Rates & Mechanisms

Experiments → Rate Law
Rate Law → Mechanism (?)

MECHANISM: “The detailed molecular processes by which a chemical reaction proceeds.” A series of “elementary steps” which combine to give an observed net reaction.

Elementary Steps

ELEMENTARY STEP: A chemical equation or reaction that describes a process as it occurs at the molecular level. A single reaction event which occurs in one simple atomic or molecular collision.

Most reactions do not occur in a single elementary step.

Reactions vs. Elementary Steps

Normal chemical equations tell us the overall stoichiometry of a reaction, e.g.,

$2 \text{C}_8\text{H}_{16} + 25 \text{O}_2 \rightarrow 16 \text{CO}_2 + 18 \text{H}_2\text{O}$

but they tells us nothing about rate or mechanism.

Equation for an elementary step looks just like a “normal” equation, but actually describes a simple molecular event.

$\text{NO}_2 + \text{NO}_2 \rightarrow \text{N}_2\text{O}_4$

Reactions vs. Elementary Steps

Not always easy to tell an elementary step from a (slightly) more complicated reaction

$2 \text{NO}_2 \rightarrow \text{N}_2\text{O}_4$

IS an elementary step

$2 \text{NO}_2 \rightarrow 2 \text{NO} + \text{O}_2$

is NOT an elementary step

You can’t really tell this from the appearance of the equations.

Types of Elementary Reactions

Unimolecular decomposition: one molecule falls apart:

$A \rightarrow \text{Product(s)}$

Bimolecular reaction: two reactant molecules collide:

$A + B \rightarrow \text{Product(s)}$

Termolecular reaction: three reactant molecules:

$A + B + C \rightarrow \text{Product(s)}$

(such steps rare in gas-phase and soln. rxns.)

NO examples of more complex elementary reactions are known.

Rates of Elementary Steps

For an elementary step, the order of the reaction will derive from the coefficients:

$A \rightarrow \text{Product(s)} \quad \text{rate} = k[A]$

$A + B \rightarrow \text{Product(s)} \quad \text{rate} = k[A][B]$

$2A \rightarrow \text{Product(s)} \quad \text{rate} = k[A]^2$

$A + B + C \rightarrow \text{Product(s)} \quad \text{rate} = k[A][B][C]$

(not for gas phase reactions)

Can ONLY do this for an elementary step!
**Rate laws & mechanisms**
- Start with overall reaction
- Guess some mechanism(s)
- Derive corresponding rate laws
- Compare with experiments
- Repeat as needed

*We need to relate rates of individual steps to the overall, observable rate laws.*

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**Rate Determining Steps**
- If a single step in a reaction mechanism is much slower than the other steps, then the *rate of the slow step is crucial* in determining overall rate.
- The rate determining step (RDS) can be thought of as a “bottleneck” in the formation of products. Steps that follow the RDS have negligible effect on the overall rate of reaction.

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**An energy profile**

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A + B → C → D + E
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- 1st step is rate-determining
- “Reaction Coordinate”

**Example: rates & mechanisms**

\[ 2 \text{NO}_2 \rightarrow 2 \text{NO} + \text{O}_2 \]

- Consider 2 mechanisms for this:
  - \[ \text{NO}_2 \rightarrow \text{NO} + \text{O} \] (slow)
  - \[ \text{O} + \text{NO}_2 \rightarrow \text{O}_2 + \text{NO} \] (fast)
  - \[ 2 \text{NO}_2 \rightarrow \text{NO}_3 + \text{NO} \] (slow)
  - \[ \text{NO}_3 \rightarrow \text{NO} + \text{O}_2 \] (fast)

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**Determining Mechanisms**
- Mechanism is plausible if:
  - it gives correct overall stoichiometry
  - predicts correct rate law
  - it is “chemically reasonable”

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**Determining Mechanisms**
- A mechanism can never be absolutely proven (but very often little doubt remains)
- In addition to consistency with the rate law, finding hypothesized intermediates of following isotopic labels through the course of a reaction strengthens the proposed mechanism
Rate Laws Can Prove a Mechanism is Wrong but Can’t Prove one Right!

2 NO + O₂ → 2NO₂ 
rate = \( k \) \([\text{NO}]^2[\text{O}_2]\)

A single step mechanism?

