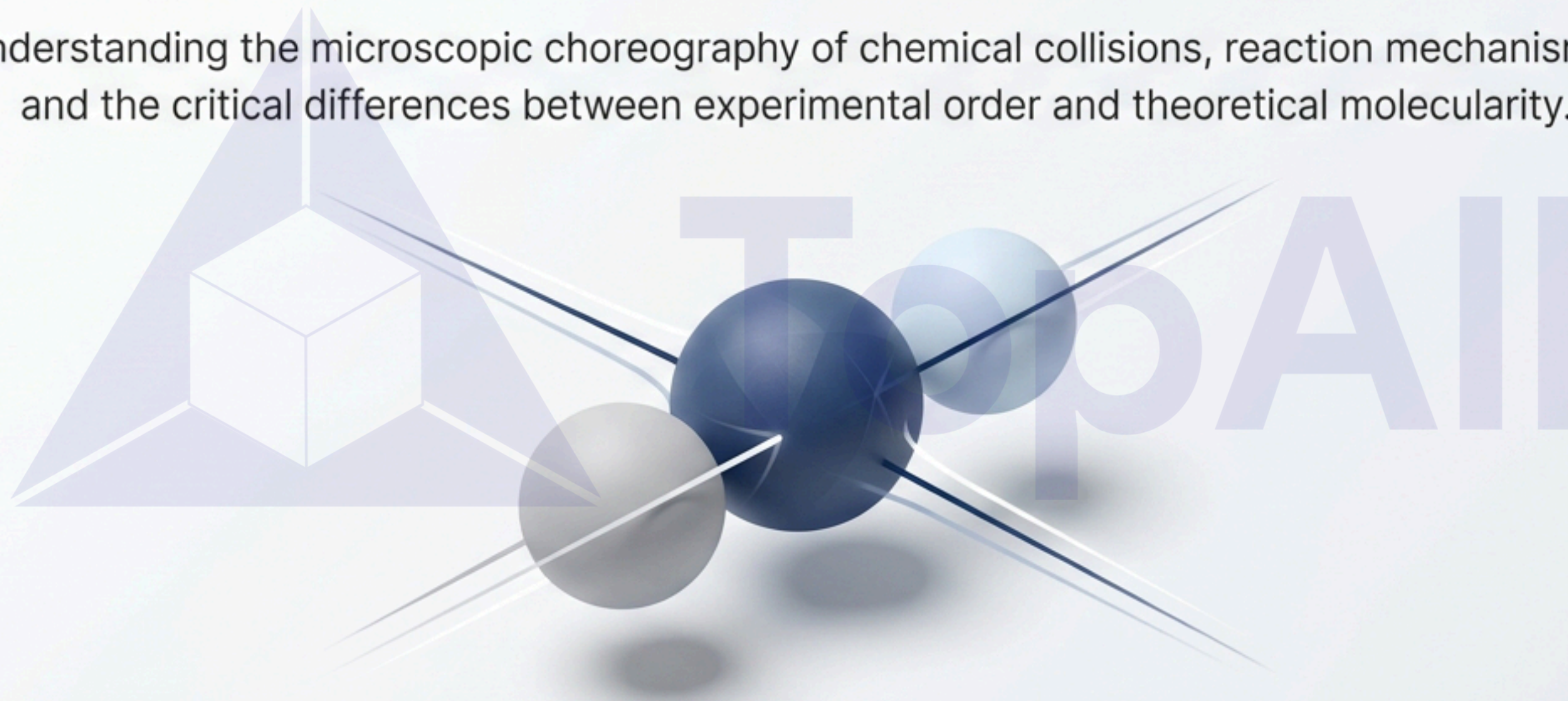


3.2.4 Molecularity of a Reaction

Understanding the microscopic choreography of chemical collisions, reaction mechanisms, and the critical differences between experimental order and theoretical molecularity.



[Exam-Smart Summary]

[7-Part Sequence]

[Concept & Comparison]

