Rate law

- Proportionality symbol can be replaced by an equal sign if a proportionality constant (*k*) is introduced.

$$\text{Rate} = k\,[A]^{n}\,[B]^{m}$$

k: reaction rate constant

The equation describing the reaction rate is called as the **rate law**.

- **“*k*” value changes only with the temperature.**

- Consider the following reaction:

$$H_2Se_2O_3 \ + \ 6\ I^- \ + \ 4\ H^+ \rightarrow 2\ Se^+ \ + \ 2\ I^{3-} + 3\ H_2O$$

- The rate law for this reaction:

$$\text{Rate} = k\,[H_2Se_2O_3]^x\ [I^-]^y\ [H^+]^z$$

- The exponents were found experimentally for the initial rate of this reaction.

$x = 1$, $y = 3$ and $z = 2$

- The order of this reaction is:
  - *first* for $H_2Se_2O_3$,
  - *third* for I,
  - *second* for H.

The overall order of this reaction for reactants is sixth.

- Rate = $k\,[H_2Se_2O_3]^{1}\ [I^{-}]^{3}\ [H^{+}]^{2}$

Example 5: What is the rate for the above decomposition reaction when the reactant concentrations are the following?

$[H_2Se_2O_3] = 2.0 \times 10^{-2}\ M$

$[I^{-}] = 2.0 \times 10^{-3}\ M$

$[H^{+}] = 1.0 \times 10^{-3}\ M$

$k = 5.0 \times 10^{5}\ L^{5}\ mol^{-5}\ s^{-1}$

Rate = $k\ [H_2Se_2O_3]^1\ [I^–]^3\ [H^+]^2$

Rate = $(5.0 \times 10^5\ L^5\ mol^{-5}\ s^{-1})\ [2.0 \times 10^{-2}]^1\ [2.0 \times 10^{-3}]^3\ [1.0 \times 10^{-3}]^2$

Answer: 8.0×10^{-11} mol L^{-1} s^{-1}

Order of reaction

- An exponent in a rate law is called the **order of the reaction** with respect to the corresponding reactant.

- Consider the decomposition reaction of nitrogen pentaoxide (N_2O_5) to nitrogen dioxide and oxygen.

$$\mathbf{2}\, N_2O_5 \rightarrow 4\, NO_2 + O_2$$

$$\mathbf{2}\ N_2O_5 \rightarrow \quad 4\ NO_2 \quad + \quad O_2$$

$$\text{Rate} = k\,[N_2O_5]^{\mathbf{1}}$$

- The **coefficient** of N_2O_5 is **2** in the overall chemical reaction.

- However, the **exponent** of N_2O_5 is **1** in the rate law, so the reaction rate is said to be ***first order*** with respect to N_2O_5.

Overall order of a reaction

- The overall order of a reaction is the **sum** of the orders with respect to each reactant (or product) in the rate law.
  - The decomposition of N_2O_5 is a ***first-order*** reaction.

- Exponents in a rate law are generally small whole numbers.
- However fractional and negative values are occasionally found.
- A negative exponent means as the concentration of reactant or product increases, the rate of reaction decreases.

Determining the Exponents in a Rate Law

- Exponents in a rate law must be determined experimentally.

- **To determine the exponents, we study how changes in the concentrations of reactants or products affect the rate of the reaction.**

Example 6: The concentrations of the reactants and rate data for the following reaction was presented in Table 1.

$$A + B \rightarrow \text{products}$$

$$\text{Rate} = k\,[A]^{n}\,[B]^{m}$$

a) Find out the exponents in rate law,

b) Calculate the *k* value for any set of data.

Table 1. Concentration-rate data for the reac. of «A + B → products»

Trial number	Initial conc. (mol L^{-1})		Initial rate of formation of products
	[A]	[B]	(mol L^{-1} s^{-1})
I	0.10	0.10	0.20
II	0.20	0.10	0.40
III	0.30	0.10	0.60
IV	0.30	0.20	2.40
V	0.30	0.30	5.40

Solution

- Notice that the conc. of B is constant for the first three sets of data. Therefore, changes in the rate are caused by changes in the conc. of A.
- When [A] is doubled, the rate doubles; when [A] is tripled, the rate triples.
- Then, the exponent of A should be 1.

- In the final three sets of data, the concentration of B changes while the concentration of A is held constant. At this time, the concentration of B affects the reaction rate.

- When [B] is doubled, the rate increases by a factor of 4; when [B] is tripled, the rate increases by a factor of 9.

- The only way that B can affect the rate this way is if its concentration is squared in the rate law. Then, the exponent of B should be 2.

- The rate law for this reaction is:

$$\text{Rate} = k\,[\text{A}]^{1}\,[\text{B}]^{2}$$

- To calculate the value of ***k***, we can use any set of data.

$$0.20 = k\,(0.10\ \text{mol L}^{-1})^{1}\,(0.10\ \text{mol L}^{-1})^{2}$$

$$k = 2.0 \times 10^{2}\ \text{L}^{2}\ \text{mol}^{-1}\ \text{s}^{-1}$$

Example 7: The concentration and rate data for the following the reaction between hydrogen and nitrogen oxide at 800°C was given in Table 1.

a) Find out the exponents of the rate law.
b) Calculate the *k* value for any set of data.

