Second order (n = 2) of reactions

- If only **one reactant** enters the reaction (monomolecular reaction), then the rate of the reaction is proportional to the second power of the concentration of the reactant.

- If **two reactants** enter the reaction (bimolecular reaction), then the rate of the reaction is proportional to the multiplication of the first power of the concentrations of these two reactants.

$$V = -\frac{dA}{dt} = k_2 A^2 \text{ (monomolecular)}$$

$$V = -\frac{dA}{dt} = k_2 A B \text{ (bimolecular)}$$

$$\frac{dA}{A^2} = - k_2 \, dt$$

The following rule of integration (power rule) is used:

$$\int \frac{dx}{x^2} = - \frac{1}{x}$$

$$\int_{-1/A_o}^{-1/A} \frac{dA}{A^2} = -k_2 \int_{t_o}^{t} dt$$

$$-\frac{1}{A} - \left(-\frac{1}{A_o}\right) = -k_2\, t \qquad \text{or;}$$

$$\frac{1}{A} = k_2\, t + \frac{1}{A_o}$$

$$\frac{1}{A} = k_2 t + \frac{1}{A_o}$$

- In second-order reactions, there is a linear relationship between the concentration (1/conc.) of the reactant or product with the time of the reaction. (in arithmetic graph paper)

$$\frac{1}{A} = k_2 t + \frac{1}{A_o}$$

Where:

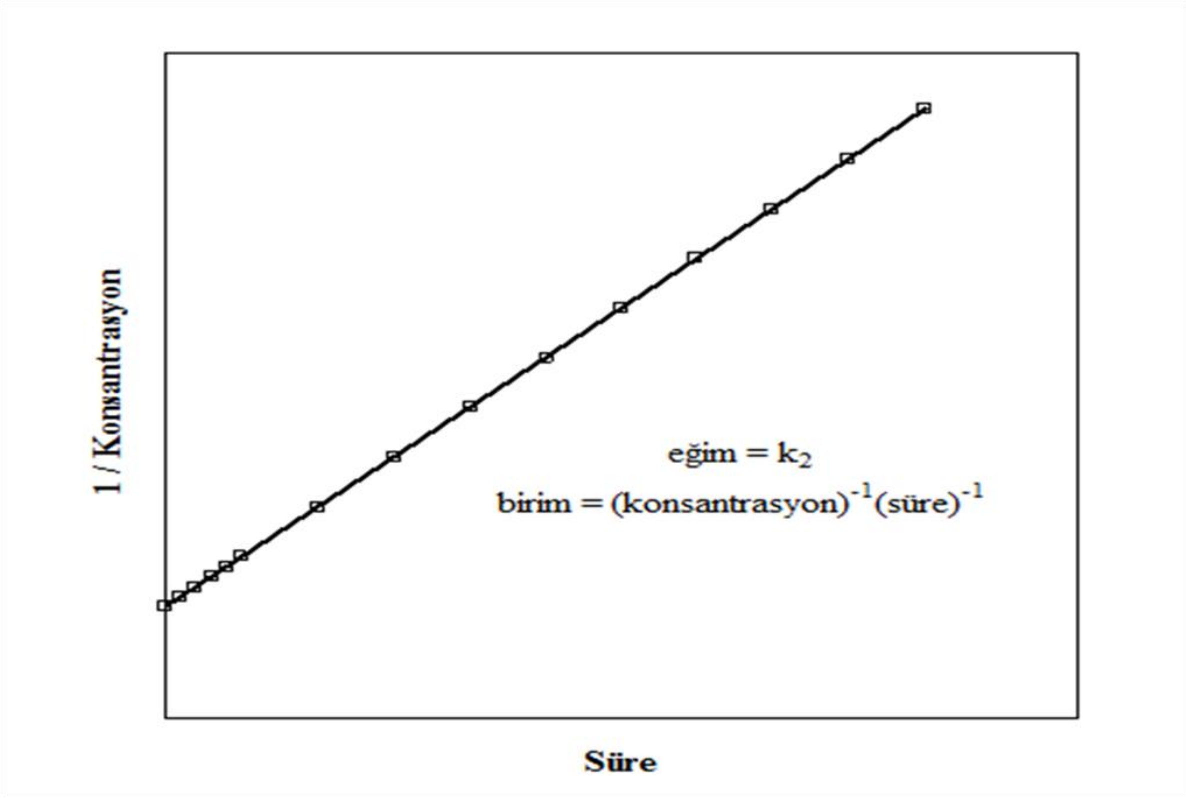
A : Concentration of reactant after *t* time,

