First-order (n = 1) Reactions

- If the rate of the reaction depends on the first power of the concentration of one of the reactants or the products, such reactions are called as «first-order reactions.»

- There is a linear relationship (decreasing or increasing) between the concentration of the reactant or product and the reaction time in semi-log graph paper.

$$V = -\frac{dA}{dt} = k_1 A^1$$

$$\int_{\ln A_o}^{\ln A} \frac{dA}{A} = -k_1 \int_{t_o}^{t} dt$$

$$\ln A - \ln A_o = -k_1 t$$

$$\ln A = -k_1 t + \ln A_o$$

$$2.303 \log \frac{A}{A_o} = -k\,t$$

$$\log \frac{A}{A_o} = \frac{-k}{2.303}\,t$$

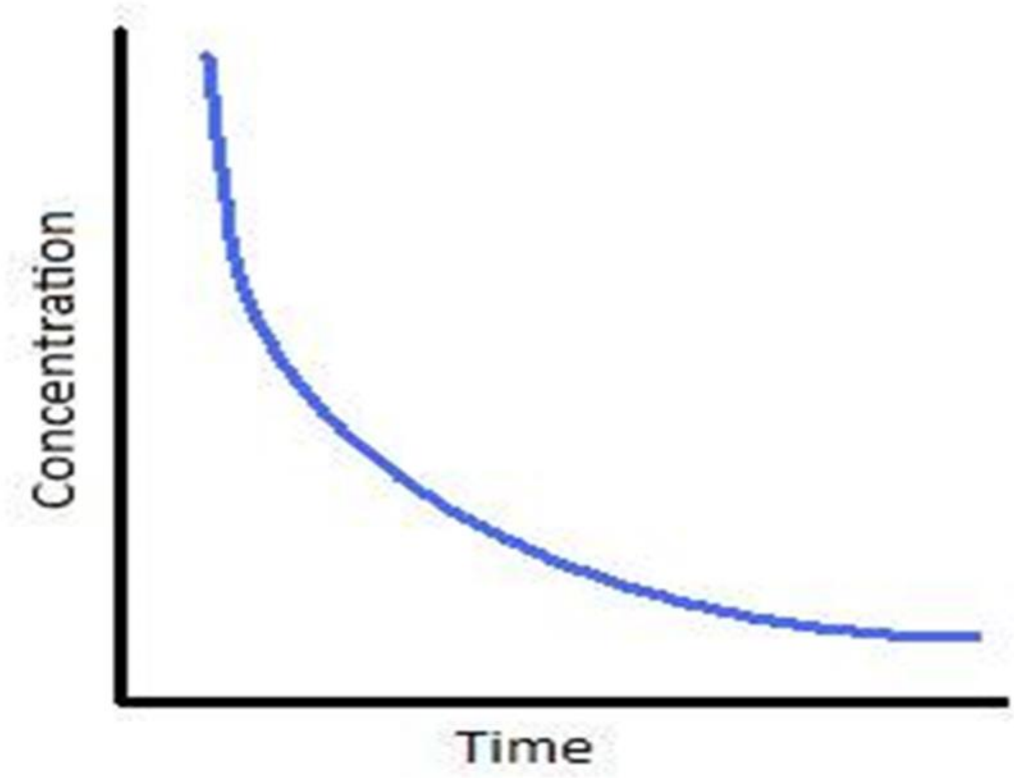
$$\log A - \log A_o = \frac{-k}{2.303}\,t$$

$$\log A = \frac{-k}{2.303}\,t \quad + \quad \log A_o$$

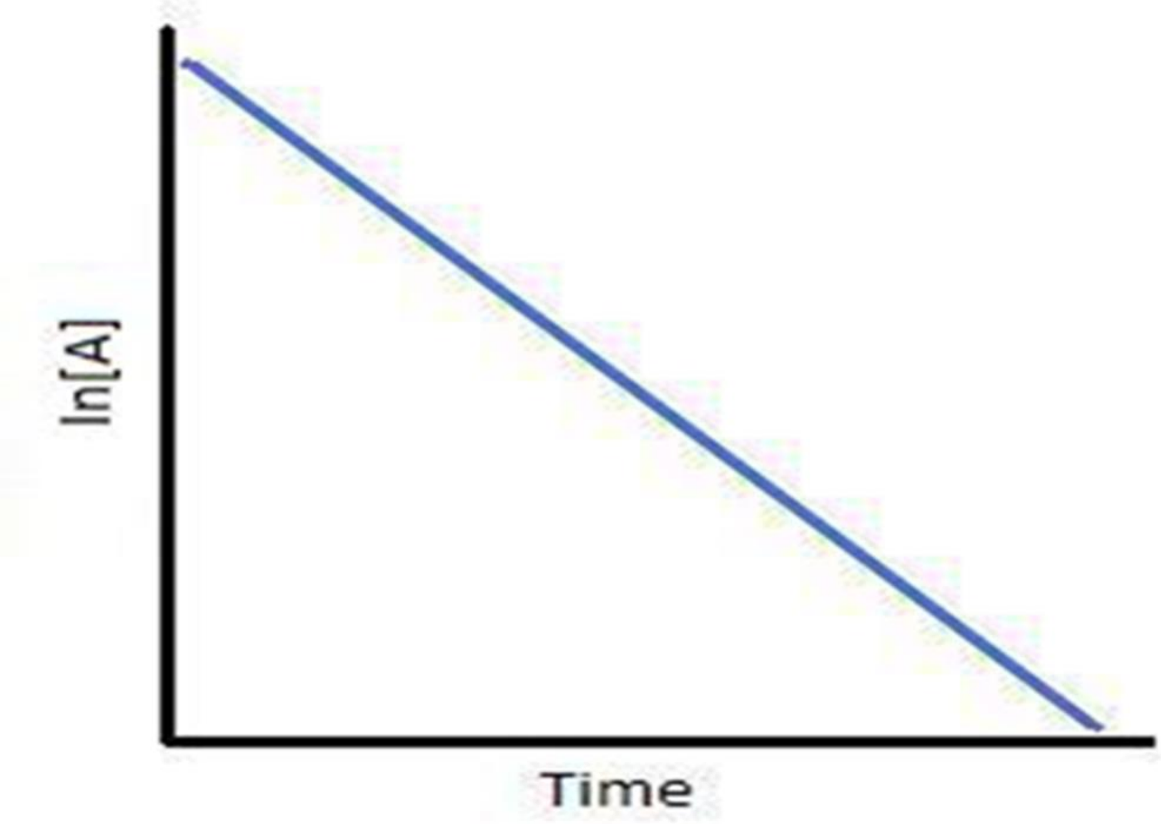
- **The same percentage** of reactant is degraded or the product is formed per unit of time. Time period will the same throughout the reaction for the same percentage (not the amount) of the reactant disappear.

- **Reaction rate depends on the reactant concentration**.

Graphing First-order Reactions (arithmetic graph paper)



Graphing First-order Reactions



Example

The degradation of anthocyanins in sour cherry juice was degraded at a rate of $k_1 = -0.00286\ min^{-1}$ in the presence of 9.3 mmol L^{-1} H_2O_2 at 20°C.

Analyzing «k» value

- Degradation of anth. in sour cherry juice in the presence of H_2O_2 at 20^oC is first-order.
- In every 1 min., 0.286% anthocyanins left from the previous min was degraded.
- For example, if there is 80 mg/L anthocyanin present, what would be the anth. con. after 2 min at 20^oC?

