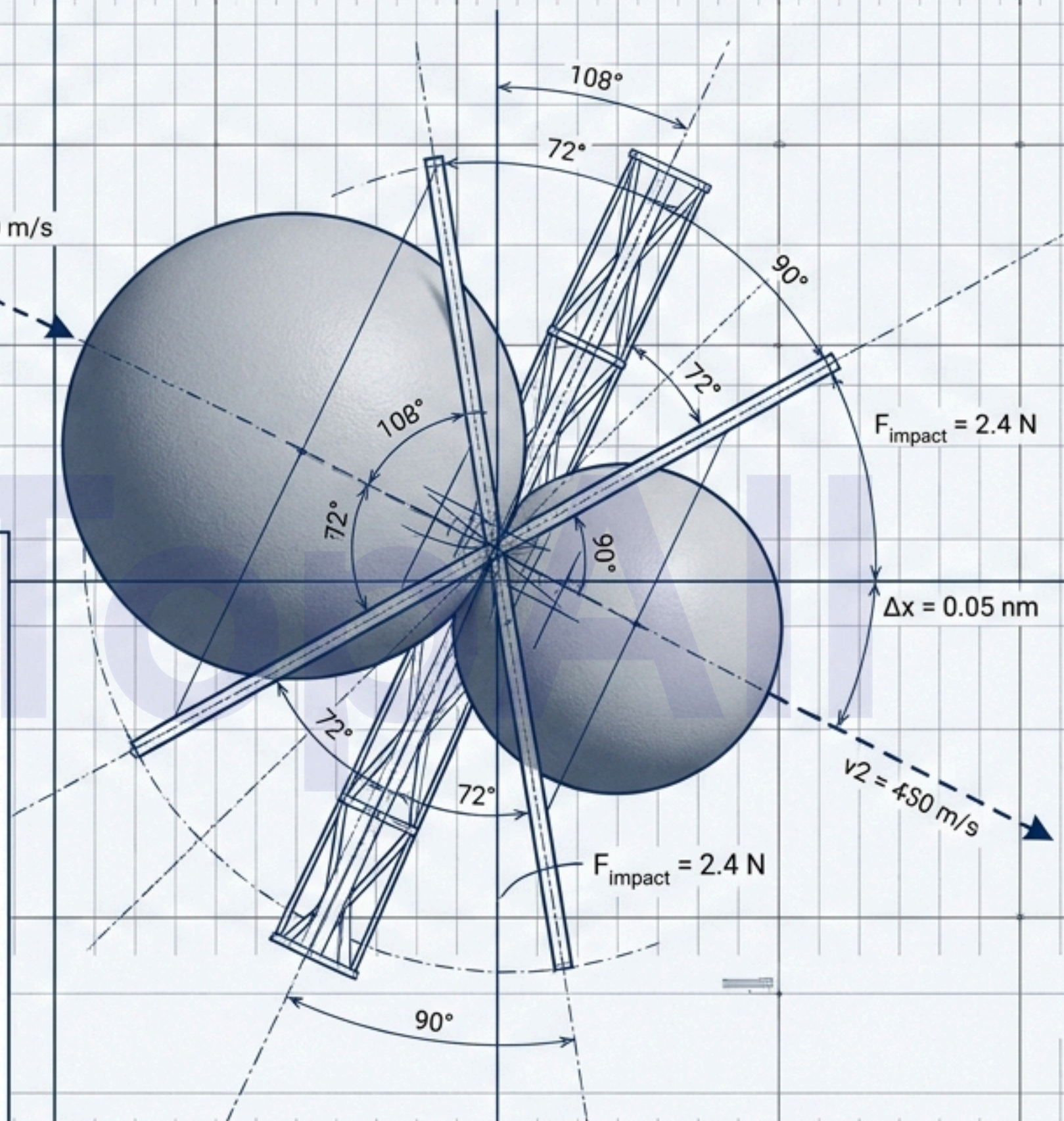


Concept 3.2.4 • Chemical Kinetics

Molecularity of a Reaction

The physical reality of molecular collisions.



