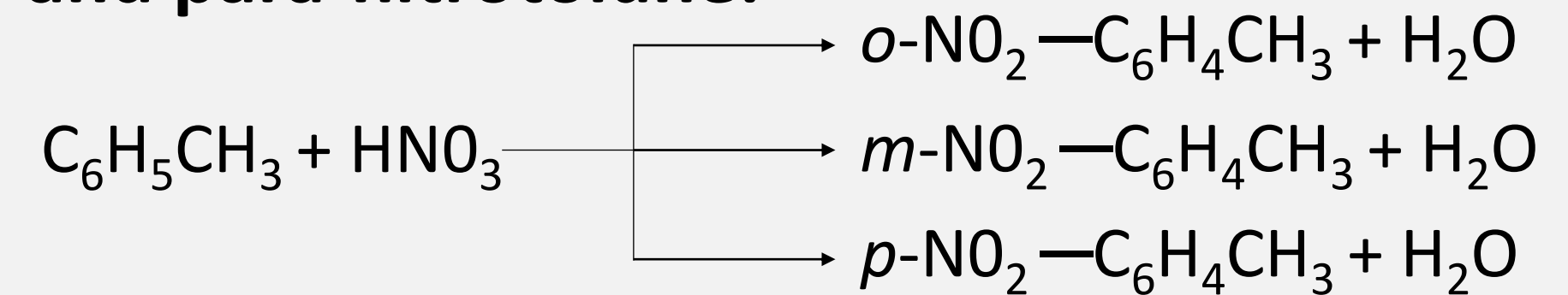


Complex Reactions: Opposite, Consecutive and Parallel Reactions

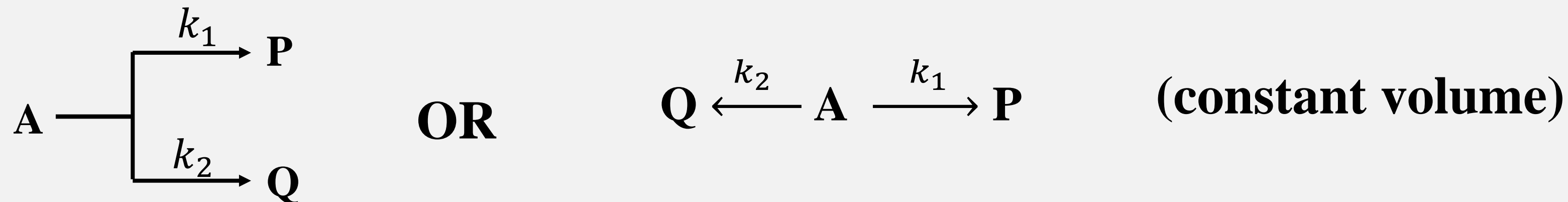
Parallel Reactions

- When the reactants participate in two or more reactions independently and simultaneously, the combination of these reactions is called a parallel reaction

Example: Nitration of toluene leads to the formation of ortho-, meta- and para-nitrotoluene:



First-Order Parallel Reactions: All the parallel reactions involved are of first order



Time	[A]	[P]	[Q]
$t=0$	$[\text{A}]_0$	0	0

For the three substances we can write the rate equations as:

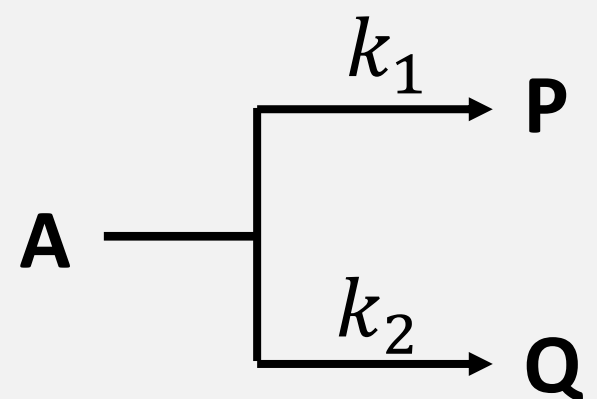
$$v_{\text{P}} = \frac{d[\text{P}]}{dt} = k_1[\text{A}]$$

$$v_{\text{Q}} = \frac{d[\text{Q}]}{dt} = k_2[\text{A}]$$

$$v_{\text{A}} = -\frac{d[\text{A}]}{dt} = v_{\text{P}} + v_{\text{Q}} = k_1[\text{A}] + k_2[\text{A}] = (k_1 + k_2)[\text{A}]$$