A_o=80 mg/L anthocyanin present,

- After 1 min., 80 x 0.00286 = 0.2288 mg of anth. was degraded and

  80 – 0.2288 = **79.7712 mg/L** of anth. is left.

- At the end of 2nd min., 79.7712 x 0.00286 = 0.2281 mg of anth. was degraded and

  79.7712 – 0.2281 = **79.5431 mg/L** of anth. is left.

Example

The reaction rate constants for the degradation of anthocyanins during heating at 80°C in black carrot and blood orange juice were found as 0.069 ve 0.1932 h^{-1} respectively.

a) Compare the heat stabilities of black carrot and blood orange juice.

b) If 100 mg/L of anthocyanins are present in both juices initially, find out the remaining of anthocyanins after heating at 80°C for 2 h.

Black carrot juice heating at 80ºC

- 100x0,069 = 6.9 mg/L, after 1 h

100 – 6.9 = 93.1 mg/L

- 93.1x0,069 = 6.4 mg/L, after 2 h

93.1 – 6.4 = 86.7 mg/L

Blood orange juice heating at 80^{o}C

- 100x0,1932 = 19.32 mg/L, after 1 h

100 – 19.32 = 80.68 mg/L

- 80.68x0,1932 = 15.59 mg/L, after 2 h

80.68 – 15.59 = 65.1 mg/L

After heating at 80^{o}C for 2 h, remaining anthocyanins:

- In black carrrot juice; 86.7 mg/L
- In blood orange juice; 65.1 mg/L

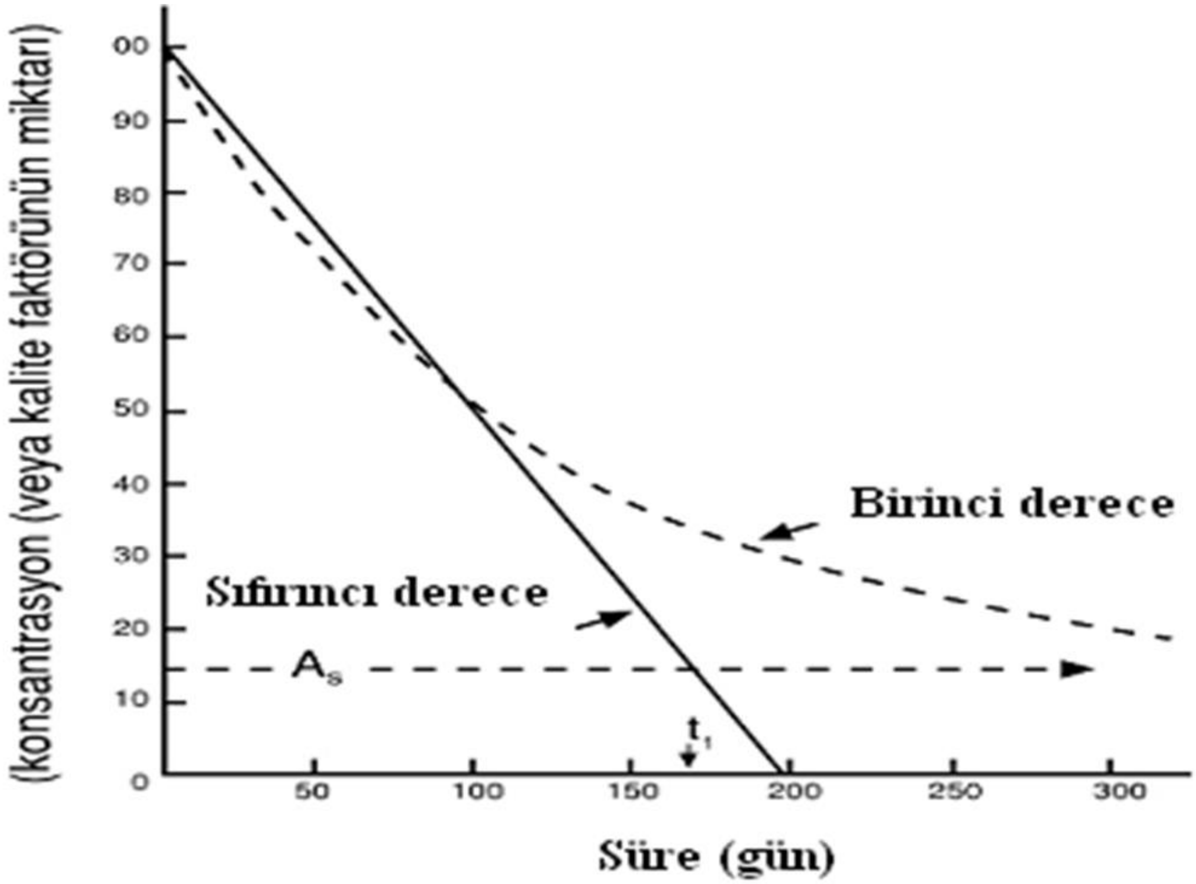
Example

Interpret the following reaction rate constants.

- $k_{95°C} = –0.76$ mg $L^{–1}$ $min^{–1}$ (degradation of ascorbic acid in orange juice)

- $k_{40°C} = –2.3$ $min^{–1}$ (degradation of anthocyanins in pomegranate juice in the presence of 0.5 ppm of H_2O_2)

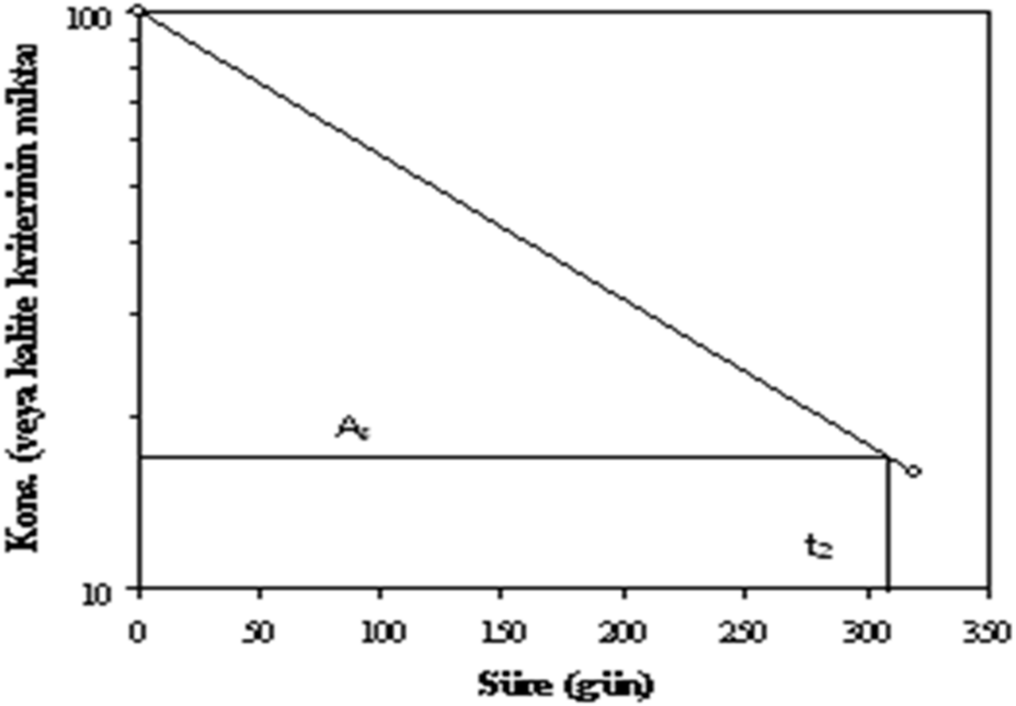
To determine if the reaction is zero- or first-order



- When the reaction is not carried far enough (<50% conversion), both zero- and first-order might be indistinguishable from the line.

