allowing for more accurate estimation of k at each temperature by eliminating the need to estimate a separate A_O for each experiment and thus increasing the degrees of freedom[21]. Another alternative is a nonlinear regression for estimating A_O, k_A and E_A/R[21,22,23]. Experimental data of concentration vs. time for all tested temperatures is used, substantially increasing the degrees of freedom and hence giving much narrower confidence intervals for the estimated parameters.

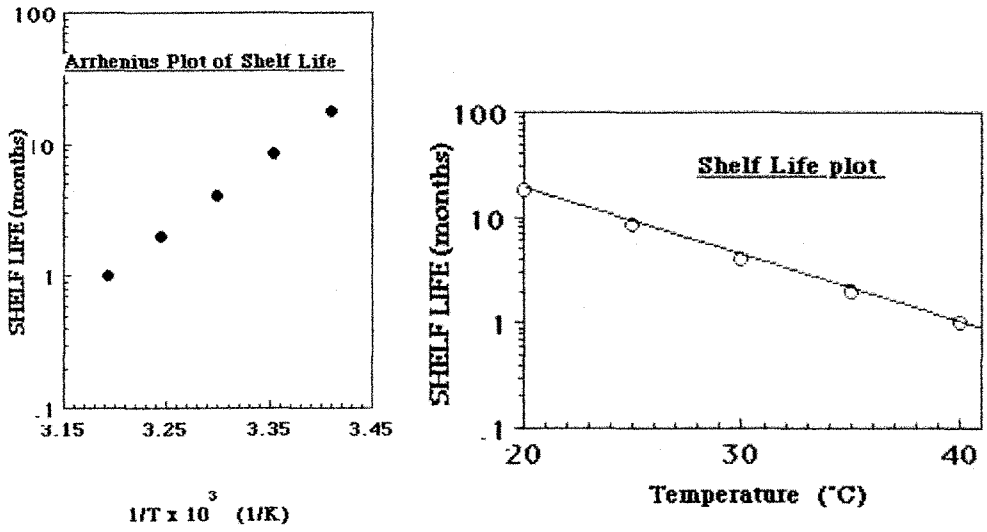
All the methods described above for the estimation of the Arrhenius parameters require isothermal kinetic experiments at three or more temperatures and a one or two step data analysis. An alternative method that has been proposed is the use of a single non-isothermal experiment. During the experiment there is a controlled increase of the temperature according to a predetermined function, T(t). This method is commonly used in the pharmaceutical industry. Yoshioka et al. (1987)[24] statistically evaluated this method and concluded that it required that a large number of samples must be taken to a higher reactant conversion than in the isothermal method. The non-isothermal method is very sensitive to experimental error in concentration measurements, not being satisfactory at a 5% precision level which is usual in the case of foods. Even at a low experimental error level (2%), the one step isothermal method with experiments at three temperatures gave better precision and accuracy for the estimation of the Arrhenius parameters than the non-isothermal method with a linearly increasing temperature at the same range and for the same total number of data points.

An alternative way of expressing temperature dependence which has been extensively used by the food industry and in the food science and biochemistry literature is the Q_{10} approach. Q_{10} is defined as the ratio of the reaction rate constants at temperatures differing by 10 °C. Equivalently Q_{10} has been defined as the change of shelf life θ_S, i.e., the time for A (or B) to reach unacceptable levels, when the food is stored at a temperature higher by 10 °C . This term called also be looked at as the temperature sensitivity of the reaction for a certain temperature range. This definition is important since the majority of the earlier food literature reports end-point data rather than complete kinetic modeling of quality loss. The Q_{10} approach in essence introduces a temperature-dependence equation of the form:

$$k(T) = k_O e^{bT} \qquad (11)$$

which implies that if ln k is plotted vs. temperature (instead of 1/T of the Arrhenius equation) a straight line is obtained. Equivalently, ln θ_S can be plotted vs.

temperature. Such plots are often called shelf life plots, where b is the slope of the shelf life plot and k_O is the intercept. The *shelf life plots* are true straight lines only for narrow temperature ranges[1] of 10 to 20 °C. For such a narrow interval, data from an Arrhenius plot will give a relatively straight line in a shelf life plot. In Figure 1 an Arrhenius plot of shelf life and a shelf life plot are compared showing good correspondence over the narrow 20°C range.



1 a **1 b**

Figure 1.(a) Arrhenius plot of shelf life of a food with 18 months shelf life at 20 °C and 1 month at 40 °C. (b) Shelf life plot of the same food.

