

16.6 Reaction Mechanisms

- Sequences of molecular level steps (called elementary reactions) that sum up to the overall reaction

- Elementary reactions (steps)** – describe individual molecular events (collisions)

Example: $2\text{O}_3(\text{g}) \rightarrow 3\text{O}_2(\text{g})$

→ Proposed 2 step mechanism:

- $\text{O}_3 \rightarrow \text{O}_2 + \text{O}$
- $\text{O}_3 + \text{O} \rightarrow 2\text{O}_2$ $\left| \begin{array}{l} \oplus \\ \Rightarrow \end{array} \right. 2\text{O}_3 \rightarrow 3\text{O}_2$ (overall)

- **Reaction intermediate** – formed in one step and used up in another (does not appear in the overall reaction) → O is an intermediate

→ Reaction intermediates are usually unstable species, but some are stable enough to be isolated

- Molecularity** – the number of reactant species involved in an elementary reaction (the number of colliding species)

Example: $2\text{O}_3(\text{g}) \rightarrow 3\text{O}_2(\text{g})$

$\text{O}_3 \rightarrow \text{O}_2 + \text{O}$ (1 reactant molecule → **Unimolecular**)

$\text{O}_3 + \text{O} \rightarrow 2\text{O}_2$ (2 reactant species → **Bimolecular**)

→ **Termolecular** reactions are very rare – very low probability for a three-particle collision with enough energy and proper orientation

→ Higher order molecularities are not known

- Rate laws for elementary reactions** – can be derived from the reaction stoichiometry

- The reaction orders are equal to the stoichiometric coefficients of the reactants



$$\text{Rate} = k[\text{A}]^i[\text{B}]^j$$

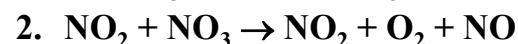
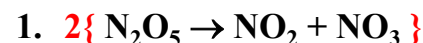
→ Applies only to elementary reactions!

⇒ Overall reaction order (i + j) = Molecularity

Table 16.6 Rate Laws for General Elementary Steps

Elementary Step	Molecularity	Rate Law
$\text{A} \rightarrow \text{product}$	Unimolecular	$\text{Rate} = k[\text{A}]$
$2\text{A} \rightarrow \text{product}$	Bimolecular	$\text{Rate} = k[\text{A}]^2$
$\text{A} + \text{B} \rightarrow \text{product}$	Bimolecular	$\text{Rate} = k[\text{A}][\text{B}]$
$2\text{A} + \text{B} \rightarrow \text{product}$	Termolecular	$\text{Rate} = k[\text{A}]^2[\text{B}]$

Example: For the following three-step mechanism, determine the rate law and molecularity of each step, identify the intermediate and write the overall balanced equation.

