

Exercise walk-through

5.8

Reaction Mechanism and Rate Law

AP Chemistry

The rate law

Found by experiment

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

The **orders** m, n come from data,
not the equation.

Method of initial rates :
double $[\text{A}]$ – rate $\times 2$ (1st), $\times 4$ (2nd),
unchanged (0th).

0 order: k in $\frac{\text{mol}}{\text{L s}}$

1st order: k in $\frac{1}{\text{s}}$

2nd order: k in $\frac{\text{L}}{\text{mol s}}$

Rate, and the constant in the rate law

Reaction rate

The **reaction rate** is the change in concentration per unit time – and it is divided by the stoichiometric coefficient so every species gives the same number.

Rate constant

The **rate constant** k in $\text{rate} = k[A]^m[B]^n$ depends on temperature and on the catalyst – never on concentration.

Its units

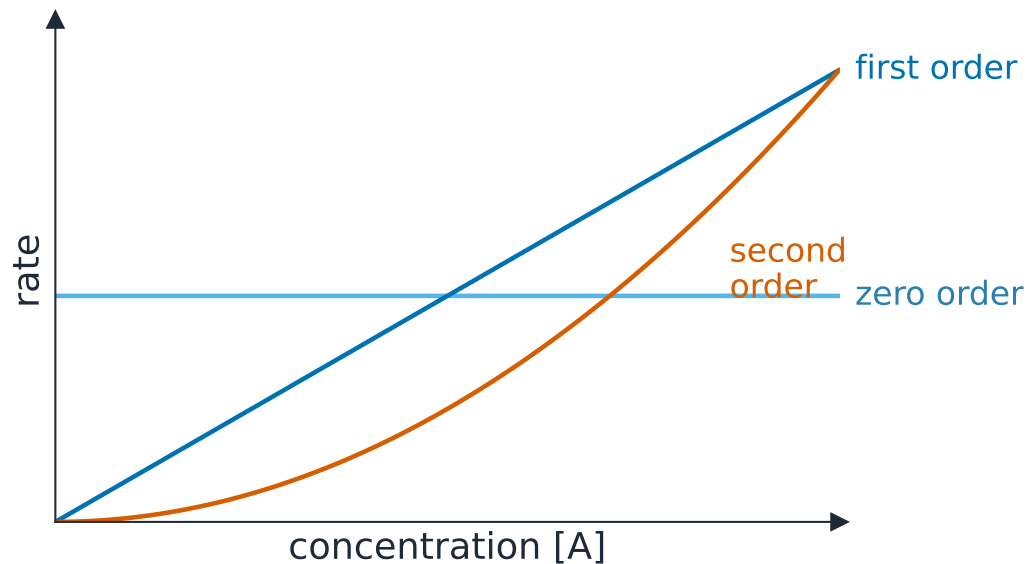
k 's units follow from the overall order, which is a useful check on an experimentally determined rate law.

Where it comes from

The orders come from experiment – initial rates or an integrated plot – never from the balanced equation.

Arrhenius: $k = Ae^{-E_a/RT}$. Temperature acts on k , which is why a rate law with fixed k describes one temperature only.

Rate against concentration for zero-



Rate against concentration for zero-, first-, and second-order reactions

Exercises 2.1-2.3

2.1 If the slow step is $A + B \rightarrow X$, write the rate law. [1]

2.2 Can the final rate law contain an intermediate? [1]

2.3 A slow first step is $2NO \rightarrow N_2O_2$. Write its rate law. [1]

Exercises 2.1-2.3

2.1 If the slow step is $A + B \rightarrow X$, write the rate law. [1]

2.1

- $\text{rate} = k[A][B]$
-

2.2 Can the final rate law contain an intermediate? [1]

2.2

- No
-

2.3 A slow first step is $2\text{NO} \rightarrow \text{N}_2\text{O}_2$. Write its rate law. [1]

2.3

- $\text{rate} = k[\text{NO}]^2$

Exercise 3.1

3.1 For a mechanism with a slow **first** step, the rate law is written from

[1]

☐

A the overall equation

B the slow first step's molecularity

C the fast step

D the products

Exercise 3.1

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A the overall equation

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3.1 B

- the slow first step's molecularity

Exercise 3.2 (a)

3.2 A mechanism for $\text{NO}_2 + \text{CO} \rightarrow \text{NO} + \text{CO}_2$ is: Step 1 (slow) $\text{NO}_2 + \text{NO}_2 \rightarrow \text{NO}_3 + \text{NO}$; Step 2 (fast) $\text{NO}_3 + \text{CO} \rightarrow \text{NO}_2 + \text{CO}_2$.

(a) Write the predicted rate law.

[2]

Exercise 3.2 (a)

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(a) Write the predicted rate law.

[2]

(a)

- $\text{rate} = k[\text{NO}_2]^2$

Exercise 3.2 (b)

3.2 A mechanism for $\text{NO}_2 + \text{CO} \rightarrow \text{NO} + \text{CO}_2$ is: Step 1 (slow) $\text{NO}_2 + \text{NO}_2 \rightarrow \text{NO}_3 + \text{NO}$; Step 2 (fast) $\text{NO}_3 + \text{CO} \rightarrow \text{NO}_2 + \text{CO}_2$.

(b) The experimental rate law is $\text{rate} = k[\text{NO}_2]^2$. Is the mechanism consistent? [1]

Exercise 3.2 (b)

3.2 A mechanism for $\text{NO}_2 + \text{CO} \rightarrow \text{NO} + \text{CO}_2$ is: Step 1 (slow) $\text{NO}_2 + \text{NO}_2 \rightarrow \text{NO}_3 + \text{NO}$; Step 2 (fast) $\text{NO}_3 + \text{CO} \rightarrow \text{NO}_2 + \text{CO}_2$.

(b) The experimental rate law is $\text{rate} = k[\text{NO}_2]^2$. Is the mechanism consistent? [1]

(b)

- Yes – it matches the experimental rate law

Exercise 3.3

3.3 Explain why the concentration of CO does **not** appear in the rate law for the mechanism in 3.2. [2]

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3.3

- CO reacts only in the fast **second** step, after the rate-determining step; the slow step (which sets the rate) does not involve CO, so it is absent from the rate law