AP CHEMISTRY
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⚡ Elementary Reactions & Mechanisms

AP Chemistry Unit 5, Topics 5.7 & 5.8

① Topic 5.7: Elementary Reactions

Most reactions don't happen in ONE simple step! They occur through a series of **elementary reactions** - the fundamental building blocks of chemical kinetics. ☐

☐ Elementary Reaction Definition

An **elementary reaction** (or elementary step) is a reaction that occurs in a **single step** at the molecular level. It describes what ACTUALLY happens when molecules collide and react.

> ⚡ Key Property: For elementary reactions ONLY, the rate law can be written directly from the balanced equation!

⚠ CRITICAL DISTINCTION

✅ Elementary Reaction	❌ Overall Reaction
$NO_2 + CO \rightarrow NO + CO_2$	$2NO_2 + F_2 \rightarrow 2NO_2F$
• Occurs in ONE step	• Occurs through multiple steps
• Actual molecular event	• Net result of mechanism
• Rate = $k[NO_2][CO]$	• Rate ≠ $k[NO_2]^2[F_2]$
• Rate law matches stoichiometry!	• Must determine experimentally!

⚠

☐ COMMON AP CHEMISTRY MISTAKE!

You CANNOT write rate laws from balanced equations UNLESS you know the reaction is elementary!

For example: If given $2H_2 + 2NO \rightarrow N_2 + 2H_2O$, you CANNOT assume Rate = $k[H_2]^2[NO]^2$ unless told it's elementary. Most likely it occurs through a multi-step mechanism!
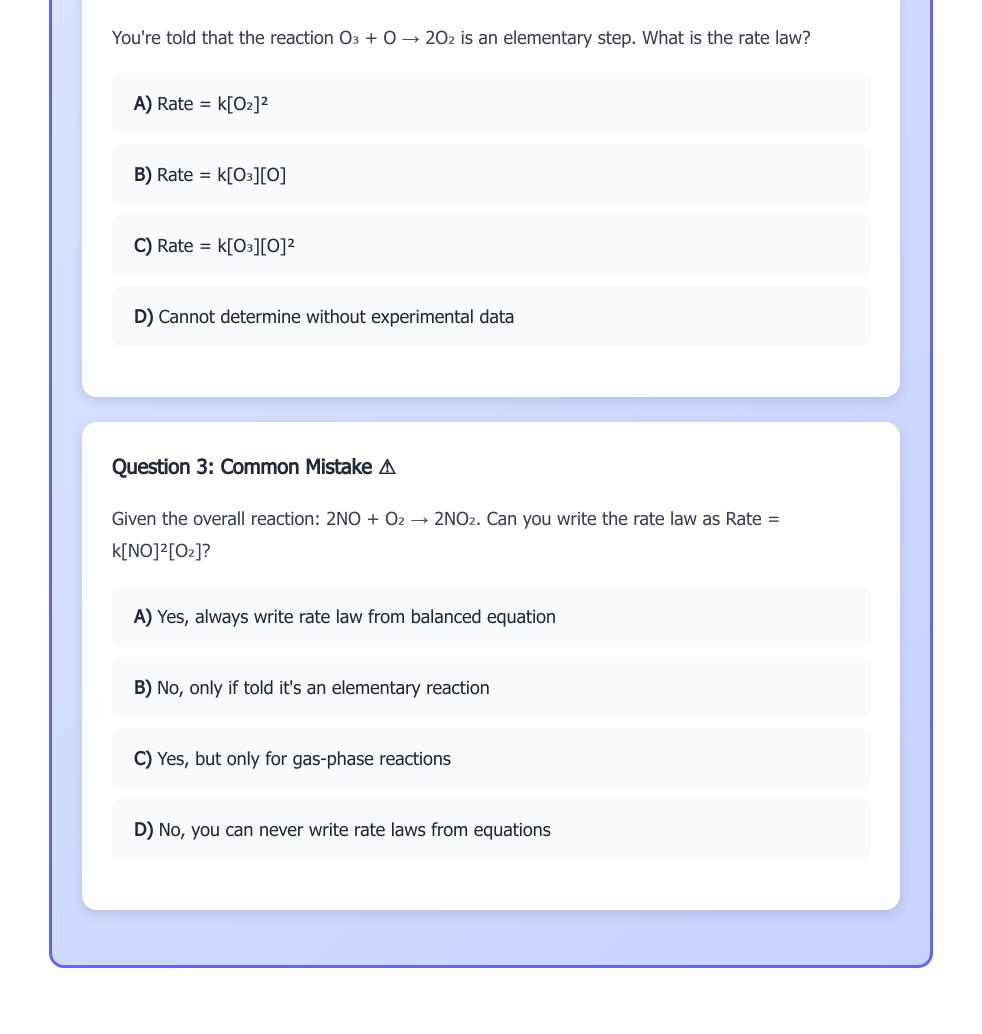
> ✓ Always check: Is this an elementary step or an overall reaction?

