Module II   Scientific Principles of Shelf Life Evaluation

Chapter 3: Use of Kinetic Analysis in Shelf Life Evaluation

In this module we will study some aspects of chemical kinetics that are useful in determining shelf life of foods. Specifically, we will examine zero-order and first-order kinetics which are commonly used to describe changes in quality attributes.

Goal: To learn principles of zero and first order kinetics and use them to predict shelf life of quality attributes.
Objective: By the end of this module you will have learnt

1) how to describe a zero order reaction
2) how to determine zero order rate constant
3) how to describe a first order reaction
4) how to determine a first order rate constant
5) how to predict shelf life of a food whose quality attribute is increasing or decreasing while following zero or first order kinetics.
6) what are some of the key concerns in using principles of chemical kinetics to describe rate of reactions.

The above package of frozen shrimp has gone well beyond its shelf life. This is a result of severe temperature fluctuations during storage and distribution.

Quality of food undergoes a change during storage and distribution. Changes in a specific quality attribute, A, with time, t, can be mathematically stated as shown in Eq (1).

$$\pm\frac{dA}{dt} \propto [A]^n \tag{1}$$

The left hand side of Eq(1) states that the rate of change of A with time, expressed as dA/dt may be increasing or decreasing, depending on whether the concentration of the quality attribute is becoming larger or smaller during storage. The rate of change is proportional to the concentration of the attribute, [A] raised to power n, where n is the reaction order. Eq (1) is a general rate equation.

In Eq (1), we remove the proportionality and introduce a constant, k. Where k is the reaction rate constant to obtain Eq (2).

$$\pm \frac{dA}{dt} = k[A]^n \tag{2}$$

3.1 Zero Order Reactions

For zero order reaction when the concentration A is decreasing, we use n = 0 to obtain,

$$-\frac{dA}{dt} = k \tag{3}$$

The differential equation given in Eq (3) is converted to a more useful form by integrating it. Before, we integrate it, we need to separate the two variables, A and t, so that they are on either side of the equation.

$$-dA = kdt \tag{4}$$

Now, it is easier to integrate, the left hand side is integrated from initial concentration, A_0 , to some final concentration, A. Similarly, the right hand side is integrated from initial time, 0, to some final time, t.

$$-\int_{A_0}^{A} dA = k\int_0^t dt \tag{5}$$

By evaluating the integrals, we obtain Eq (6).

$$-|A|_{A_0}^{A} = k|t|_0^t \tag{6}$$

Or,

$$A_0 - A = kt \tag{7}$$

The left hand side, A_0-A is an indication of how much the concentration of the quality attribute has changed from the initial value, A_0 to some value, A, at time t.

The left hand side of Eq (7) is also called the **extent of reaction** in chemical kinetics.

Next, we will relate this extent of reaction to the shelf life.

The extent of reaction can be thought of as equivalent to the change in a quality attribute as it reaches its end of shelf life. Thus, we obtain Eq(8) from Eq(7) by replacing A with concentration of quality attribute at the end of shelf life, A_e, and t with t_s, the time when the attribute has reached the end of its shelf life.

$$A_0 - A_e = kt_s \tag{8}$$

Eq (8) may be rearranged to write it in terms of the shelf life as given in Eq (9), where t_s is given as the change in quality attribute from A_0 to A_e divided by the zero order rate constant, k.

$$t_s = \frac{A_0 - A_e}{k} \tag{9}$$

Eq (7) is also useful in determining whether a reaction is following zero order. By rewriting Eq (7) and comparing it with an equation of a straight line, we note that the slope of the straight line will give the zero order rate constant, k.

Also, if we fit data on the change in concentration of a quality attribute, A, with time, to a straight line, then, the degree of fit can tell us whether the reaction is following zero order reaction. A good fit, determined by R^2 is what we need to know to decide.

