Appendix C

Technological Evaluation of Shelf Life of Foods

INTRODUCTION

Appendix B covered the major modes of deterioration and the principles of processing foods. It can be concluded from that appendix that one of the major environmental factors resulting in increased loss of quality and nutrition for most foods is exposure to increased temperature. The higher the temperature, the greater the loss of food quality. Thus, in order to predict the extent of high-quality shelf life so as to be able to put a shelf-life date on a product, a knowledge of the rate of deterioration as a function of environmental conditions is necessary. * Coupled with this would be the need for knowledge of the actual environmental conditions to which the various classes of foodstuffs are exposed.

Basically, for each food item, each mode of deterioration was studied at several temperatures for up to 3 years. In addition, information as to temperatures in warehouses, boxcars, etc., was gathered. Many reports and tables resulted from the study. However, much is not applicable today because the various types of foods are processed differently, different packaging systems are used, the distribution system has changed, etc. Nevertheless, one interesting outcome of the report was a nomograph (figure C-1), which gives the prediction of quality for various food classes based on some rate of deterioration and a desired shelf life. What this graph says is that given a certain rate of loss, if it is constant, one can predict the amount of change. Unfortunately, this simple method is not correct for many foods and for many modes of deterioration such as nutrient loss, color change, and flavor change. This appendix covers the basic principles of how temperature and other environmental factors affect the rate of food deterioration and how this can be used to predict the sell-by, best-if-used-by, or use-by date. These methods are not needed for a pack date.

*The U.S. Army supported some major studies during the late-1940's through 1953 to gain this information for the military food supply. The studies are summarized in S. R. Cecil's and J. G. Woodroof's (1962) “Long Term Storage of Military Rations” (Ga. Exp't Station Tech. Bull. 25).
Figure C-1.—Nomogram of Temperature, Time, and Quality for the Military Ration Items Used in the Long-Term Storage Tests

Use of the nomogram (as illustrated by dotted lines):

(a) The $k$ values given for storage of individual items (figures 9-80) may be used with scales $k$, $t$, and $Q_k$. For example, a $k$ value of 3.5 percent per 6 months resulted in a quality level in the upper range of "good" after 1.5 years of storage, as shown by the point at which the $Q_k$ scale is intercepted by a straight-edge passing through 3.5 on the $k$ scale and 1.5 on the $t$ scale.

(b) The scales for types of products are used in matched pairs. For example, vegetable or fruit products stored at 70°F (corresponding to an average $k$ value of 6.5 as shown) for 3 years had an average quality rating in the upper range of "fair," since the $V$ scale quality is intercepted at this level by the line passing through 70 on the $V$ temperature scale and 3 on the $t$ scale.
Appendix C— Technological/ Evaluation of Shelf Life of Foods

PRINCIPLES FOR THE RATE

General Rate of Loss of Quality Equation

The loss of food quality for most foods can be represented by mathematical equation 1:

\[
\text{rate} = \frac{dA}{dt} = kA^n
\]

where:
- \(A\) = the quality factor measured
- \(\theta\) = time
- \(k\) = a constant that depends on temperature and water activity
- \(n\) = a power factor called the order of the reaction, which defines whether the reaction rate is independent of the amount of quality left
- \(\frac{dA}{dt}\) = the rate of change of \(A\) with time. A negative sign is used if the deterioration is a loss of \(A\) and a positive sign if it is for production of an undesirable end product

Usually, results of shelf-life studies are not obtained as a rate but rather as the amount of \(A\) left or produced as a function of time.

Constant Loss of Shelf Life

Based on equation 1, much of the food literature assumes (without truly measuring it) that the value of \(n = 0\). This assumption, called a zero-order reaction scheme, then implies that the rate of loss is constant with time as shown in equation 2 for some constant temperature.

\[
\text{rate of loss} = \frac{dA}{d\theta} = k = \text{constant at some constant temperature}
\]

What equation 2 means is that the percent of shelf life lost per day is constant at some constant temperature. This is the assumption used in the nomograph of figure C-1. Mathematically, if equation 2 were integrated, the amount of quality left with time as a function of temperature becomes equation 3:

\[
\text{amount left (A)} = \text{initial amount (A)}_0 - k\theta
\]

In terms of shelf life, this becomes equation 4:

\[
\theta = \frac{A_0 - A_f}{k}
\]

where:
- \(A_0\) = initial (zero time) value of quality factor
- \(A_f\) = value of \(A\) at end of shelf life (could be zero or any other defined value as measured in a consumer test)

\(\theta\) = shelf life in days, months, years, etc

In many cases, \(A\) is not a very quantifiable, chemically, or measurable value and must be based solely on human panel evaluation. In this case, \(A_0\) is assumed to be 100-percent quality and \(A_f\) is just unacceptable quality. Thus, the rate of deterioration becomes the rate constant in equation 5:

\[
\text{rate of quality loss} = \frac{100\%}{\theta} = \text{constant}\%\ \text{loss per day}
\]

This is the assumption used in figure C-1. Technically, the major problem in shelf-life testing is to verify that indeed \(n = 0\) so that equation 4 or 5 can be used. This is not easy to do, although some modes of deterioration are directly applicable to zero-order kinetics. These include:
- Enzymatic degradation (fresh fruits and vegetables, some frozen foods, some refrigerated doughs);
- Nonenzymatic browning (dry cereals, dry dairy products, dry pet foods, and loss of protein nutritional value); and
- Lipid oxidation (rancidity development in snacks, dry foods, pet foods, frozen foods).