A_o: Initial concentration of reactant,

k_2 : Second order reaction rate constant.

Unit: $(\text{concentration})^{-1}\ (\text{time})^{-1}$

Graphing Second-order Reactions



Examples for Second-Order Reactions

- Limited number of reactions in foods follow second-order reaction kinetics.

Examples are:

- Changes in amino acids during Maillard reaction. For example, lysine loss in milk during Maillard reaction.
- Tiamine loss in milk
- Ascorbic acid loss in baby foods and lemon juice.
- Tiosulfanote loss (indicates loss of pungency) during drying and storage of onion rings.

Example 3.20

- The loss of lysine (essential amino acid) is studied during the heating of milk at 160°C. The results from this experiment are presented in Table 3.14.

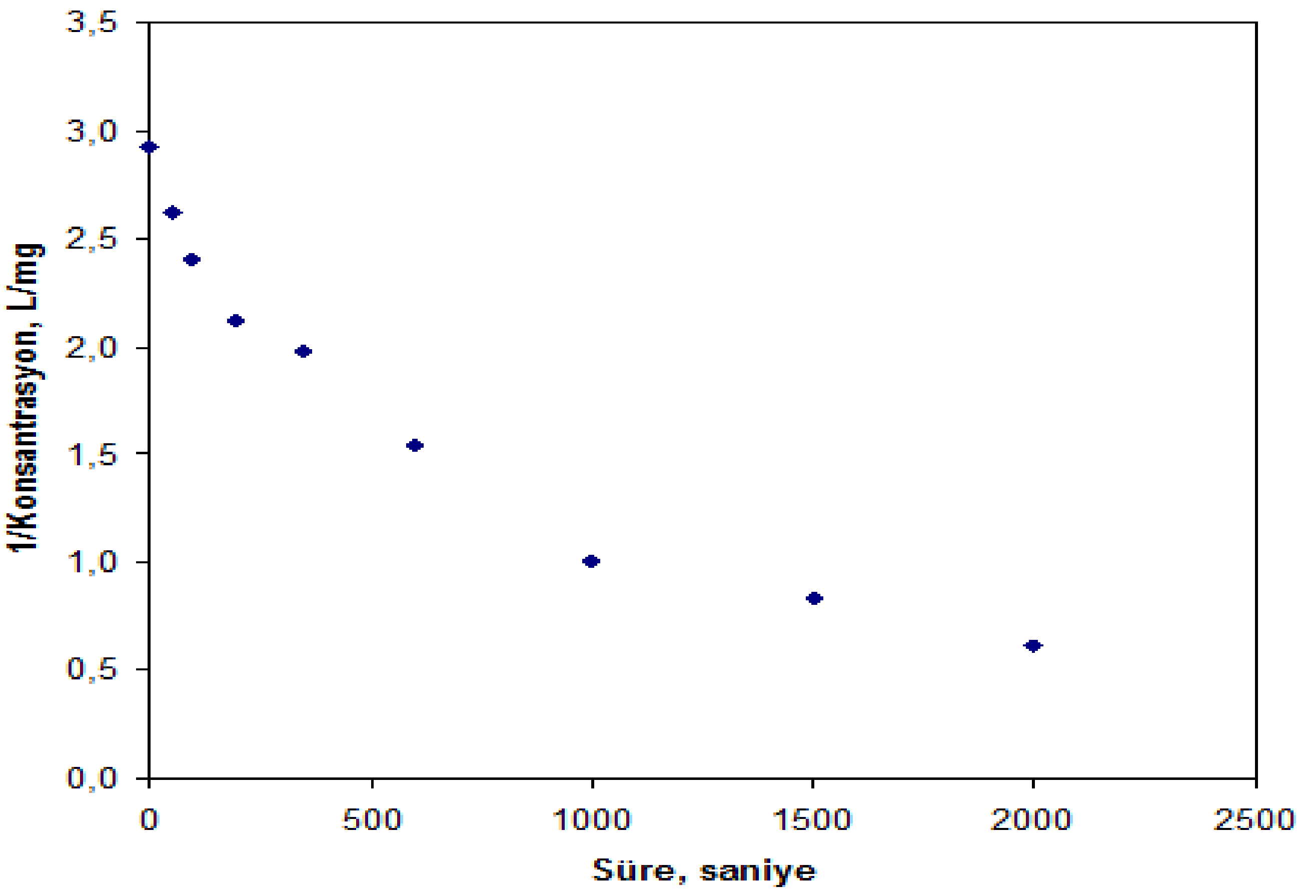
Note: The unit of slope in an aritmetic paper for the degradation of lysine is found to be L/(mg s).