✅ Check Your Understanding: Elementary vs. Overall

Question 1: Definition Check ☐

What makes a reaction "elementary"?

A) It has simple stoichiometry

B) It occurs in a single step at the molecular level

C) It's a fast reaction

D) It's taught in elementary school

You're told that the reaction $O_3 + O \rightarrow 2O_2$ is an elementary step. What is the rate law?

A) Rate = $k[O_2]^2$

B) Rate = $k[O_3][O]$

C) Rate = $k[O_3][O]^2$

D) Cannot determine without experimental data

Question 3: Common Mistake ⚠

Given the overall reaction: $2NO + O_2 \rightarrow 2NO_2$. Can you write the rate law as Rate = $k[NO]^2[O_2]$?

A) Yes, always write rate law from balanced equation

B) No, only if told it's an elementary reaction

C) Yes, but only for gas-phase reactions

D) No, you can never write rate laws from equations

2 Molecularity: Counting Collision Partners

Molecularity tells us how many molecules (or atoms) must collide simultaneously for an elementary reaction to occur. ☐

☐ Molecularity Definition

Molecularity = the number of reactant particles (molecules, atoms, or ions) that participate in an elementary reaction.

Important: Molecularity ONLY applies to elementary reactions, not overall reactions!

Unimolecular

☐

ONE molecule reacts

```
A → Products
```

Example:

$O_3^* \rightarrow O_2 + O$

(excited ozone decomposes)

Rate = $k[O_3^*]$

Usually involves molecule rearrangement or decomposition

Bimolecular (Most Common!)

☐ + ☐

TWO molecules collide

```
A + B → Products
```

Example:

$NO_2 + CO \rightarrow NO + CO_2$

Rate = $k[NO_2][CO]$

$2NO_2 \rightarrow NO_3 + NO$

(two NO_2 molecules collide)

Rate = $k[NO_2]^2$

~90% of elementary reactions are bimolecular!

Termolecular (Rare!)

☐ + ☐ + ☐

THREE molecules collide
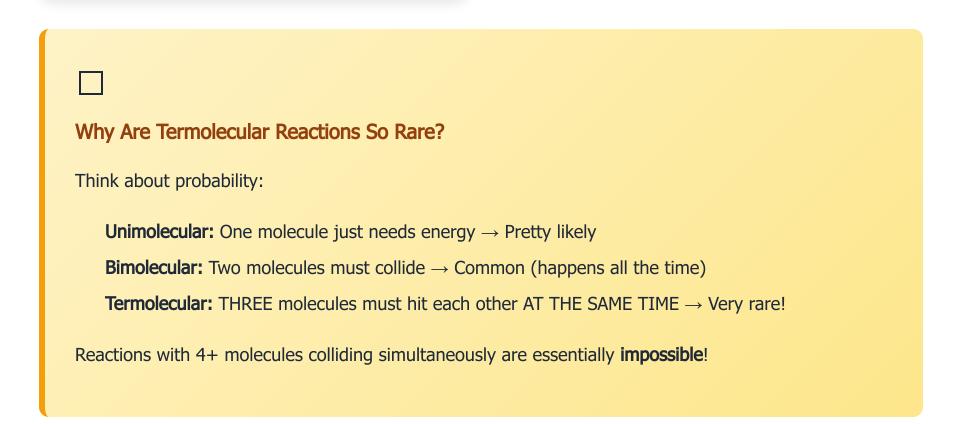
```
A + B + C → Products
```

Example:

$2NO + O_2 \rightarrow 2NO_2$

(if elementary)

Rate = $k[NO]^2[O_2]$

Accept   Decline

☐

Why Are Termolecular Reactions So Rare?