Based on this knowledge, one can predict the shelf life of a food at a given single temperature if the amount of loss at any time is known. For example, if it is known that a certain food has lost 50 percent of its quality in 100 days if held at some constant temperature, then:

\[
k = \frac{30}{100} = 0.30 = 0.5\%\ \text{per day}
\]

Based on this, we could construct figure C-2 which gives the shelf life left as a function of time (\(k\) is the slope of the line). As seen at 40 days, there is 80-percent shelf life left: at 160 days, there is 20 percent left: etc.

The main problem in establishing this graph is determining the criteria of what is to be measured. That is, what is \(A\) or how much of \(A\) must be lost to give an end of shelf life as perceived by the consumer. It must be noted that shelf life is not a function of time; rather, it is a function of the environmental conditions and the amount of quality change that can be allowed. The second problem is that since food distribution occurs at variable temperatures, this data must be collected at sev-
eral temperatures to be useful. Methods to apply this graph to variable conditions are described later.

Quality-Dependent Shelf-Life Loss Function

As discussed above, the shelf life in many cases does not follow a simple constant rate of deterioration. In fact the value of \( n \) can range for many reactions from zero to any fractional value or whole value up to 2. In fact many foods that do not deteriorate at a constant rate follow a pattern where \( n = 1 \), which results in an exponential decrease in rate of loss as the quality decreases. This does not necessarily mean that the shelf life of foods that follow this scheme is longer than those with a constant loss rate, since the value of the rate constant is very important. Mathematically, the rate of loss is, as shown in equation 6:

\[
\text{rate of loss} = - \frac{dA}{d\theta} = k(A) \tag{6}
\]

Integrating equation 6 gives a logarithmic function as shown in equation 7:

\[
\ln \left( \frac{A}{A_0} \right) = -k\theta \tag{7}
\]

where
- \( A \) = amount of quality left at time \( \theta \)
- \( A_0 \) = initial quality
- \( k \) = the rate constant in units of reciprocal time

A graphical representation of the amount of quality left as a function of time is not a straight line as illustrated in figure C-3. If 50 percent is lost in 100 days as in the previous example, then at 40 days, there is 76 percent of the quality left. For a constant rate of loss, there would be 80 percent left. At 100 days, both mechanisms give the same percent left, but after this time, the quality loss slows down for the exponential mechanism and theoretically never reaches a zero value. For example, at 160 days, there is 33 percent left, and at 300 days, there is still 12.5 percent left. The types of deterioration that follow an exponential equation include:

- rancidity (in some cases, as in salad oils or dry vegetables);
- microbial growth (fresh meat, poultry, fish, and dairy products);
- microbial death (heat treatment and storage);
- microbial production of off-flavors, slime, etc. (fresh meat, poultry, fish, and dairy products);
- vitamin losses (canned, semimoist, and dry foods); and
- loss of protein quality (dry foods).

Another way of representing exponential decay in figure C-3 is to plot it in semilog as in figure C-4. The slope of this line is the rate that is constant at constant temperature. Typically, for exponential decay mechanisms, the rate constant can be represented by \( \theta_c \), which is called the half life. Mathematically, if one knows the amount of deterioration at any time at some constant temperature and if it follows a first-order reaction, figure C-4 can be easily constructed.
Appendix C— Technological Evaluation of Shelf Life of Foods

Figure C-4.—First-Order Log Plot

![First-Order Log Plot]

**Other Mechanisms of Shelf-Life Loss**

Very little data exists that describes food deterioration by orders other than zero or first. Lee et al. (J. Food Sci. 42:640, 1977) and Sing et al. (J. Food Sci. 41:304, 1976) have described the deterioration of vitamin C in liquid foods such as tomato juice or canned infant formulas by a second-order reaction. In this case, the reaction is dependent on both ascorbate and oxygen—as the oxygen is depleted, the rate of loss of ascorbate becomes less than that predicted by a first-order reaction.

Labuza (Critical Rev. Food Tech. 3:355, 1971) has reviewed the area of lipid oxidation kinetics and has found that oxygen uptake generally follows a half-order reaction with respect to oxygen for relatively pure lipids. However, addition of antioxidants changes the order to first order. In complex foods, however, the data best fit zero-order kinetics.

When sensory quality change is plotted against time, not infrequently the axiom “fresh is best” is violated. For example, Kramer et al. (J. Food Qual. 1:23, 1977) found an improvement in sensory quality of certain prepared frozen foods after frozen storage for 3 months. After 6 months of storage, sensory quality began to deteriorate and continued by approximately a first-order reaction. The entire curve, however, could best be fitted as a cubic polynomial. Similar results were obtained with reportable-pouch packed items by Salunkhe and Giffee (J. Food Qual. 2:76, 1978). A typical curve for this type of response is shown as figure C-5.