The Blueprint Legend

Molecularity

Number of reacting species (atoms/ions/molecules) colliding simultaneously in an elementary step.

Elementary Reaction

A reaction taking place in exactly one step.

Complex Reaction

A sequence of elementary reactions (a mechanism) giving the final products.

Rate-Determining Step

The slowest step in a sequence; controls the overall rate.

Intermediate

A species formed during the reaction but absent in the final balanced equation.

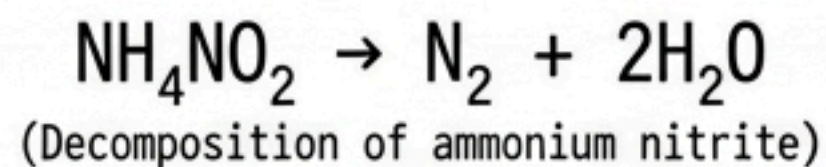
The Molecularity Gallery

1



Unimolecular

One reacting species.

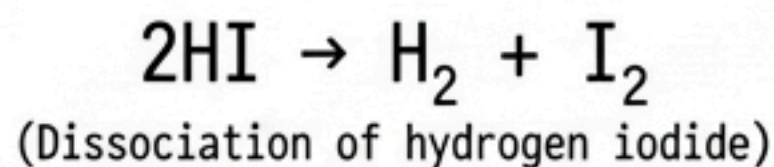


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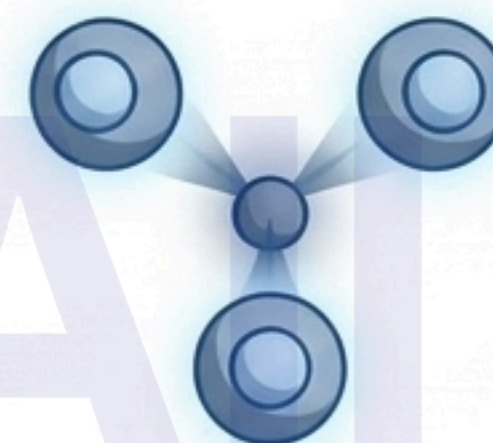


Bimolecular

Two species colliding.

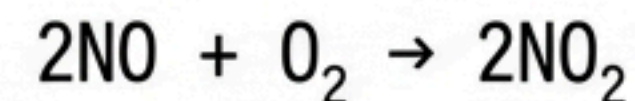


3



Trimolecular

Three species colliding.



Why is >3 rare? The probability of more than three molecules colliding simultaneously with proper orientation is practically zero.



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$$E=mc^2$$



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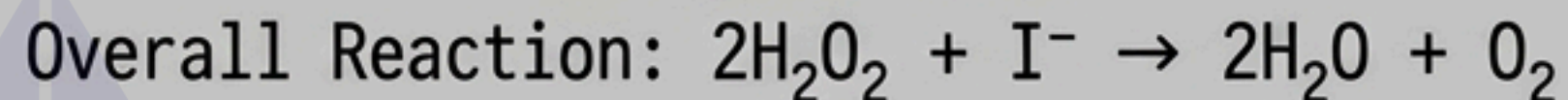
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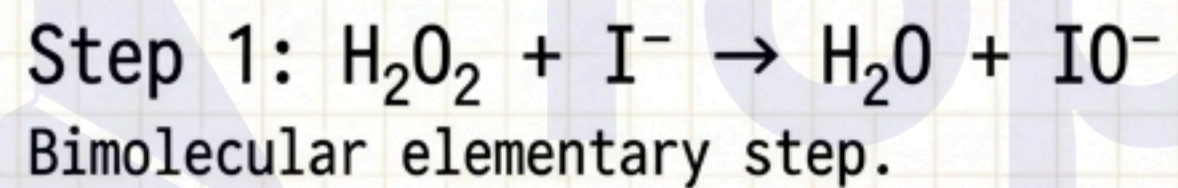


Zooming Under the Hood: Complex Mechanisms

The Illusion



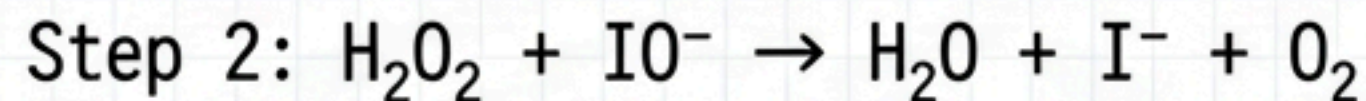
The Bottleneck



[slow — rate-determining]

The species IO^- is an **Intermediate**—it is created in Step 1 and consumed in Step 2.

