

Mechanisms, catalysts and activation energy

AP Chemistry · Worksheet answers

Each answer shows the reasoning: steps added and cancelled, formulas, substitutions and the final result in bold. For mechanism problems, always check two things: the steps must add up to the overall equation, and the predicted rate law must match experiment.

Level: AP Chemistry · **Curriculum:** AP Chem Unit 5

Problem 1 Molecularity and rate laws

1. Unimolecular; rate = $k[\text{O}_3]$.
2. Bimolecular; rate = $k[\text{NO}][\text{O}_3]$.
3. Bimolecular (two molecules collide); rate = $k[\text{NO}_2]^2$.

Problem 2 Naming the species

1. X is an **intermediate** (made, then used). Y is a **catalyst** (used, then re-formed).
2. **Neither** appears: both cancel.
3. The **transition state**.

Problem 3 Adding the steps

1. $\text{Cl} + \text{O}_3 + \text{ClO} + \text{O} \rightarrow \text{ClO} + \text{O}_2 + \text{Cl} + \text{O}_2$. Cancel Cl and ClO: $\text{O}_3 + \text{O} \rightarrow 2 \text{O}_2$. Atom check: 4 O on each side.
2. Catalyst **Cl**; intermediate **ClO**.

Problem 4 Reading an energy diagram

1. $E_a(\text{forward}) = 100 - 40 = \mathbf{60 \text{ kJ}}$.
2. $\Delta H = 10 - 40 = \mathbf{-30 \text{ kJ}}$ (exothermic).
3. $E_a(\text{reverse}) = 100 - 10 = \mathbf{90 \text{ kJ}}$.

Problem 5 True or false about catalysts

1. **False**: ΔH is unchanged.
2. **True**.
3. **False**: it speeds both directions and does not change the equilibrium position.
4. **False**: it is restored.

Problem 6 Slow step and rate law

1. $\text{A} + \text{B} + \text{C} + \text{B} \rightarrow \text{C} + \text{D}$ gives $\mathbf{\text{A} + 2 \text{B} \rightarrow \text{D}}$ after cancelling C.

- The intermediate is **C**.
- The slow step is bimolecular, so rate = **$k[A][B]$** .

Problem 7 Why heat speeds reactions

At the higher temperature, particles move faster, so collisions are more frequent. More importantly, a larger fraction of collisions have energy of at least E_a . Both effects increase the number of **successful collisions per second**, and the second effect dominates.

Problem 8 Checking a mechanism for nitric oxide

- $2 \text{ NO} + \text{H}_2 + \text{H}_2\text{O}_2 + \text{H}_2 \rightarrow \text{N}_2 + \text{H}_2\text{O}_2 + 2 \text{ H}_2\text{O}$. Cancel H_2O_2 : **$2 \text{ NO} + 2 \text{ H}_2 \rightarrow \text{N}_2 + 2 \text{ H}_2\text{O}$** .
- The intermediate is **H_2O_2** .
- Rate = $k[\text{NO}]^2[\text{H}_2]$: **third order overall**.

Problem 9 Choosing between mechanisms

- I: rate = $k[A][B]$. II: rate = $k[A]^2$.
- Mechanism I** fits.
- Several different mechanisms can predict the same rate law, and only the rate law is tested, so agreement does not prove it. Other evidence (detecting X) would be needed.

Problem 10 Fast equilibrium first

- $\text{A} + \text{B} + \text{AB} + \text{B} \rightarrow \text{AB} + \text{C}$ gives **$\text{A} + 2 \text{ B} \rightarrow \text{C}$** .
- Rate = $k_2[\text{AB}][\text{B}]$, with $[\text{AB}] = K[\text{A}][\text{B}]$, so rate = $k_2K[\text{A}][\text{B}]^2$.
- $k = 0.50 \times 4.0 = \mathbf{2.0 \text{ M}^{-2} \text{ s}^{-1}}$. Rate = $2.0 \times 0.10 \times (0.20)^2 = \mathbf{8.0 \times 10^{-3} \text{ M/s}}$.

Problem 11 Two-step profile

- Step 1: $85 - 0 = \mathbf{85 \text{ kJ/mol}}$. Step 2: $60 - 30 = \mathbf{30 \text{ kJ/mol}}$.
- Step 1**, with the larger barrier.
- $\Delta H = -45 - 0 = \mathbf{-45 \text{ kJ/mol}}$.
- Reverse of step 1: $85 - 30 = \mathbf{55 \text{ kJ/mol}}$.