Table 1. Concentration-rate data

	Initial conc. x 10^3 (torr)		**Initial rate**
Trial number	**[NO]**	**[H_2]**	**(torr min^{-1})**
I	6.00	1.00	20
II	6.00	2.00	40
III	6.00	3.00	60
IV	1.00	6.00	3
V	2.00	6.00	12
VI	3.00	6.00	27

Solution

- Notice that the conc. of NO is constant for the first three sets of data. Therefore, changes in the rate are caused by changes in the conc. of H_2.
- When $[H_2]$ is doubled, the rate doubles; when $[H_2]$ is tripled, the rate triples.
- Then, the exponent of H_2 should be 1.

- In the final three sets of data, the concentration of NO changes while the concentration of H_2 is held constant. At this time, the concentration of NO affects the reaction rate.
- When [NO] is doubled, the rate increases by a factor of 4; when [NO] is tripled, the rate increases by a factor of 9.
- The only way that NO can affect the rate this way is if its concentration is squared in the rate law. Then, the exponent of NO should be 2.

- The rate law for this reaction is:

$$\text{Rate} = k\,[\text{NO}]^{2}\,[\text{H}_2]^{1}$$

Rate law

- Rate law tells us how the rate of reaction changes with the conc. of the reactants or the products.

$$A + B \rightarrow C + D$$

$$\text{Rate} = -k\,[A]^{n}\,[B]^{m}$$

$$\text{Rate} = +k\,[C]^{x}\,[D]^{y}$$

Concentration and time

However, we may need to know the conc. of a compound during processing or storage at a given time. For instance;

- **Producing a chemical compound**: We need to know the conc. of the compound (eg. soap) at a specified time during processing.
- **Preserving a quality parameter**: We need to know the conc. of the compound (eg, anthocyanin) at a specified time during processing or storage.

Example

We may need to know the amount af anthocyanins in sour cherry juice stored at 10^{o}C for 6 months

- To obtain such data, expression about the conc. with time is needed.
- This expression is derived from rate law.

- **Rate law** is actually a differential equation between concentration and time and is obtained by integration.

$$v\ (\text{rate}) = -\frac{dA}{dt} = k\ [A]^n$$

- "–" sign, showing the reduction in the conc. of A with time.

$\frac{dA}{dt}$: Differential of A conc. to *t*. It shows the change in the conc. of A to time in small time increments,

k: reaction rate constant,

[A]: concentration of A at any (*t*) time,

n: order of reaction.

Reaction order

- To follow the changes in the quality of foods during processing and storage, the best way is to describe the experimental data in the form of mathematical models.

- To accomplish this goal, reaction order of a given reaction is described.

- **“Reaction order” is a mathematical tool to evaluate the experimental data.** It does not give any explanation about the mechanism of reaction.

decrease (loss):

$$V = -\frac{dA}{dt} = k_n A^n$$

increase **(formation):**

$$V = +\frac{dC}{dt} = k_n C^n$$

where:

dA/dt : Decrease or increase in concentration of the components for a period of time or change in concentration over time,

A : Concentration of reactant,

V : Rate of the reaction with respect to the degraded reactant or formed product,

k : Reaction rate constant,

n : Order of reaction

- The order of reactions generally starts from zero to go to «n.»

- In foods, the order of reactions in foods are limited. **Most reactions in foods fits first-order and some fits zero-order**.

- Small fractions of the reactions in foods fit **second-order**.

Zero-order (n = 0) Reactions

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

- In zero-order reactions, there is a linear relationship (decreasing or increasing) between the concentration of the reactant or product and the reaction time in aritmetic graph paper.

$$-\frac{dA}{dt} = k_o\,[A]^o \;\Rightarrow\; [A]^o = 1 \Rightarrow -\frac{dA}{dt} = k_o$$

$$\int_{A_o}^{A} dA = -k_o \int_{t_o}^{t} dt \qquad t_o = 0 \quad \text{ise,}$$

$$\mathbf{A} = -k_o\,\boldsymbol{t} + A_o$$ (Integrated form of the rate law)

This form allows us to find the conc. of reactant at any time after the start of the reaction.