Think about probability:

Unimolecular: One molecule just needs energy → Pretty likely

Bimolecular: Two molecules must collide → Common (happens all the time)

Termolecular: THREE molecules must hit each other AT THE SAME TIME → Very rare!

Reactions with 4+ molecules colliding simultaneously are essentially **impossible**!

☐ Key Pattern: Rate Law from Molecularity

Molecularity	Elementary Reaction	Rate Law
Unimolecular	A → Products	**Rate = k[A]**
Bimolecular	A + B → Products	**Rate = k[A][B]**
Bimolecular	2A → Products	**Rate = k[A]²**
Termolecular	A + B + C → Products	**Rate = k[A][B][C]**
Termolecular	2A + B → Products	**Rate = k[A]²[B]**

Remember: The coefficients become exponents in the rate law!

✅ Check Your Understanding: Molecularity

Question 1: Identify Molecularity ☐

The elementary step is: $O + O_2 + M \rightarrow O_3 + M$. What is the molecularity?

A) Unimolecular

B) Bimolecular

C) Termolecular

D) Quadmolecular

Question 2: Rate Law from Elementary Step ✍

For the elementary reaction $2NO_2 \rightarrow NO_3 + NO$, what is the rate law?

A) Rate = k[NO₂]

B) Rate = k[NO₂]²

C) Rate = k[NO₃][NO]

D) Cannot determine

Question 3: Why So Rare? ☐

Why are termolecular elementary reactions rare?

A) They require high temperatures

B) Three molecules colliding simultaneously is very improbable

C) They're forbidden by thermodynamics

D) They have high activation energies

3 **Topic 5.8: Reaction Mechanisms**

Most chemical reactions occur through a **series of elementary steps** called a **reaction mechanism**. Understanding mechanisms reveals the TRUE story of how reactions happen! □

□ **Reaction Mechanism Definition**

A **reaction mechanism** is the sequence of elementary steps that describes the pathway from reactants to products at the molecular level.

Think of it as the "recipe" showing exactly how reactants transform into products, step-by-step!

□ **Example: Real Mechanism**

Overall Reaction: $2NO_2 + F_2 \rightarrow 2NO_2F$

This reaction doesn't happen in one collision! It occurs through these steps:

1

Step 1 (slow):

$$NO_2 + F_2 \rightarrow NO_2F + F$$

$Rate_1 = k_1[NO_2][F_2]$

SLOW STEP = Rate-Determining Step (RDS)

2

Step 2 (fast):

$$NO_2 + F \rightarrow NO_2F$$

$Rate_2 = k_2[NO_2][F]$

Fast - happens quickly once F is available

Add the steps together:

```
Step 1: NO₂ + F₂ → NO₂F + F
Step 2: NO₂ + F → NO₂F
```

Overall: $2NO_2 + F_2 \rightarrow 2NO_2F$

Notice: F appears and cancels out (it's an intermediate!)

✅ **Valid Mechanism Requirements**

For a mechanism to be valid, it MUST satisfy TWO criteria:

1□ **Elementary steps must add to overall reaction**

When you sum all elementary steps, intermediates cancel out and you're left with the balanced overall equation.

2□ **Mechanism must match experimental rate law**

The rate law predicted by the mechanism must agree with the experimentally determined rate law.

✅ **Check Your Understanding: Mechanisms Basics**

Question 1: Definition □

What is a reaction mechanism?

A) The balanced chemical equation

B) The sequence of elementary steps from reactants to products

C) The rate law for the reaction

Question 2: Validity Check ✅

What must be true for a proposed mechanism to be valid?

A) All steps must be fast

B) It must have at least three steps

C) Steps must add to overall reaction AND match experimental rate law

D) It must involve intermediates

Question 3: Multiple Mechanisms ☐

Can more than one mechanism be consistent with the same overall reaction?

