 - k_1 = 10 \\
\frac{k_2}{k_1} &= \left(\frac{\mathrm{e}^{-E_\mathrm{a}/RT_2}}{\mathrm{e}^{-E_\mathrm{a}/RT_1}}\right) \qquad (7.6) \\
\ln\left(\frac{k_2}{k_1}\right) &= \ln\left(\frac{\mathrm{e}^{-E_\mathrm{a}/RT_2}}{\mathrm{e}^{-E_\mathrm{a}/RT_1}}\right) \\
&= \ln\left(\mathrm{e}^{-E_\mathrm{a}/RT_2}\right) - \ln\left(\mathrm{e}^{-E_\mathrm{a}/RT_1}\right) \\
\ln\left(\frac{k_2}{k_1}\right) &= \frac{E_\mathrm{a}}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)
\end{aligned}
$$

Two important factors have to be noted; Q_{10} is dependent on the activation energy (E_a) value, and its intrinsic value will change with temperature – a ten-degree difference at 350°K will usually be substantially different than a ten-degree difference at 250°K for any value of E_a.

Once the Q_{10} value is found, the approximation of temperature-dependent shelf-life testing can be done as shown in Table 7.1. As shown in the table, with a Q_{10} value of 3, a shelf life of 26 weeks at 20°C (293°K) can theoretically be simulated in approximately 7 days at 50°C (323°K). Similarly, accelerated degradation can be reversed into an estimate of shelf-life parameters using similar tabulation or curves available, such as Figure 7.1.

Table 7.1. Effect of Q_{10} on Product with 26-Week Shelf Life at 20°C

Temperature °C	$Q_{10} = 2$	$Q_{10} = 2.5$	$Q_{10} = 3$	$Q_{10} = 4$	$Q_{10} = 5$
30	13.0	10.5	8.7	6.5	5.2
40	6.5	4.2	2.9	1.6	1.0
50	3.25	1.7	1.0	0.4	0.2

Although the Q_{10} curve appears to be a tantalizing means to shorten shelf-life testing, it must be treated with great care for these and many other reasons – certainly, a simple ice cube behaves very differently at −5°C than it does at +5°C! Similarly, phase changes or state transitions may occur in food components, secondary reactions may hamper or accelerate the product parameters that one is measuring, or some unanticipated secondary factor may be introduced, such as exceeding the glass transition temperature of a plastic packaging material and having a severe change in permeation [2]. It is possible to match estimated degradation rates against short-term data as an initial check, but results from accelerated shelf-life testing must be treated with great care and should always be verified against real-world data. In the hurry to get a product into production, it is a false economy to rush an unsafe or unsalable product to market, only to have to recall it or deal with the human and economic consequences of spoilage.

Amplification of Estimation Errors in Accelerated Shelf-Life Testing

One of the underlying problems with accelerated shelf-life testing is that the small exposure time that is used to extrapolate long-term effects also amplifies the effects of any error in measurement or procedure, or variability in samples. As shown in Figure 7.2, this can have a dramatic effect on the final results and cause severe misestimation of the product's shelf life.

Shelf-Life Testing Follow-up

The final step in any modeling exercise is "closing the loop" by validating the model. In the case of extending the shelf life of a product, the final results must be carefully monitored in order to assure that the product has maintained a proper quality and safety level. This may require field work to sample the *shelf duration* and stock rotation of products in the retail environment. This requirement is doubly important when accelerated shelf-life testing is used because it will

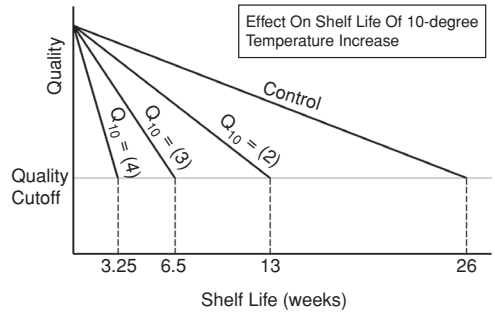


Figure 7.1. Graph of Quality Changes Due to 10°C Temperature Change at Different Q_{10} Values

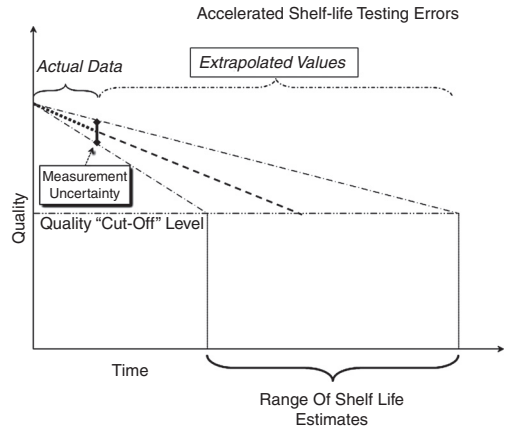


Figure 7.2. Graph of Shelf Life Estimate Error Amplification

give a strong indication of whether or not the shelf-life model is accurate. In any case, any data from real-world products, whether they have been sent through the distribution cycle or are stored under standardized conditions and then sampled, will be useful in improving the shelf-life testing process.

Examples of Specific Chemical Degradation Reactions

Browning of Foods

One of the more immediate reactions of foods to environmental exposure is browning, whether enzymatic or non-enzymatic. The difference is important, and both are strongly correlated with water content as well as temperature, water activity, and water mobility, which are discussed later in this chapter. Most browning reactions require a polyphenolic substrate such as a flavor constituent (cinnamic acid, for example), a coloring agent (such as anthocyanins), or other flavonoid-like compounds.

Enzymatic browning can cause both beneficial reactions such as those which create the distinctive properties of cocoa, tea, and coffee as well as raisins and other dried fruits. It can also cause harmful reactions such as those caused by browning and discoloration (pigmentation) in fruits, vegetables, and seafood. Most enzymatic reactions are caused by polyphenol oxidase or other similar enzymatic compounds that break down critical polyphenolic flavor, color, and occasionally texture compounds in foods. Enzymatic browning breaks these polyphenolic compounds down into melanins, creating the dark colors associated with the reaction.

Control or inhibition of enzymatic browning may involve lowering the pH of the product (such as the practice putting acidic juice on a piece of cut fruit), addition of a chemical preservative, elimination of oxygen availability to the product, or by blanching in order to inactivate the enzyme responsible for the reaction. Other control measures may include refrigeration to slow down degradation or freezing to below -18°C, although the exact mechanism of this is the subject of some debate. Rapid freezing both for direct production of frozen foods and the freeze-drying of foods is necessary to reduce browning in the final product. Because of the role of copper in polyphenolic oxidases, chelating agents can also control browning as well as

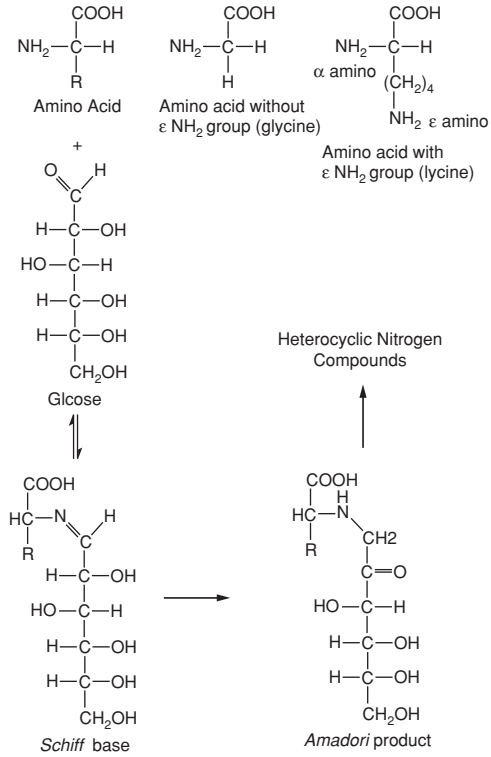


Figure 7.3. Basic Maillard Pathway
Source: U.S. Geological Survey, Scientific Investigations Report 2004–5121. "Evaluation of Conceptual Models of Natural Organic Matter (Humus) From a Consideration of the Chemical and Biochemical Processes of Humification"

modification of the product that enzyme is acting upon. More involved methods for the control of enzymatic browning, such as irradiation, pressure treatment, and other alternative processing methods as discussed in Chapter 6, have been evaluated for the reduction of enzymatic browning with varying degrees of success.

The most common forms of non-enzymatic browning are caramelization and the Maillard reaction (often called *Maillard browning*). Both reactions require thermal input and are often involved in the browning or coloring of cooked foods. Caramelization – a dehydration and pyrolysis reaction that results in oxidized sugars with low water availability – is used extensively in cooking to intentionally produce both flavor and color changes, the most easily recognized being the enediols and dicarbonyls of the caramel compounds. In most instances, caramelization is controlled by careful measuring of the amount of heat or sugar available during processing. The Maillard reaction (Figure 7.3), on the other hand, is a complex polymerization reaction between sugars, water, and protein's amino acids, which generates changes in the color and flavor of the product. It can affect the color, flavor, aroma, and nutritional content of the food, such as the browning of bread crusts, coffee, and cocoa, as well as undesirable changes such as flavor loss and the creation of toxic or mutagenic compounds and precursors.

Because the Maillard reaction is determined by the sugar and amino acid involved, these may be manipulated to control the reactions or to produce a wide variety of flavors and aromas,

both natural and synthetic. Further control of Maillard browning is achieved by controlling the reactants, pH, and water availability (Maillard browning peaks in the $0.6 < A_w < 0.7$ range), as well as thermal energy available for the reactions by controlling temperature.

Other Discoloration Reactions

With the continued high demand for natural food colorants that do not have to undergo strict regulatory review, the stability of natural colors may be critical in maintaining consumer acceptance of a product. Oxidation and degradation of other natural color compounds such as carotenoids, anthocyanic compounds, and the like are usually more direct breakdowns of the complex pigmenting compounds and are directly affected by oxygen availability, temperature, light exposure, and pH, as well as many naturally occurring processes such as enzymatic attack or microbial growth. Stabilization of natural colors often involves reducing the availability of moisture or the addition of a preservative such as sulfur dioxide, which is commonly used to prevent discoloration of dried fruits.

Rancidity and Oxidation of Fats and Oils

Rancidity of lipids may occur by three general mechanisms: hydrolytic, microbial, and oxidation resulting from the action of water, microbial enzymes, and oxygen, respectively. Free radical lipid autoxidation – an oxidation of fats and oils that usually causes some type of quality loss – follows a well-documented reaction pathway [3]. In general, the reaction proceeds in a manner similar to the synthetic plastics polymerization reactions discussed in Chapter 4, with initiation providing active sites for a continued reaction that only terminates when the material has been depleted or the reaction is quenched by antioxidants or other compounds. Some oxidation reactions are used as a low-rate type of polymerization for thickening and binding items such as oil finishes and the pigment in vegetable oil artist's colors used in the past. The lipid oxidation reaction, shown in Figure 7.4, begins with the loss of a hydrogen atom because of heat, radiation,

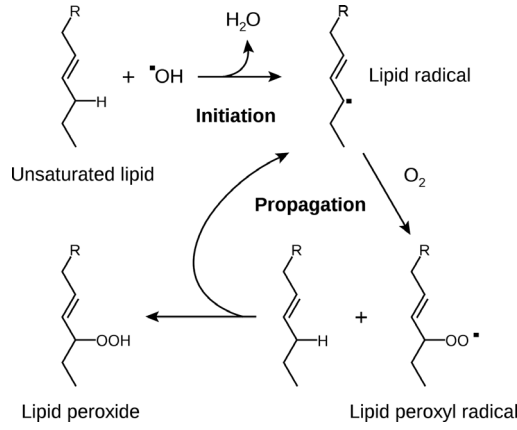


Figure 7.4. Lipid Peroxidation Pathway
Source: Tim Vickers, after Young IS, McEneny J (2001). "Lipoprotein oxidation and atherosclerosis". *Biochem Soc Trans* 29 (Pt 2): 358–62. PMID 11356183

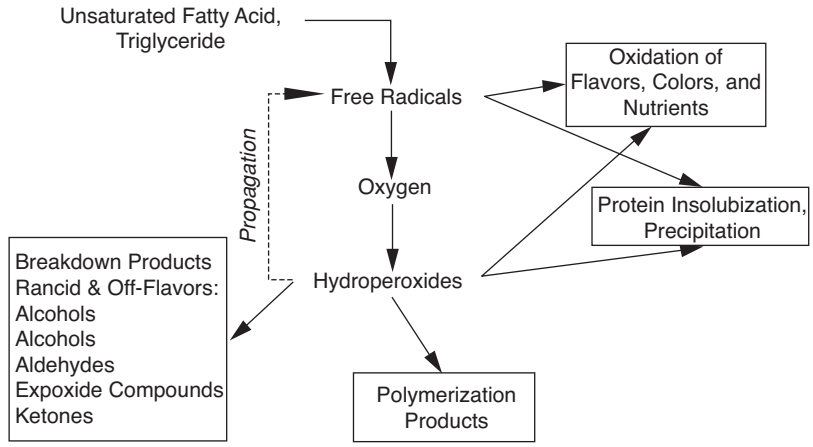


Figure 7.5. Lipid Oxidation By-products

enzymes (lipogenases), or metallic compounds. The lipid material then becomes a free radical, with a binding site available to bond to oxygen, forming a peroxy radical that then reacts with other lipid compounds to form hydroperoxides. The ongoing reaction terminates by combining radicals to form more stable reaction products.