Equation of straight line:

$$y = mx + c \tag{10}$$

y represents the ordinate, x the abcissa, m is the slope and c is the intercept

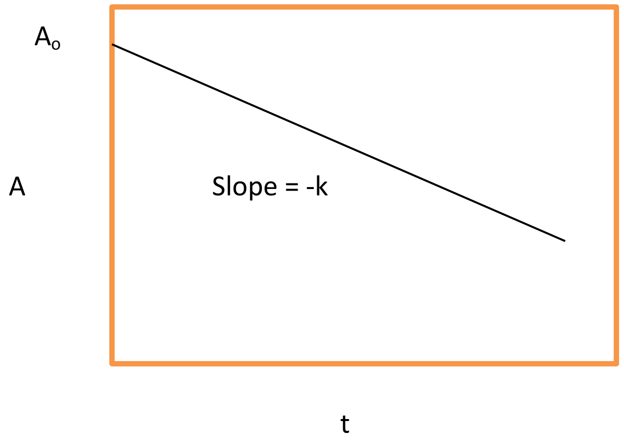


Figure 1 Change in the concentration of a quality attribute with time for a zero order reaction.

Example:

Let us consider an example with some data obtained for browning of fruit juice during storage. An aseptically processed juice is being evaluated for its shelf life. It has been determined that the key quality attribute affecting the shelf life is browning. Therefore, a shelf life study was designed to store the product for 60 days and measure the optical density (at 420 nm) at ten day intervals. The following data were obtained. Determine if the browning reaction may be characterized by pseudo zero-order kinetics. Calculate the shelf life if an optical density of 0.24 signifies the end of shelf life.

Time (days)	Browning (optical density)
0	0.05
10	0.071
20	0.089
30	0.11
40	0.128
50	0.149
60	0.17

Solution

We will use a spreadsheet to solve this problem.

1) enter the data in two columns.

2) plot it as an xy scatter plot

3) Use the Trend line feature, intercept at 0.05 and choose to display equation and R^2 value

4) Your plot should appear as shown in the right.

5) Compare the trend line equation shown in the Figure with Eq (3). Note that the slope is positive in this example since there is an increase of browning over time.

6) The high R^2 of 0.9996 suggests that the reaction is following a zero order. The slope represents the rate constant value of 0.002 units/day

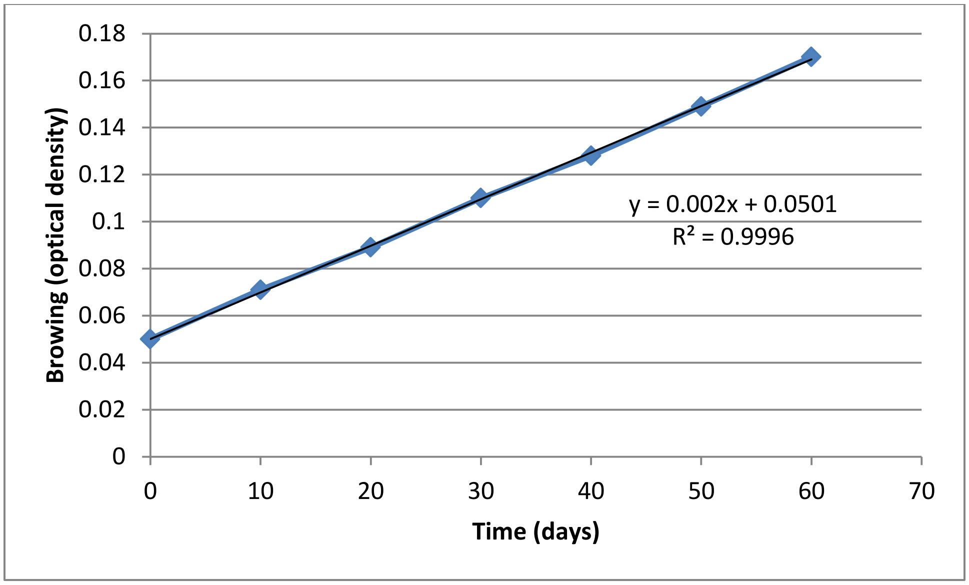


Figure 2. Browning reaction in stored orange juice

Shelf life is obtained by using Eq (9)

$$shelf\ life = \frac{A_e - A_0}{k} = \frac{0.24 - 0.051}{0.002}$$

Shelf life = 95 *days*

Thus, it will take 95 days for the browning reaction to cause the product to become unacceptable.