The Follow-through



[fast]

The Mathematical Consequence

The rate law ignores the overall equation. It only “sees” the rate-determining step.

Formula Bank



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

Derived entirely from the slow step.

This reaction is first order with respect to both H_2O_2 and I^- . Overall order = 2.

The Diagnostic Matrix: Order vs. Molecularity

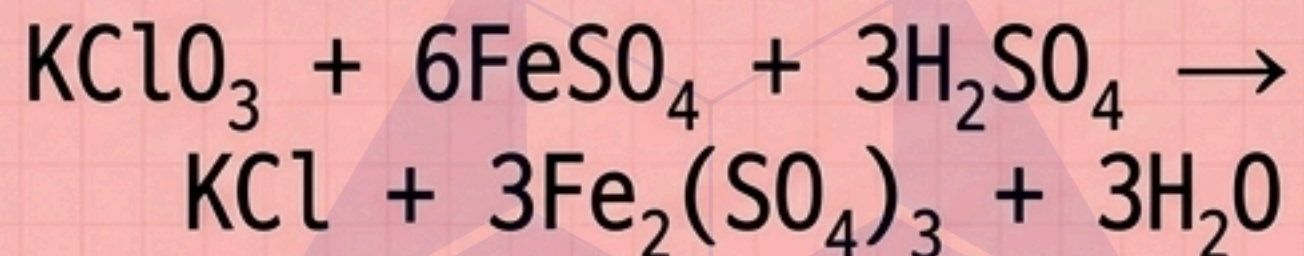
	Order	Molecularity
Origin	Experimental quantity.	Theoretical concept.
Values	Can be 0, fractions, or whole numbers.	Whole numbers 1 to 3 only (never zero).
Applicability	Applies to both elementary and complex reactions.	Applies ONLY to elementary reactions.
Complex Reactions	Determined by the slowest step.	Has NO MEANING for the overall complex reaction.



JEE / NEET Trap Alert

The Trap: Assuming the Rate Law follows the overall balanced equation.

The 10th-Order Illusion



Student Mistake: “1 + 6 + 3 = 10 reacting molecules. It must be a 10th order reaction with a molecularity of 10!”

The Reality

Reactions involving >3 molecules must take place in multiple steps.

This specific reaction is actually **second order**, dictated entirely by a hidden, slow elementary step.

Molecularity of 10 is physically impossible.

This reaction is actually second order due to a rate-determining step.

Practice Check

For a complex reaction, which of the following statements regarding molecularity is strictly accurate?

- ☐ A. It is determined by adding the stoichiometric coefficients of the overall balanced equation.
- ☐ B. It is synonymous with the overall experimental order of the reaction.
- ☐ C. It is equal to the molecularity of the fastest step in the mechanism.
- ☒ D. It has no meaning for the overall reaction, as it applies only to individual elementary steps.

Submit →

Correct Answer: D. Molecularity strictly describes simultaneous physical collisions in a *single* step. For complex (multi-step) reactions, overall molecularity does not exist.

The Blueprint: Key Takeaways



Molecularity is a physical reality:

It counts the exact number of species colliding simultaneously in a single step (max 3).



Complex = Multi-step:

Any reaction with >3 reactants is a complex reaction occurring in multiple elementary steps.



The Bottleneck rules all:

The slowest step (Rate-Determining Step) entirely dictates the overall rate of a complex reaction.



Experiment vs. Theory:

Order is measured in the lab (can be fractions/zero).
Molecularity is derived from the theoretical mechanism (1, 2, or 3 only).





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