a) Find out the reaction order for the thermal degradation of lysine.
b) Calculate the reaction rate constant for the degradation of lysine.

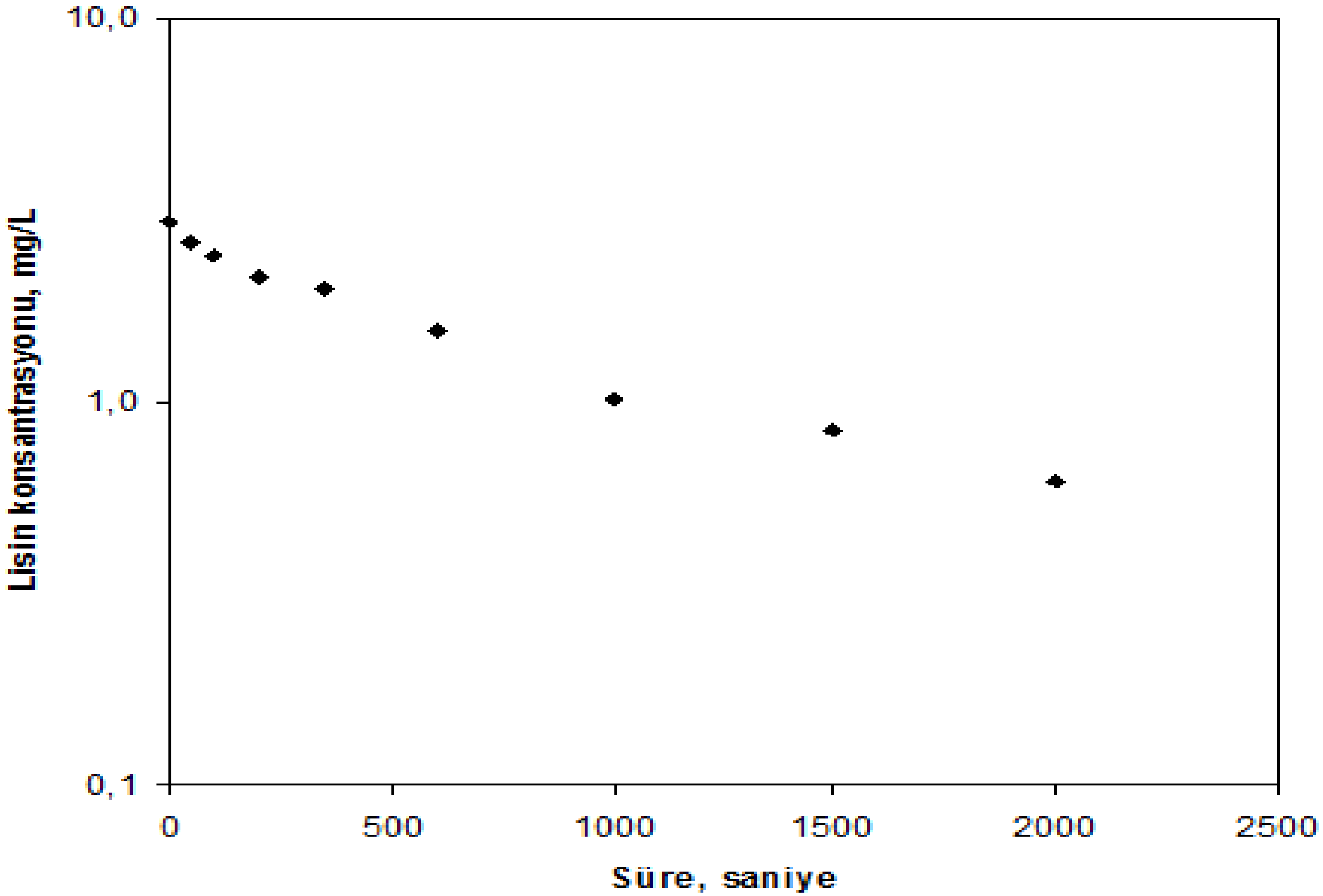
Tablo Lysine losses in milk heated at 160°C

