Section 3: Reaction Rate Laws

Writing Reaction Rate Laws

The word **average** is important since most chemical reactions slow down as the reactants are consumed and fewer particles are available to collide.

A **rate law** expresses the relationship between the rate of a chemical reaction and the concentration of reactants. A rate law must be determined experimentally.

The reaction A ⟶ B is a one-step reaction.

One-Step Reaction Rate Law

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

[A] represents the concentration of a reactant; *k* is a constant.

The symbol k is the **specific rate constant**, a numerical value that relates the reaction rate and the concentrations of reactants at a given temperature.

- K is unique for every reaction.
- K can have a variety of units including L/(mol.s), $L^2/(mol^2.s)$, and s^{-1}. This unit depends on the reaction order.

The unit of the rate is concentration/time , consider the concentration is M or mol/L. Complete the table

Rate law	Reaction order	Unit of K
Rate = $K[A]^0$		
Rate = K[A]		
Rate = $K[A]^2$		
Rate = $K[A]^3$		

- K does not change with concentration; however, k does change with temperature.

The rate law shows that the reaction rate is .... proportional to the molar concentration of A.

A large value of K means that ....

First-order reaction rate laws

Rate = k[A] ⟶ Rate = $k[A]^1$

The **reaction order** for a reactant defines how the rate is affected by the concentration of that reactant.

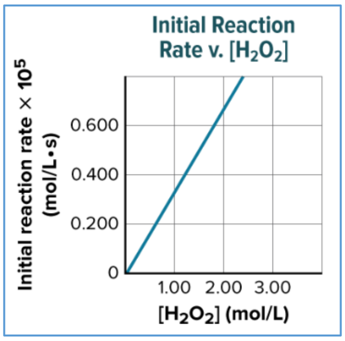
Rate = $k[H_2O_2]$. The decomposition of H_2O_2 is said to be **first order** in H_2O_2. What does it mean?

....

....

....

The graph shows a direct relationship between the concentration of H_2O_2 and the rate of the decomposition. Complete this table.



[H_2O_2] (mol/L)	Initial reaction rate × 10^5 (mol/L·S)
1.00	
2.00	
3.00	

Get It?

If the reaction order for a reactant is first order, how will the rate of the reaction change if the concentration of the reactant is **tripled**? ....

Other-order reaction rate laws

The overall reaction order of a chemichal reaction is the sum of the orders for the individual reactants.

Many chemical reactions, particularly those that have more than one reactant, are not first-order.

The General Rate Law

$$rate = k[A]^m[B]^n$$

[A] and [B] represent the concentrations of reactants A and B. The exponents *m* and *n* are the reaction orders.

If **aA + bB ⟶ products**

If the reaction between A and B occurs in a single step (and with a single activated complex) does m = a and n = b. However, single-step reactions are not common.

If **$2NO(g) + 2H_2(g) \longrightarrow N_2(g) + 2H_2O(g)$** **rate = $k[NO]^2 [H_2]$**

Is it a single step reaction? .... because ....

The reaction is described as .... order in NO, ... order in H_2 , and .... order overall.

$[NO]^2$ means: ....

[H_2] means: ....

If one of the reactants is not part of the rate law expression, changing the concentration of that reactant will have no effect on the rate of the reaction. The exponent of this type of reactant would be ....

The rate law for the decomposition of H_2O_2 is expressed by **Rate = $k[H_2O_2]^1$** **How the chemical rate changes if the H_2O_2 concentration decreases to one-half?** **A. Increases by one and half** **B. decreases by one-half** **C. Increase by one-half** **D . No change**	يُعبر عن قانون سرعة تفاعل تفكك H_2O_2 بالمعادلة التالية: **Rate = $k[H_2O_2]^1$** كيف تتغير سرعة التفاعل إذا انخفض تركيز H_2O_2 إلى النصف؟ A . تزداد بمعدّل مرة ونصف B . تقل بمعدّل النصف C . تزداد بمعدل النصف D . لا تتغير

Determine Reaction Order

The **method of initial rates** determines reaction order by comparing the initial rates of a reaction carried out with varying reactant concentrations.

Consider the general reaction **aA + bB ⟶ products**

Trial	Initial [A](*M*)	Initial [B](*M*)	Initial Rate (mol/(L • s))
1	0.100	0.100	2.00×10^{-3}
2	0.200	0.100	4.00×10^{-3}
3	0.200	0.200	16.00×10^{-3}

How can we write the general rate law for this reaction? ....

We need to find the exponents of [A] and [B] by choosing two trials to compare each time.

To find the component of [A] . In which trials we can see [B] remains constant? ....

Divide the higher by the lower.

Find the exponent.

To find the component of [B] . In which trials we can see [A] remains constant? ....