Complex Reactions: Opposite, Consecutive and Parallel Reactions

Integrated Rate Equation of First-Order Parallel Reactions



$$\frac{d[A]}{dt} = -(k_1 + k_2)[A] \Rightarrow [A] = [A]_0 e^{-(k_1 + k_2)t}$$

$$\frac{d[P]}{dt} = k_1[A] = k_1[A]_0 e^{-(k_1 + k_2)t}$$

Integrating,

$$[P] = \frac{-k_1[A]_0}{(k_1 + k_2)} e^{-(k_1 + k_2)t} + cont.$$

$$\text{At } t = 0, [P] = 0 \Rightarrow cont = \frac{k_1[A]_0}{(k_1 + k_2)}$$

$$\Rightarrow [P] = \frac{k_1[A]_0}{(k_1 + k_2)} (1 - e^{-(k_1 + k_2)t})$$

$$\frac{d[Q]}{dt} = k_2[A] = k_2[A]_0 e^{-(k_1 + k_2)t}$$

Integrating,

$$[Q] = \frac{-k_2[A]_0}{(k_1 + k_2)} e^{-(k_1 + k_2)t} + cont.$$

$$\text{At } t = 0, [Q] = 0 \Rightarrow cont = \frac{k_2[A]_0}{(k_1 + k_2)}$$

$$\Rightarrow [Q] = \frac{k_2[A]_0}{(k_1 + k_2)} (1 - e^{-(k_1 + k_2)t})$$

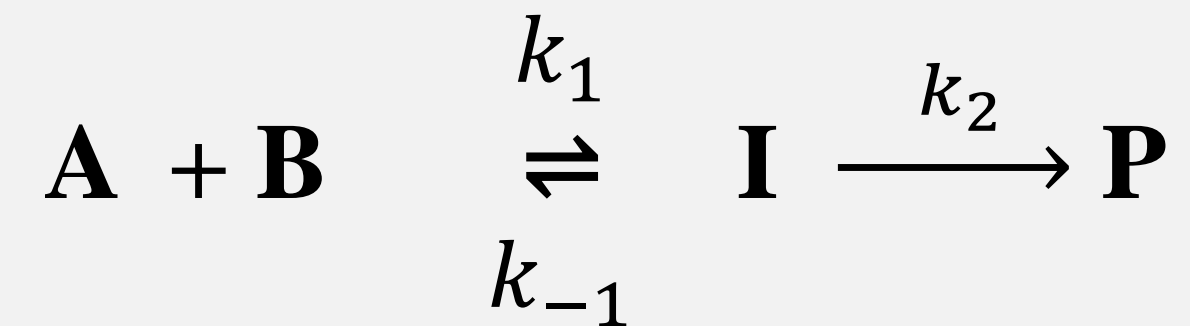
Note that at all times

$$\frac{[P]}{[Q]} = \frac{k_1}{k_2}$$

- This means the composite reaction involves a pre-equilibrium

Reaction mechanisms: steady-state approximation, pre-equilibria, unimolecular reactions

Pre-equilibria



- Consider the above sequence of consecutive reactions in which 'I' reaches an equilibrium with the reactants 'A' and 'B'

- This means the composite reaction involves a pre-equilibrium

- Pre-equilibrium can arise when rate of decay of the intermediate back to the reactants is much faster than the rate at which it forms the products

$$k_{-1} \gg k_2$$

- Since A, B and I are assumed as in equilibrium

$$K = \frac{k_1}{k_{-1}} = \frac{[\text{I}]}{[\text{A}][\text{B}]}$$

- It is also assumed that I to P is too slow to affect this equilibrium

- The rate of formation of P

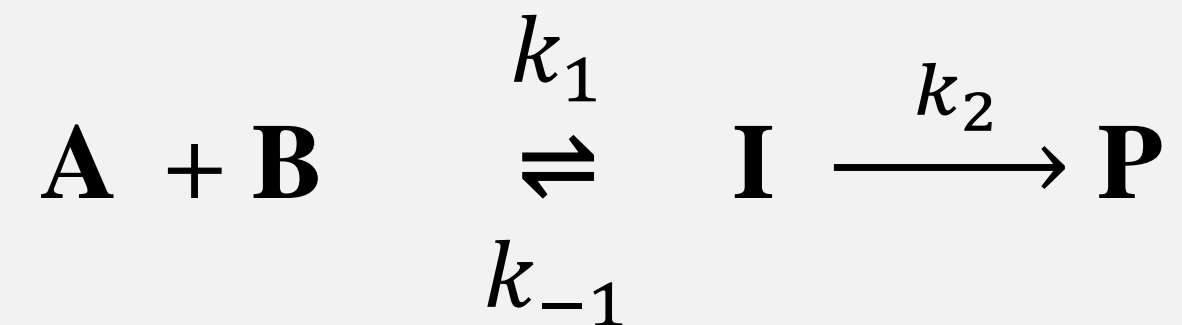
$$\frac{d[\text{P}]}{dt} = k_2[\text{I}] = k_2 K [\text{A}][\text{B}]$$

$$\Rightarrow \frac{d[\text{P}]}{dt} = k[\text{A}][\text{B}] \quad \text{where} \quad k = k_2 K = \frac{k_1 k_2}{k_{-1}}$$