Decomposition of these hydroperoxides can result in either polymerization products that can be toxic, or breakdown products that are often volatile and may affect product quality. Hydroperoxides can also react with proteins, membranes, and enzymes to affect cell function [4].

Photooxidation reactions require the photochemical production of a triplet sensitizer that interacts either with a substrate or with oxygen. In the latter case, a singlet oxygen is produced that is very reactive and is thought to be capable of initiation of the autoxidation, and will produce hydroperoxides and breakdown products in a manner similar to radical-initiated photooxidation [5].

Regardless of the pathway, lipid oxidation will produce a broad spectrum of aldehydes, esters, peroxides, and free radicals that may damage other food components such as vitamins and proteins, as shown in Figure 7.5.

Control of lipid oxidation involves control of oxygen, control of light, heat, and the addition of reaction-controlling additives such as antioxidants and finally water, which at high A_w values will quench the reaction, and at very low levels is correlated with low reaction rates.

Environmental Agents and Shelf Life Reduction

Gas Permeation and Exposure

As mentioned in the preceding discussion on oxidation, oxygen remains a powerful environmental agent that may degrade product quality over time. Oxygen is usually excluded from food materials, often by a combination of packaging, treatment during processing, and the *scavenging* effects of both the product oxidizing remaining oxygen during storage and intentionally included in-package devices and materials. As modified atmosphere packaging (MAP) processes become more prevalent, the ability of a package to retain and maintain a stable desired

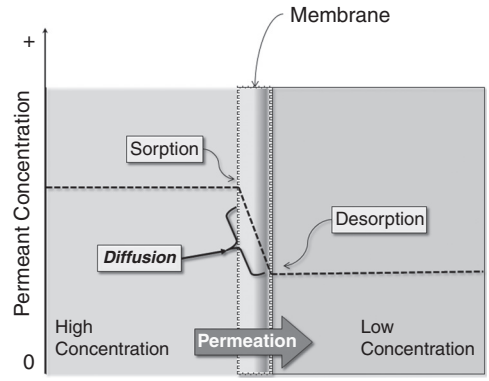


Figure 7.6. Permeation Model Based on Fickian Diffusion

microatmospheric mix, not only with regard to oxygen content but other gasses such as CO_2 and ethylene, will become more important as well.

Gas permeation is traditionally modeled using the basic Fickian diffusion model where permeation occurs along a concentration gradient and involves surface sorption-desorption phenomena as well as bulk diffusion within the polymer matrix that is driven by the concentration differential, as shown in Figure 7.6.

The Fickian diffusion model described in Chapter 2 assumes a steady-state, isothermal, and linear (permeant concentration and thickness independent) coefficients, and can be written as:

$$J = -D\frac{\delta c}{\delta x} \tag{7.7}$$

J: Diffusive Flux, $\dfrac{\text{mol}}{\text{m}^2/\text{s}}$

D: Diffusion Coefficient, m^2/s

$\dfrac{\delta c}{\delta x}$: differential concentration across the structure's thickness, $\dfrac{\delta\left(\frac{\text{mol}}{\text{m}^3}\right)}{\delta m}$

The solubility coefficient, the ratio between the partial pressures of the permeant (P) and the concentration at the surface of the solid phase (C), can be given as:

$$S = \frac{C_1}{P_1} = \frac{C_2}{P_2} \tag{7.8}$$

It is generally considered that there is a small discontinuity between the concentration of the bulk permeant and the surface concentration. The experimental determination of D and S is most commonly achieved by using an isostatic or quasi-isostatic permeation cell, as shown in Figure 7.7.

The measurement of gas concentration increase on the *static* side of the solid-phase membrane will give both a steady-state rate of concentration increase and a time lag that may be used to estimate values for D and S, as shown in Figure 7.8, which is often sufficient for simple, steady-state models and initial estimates of values.

Calculation of the P and S value estimates may be taken from the data compiled for the particular permeant-matrix combination and converted using the known thickness of the material

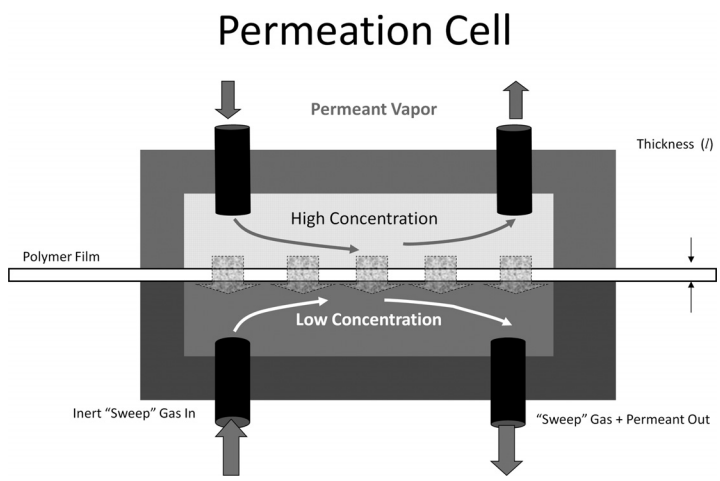


Figure 7.7. Cross-Sectional View of Gas Permeation Cell

(l) and the lag time to establish steady-state permeation rate through the film.

$$L = \frac{l^2}{6D} \tag{7.9}$$

$$D = \frac{l^2}{6L}$$

$$D = \frac{\bar{P}}{\bar{S}}$$

$$\bar{S} = \frac{\bar{P}}{D}$$

l: thickness, m
D: Diffusivity,
L: Lag Time, s
$\bar{P}$: Steady State Permeation Rate
$\bar{S}$: Solubility Coefficient

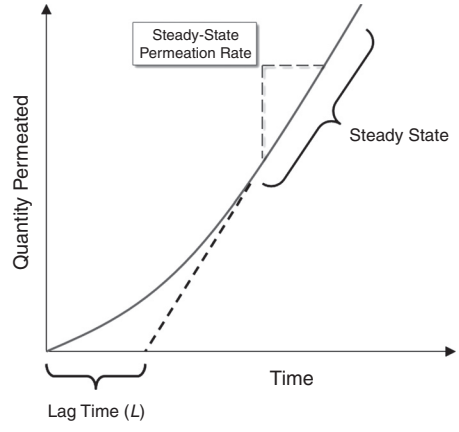


Figure 7.8. Permeation Rate and Lag Time Used to Determine Solubility and Diffusion Coefficients

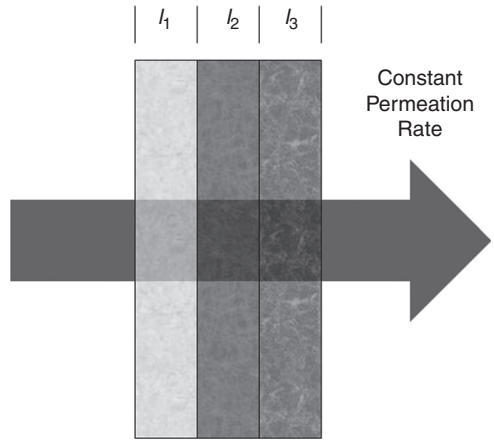


Figure 7.9. Multilayer Permeation

In more practical terms, gas and vapor transmission through packaging matrixes is usually expressed as a permeation rate, and is often expressed in odd and sometimes very mixed unit sets – there appears to be no standard beyond a basic (quantity)/(time) ratio.

$$\bar{P} = \frac{\Delta Q \cdot l}{\Delta t \cdot A \cdot p_{\mathrm{p}}} \tag{7.10}$$

$\bar{P}$: permeation rate
ΔQ: quantity of material permeated,
l: thickness of the material,
Δt: reference time period
A: membrane(film) area
p_{p}: partial pressure differential of permeant
Note that mixed units systems are common.

For laminates and co-extrusions such as shown in Figure 7.9, the mass-transfer parallels with heat transfer can be extended to give an overall permeability of a layered material as:

$$\frac{\Delta x_1 + \Delta x_2 + \Delta x_3 + \cdots + \Delta x_n}{\bar{P}_{\mathrm{composite}}} = \frac{\Delta x_1}{\bar{P}_1} + \frac{\Delta x_2}{\bar{P}_2} + \frac{\Delta x_3}{\bar{P}_3} + \cdots + \frac{\Delta x_n}{\bar{P}_n}$$

Or

$$\bar{P}_{\mathrm{composite}} = \frac{\Delta x_1 + \Delta x_2 + \Delta x_3 + \cdots + \Delta x_n}{\left(\frac{\Delta x_1}{\bar{P}_1} + \frac{\Delta x_2}{\bar{P}_2} + \frac{\Delta x_3}{\bar{P}_3} + \cdots + \frac{\Delta x_n}{\bar{P}_n}\right)} = \frac{\Delta x_{\mathrm{overall}}}{\left(\frac{\Delta x_1}{\bar{P}_1} + \frac{\Delta x_2}{\bar{P}_2} + \frac{\Delta x_3}{\bar{P}_3} + \cdots + \frac{\Delta x_n}{\bar{P}_n}\right)} \tag{7.11}$$

Some Fallacies of the Steady-State Model

The steady-state permeability and diffusion models work well with simple permeants and diffusion through fairly inert matrixes, but in real-world applications, many factors can crop up to cause large deviations from predicted values. The largest of these is confusion between permeation processes, which are controlled by diffusion mechanisms, and bulk flow occurring

through a large opening or defect in a material and controlled by pressure differential. If bulk flow is occurring, it will overwhelm any sort of diffusion-mediated transfer. It is not unheard of for analytical laboratories to be asked for permeation rates of packages that are perforated or have large ports cut into them, which means that the values are entirely dependent on the mass flow rate of leaks rather than the permeability materials being tested. The analysis of microperforated films as described in Chapter 4 represents a borderline case where the actual mechanism may be pressure- or diffusion-regulated, and in practical terms an effective permeation rate must be known.

Another common phenomenon is interaction between the permeant (or a co-permeant) and the diffusion coefficient of the barrier matrix. Non-linear permeation can be said to occur when the permeability depends on permeant concentration, thickness of material, time-related changes in materials, or some other external factor. One of the most common examples of this phenomenon is plasticization of a polymer matrix in a food packaging system by a volatile constituent (usually a flavor compound) or by a fat or oil contained in the product.

Factors That Can Influence Permeation

Permeant Characteristics

Typically, larger and more complex molecules will have a slower diffusivity than smaller, simpler compounds. The extreme example of this is hydrogen, which can diffuse through metals and glass. The solubility of the permeant in the polymer matrix (which implies interaction with the molecular structure of the polymer), as well as the presence of co-permeants, can markedly affect the diffusion of the permeants and significantly change the permeation rates. Organic solvents, for example, have a very high permeation rate through many hydrocarbon-based polymers, whereas inorganic gasses such as nitrogen may have a much slower rate, even though their molecular size is smaller.

Polymer Functional Groups and Additives

More complex functional groups, such as hydroxyl groups on a carbon backbone, have been shown to produce a much lower oxygen permeation rate than simpler alkanes, with other groups producing intermediate values. Inert additives may or may not change the barrier characteristics depending on how well they are bonded to the polymer matrix. Simple, inert additives are thought to create microvoids that allow a higher permeation rate. Other additives such as plasticizers and modifiers will increase chain segmental mobility and allow chain movement, increasing the permeation rate.

Structure and Morphology

Simple, linear HDPE will have a much lower permeation rate than polypropylene or more variants with high degrees of branching. Similarly, complex and cross-linked materials will have a much lower permeation rate than shorter, simpler materials. This is presumed to be an effect of the free volume created in the less densely packed linear structures. Similarly, a low level of amorphous structure or a high degree of orientation will reduce permeation as well, because both of those states will allow a higher degree of close-order packing and therefore less free volume for permeant penetration.

Environmental Conditions

Temperature is the most obvious environmental factor that will affect the barrier characteristics of a polymer. Below the glass transition temperature (T_g), the inflexibility and lack of segmental rotation in the polymer chains will prevent the rapid diffusion of many permeants, but as the temperature increases and the polymer achieves a rubbery state, the permeation rate will jump dramatically. Humidity will also play an enormous role, particularly with hygroscopic polymers such as nylon and water soluble-barriers such as the vinyl alcohol (PVA) compounds. Longer-term effects can result from the degradation of the polymer by sunlight or oxidation, as well as the effects of mechanical abuse.

Water Vapor Permeation

Water vapor permeation shares many of the characteristics of the simple gas permeation models, but with the added complication that the partial pressure across the barrier will probably not remain constant. With the permeation of gasses, particularly oxygen, the assumption is made that the gas will be bound up in reaction products. For a simple Water Vapor Transmission Rate (WVTR) in plastic films, this assumption is maintained during testing by creating a constant partial pressure across the film membrane with desiccants, as shown in Figure 7.10, with results usually reported in g $H_2O/m^2/24h$, although this may vary widely and may mix unit systems.