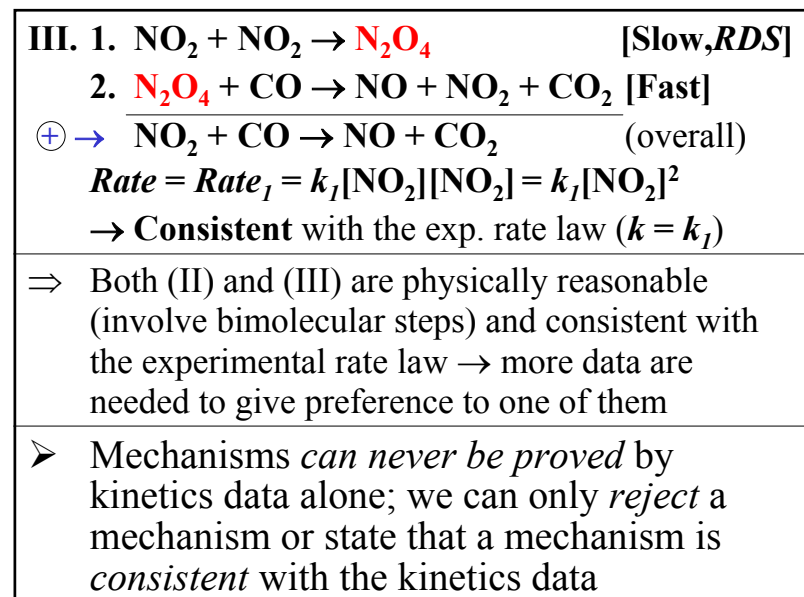
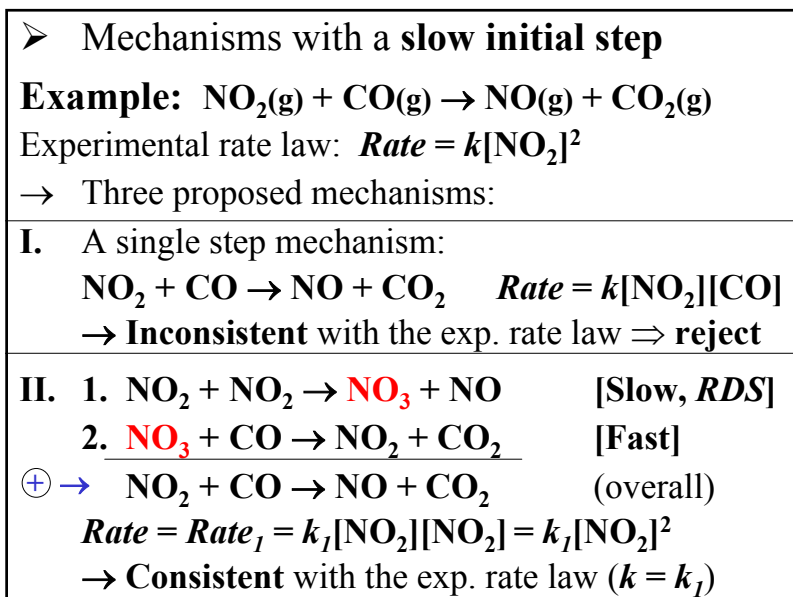
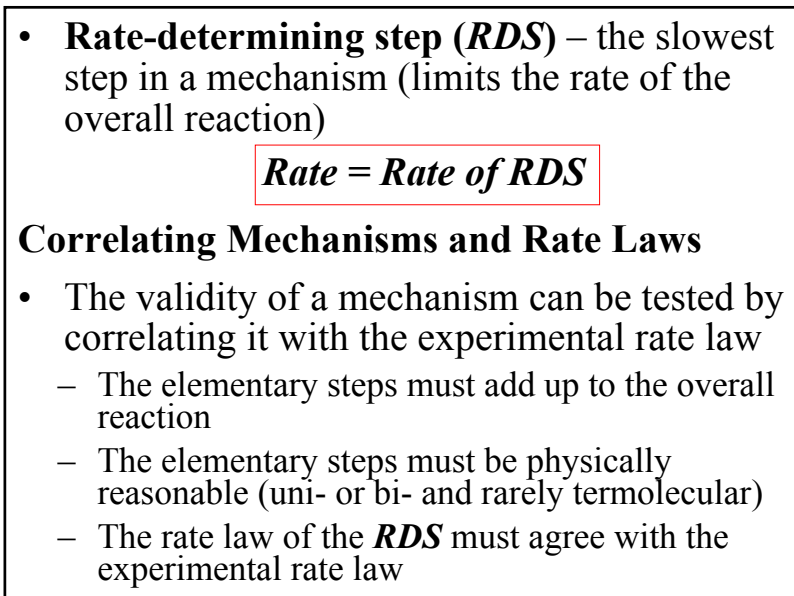
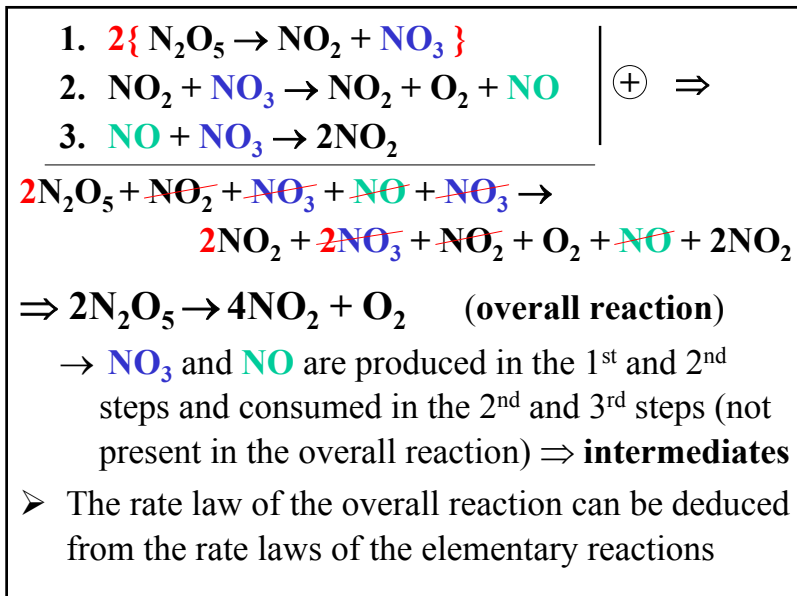


→ $2\{\dots\}$ – the 1st equation is taken twice

1. $\text{Rate}_1 = k_1[\text{N}_2\text{O}_5]$ → unimolecular

2. $\text{Rate}_2 = k_2[\text{NO}_2][\text{NO}_3]$ → bimolecular

3. $\text{Rate}_3 = k_3[\text{NO}][\text{NO}_3]$ → bimolecular



➤ Mechanisms with a **fast initial step**

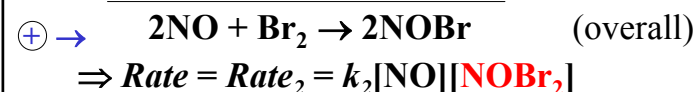
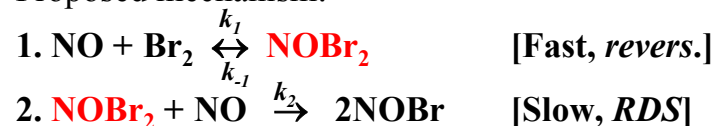
$A \xrightarrow{k_1} \text{Int}$	[Slow]	[Fast]
$\text{Int} \xrightarrow{k_2} B$	[Fast]	[Slow]
⊕ → $A \rightarrow B$	$Rate = k_1[A]$	$Rate = k_2[\text{Int}]$