Such sensory responses can be explained on the basis of psychophysical characteristics inherent in sensory evaluations. They do not contradict the above general principles of the kinetics of shelf-life loss. All that is indicated is that consumers prefer (best) what they are accustomed to, which is not always the freshest product. Thus, in the case of preference for 3-month-old frozen foods, the reason was that the products were initially overspiced and reached an optimal flavor blend and intensity after 3 months’ storage. In the case of the pouch/canned products, consumers preferred products that were slightly degraded over the fresh. These not-unusual sensory responses indicate first the great difficulty in attempting a generalized prediction equation for shelf life and the need to study each product individually. They also indicate that freshest is not always best, although open dating is predicated on the assumption that consumers are convinced that freshness and sensory quality are the same.

**Figure C-5.—Initial Quality Gain Prior to First-Order Degradation**

![Initial Quality Gain Prior to First-Order Degradation]
TEMPERATURE DEPENDENCE OF RATE OF DETERIORATION

The above analyses of loss of quality were derived for a constant temperature situation. The temperature-dependent part of the rate of loss equation is the rate constant $k$. Theoretically, it obeys the Arrhenius relationship which states that the rate constant (or rate) is exponentially related to the reciprocal of the absolute temperature. A plot of the rate constant on semilog paper as a function of reciprocal absolute temperature ($1/T$) gives a straight line. A steeper slope means the reaction is more temperature-dependent—that is, as the temperature increases, the reaction is faster. It is possible that food can deteriorate by two different mechanisms with different temperature dependencies. For example, dry potatoes can go rancid and can become brown. The rates of each would have different temperature functions. What this means is the dominant mode of deterioration could change with increasing temperature to the faster reaction. This could be a problem in predicting shelf life.

Most data for modes of deterioration in the literature do not give rates or rate constants but rather are in the form of overall shelf life as a function of temperature. Mathematically, if only a small temperature range is used (no more than 20° to 400° C range), the data will give a fairly straight line if the shelf life for some quality measurement is plotted on semilog paper as a function of temperature as in figure C-6. This figure illustrates the temperature sensitivity of two foods or two modes of deterioration, both giving a shelf life of 200 days at 25° C. Theoretically, to construct this plot one needs: 1) some measure of loss of quality, 2) some endpoint value for consumer unacceptability, 3) data to measure the time to reach this endpoint, and 4) experiments to measure this loss for at least two temperatures so the line can be constructed. The more temperatures used, the better the statistical significance of the data.

It is obvious from the graph that the steeper the slope, the more sensitive is the food (or the reaction) to temperature. A measure of this sensitivity is called the $Q_{10}$ of the reaction that is defined in equation 8:

\[
Q_{10} = \frac{\text{rate of loss of quality at temperature (T + 10°C)}}{\text{rate of loss of quality at temperature T°C}} \quad (8)
\]

The $Q_{10}$ can also be calculated from the shelf-life plot as in equation 9:

\[
Q_{10} = \frac{\text{shelf life at T°C}}{\text{shelf life at (T+ 10°C)}} \quad (9)
\]

which assumes that the rate is inversely proportional to the shelf life.

As an example from figure C-6, it can be calculated that for food A, the $Q_{10}$ is:

\[
Q_{10} = \frac{\theta_{A} \text{ at 25° C}}{\theta_{A} \text{ at 35° C}} = \frac{200}{50} = 4
\]

For food B, the $Q_{10}$ is:

\[
Q_{10} = \frac{800}{3} = 266
\]

Thus, food B or reaction B is much more sensitive to an increased temperature than is A.

This graph has practical applications in studying loss of shelf life. To illustrate, if studies at two different temperatures are made, the shelf life at some lower temperature can be predicted if the line is assumed to be straight. One cannot, however, study the deterioration at only one temperature, since it is not possible to predict beforehand.
the shape of the line or the $Q_{10}$ exactly. Table C-1 illustrates how important the $Q_{10}$ would be in predicting shelf life at lower temperatures. It should be noted that since different reactions may occur at different temperatures to cause end-of-product acceptability, the projected line might be incorrect. For example, in figure C-6, reaction B would cause end of shelf life in 12 days at $30^\circ C$, but below $25^\circ C$, reaction A is faster and thus would be the controlling factor in end of shelf life if the figure referred to two major deterioration modes of a single food item.

### SHELF-LIFE Prediction FOR VARIABLE TEMPERATURE

Given that data as to the mathematical representation of the reaction causing end of shelf life can be obtained and a shelf-life plot constructed, some simple expressions can be derived to predict the extent of deterioration as a function of variable time/temperature storage conditions. From this, either a use-by date can be calculated or a sell-by date evaluated in which some shelf life left for home storage is figured in.

**Zero-Order Reaction Prediction**

For zero order, the expression is as follows in equation 10:

$$\text{amount left} = \text{initial amount} \left(1 - \frac{k \theta_i}{1 + n} \right)$$

where

$$\sum_{i=0}^{n} k \theta_i = \text{amount lost in variable period which is equal to the sum of the product of the rate constant (k, at each given temperature $T_i$) times the time interval ($\theta_i$) at the average temperature $T_i$, for the given time period $\Delta t$. (The whole sequence being broken into n segments of time)}$$

If the time/temperature history is broken up into suitable time periods as illustrated in figure C-7, the average temperature in that time period can be found. The rate constant for that temperature is then calculated from the shelf-life plot using a zero-order reaction, and this rate constant is multiplied by the time during the period. These are then added up to get the amount lost for a total of n segments.