Although this method will produce good data and can be used in the same way as the gas permeation method to determine diffusion and sorption data, real-world applications may be more complex.With moisture permeation, the assumption that a constant partial pressure exists is usually invalid because the partial pressure will change as the product becomes hydrated and its water activity changes. This change in water activity with increasing hydration is usually modeled using a moisture sorption/desorption isotherm (Figure 7.11), which must be experimentally determined.

Creating a moisture isotherm is usually achieved by storing product at a particular relative humidity and measuring its equilibrium uptake in comparison to a desiccated sample. The equipment for this may be quite complex, but adequate measurements may be made by using sealed containers that are humidified with saturated solutions of specific salts, as shown in Figure 7.12, an oven (preferably with vacuum) for desiccation, and an accurate scale to measure the weight difference between the hydrated and desiccated samples.

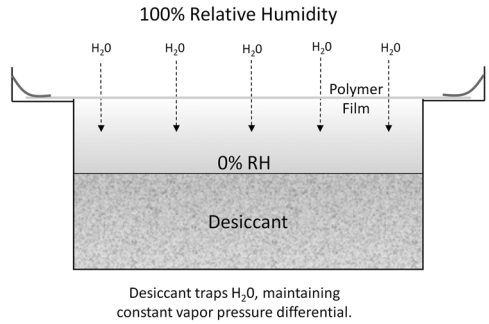


Figure 7.10. Moisture Permeation Testing Cup

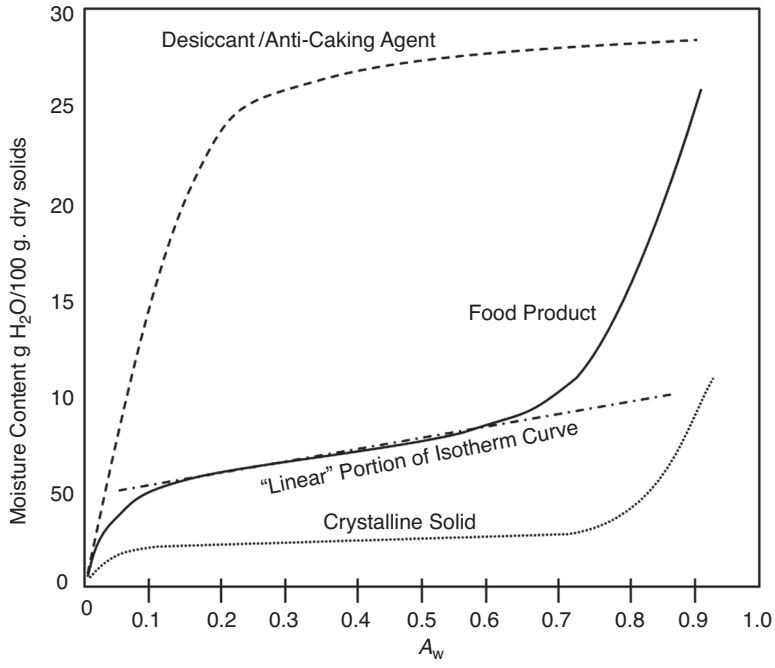


Figure 7.11. Moisture Isotherms

Because of differential binding of moisture during sorption or desorption, hysteresis usually exists between the sorption and desorption isotherm curves, as shown in Figure 7.13, and the results should be considered in relation to whether moisture gain or loss is likely to occur in the product.

Additionally, the surface area of the product must be considered. Grated cheese products have a huge, slightly hydrophilic surface that can create a rapid mold growth problem even if the larger block of the same cheese shows little immediate tendency for it. The difference is that the grated cheese product has an enormous surface area such that the binding of a small amount

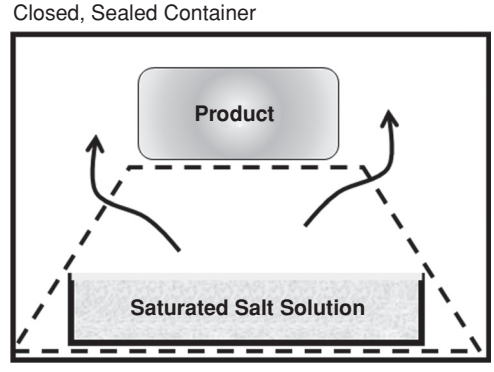


Figure 7.12. Humidification of Product Using Saturated Salt Solutions in Closed Container

Table 7.2. Relative Humidities of Various Salt Solutions

Temperature °C				
Salt	15.0	20.0	25.0	30.0
Phosphorus Pentoxide*	0	0	0	0
Sodium Hydroxide	9.6	8.9	8.2	7.6
Lithium Chloride	11.3	11.3	11.3	11.3
Magnesium Chloride	33.3	33.1	32.8	32.4
Potassium Carbonate	43.2	43.2	43.2	43.2
Magnesium Nitrate	55.9	54.4	52.9	51.4
Potassium Iodide	71.0	69.9	68.9	67.9
Sodium Chloride	75.6	75.5	75.3	75.1
Potassium Chloride	85.9	85.1	84.3	83.6
Potassium Nitrate	95.4	94.6	93.6	92.3
Distilled Water	1.0	1.0	1.0	1.0

*Not Recommended
Source: Greenspan. L. (1977), "Humidity Points of Binary Saturated Aqueous Solutions." *Journal of Research of the National Bureau of Standards* 81A(1): 89–96.
Available from NIST at http://nvl.nist.gov/nvl3.cfm?doc_id=89&s_id=117.

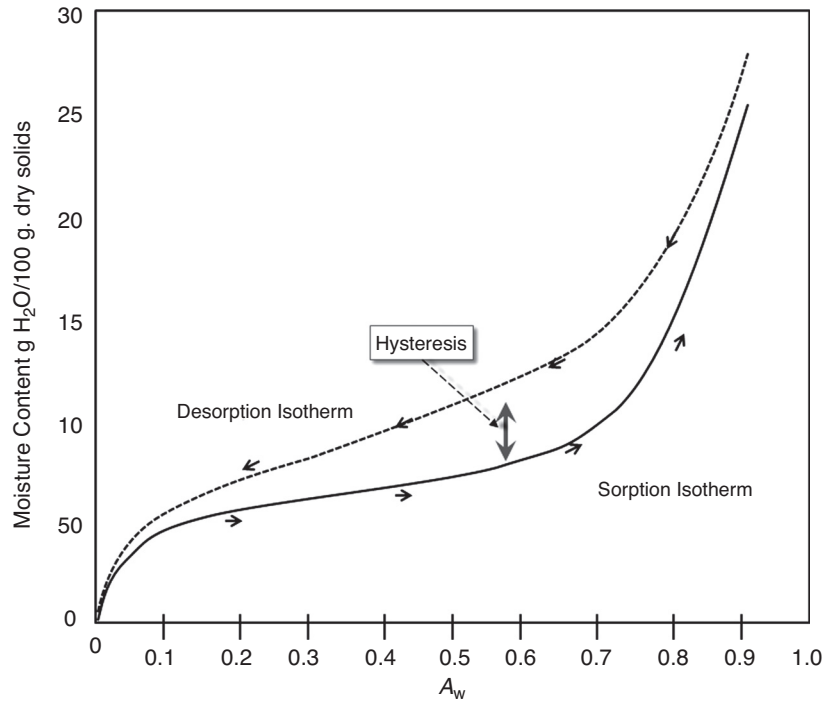


Figure 7.13. Sorption and Desorption Isotherms Showing Hysteresis

of moisture over the large area will create a much larger capacity for crossing the minimum moisture threshold and of supporting growth, particularly of molds.

Many studies have been done to fit a generalized equation to moisture-sorption isotherms, and there is a wealth of literature on these and their modifications. One of the most common and most broadly applicable is the Guggenheim-Anderson-DeBoeur (GAB) equation:

$$M = \frac{M_m C k a_w}{(1 - k a_w)(1 - k a_w + C k a_w)} \tag{7.12}$$

M: equilibrium Moisture Content, dry solids basis, g/g
M_m: monolayer Moisture Content, dry solids basis, g/g
a_w: water Activity, g/g

$$C = C' e^{(H_1 - H_m)/RT}$$
$$k = k' e^{(H_1 - Hq)/RT}$$

H_1: heat of condensation of water
H_m: heat of monolayer sorption
H_q: heat of multilayer sorption
C', k': experimentally determined coefficients

Moisture-Related Degradation Reactions

In addition to the lipid oxidation, enzymatic, and browning reactions that have been previously discussed, the growth of microorganisms in foods is intimately associated with the level of available moisture, with mold growth occurring at approximately $A_w > 0.6$ and bacterial growth beginning at approximately $A_w > 0.9$, with toxin production somewhat above that. Similarly, oxidation, browning, and other degradation forms will vary with water availability, as shown in Figure 7.14.

Predictive Models of Moisture Sorption

Because the moisture sorption model is assumed to be non-linear in that the partial pressure of moisture vapor changes with the ongoing humidity change in the package, creating a predictive model is much less direct than the simple calculations performed for simple gas permeation models. Although the GAB model and others provide an analytical approximation to use in other calculations, creating a practical model with experimental data is most readily accomplished with the aid of simple spreadsheets or even a good programmable calculator. In most cases, if the permeation rate of the polymer film is known, the partial pressure can be adjusted in an ongoing progression of values to achieve the equivalent of a stepwise integration along the sorption isotherm curve as it approaches equilibrium.

The flowchart in Figure 7.15 shows the general programming layout for a moisture sorption estimation equation.

Water Activity and Water Mobility

Water activity has been used to predict and explain a large number of phenomena and serves very well for a number of everyday reactions and processes. Additionally, it has the advantage of being easily (and cheaply) measured. Unfortunately, it is difficult to measure the water activity

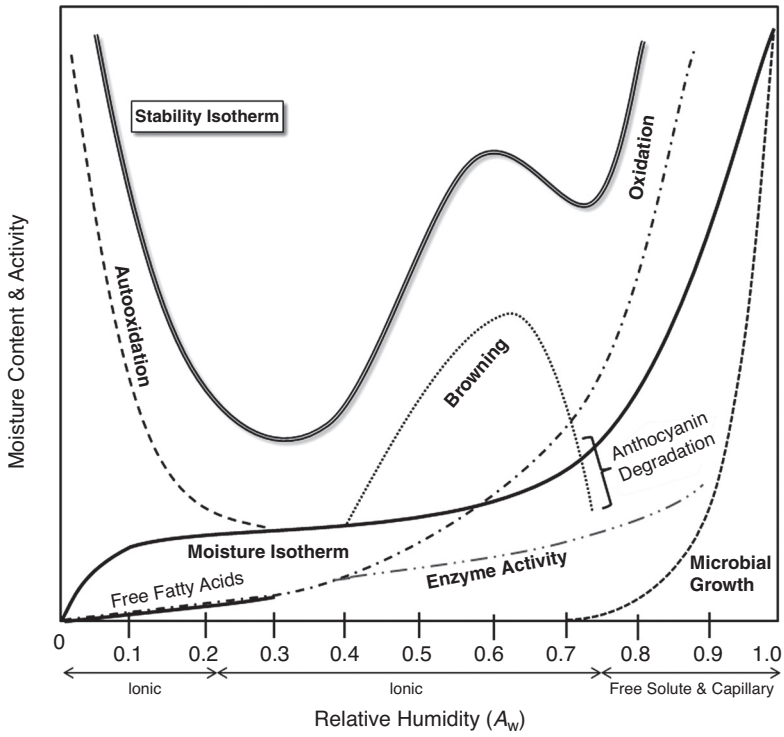


Figure 7.14. Relationship of Water Activity to Spoilage Mechanisms
Source: Labuza, T. P. and Nelson, K. A. "Water Activity and Food Polymer Science: Implications of State on Arrhenius and WLF Models in Predicting Shelf Life." *Journal of Food Engineering*, 22: 271–89. Used With Permission

