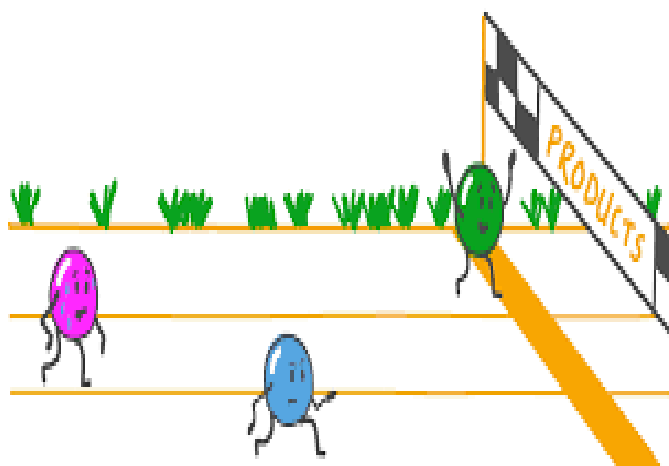


RATES OF REACTIONS



Chapter: Reaction Rates

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section 3 : Reaction Rate Laws

Writing Reaction Rate Laws

- **A rate law** : is the relationship between the rate of a chemical reaction and the concentration of reactants.
- For example, the reaction $A \rightarrow B$ is a one-step reaction. The rate law for this reaction is expressed as follows.

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

- A rate law must be determined experimentally.
- The rate law shows that the reaction rate is directly proportional to the molar concentration of A.
- **The specific rate constant(K)**: a numerical value that relates the reaction rate and the concentrations of reactants at a given temperature.
- **Properties the specific rate constant:**
- The specific rate constant is unique for every reaction and can have a variety of units including $L/(\text{mol}\cdot\text{s})$, $L^2/(\text{mol}^2 \cdot \text{s})$, and s^{-1} .
- The specific rate constant, k , does not change with concentration.
- However, k does change with temperature.
- A large value of k means that A reacts rapidly to form B.

First-order reaction rate laws

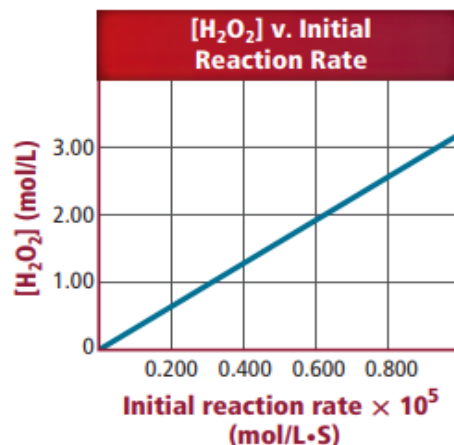
- In the expression $\text{Rate} = k[A]$, it is understood that the notation $[A]$ means the same as $[A]^1$.
- For reactant A, the understood exponent 1 is called **the reaction order**.
- **The reaction order** : for a reactant defines how the rate is affected by the concentration of that reactant.
- For example, the rate law for the decomposition of H_2O_2 is expressed by the following equation.

$$\text{Rate} = k [\text{H}_2\text{O}_2]$$

- Because the reaction rate is directly proportional to the concentration of H_2O_2 raised to the first power ($[\text{H}_2\text{O}_2]^1$).
- The decomposition of H_2O_2 is said to be first order in H_2O_2 .
- Because the reaction is first order in H_2O_2 , the reaction rate changes in the same proportion that the concentration of H_2O_2 changes.
- So, if the H_2O_2 concentration decreases to one-half its original value, the reaction rate is also reduced by one-half.
- The reaction rates are determined from experimental data. Because reaction order is based on reaction rates, it follows that reaction order is also determined experimentally.

- Finally, because the rate constant, k , describes the reaction rate, it must also be determined experimentally.

- The graph shows how the initial reaction rate for the decomposition of H_2O_2 changes with the concentration of H_2O_2 .



- 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

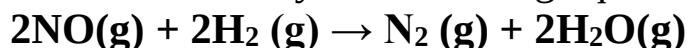
- The overall reaction order of a chemical reaction:** is the sum of the orders for the individual reactants in the rate law.
- Many chemical reactions, particularly those that have more than one reactant, are not first-order.
- Consider the general form for a chemical reaction with two reactants. In this chemical equation, a and b are coefficients.



- The General Rate Law

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

- The rate of a reaction** : is equal to the product of k and the concentrations of the reactants each raised to a power (order) that is determined experimentally.
- Only if the reaction between A and B occurs in a single step (and with a single activated complex) does $m = a$ and $n = b$.
- That is unlikely, however, because single-step reactions are not common.
- For example, consider the reaction between nitrogen monoxide (NO) and hydrogen (H_2), which is described by the following equation.