Divide the higher by the lower.

Find the exponent.

Write the rate law now: The overall reaction order is

Practice problems:

Write the rate law for the reaction aA ⟶ bB if the reaction is third order in A. [B] is not part of the rate law.

The rate law for the reaction $2NO(g) + O_2(g) \longrightarrow 2NO_2(g)$ is first order in O_2 and third order overall. What is the rate law for the reaction?

Given the experimental data below, use the method of initial rates to determine the rate law for the reaction

aA + bB ⟶ products.

Trial	Initial [A](*M*)	Initial [B](*M*)	Initial Rate (mol/(L•s))
1	0.100	0.100	2.00×10^{-3}
2	0.200	0.100	2.00×10^{-3}
3	0.200	0.200	4.00×10^{-3}

22. CHALLENGE The rate law for the reaction $CH_3CHO\,(g) \rightarrow CH_4\,(g) + CO\,(g)$ is given by the following expression:

$\text{Rate} = k[CH_3CHO]^2$.

Use this information to fill in the missing experimental data below.

Trial	Initial $[CH_3CHO]\,(M)$	Initial Rate $(\text{mol}/(\text{L} \cdot \text{s}))$
1	2.00×10^{-3}	2.70×10^{-11}
2	4.00×10^{-3}	1.08×10^{-10}
3	8.00×10^{-3}	
4	6.00×10^{-3}	
5		6.75×10^{-10}
6		9.72×10^{-10}

Given the experimental data below, use the method of initial rates to determine the reaction order.

aA + bB → products.

Experimental Data

Trial	Initial [A] (M)	Initial [B] (M)	Initial Rate (mol/(L·s))
1	0.100	0.100	2.00×10^{-3}
2	0.200	0.100	2.00×10^{-3}
3	0.200	0.200	4.00×10^{-3}

بمعرفة البيانات التجريبية أدناه، استخدم طريقة السرعات الابتدائية لتحديد الرتبة الكلية للتفاعل:

aA+ bB→ نواتج

البيانات التجريبية

تجربة	التركيز الابتدائي [A] (M)	التركيز الابتدائي [B] (M)	السرعة الابتدائية (mol/(L·s))
1	0.100	0.100	2.00×10^{-3}
2	0.200	0.100	2.00×10^{-3}
3	0.200	0.200	4.00×10^{-3}

A. 1
B. 2
C. 3
D. 4

1 . A
2 . B
3 . C
4 . D

Given the experimental data below, use the method of initial rates to determine the reaction order.

aA + bB → products.

Experimental Data

Trial	Initial [A](M)	Initial [B](M)	Initial Rate (mol/(L·s))
1	0.100	0.100	2.00×10^{-3}
2	0.200	0.100	2.00×10^{-3}
3	0.200	0.200	4.00×10^{-3}

A. 1
B. 2
C. 3
D. 4

بمعرفة البيانات التجريبية أدناه، استخدم طريقة السرعات الابتدائية لتحديد الرتبة الكلية للتفاعل:

aA+ bB→ نواتج

البيانات التجريبية

تجربة	التركيز الابتدائي [A](M)	التركيز الابتدائي [B](M)	السرعة الابتدائية (mol/(L·s))
1	0.100	0.100	2.00×10^{-3}
2	0.200	0.100	2.00×10^{-3}
3	0.200	0.200	4.00×10^{-3}

1 . A
2 . B
3 . C
4 . D

The rate law for the decomposition of H_2O_2 is expressed by

$$Rate = k[H_2O_2]^1$$

How the chemical rate changes if the H_2O_2 concentration decreases to one-half?

A. Increases by one and half
B. decreases by one-half
C. Increase by one-half
D . No change

يُعبر عن قانون سرعة تفاعل تفكك H_2O_2 بالمعادلة التالية:

$$Rate = k[H_2O_2]^1$$

كيف تتغير سرعة التفاعل إذا انخفض تركيز H_2O_2 إلى النصف؟

A . تزداد بمعدّل مرة ونصف
B . تقل بمعدّل النصف
C . تزداد بمعدل النصف
D . لا تتغير