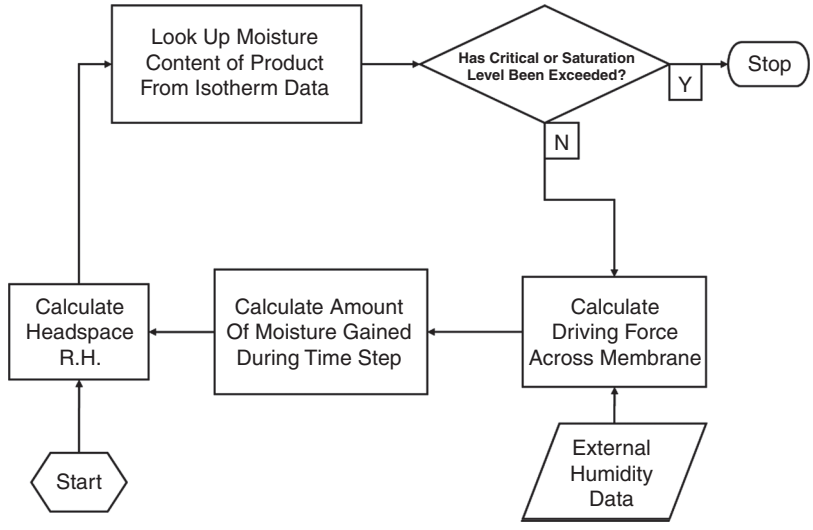


Figure 7.15. Flowchart for Shelf Life Estimation Program

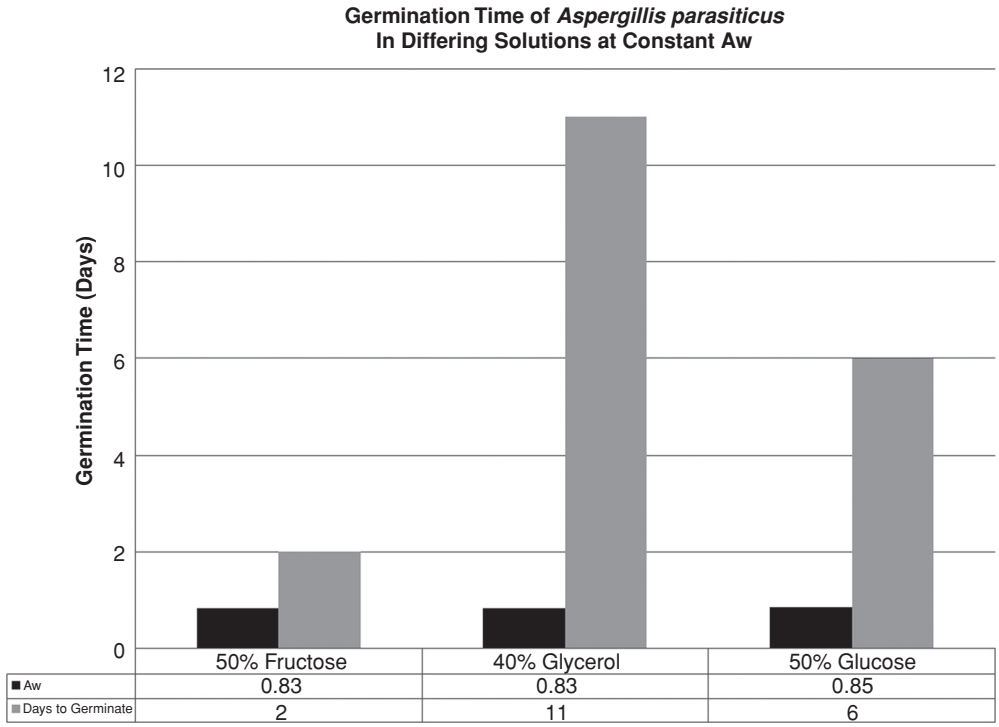


Figure 7.16. Germination Time Differing By Media Type Rather Than Aw

of frozen foods at very cold temperatures even though moisture migration and browning are occurring, and there are a number of unexplained phenomena, such as a study that produced wildly disparate germination data for *aspergillis parasiticus* held at the same water activity with growth media that differed only in their ability to bind water, as shown in Figure 7.16 [6].

A better explanation is the concept of *water mobility*, which gives the phase of water-containing compounds as an explanation of whether water is available for degradation or other processes. In an amorphous food product, water will act as a plasticizer and the product will exhibit many of the same characteristics as other polymers, showing glassy, rubbery, and melt states with increasing water mobility. As an example, see a generalized phase diagram for a standard-pressure solids-water system shown in Figure 7.17.

It can be shown that a small change in temperature at a particular weight fraction of water (shown as A-B) will cause a shift in phase from glassy to rubbery in both laboratory models of starch-water systems and frozen foods, with a marked increase in water mobility and an attendant increase in product degradation. Similarly, the transition from glassy directly to a melt state above the freezing point of water can be quite marked. This principle has been borne out in subsequent studies of frozen foods, which show that a repeated transition into the rubbery region, even though the food is still apparently frozen solid, will result in the acceleration of freezer burn and increased degradation of color and quality.

More complete diagrams are available showing that the state of water in foods may be a great deal more complex than was originally thought, and that both measuring it and determining the final outcomes may be a great deal more difficult than the simple use of A_w. The advantages

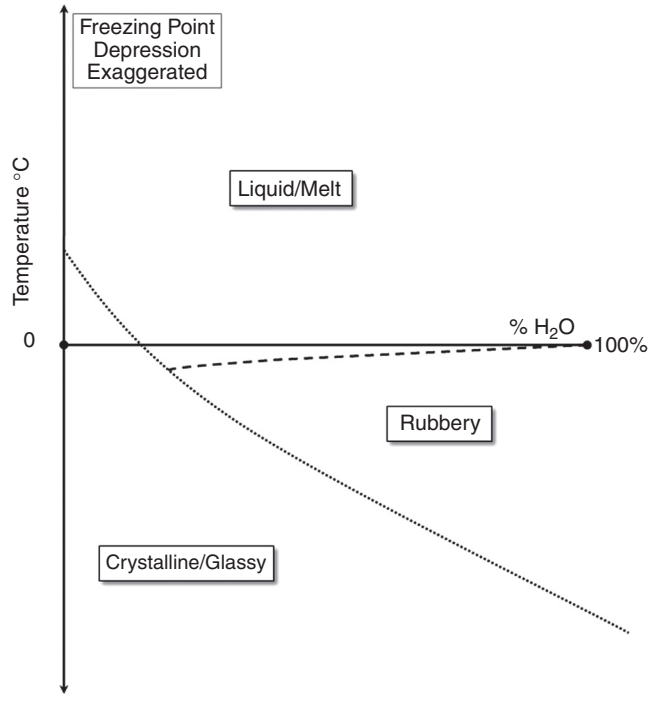


Figure 7.17. General Phase Diagram of Water in Foods

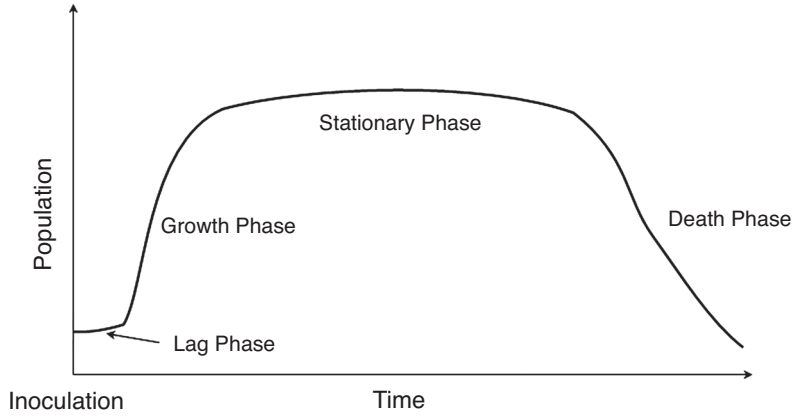
outweigh the difficulties, in that the predictive model has both a practical result and a better theoretical explanation.

What is clear is that the prediction of degradation mechanisms must take the state of water into account when anomalous behavior occurs, and that the changes in temperature and solvent/solute ratios that would not cause a great effect in A_w values may significantly alter the water availability for degradation. Indeed, the formation of intracellular glassy compounds is the mechanism by which many of the grains and plants (or their seeds, which we often eat) resist denaturation and survive dry periods, and more astonishingly how some seeds may be viable after millennia of dry storage while other species that cannot do this show no drought tolerance at all [7].

The great disadvantage in using the water state or water mobility concepts for practical applications is that the values may be difficult, time-consuming, or expensive to measure. Current measurement methods revolve around differential scanning calorimetry (DSC), nuclear magnetic resonance and magnetic resonance imaging (NMR, MRI), and Fourier transform infrared spectroscopy (FTIR). Development of fast, inexpensive scanners is ongoing, and there has been limited success with devices such as small portable MRI instruments to determine the state of water in frozen foods [8].

Microbial Product Changes

Microbial action both creates and destroys certain food products, and may help or hinder long-term food storage depending on the type of organism and whether or not it is considered part of the food product. In addition, microbial biopreservation technologies offer the promise of using



Lag Phase	Little Reproduction	Adjustment to growth media and initial reproduction.
Exponential (Growth) Phase	Reproduction >> Deaths	Few competitors, lots of nutrients.
Stationary Phase	Reproduction ≈ Deaths	Competition, waste products, and nutrient supply limits growth
Death Phase	Reproduction << Deaths	Nutrient depletion, waste saturation.

Figure 7.18. Microbial Growth Curve

cultures of microorganisms that are added to extend the shelf life or enhance the safety of food products.

Food microbiology, like food chemistry, is its own discipline and can only be generally discussed here. The types of microorganisms that are of most interest in food processing are bacteria, yeasts, and molds, and all exhibit the same general growth patterns shown in Figure 7.18.

Inoculation

Although this may bring syringes to mind, it simply refers to the initial introduction of the microbial species to its growth media (usually the food product).

Lag Phase

A period of low, metastable population level that occurs as microorganisms adjust to the new environment. The slow growth rate is often due to metabolic adjustments or population selection.

Logarithmic (Growth) Phase

A period of rapid (usually exponential) population growth as the microbial population expands into the nutrient supply and has little accumulated waste.

Plateau Phase

Microbial growth and deaths are approximately equal as nutrient availability decreases and waste accumulates.

Death Phase

Death rate exceeds new organism production, usually as a result of nutrient starvation or the accumulation of waste products.

Because all populations of microorganisms have different growth characteristics in the various growth media provided by most foods, it would be impossible to offer anything but the most general description of growth factors for several typical organisms.

Factors Used for Preservation by Affecting Microbial Growth

pH

Acidity will affect the type of microbial growth that can occur, and foods below a pH value of approximately 4.6 are considered high-acid foods where all food poisoning and most food spoilage organisms will not grow, which makes acidification, as with some types of pickling, some of the oldest and most effective preventatives of microbial growth, although acidified high-acid foods with a high water activity are still considered at risk and may require thorough thermal processing. In rare instances, processing with alkaline materials may be used to produce stable foods such as lutefisk from relatively pH-neutral (and therefore spoilage-prone) fish products. Additionally, naturally produced low pH can be generated by fermentation that will produce other antimicrobial products such as ethanol.

Water Availability and Osmotic Pressure

Although the concepts of water activity and mobility have been previously discussed, the methods of controlling them have not. Generally, drying, freezing, or using preservatives such as salt will immobilize water to the point where microbial growth is slowed or prevented. Osmotic pressure gradients that desiccate pathogens can be built up by preservation in high-sugar syrup with or without ethanol's combination of toxicity and osmotic differential to produce similar effects.

Oxygen Availability, Oxidation-Reduction Potential, and Microbial Growth

The availability of oxygen may determine what kind of organism may or may not grow in the product. Because the exclusion of oxygen has been a long-standing practice in many packaged foods to reduce degradation both from oxidation and from aerobic organisms, the possibility of anaerobic organisms such as *C. Botulinum* as well as microaerophiles such as *Camphylobacter jejuni* makes the proper processing of packaged foods a critical step. Relatively recent developments such as bagged salads that have matched moderate oxygen transmission rate package structures, gas-flushed modified atmosphere packaging (MAP), and respiring produce products create yet another challenge in oxygen level management.

Microorganisms are also sensitive to the oxidation-reduction potential (Eh) that their environment provides. The potential for electron exchange can be expressed in millivolts (mV), with high-oxidation states represented by a high positive potential and high-reducing state represented by a high negative potential. As one might expect, aerobic organisms require an oxidized

(high positive potential) environment to grow well and anaerobes require reduced (negative potential) environments. The Eh value, defined as 1.0 Eh = 1.0 mV of reduction potential, can be estimated by use of the Nernst equation and is usually referenced to a platinum electrode standard. Generally, the Eh value of a material will vary with both pH and with the presence of secondary compounds such as hydrogen sulfide (H_2S) that has the potential to lower the Eh value to approximately −300 mV. The state of the food materials will affect the Eh value, with freshly slaughtered meats having a high Eh value that prevents the immediate growth of anaerobic organisms, but decreases over time, and many foods and particularly plant foods and juices have a high Eh value that favors aerobic spoilage.

Note that the complex electrochemistry of cans and canned foods, discussed in Chapter 4, is an integral part of the electrochemical balance. Food stability as well as the stability of the can structure are intimately interrelated and present a challenge to provide structures that are stable and do not degrade or adulterate the product.

Shelf Life Extension by Preservative Agents

Preservative agents have also been used since antiquity, although most of these such as salt, fermentation acids and alcohol, and sugar are not commonly considered preservatives in the same sense as newer synthetic chemicals. Most of these traditional pickling and preservation agents work by providing a hostile environment for microbial growth either by immobilizing water or by raising the pH or alcohol content of the product to the point where pathogen growth is inhibited. A brief description of some common antimicrobial preservatives is provided in Table 7.3, but it is important to remember that there are a huge number of materials that are approved for use as food preservatives, and the table is by no means comprehensive.