$$A = -k_o t + A_o \quad \text{(degradation)}$$

$$C = k_o t + C_o \quad \text{(formation)}$$

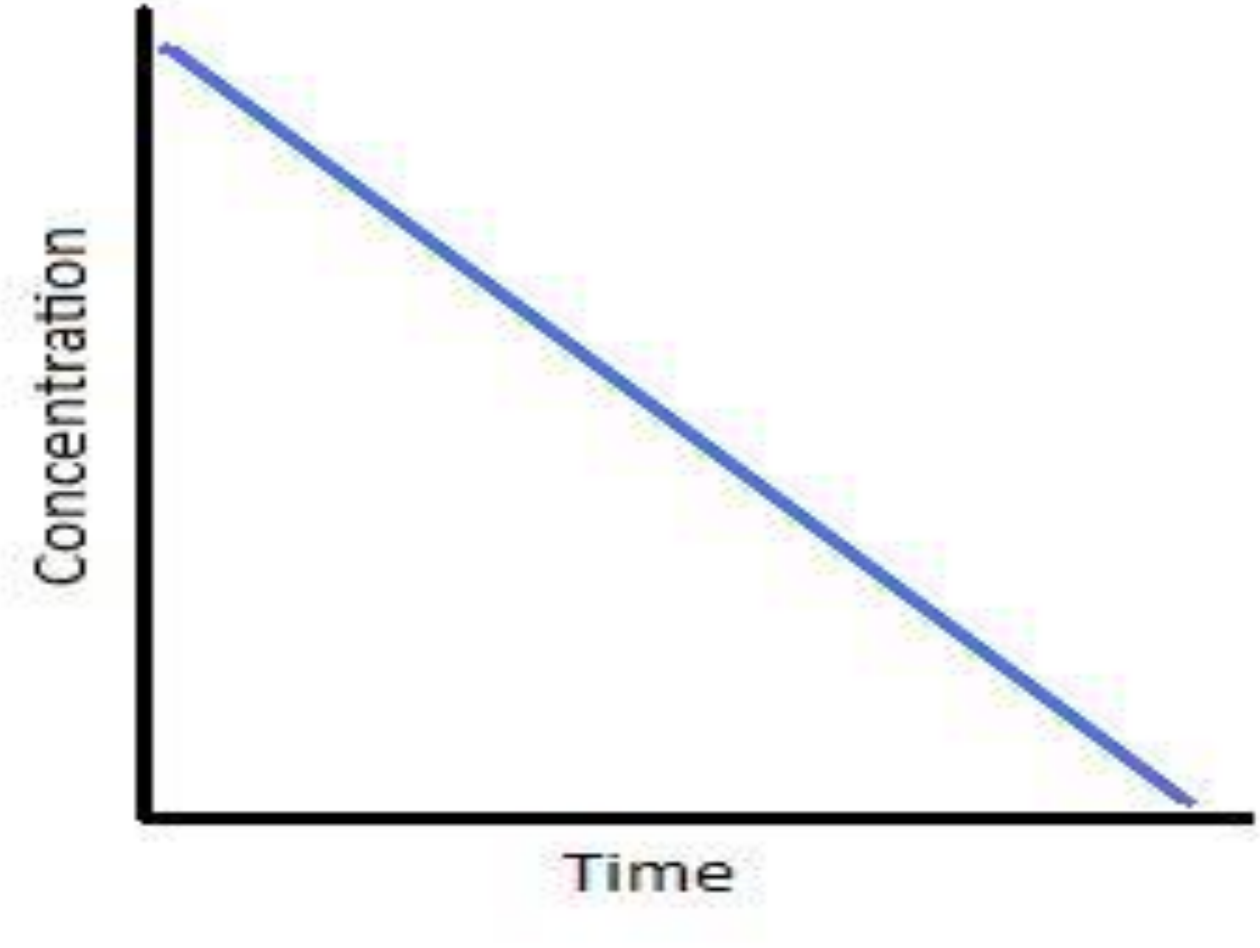
A : Concentration of A at some time (*t*) after the start of the reaction,

A_o: Initial concentration of A (*t*=0),

k_o : Zero-order reaction rate constant, {(concentration) / (time)}

t : Time.

Graphing Zero-order Reactions (arithmetic graph paper)



- **Zero-order reactions** proceed at a rate that is **independent of reactant concentration**. With increasing or decreasing reactant concentration, reaction rate **does not** change.

- In zero-order reactions, the amount of product is so small compared to the amount of reactant. As a result, reactant concentration is accepted as unchanged.

- In **zero-order reactions**, **the same amount** of the reactant was degraded or the same amount of product is formed per unit of time (look at the unit of **slope**).
- **For example**, the removal of ethyl alcohol from liver.

Regardless of ethyl alcohol level in blood, the liver processes the same amount of ethyl alcohol per unit of time. As a result, it will take some for your being sober depending upon your consumption of alcohol level!!!! Watch out when drinking☺))

Example

- The degradation rate constant (***k***) for the ascorbic acid in orange juice at 95°C is found as –0.76 mg L^{-1} h^{-1}. Analyze the ***k*** value.

Analyzing *k* value

- **unit of *k*:** The degradation of ascorbic acid in orange juice at 95°C is said to be «zero order.»
- **Numeric value of *k*:** Every 1 h, 0.76 mg of ascorbic acid is degraded at 95°C from 1 L of orange juice.

- Independent from aa concentration, **the same amount of aa** is degraded in orange juice per unit of time (h) throughout the reaction. (a lot of aa, as compared to dehydro aa)

- As the sufficient amount of time is past, all the aa will be degraded.
  (**AA conc.** will eventually come to **zero**).