## **Reaction Mechanisms**: Elementary, my dear Watson!

Collision theory assumes that most reactions occur in a series of steps where one or more reactant particles collide, known as the reaction mechanism.

**Example**

Overall reaction

$$2NO_2(g) + F_2(g) \rightleftharpoons 2NO_2F(g)$$

Reaction Mechanism

intermediate!

Step 1: $NO_2(g) + F_2(g) \rightleftharpoons NO_2F(g) + \boxed{F(g)}$

Step 2: $NO_2(g) + \boxed{F(g)} \rightleftharpoons NO_2F(g)$

**Elementary steps**: each single step in the mechanism: cannot be broken down into simpler steps

- Elementary steps occur exactly as written: they represent the chemical species that are directly interacting.
- Because F(g) is made and then consumed, F(g) does NOT show up in the overall reaction: species that are products in an earlier step but then used up as reactants in a later step are called intermediates.
- When all elementary steps are added together, they must add up to be the overall balanced reaction.

**Molecularity** (number of molecules participating in an elementary step)

- Unimolecular: 1 reactant particle is involved in an elementary step (it may collide with a solvent molecule or other non-reactive particle that is present)
- Bimolecular reaction: 2 reactant particles are involved in an elementary step
- Termolecular reaction: 3 reactant particles are involved in an elementary step (*very* rare!, since three particles would need to simultaneously collide with correct orientation and sufficient energy)

**Rate Laws for Elementary Steps**

- Each elementary step in the mechanism has its own activation energy and its own rate law.
- Although the rate law and orders for an overall reaction MUST be determined experimentally, the rate laws and orders of an elementary step can be derived from the stoichiometry of that specific elementary step.

**Example**

Overall reaction

$2NO_2(g) + F_2(g) \rightleftharpoons 2NO_2F(g)$ $\quad rate = k_0[NO_2]^{\text{from exp.data}}[F_2]^{\text{from exp.data}}$

Reaction Mechanism

Step 1: $NO_2(g) + F_2(g) \rightleftharpoons NO_2F(g) + F(g)$ $\quad rate = k_1[NO_2]^1[F_2]^1$ from step 1 coefficients

Step 2: $NO_2(g) + F(g) \rightleftharpoons NO_2F(g)$ $\quad rate = \cancel{k_1}\, k_2[NO_2]^1[F]^1$ from step 2 coefficients

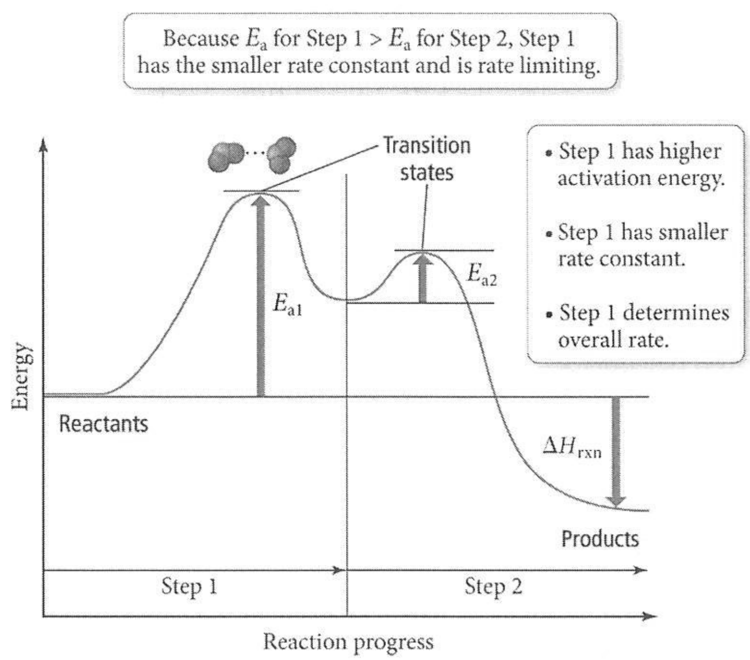
**In Summary:**

| Elementary Step | Molecularity | Rate Law |
|---|---|---|
| A $\longrightarrow$ products | 1 (uni) | Rate $= k[A]$ |
| A + A $\longrightarrow$ products | 2 (bi) | Rate $= k[A]^2$ |
| A + B $\longrightarrow$ products | 2 (bi) | Rate $= k[A][B]$ |
| A + A + A $\longrightarrow$ products | 3 (rare) (ter) | Rate $= k[A]^3$ |
| A + A + B $\longrightarrow$ products | 3 (rare) (ter) | Rate $= k[A]^2[B]$ |
| A + B + C $\longrightarrow$ products | 3 (rare) (ter) | Rate $= k[A][B][C]$ |

**Rate-Determining Step** (RDS): the Slowest elementary step in the reaction mechanism

- In a reaction mechanism, product production cannot occur any faster than the Slowest step, so this step determines the rate of the overall reaction.
- The slowest, or rate determining step, has the largest activation energy.
- To determine the rate of the overall reaction, you must combine the rates of ALL elementary steps up to and including the slowest step in the mechanism.

**Energy Diagram for a Two-Step Mechanism**




To validate a reaction mechanism, two conditions must be met:

1. Elementary steps must Sum to overall reaction.
2. Rate law predicted by the mechanism (the combined rates of all elementary steps up to and including slowest step (RDS) in the mechanism) must be consistent with the experimentally observed rate law.

of the overall rxn

**To get credit for free response:**

You MUST relate the Coefficients from the balanced RDS (Slow step) to the exponents of the rate law to justify the mechanism!
(i.e., order)

Key phrase: rate law of RDS matches experimentally determined rate law of overall rxn

**Guided Practice**

1. Consider the following two step mechanism:

Reaction Mechanism

| | | |
|---|---|---|
| Step 1: | $2\,A \rightarrow A_2$ | slow ] RDS |
| Step 2: | $A_2 + B \rightarrow A_2B$ | fast |

a. Determine the overall reaction.

$$\begin{array}{l} 2A \rightarrow \cancel{A_2} \\ \cancel{A_2} + B \rightarrow A_2B \quad + \\ \hline 2A + B \rightarrow A_2B \end{array}$$

b. Predict the rate law for the overall reaction. Justify your answer. rate = $k[A]^2$, b/c the first step is the rate determining step (RDS), so the overall rate law can be determined from the stoichiometry of step 1 (2 A ⇒ $2^{nd}$ order w/ respect to A, no B ⇒ $0^{th}$ order w/ respect to B)

c. Identify the intermediate in the mechanism. Justify your answer.

$A_2$ is an intermediate b/c it is formed in an earlier step + consumed in a later step.

**Independent Practice**

2. The balanced equation for the reaction of the gases nitrogen dioxide and fluorine is: $2\,NO_2(g) + F_2(g) \rightarrow 2\,NO_2F(g)$

A suggested mechanism for this reaction is

both bimolecular!

Step 1: $NO_2(g) + F_2(g) \rightleftharpoons NO_2F(g) + F(g)$

Step 2: $NO_2(g) + F(g) \rightleftharpoons NO_2F(g)$

a. Label each step of the reaction mechanism with its molecularity.

b. The experimentally determined rate law is: Rate = $k[NO_2][F_2]$. Which of the two steps in the mechanism shown above is the slow step? Explain your reasoning.

Step 1 is the slow step, b/c the rate law derived from the stoichiometry of step 1 matches the rate law of the overall rxn.