A) No, each reaction has only one possible mechanism

B) Yes, multiple mechanisms can be proposed, but only the one matching the rate law is valid

C) No, once you write the balanced equation, the mechanism is determined

D) Yes, and they're all equally valid

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4 Intermediates & Rate-Determining Step

Two crucial concepts in mechanisms: **intermediates** (species formed and consumed) and the **rate-determining step** (the bottleneck). ☐

☐ Intermediates

An **intermediate** is a species that is produced in one step and consumed in a later step. It appears in the mechanism but NOT in the overall equation.

Key Properties of Intermediates:
- Formed in an early step
- Consumed in a later step
- Cancel out when steps are added
- NOT in overall equation
- Often unstable/reactive

⚠️
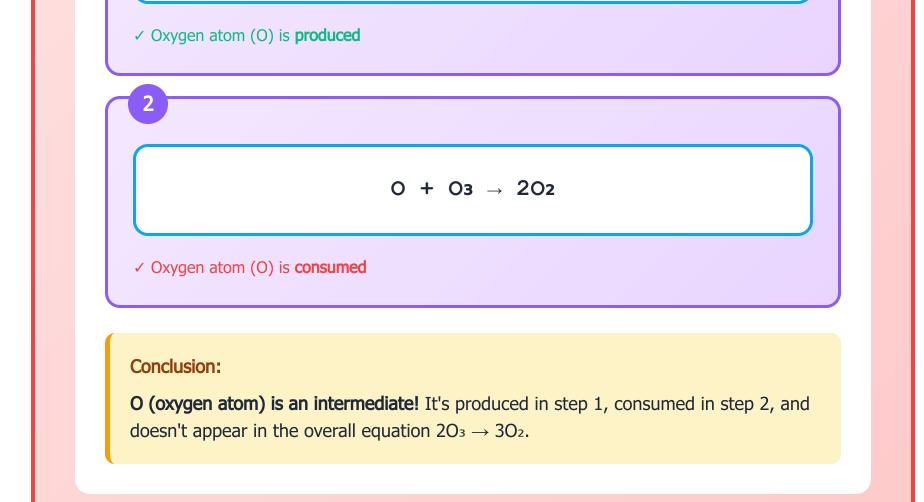
⚠ Don't Confuse: Intermediate vs. Catalyst

Property	Intermediate	Catalyst
Formed when?	During reaction	Present at start
Role	Produced then consumed	Consumed then regenerated
In overall equation?	NO	NO
Position in mechanism	Product side → Reactant side	Reactant side → Product side

☐ Example: Identifying Intermediates

Mechanism for: $2O_3 \rightarrow 3O_2$

1

✓ Oxygen atom (O) is **produced**

2

$$O + O_3 \rightarrow 2O_2$$

✓ Oxygen atom (O) is **consumed**

Conclusion:

O (oxygen atom) is an intermediate! It's produced in step 1, consumed in step 2, and doesn't appear in the overall equation $2O_3 \rightarrow 3O_2$.

☐ Rate-Determining Step (RDS)

The **rate-determining step** is the SLOWEST step in a mechanism. It acts as the "bottleneck" that controls the overall reaction rate.

☐ Critical Rule:

The overall rate law is determined by the rate-determining step (plus any fast pre-equilibrium steps before it).

☐

Analogy: Traffic Bottleneck ☐

Imagine a highway with three sections:

Section 1 (fast): 4 lanes, traffic flows at 70 mph
Section 2 (SLOW): Only 1 lane, traffic crawls at 20 mph ⚠
Section 3 (fast): 4 lanes, traffic flows at 70 mph

What determines how fast cars get through the entire highway?

The SLOW section! Even though sections 1 and 3 are fast, everyone must go through the bottleneck at section 2.

Same with reactions: The slowest step controls the overall rate!

☐ Example: RDS Determines Rate Law

Overall: $2NO_2 + F_2 \rightarrow 2NO_2F$

1

Step 1 (SLOW - RDS):

$$NO_2 + F_2 \rightarrow NO_2F + F$$

$Rate_1 = k_1[NO_2][F_2]$

THIS CONTROLS THE OVERALL RATE!

2

Step 2 (fast):

$$NO_2 + F \rightarrow NO_2F$$

$Rate_2 = k_2[NO_2][F]$ (but F is intermediate, so this doesn't affect overall rate law directly)

✓ **Overall Rate Law:**

$$Rate = k[NO_2][F_2]$$

The rate law comes directly from the slow step! Notice it's first-order in NO_2, NOT second-order (even though the overall equation has $2NO_2$).