- If the experiment is carried out at least 50% conversion and preferably 75%, it is usually easy to determine which reaction order gives the best fit (or to determine the reaction order).

To determine the shelf-life for first-order reaction



R^2 is used to determine the reaction order

- R^2 from linear regression is used to determine the reaction order.

- In practice, determine R^2 for zero-, first and second order reactions by linear regression, then compare R^2 values and find out the reaction order by selecting R^2 value which is closer to 1.

Example 3.16

The storage stability of ascorbic acid (aa) in frozen spinach stored at –6.7°C (20°F) for 180 days was studied. The aa contents were given in Table 3.10.

a) Determine the reaction order for the degradation of aa in spinach stored at –6.7^{o}C.
b) Calculate the reaction rate constant (*k*),
c) Find out "aa degraded (%)" after 160 days of storage.

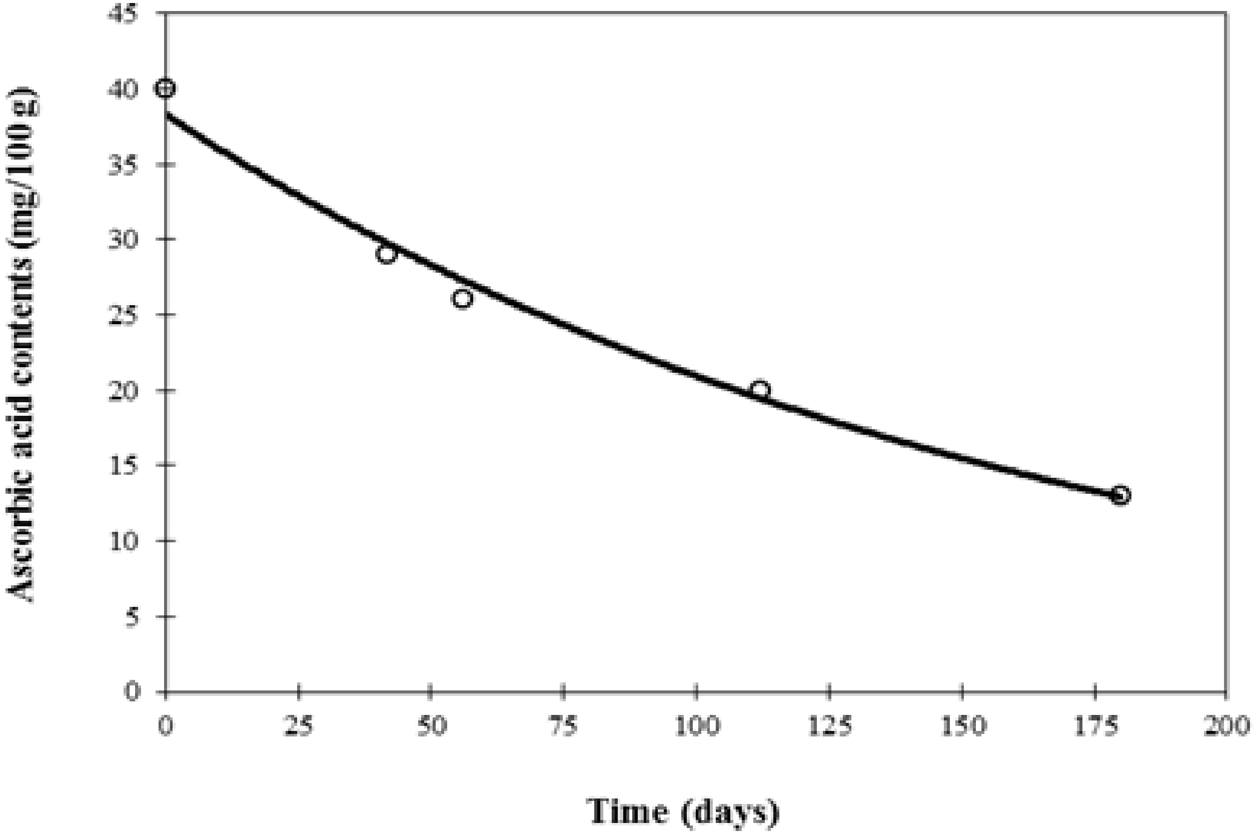
Table 3.11 AA contents in frozen spinach stored at –6.7°C

Time (days)	AA content (mg 100 g^{-1})
0	40
42	29
56	26
112	20
180	13

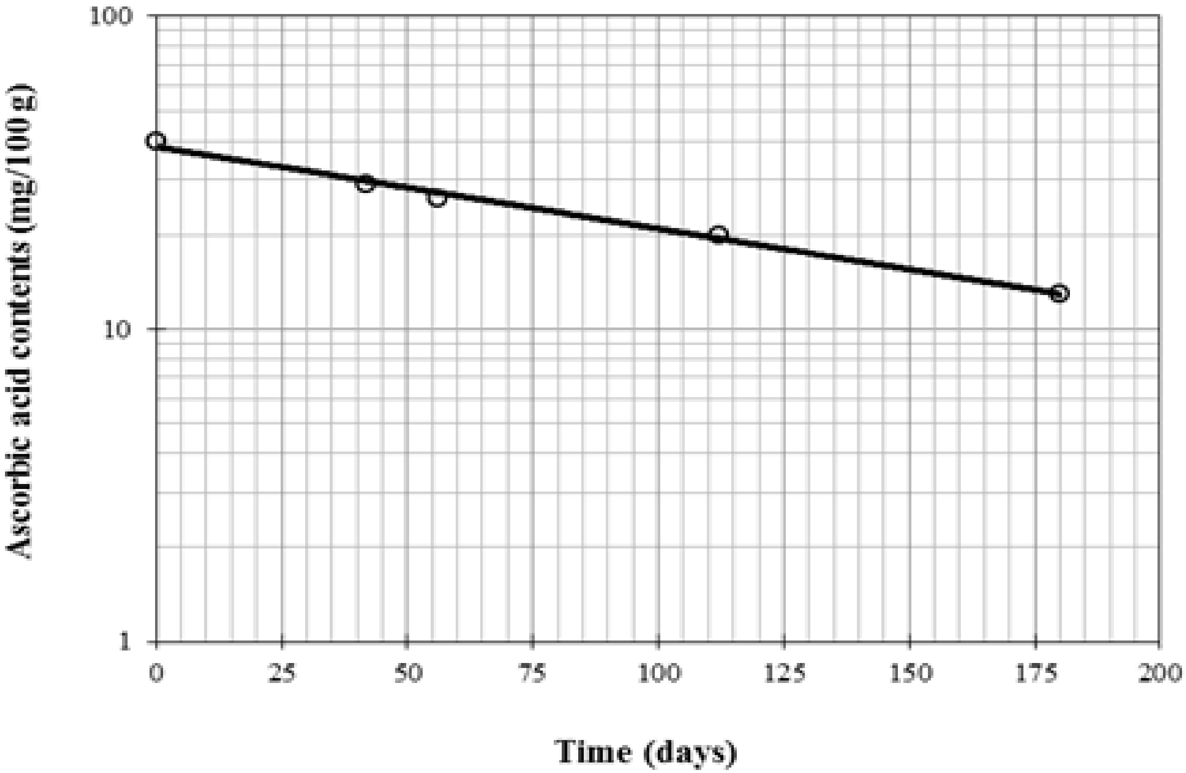
Solution (reaction order)

- Data is plotted on an arithmetic graph paper.
- Investigate whether or not the line is straight.
- Then, plot data on a semi-log graph paper.
- If there is a doubt, then carry out he regression analysis and find out the R^2.