- This reaction occurs in more than one step, and has the following rate law.

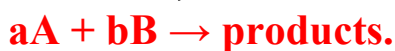
$$\text{rate} = k[\text{NO}]^2[\text{H}_2]$$

- The rate law was determined from experimental data that indicate that the rate depends on the concentration of the reactants as follows:
- If $[\text{NO}]$ doubles, the rate quadruples; If $[\text{H}_2]$ doubles, the rate doubles.
- The reaction is described as second order in NO , first order in H_2 , and third order overall.

- The overall order is the sum of the orders for the individual reactants (the sum of the exponents), which is (2 + 1), or 3.

Determining Reaction Order

- **The method of initial rates:** is one common experimental method of evaluating reaction order .
- The method of initial rates determines reaction order by comparing the initial rates of a reaction carried out with varying reactant concentrations.
- The initial rate measures how fast the reaction proceeds at the moment at which the reactants are mixed and the concentrations of the reactants are known.
- To understand how this method works, consider the general reaction



- Suppose that the reaction is carried out three times with varying concentrations of A and B and yields the initial reaction rates shown in Table .
- Recall that the general rate law for this type of reaction is as follows.

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

- To determine m, the exponent of [A], compare the concentrations and reaction rates in Trials 1 and 2.
- As you can see from the data, while the concentration of B remains constant, the concentration of A in Trial 2 is twice that of Trial 1.
- Note that the initial rate in Trial 2 is twice that of Trial 1.
- Because doubling [A] doubles the rate, the reaction must be first order in A.
- That is, because $2^m = 2$, m must equal 1.
- The same method is used to determine n, the exponent of [B], except this time Trials 2 and 3 are compared.
- Doubling the concentration of B causes the rate to increase by four times. Because $2^n = 4$, n must equal 2.
- This information suggests that the reaction is second order in B, giving the following overall rate law. **rate = k[A]¹ [B]²**
- The overall reaction order is third order (sum of exponents 2+1=3).

Table 16.2		Experimental Initial Rates for $aA + bB \rightarrow \text{products}$	
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}

1- Write the rate law for the reaction $aA \rightarrow bB$, if the reaction is third order in A. [B] is not part of the rate law.

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

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3- Given the experimental data below, use the method of initial rates to determine the rate law for the reaction $aA + bB \rightarrow \text{products}$. (Hint: Any number to the zero power equals one. For example, $(0.22)^0 = 1$)

Practice Problem 21 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}

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4- Challenge. The rate law for the reaction $CH_3CHO(g) \rightarrow CH_4(g) + CO(g)$ is $\text{Rate} = k [CH_3CHO]^2$. Use this information to fill in the missing experimental data below.

Practice Problem 22 Experimental Data		
Trial	Initial $[CH_3CHO](M)$	Initial Rate (mol/(L·s))
1	2.00×10^{-3}	2.70×10^{-11}
2	4.00×10^{-3}	10.8×10^{-11}
3	8.00×10^{-3}	

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5- **Explain** what the rate law for a chemical reaction tells you about the reaction.

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6- **Apply**, the rate-law equations to show the difference between a first-order reaction with a single reactant and a second-order reaction with a single reactant.

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7- **Explain**, the function of the specific rate constant in a rate-law equation.

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8- **Explain**, Under what circumstance is the specific rate constant (k), not a constant. What does the size of k indicate about the rate of a reaction?

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9- **Suggest**, a reason why, when given the rate of a chemical reaction, it is important to know that the reaction rate is an average reaction rate.

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10- **Explain**, how the exponents in the rate equation for a chemical reaction relate to the coefficients in the chemical equation.

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11- **Determine**, the overall reaction order for a reaction between A and B for which the rate law is $\text{rate} = k[\text{A}]^2[\text{B}]^2$.

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12- **Why** must the rate law for a chemical reaction be based on experimental evidence rather than the balanced equation for the reaction?

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13- Assume, that the rate law for a generic chemical reaction is $\text{Rate} = [\text{A}][\text{B}]^3$. What is the reaction order in A, the reaction order in B, and the overall reaction order?

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14- Consider, the generic chemical reaction: $\text{A} + \text{B} \rightarrow \text{AB}$. Based on experimental data, the reaction is second order in Reactant A. If the concentration of A is halved, and all other conditions remain unchanged, how does the reaction rate change?

