Shelf Life Primer

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Basis of Kinetics

The shelf life of most products depends on initial products characteristics, processing parameters, packaging characteristics and environmental conditions a product is exposed to during distribution to the final user. Of importance to food, drugs, diagnostics, flowers, paint etc is the temperature, and in some cases, the humidity the product is exposed to. In some cases, for example fresh roasted ground coffee, the oxygen level in the package is also a factor. With liquid products in an impermeable jar, can or pouch, the major factor is temperature abuse.

S. Arrhenius was the first in 1887 to study the basis for the increase in rate of reactions (he worked on enzymatic and acid hydrolysis of sucrose). He developed an empirical approach showing that the rate increase as an exponential function of temperature. In that equation he coined a term, Ea, which is the activation energy and directly related to the sensitivity of the reaction to temperature through a function on Ln k (natural log of rate constant) vs 1/T (where T is temperature in K (Arrhenius, S., Z. Physik. Chem., 1:1101; 1887). The steeper the slope the more sensitive to a temperature change was the reaction. The slope is equal to Ea/R (R is gas constant).

My lab with Dr Marc Karel at MIT in the 1960s under contract from the DOD and NASA showed that the Arrhenius relation can be applies to both foods and drug stability. They simplified the mathematics and showed that one could describe a shelf life plot for a product as a semi log plot of shelf life (based on a set upon criteria) as shown in Figure 1 below.

An alternative way of expressing temperature dependence which has been extensively used by both the drug and 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 Q_S, i.e., the time for the product to reach an unacceptable level when t stored at a temperature higher by 10 °C. This term can 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 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, θ_S (shelf life time) can be plotted (again on semilog paper) 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 of 20 to 40 °C difference. For such an 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 20°C range. Mathematically we can calculate the E_a and Q_{10} from each other.

References are included at the end of this document from the drug field. In the food area it is generally difficult to find a chemical marker related to sensory quality while in drugs and diagnostics the loss of one critical component through chemical reaction can be measured. The US FDA requires that drug shelf life be based on no more than a 10% loss below label value based on the 95% lower confidence limit. Note that $\ln Q_{10} = 10b$ where b is the slope of the shelf life plot.

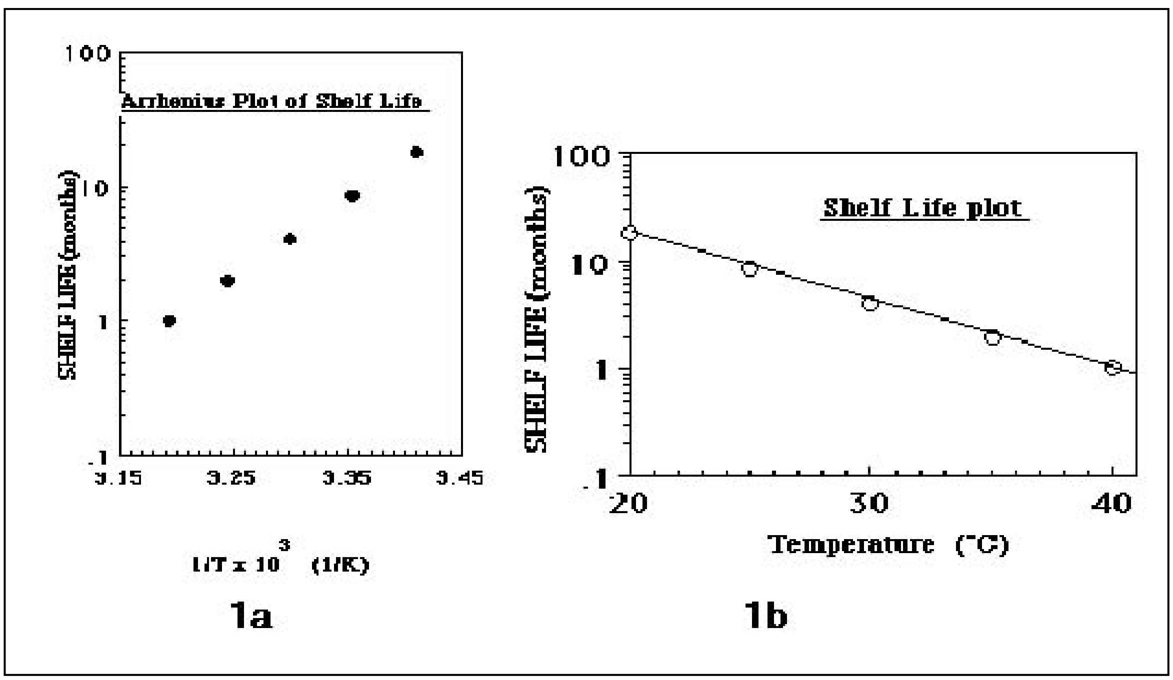


Figure 1.(a) Arrhenius plot of shelf life of a product with 18 months shelf life at 20 °C and 1 month at 40 °C. (b) Shelf life plot of the same product.