Basically Q_{10} and b are functions of temperature and depend on the temperature range for equation (11). The activation energy of a food quality loss reaction, Q_{10} and b are interrelated through :

$$\ln Q_{10} = 10\, b = \frac{E_A}{R} \frac{10}{T(T+10)} \qquad (12)$$

The variation of Q_{10} with temperature for reactions of different activation energy is shown in Table 2.

Table 2. Q_{10} Dependence on E_A and Temperature

E_A kcal/mol	Q_{10} at 5° C	Q_{10}	Q_{10} at 20 °C	at40 °C
10	1.87	1.76	1.64	
20	3.51	3.10	2.70	
30	6.58	5.47	4.45	

Nevertheless, there are factors relevant to food and food quality loss reactions that can cause significant deviations from an Arrhenius behavior with temperature. These factors were outlined by Labuza and Riboh (1982)[25]. The most important is a temperature caused change in the reaction conditions (E_j) that are assumed constant. Phase changes are often involved. Fats may change to the liquid state contributing to the mobilization of organic reactants or vice versa[26]. In frozen foods the effect of phase change of the water to ice in a food causes a pronounced rate increase in the immediate subfreezing temperature range. The rate increase is especially notable for reactants of low initial concentration and is related basically to the freeze-concentration effect. It is prominent in the temperature zone of maximum ice formation, the width of which will depend on the type of food but generally will be in the range of -1 °C to -10° C. Experimental studies showing this negative temperature effect were reviewed by Singh and Wang (1977)[27]. Other phase change phenomena are also important. Carbohydrates in the amorphous state may crystallize at lower temperatures, creating more free water for other reactions but reducing the amount of available sugars for reaction [28]. Denaturation of proteins can increase or decrease their susceptibility to chemical reactions depending upon the stereochemical factors that affect these reactions, another factor that can cause non-Arrhenius behavior.

When two reactions important to food quality and with different E_A are occurring in the food, it is possible that each of them will predominantly define quality in a different temperature range. Thus, for example, if quality is measured by an overall flavour score, the quality change rate vs. 1/T will have a different slope in each of these regions. A typical example of such a behaviour is quality loss of dehydrated potatoes[1] where lipid oxidation and loss of fat soluble vitamins predominates up to 31 °C and nonenzymatic browning and lysine loss above 31 °C .For reactions that involve enzymatic activity or microbial growth the temperature dependence plot shows a maximum rate at an optimum temperature, below which an Arrhenius type

behaviour is exhibited while above it an inverse Arrhenius behaviour is followed (ln k decreases directly with 1/T).

A temperature increase increases the water activity at the same moisture level or enhances the moisture exchange with the environment in cases of foods in moisture permeable packages, affecting the reaction rate as will be discussed in the next section. Solubility of gases, especially of oxygen, changes with temperature (25% decrease with every 10 °C increase for O_2 in water), thus affecting oxidation reactions where the oxygen is limiting.

Taking into account the described limitations and the possible sources of deviation, the Arrhenius equation can still be used to model food degradation for certain ranges of temperatures. This model can be used to predict reaction rates and shelf life of the food at any temperature within the range, without actual testing. Equally important, it allows the use of the concept of accelerated shelf life testing (ASLT).

ASLT, as described previously, involves the use of higher testing temperatures in food quality loss and shelf life experiments and extrapolation of the results to regular storage conditions through the use of the Arrhenius equation. That cuts down very substantially the testing time. A reaction of an average E_A of 20 kcal/mol may be accelerated by 9 to 13 times with a 20 °C increase in the testing temperature, depending on the temperature zone. In Figure 2 the ASLT time needed at 104 °F for a food that has a shelf life of 18 months at 72 °F is shown based on different Q_{10}'s.