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15- The instantaneous rate data in Table were obtained for the reaction $\text{H}_2(\text{g}) + 2\text{NO}(\text{g}) \rightarrow \text{H}_2\text{O}(\text{g}) + \text{N}_2\text{O}(\text{g})$ at a given temperature and concentration of NO. How does the instantaneous rate of this reaction change as the initial concentration of H_2 is changed? Based on the data, is $[\text{H}_2]$ part of the rate law? Explain.

Table 16.3 Reaction Between $\text{H}_2(\text{g})$ and $\text{NO}(\text{g})$	
$[\text{H}_2]$ (mol/L)	Instantaneous Rate (mol/L·s)
0.18	6.00×10^{-3}
0.32	1.07×10^{-2}
0.58	1.93×10^{-2}

16- Suppose, that a chemical reaction has the rate law of $\text{rate} = [\text{A}]^2 [\text{B}]^3$ and that the reaction rate is $4.5 \times 10^{-4} \text{ mol}/(\text{L} \cdot \text{min})$. If the concentrations of both A and B are doubled and all other reaction conditions remain constant, how will the reaction rate change?

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17- The data in Table were obtained for the decomposition of azomethane ($\text{CH}_3\text{N}_2\text{CH}_3$) at a particular temperature according to the equation $\text{CH}_3\text{N}_2\text{CH}_3(\text{g}) \rightarrow \text{C}_2\text{H}_6(\text{g}) + \text{N}_2(\text{g})$. Use the data to determine the reaction's experimental rate law.

Table 16.4 Decomposition of Azomethane		
Experiment Number	Initial $[\text{CH}_3\text{N}_2\text{CH}_3]$	Initial Reaction Rate
1	0.012M	$2.5 \times 10^{-6} \text{ mol}/(\text{L} \cdot \text{s})$
2	0.024M	$5.0 \times 10^{-6} \text{ mol}/(\text{L} \cdot \text{s})$

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18-Use the data in previous Table to calculate the value of the specific rate constant, k.

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19- At the same temperature, predict the reaction rate when the initial concentration of $\text{CH}_3\text{N}_2\text{CH}_3$ is 0.048M. Use the data in previous Table.

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20- Dinitrogen pentoxide decomposes in chloroform at a rate of 2.48×10^{-4} mol/(L·min) at a particular temperature according to the equation $2\text{N}_2\text{O}_5 \rightarrow 4\text{NO}_2 + \text{O}_2$. The reaction is first order in N_2O_5 . Given an initial concentration 0.400 mol/L, what is the rate constant for the reaction? What is the approximate $[\text{N}_2\text{O}_5]$ after the reaction proceeds for 1.30 h?

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21-Radioactive decay is first order in the decaying isotope. strontium-90 contained in fallout from nuclear explosions decays to yttrium-90 and a beta particle. Write the rate law for the decay of strontium-90.

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22- The following reaction takes place in an automobile's engine and exhaust system. $\text{NO}_2(\text{g}) + \text{CO}(\text{g}) \rightarrow \text{NO}(\text{g}) + \text{CO}_2(\text{g})$. The reaction's rate law at a particular temperature is $\text{Rate} = 0.50 \text{ L}/(\text{mol} \cdot \text{s})[\text{NO}_2]^2$. What is the reaction's initial, instantaneous rate when $[\text{NO}_2] = 0.0048 \text{ mol/L}$?

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23-The concentrations in a chemical reaction are expressed in moles per liter, and the time is expressed in seconds. If the overall rate law is third-order, what are the units for the rate and the rate constant?

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24-Heating cyclopropane (C_3H_6) converts it to propene ($\text{CH}_2 = \text{CHCH}_3$). The rate law is first order in cyclopropane. If the rate constant at a particular temperature is $6.22 \times 10^{-4} \text{ s}^{-1}$ and the concentration of cyclopropane is held at 0.0300 mol/L , what mass of propene is produced in 10.0 minutes in a volume of 2.50 L?

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25-The rate law is $\text{Rate} = k[\text{phenolphthalein}]$. If the rate constant for the reaction is $1.0 \times 10^{-2} \text{ s}^{-1}$, what is the instantaneous rate of reaction when the concentration of phenolphthalein is 0.0025M ?

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26-The rate law for $\text{A} + \text{B} + \text{C} \rightarrow \text{products}$ is: $\text{rate} = k[\text{A}]^2 [\text{C}]$. If $k = 6.92 \times 10^{-5} \text{ L}^2 / (\text{mol}^2 \cdot \text{s})$, $[\text{A}] = 0.175\text{M}$, $[\text{B}] = 0.230\text{M}$, and $[\text{C}] = 0.315\text{M}$, what is the instantaneous reaction rate?

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