Rate Law is consistent, but highly unlikely.

Example

2 NO + 2 H₂ → N₂ + 2 H₂O
One possible mechanism:

1. NO + NO ⇌ N₂O₂ (fast equilibrium)
2. N₂O₂ + H₂ → N₂O + H₂O (slow)
3. N₂O + H₂ → N₂ + H₂O (fast)

Rate Law for this mechanism?

Is it plausible?

Example, continued

2 NO + 2 H₂ → N₂ + 2 H₂O
rate = rate of slow step
= \( k_2[\text{N}_2\text{O}_2][\text{H}_2]\)
- But N₂O₂ is neither a reactant nor product
- We want to eliminate it from the rate law

Example, continued: Reversible Steps

2 NO ⇌ N₂O₂ (fast)

While “waiting” for the RDS, the rates of the forward and back reactions will become equal

rate forward = \( k_1[\text{NO}]^2\)
rate reverse = \( k_{-1}[\text{N}_2\text{O}_2]\)

Reversible Steps that come before the rate determining step

- What if the rate determining step (RDS) isn’t the first step?
- Earlier steps can run forward and in reverse many times while “waiting” for the RDS.
- This leads to an equilibrium being established between reactants and products of earlier steps.
- The RDS still controls the overall rate.
**Example, continued: Reversible Steps**

\[ 2 \text{NO} \rightleftharpoons \text{N}_2\text{O}_2 \] (fast)

Set them equal: rate forward = rate reverse
\[ k_f[\text{NO}]^2 = k_r[\text{N}_2\text{O}_2] \]
Use this to get an expression for \([\text{N}_2\text{O}_2]\):
\[ [\text{N}_2\text{O}_2] = \left(\frac{k_1}{k_r - 1}\right)[\text{NO}]^2 \]

What does a plot of the concentrations of NO and N\(_2\)O\(_2\) look like vs. time as this reaction proceeds?

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\[ 2 \text{NO} + 2 \text{H}_2 \rightarrow \text{N}_2 + 2 \text{H}_2\text{O} \], cont...

\[ 2 \text{NO} \rightleftharpoons \text{N}_2\text{O}_2 \] (fast)
\[ \text{N}_2\text{O}_2 + \text{O}_2 \rightarrow 2\text{NO}_2 \] (slow)

Make the substitution: \([\text{N}_2\text{O}_2] = \left(\frac{k_1}{k_r - 1}\right)[\text{NO}]^2\)

Rate = \(k_2[\text{N}_2\text{O}_2][\text{H}_2] = k_2(\frac{k_1}{k_r - 1})[\text{NO}]^2[\text{H}_2]\)

Overall rate law = \(k_{\text{observed}}[\text{NO}]^2[\text{H}_2]\)

Overall rate constant, \(k_{\text{observed}} = k_2(\frac{k_1}{k_r - 1})\)

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**Equilibrium:** \[ 2 \text{NO} \rightleftharpoons \text{N}_2\text{O}_2 \]

The interconversion of products and reactants are an example of equilibrium

Set: rate forward = rate backward
\[ k_f[\text{NO}]^2 = k_r[\text{N}_2\text{O}_2] \]

The Equilibrium Constant, \(K_{\text{eq}}\), is defined as:
\[ \frac{k_f}{k_r} = \frac{[\text{N}_2\text{O}_2]}{[\text{NO}]^2} = \text{constant} = K_{\text{eq}} \]

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**Example (from old exam)**

Consider the reaction between reactants A and B to give products D and E — the energy diagram here applies. C is an intermediate product that is not present when the reaction is over.

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**Example, continued…**

Which step is rate determining?

The overall reaction is…

Endothermic? Exothermic?
Neither? No way to tell?
Catalyst $P$ increases the rate of the second step ($C \rightarrow D + E$), but does not affect the first step ($A + B \rightarrow C$).

Catalyst $Q$ increases the rate of the first step ($A + B \rightarrow C$), but does not affect the second step ($C \rightarrow D + E$).

Which catalyst will be most effective in increasing the rate of the overall reaction ($A + B \rightarrow D + E$)?

Any details to add concerning the mechanism?

What is the rate law?