Problem 12 Catalyst and rate constant

- $k(\text{cat})/k = e^{(25000/(8.314 \times 298))} = e^{(10.09)} = \mathbf{2.4 \times 10^4}$.
- The reverse reaction is sped up **by the same factor** (its barrier is lowered by 25 kJ/mol too).
- ΔH is **unchanged**.

Problem 13 Activation energy from a rule of thumb

- $E_a = R \ln 2 / (1/300 - 1/310) = 8.314 \times 0.693 / (1.075 \times 10^{-4}) = 5.36 \times 10^4 \text{ J/mol}$.

2. $E_a \approx 54 \text{ kJ/mol}$.

Problem 14 Predicting a rate constant

1. $\ln(k_2/k_1) = (80000/8.314)(1/298 - 1/318) = 9622 \times 2.110 \times 10^{-4} = 2.031$, so $k_2/k_1 = 7.62$ and $k_2 = 1.5 \times 10^{-5} \times 7.62 = \mathbf{1.1 \times 10^{-4} \text{ s}^{-1}}$.

2. About **7.6 times** faster.

Problem 15 Reading an Arrhenius plot

1. Slope = $(-4.75 - (-2.15))/(0.0035 - 0.0031) = -2.60/0.0004 = \mathbf{-6.5 \times 10^3 \text{ K}}$.

2. $E_a = -\text{slope} \times R = 6500 \times 8.314 = 5.4 \times 10^4 \text{ J/mol} = \mathbf{54 \text{ kJ/mol}}$.

3. $\ln A = -2.15 + 6500 \times 0.0031 = \mathbf{18.0}$, so $A = e^{18.0} = \mathbf{6.6 \times 10^7 \text{ s}^{-1}}$.

Problem 16 Catalytic decomposition of peroxide

1. $\text{H}_2\text{O}_2 + \text{I}^- + \text{H}_2\text{O}_2 + \text{IO}^- \rightarrow \text{H}_2\text{O} + \text{IO}^- + \text{H}_2\text{O} + \text{O}_2 + \text{I}^-$. Cancel I^- and IO^- : **$2 \text{H}_2\text{O}_2 \rightarrow 2 \text{H}_2\text{O} + \text{O}_2$** .

2. Catalyst I^- ; intermediate IO^- .

3. Rate = $k[\text{H}_2\text{O}_2][\text{I}^-]$. Only one H_2O_2 takes part in the slow step; the second reacts after it.

4. Rate = $0.0115 \times 0.50 \times 0.020 = \mathbf{1.2 \times 10^{-4} \text{ M/s}}$.

Problem 17 Designing an experiment

1. Measure initial rates at fixed $[\text{A}]$ while changing $[\text{B}]$ (for example 0.10 M to 0.30 M).

2. X: rate unchanged. Y: rate multiplied by the same factor as $[\text{B}]$.

3. $[\text{B}] \times 3$ gives rate $\times 3$ ($3.6 \times 10^{-3}/1.2 \times 10^{-3}$): **mechanism Y**. $k = 1.2 \times 10^{-3}/(0.10^2 \times 0.10) = \mathbf{1.2 \text{ M}^{-2} \text{ s}^{-1}}$.

4. Another mechanism could give the same rate law; evidence can disprove a mechanism but only support one.

Problem 18 Food spoilage and temperature

1. $\ln \text{ratio} = (65000/8.314)(1/277.15 - 1/298.15) = 7818 \times 2.541 \times 10^{-4} = 1.987$; ratio = **7.3**.

2. Time = $4.0/7.3 = \mathbf{0.55 \text{ days}}$ (about 13 hours).

Problem 19 Matching a catalysed rate

1. Factor = $e^{(40000/(8.314 \times 300))} = e^{(16.04)} = \mathbf{9.2 \times 10^6}$.

2. Equal k needs equal E_a/T : $100/T = 60/300$, so $T = \mathbf{500 \text{ K}}$ (227 °C).

3. A catalyst works at low temperature, saving energy and avoiding decomposition of products, while heating by 200 K costs energy.

Problem 20 Surface catalysis and zero order

1. At high pressure all active sites on the gold are occupied, so the surface works at maximum capacity; extra gas does not raise the rate.
2. The rate rises linearly at low $[\text{N}_2\text{O}]$ then **levels off to a horizontal line**.
3. $t = [\text{N}_2\text{O}]_0/k = 0.012/(3.0 \times 10^{-5}) = \mathbf{4.0 \times 10^2 \text{ s}}$.
4. As the gas is used up, the pressure falls to the low region where sites are no longer saturated, and the rate begins to depend on $[\text{N}_2\text{O}]$.