Plotting the experimantal data on an arithmetic graph paper



Plotting the experimantal data on a semi-log graph paper (how can you plot this graph in order to be visually more correct graph?)



Reaction order by R^2

Zero order: $R^2 = 0.9377$

First-order: $R^2 = 0.9868$

Zero order: $R^2 = 0.9377$

First-order: $R^2 = 0.9868$

a) Comparing R^2 values, ascorbic acid degradation in frozen spinach at –6.7°C for 180 days follows **first-order** reaction kinetics.

Coefficients calculated by semi-log regression

b) Calculate the reaction rate constant (*k*),

$a = -0.00262\ day^{-1}$

$b = 1.583$

$R^2 = 0.9868$

k = ???

c) Find out “aa degraded (%)” after 160 days of storage.

A = 14.6 (aa remaining after 160 days of storage)

Answer: 61.9%

Example 3.17

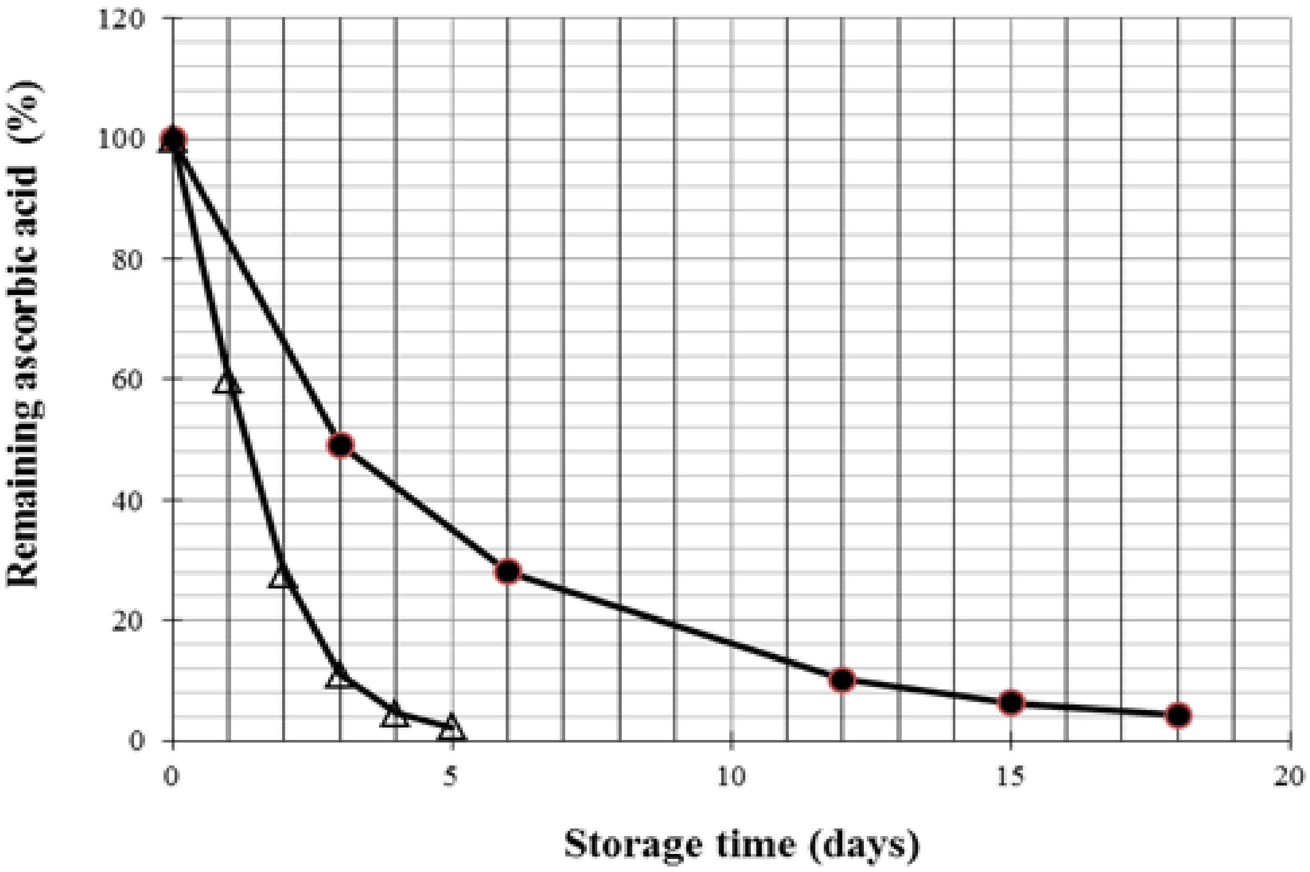
- Ascorbic acid losses were studied in guava slices at different water activities (a_w) at 50°C. Periodically samples were drawn from the storage and analyzed for ascorbic acid contents. The data were given in Table 3.11.

a) Find out the reaction order for the degradation of aa.
b) Calculate reaction rate constants
c) Compare the stability of aa at two different a_w's by taking into consideration of *k* values.