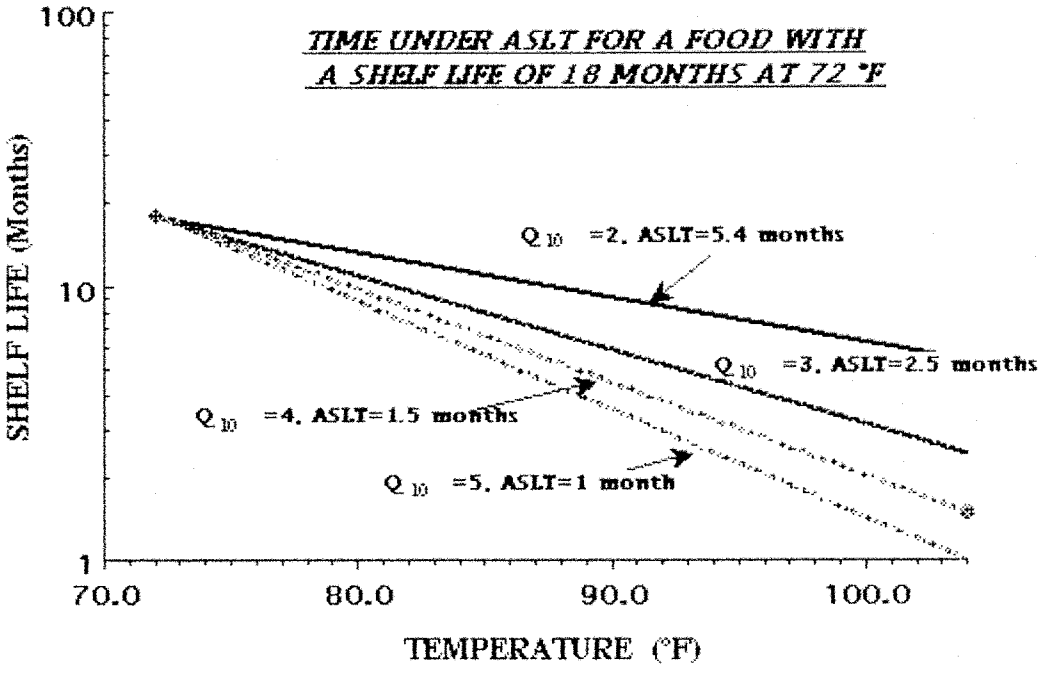


Figure 2. Effect of Q_{10} on ASLT times for a food of 18 months shelf life at room temperature (72 °F). The ASLT is conducted at 104 °F (40 °C).

Thus testing at room temperaturee would requite 1 1/2 years to reach end of shelf life whereas if the Q_{10} were high (4 to 5), the test can be completed in about a month. This principle and the methodology in conducting effective ASLT are described by Labuza (1985)*5* and Labuza and Schmidl (1985)*29*. Unfortunately a product development scientist does not know what the temperature sensitivity is before hand, so several test temperatures are required and the test may last 3 to 6 months.

Effects of other Environmental Factors

The relative humidity of the immediate enviroment which directly affects the moisture content and water activity (a_w) of a food is the second most important enviromental factor that affect the rate of food deterioration reactions*30*. Water activity describes the degree of boundness of the water contained in the food and its availability to act as a solvent and participate in chemical reactions*31*. Critical levels of a_w can be established above which undesirable deterioration of food occurs such as microbial growth or textural changes. Controlling the a_w is the basis for preservation of dry and intermediate moisture foods (IMF)*32*. Besides the specific critical a_w limits,

water activity has a pronounced effect on chemical reactions in these foods. Generally, the ability of water to act as a solvent, reaction medium and as a reactant itself increases with increasing a_W. As a result, many deteriorative reactions increase exponentially in rate with increasing a_W above the value corresponding to the monolayer moisture, the value at which most reactions have a minimum rate. For lipid oxidation the rate increases again as the a_W decreases below the monolayer.

The proposed theories that attempt to explain the effect of a_W on food deterioration reaction as well as ways to systematically approach and model this effect were discussed by Labuza (1980)[33]. The moisture content and water activity can influence the kinetic parameters (k_A, E_A), the concentrations of the reactants and in some cases even the apparent reaction reaction order, n. Most relevant studies have modeled either k_A as a function of a_W[34] related to the change of mobility of reactants due to a_W dependent changes of viscosity, or E_A as a function of a_W [34,35]. The inverse relationship of E_A with a_W (increase in a_W decreases E_A and vice versa) could be theoretically explained by the proposed phenomenon of enthalpy-entropy compensation. The applicability of this theory and data that support it have been discussed by Labuza(1980)[36].

Mathematical models that incorporate the effect of a_W as an additional parameter can be used for shelf life predictions of moisture sensitive foods. Also ASLT methods have been used to predict shelf life at normal conditions based on data collected at high temperature and high humidity conditions[35]. For example Figure 3 shows that a semilog plot of shelf life (in this case the half life of aspartame in a formulated model system) vs water activity also gives a straight line. This then allows one to use higher a_W's to project to shelf life at lower a_W's. Also noted in Figure 3, is the effect of initial pH of the system. As seenthe higher pH gives a somewhat longer shelf life at the lower water activities.