3.2 First Order Reactions

Now we will consider reactions that are described by the first order. Recall that for a general reaction scheme, as shown in Eq (1), the rate of change in concentration of A is proportional to the concentration of A raised to power n. By removing the proportionality, we introduce the rate constant, k.

For first order reaction, n=1, then A raised to power one will be A.

$$-\frac{dA}{dt} = kA \tag{11}$$

Therefore, in Eq (11), the rate of change in concentration A, is a function of both the concentration and the first order rate constant (Note, that in zero order reaction, the rate of change in concentration was a function only of the zero-order rate constant). We assume that the concentration of A decreases with time, therefore, we have -ive sign for the rate in Eq (11).

Next we will integrate Eq (6) to obtain the rate constant, k. In order to integrate Eq (11), we first separate the variables A and t on either side of the equation.

$$-\frac{dA}{A} = kdt \tag{12}$$

Then,

$$-\int_{A_0}^{A}\frac{dA}{A} = k\int_0^t dt \tag{13}$$

The integral of dA/A is *ln* A, and integral of dt is t. The integrated terms are evaluated from A_o at time zero to A at time t.

$$-|lnA|_{A_0}^{A} = k|t|_0^t \tag{14}$$

$$lnA_0 - lnA = kt \tag{15}$$

The integrated expression is shown in Eq (15). Note the difference with zero order reaction, now we have natural logarithm term. With today's computers, equations with logarithm can be evaluated quite easily as we will see later with an example.

Equation (15) also suggests that the right hand side is the extent of reaction, representing the decrease in the concentration of A from some initial value to A at time t.
We will use extent of reaction to determine the shelf life. First we rewrite the left hand side of equation (15) in Eq (16) by using a property of logarithms.

$$ln\frac{A_0}{A} = kt \tag{16}$$

Next we obtain Eq (17), by noting that at the end of the shelf life, t_s, the concentration of the quality attribute will reach A_e.

$$ln\frac{A_0}{A_e} = kt_s \tag{17}$$

Then the shelf life for a quality attribute following first order kinetics will be described by Eq (18).

$$t_s = \frac{ln\frac{A_0}{A_e}}{k} \tag{18}$$

Note that k in equation (18) is the first order rate constant.

Next we will use Eq (15) to determine the first order rate constant, k. By comparing this equation with an equation of a straight line, we note that the slope will give us the first order rate constant, k.
Also, if we fit data on the natural logarithm of the changing concentration of a quality attribute, A, with time, to a straight line (Eq (10)), then, the degree of fit can tell us whether the reaction is following the first order reaction.

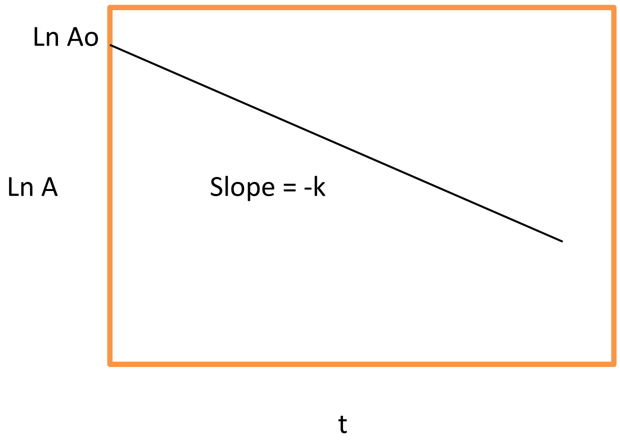


Figure 3. Change in the concentration of a quality attribute following first order reaction.

A good fit, determined by R^2 is what we need to know to make that decision.