Shelf Life Used Calculation

The equation below can be used to determine the effect of a small segment of time at a given temperature—irrespective of the order of the reaction. This is a key component for electronic tags as they can be set for an optimum sampling time (12 to 15 min) to minimize power use and still give accurate results. Figure 2 below is a shelf life plot for sea bream, an expensive Mediterranean fish that experienced a 15% shrink in the Greek to Italy chain.

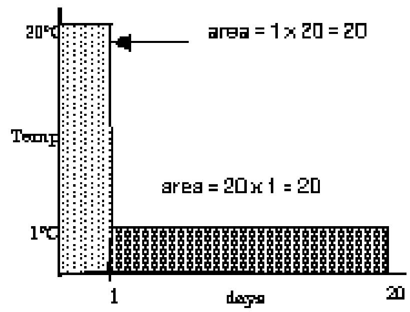


Figure 2 Two time temperature distributions.

In this distribution a product is subjected to two different legs in the distribution, 1 day at 20 C and 20 days at 1 °C. They both have the same area under the time temperature graph, ie 20 Degree-Days, yet they have vastly different effect depending on the Q_{10} or E_a of the product. For example the sea bream mentioned above gave an Arrhenius plot based on sensory score as shown in figure 3.

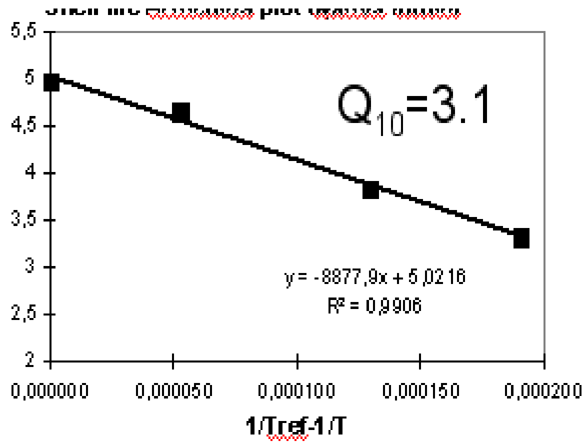


Figure 3 Arrhenius Plot for sensory shelf life of seabream

From the slope of the Arrhenius plot the Ea and Q10 can be calculated. As seen here the Q_{10} = 3.1, ie a 10 C increase in temperature increases the rate 3.1 fold. In addition from the plot one can choose a shelf life at a reference temperature, in this case we will choose) °C with a shelf life determined to be 28 days.

Equation 1 below shows the simplified equation for the % of quality lost for a given time where the temperature is assumed to be constant.

$$\%f_{consumed} = (100/\ t_{s0°C})x\ Q_{10}^{\ T/10}\ x\ time$$

In this case $t_{s0•C}$ is the shelf life at the reference temperature which was noted above and the Q_{10} = 3.1. The ∆T is the difference in actual temperature minus the reference temp. Thus:

at 20 C for 1 day

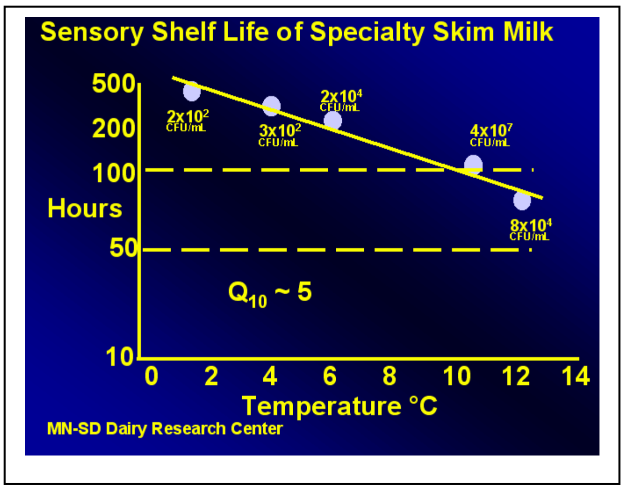
$$\%f_{consumed} = \frac{100}{28} x 3.1^{\frac{20}{10}} x 1 = 34\%$$

at 1 C for 20 days

$$\%f_{consumed} = \frac{100}{28} x 3.1^{\frac{1}{10}} x 20 = 80\%$$

As seen, the short time at higher temperature of 20° C had a ~ 50% less lost. Studies for ESL milk done in our lab, (Figure 4), show that it has a Q_{10} of 5 and with the same shelf life of 28 days at 0°C. The 20 days at 1°C give a loss of 85% or ~ 5 days left while at 20 °C for 1 day the milk is spoiled with a calculation of 128% lost. The value of an electronic TTI is that you can do this on the board and reader at a distance with a reader and get both the history and the fraction of shelf life lost in each segment.

Figure 4 Shelf life of ESL Milk as a function of temperature



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