N10 - KINETICS

Mechanisms

Link to YouTube Presentation: https://youtu.be/elfsdYUnk8E

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Mechanisms

Target: I can use rate laws to determine the slow step in a reaction, and can write rate laws based on reaction mechanism information.

Rate Laws

Reaction Mechanism

The series of elementary steps by which a chemical reaction occurs.

Elementary Steps = individual, single steps

Rate Laws

To validate (not prove) a mechanism, two conditions must be met:

1. The elementary steps must sum to the overall balanced equation (sometimes called the “stoichiometric equation.”)
2. The rate law predicted by the mechanism must be consistent with the experimentally observed rate law.

Rate Laws

Rate Determining Step

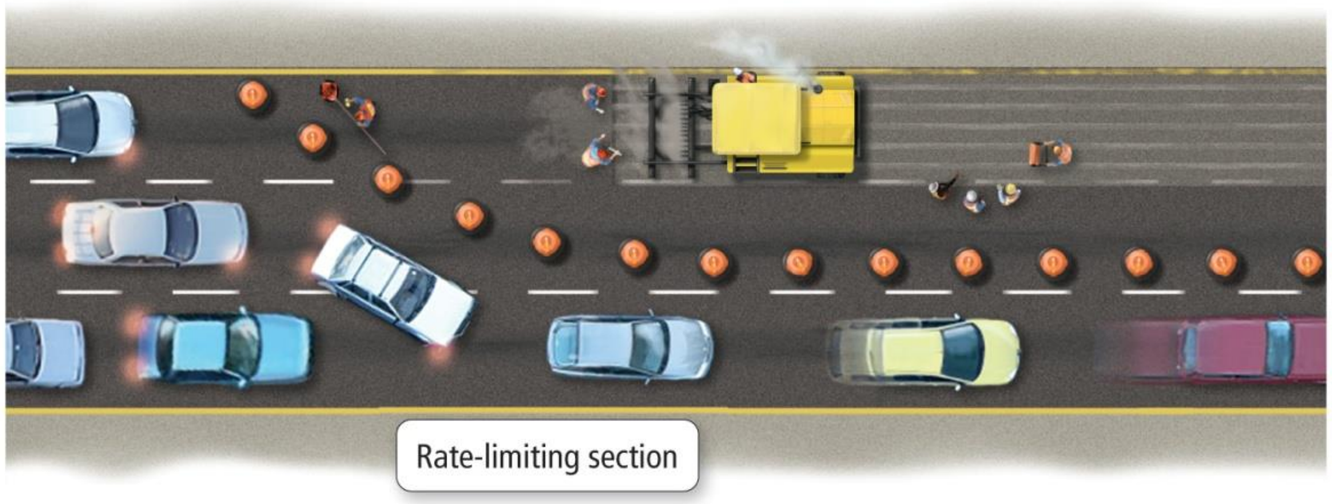
The slowest step in the reaction mechanism.

It therefore determines the rate of the reaction.

The experimental rate law
must agree with the rate-determining step!

Rate Laws

- In most mechanisms, one step occurs slower than the other steps.
- The result is that product production cannot occur any faster than the slowest step; the step determines the rate of the overall reaction.
- We call the slowest step in the mechanism the rate determining step.
  - **The slowest step has the largest activation energy.**
- The rate law of the rate determining step determines the rate law of the overall reaction.



Can't go faster than the slowest step!

https://youtu.be/NkQ58I53mjk

Another Reaction Mechanism

1

$NO_{2(g)} + CO_{(g)} \rightarrow NO_{(g)} + CO_{2(g)}$

1. $NO_{2(g)} + NO_{2(g)} \rightarrow NO_{3(g)} + NO_{(g)}$
2. $NO_{3(g)} + CO_{(g)} \rightarrow NO_{2(g)} + CO_{2(g)}$