For many types of preservatives, it is important to determine whether the preservative agent will be lost in processing, and whether it will affect the packaging material either by direct action, as with an acid- or alcohol-containing product, or by indirect mechanisms such as the uptake of the preservative into the packaging material matrix.

Shelf Life Extension by Packaging

Although packaging can control the transmission of materials in and out of a product, the packaging microenvironment may be more complex and subtle than one might initially imagine.

Table 7.3. Food Antimicrobial Compounds

Compound	Use
Acetic Acid, Potassium-, Sodium-, and Calcium Acetate, and Sodium Diacetate	Pickling, antimold agents, sauces, antibacterial additives.
Benzoic Acid	Acid food preservation.
Propionic Acid, Sodium, Calcium Proprionate	Bakery preservation; occurs naturally in Swiss cheese.
Sulfur and Sulfur Dioxide	Reduces nonenzymatic browning, antioxidant, antimicrobial.
Sorbic Acid	Mold and yeast control.
Nitrites, Nitrates	Meat curing
Methy-, Propyl- and Heptyl-Parabens	Antimicrobial in baked goods, drinks, jams, syrups.
Ethylene, Propylene Oxide	Chemical sterilants. Used on dry foods (nuts, grain, and spices) and to sterilize packaging materials. Also used to sterilize bandages and surgical instruments and materials.

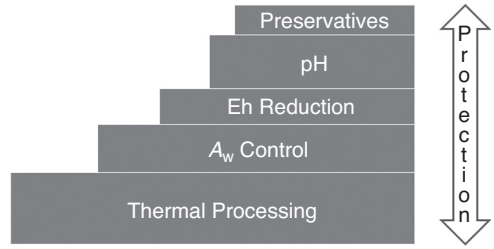


Figure 7.19. Staircase (Hurdle) Preservation Principles

Meat producers are carefully matching oxygen and gas transmission rates with modified atmosphere gas flushing to extend the shelf life of fresh cuts of meat. Fresh produce may be stored in a controlled-atmosphere macroenvironment before being shipped under carefully controlled conditions to market, and processed foods are often stored and shipped with carefully engineered packaging systems that have components that actively work to absorb gasses and moisture and to stabilize the product.

For fresh and processed foods, there are many additional post-packaging systems available for the extension of shelf life. Most of these depend on the establishment and maintenance of a microenvironment within the package that is optimal for the extension of shelf life of the product, and this, in turn, depends on careful management of many contributing factors for each particular type of product. For many types of fresh products, control of initial microbial load and then temperature control during storage and distribution is one of the most effective means of shelf-life extension, but further gains can be obtained by controlling the gas mixture within the package as well as other manipulations of the microenvironment.

Modified-atmosphere packaging (MAP) and active packaging are examples of tools used to ensure layered levels of impediment to microbial growth and reduction of processes such as oxidation, ripening, or staling, as shown in Figure 7.19 [9]. These are often termed *hurdles*, although a progressive staircase is a better metaphor, because microorganisms and degradation mechanisms must face progressive rather than successive layers of restraint.

Initial sterilization or microbial load reduction may be accomplished by many different means depending on the product type and the desired effect. The simplest of these is to ensure that processing conditions do not contribute to a relatively low initial load, but for most products, an initial antimicrobial wash or spray, or some other type of reduction may be useful. Continued maintenance of shelf life will then be dependent on the type and particular variety of product involved. For example, although the degradation mechanisms of pork and beef are quite similar, the optimum mix of gas treatment and package type may differ significantly, and even these will vary somewhat, depending on species.

Package-Product Interaction

Apart from the simple barrier function that most packages are presumed to provide, the package and product often interact with one another. Package-product interaction can be arbitrarily segmented into movement of materials either into or out of the package, as well as reaction with the packaging material itself. These interactions are the subject of both a great deal of development and engineering effort on the part of the food packaging industry, and the subject of some degree of concern among consumer advocates, toxicologists, and regulators. From a

legal perspective, harmful materials being transferred into a product from a package structure or material will render it adulterated and therefore unfit for sale or use. From an engineering standpoint, materials transferred into a package material from the product such as the previously discussed materials that may affect the barrier properties, or an oily compound that acts as a plasticizer, can be a significant concern.

Extraction of Packaging Materials into Products

The extraction of materials into products, particularly food, drug, and cosmetic products, can have both toxicological and organoleptic consequences. Situations such as questions of health effects from the extraction of di(2-ethylhexyl)phthalate (DEHP) plasticizers into PVC blood bags and medical devices, vinyl chloride monomer (VCM) into containers for hot beverages, and bisphenol-A (BPA) compounds from plastic containers into food products have gotten a good deal of press exposure from time to time. More subtle effects such as the flavor or odor changes from printing inks used on packages or volatile compounds from paper formulations can also affect the salability of the product.

Extraction of compounds from packaging into the product can also have positive effects with items such as corrosion-preventative wraps for machinery and antioxidant-containing packages for cereals, butter, and margarine sticks. These intentional interactions are regarded in the United States as indirect food additives and must be declared on the label. In general, food packaging materials and food contact items along with ingredients and direct or indirect additives must either belong to a list of approved additives or the "Generally Recognized as Safe" GRAS list, European Commission-approved additives list or similar compilation. Since it would be tedious, if not silly, to test every traditional food material (water, for instance) as a hazardous additive, most regulatory systems exempt simple, naturally derived compounds from rigorous testing. Food additives that have been heavily modified or have a synthetic origin most often must undergo an approval process that will approve use at all levels, at limited exposures, or will prohibit their use altogether. In the United States, unapproved additives and food contact materials that release unapproved compounds must go through an approval process that is described in detail in Chapter 10.

Antimicrobial Packaging

The incorporation of antimicrobial agents into films has shown a good deal of promise, and there is a vast array of possible materials that might be used for this purpose [10], but the application suffers from the disadvantage of many components being non-diffusive and thus having no effect on product that may not be in touch with the film's surface. This would be problematic for items such as cheeses and sliced meats, which will be likely to have irregular surfaces, but using a diffusive microbial may have enough effect on the localization to make the technology more widespread.

Endocrine Disruptors

Endocrine disruptors are, as the name suggests, substances that interfere with the normal endocrine functions in an organism. Discoveries that industrial effluents impaired the normal development of animal species have called into question the effects on human health and development by many compounds that are not directly toxic or carcinogenic. In general, endocrine

disruptors operate by closely mimicking natural hormones and either obstructing the proper response to endocrine functions or by triggering them inappropriately. One of the larger current debates is the migration of compounds from plastic films and molded containers as well as from paper structures. It is not clear at this point whether there is certainty of the effect on humans, but there is enough concern about findings with animal models and cell lines that Canada has largely banned BPA plasticizers, particularly in polycarbonate structures such as baby bottles, because of concerns about neonatal and possible teratogenic effects. Additionally, the US FDA Centers for Devices and Radiologic Health issued a Public Health Notification regarding medical devices containing PVC plasticized with DEHP [11]. Other sources of BPA are in can linings, including those used for infant formulas, and some dental resins. Additional concerns stem from the presence of BPA in wastewater and groundwater runoff.

Extraction of Product Components into Packaging Materials and Structures

As with many package-product interactions, the extraction of components from a product can be either helpful or harmful, depending on the product and the compounds that are being transferred. Undesirable extractions will include the removal of volatile flavor and odor constituents, often referred to as scavenging or stripping, resulting in loss or change of flavor as well as the previously described changes such as increased permeation or loss of rigidity in the structure. Food products that have ingredients similar to compounds used in packaging materials can present problems as well. A good example has been the development of plastic containers for both food and lubricating oils. Initial moldings were found to absorb the oils (which are often used as plasticizers themselves) and weaken to the point where they would lose structural integrity, and it required the development of more stable resins before plastic oil containers were commercially feasible.

Desirable interactions have been the subject of a good deal of development work, ranging from absorbent pads to bind the "weep" from fresh-cut meats and vegetables to complex scavengers and absorbers intended to reduce the amount of oxygen, moisture, or other compound responsible for degradation of the product. When used in combination with gas flushing to create an initially favorable microclimate in the package, remarkable shelf life and quality improvements can be seen.

Successful controlled- or modified-atmosphere packaging for non-metabolizing products depends on several steps. It is important to control the initial concentration of the headspace gasses that will affect the product without bringing them to the point of anaerobic growth, as shown in Figure 7.20.

Usually this involves using a nitrogen or mixed gas flush or overpack and possibly processing of the product under a controlled atmosphere as well, and all of these factors must be carefully matched to the product characteristics as shown in Figure 7.21.

The permeation rates of the package then must be matched to the product and desired shelf life effect, usually resulting in a low oxygen permeation rate coupled with the ability to rid or bind metabolic by-products such as ethylene or CO_2.

Very often, the control of permeated or by-product gasses requires the addition of either an active packaging material or component, usually in the form of a small sachet of material containing an active ingredient, as shown in Table 7.4. The most common of these is an oxygen binder that consists mainly of finely powdered iron similar to that used in the fabrication of magnetic recording media, and reacts with oxygen and atmospheric water to bind small

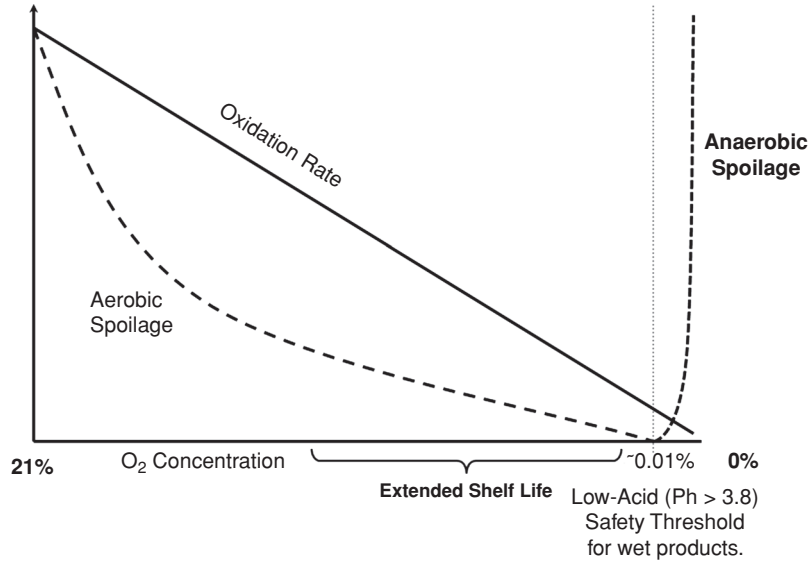


Figure 7.20. Degradation of Non-Metabolizing Products

amounts of oxygen into iron oxide. Moisture scavengers also can be added to prevent moisture from contacting the product.

Active Packaging

Active packaging is distinguished by its capacity to proactively affect some aspect of the package's operation beyond providing a simple, inert container or barrier material. Although the definition could be extended to the tin coating on steel cans and other traditional structural features, it is more commonly taken to mean proactive components that remove components

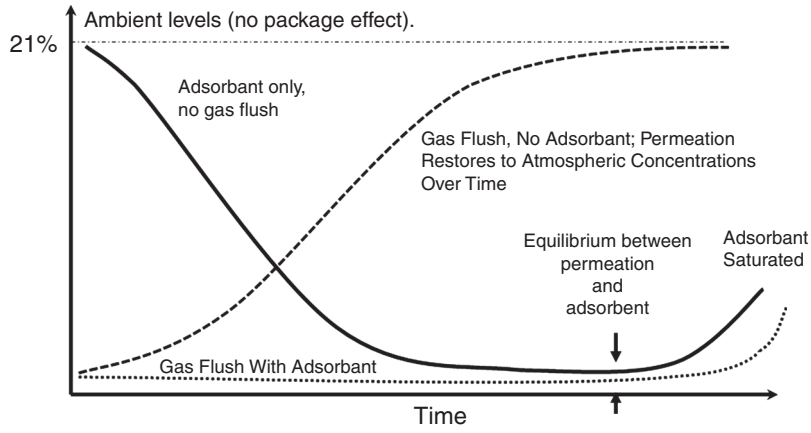


Figure 7.21. Oxygen Concentration in Package with Scavenger and Gas Flush

Table 7.4. Packaging Scavenger Compounds

Scavenger Target Compound	Type of Scavenger Used
H_2O	Adsorbing desiccant (silica gel, calcium chloride, clay)
O_2	Fe oxidation, antioxidants such as ascorbic acid
CO_2	Ca(OH)/NaOH blends, Na_2CO_3, LiOH
C_2H_4	Potassium permanganate ($KMnO_4$)

from the package headspace and react to changes in the product or the distribution environment either by indication or by proactively compensating for a deleterious effect. Active packaging is one of the ongoing areas where material science and other technologies such as nanomaterials, sorbents, and dispersants, as well as reactive substances, are being investigated as a means of improving performance or reducing the cost of packaging materials.

Absorbants and Dispersants

These are typically small sachets, patches, or layers of material that will bind up oxygen, moisture, ethylene, or other specific components that are either produced by the product itself or permeate in through the packaging material. Dispersants (often termed *reactors*) may release CO_2 to preserve fruit, ethanol to preserve baked goods, or release other flavor or odor constituents to maintain product quality, although these represent an indirect food additive that may need to be mentioned in the ingredients list or product label.