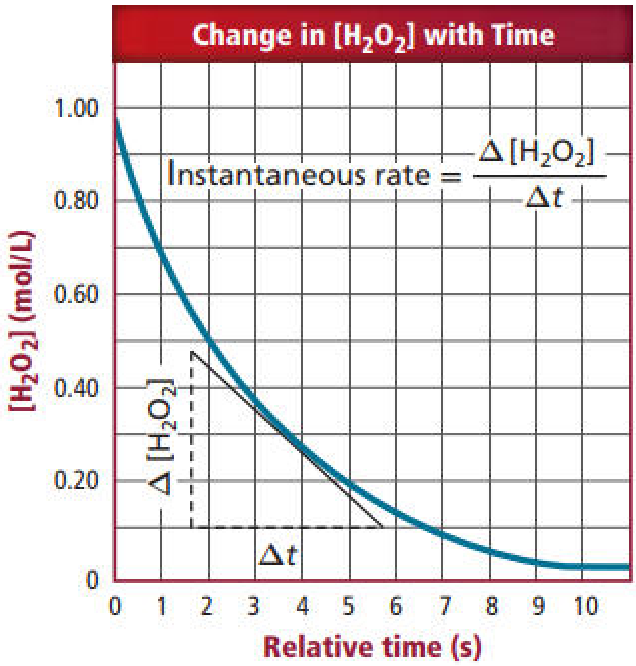
Consider the decomposition of hydrogen peroxide (H2O2)

$$2H_2O_2(aq) \rightarrow 2H_2O(l) + O_2(g)$$

For this reaction, the decrease in H_2O_2 concentration over time is shown in **Figure 16.17.** The curved line shows how the reaction rate decreases as the reaction proceeds. The **instantaneous rate** is the slope of the straight line tangent to the curve at a specific time. The expression $\Delta[H_2O_2]/\Delta t$ is one way to express the reaction rate. In other words, the rate of change in H_2O_2 concentration relates to one specific point (or instant) on the graph.

You can determine the instantaneous rate for a reaction in another way if you are given the reactant concentrations at a given temperature and know the experimentally determined rate law and the specific rate constant at that temperature.

Figure 16.17 The instantaneous rate for a specific point in the reaction progress can be determined from the tangent to the curve that passes through that point.



Slope of line $= \frac{\Delta x}{\Delta y}$

Instantaneous rate $=$ Δ

$\frac{\Delta x}{\Delta y} = \frac{\Delta[H_2O_2]}{\Delta t}$

Graph Check

Identify the variables that are plotted on the *y*-axis and on the *x*-axis.

Consider, the decomposition of dinitrogen pentoxide (N_2O_5) into nitrogen dioxide (NO_2) and oxygen (O_2), which proceeds as follows.

$$2N_2O_5(g) \rightarrow 4NO_2(g) + O_2(g)$$

The experimentally determined rate law for this reaction is

$$\text{rate} = k[N_2O_5]$$

where $k = 1.0 \times 10^{-5}\ s^{-1}$. If $[N_2O_5] = 0.350M$, the instantaneous reaction rate would be calculated as

$$\text{rate} = (1.0 \times 10^{-5}\ s^{-1})(0.350\ mol/L) = 3.5 \times 10^{-6}\ mol/(L \cdot s)$$

The following reaction is first order in H2 and second order in NO with a rate constant of

2.90×10^2 ($L^2/(mol^2 \cdot s)$).

$$2NO(g) + H_2(g) \rightarrow N_2O(g) + H_2O(g)$$

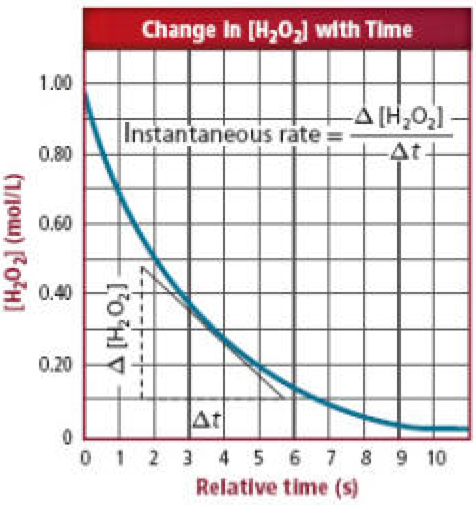
Calculate the instantaneous rate when the reactant concentrations are [NO] = 0.00200*M* and $[H_2]$ = 0.00400*M*.

Calculate the instantaneous rate for the reaction between NO and H2

1. [NO] = 0.00500*M* and $[H_2]$ = 0.00200*M*
2. [NO] = 0.0100*M* and $[H_2]$ = 0.00125*M*

Challenge Calculate [NO] for the reaction in Example Problem 16.2 if the rate is 9.00×10^{-5} mol/(L • s) and $[H_2]$ is 0.00300*M*.

. In the reaction of hydrogen peroxide, what happens to the instantaneous rate as time passes?



Slope of line = $\frac{\Delta x}{\Delta y}$

Instantaneous rate = $\frac{\Delta [H_2O_2]}{\Delta t}$

$\frac{\Delta x}{\Delta y} = \frac{\Delta [H_2O_2]}{\Delta t}$

A. ○ the rate increases

B. ○ the rate decreases

C. ○ the rate stays the same

D. ○ the rate doubles