Question 1: Identify Intermediate ☐

Step 1: A + B → C + D
Step 2: D + E → F
Overall: A + B + E → C + F

Which species is an intermediate?

> **A)** A

> **B)** C

> **C)** D

> **D)** F

Question 2: Rate-Determining Step ☐

What is true about the rate-determining step?

> **A)** It's always the first step

> **B)** It's the slowest step and controls the overall rate

> **C)** It's the step with the most molecules

> **D)** It must involve an intermediate

Question 3: Intermediate vs. Catalyst 🆚

How can you distinguish an intermediate from a catalyst in a mechanism?

> **A)** Intermediates are consumed first then produced; catalysts are produced first then consumed

> **B)** Intermediates are produced first then consumed; catalysts are consumed first then regenerated

> **C)** They're the same thing

> **D)** Intermediates appear in the overall equation; catalysts don't

5 Deriving Rate Laws from Mechanisms

Here's where everything comes together! We'll learn how to predict the rate law from a proposed mechanism. This is a KEY AP Chemistry skill! ☐

☐ Step-by-Step Process

Identify the rate-determining step (RDS) - usually labeled "slow"

Write the rate law for the RDS using its stoichiometry

Check for intermediates in the rate law

If intermediate present: Use fast equilibrium steps before RDS to substitute

Simplify to express rate law in terms of reactants only

☐ Example 1: Simple Case (No Intermediates in RDS)

Overall: $2NO_2 + F_2 \rightarrow 2NO_2F$

1

Step 1 (SLOW - RDS):

Rate-determining!

2

Step 2 (fast):

$$NO_2 + F \rightarrow NO_2F$$

Solution:

Step 1: RDS is step 1 (slow)

Step 2: Rate law from RDS stoichiometry: Rate = $k_1[NO_2][F_2]$

Step 3: Check for intermediates: NO_2 and F_2 are both reactants ✓

Step 4: No intermediates present!

Step 5: Done!

$$\text{Rate} = k[NO_2][F_2]$$

(where $k = k_1$)

☐ Example 2: With Fast Pre-Equilibrium

Overall: $2NO + O_2 \rightarrow 2NO_2$

1

Step 1 (fast equilibrium):

$$2NO \rightleftharpoons N_2O_2$$

Forward: $\text{Rate}_f = k_1[NO]^2$
Reverse: $\text{Rate}_r = k_{-1}[N_2O_2]$

2

Step 2 (SLOW - RDS):

$$N_2O_2 + O_2 \rightarrow 2NO_2$$

Rate-determining!

Rate = $k_2[N_2O_2][O_2]$

Problem: N_2O_2 is an intermediate!

We can't have intermediates in the final rate law. We need to express $[N_2O_2]$ in terms of reactants using the fast equilibrium!

Solution using Fast Equilibrium:

Step 1: At fast equilibrium: $\text{Rate}_{forward} = \text{Rate}_{reverse}$

$k_1[NO]^2 = k_{-1}[N_2O_2]$

Step 2: Solve for intermediate $[N_2O_2]$:

$[N_2O_2] = (k_1/k_{-1})[NO]^2$

Step 3: Substitute into RDS rate law:

Rate = $k_2[N_2O_2][O_2]$
Rate = $k_2 \times (k_1/k_{-1})[NO]^2 \times [O_2]$

Step 4: Combine constants:

Rate = $k[NO]^2[O_2]$

$$\text{Rate} = k[NO]^2[O_2]$$

where $k = k_1k_2/k_{-1}$

Use the pre-equilibrium approximation when:

A **fast step comes BEFORE** the slow (RDS) step

The slow step contains an **intermediate** from the fast step

The fast step is **reversible** (shown with ⇌)

Key: Assume the fast step reaches equilibrium quickly, so Rate$_{forward}$ = Rate$_{reverse}$

✅ Check Your Understanding: Rate Laws from Mechanisms

Question 1: Simple RDS ☐

Step 1 (fast): A + B ⇌ C
Step 2 (slow): C + D → E

The rate-determining step is:

A) Step 1

B) Step 2

C) Both steps

D) Neither step

Question 2: Rate Law with Intermediate ☐

Step 1 (slow): X + Y → Z
Step 2 (fast): Z + W → Products

What is the rate law?