These applications must be balanced against the needs of the product, as well as the overall barrier properties of the package structure to prevent premature saturation or depletion of the active component. As previously mentioned, improper barrier selection may result in the premature expiration of the product's shelf life or an imbalance in the microclimate of the package that may result in package collapse or billowing. For films and structures that incorporate an oxygen-scavenging component, for example, a poor seal or constructing the rest of the structure of a low-barrier material will result in over-dependence on the absorption of oxygen by the scavenger and will be an inefficient use of materials.

Other active materials may be used beyond simple adsorbant and dispersive types, although these are often very specifically targeted toward singular problems.

Pitfalls in Using Active Packaging

One of the earliest lessons learned by packaging operations seeking to extend shelf life with the use of scavengers and other active components was that removing oxygen completely from a product, or increasing the rate of removal above the rate of permeation into the package, can drive the packaging into an anaerobic state, risking anything from fermentation to botulism. Additionally, when active packaging materials or additions are used, consideration must be given to the product's headspace circulating internal gasses freely so that the permeant does not travel through the product before it is absorbed. Products have been tested with absorbent materials and have been found to discolor or spoil everywhere except in the proximity of the absorbent, simply because the package was not capable of providing oxygen any other pathway to the product. The absorbent materials also have a finite capacity and may saturate and cause the product to abruptly degrade.

Processing of Product by Advanced Packaging Materials

One intriguing possibility that has evolved and which shows interesting possibilities is the advanced use of the package material or structure as part of the food processing operation. An example of this is the use of naringase on cellulose acetate film to reduce bitterness in grapefruit juice during storage to break down naringen, a glycosidic flavonone that causes bitterness [12]. Although the treatment could have been done during processing, doing so would have resulted in repeated clogging of equipment and an unacceptable increase in cost. In this application, the package itself became part of the processing system, and the concept represents an intriguing range of possibilities for specific treatments of products, such as the degradation of lactose in milk for lactose-intolerant customers using lactase-treated packaging. This may be where many of packaging materials research projects and particularly those that are nanotechnology-centered may find practical application.

Packaging and Shelf Life of Specific Food Types

While it would be impossible to contend with every single kind of food product, there are several larger categories that have some broad packaging requirements that should be included.

Meat and Poultry Products

Freshly cut meat products often produce water because of the reduced water-holding capacity of cut surfaces and degenerating cell structures. This "weep" is usually controlled by adding an absorbent material to the overwrapped package, or wrapping the meat in a moisture-proof bag at the point of sale. More important is meat coloration; consumers regard meat color as an indication of its freshness and desirability. Color "ideals" for different types of meats will vary from light pink in lamb to deep red in beef, and as will be shown, consumer preferences are generally slanted toward meats that have been allowed to "age" for short periods in the presence of oxygen. Meat color is based on many factors, but the controlling system is that of the heme structure in myoglobin (Figure 7.22) that is concentrated in the muscle fibers of meats, and is analogous to the same structure in the oxygen-carrying hemoglobin in blood.

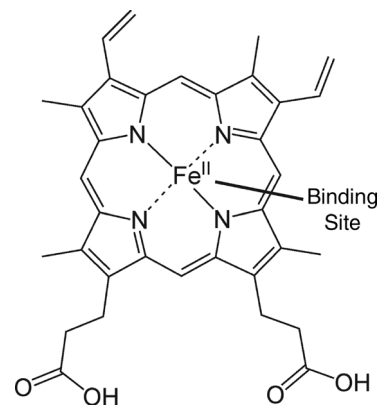


Figure 7.22. Heme Molecule with Binding Site
Source: Lennert B, Public Domain

Table 7.5. Myoglobin Coloration

Bonds	Compound	Color	Name
FE^{++} Ferrous	$:H_2O$	Purple	Reduced Myoglobin
	$:O_2$	Red	Oxymyoglobin
	:NO	Cured Pink	Nitric Oxide Myoglobin
	:CO	Red	Carboxymyoglobin
FE^{+++} Ferric (ionic bond)	−CN	Red	Cyanmetmyoglobin
	−OH	Brown	Metmyoglobin
	−SH	Green	Sulfmyoglobin
	$-H_2O_2$	Green	Choleoglobin

Myoglobin can assume many different types of coloration, depending on its chemical state, which in turn is usually caused by environmental conditions, preservative treatments, or microbial activity, as shown in Table 7.5.

The usual pathway for fresh meat is to begin with reduced myoglobin, oxygenate it to oxymyoglobin that is the state in which fresh meat is most appealing, before turning brown through conversion to metmyoglobin. This pathway may repeat itself as shown in Figure 7.23, but more commonly the meat is discarded or reprocessed in the metmyoglobin stage.

Bacteria may produce discoloration as well via the reactions shown in Table 7.6, which will depend on the species of bacteria as well as the conditions under which they grow. Two of these produce the characteristic green coloration of spoiled meat by producing choleoglobin and sulfmyoglobin.

Curing meats by adding nitrite compounds causes the meat to stabilize the color change cycle and will produce the characteristic pinkish colors of cured lunch meats. In curing, the myoglobin, oxymyoglobin, and metmyoglobin all stabilize to nitric oxide myoglobin, which is then converted to pink-colored nitrosylhemochromogen when heated.

Packaging of fresh meats thus presents a paradox – the extension of shelf life by restricting oxygen uptake while allowing the product to absorb enough oxygen to "bloom" and become attractive to consumers. Discoloration of meats during storage is a persistent concern, particularly as the industry moves toward more centralized production of consumer-packaged meat products, termed case-ready meats, that are prepared well in advance of store display and therefore more in danger of exceeding the time limit for optimal color. Solutions have been sought in modified-atmosphere packaging, particularly using carbon monoxide-based mixes

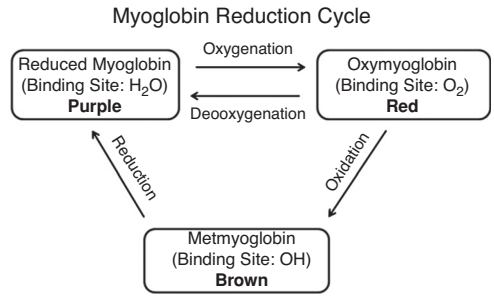


Figure 7.23. Myoglobin Cycle

Table 7.6. Bacterial Discoloration of Myoglobin

Pigment	Catalyst	New Pigment
Oxymyoglobin	Oxidation and Bacteria	Metmyoglobin
Metmyoglobin	Bacteria	Choleoglobin
Metmyoglobin	Bacteria	Sulfmyoglobin

that produces a stable pink color, and in carefully engineering the films used to optimize the best combination of barrier packaging. Degradation of cured meat products is usually the result of longer exposure to oxygen, light, or bacteria and will typically result in growth or graying on the exposed surface.

Often, this is due to light exposure, and particularly as a result of the high-energy blue spectra that exists in most fluorescent lighting systems in grocery stores. The light-related discoloration may be controlled by packaging and storage conditions, but has been hampered somewhat by marketing and legal requirements that often limit the packaging systems that may be used. Bacon is permitted to be packaged in a light-opaque overwrap so long as there is the ability to inspect the product through the outer packaging. Other "fresh" meats may have to have clear overpacks, allowing both inspection of the product and light degradation. Newer fully processed meat products such as cooked chicken and steak strips are packaged in a light-opaque container or a clear container with an overwrap. The degradation of meat and poultry products is a complex function of time, temperature, and environment, particularly oxygen availability and light exposure. With most meat products, the safe shelf life is determined by microbial growth, but in many cases, the product has changed and become undesirable to the consumer because of color changes long before any critical level of pathogen growth occurs.

Different cultures regard different colors of meat desirable, but in western countries, the primary preference is for a deep red color before cooking and various shades of red to brown after cooking. Unfortunately, because of the ongoing metabolism that occurs in the presence of the oxygen required to make meat "bloom" – to produce a "fresh" red color – oxidation occurs very quickly, causing discoloration and rancidity in the fats and limiting the shelf life. To extend the shelf life of meat products, they are usually chilled and vacuum-packed to reduce both the metabolic rate and the amount of oxygen available, which produces a deep purple color in the meat product, which consumers find unappealing.

Until recently, the result of this has been that carcasses, or sides or quarters of carcasses, were shipped in a vacuum-packed high-barrier bag from a central slaughterhouse, then further butchered at the retail store in order to provide enough shelf life to sell the meat before the color degraded. The open-air butchering and oxygen-permeable packaging provided a means for the meat to bloom red from its previous purple color at the cost of a fairly short shelf life. With a push toward centralized manufacturing from meat manufacturers and large retailers seeking to further cut costs, the butchering and packaging would be done in a centralized facility. This adds the complexity of trying to accommodate the conflicting goals of red coloration and long shelf life.

Several solutions have evolved to deal with this situation. One solution has been to provide a high-barrier overwrap of one or several display trays of meat that can be removed prior to display in order to allow the meat to bloom. This works reasonably well at the added cost and complexity of an overwrap. A complementary solution has been to add a gas mixture to the display package, typically a mix of carbon monoxide and carbon dioxide, to extend the

coloration by converting myoglobin to carboxymyoglobin, extending the red coloration of the meat and reducing the visible growth of spoilage organisms. The great danger with this, as with many MAP solutions, is that spoilage does not occur but pathogen growth may continue, providing an apparently unspoiled but microbially dangerous product, so these methods must be implemented very carefully. A further extension of the MAP concept adds a scavenger to reduce oxygen levels in the product to reduce browning and rancidity, and can utilize antioxidants to further preserve taste and color.

Seafood

Seafood differs from many other meat products in that the initial microbial load and fat content is often intrinsically much higher, and the products are particularly sensitive to temperature changes and exposure to oxygen. Consumers prefer fish that is as freshly caught as possible, and will avoid fish that smell of the tri- and dimethylamines that are produced by the enzymatic degradation of the trimethylamine oxide in saltwater fish species. Additionally, odor production from autooxidation of fatty acids in fish, as well as the loss of flavor and color, is taken to be signs of reduced product quality [13]. Frozen seafood, although much more stable, suffers from quality loss due to temperature variation, light exposure, and oxygen availability, although this occurs much more slowly than with other products [14].

To extend the very short shelf life of seafood, many different tactics have been employed, but some of the first historical methods – rapidly shipping live seafood, or chilling and rapid shipment, or freezing – are still the most effective. This has created an enormous seafood rapid-shipment infrastructure with seemingly anomalous features such as the shipment of 30,000 pounds per week of lobster from very-landlocked Louisville, Kentucky, to various points in the United States because of the availability of access to a rapid air shipment terminal [15].

Packaging systems that have evolved to extend the shelf life of fresh and processed seafood require very strict control of both temperature and package microenvironment, but have the capacity to provide a very-high-quality product for an extended period of time. In the United States, the primary required means of controlling spoilage remains reduced temperature but secondary measures or multiple hurdles to microbial growth are required because of fears of temperature abuse and the resulting growth of potent pathogens such as C. Botulinum Type E [16]. The results of these types of packaging technologies vary widely among species and gas mixtures, with the best results being an approximately threefold extension of shelf life, typically using CO_2/N_2 mixtures, as shown in Figure 7.24 [17].

Larger-scale distribution systems include live, iced, and frozen distribution, as well as dedicated systems of controlled temperature and atmosphere shipping containers and racks, as well as high-barrier master packs containing retail packs that can reduce the temperature fluctuations, light exposure, and degradative microbial and chemical processes significantly.

Fresh Fruits and Vegetables

Fresh fruits and vegetables have the nearly unique qualification of being living (though usually senescent) organisms almost until the time that they are consumed. Because of this, it is important that a basic understanding of the maturation process as well as the storage and transportation conditions be understood.

