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Topic 5.4: Elementary Reactions

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UNIT 5 · KINETICS

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A Single Molecular Event

An elementary reaction is a reaction that takes place in one single step, exactly as its equation is written.

One molecular event occurs: reactant particles collide, or a single particle breaks apart, and bonds rearrange in that one event, with no hidden sub-steps. Its coefficients count the actual particles involved, not merely atoms that must balance.

The step must balance exactly as written, since its particles are the very ones rearranged into the products.

Most reactions are not elementary. Their overall equations are the sum of two or more elementary steps, a sequence called a mechanism, so it shows only the net change.

Molecularity: Counting the Reactant Particles

Molecularity is the number of reactant particles taking part in a single elementary step, counted from the step's equation, coefficients included. It is always a whole number: 1, 2 or 3.

A unimolecular step has one reactant particle, A → products, which breaks apart or rearranges on its own: $O_3 \rightarrow O_2 + O$ and $Br_2 \rightarrow 2Br$ are unimolecular.

A bimolecular step has two reactant particles colliding, either different particles, A + B → products, as in $NO + O_3 \rightarrow NO_2 + O_2$, or identical particles, 2A → products, as in $2NO \rightarrow N_2O_2$.

A termolecular step has three reactant particles in one event: A + B + C, 2A + B, or 3A, as $2NO + O_2 \rightarrow 2NO_2$ would be if it occurred in one step.

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Only reactant particles count, not products and not the atoms inside a particle: $O_3 \rightarrow O_2 + O$ is unimolecular even though two products form.

Molecularity belongs to elementary steps only: an overall reaction is not one event, so no molecularity can be assigned to it.

Why Termolecular Steps Are Extremely Rare

A step requires its particles to arrive at the same place at the same moment, with enough energy and the correct orientation.

Two-particle collisions happen constantly, but a third particle arriving at the same instant, equally energetic and correctly oriented, is so improbable that termolecular steps almost never occur.

A change needing three particles therefore almost always happens as a sequence of unimolecular and bimolecular steps.

So $2H_2 + O_2 \rightarrow 2H_2O$, though balanced, cannot be a single elementary step, and steps needing four or more particles are not elementary at all.

The Rate Law of an Elementary Step

For an elementary step, and only for an elementary step, the rate law is written directly from its equation: the order in each reactant equals that reactant's coefficient.

A unimolecular step A → products has rate = k[A], first order, with k in s^{-1}.

A bimolecular step has rate = k[A][B] for A + B → products, or rate = $k[A]^2$ for 2A → products. Both are second order overall, with k in $M^{-1}\ s^{-1}$.

A termolecular step 2A + B → products has rate = $k[A]^2[B]$, third order overall, with k in $M^{-2}\ s^{-1}$.

Products never appear in a step's rate law: only reactant concentrations control how often the particles can meet or break apart.

For any elementary step, the molecularity and the overall order of its rate law are numerically equal, because both count the same reactant particles.

Overall Reactions: Why the Shortcut Stops

An overall equation reports the net change after all its steps are added together. Its coefficients balance atoms for that net change; they say nothing about any single collision.

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So an overall rate law cannot be read from its equation; it must be determined by experiment, using initial rate measurements of the kind used in Topic 5.2.

An overall equation such as 2A + B → products might turn out to be first order in A and zero order in B; no inspection of the equation can reveal that.

The signal that coefficients may be used as orders is the word elementary, or one line of a mechanism shown as a step. Without that signal, the shortcut is forbidden.

Adding steps together also identifies two special species: an intermediate, formed in one step and consumed in a later step, and a catalyst, consumed in an early step and regenerated in a later step.

Both cancel on addition, so neither appears in the overall equation.

Worked Examples

Example 1: Rate law and k for a bimolecular step. The step $NO_2 + CO \rightarrow NO + CO_2$ is elementary and bimolecular (two reactant particles), so its rate law is rate = $k[NO_2][CO]$. The measured rate is 6.0×10^{-3} M/s when $[NO_2] = 0.20$ M and [CO] = 0.30 M, so $k = 6.0 \times 10^{-3} \div (0.20 \times 0.30) = 6.0 \times 10^{-3} \div 0.060 = 0.10\ M^{-1}\ s^{-1}$. At $[NO_2] = 0.40$ M and [CO] = 0.30 M, rate = $0.10 \times 0.40 \times 0.30 = 0.012$ M/s.