A) Rate = k[X][Y][W]

B) Rate = k[Z][W]

C) Rate = k[X][Y]

D) Rate = k[X][Y] + k[Z][W]

Question 3: Pre-Equilibrium Application ☐

Step 1 (fast): 2A ⇌ B (K$_{eq}$ = [B]/[A]^2)
Step 2 (slow): B + C → D

If the slow step has Rate = k$_2$[B][C], and we need to eliminate intermediate B, what is the final rate law?

A) Rate = k[A][C]

B) Rate = k[A]^2[C]

C) Rate = k[B][C]

D) Rate = k[A][C]^2

☐ Final Mastery Quiz: Topics 5.7 & 5.8

Test your complete understanding of elementary reactions and mechanisms!

Question 1: Elementary vs. Overall ☐

The reaction H$_2$ + I$_2$ → 2HI is found experimentally to have Rate = k[H$_2$][I$_2$]. This means:

A) The reaction must be elementary

C) The reaction must be multi-step

D) The reaction is zero-order

Question 2: Molecularity ☐

An elementary step has the equation: $2NO + Cl_2 \rightarrow 2NOCl$. The molecularity is:

A) Unimolecular

B) Bimolecular

C) Termolecular

D) Cannot determine

Question 3: Rate Law from Elementary Step ✎

For the elementary reaction $O + O_3 \rightarrow 2O_2$, the rate law is:

A) Rate = $k[O_2]^2$

B) Rate = $k[O][O_3]$

C) Rate = $k[O]^2[O_3]$

D) Cannot be determined from the equation

Question 4: Identify Intermediate ☐

Given mechanism:
Step 1: $A + B \rightarrow C + D$
Step 2: $C + E \rightarrow F$
Overall: $A + B + E \rightarrow D + F$

Which is an intermediate?

A) A

B) B

C) C

D) F

Question 5: Rate-Determining Step ☐

In a multi-step mechanism, the rate-determining step:

A) Must be the first step

B) Is the slowest step and controls the overall rate

C) Must involve a catalyst

D) Is always bimolecular

Question 6: Mechanism Validity ✓

A proposed mechanism is valid if:

A) It has at least two steps

B) All steps are elementary

C) Steps add to overall reaction AND predicted rate law matches experimental

D) It involves intermediates

Question 7: Simple Rate Law Derivation ☐

Mechanism:
Step 1 (slow): $X_2 \rightarrow 2X$
Step 2 (fast): $X + Y \rightarrow XY$

The rate law for the overall reaction is:

A) Rate = k[X][Y]

B) Rate = k[X$_2$]

C) Rate = k[X$_2$][Y]

D) Rate = k[X]²[Y]

Question 8: Pre-Equilibrium Concept ☐

Fast pre-equilibrium approximation is used when:

A) All steps are fast

B) A fast reversible step comes before the slow step, and slow step contains intermediate

C) The slow step comes first

D) There are no intermediates

Question 9: Intermediate vs. Catalyst 🆚

The key difference between an intermediate and a catalyst is:

A) Intermediates are produced then consumed; catalysts are consumed then regenerated

B) They're the same thing

C) Only catalysts appear in the rate law

D) Intermediates appear in the overall equation; catalysts don't

Question 10: Complex Mechanism Challenge ☐

Mechanism:
Step 1 (fast): $2NO \rightleftharpoons N_2O_2$ (K = [N$_2$O$_2$]/[NO]²)
Step 2 (slow): $N_2O_2 + H_2 \rightarrow N_2O + H_2O$
Step 3 (fast): $N_2O + H_2 \rightarrow N_2 + H_2O$

The rate law for the overall reaction is:

A) Rate = k[NO]²[H$_2$]

B) Rate = k[N$_2$O$_2$][H$_2$]

C) Rate = k[NO][H$_2$]²

D) Rate = k[NO]²[H$_2$]²

☐ Outstanding Work!

You've mastered elementary reactions and reaction mechanisms! You can now identify molecularity, recognize intermediates, find rate-determining steps, and derive rate laws from multi-step mechanisms. These are crucial skills for AP Chemistry success! ☐