If shelf life is based simply on some time to reach unacceptability, equation 10 can be simplified to give equation 11:

$$t_i = \text{fraction shelf-life consumed} = \sum_{i=0}^{n} \left( \frac{\theta_i}{\theta_f} \right) T_i$$

This equation says that the fraction of shelf life lost for holding the product at some temperature is equal to the time ($\theta_i$) held at that temperature divided by the total time ($\theta_f$) a fresh product would last if held at that temperature.

To employ this method, the temperature history is divided into n suitable time periods; the average temperature $T_i$ at each time period is evaluated; the time held at that temperature $\theta_i$ is then divided by the shelf life $\theta_f$ for that given tempera-

### Table C-1.—Weeks of Shelf Life at a Given Temperature for Given $Q_{10}$

<table>
<thead>
<tr>
<th>Temperature</th>
<th>2</th>
<th>2.5</th>
<th>3</th>
<th>4</th>
<th>5</th>
</tr>
</thead>
<tbody>
<tr>
<td>50°C</td>
<td>2</td>
<td>2</td>
<td>2</td>
<td>2</td>
<td>2</td>
</tr>
<tr>
<td>40°C</td>
<td>4</td>
<td>5</td>
<td>6</td>
<td>8</td>
<td>10</td>
</tr>
<tr>
<td>30°C</td>
<td>8</td>
<td>12.5</td>
<td>18</td>
<td>32</td>
<td>50</td>
</tr>
<tr>
<td>20°C</td>
<td>16</td>
<td>31.3</td>
<td>54</td>
<td>2.5</td>
<td>4.8</td>
</tr>
</tbody>
</table>
ture. The fractional values are then summed up to give the total fraction of shelf life consumed. The time left at any storage temperature at which the consumer may hold the product is the fraction of shelf life remaining \((1 - f)\) times the shelf life at that storage temperature from the shelf-life plot.

The U.S. Department of Agriculture (USDA) developed this method, referred to as TTT, or time/temperature/tolerance method (Conference of Food Quality, Nov. 4, 1960, USDA Agr. Res. Service, Albany, Calif.). Extensive references to its use can be found in the literature. For example, Gutschmidt (Lebensmittel Forschung und Technol. 7:137, 1974) applied this to storage-life prediction of frozen chicken with excellent results. It must be remembered, however, that this only applies for reactions with a zero-order de- teriorative mechanism—a constant rate of loss at constant temperature.

Zero-Order Shelf-Life Devices—Present Technology

A device that can be attached to a frozen food package to integrate time/temperature exposure in the manner discussed above has been developed (Kockums Chemical Company, Biomedical Science Division, Reston, Va.). Unfortunately, the device (i-point TTM) can only be used for reactions with the same temperature sensitivity or \(Q_{10}\) if shelf life is to be predicted. Those available in 1977 were i-point #1 \(Q_{10} = 140\); i-point #2 \(Q_{10} = 6\); i-point #3 \(Q_{10} = 36\). These devices could be used, however, to evaluate abuse during storage, and modifications can be made to get other \(Q_{10}\)'s.

The i-point device is based on an enzymatic reaction that is activated by breaking a seal which mixes the enzyme with a substrate. Color changes that occur with the subsequent reaction can indicate the days of shelf life left or the extent of degradation. Unfortunately, these devices have temperature responses that change above about \(-10^\circ\) C, resulting in a different \(Q_{10}\) (of about 2.2). They also have very rapid response times above \(+10^\circ\) C, so they cannot be used for foods with long shelf life (e.g., dehydrated foods).

The present cost of these devices prohibits their use on individual packages, but they can be put on cases or pallets to evaluate abuse conditions. Of course, if they are on the outside of a food carton, they will respond to temperature change more rapidly than does the bulk of the food, so the predicted shelf life would be less than the period of time the food could actually last.

A different device using the gas diffusion principle, which also integrates time and temperature, is available (Info-Chem, Fairfield, N.J.). After activation, a gas crosses a permeable barrier in the device to react with another chemical, causing a color change along a scale. The barrier property controls the temperature sensitivity. The \(Q_{10}\)'s are: \(T T W\) \(Q_{10} = 1.68\); \(T T W\) \(Q_{10} = 2.29\); \(T T W\) \(Q_{10} = 2.88\); and \(T T W\) \(Q_{10} = 4.03\).

A factor limiting the use of these latter devices is that they respond much too slowly at temperatures below freezing, so they probably cannot be used for refrigerated frozen foods. Even at \(4^\circ\) C, the devices all have a response life of 750 days. If the reaction rate was faster or the indicator was made more sensitive, they could be especially useful for very sensitive refrigerated pharmaceuticals to indicate if the drugs have been abused by holding at high temperatures. However, the devices are applicable for semiperishable foods with a shelf life of 30 days to 1 year at \(15^\circ\) to \(38^\circ\) C.

Other devices are available that integrate time and temperature but have much shorter response times. The 3-M Company (Minneapolis, Minn.) and Tempil Company (South Plainfield, N.J.) have developed abuse temperature/time integrators. These devices use the melting-point principle in which a waxy material melts at a given response temperature and is absorbed by a wick that develops a color along a visible scale (much like a thermometer) as long as the device is held above this critical response temperature. The device does not integrate absolute shelf life as the other devices: rather, it integrates exposure to some temperature above a set limit. This, however, is useful if the product has a very high \(Q_{10}\) (i.e., the food is very sensitive to high temperature). The devices are also useful for products with a shelf life of less than 1 week.