- **[Int]** can not be in the rate law (intermediate) and must be expressed through the concentrations of the reactants (or products) in the overall reaction
- If the first reaction is **fast and reversible**, it quickly reaches equilibrium and the rate of formation of the intermediate is equal to the rate of its consumption (steady state approximation)
- The **steady state approximation** allows the calculation of **[Int]**

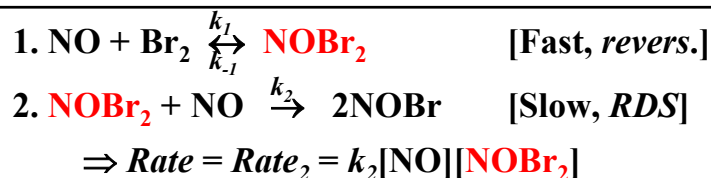
Example: $2\text{NO}(\text{g}) + \text{Br}_2(\text{g}) \rightarrow 2\text{NOBr}(\text{g})$

Experimental rate law: $Rate = k[\text{NO}]^2[\text{Br}_2]$

→ Proposed mechanism:



- **NOBr₂** is an intermediate and must be expressed through the reactants
- The 1st step reaches equilibrium so the rates of the forward ($Rate_1$) and reverse ($Rate_{-1}$) reactions are equal

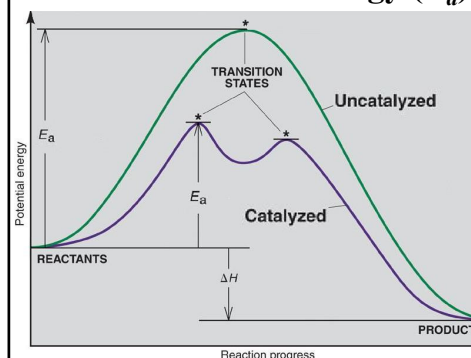


→ $Rate_1 = Rate_{-1} \rightarrow k_1[\text{NO}][\text{Br}_2] = k_{-1}[\text{NOBr}_2]$
 → $[\text{NOBr}_2] = (k_1/k_{-1})[\text{NO}][\text{Br}_2]$
 $\Rightarrow Rate = k_2[\text{NO}][\text{NOBr}_2] = k_2[\text{NO}](k_1/k_{-1})[\text{NO}][\text{Br}_2]$
 $\Rightarrow Rate = (k_2k_1/k_{-1})[\text{NO}]^2[\text{Br}_2] = k[\text{NO}]^2[\text{Br}_2]$

- Experimental rate law: $Rate = k[\text{NO}]^2[\text{Br}_2]$
- **Consistent** with the exp. rate law ($k = k_2k_1/k_{-1}$)

16.7 Catalysis

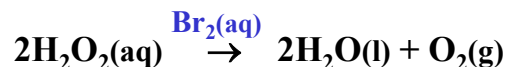
- **Catalyst** – a substance that increases the reaction rate without being consumed in it
 - In general catalysts increase the rate by **lowering the activation energy (E_a)** of the reaction



- Catalysts provide a different mechanism for the reaction
- Catalysts speedup both the forward and reverse reactions
- Catalysts don't change the ΔH_r

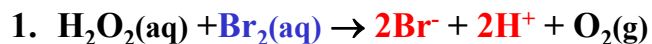
- **Homogeneous catalysis** – the catalyst is in the same phase as the reactants

Example: Decomposition of H_2O_2



→ $\text{Br}_2(\text{aq})$ is in the same phase as $\text{H}_2\text{O}_2(\text{aq})$

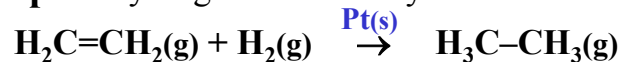
→ Br_2 catalyses the reaction by providing a two step mechanism with lower E_a



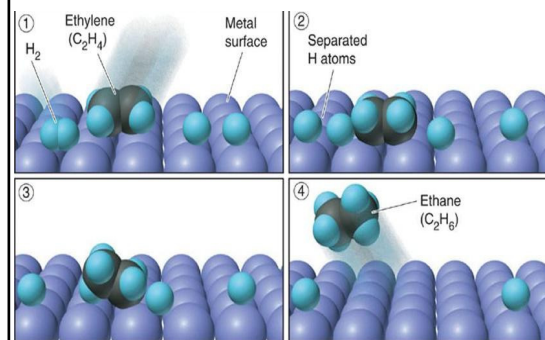
→ Br_2 is not consumed in the reaction

- **Heterogeneous catalysis** – the catalyst is in a phase different from that of the reactants

Example: Hydrogenation of ethylene



→ $\text{Pt}(\text{s})$ is in a different phase (solid)



→ The reactants are adsorbed over the Pt and their bonds are weakened (H_2 splits into 2H)