What Molecularity Means

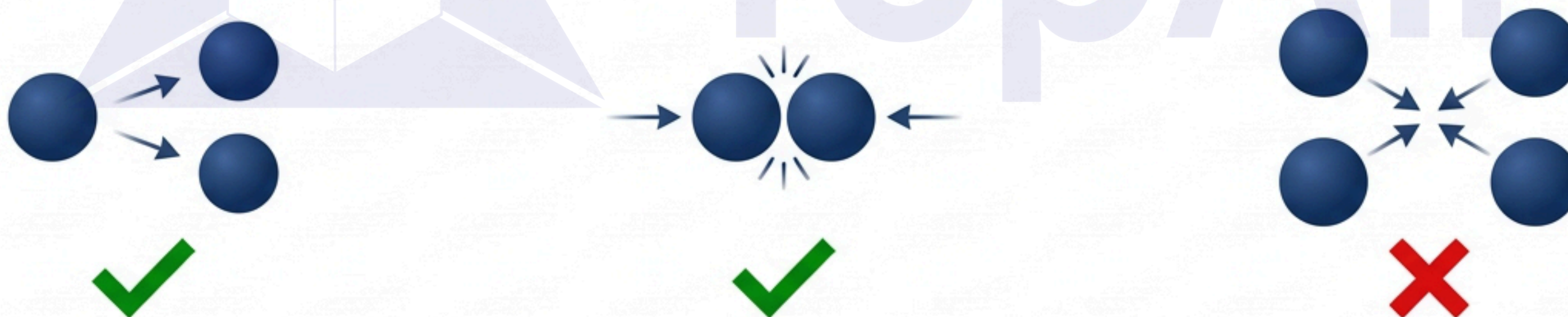
The molecularity of a reaction is defined as the exact number of reacting species taking part in an elementary reaction, which must collide simultaneously in order to bring about a chemical change.

[Atoms]

[Ions]

[Molecules]

The Simultaneous Collision Rule: A microscopic view of physical reality



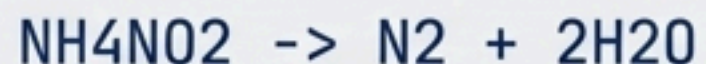
Molecularity is a purely **theoretical concept** derived from proposing a reaction mechanism, unlike reaction order which is strictly experimental.

Unimolecular, Bimolecular, and Termolecular Reactions

Unimolecular (Molecularity = 1)

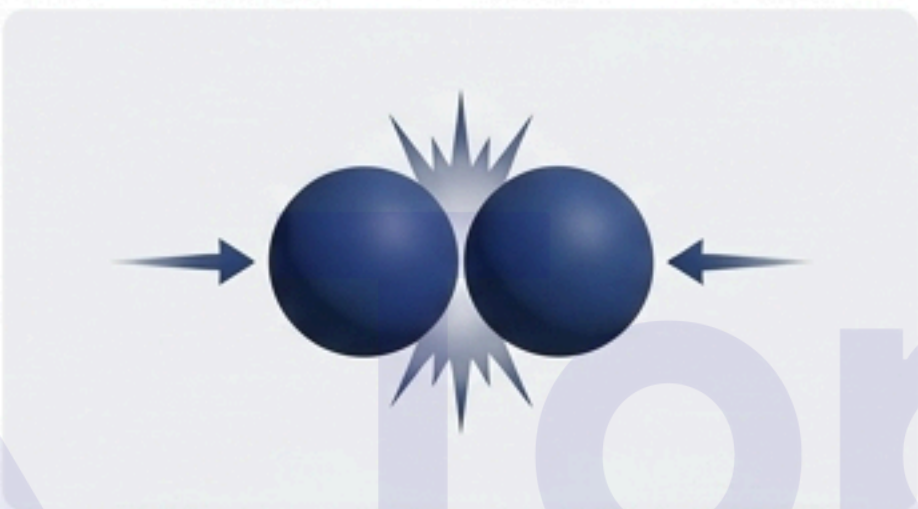


One reacting species is involved. It typically undergoes decomposition or rearrangement.

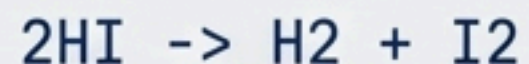


Decomposition of ammonium nitrite

Bimolecular (Molecularity = 2)



Involves the simultaneous collision between two reacting species. This is the most common type of elementary reaction.

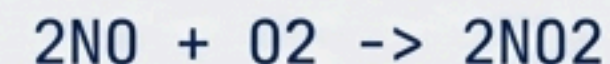


Dissociation of hydrogen iodide

Termolecular (Molecularity = 3)



Involves the simultaneous collision between three reacting species. These are rare and proceed slowly.



Oxidation of nitric oxide



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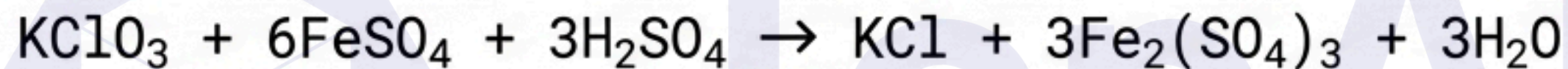
Why Molecularity Applies Only to Elementary Reactions

Elementary Reactions

Complete in a single step. Molecularity describes the exact physical collision taking place.