Several studies in the past have been made to test the reliability of these time/temperature integrators (K. Hu, Food Technology, August 1972; K. Hayakawa, ASHRAE J., April 1974; C. Byrne, Food Technology, June 1976; and A. Kramer and J. Farquhar, Food Technology, February 1976). In essence, they have found that many of these indicators become unreliable if they are exposed to high temperature prior to activation. In addition, the response characteristics in many cases do not match manufacturers’ specifications.

Since these studies were published, the indicators have been modified, so performance may be better although there is nothing available in the scientific literature. However, the major problem
is still to develop an indicator that exactly matches the $Q_{10}$ for the food if it is to be used on an individual food package to indicate amount of shelf life left. The Australians have devised such an indicator that has the capability of electronically setting the exact $Q_{10}$ desired (J. Olley, Int’l Inst. of Refrigeration, Australian National Committee, Joint Meeting of Commissions, Melbourne, Australia, September 1976). The device is useful as a research tool for monitoring a distribution system but is not practical for everyday use on packages. The significance in stimulating further development of shelf-life devices is that they could give the shelf life directly and would be a major benefit to the consumer.

**Exponential Decay Shelf-Life Prediction**

As with the mechanism measuring the constant loss of shelf life, an equation can be developed to predict the amount of shelf life used up as a function of variable temperature storage for foods that decay by an exponential mechanism. Equation 12 is:

$$A = A_0e^{-\frac{1}{k_{th}t}}$$

where $A$ is the amount left at the end of the time/temperature distribution, and $k_{th}$ is as was discussed for the constant-loss equation. Unfortunately, there are no reports in the literature for testing the validity of this equation in the measurement of shelf life as has been done for constant loss rates for frozen foods. However, application of this equation to the calculation of quality losses, nutrient destruction, and microbial death during the thermal processing of canned foods has been successful (M. Lenz and D. Lund, J. Food Sci. 42: 989, 1977; J. Food Sci. 42: 997, 1977; and J. Food Sci. 42: 1002, 1977). Therefore, there is no reason to believe that this equation and approach is not applicable to predicting storage life of foods.

Currently there are no devices that have a first-order response, and the zero-order devices mentioned above should not be used for a food which decays by first order unless the extent of reaction which terminates shelf life is only a small fraction of the total reaction that can occur. Further research is needed in this area.

**Sequential Fluctuating Temperatures**

In some cases, a product may be exposed to a sequential regular fluctuating temperature profile, especially if held in boxcars, trucks, and certain warehouses. This is because of the daily day/night pattern. Many of these patterns can be assumed to follow either a square-wave or sine-wave form as shown in figure C-8. The amount of deterioration occurring in this storage sequence can be calculated by the formulas previously presented if the proper order of reaction is used.

There have been some papers published that have developed formulas for calculating the amount deteriorated for either square-wave or sine-wave functions. The classic papers have been by Hicks (J. Coun. Sci. Ind. Research, Australia 17:111, 1944), Schwimmer et al. (Eng. Chem. 47:1149, 1955), and Powers (J. Food Sci. 30:520, 1965). Although not stated exactly in these papers, the derivations they presented were all for zero-order reactions. Unfortunately, subsequent work by some researchers has unknowingly used these equations for predicting changes that occur for first-order reactions such as microbial growth and vitamin C degradation. Recently, Labuza (J. Food Sci. 44, 1979) has derived the applicable functions for exponential reactions, but they have not been tested as of yet.

It also should be noted that using the mean temperature for either the sine or square wave to predict the loss that occurs does not give the same results as the actual amount of degradation. This is because the shelf life (or the reactions causing it) are exponentially related to temperature; thus the actual amount of degradation is always more.

**Figure C-8.—Sequential Regular Fluctuating Profile**
Based on this, the reaction can be assumed to be occurring at some effective temperature that is greater than $T$ mean. In the same paper Labuza (1979) has derived the necessary equations.

**Other Temperature Effects**

Two other phenomena can occur in foods as a function of temperature that lead to loss of shelf life—namely, staling and phase change. Staling is a process which occurs in bakery items and is related to the crystallization of starch components. In staling, the rate of loss of shelf life increases as temperature decreases. The kinetics are exponential in nature with a $Q_{10}$ of around 2 to 3. For a recent review of staling, see W. Knightly, Bakers’ Digest, No. 5, 51: 52, 1977.

A second area is that of phase change including thawing, freezing, and fat-melting—solidifying phenomena. Although no mathematical models can be developed to predict how these would affect loss of shelf life, it is known that thawed frozen foods are very subject to microbial deterioration, and the melted fat can oxidize faster as well as cause loss in desired texture. Commercial devices that indicate whether a frozen product has been exposed at temperatures where it can possibly thaw have been developed by the same companies that have made the time/temperature integrators. These are cheap enough to be used on individual food packages and would be useful to indicate abuse. However, a major drawback is that the device could melt before the food does and thus would not be truthful.

