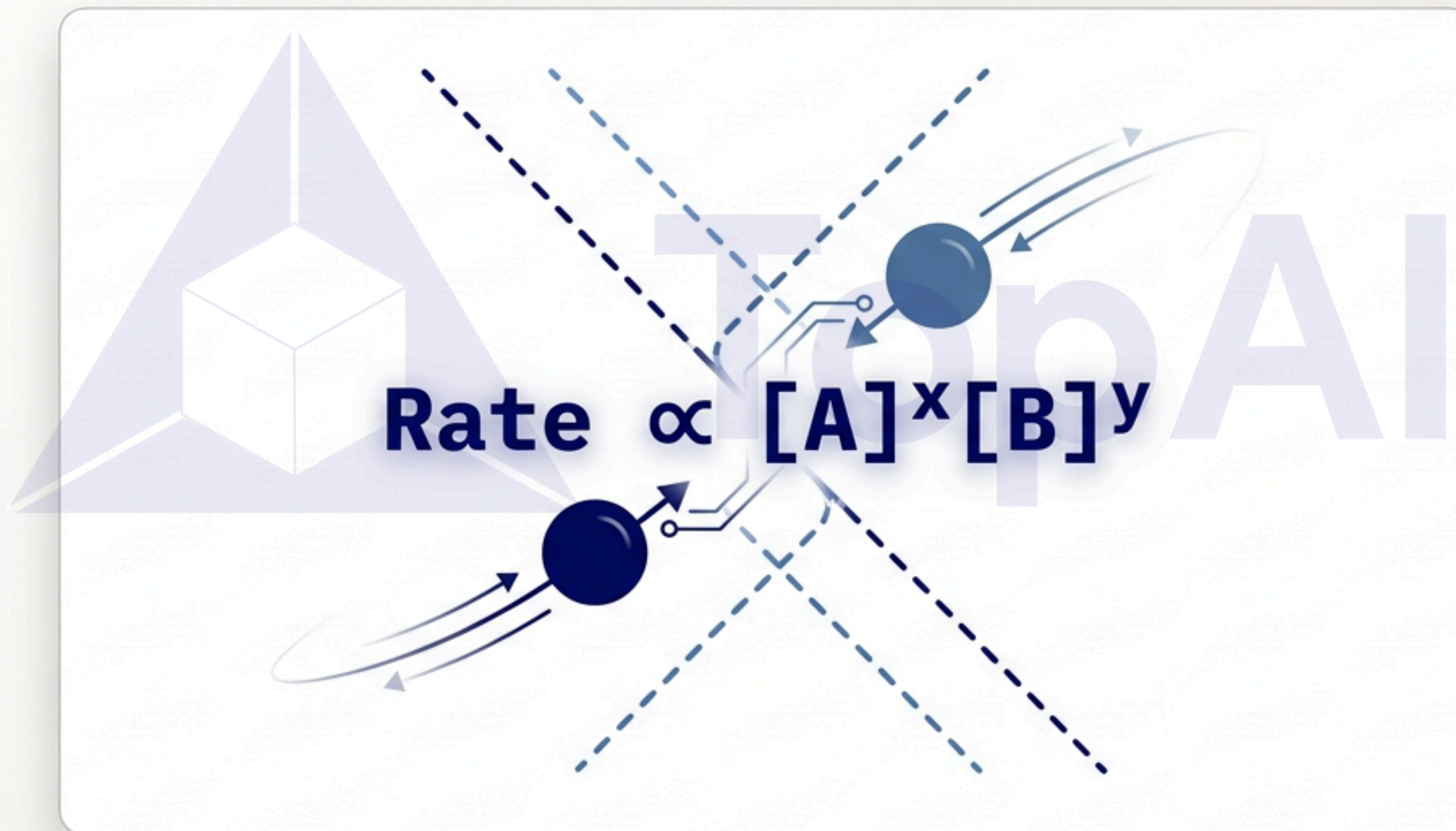


3.2.2 Rate Expression and Rate Constant



General Form of the Rate Law

For a general reaction $aA + bB \rightarrow cC + dD$, the rate law expresses the reaction rate in terms of molar concentrations.