Time (s)	**Lysine concentration (mg L^{-1})**
0	2.93
50	2.62
100	2.40
200	2.12
350	1.98
600	1.54
1000	1.01
1500	0.84
2000	0.62

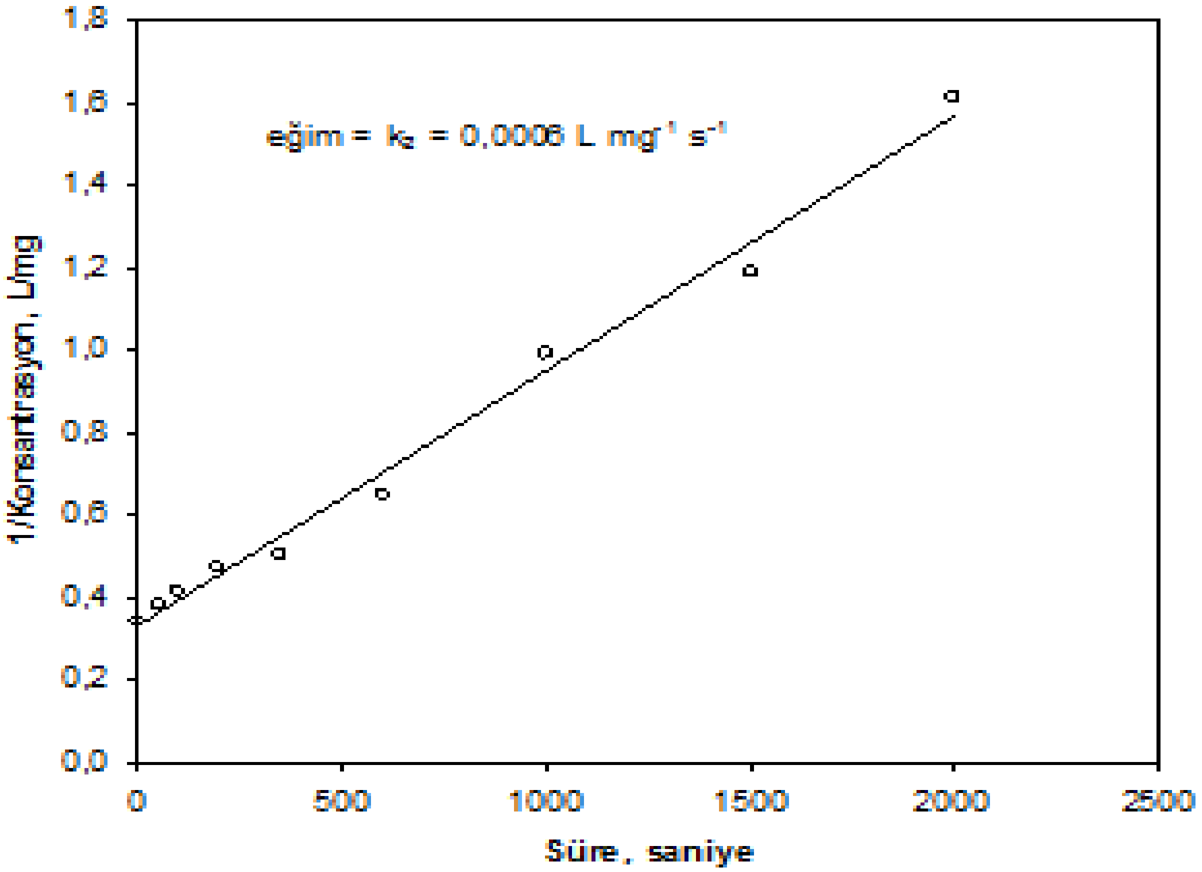
Plotting data in arithmetic graph paper (conc. vs time)