Next, we will consider an example of some data obtained for reduction of vitamin C in a juice during storage. The loss of Vitamin C in kiwi juice is known to follow first order kinetics. The following data were collected for ascorbic acid concentration over 18 day storage period. Determine the rate constant. The manufacturer would like to declare a vitamin C concentration of 15 mg/100mL on the label. For how long would her claim be valid from the day of manufacture?

Time (days)	Ascorbic Acid (mg/100 mL)
0	50
3	40

6	35
9	30
12	25
15	22
18	20

Solution

We will use a spreadsheet to solve this problem.

1) Enter the time and concentration data in two columns.
2) Create a new column for ln(concentration)
3) plot it as an xy scatter plot
4) Use the Trend line feature, intercept at 0.05 and choose to display equation and R^2 value
5) Your plot should appear as shown in the right.
6) Compare the trend line equation shown in the Figure with Eq(15).
7) The high R^2 of 0.9904 suggests that the reaction is following a first order.

Time (days)	Ascorbic Acid (mg/100 mL)	ln(A)
0	50	3.9120
3	40	3.6889
6	35	3.5553
9	30	3.4012
12	25	3.2189
15	22	3.0910
18	20	2.9957

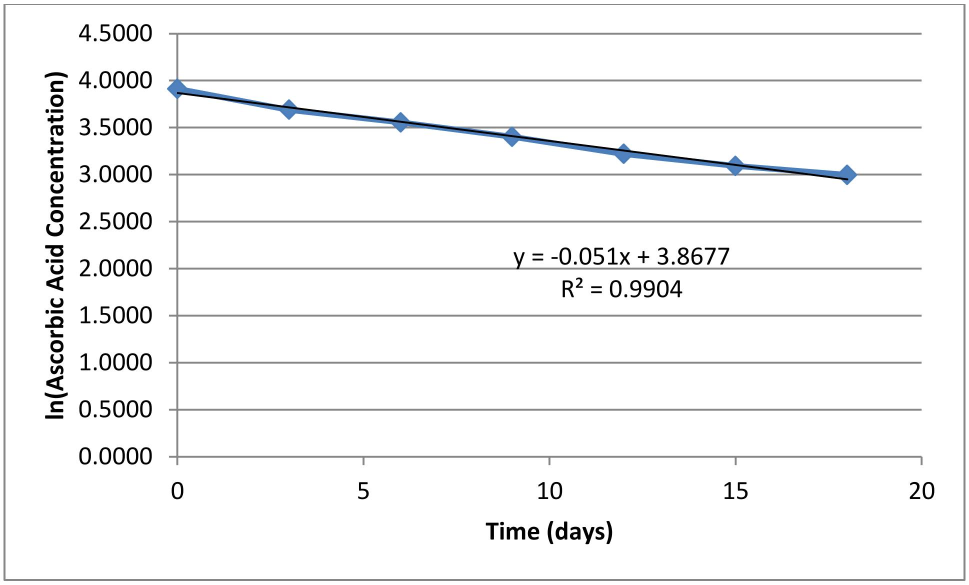


Figure 4 Change in ascorbic acid concentration in kiwi juice with time during storage

From the preceding Figure, rate constant = 0.051 $(\text{day})^{-1}$

Using Eq (18),

Time to reach 15 mg/100 mL $= \frac{ln\frac{50}{15}}{0.051}$

Answer = 23.6 days

3.3 Caution in Using Kinetic Analysis

In determining rate constants, it is important to pay attention to the analytical precision of measurement and the change in reactant species monitored. As shown below, if the analytical precision is low, then one must let more change in the reactant species to occur otherwise the error in estimation of rate constant k will be high.