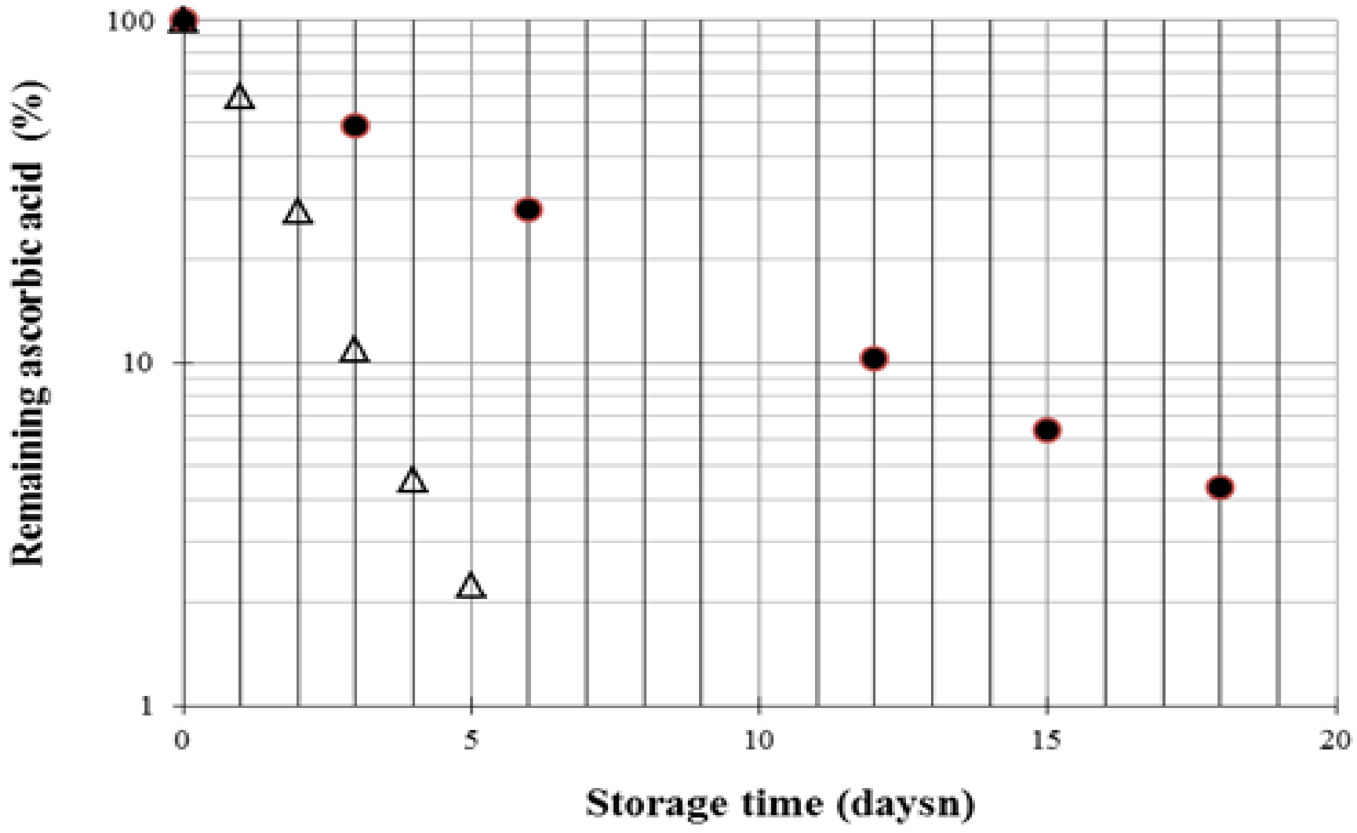
Table 3.11 Ascorbic acid contents of guava slices at different a_w values and stored at 50°C.

Time (day)	a_w = 0.43 Remaining aa (%)	Time (day)	a_w =0.81 Remaining aa (%)
0	100	0	100
3	49.24	1	59.96
6	28.03	2	27.69
12	10.25	3	10.98
15	6.39	4	4.54
18	4.31	5	2.25

Plotting the experimantal data on an arithmetic graph paper



Plotting the experimantal data on a semi-log graph paper



a) Find out the reaction order for the degradation of aa.

Answer:

b) Calculate reaction rate constants.

Answer:

- **At a_w = 0.43:** slope = $$\frac{\log 20 - \log 10}{8.4 - 12.4}$$ = –0.07526 day^{-1}

- **At a_w= 0.43:** slope = $$\frac{\log 10 - \log 4}{2.46 - 4.18}$$ = –0.2300 day^{-1}

k values= ??????

Calculation of *k* values

- **At a_w = 0.43:**

$$k_1 = -0.07526 \times 2.303 = -0.1733 \text{ day}^{-1}$$

- **At a_w = 0.81:**

$$k_1 = -0.2300 \times 2.303 = -0.5359 \text{ day}^{-1}$$

c) Compare the stability of aa at two different a_w's by taking into consideration of *k* values.

Answer:

Example 3.18

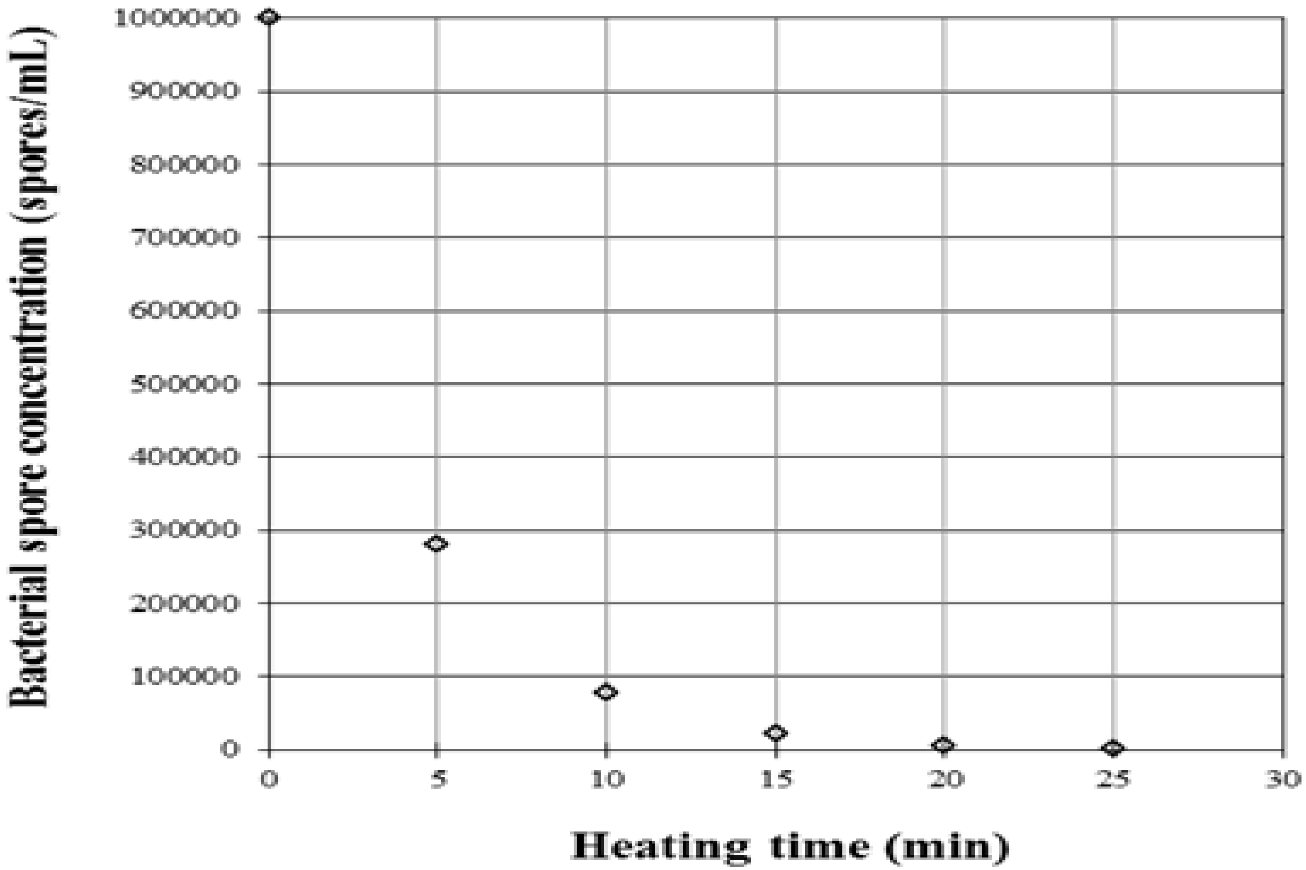
- Bacterial spores were subjected to heat at 242°F and the results were given in Table 3.12.

a) Find out the inactivation rate constant for this bacteria.
b) Time needed to inactivate 50 and 90% of this bacteria.