Plotting data in semi-log graph paper (conc. vs. time)



Plotting data in aitmetic graph paper (1/conc. vs time)



Reaction order

- We found the straight line in **arithmetic garph paper** (**1/conc. vs time**). Therefore, the degradation of lysine during heating of milk at 160°C follows **second order reaction** kinetics.

Slope and reaction rate constant (from graph)

$$\text{Slope} = \frac{1/C_2 - 1/C_1}{t_2 - t_1}$$

Slope = k_2 = ????

Intercept = ?????

Regression data

X (time)	Y (1/lysine con)	X^2	Y^2	XY
0	0.341	0	0.116	0
50	0.382	2500	0.146	19.10
100	0.417			
200	0.472			
350	0.505			
600	0.649			
1000	0.990			
1500	1.190			
2000	1.613			
$\Sigma X = 5800$	$\Sigma Y = 6.559$	$\Sigma X^2 = 7785000$	$\Sigma Y^2 = 6.333$	$\Sigma XY = 6722.35$

Slope and intercept
(from regression)

a = 0.00062 L mg^{-1} s^{-1}

b (1/b) = 0.3314 L mg^{-1}

Reaction rate constant

Equation describing the reaction:

$$\frac{1}{A} = k_2 t + \frac{1}{A_o}$$

$$\frac{1}{A} = 0.00062\, t + 0.3314$$

Homework

Calculate the R^2 at home!!!

(Answer: $R^2 = 0.991$)

Example 3.21

- Color and pungency (acılık) are the most important quality criteria in dried onions and garlics. The loss of pungency in dehydrated onions is followed by the loss in *thiosulfinate* concentration. "American Dehydrated Onion and Garlic Association (ADOGA)" specifies that dehydrated onions should minimum contain *thiosulfinate* at "5 μmole/g" level. In a study, the *thiosulfinate* loss is studied in dried onions during storage at 20°C. The initial *thiosulfinate* concentration was 13 μmole/g and the reaction rate constant for the loss of *thiosulfinate* was found as "2.24 x 10^{-4} g/(μmole day)."

a) Find out the *thiosulfinate* concentration remaining after 6 mo of storage for 1 kg dehydrated onions.
b) Calculate the storage time when thiosulfinate concentration reaches to the acceptable minimum pungency level (shelf-life!)