Example 2: Two identical particles. The step $2NO \rightarrow N_2O_2$ is elementary: two NO particles must collide, so it is bimolecular with rate = $k[NO]^2$, even though only one reactant species appears. With $k = 0.50\ M^{-1}\ s^{-1}$ and [NO] = 0.10 M, rate = $0.50 \times (0.10)^2 = 5.0 \times 10^{-3}$ M/s. Doubling [NO] to 0.20 M gives rate = $0.50 \times (0.20)^2 = 0.020$ M/s, four times larger, because [NO] enters the law twice.

Example 3: Adding two steps. Step 1: $NO_2 + NO_2 \rightarrow NO_3 + NO$ (bimolecular). Step 2: $NO_3 + CO \rightarrow NO_2 + CO_2$ (bimolecular). Adding the steps and cancelling species on both sides removes NO_3 and one NO_2, leaving $NO_2 + CO \rightarrow NO + CO_2$ overall. NO_3 is formed in step 1 and consumed in step 2, so NO_3 is an intermediate. Each step keeps its own rate law from its own equation; the overall equation, a sum of steps, would need its rate law measured.

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Example 4: Testing a proposed single step against a rate law. An overall reaction has the experimental rate law rate = $k[NO]^2[O_2]$. The step $NO + O_2 \rightarrow NO_2 + O$ would give rate = $k[NO][O_2]$, and $2NO \rightarrow N_2O_2$ would give rate = $k[NO]^2$; neither matches. Only $2NO + O_2 \rightarrow 2NO_2$ gives rate = $k[NO]^2[O_2]$. That step is termolecular, overall order 3, so k carries units $M^{-2}\ s^{-1}$; with k = 2.0 $M^{-2}\ s^{-1}$, [NO] = 0.10 M and $[O_2]$ = 0.20 M, the rate would be $2.0 \times (0.10)^2 \times 0.20 = 4.0 \times 10^{-3}$ M/s. Matching is necessary, not proof: termolecular steps are so rare that a sequence of simpler steps giving the same law is more likely.

Traps That Cost Marks in Topic 5.4

Reading orders from an overall equation. Coefficients act as orders only for an elementary step. For an overall reaction the orders come from experiment, whatever the coefficients are.

Counting products or atoms as molecularity. Molecularity counts reactant particles only. $O_3 \rightarrow O_2 + O$ is unimolecular: one particle reacts, even though two products form.

Calling 2A unimolecular. One reactant species is not one particle: two A particles collide, so the step is bimolecular with rate = $k[A]^2$.

Assigning a molecularity to an overall reaction. Overall reactions have no molecularity: only a step describes one collision or one particle breaking apart.

Assuming a balanced three-reactant equation is one step. A termolecular collision is vanishingly unlikely, so $2H_2 + O_2 \rightarrow 2H_2O$ must be the sum of several steps, never one elementary event.

Putting products into a step's rate law, or mixing up intermediates and catalysts. A step's rate law contains reactants only, never products. An intermediate is made first, used later; a catalyst is used first, remade later; both cancel from the overall equation.

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Key Relationships to Remember

- Elementary reaction: a single molecular event that occurs exactly as its equation is written, with no hidden sub-steps
- Molecularity: the number of reactant particles in an elementary step: 1 is unimolecular, 2 is bimolecular, 3 is termolecular
- Rate law of an elementary step: the order in each reactant equals its coefficient in the step's equation
- Bimolecular rate laws: rate = $k[A][B]$ for A + B, and rate = $k[A]^2$ for 2A; termolecular: rate = $k[A]^2[B]$ for 2A + B
- Molecularity of a step equals the overall order of that step's rate law
- Units of k follow the step's overall order: s^{-1} for first order, $M^{-1}\ s^{-1}$ for second order, $M^{-2}\ s^{-1}$ for third order
- Overall reactions: rate laws are determined by experiment only, and molecularity does not apply
- Intermediate: formed in one step, consumed in a later step; catalyst: consumed early, regenerated later; both cancel from the overall equation

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