**UTILIZATION OF TEMPERATURE-DEPENDENCE EQUATIONS**

The previous section outlined the means by which equations could be used to predict shelf life. Obviously, these equations could be used to set a sell-by date in which the fraction of shelf life used up in the distribution/marketing system could be calculated. From this, information could be included on the package that would indicate the expected shelf life for given storage conditions in the home. Similarly, the same calculations including specified home storage could be used to set a use-by date. However, some of the problems that could occur which would make these calculations meaningless are:

1. The product used to develop the shelf-life data or graph may not be the final product marketed, since the shelf-life studies should start early in the product development.
2. As in 1, the product tested may be produced in the lab or pilot plant and therefore will not be subjected to the same conditions as would the product produced in the plant.
3. The ingredients can vary because of growth conditions, rain, sunshine, etc., as well as genetic variety. The ingredients may also be stored for variable times.
4. Labels must usually be made early in the year prior to the growing season so that if effects as in 3 occur, it would be impossible to account for them.
5. The calculations to set the date must be developed for the average conditions. Some products thus will be out-of-date before the time on the label just because of statistical variation.
6. Some products may be mishandled by distributors and supermarket personnel and thus could lose shelf life before the label date.
7. Product shelf-life tests can only be done on individual packages. During a large part of the distribution time, though, these packages are in cartons, which in turn are in cases, which are in pallets. Therefore, exposure to the external conditions is not so drastic—especially for those cartons in the center—and the product may have a shelf life greater than the label states. Good food could then be wasted.

Since other factors could also be included in this discussion, it is obvious that setting a true shelf-life date for each package cannot be done. Only averages can be calculated, and these only where good data exist. Collecting this data is a very time-consuming and expensive process, especially where sensory panel evaluations must be used. Thus, it is probably best to not require open dating of all food products but to mandate what can be put on the label if open dating is used. Based solely on kinetic implications with respect to temperature, a sell-by date with home-storage information or a best-if-used-by date seems most logical.
MOISTURE EFFECTS ON SHELF-LIFE PREDICTIONS

Moisture Gain or Loss Equation to Reach Critical Value

Moisture gain by dry or semidry foods can lead to several modes of deterioration, including microbial growth, loss of crispness, loss of softness, hardening, and caking. The moisture gain or loss for a food held at constant temperature and exposed to a given external relative humidity can be predicted from simple engineering relationships as reviewed by Labuza et al. (Trans. ASAE 15: 150, 1972). The basic equation 13 is:

\[
\frac{dw}{d\theta} = \frac{k}{x} \frac{A}{P_{rev}} (P_{out} - P_{in})
\]

where

- \(dw\) = grams water gained or lost per day
- \(k\) = package permeability to water
- \(P_{out}\) = vapor pressure outside the package
- \(P_{in}\) = vapor pressure inside the package — i.e., the vapor pressure of water from the food
- \(A\) = package surface area

As with temperature, an increase in external humidity conditions would decrease the time it would take for a given packaged dry food to reach the undesirable moisture content. The factors that would be needed to predict this time include:

- The moisture absorption isotherm as in figure B-1.
- The package film permeance \(k/x\). Manufacturers usually list a range of values for a given packaging film. However, actual values can be obtained by simple tests.
- The ratio of the package area \(A\) to dry weight \(W\) contained.
- The initial moisture content \(m_0\) and critical moisture \(m_c\) above or below which one should not go. The critical moisture \(m_c\) — the point of unacceptability — must be found from studies of the food at different moisture.
- The relative humidity and temperature to which the product will be subjected. From this and the isotherm equation \(m_t\), the moisture content the food would achieve if it had no package can be found. In addition, the value of the vapor pressure of water \(P_v\) at the temperature of the test can be obtained from standard tables.

Given these values, equations 14 and 15 can be found, which give the time \((\theta)\) to reach a certain moisture content \((m)\). The exponential term of moisture is plotted as a function of time in figure c-9.

\[
\ln \frac{m - m_c}{m_0 - m_c} = \frac{kA}{xW} \frac{P_v}{P_{in}} \theta
\]

As indicated in figure C-9, if condition III were the actual food-package system, storage under condition I would decrease the time to reach the critical moisture by a factor of 11-2, or 5.5 times. This would occur if the film used had 5.5 times greater water permeability. The same acceleration in loss of shelf life would occur if the product were stored at a temperature that would raise the vapor pressure of water \(P_v\) by 5.5 times. At 100-percent relative humidity, the vapor pressure of water ranges from about 17 mm Hg (at 20° C) to 72 mm Hg (at 45° C). Therefore, a decrease in the loss of shelf life of about 4.5 times would occur if the product were stored at the higher temperature and same relative humidity.

Food package size also can affect shelf life with respect to moisture gain. Since the ratio of package area to food weight contained \((A/W)\) decreases by one-third \(R\) (where \(R\) is the average
radius), a package of smaller size has a shorter shelf life as compared to a larger one.

In practice, in testing for shelf life of foods, researchers use a combination of higher humidity (percent RH) and temperature \( (T) \) than the food would normally be subjected to. Most food processors suggest, for dry foods, that the average temperature/humidity during distribution is 21° C at 50-percent RH and thus apply some factor by which the food shelf life under the adverse condition is multiplied to give the average shelf life.