- The rate law has a form of second order rate law with composite rate constant

Reaction mechanisms: steady-state approximation, pre-equilibria, unimolecular reactions

Pre-equilibria



- **Argument: What if “I” to “P” conversion is not too slow and “I” is slowly converting to “P”**

$$\frac{d[\mathbf{P}]}{dt} = k_2[\mathbf{I}]$$

$$\frac{d[\mathbf{I}]}{dt} = k_1[\mathbf{A}][\mathbf{B}] - k_{-1}[\mathbf{I}] - k_2[\mathbf{I}]$$

- Invoking steady state approximation

$$\frac{d[\mathbf{I}]}{dt} \approx 0 \Rightarrow [\mathbf{I}] \approx \frac{k_1[\mathbf{A}][\mathbf{B}]}{k_2 + k_{-1}}$$

Thus, the rate of formation of P

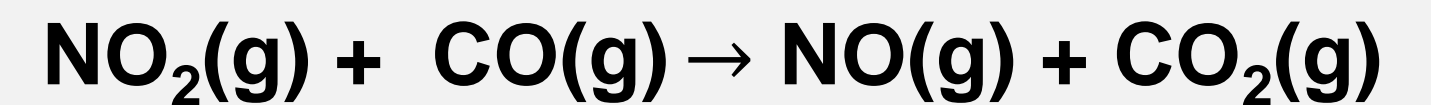
$$\frac{d[\mathbf{P}]}{dt} = k_2 [\mathbf{I}] \approx k_2 \frac{k_1[\mathbf{A}][\mathbf{B}]}{k_2 + k_{-1}} = k[\mathbf{A}][\mathbf{B}] \quad \text{where} \quad k = \frac{k_1 k_2}{k_2 + k_{-1}}$$

- The rate law again has a form of second order rate law with composite rate constant

Reaction mechanisms: steady-state approximation, pre-equilibria, unimolecular reactions

Reaction mechanisms: The rate-determining step

- Most reactions do not take place in a single step, instead they are involved several steps
- We often write only the overall reaction in which the substances present in the beginning and formed by the reaction are mentioned
- The sequence of individual reactions steps by which the overall reaction occurs is termed as reaction mechanism
- Each step in a reaction mechanism is an elementary step
- The individual steps in a valid reaction mechanism must add to the overall reaction



Experimentally determined rate law:

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

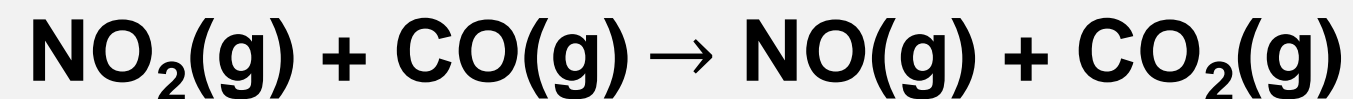
If it was a single-step reaction, the rate would have been

$$\text{Rate} = k [\text{NO}_2][\text{CO}]$$

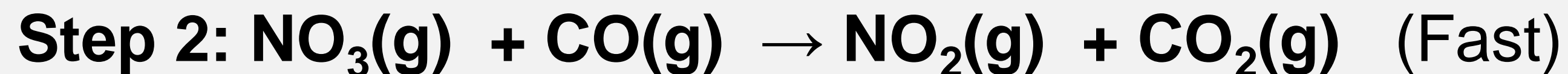
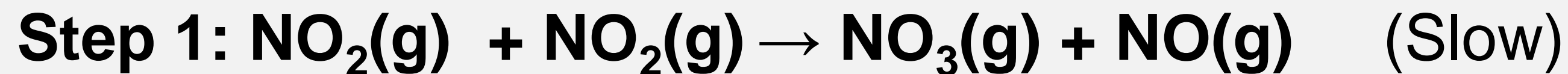
The reaction involves more than one step!