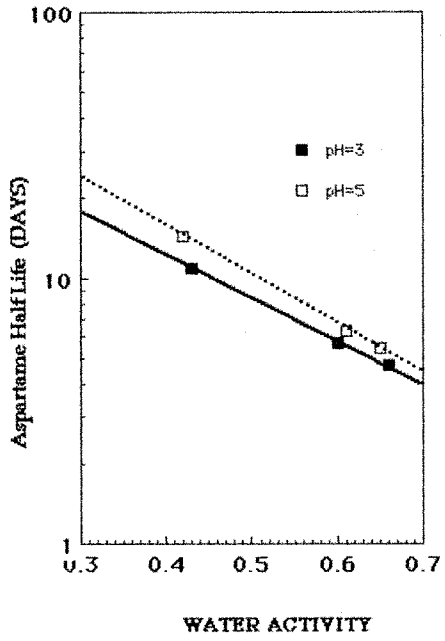


Figure 3. Half life of aspartame in a model food system plotted as a function of water activity

Such information can be applied to packaged foods in conjunction with moisture transfer models developed based on the properties of the food and the packaging materials . In packaged foods there exists a dynamic state of moisture exchange with the environment that tends to equilibrate the food's a_w to the external relative humidity. The moisture transport models allow the computation of the a_w of the food with time depending on the ambient relative humidity and temperature, the barrier properties of the selected package and the moisture isotherm of the food[37]. Knowledge of the temperature and a_w values in turn can be used in a computer model to estimate the loss of quality and the shelf life of the food/package system under any distribution or storage conditions. Thus, tests to study the effect of different packaging materials with the food and select the optimum configuration are really not needed as long as the foods deterioration kinetics are known along with the moisture permeability of the film.

Gas composition is an additional factor that may play a significant role in some quality loss reactions. Oxygen availability is very important for oxidative reactions and can affect both the rate and reaction apparent order depending upon whether it is limiting or in excess[12]. It also affects the respiration rates and senescence of plant materials and microbial growth depending on the redox potential. Vacuum packaging and nitrogen flushing is based on slowing down undesirable

reactions by limiting the availability of O_2. Further, the presence and relative amount of other gases, especially carbon dioxide, strongly affects biological and microbial reactions in fresh meat and fruit and vegetables. The mode of action of CO_2 has not been completely elucidated but is partly connected to surface acidification[38]. Different commodities have different optimum O_2 - CO_2 - N_2 gas composition requirements for maximum shelf life. Excess CO_2 in many cases is detrimental. Other important gases are ethylene and CO. Controlled and modified atmosphere packaging is based on these principles. Ideally by selecting a packaging material with the desirable permeance properties, the concentration of gases and the RH inside the package can be kept within predictable limits determined by the conditions set at processing. Gas transport models that incorporate the oxygen uptake and CO_2 generation by the food allow the calculation of packaging requirements. Unfortunately very few, if any, polymer films satisfy the requirements for both O_2 and CO_2 control. Alternatively, active control can be exerted through the use of enzymatic or chemical scavengers, a novel approach[39]. They can be added in the system in the form of sachets or integrated in the packaging material. A comprehensive review of CAP/MAP foods technology as well as the kinetic methods to predict their shelf life, is given by Labuza and Breene (1989)[40].

Quality Indices: Sensory vs. Instrumental Evaluation

In the previous sections the approaches to modeling quality loss of a food product were outlined. An important requirement for obtaining a reliable model was in all cases the definition of an appropriate index that measures or directly corresponds to food quality as evaluated by the final consumer, ie is the taste acceptable or not.

Chemical, microbiological and physical tests are used widely in the study of food quality. Characteristics used by the consumer for evaluation of a product, such as flavor, color and textural properties can be measured instrumentally or chemically. Careful evaluation of the chemical and biological reactions and physical changes that occur in the food during and after processing, based on the accumulated knowledge in food science, allows the recognition of the ones that are most important to its safety, integrity and overall quality [5]. The values of these analytically determined parameters must then be correlated to sensory results for the same food and a limit that corresponds to the lowest acceptable organoleptic quality can be set. In Figure 4 the loss of Vitamin C in frozen spinach and end of shelf life based on sensory quality is plotted vs temperature.