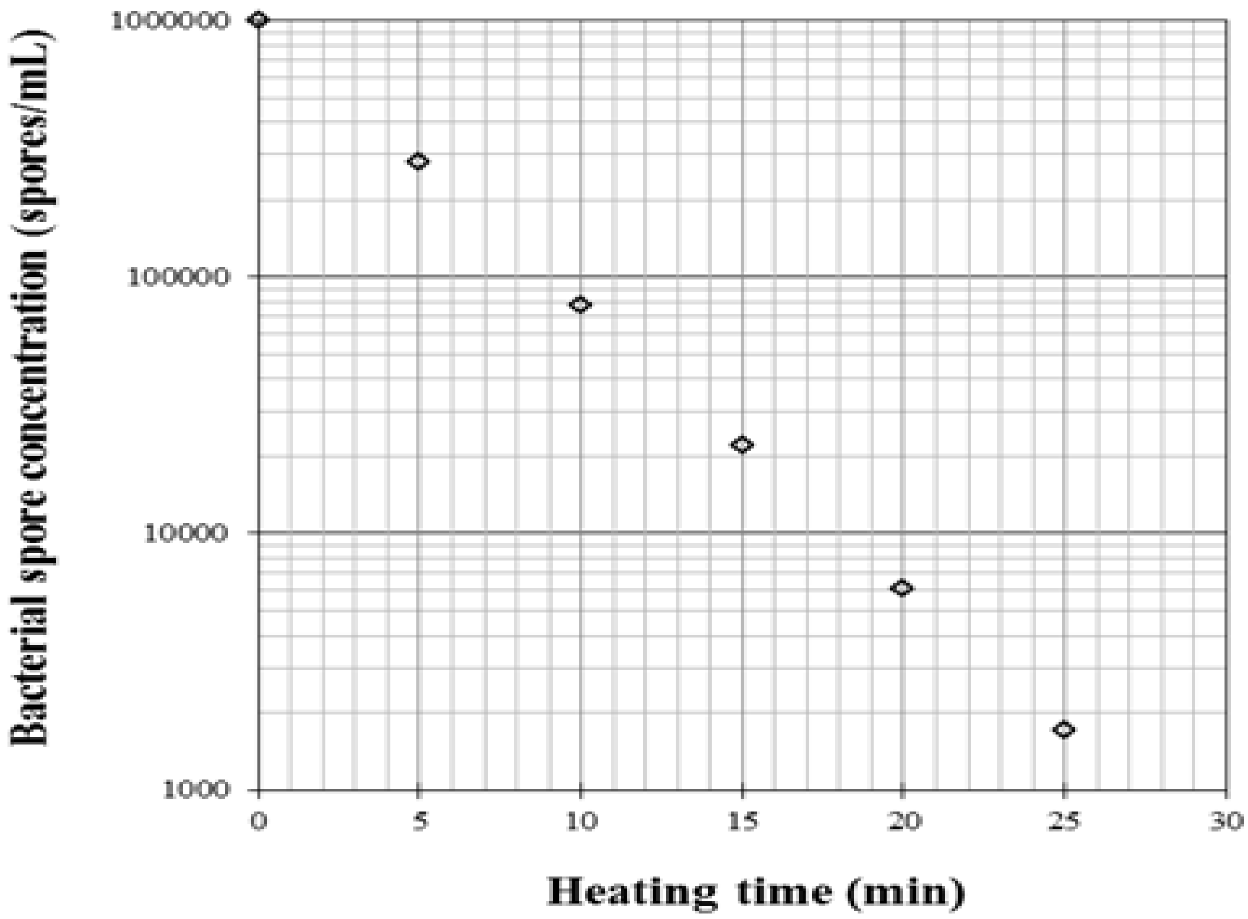
Table 3.12 Bacterial spore concentration after heating at 242°F

Time (min)	Spore concentration (number of spores mL^{-1})
0	1.0×10^6
5	2.8×10^5
10	7.8×10^4
15	2.2×10^4
20	6.1×10^3
25	1.7×10^3

Plotting the experimantal data on an arithmetic graph paper



Plotting the experimantal data on a semi-log graph paper



Coefficients calculated by regression analysis (EXTRA):

- a = -0.1108 min^{-1}
- b = 101.8 spores mL^{-1}
- $R^2 = 0.9999$

The term for the bacterial spores to inactivate by 50% implies that bacterial spores decrease from 100 (initial) to 50 (after *t* min of heating).

The term for the bacterial spores to inactivate by 50% implies that bacterial spores decrease from 100 (initial) to 50 (after *t* min of heating).

$$\ln A = k\,t + \ln A_o$$

$$\ln 50 = -0.2503\,t + \ln 100$$

t = 2.8 min

The term for the bacterial spores to inactivate by 90% implies that bacterial spores decrease from 100 (initial) to 10 (after t min of heating).

The term for the bacterial spores to inactivate by 90% implies that bacterial spores decrease from 100 (initial) to 10 (after *t* min of heating).