Reaction mechanisms: steady-state approximation, pre-equilibria, unimolecular reactions

Reaction mechanisms: The rate-determining step

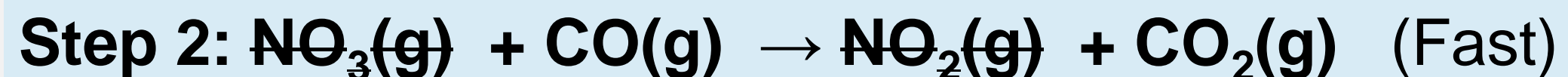
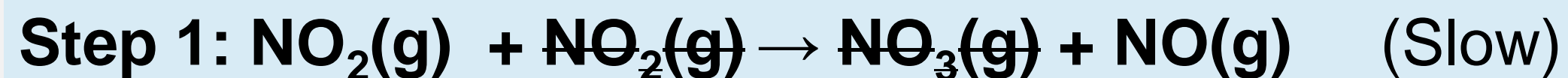


Possible mechanism:

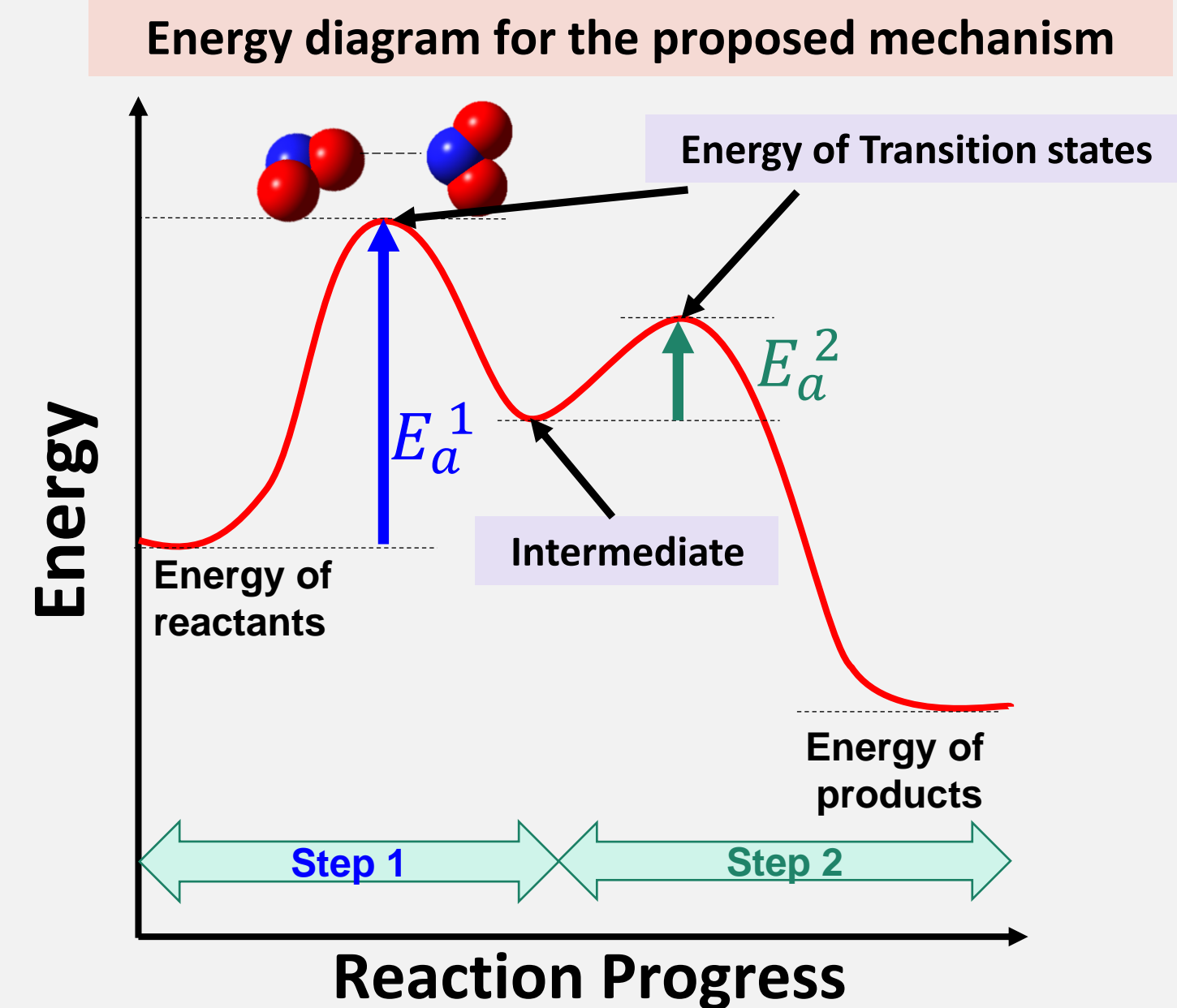


1. The elementary steps in the mechanism must add up to the overall reaction
2. The rate law predicted by the mechanism must match with the experimentally observed rate law