Nearly all fruits and vegetables, once harvested, shift from a photosynthetic metabolism combined with respiration to solely respiration, requiring oxygen and moisture to maintain cell

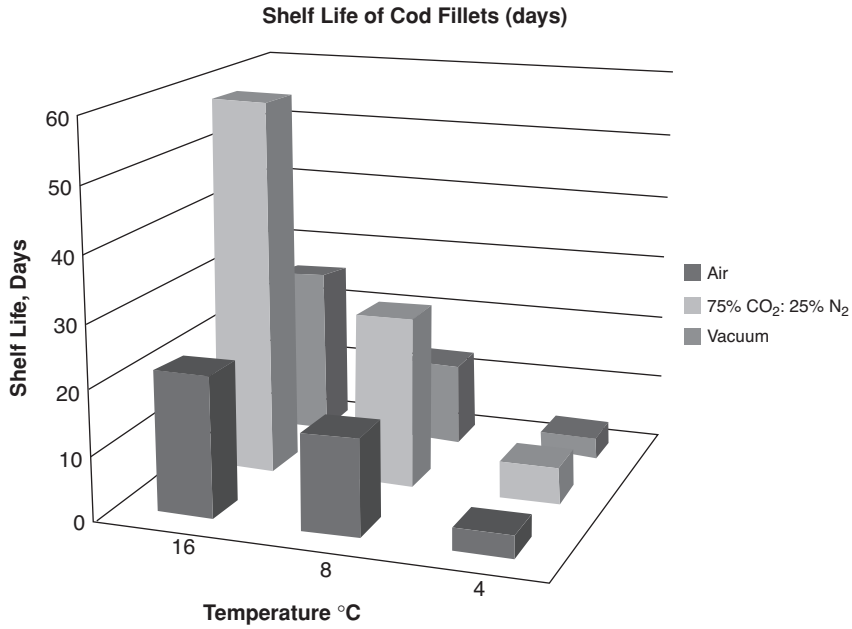


Figure 7.24. Shelf Life of Cod Fillets Stored in Different Gas Mixtures

turgidity and emitting carbon dioxide as a by-product that must be eliminated. Additionally, many fruits and vegetables emit ethylene gas as both a ripening trigger signal and a ripening by-product – a process that can also be triggered by damaging the fruit tissue or by artificially introducing an ethylene source to the fruit. To understand how these methods can control maturation and extend the post-harvest shelf life of fruits, vegetables, flours, and other plant organisms, it is necessary to understand the general importance of ethylene production within the crop. Ethylene biosynthesis both controls and is controlled by the presence of low levels of gaseous ethylene. First discovered in the 1920s by lemon growers who would use kerosene heaters (and their emissions) to store and ripen unripe lemons, the control and use of ethylene has become central to post-harvest handling of fresh crops. Exposing ethylene-sensitive fruit to an elevated level of ethylene gas triggers maturation and ripening. A common household version of this is placing unripe tomatoes (which are a fruit that ripen in the presence of ethylene) with bananas, which are high ethylene producers, in an oxygen-permeable container, typically a paper bag. The result is that the immature tomatoes will "artificially" ripen indoors after picking.

This same process allows control of aging and maturation through control of both the respiratory gasses and temperature in commercial large-scale controlled-atmosphere (CA) facilities. This effect can be obtained using refrigeration and ethylene-absorbent packaging materials or sachets for individual fruit packages to produce MAP that extend shelf life for whole fruits and vegetables, although the latter is currently not common in the United States. This must be done with caution because exposing produce to a gas mixture outside of their range of tolerance will create stresses that, in turn, will increase ethylene production and other detrimental processes.

Controlled-atmosphere (CA) storage involves the large-scale implementation of control over both temperature and atmospheric gas mixture during storage, and, if done properly, will slow the respiration and ethylene production rates. Purpose-built warehouses control oxygen

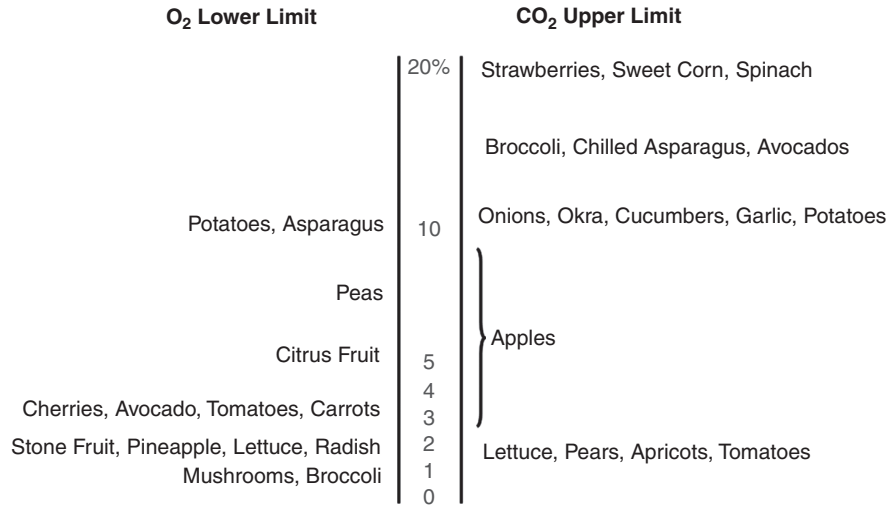


Figure 7.25. Produce Gas Tolerance

level and temperature and scavenge ethylene and CO_2 by the use of adsorbants that may be employed as pads or trays in the ventilation systems of the facilities. Potassium permanganate or activated carbon is commonly used to control ethylene, and lime is used to control CO_2. Similar technologies may be used on a smaller scale in packages or even incorporated into or coated onto packaging materials.

When the produce is to be shipped, it is briefly exposed to high levels of ethylene gas to "wake up" the fruit so it begins to mature during shipment, with final ripening occurring at the retail level or in the consumers' home. The delay of maturation makes distribution over long distances possible, because unripe fruit is usually physically stronger than ripe fruit, and vegetables often cannot withstand handling and shipping without severe damage or complete loss.

Since plant-based organisms vary widely in their respiration rates and requirements for preservation, the specific factors and results for extending shelf life will vary widely. The storage life of some types of fruit such as apples and tomatoes will be extended by many months; bananas may be extended for some weeks, and fresh-cut flowers only by a few days, as shown in Figure 7.25. In general, controlled-atmosphere storage to extend shelf life involves reducing oxygen concentration to reduce the rate of respiration, reducing temperature to similarly slow respiration and maturation, and removing ethylene to delay the onset of maturation. Cut fruits and vegetables have also benefited from a booming implementation of MAP systems that allow processing in central facilities and regional or national distribution for bagged salads and mixed fruit.

The extension of shelf live and the delay of the onset of maturity is a balancing act, as shown in Figure 7.26, because many plants' respiratory metabolism will fail at very low levels of oxygen, and the product will begin anaerobic fermentation. Similarly, the accumulation of CO_2 must be limited because extreme levels will poison the respiratory metabolism of the product.

To achieve this balance, the initial atmosphere of the package may have to be modified, and there must be a match between the metabolisms of the products and the permeation rates of the package. This may be further modified by temperature control of the product, but this is usually

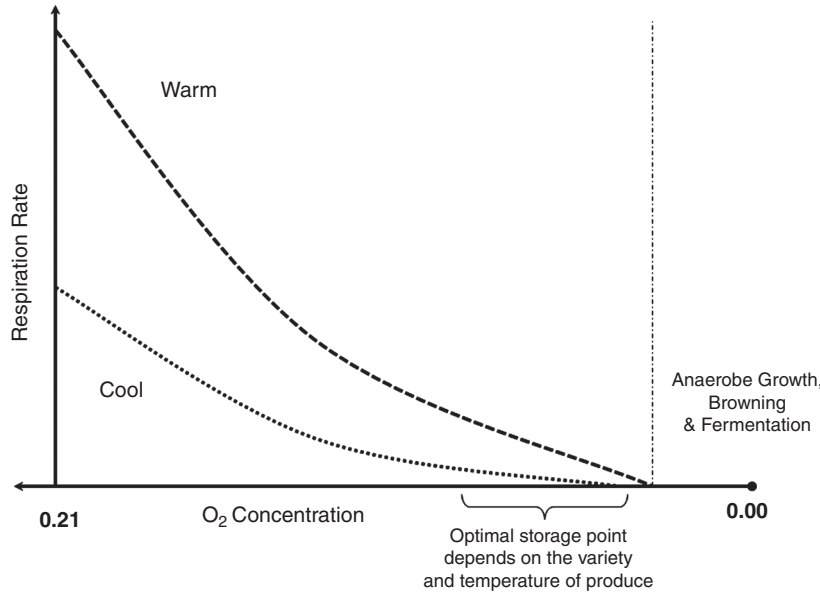


Figure 7.26. Degradation of Metabolizing (Vegetable) Products

achieved with temperature-controlled distribution rather than packaging. A more detailed list of environmental requirements is given in Appendix 7.1.

Control of Fruit Maturation using 1-methylcyclopropene (1-MCP)

Work is being done with a polyamine treatment, 1-methylcyclopropene (1-MCP), as an agent to slow maturation or to extend the mature phase of fruit's development and thus extend its shelf life by interfering with ethylene's biosynthetic pathway, which shares a common intermediate (S-adenosylmethionine). It effectively disrupts the ethylene sensitivity of an organism, putatively by interacting with ethylene receptors in the vegetable tissue and successfully competing for binding sites. This, in turn, delays maturation and has been shown to slow both phenolic and respiratory metabolic rates (and nearly every other process) in the organism [18]. Because its toxicity is extremely low and it disperses as a gas after treatment, current research shows little to no health affect from its use, and 1-MCP has been approved for the treatment of fruits, vegetables, and cut flowers in both indoor and outdoor uses [19]. Although this might be seen as a food additive and has been the subject of some controversy, its effects on the general CA and MAP treatments of flower, fruit, and vegetable handling, packaging, and distribution are likely to be profound.

Dairy Products

By definition, dairy products all involve a large liquid-milk component as their starting points. From there, the applications move outward to liquid products such as milk and cream products, thicker derivatives and cultured products such as sour cream, yogurt, and cottage cheese, and then on to solid and semi-solid products such as butter, cheese, and ice cream. With nearly

Table 7.7. Milk Process Type and Shelf Lives

Milk Process Type	Heat Treatment		Shelf Life
Pasteurized	72–75°C	15–40 sec.	~ 7–10 days when chilled
ESL	~125°C*	3 sec.	21+ days when chilled
UHT	135–150°C	4–20 sec.	6+ months at ambient
Sterilized	115–125°C	10–40 min.	9+ months at ambient

* i.e., regenerative heating to 75°-80°C, flash heat to 125°C, flash cooling to 70°–85°C.
Note: These reflect both European and American processing parameters and have broader values than shown in Table 6.2.

all of these products, the two most common degradation processes are oxidation and microbial action. To extend the shelf life of most of these products, treatments ranging from pasteurization to UHT sterilization are applied to lower the microbial count, with the exception of raw-milk cheeses that must be aged for at least 60 days.

Liquid milk products may be pasteurized then chilled and distributed through temperature-controlled systems including refrigerated dairy cases in retail outlets and consumers' refrigerators. These are usually packaged in coated paper or blow-molded containers that are often opaque to shield the product from light. Shelf-stable liquid milk has been available for some time and is sterilized via a UHT process as described in Chapter 6, and then aseptically packaged, but the caramelized sugars in this product have kept it from achieving a large market share in competition with "fresh" refrigerated milk, although it does well in areas that do not have access to reliable refrigeration. An intermediate version – extended shelf life (ESL) milk – may combine filtration, separation, a modified pasteurizer with several stepped temperatures, and sterile filling to provide an extended shelf life for refrigerated milk with no substantial change in taste. Values for many types of processes and their respective shelf lives are shown in Table 7.7. To prevent oxidation, this is usually combined with a thicker, opaque container, often made of HDPE or paper/foil/polymer laminate in order to reduce oxidation and prevent light from degrading the vitamin A content.

Butter, which is extremely prone to oxidative rancidity as well as mold-induced ketonic rancidity, is usually wrapped in an antioxidant-containing barrier package to prevent contamination and reduce the oxidative hardening and off-flavor at the surface during storage and distribution.

Cheese, which is moderately shelf-stable so long as surface moisture sorption and mold growth are avoided, can be pasteurized as previously mentioned or simply sold as sliced, grated, and block product in a protective covering. Because the moisture level in most hard cheeses is fairly low, mold growth on the surface is the largest immediate concern when no other major contamination (inadequate pasteurization or the inclusion of a contaminated additive) exists, and this is controlled by moisture barrier films. For shredded products, the large surface area adds the possibility of surface adsorption of moisture, causing problems throughout the product, so handling and pre-packaging preparation are also important. Some cheeses, particularly Swiss cheese, exhibit CO_2 outgassing as a function of the microbial action that is an integral part of the product, and a high-gas-transmission packaging material must be used to avoid unappealing inflated packages in retail displays.

Cultured products may be somewhat self-stabilizing but must be kept cold, and often products such as yogurt must actually contain an active culture to meet label claims linked to claimed health benefits. Most of these products are sold in high-barrier formed tubs and cups with a film seal to prevent contamination and indicate tampering.

Frozen products such as ice cream will not support microbial growth but will eventually develop "iciness" as the product coalesces into large, coarse crystals. Because ice cream is technically both an emulsion and a foam, this is primarily prevented by proper manufacturing processes and avoiding temperature abuse during distribution and storage, because components' change may allow water to migrate and crystallize. High-barrier packaging can help this slightly by retarding moisture loss at the surface of the product, but the effect is limited.

Bakery Products

Most of the foods considered in this chapter are in a nearly unprocessed state, but bakeries represent a multibillion-ton food source for the United States alone. Breads, pastries, cakes, cookies, pies, and other types of baked goods, often filled with fruits, nuts, meats, cheese, and other dairy fillings, will complicate the matter with spoilage concerns of their own. Historically, these products have had a very short shelf life, requiring consumption soon after purchasing and therefore a large number of small-output bakeries to supply them. The drive to larger, centralized bakeries for many mass-distribution products has prompted several routes to extend shelf life, preserve quality, and maintain microbial safety of bakery products.

In general, staling is any non-microbial process that degrades the product quality and is thought to be a function of changes in the starch structure of baked goods, associated with moisture changes but more complex than simple moisture loss or drying of the product.