$Rate_{obs} = k[NO_2]^2$

$Rate = k_1[NO_2]^2$ **Slow**

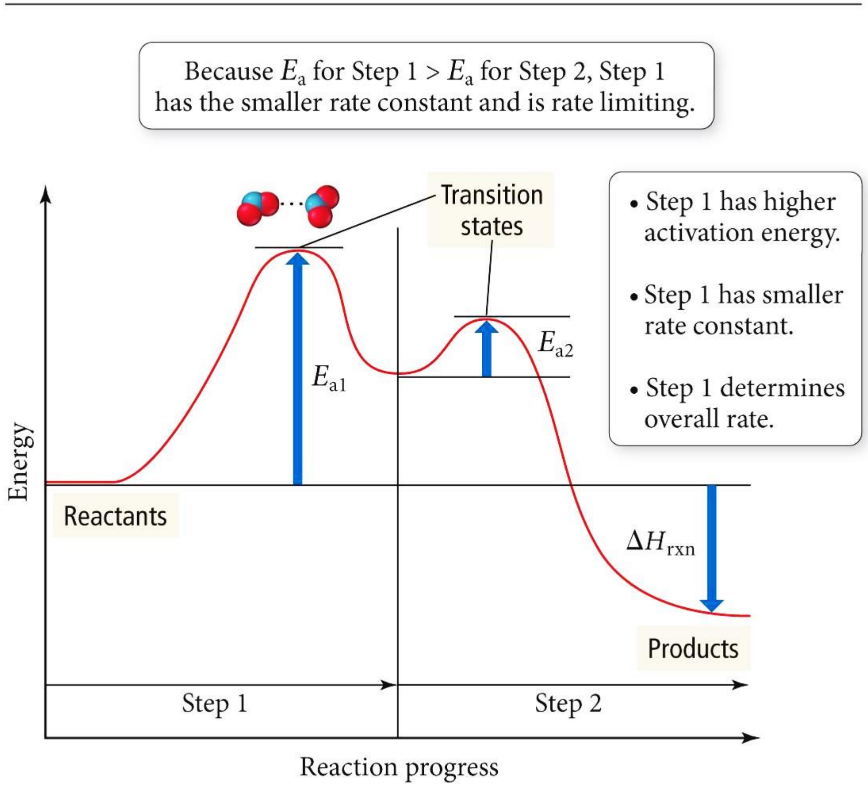
$Rate = k_2[NO_3][CO]$ **Fast**

The first step is slower than the second step because its activation energy is larger.

The first step in this mechanism is the **rate determining step.**

The rate law of the first step is the same as the rate law of the overall reaction.

Energy Diagram for a Two-Step Mechanism



Identifying the Rate-Determining Step

2

$2H_2(g) + 2NO(g) \rightarrow N_2(g) + 2H_2O(g)$

The experimental rate law is:

$R = k[NO]^2 [H_2]$

Which step in the rxn mechanism is the rate-determining step?

Step #1 $H_2(g) + 2NO(g) \rightarrow N_2O(g) + H_2O(g)$

Step #2 $N_2O(g) + H_2(g) \rightarrow N_2(g) + H_2O(g)$

Step #1 agrees with the experimental rate law

Identifying Intermediates

$$2H_2(g) + 2NO(g) \rightarrow N_2(g) + 2H_2O(g)$$

Intermediates – substances that are made during one step of the mechanism and then get used up

– they do not show up in the final, balanced equation because they were not an original reactant, or a final product.

Step #1 $H_2(g) + 2NO(g) \rightarrow \boxed{N_2O(g)} + H_2O(g)$

Step #2 $\boxed{N_2O(g)} + H_2(g) \rightarrow N_2(g) + H_2O(g)$

$$2H_2(g) + 2NO(g) \rightarrow N_2(g) + 2H_2O(g)$$

$\therefore$ $N_2O(g)$ is an intermediate

Mechanism with a Fast Initial Step

- **We don't like reaction rates to have intermediates in them. So we will rearrange/substitute to write it without them.**
- When a mechanism contains a fast initial step, the rate limiting step may contain intermediates.
- When a previous step is rapid and reaches equilibrium, the forward and reverse reaction rates are equal, so the concentrations of reactants and products of the step are related and the product is an intermediate.
- Substituting into the rate law of the RDS will produce a rate law in terms of just reactants.

A (not so fun) Game of Substitution!

Note: for each elementary step, coeff. = orders

3

$$Rate = k_2[H_2][N_2O_2]$$
$$Rate = k_2[H_2]\frac{k_1}{k_{-1}}[NO]^2$$
$$Rate = \frac{k_2 k_1}{k_{-1}}[H_2][NO]^2$$

Step		Rate
1. $2\,NO_{(g)} \underset{k_{-1}}{\overset{k_1}{\Leftrightarrow}} N_2O_{2(g)}$	Fast	
2. $H_{2(g)} + N_2O_{2(g)} \rightarrow H_2O_{(g)} + N_2O_{(g)}$	Slow	Rate = $k_2[H_2][N_2O_2]$
3. $H_{2(g)} + N_2O_{(g)} \rightarrow H_2O_{(g)} + N_{2(g)}$	Fast	

$2\,H_{2(g)} + 2\,NO_{(g)} \rightarrow 2\,H_2O_{(g)} + N_{2(g)}$ $\quad Rate_{obs} = k\,[H_2][NO]^2$

$$For\ Step\ 1,\ Rate_{forward} = Rate_{reverse}$$
$$k_1[NO]^2 = k_{-1}[N_2O_2]$$

$$[N_2O_2] = \frac{k_1}{k_{-1}}[NO]^2$$

Now plug this in anywhere you see $[N_2O_2]$ in the slow step rate law!

$$Rate = k_2[H_2][N_2O_2]$$

$$Rate = k_2[H_2]\frac{k_1}{k_{-1}}[NO]^2$$

k′

$$Rate = \frac{k_2 k_1}{k_{-1}}[H_2][NO]^2$$

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