$$\ln A = k\,t + \ln A_o$$

$$\ln 10 = -0.2503\,t + \ln 100$$

t = 9.2 min

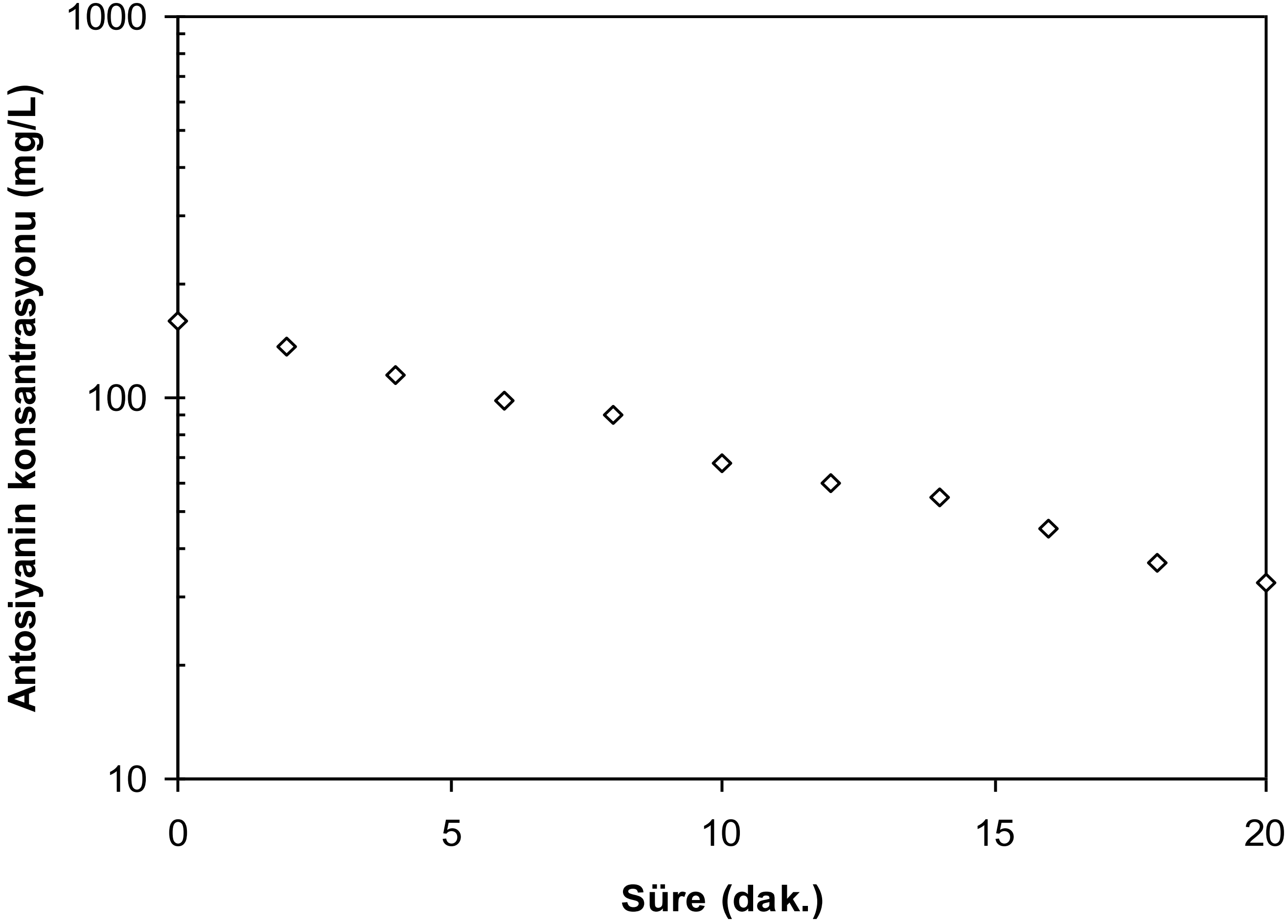
Example

The losses of anthocyanins from sour cherry juice heated at 80°C for various times were determined and the results were given in the following table.

a) Plot the data to an appropriate graph paper.
b) Determine the reaction order.
c) Determine the slope and intercept.
d) Determine the degradation rate constant.

Anthocyanin contents of sour cherry juice heated at 80^oC for various times

Time (h)	Anthocyanin content (mg/L)		Time (h)	Anthocyanin content (mg/L)
0	160		12	60
2	136		14	55
4	115		16	45
6	98		18	37
8	90		20	33
10	67			


1000
100
10
0
5
10
15
20
Antosiyanin konsantrasyonu (mg/L)
Süre (dak.)

Regression values and *k* value

- Slope (a) = -0.0803 unit?
- Intercept (b) = 2.206

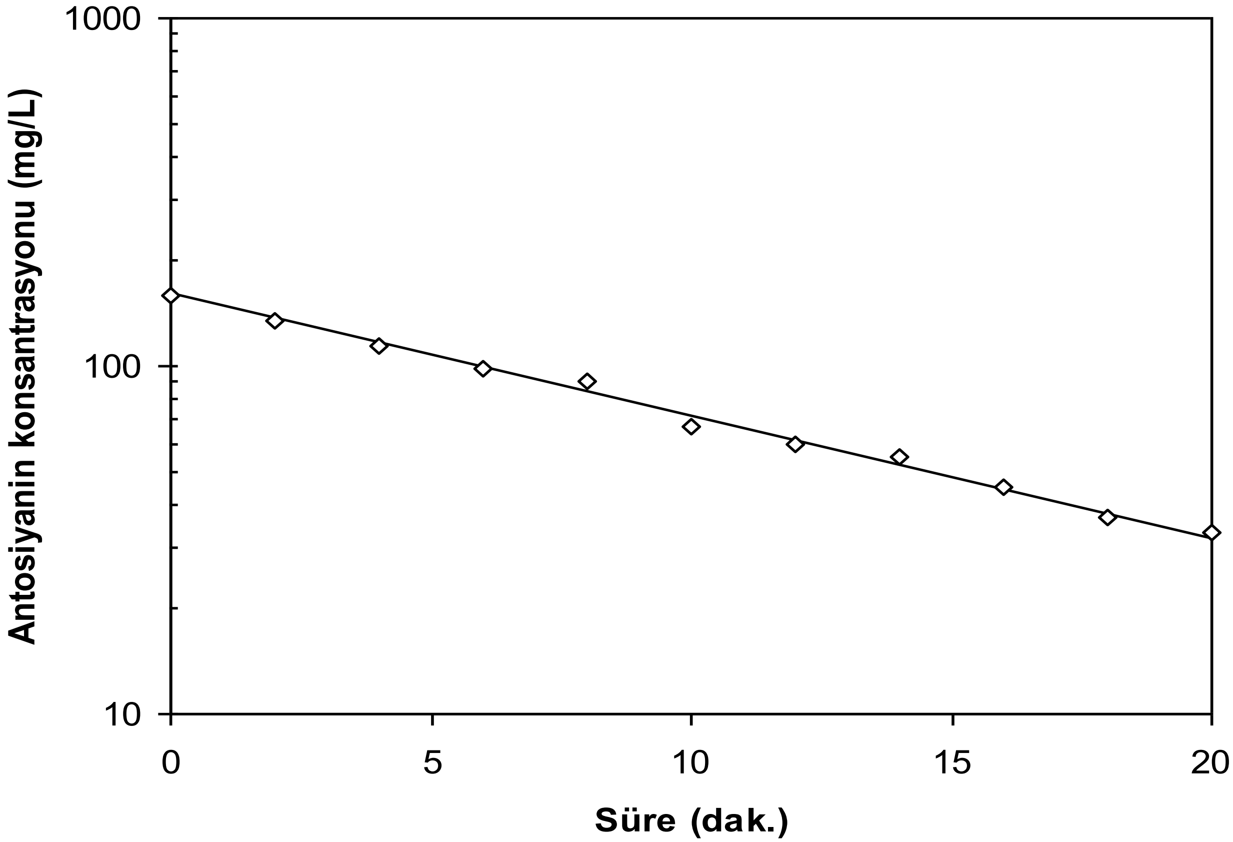
  b= ???unit

- R^2 = 0.9949

  Equation ??????