Microbial spoilage is most often thought of as a function of molds growing on bakery products because molds can grow at relatively low water-activity levels. Other types of microbial spoilage can occur, such as yeast spoilage causing blooming or fermentation of products and bacterial infestation, particularly in bakery products that have meat, dairy, or other components. The relatively neutral pH range (approximately 4.5–8.5) allows products to support a broad range of organisms.

Chemical spoilage apart from staling usually occurs via either oxidative rancidity of unsaturated fatty acids in the presence of oxygen or hydrolytic rancidity of triglycerides in its absence. In either case, the result is off-odor and off-flavor compounds that may interact with other ingredients in the product.

Shelf life extension and preservation is most often provided by a combination of preservatives in the product formulation and increasingly by modified-atmosphere packaging of the bakery product itself. In the case of baked goods that make an "all natural" or "no preservatives" label claim, the packaging becomes a critical part of maintaining product quality. Post-packaging treatment of the products to eliminate post-baking contamination has had some success with irradiation and high-intensity light exposure, but many of the processes such as infrared heating and high pressure treatment are too destructive to the product itself to be practical.

Modified-atmosphere packaging of baked products can extend the life of many types of baked goods by reducing mold growth (see Table 7.8) and can extend shelf life from days to weeks in many cases, but may not retard staling [20]. The gas mixture must be matched with a suitably selective permeable film, because excess levels of carbon dioxide can dissolve into the product and collapse both the package and the product. The presence of even small amounts of oxygen can lead to mold growth, and moisture permeation can lead to very rapid drying of the products. Additional protection may be achieved by oxygen-absorbent materials or components in the package. These will help maintain the low-oxygen atmosphere in the package and maintain and extend shelf life, and can be used with or without a mixed gas treatment, though a synergistic approach is the most effective [21].

Table 7.8. Gas Mixtures Used with Bakery Products

Product Type	CO_2	N_2
Breads, Buns, Cakes, Croissants	100	
Danish, Sweet Rolls, Tea Cakes	50	50
Pita Bread	73–99	1–24

Adapted from: Smith, J. P. et al. (2004), "Shelf Life and Bakery Products, A Review." *Critical Reviews in Food Science and Nutrition* 44(1): 19–55.

Potato Chips and Crisp Snacks

Crisp snacks, which are most often cooked in oils or have high oil content, have a twofold problem in terms of maintaining product quality, oxygen, and moisture. Moisture causes both loss of texture (sogginess) as well as being involved in oxidation processes of fats, whereas oxygen is the primary culprit of fat oxidation that may lead to off-flavors and staling. To prevent these problems, several simultaneous solutions are usually implemented: control of headspace gasses and the use a high-vapor-barrier, opaque film as the preferred packaging material. The exclusion of light, moisture, and oxygen will reduce oxidation of the fats significantly, but the modification of the "headspace" gas (which includes a good deal of interstitial volume in many products) can extend the shelf life of products significantly.

Because there are two simultaneous reactants working against the shelf life, the solution may be somewhat counterintuitive. Development of mathematical models must account for the interaction between the reactants, which in the case of fat oxidation involving oxygen and water availability can be very complex [22]. Studies have found that a modest water vapor concentration in the headspace may actually prolong shelf life with potato chips in high-barrier bags, although the textural changes implicit in this argue for careful control of headspace/interstitial gasses [23].

Beer and Wine Spoilage

Because beer and wine are already fermented, they provide both a modest degree of antimicrobial protection and a ripe growth media for competing organisms. The chief degradation mechanisms for beer that is produced using a good recipe and correct yeast cultures in a properly sanitized facility are usually the result of oxygen exposure, light degradation of isohumulone components in hops (resulting in a distinctive "skunking" off-odor), and temperature abuse. The usual protection methods beyond pasteurization, if used, include minimizing exposure to high temperatures, storage in light-blocking bottles, and reducing oxygen exposure. Some bottle caps for the brewing industry have been produced with an oxygen-scavenging seal because it is the only mode of oxygen ingress for a glass bottle with a metal crown cap.

Wine spoilage is compounded by several factors: long storage life occasionally exceeding a decade or more, the porous nature of traditional corks, and the intrinsic slow change of flavor characteristics over a wine's storage life. Light and temperature abuse as previously described for beer are common quality-degradation factors. Oxidation of anthocyanins and various phenolic compounds can change the flavor, aroma, and color of wine, and contamination by a variety of spoilage yeasts as well as sulfur compound formation and degradation can contribute to quality changes.

Natural cork materials also contribute both to the degradation and controversy of wine storage, with *cork taint* that results from the degradation of chlorine-bleached cork by filamentious fungi [24]. This produces a host of microbial breakdown products, most notably trichloroanisole (TCA) via the breakdown of trichlorophenol compounds, although other resulting by-products may be present [27, 28].

Appendixes

Appendix 7.1. Oxygen and Water Permeability of Plastic Films

Examples of Permeability of Polymer Films to Oxygen and Water Vapor		
(cc*mm) × 10^8/(cm^2*s*cm Hg partial pressure)		
Material	Oxygen Permeation	Water Vapor Permeation
Polyethylene, Low Density	55	9.0
Polyethylene, High Density	0.5	1.2
PVC – Plasticized	6	6.1
PVC – Unplasticized	1.2	N/A
Polystyrene	15–250	12
Oriented Polypropylene	21	5.1
PET	0.30	13
Nylon 6	0.38, varies with humidity	0.05
EVOH (Ethylene Vinyl Alcohol)	0.8–1.9, varies with humidity	100+
PVDC (Saran®)	0.05	0.3

Note: These are approximate values only, and should only be used as an illustration of relative values. Each supplier, product, product grade, and processing treatment will differ substantially from these values. Surface modifications such as metallization, coating, or printing will affect them as well.

Appendix 7.2. Ethylene Sensitivity of Various Produce Products.

ETHYLENE PRODUCTION/SENSITIVITY CHART				
	RECOMMENDED TEMPERATURE SETTING			
COMMODITY	C	F	ETHYLENE PRODUCTION RATE	SENSITIVITY TO ETHYLENE ACTION
FRESH FRUIT & VEG.				
Apple (non-chilled)	1.1	30	VH	H
Apple (chilled)	4.4	40	VH	H
Apricot	−0.5	31	H	H
Artichoke – Globe/Jerusalem	0.0	32	VL	L
Asian Pear	1.1	34	H	H
Asparagus	2.2	36	VL	M
Avocado – California	3.3	38	H	H
Tropical	10.0	50	H	H
Banana	14.4	58	M	H

(*Continued*)

Appendix 7.2. (*Continued*)

ETHYLENE PRODUCTION/SENSITIVITY CHART				
	RECOMMENDED TEMPERATURE SETTING		ETHYLENE PRODUCTION RATE	SENSITIVITY TO ETHYLENE ACTION
COMMODITY	C	F		
Beans – Lima	0.0	32	L	M
Snap/Green	7.2	45	L	M
Belgian Endive	2.2	36	VL	M
Berries – Blackberry	−0.5	31	L	L
Blueberry	−0.5	31	L	L
Cranberry	2.2	36	L	L
Currants	−0.5	31	L	L
Dewberry	−0.5	31	L	L
Elderberry	−0.5	31	L	L
Gooseberry	−0.5	31	L	L
Loganberry	−0.5	31	L	L
Raspberry	−0.5	31	L	L
Strawberry	−0.5	31	L	L
Breadfruit	13.3	56	M	M
Broccoli	0.0	32	VL	H
Brussels Sprouts	0.0	32	VL	H
Cabbage	0.0	32	VL	H
Cantaloupe	4.4	40	H	M
Cape Gooseberry	12.2	54	L	L
Carrots – topped	0.0	32	VL	L
Casaba Melon	10.0	50	L	L
Cauliflower	0.0	32	VL	H
Celery	0.0	32	VL	M
Chard	0.0	32	VL	H
Cherimoya	12.8	55	VH	H
Cherry – Sour	−0.5	31	VL	L
Sweet	−1.1	30	VL	L
Chicory	0.0	32	VL	LH
Chinese Gooseberry	0.0	32	L	H
Collards	0.0	32	VL	M
Crenshaw Melon	10.0	50	M	H
Cucumbers	10.0	50	L	H
Eggplant	10.0	50	L	L
Endive (Escarole)	0.0	32	VL	M
Feijoa	5.0	41	M	L
Figs	0.0	32	M	L
Garlic	0.0	32	VL	L
Ginger	13.3	56	VL	L
Grapefruit – AZ/CA/FL/TX	13.3	56	VL	L
Grapes	−1.1	30	VL	L
Greens	0.0	32	VL	H
Guava	10.0	50	L	M
Honeydew	10.0	50	M	H
Horseradish	0.0	32	VL	L
Jack Fruit	13.3	56	M	M

Appendix 7.2. (*Continued*)

ETHYLENE PRODUCTION/SENSITIVITY CHART				
	RECOMMENDED TEMPERATURE SETTING		ETHYLENE PRODUCTION RATE	SENSITIVITY TO ETHYLENE ACTION
COMMODITY	C	F		
Kale	0.0	32	VL	M
Kiwi Fruit	0.0	32	L	H
Kohirabi	0.0	32	VL	L
Leeks	0.0	32	VL	M
Lemon	12.2	54	VL	M
Lettuce – Butterhead	0.0	32	L	M
Head/Iceberg	0.0	32	VL	H
Lime	12.2	54	VL	M
Lychee	1.7	35	M	M
Mandarine	7.2	45	VL	M
Mango	13.3	56	M	H
Mangosteen	13.3	56	M	H
Mincola	3.3	38	L	L
Mushrooms	0.0	32	L	M
Nectarine	−0.5	31	H	H
Okra	10.0	50	L	H
Olive	7.2	45	L	M
Onions – Dry	0.0	32	VL	L
Green	0.0	32	VL	M
Orange – CA/AZ	7.2	45	VL	M
FL/TX	2.2	36	VL	M
Papaya	12.2	54	H	H
Paprika	10.0	50	L	L
Parsley	0.0	32	VL	H
Parsnip	0.0	32	VL	L
Passion Fruit	12.2	54	VH	H
Peach	−0.5	31	H	H
Pear – Anjou/Bartlett/Bose	−1.1	30	H	H
Prickley	5.0	41	N	L
Peas	0.0	32	VL	M
Pepper – Bell (Sweet)	10.0	50	L	L
Chili	10.0	50	L	L
Persian Melon	10.0	50	M	H
Persimmon – Fuyo	10.0	50	L	H
Hachiya	0.5	41	L	H
Pineapple	10.0	50	L	L
Guava	5.0	41	M	L
Plantain	14.4	58	L	H
Plum/Prune	−0.5	31	M	H
Pomegranate	5.0	41	L	L
Potato – Processing	10.0	50	VL	M
Seed	4.4	40	VL	M
Table	7.2	45	VL	M

(*Continued*)

Appendix 7.2. (*Continued*)

ETHYLENE PRODUCTION/SENSITIVITY CHART				
	RECOMMENDED TEMPERATURE SETTING		ETHYLENE PRODUCTION RATE	SENSITIVITY TO ETHYLENE ACTION
COMMODITY	C	F		
Pumpkin	12.2	54	L	L
Quince	−0.5	31	L	H
Radishes	0.0	32	VL	L
Red Beet	2.8	37	VL	L
Rambutan	12.2	54	H	H
Rhubarb	0.0	32	VL	L
Rutabaga	0.0	32	VL	L
Sapota	12.2	54	VH	H
Spinach	0.0	32	VL	H
Squash – Hard Skin	12.0	54	L	L
Soft Skin	10.0	50	L	M
Summer	7.2	45	L	M
Zucchini	7.2	45	N	N
Star Fruit	8.9	48	L	L
Swede (Rutabaga)	0.0	32	VL	L
Sweet Corn	0.0	32	VL	L
Sweet Potato	13.3	56	VL	L
Tamarillo	0.0	32	L	M
Tangerine	7.2	45	VL	M
Taro Root	7.2	45	N	N
Tomato – Mature/Green	13.3	56	VL	H
Brkr/Lt. Pink	10.0	50	M	H
Tree – Tomato	3.9	39	H	M
Turnip – Roots	0.0	32	VL	L
Greens	0.0	32	VL	H
Watercress	0.0	32	VL	H
Watermelon	10.0	50	L	H
Yam	13.3	56	VL	L
Live Plants				
Cut Flowers – Roses	0.0	32	VL	H
Chrysanthemums	0.0	32	VL	H
Gladioli	2.2	36	VL	H
Carnations	0.0	32	VL	H
Potted Plants	−2.8-18.3	27/65	VL	H
Nursery Stock	−1.1/4.4	30/40	VL	H
Christmas Trees	0.0	32	N	N
Flower Bulbs – Bulbs/Corns/Rhizomes/Tubers	7.2/15	45/59	VL	H

N = NONE, L = LOW, H = HIGH, VL = VERY LOW, M = MEDIUM, VH = VERY HIGH.
Source: Dry Pak Industries Inc. Used With Permission.

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