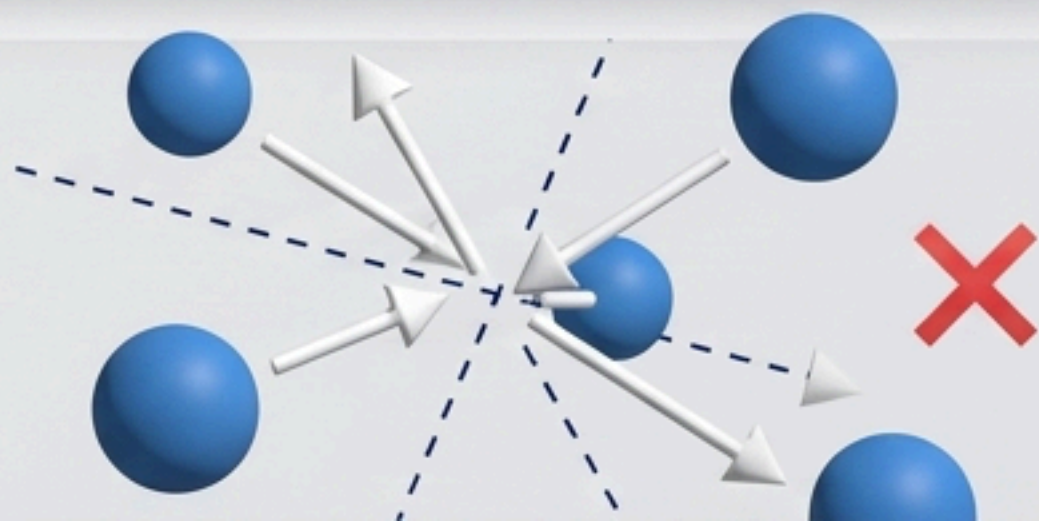
Complex Reactions

Proceed in a sequence of multiple steps (mechanism). Overall molecularity is meaningless.



[Apparent Order: 10th?] → [Actual Order: 2nd]

This balanced equation implies 10 molecules reacting at once! But probability dictates this is impossible. It must take place in several smaller, bimolecular steps.



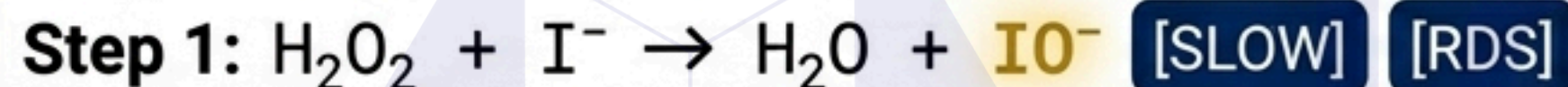
The probability that more than three molecules can collide and react simultaneously with the proper orientation and energy is virtually zero. Molecularity > 3 is not observed.

Order vs Molecularity

	Order (Macro / Lab)	Molecularity (Micro / Theory)
Nature of Concept	Experimental Derived entirely from lab data (rate law).	Theoretical Derived from the proposed reaction mechanism.
Possible Values	Can be zero, a fraction, or an integer (1, 2, 3...).	Must be a positive integer (1, 2, 3). Cannot be zero or a fraction.
Applicability	Applies to both elementary and complex overall reactions.	Applies only to elementary steps (meaningless for complex overall reactions).
Derivation	Sum of powers of concentration terms in the rate law.	Number of colliding species in the balanced elementary step.

Rate Determining Step and Intermediate

Decomposition of H_2O_2 (catalyzed by I^- in alkaline medium)



The Rate Determining Step (RDS)

The overall rate is controlled by the slowest elementary step—just like a relay race team's time depends on its slowest runner.



The Intermediate (IO^-)

Formed during the course of the reaction but consumed before the end. It never appears in the overall balanced equation.

Final Recap: Two Perspectives on Reaction Speed

The Macroscopic View



Experimental Order

What we observe in the lab. It tells us how sensitive the reaction rate is to changes in reactant concentrations for the entire process.

$$\text{Rate} = k[A]^x [B]^y \quad (\text{Order} = x + y)$$

The Microscopic View



Mechanistic Molecularity

What we propose happens at the atomic level. It tells us exactly how many distinct particles must physically collide in a single elementary step.

Strictly limited to 1, 2, or 3 species.

Key-Takeaway: Rule of Thumb: For simple elementary reactions, **Order and Molecularity are identical**. For complex reactions, the overall experimental Order reflects the **Molecularity of the slowest step**!



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