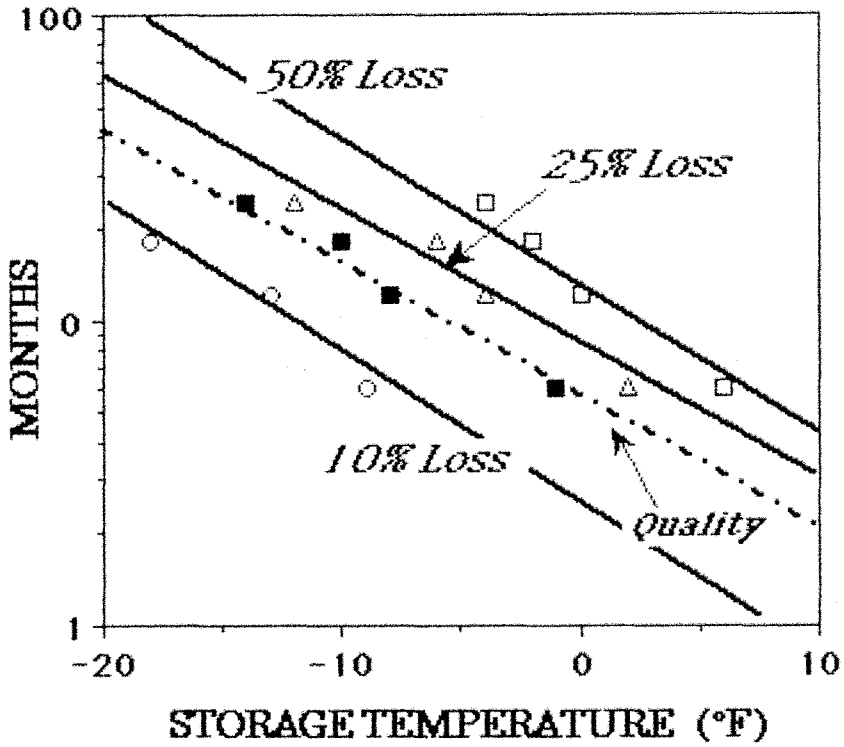


Figure 4. Plot of time to reach different levels of Vitamin C loss in frozen spinach vs temperature. Loss of quality (end of shelf life) by sensory evaluation is superimposed. (From data of Kramer (1974)[44]).

It can be seen that about 22% loss of the vitamin corresponds to the end of the shelf life based on sensory . However, caution should be drawn to the fact that correlation of values of individual chemical parameters to sensory data is often not straightforward because overall organoleptic quality is a composite of a number of changing factors[45]. The relative contribution of each factor to the overall quality may be different at different levels of quality or at different storage conditions. There are a number of publications that can serve as sources of information on food quality loss kinetics and sensory shelf life of foods. Reccomended comprehensive sources are: "Shelf-Life Dating of Foods" (Labuza, 1982)[1]; "Handbook of Food and Beverage Stability" (Charalambous, 1986)[46]; "Physical and Chemical Properties of Food" (Okos, 1986)[47].

Sensory evaluation during product development testing stages is usually doneby a trained panel to get a good estimate of the overall quality state of a food at each test time. Some sensory tests are designed to reveal, at a certain level of probability, that a product has changed or has reached the end of its shelf life

(difference tests). Hence they give "end point" information and do not allow for modeling quality loss with time. However one can construct a shelf life plot, if testing has been performed at different temperatures, and estimate a temperature sensitivity value. Another lapproach is to assign the zero time value as 100% quality and the end of shelf life value as 0% quality. Thus by testing at zero time and a few more times in between, an estimate of the end of shelf life (0% quality) can be made. This is based on the assumption that the sensory response is linear with time (ie zero order), which is often not true. A somewhat different approach is to attempt to model the progressive loss of overall quality characteristics, using a graded hedonic scale (eg a 9 (like highly to 1 (dislike highly) with just accptable at 5). If hedonic testing is properly conducted, the value of the perception y can be used as a quality index and plotted against time t. However, for hedonic testing, the requirements on the sensory panel for uniformity, experience and size are stricter than the difference tests and often these requirements are not met resulting in unreliable results. There are other problems concerning this approach. There is considerable difficulty in establishing a meaningful scale for each food product. In addition, an expert panel is not necessarily representative of consumers, let alone different consumer segments[41]. Even if that assumption can be made, a cut-off level of acceptability has to be decided upon. The time at which a large (but preset) percentage of panelists judge the food as being at or beyond that level is the end of shelf life . A criterion like that includes an indication of the proportion of the consumers to which the product must be acceptable until the end of shelf life, another variable to which reference or agreement is required.

The different statistical and graphical approaches for using sensory data in shelf life testing were evaluated by Labuza and Schmidl (1988)[42]. The maximum likelihood graphical procedure (Weibull method)[2,3] that is widely used in the electrical and machinery industries but has been scarcely used for food, was described as a good systematic approach to sensory testing.The Weibull method is simple in that it asks only "Is the product acceptable". The intensity of testing is increased near the end of shelf life so that a true shelf life is determined.

Besides the practical problems with regards to using sensory data in shelf life modeling further factors are the high cost that is involved with large testing panels and the questions connected to tasting spoiled or potentially hazardous samples. In some cases microbial growth or nutrient degradation could reach unacceptable levels while the food is still judged organoleptically acceptable. Sensory data are not "objective" enough for regulatory purposes and in cases of legal action or dispute. Sometimes consumers can be "trained" to accept lower standard products by being