$$\frac{1}{A} = k_2 t + \frac{1}{A}$$

- A = 8.53 μmole/g

$$A = 8.53 \frac{\mu mole}{g} \cdot \frac{1000}{1000} = 8530 \frac{\mu mole}{1000\ g} = 8530\ \mu mole/kg$$

- $t =$ 549 days, or **18.3 mo**

Example 3.22

Ascorbic acid loss was studied in baby food fortified with aa during storage at 20°C. Reaction rate was found to be directly proportional to the square of aa concentration. After 5 mo of storage at 20°C, aa content decreased from initial 15 mg/100 g to 8.4 mg/100 g. Calculate the aa remaining (%) in this product at the end of 1 year of storage at 20°C.

- Figure out the order of reaction!!!!

k value for the aa degradation in this food product is calculated from following equation:

$$\frac{1}{A} = k_2 t + \frac{1}{A}$$

- ....

Answer: k_2 = 1.05 x 10^{-2} unit?

AA remaining (%) in this product at the end of 1 year of storage at 20°C is calculated from the following equation:

- ……………………..

Answer: A = 5.2 mg/100 g

$$\text{AA remaining, \%} = \frac{5.2}{15}(100) = 34.7\%$$

Example 3.23

- Nitrosyl chloride (NOCl), decomposes slowly to NO and Cl_2 gaseous. The rate constant (*k*) equals 0.02 L $mole^{-1}$ s^{-1} at a certain temperature. The initial concentration of NOCl in a closed reaction vessel is 0.05 *M*.

  a) What will the NOCl concentration be after 30 min?

  b) Determine the time in minutes to drop NOCl concentration to 0.01 *M*.

Answers

- A_t = 0.018 mole L^{-1}
- t = 4000 s = 66.7 min

Summary of Reaction Orders

Reac. orders	Differential rate laws	Integrated equations	Straight lines	Units of *k*
Zero	$-d[C]/dt = k\,[C]^0$	$[C] = -k_o t + [C]_0$	[C] vs. t *slope* = k_0	conc./time
First	$-d[C]/dt = k\,[C]^1$	$\ln[C] = -k_1 t + \ln[C]_o$ $\log[C] = -k_1/2.303\ t + \log[C]_o$	ln [C] vs. t *slope* = k_1 log [C] vs. t slope x 2.303 = k_1	1/time
Second	$-d[C]/dt = k\,[C]^2$	$1/[C] = k_2 t + 1/[C]_o$	1/[C] vs. t *slope* = k_2	1/(conc. time)

Example 3.24

The reaction rate constant for the degradation of endogenous toxin in crabs during cooking was found as 0.05. Assume that the degradation of this toxin occurs for zero-, first- and second-order reaction kinetics. If the initial concentration of this toxin is 15 mg/kg, find out the toxin concentration for each of the reaction order at the end of 1 h of cooking.

Note: *The unit of reaction rate constant depends on the order of reaction and the unit of time will be taken as min.*

Crab

Units of reaction rate constants for each reaction order

- *Zero-order* $\rightarrow k_o =$
- *First-order* $\rightarrow k_1 =$
- *Second-order* $\rightarrow k_2 =$

- *Zero-order* $\rightarrow$ k_o = 0.05 mg kg^{-1} min^{-1}
- *First-order* $\rightarrow$ k_1 = 0.05 min^{-1}
- *Second-order* $\rightarrow$ k_2 = 0.05 kg mg^{-1} min^{-1}

Zero-order reaction

$$[C] = -k_o\, t + [C]_o$$

$$[C] = \mathbf{12\ mg\ kg^{-1}}$$

First-order reaction

$$\ln[C] = -k_1 t + \ln[C]_o$$

$$[C] = \mathbf{0.747\ mg\ kg^{-1}}$$

Second-order reaction

$$1/[C] = k_2 t + 1/[C]_o$$

$$[C] = \mathbf{0.326\ mg\ \ kg^{-1}}$$