Using this method and equation 13, the shelf life of a food for which the mode of deterioration is moisture gain or loss can be predicted if the external conditions of distribution and marketing are presumed to remain constant. However, in the real world, the humidity can vary as well as the temperature. Fluctuating temperature effects were discussed previously. In general, higher humidities are associated with higher temperature, but no exact pattern of correlation exists. For example, if a \( T/\text{percent RH} \) distribution were known as in figure C-10, the time \( \theta \) to reach a given change in moisture would have to be calculated by breaking up total time into \( n \) small \( \Delta \theta \) parts. For each \( \Delta \theta \), a \( T \) and percent RH \( \text{RH}_i \) could be read off the graph. Then to get the change in moisture for that segment of time (starts at \( m_i \) and ends at \( m_{i+1} \)), one must:

- Determine the vapor pressure \( P \) from a standard table.
- Derive a new \( m \) from the isotherm for the new external percent RH. If \( m \) is less than \( m \) at \( \Delta \theta_i \), the loss equation would be used; if it is greater than \( m \), the gain equation is used.

From these steps, the value of \( m \) as a function of time could be calculated, and thus \( \theta \) could be found. These calculations, in fact, could be used to predict the net-weight losses of cereals and flour under given variable external conditions—another currently controversial regulatory issue.

**Constant Weight Loss Prediction**

Two situations exist in which a more simplified version of weight loss can be derived: 1) loss of moisture from frozen foods and 2) loss of moisture from fresh produce such as meats, fish, vegetables, and fruits. In both cases, a constant external humidity and constant temperature are assumed, based on the fact that either frozen or refrigerated storage is used. The solution for both situations is based on equation 13.

\[
\frac{dW}{d\theta} = k \frac{A}{x} (P_{in} - P_{out}) = \frac{\text{grams H}_2\text{O}}{\text{day}}
\]

Given that \( k/x \), the area \( A \), the external humidity and \( P_{\text{out}} \) are constant, the question is to determine if \( P_{\text{in}} \) is constant. By definition, \( P \) is the vapor pressure of water in the food. For a frozen food, \( P_{\text{in}} \) is determined solely by the temperature that pure ice would have at the storage temperature and thus could be read from a standard table. Since fresh produce have moisture contents in the range of 60 to 98 percent and the loss of weight to reach an unacceptable quality is not large, the vapor pressure \( P \) is equivalent to that for liquid water at the storage temperature. Thus equation 13 becomes equation 16:

\[
\frac{\text{constant loss}}{\text{of moisture}} = \frac{dW}{d\theta} = k \frac{A}{x} \Delta \rho = \frac{\text{grams of water}}{\text{day}}
\]

If \( m \) is the critical moisture content as set by net-weight limitations or by quality and \( m \) is the initial moisture for a package containing \( W \) grams of dry solids of a food, the time to reach end of shelf life is determined by equation 17:

\[
\eta = \frac{(m_i - m_c)W}{k \frac{A}{x} \Delta \rho}
\]

This equation could be used to predict how long a food would last for certain conditions. For example, for a vegetable like celery in a package for which we would want 12 weeks of shelf life before it lost enough water to lose crispness, at a refrig-
erated storage of 5° C, the following conditions could prevail:

\[
P_{in} = 654 \text{ mm Hg}
\]

\[
P_{out} = 80 \text{ percent R.H.} \times 6.54 = 523 \text{ mm Hg}
\]

\[
\Delta P = 1.31 = 654 - 523
\]

If the celery had an initial moisture content of 95 percent and there were 10 ounces in the bag, the dry weight \(W_s\) would be 14 grams. Celery loses its crispness when it loses about 5 percent of its weight in water (\(m = 18; m_i = 19\)). Using polyethylene with a \(k/x = 1\) and a bag of 0.1 m\(^2\), the shelf life would be about 3 months based on water loss, thus achieving the 12 weeks. Of course, in this time, microbial growth could decay the food.

The realistic problem is defining some critical moisture content for the particular food. In real life, both temperature and humidity vary: thus an iterative procedure as described earlier must be used based on a constant weight loss by equation 16 for each of these periods.

### Moisture Change for Constant External Temperature and Humidity Conditions

In a classic research endeavor, Karel and Labuza developed the mathematical techniques that combined the equations for prediction of moisture change with the reaction kinetics of various modes of deterioration as a function of \(a_w\) (Air Force Contract F 41-609-68-C-0015, February 1969, Optimization of Protective Packaging of Space Foods). These theories were tested in detail by Mizrahi et al. for predicting loss of shelf life of dehydrated cabbage undergoing nonenzymatic browning by a zero-order mechanism (J. Food Sci. 35:799, 1970, J. Food Sci. 35:804, 1970). The results were extremely satisfactory.

The basic steps needed to be able to predict end of shelf life under these conditions are:

- Store the dehydrated product at several constant temperatures and various relative humidities and measure extent of deterioration with time. Much data like this is available in the literature for dehydrated foods, especially concerning vitamin loss. At least three humidities \((a_w)\)'s are required. The reaction order must be determined.
- Decide what extent of deterioration is considered to be unacceptable. Plot the log of the time to reach this extent for constant temperature versus the \(a_w\) of the product as in figure C-11. Generally, a straight line above the monolayer water activity should be obtained at constant temperature.
- Using either the moisture gain or loss equation and proceeding step by step as previously described, predict the moisture content change as a function of time for some constant external temperature and humidity (figure C-12).
- Using the \(m\) versus \(\theta\) graph, divide the time into small \(\Delta\theta\) segments (figure C-12) and measure the average moisture content in this time period.
- For each moisture content and temperature, calculate the change in quality using the previously developed equations.