Table 1: Accuracy in Estimating Rate Constant

Analytical Precision (%)	**Percent Error in Reaction Rate Constant**						
	Change in reactant species monitored						
	1%	5%	10%	20%	30%	40%	50%
±0.1	14	2.8	1.4	0.7	0.5	0.4	0.3
±0.5	70	14	7	3.5	2.5	2	1.5
±1.0	>100	28	14	7	5	4	3

±2.0	>100	56	28	14	10	8	6
±5.0	>100	>100	70	35	25	20	15
±10.0	>100	>100	>100	70	50	40	30

Benson(1960)

Example:

Using the table, determine the error in estimating % error in rate constant k, if the change in reactant species is monitored to be 10%, and the analytical precision is 0.5%, 2%, 5% and 10%

Solution

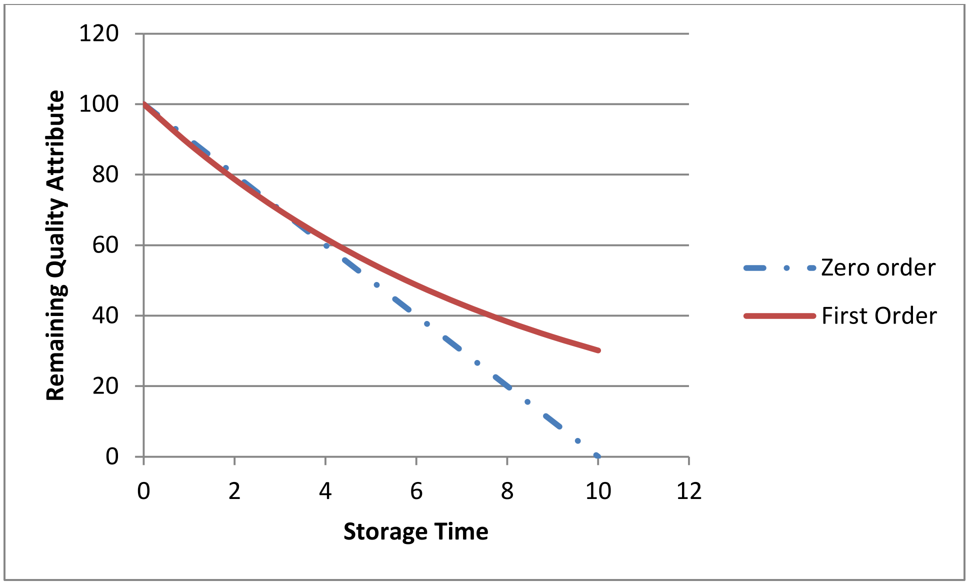
Keeping change in reactant species fixed at 10%, we get

Analytical Precision	Percent Error in k
±0.5	7
±1.0	14
±2.0	28
±5.0	70

3.4 Another Important Issue in Kinetic Analysis

When data are analyzed to determine either zero or first order rate constants, it is important to note that the quality attribute must have changed sufficiently. If not, the data may overlap, and either zero or first order kinetics may seem appropriate. But if one determines a zero order rate constant for data that in its entirety would have followed first order kinetics, then predictions would be flawed.

As shown in figure, for a quality change that follows first order kinetics, if only 60% change was monitored, then one may wrongfully conclude zero order kinetics. However, note that after 60% change, the two curves diverge, and zero-order kinetics would suggest a reduction in the attribute at a much faster rate than for the actual first order kinetics.



3.5 Summary

In this module, we learnt zero and first order rate kinetics. Since most reactions that influence shelf life of foods follow these two types of kinetic models, learning how to determine rate constants for either case is important.

By using a spreadsheet, we can easily determine whether a reaction is following, zero or first order kinetics.

We noted two important issues in kinetic analysis that can cause problems in the analysis.

1) Analytical precision and the amount of change of a reactant species influence the accuracy in estimating rate constants, and

2) The change in species must be sufficient; otherwise a wrong kinetic model may be deduced.

3.6 Review Questions:

1) What is an extent of reaction? How is it used in determining shelf life of foods.

2) Why should one be concerned about analytical precision in chemical kinetic analysis?

3) Why should one wait for a change in species of more than 50% to determine the order of reaction?

3.7 References and Additional Reading:

Benson S. W. (1960). *The Foundations of Chemical Kinetics*. McGraw Hill Book Co. New York.

Singh, R. P. and Heldman, D.R. (2008) *Introduction to Food Engineering*. 4th edition. Elsevier Publishing, London, United Kingdom.