Rate Constant
(Proportionality constant)

Exponents
(Reaction Order)



Molar Concentrations
(Reactants)

The Meaning of Exponents

Exponents indicate how sensitive the reaction rate is to a change in a specific reactant's concentration.

Individual Order



x is the order with respect to reactant A. y is the order with respect to reactant B.

Overall Order

$$n = x + y$$

The sum of the powers of the concentration of the reactants is the Overall Order of Reaction.

Recap Box: Reaction orders can be **0, 1, 2, 3**, or even a fraction. A zero-order reaction means the rate is completely independent of that reactant's concentration.



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The Differential Rate Equation

Instantaneous rate
proportional to concentrations

$$-d[R]/dt \propto [A]^x[B]^y$$

Insert Proportionality Constant (k)

$$-d[R]/dt = k[A]^x[B]^y$$

Replacing the proportionality sign with k creates the definitive **Differential Rate Equation**. It directly links the instantaneous rate of reactant disappearance to current concentrations.

Experimental Determination of Exponents



	[NO] (mol/L)	[O ₂] (mol/L)	Initial Rate (mol/L·s)	
1	0.30	0.30	0.096	
2	0.60	0.30	0.384	$2^x = 4 \rightarrow x = 2$
3	0.30	0.60	0.192	$2^y = 2 \rightarrow y = 1$

Diagram illustrating the experimental determination of exponents for the reaction $2\text{NO}(\text{g}) + \text{O}_2(\text{g}) \rightarrow 2\text{NO}_2(\text{g})$. The table shows three experiments with varying initial concentrations of NO and O₂, and the resulting initial rates. Arrows indicate the changes in concentration and rate between experiments to determine the reaction order.

- From Experiment 1 to Experiment 2: [NO] doubles (0.30 to 0.60), [O₂] remains constant (0.30), and the Initial Rate increases by a factor of 4 (0.096 to 0.384). This indicates a second-order dependence on [NO] ($2^x = 4 \rightarrow x = 2$).
- From Experiment 1 to Experiment 3: [NO] remains constant (0.30), [O₂] doubles (0.30 to 0.60), and the Initial Rate doubles (0.096 to 0.192). This indicates a first-order dependence on [O₂] ($2^y = 2 \rightarrow y = 1$).

$$\text{Rate} = k[\text{NO}]^2[\text{O}_2]^1$$

What the Rate Constant (k) Represents

Mathematical Proof

$$\text{Rate} = k[A]^x[B]^y$$

$$\text{Rate} = k[1]^x[1]^y$$

Substitute 1M standard concentrations


$$\text{Rate} = k$$

The **rate constant k** is numerically equal to the rate of reaction when the **concentration of all reactants is unity** (1 mol L⁻¹).

Theory vs. Kinetic Reality

The Balanced Equation



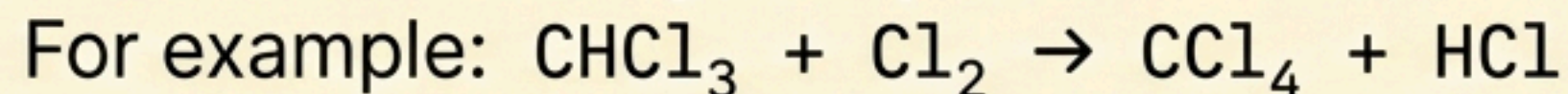
Stoichiometric coefficients (a, b) only dictate theoretical proportions, not the speed of the reaction.

The Experimental Rate Law

$$\text{Rate} = k[A]^x[B]^y$$

Exponents (x, y) represent kinetic reality and must be determined experimentally in the lab.

Theoretical stoichiometry rarely matches kinetic reality.



...but the actual experimental rate is proportional to $[\text{Cl}_2]^{1/2}$.



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