As noted, these steps have been tested and found to be very good in predicting shelf life, Mizrahi and Karel (J. Food Sci. 42:958, 1977) have recently shown that this procedure can be simplified by storing the food in a very permeable material at a given high-relative humidity and
comparing the extent of degradation to any other condition by a ratio method. As in the above solutions, this assumes constant external temperature and humidity.

**Moisture Change Under Variable External Temperature and Humidity Conditions**

The previous section described predicting the loss of shelf life for constant external humidity conditions. The same procedures can be used to calculate the extent of reaction for variable temperature and humidity conditions applying the kinetic derivations as a function of temperature from the section “Shelf-Life Prediction for Variable Temperature.” The first step would be calculating the moisture content as a function of time for a variable time/temperature/humidity distribution as previously shown. Then, applying either zero- or first-order kinetics, the extent of degradation is calculated for small time segments knowing the moisture content, \( a_w \), temperature, and external relative humidity at that point.

Although this is the real world situation, no literature exists that has tested this idea, so it is not known how good the predictions would be for estimating a shelf-life date that could be used on a food package. Even more critical is the fact that the external humidity distribution is even less well-known for food systems and is not as easily predicated as is the external temperature distribution. Therefore, only rough estimates can be made of the actual loss of shelf life.

Of course, another way that this could be controlled would be to use a pouch with a very low water permeability, thereby eliminating the moisture-change problem. This could extend food shelf life, but at the expense of using more precious raw materials (petroleum, aluminum, etc.) and at greater cost to the consumer. It is this tradeoff that the consumer must make in terms of food purchase—that is, a longer guaranteed shelf life at a greater cost, or a possible out-of-date food at lower cost. In addition, no devices exist that can integrate time/temperature/humidity conditions with respect to shelf life.

**OXYGEN EFFECTS ON SHELF LIFE**

**Introduction**

Oxygen availability is another factor that can affect the time to reach end of shelf life and thus the open date put on a food package. Several reactions in which the rate is a function of oxygen availability include:

- microbial growth,
- senescence of fruits/vegetables,
- browning of fresh meat,
- rancidity (lipid oxidation), and
- vitamin C deterioration.

Very little information is available on the use of shelf-life prediction equations with respect to oxygen as well as temperature and moisture content. Karel (Food Technol. 28:50, 1974) has reviewed this area. Part of this void is caused by the difficulty in 1) designing simple equipment to control oxygen levels during experiments that utilize oxygen as one parameter and 2) measuring and controlling oxygen in food packages.
Fruit and Vegetable Senescence

Once fresh produce is harvested, it continues its biological processes of drawing upon internal starch and sugar stores for an energy supply. This will continue until the supplies are depleted or the buildup of breakdown products affects the tissue in such a way that spoilage or microbial attack occurs. This rate of biological reactivity is a function of oxygen availability in terms of oxygen pressure as described by figure C-13. As seen, the lower the oxygen pressure ($P_{O_2}$), the lower the rate of oxygen uptake via respiration, or conversely, the lower the rate of loss of stores. Thus, a low $P_{O_2}$ will give a longer shelf life. Unfortunately, below a certain $P_{O_2}$ level, an anaerobic process of incomplete breakdown occurs in which acids and alcohols are produced that also destroy the food quality. Thus, a lower limit exists.

Some fresh produce is preserved using this principle of limiting oxygen availability by: 1) holding under partial vacuum (hypobraric storage), 2) flushing the truck or storehouse with nitrogen to force out the oxygen, or 3) flushing and sealing in a semipermeable pouch. In addition, CO$_2$ may also be added. This slows the rate of oxidation by mass action, since CO$_2$ is a product of the oxidation process. Jurin and Karel (Food Technol. 17:104, 1963) have done some of the classic work in this area. They showed that the shelf life of a food in a pouch can be predicted graphically.

Figure C-13.—Senescence Rate as a Function of $O_2$

Figure C-14.—Rates of Permeation and Respiration of $O_2$
alyzed as a function of temperature also, utilizing the techniques described previously.

**Rancidity**

Labuza (Critical Reviews of Food Technol. 3, 1977) reviewed the relationship of oxygen to stability of foods with respect to rancidity. A situation similar to that of respiration exists in that the oxygen uptake follows the same pattern. However, there is no lower oxygen critical limit—the lower, the better, in fact—and CO₂ does not slow the reaction.

Simon et al. (J. Food Sci. 36:280, 1971) was the first to apply this to oxidation of a dehydrated shrimp product using the same type of mathematical and graphical analysis. Karel’s group (J. Food Sci. 37:679, 1972) did a more in-depth study in which moisture was also simultaneously diffusing into the package for potato chips stored at constant temperature and external humidity. Very elegant computer-based solutions were presented. However, the time to develop the necessary data for equation development for most foods would be far in excess of that desirable in shelf-life testing or product development.

Basically, it can be stated that methods can be developed to predict the end of shelf life when caused by oxygen-sensitive reactions that also depend on aₙ and temperature.