  k = ???? unit

Regression line

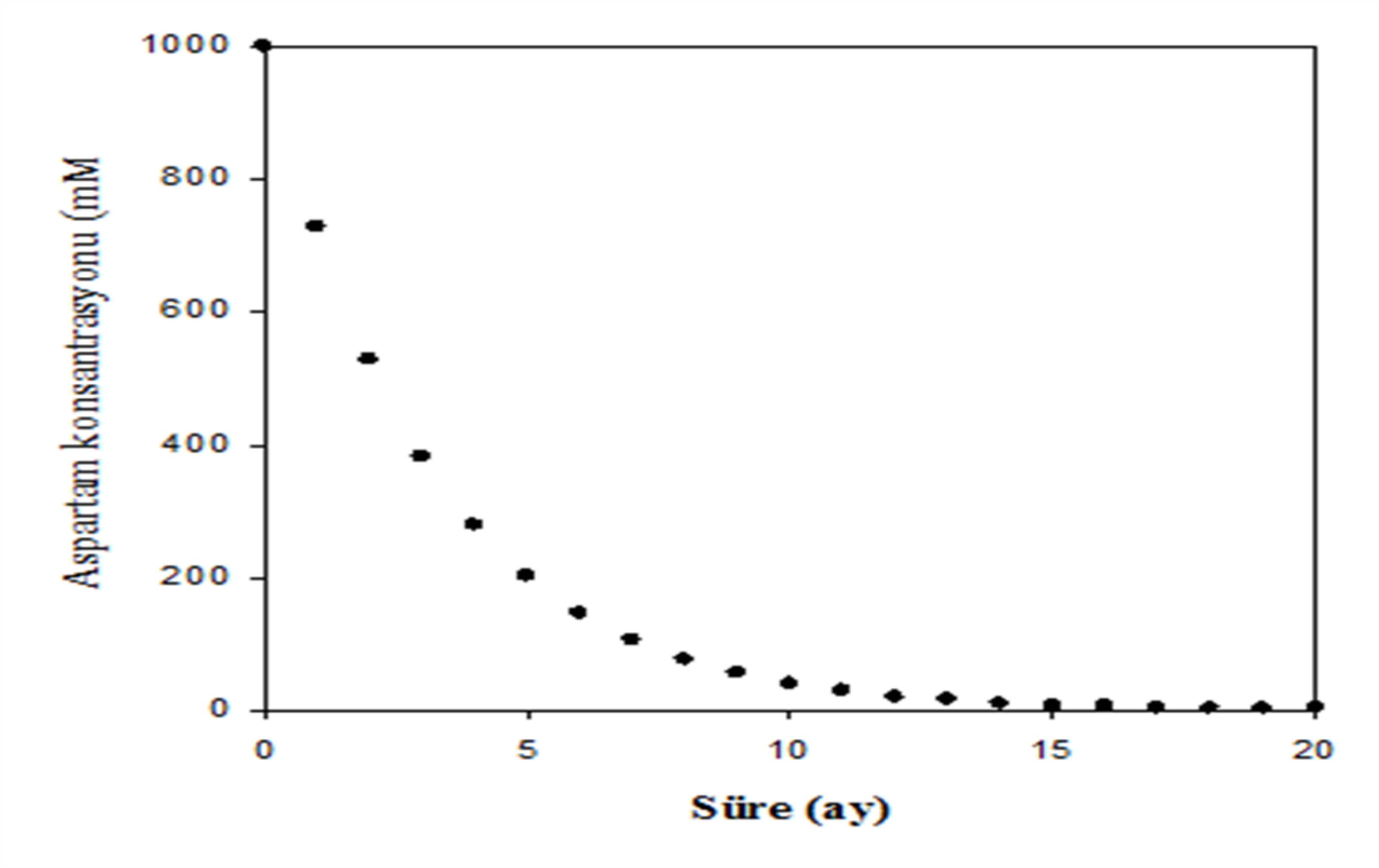


Example

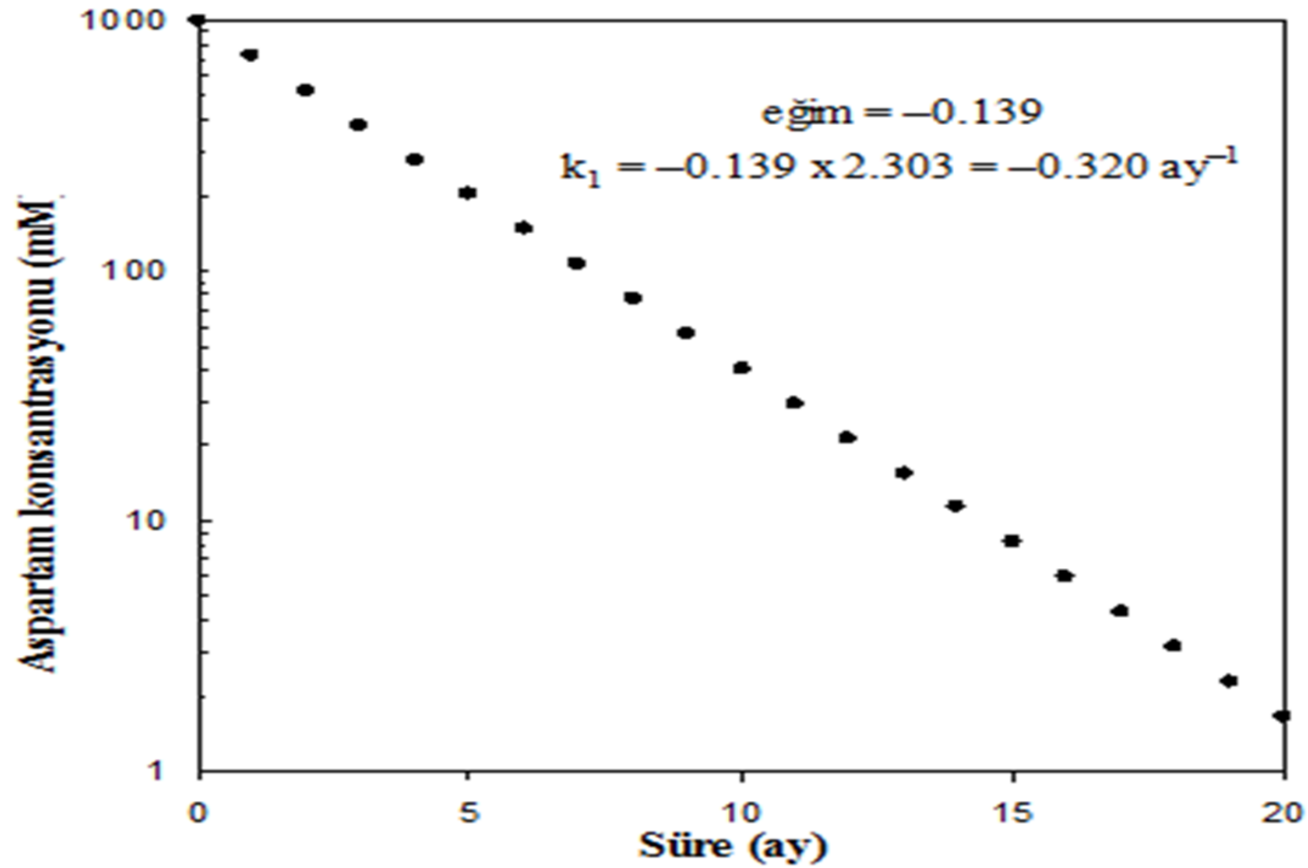
Aspartame is used as an artificial sweetener in carbonated beverages, marmalades and jams and bakery products. Studies showed that aspartame is degraded during storage and sweetness is lost as a result of this degradation. Aspartame losses was studied in a carbonated beverage sweetened with aspartame during storage. Find out the time needed to degrade 40% of the aspartame.

Time (month)	Aspartame conc. (m*M*)	Time (month)	Aspartame conc. (m*M*)
0	1000.00	11	29.60
1	726.15	12	21.49
2	527.29	13	15.61
3	382.89	14	11.33
4	278.04	15	8.23
5	201.90	16	5.98
6	146.61	17	4.34
7	106.46	18	3.15
8	77.30	19	2.29
9	56.13	20	1.66
10	40.76		

Plotting data on an arithmetic graph paper



Plotting data on a semi-log graph paper



Time needed for 40% degradation of astpartame is found from the following formula:

$$\ln A = k\,t + \ln A_o$$

$$\ln 60 = -0.320\ \text{mo}^{-1}\, t + \ln 100$$

t = 1.6 mo