Test 1:

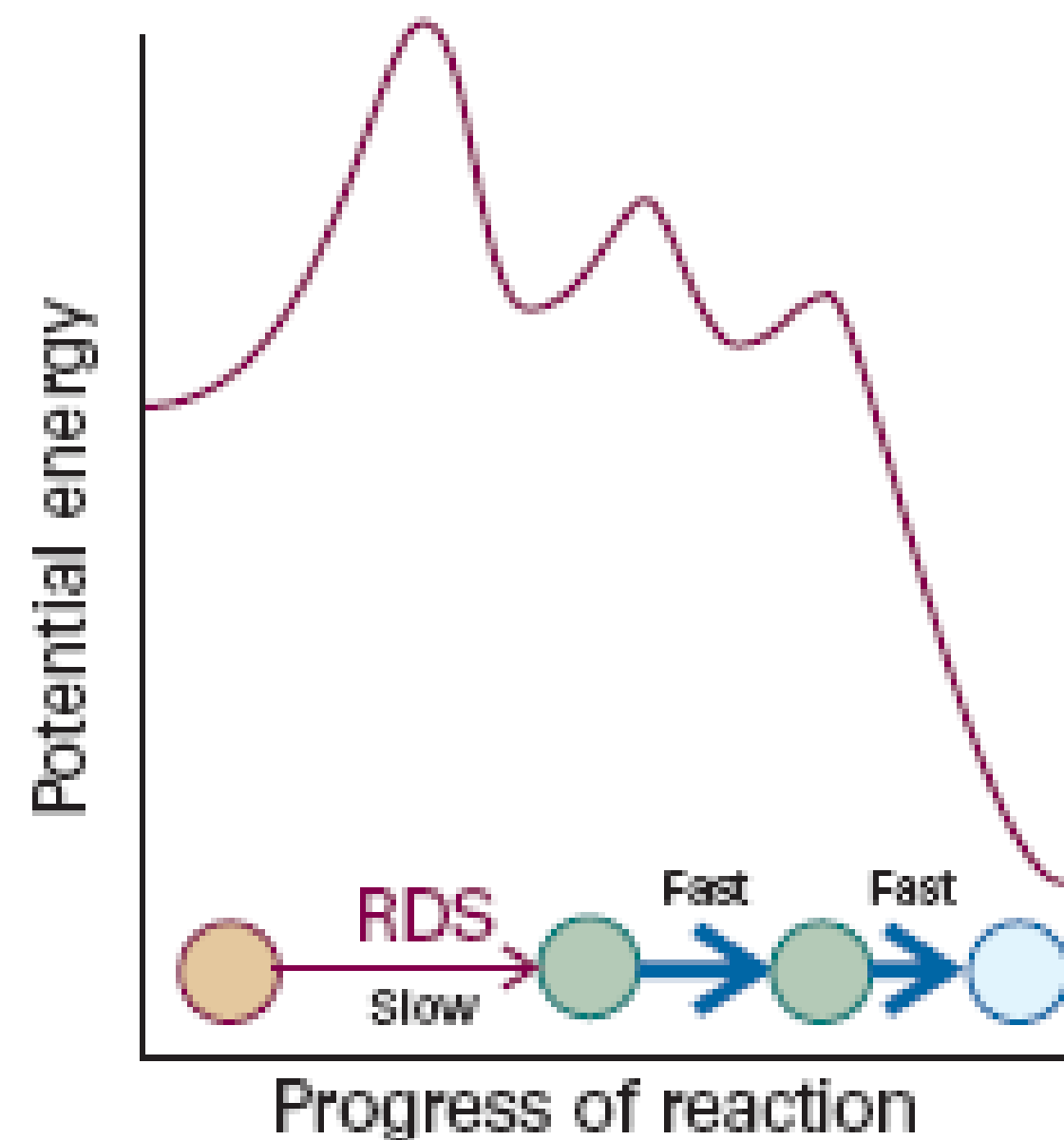


- The first step determines the overall rate of the reaction, the predicted rate law is **Rate** = $k[\text{NO}_2]^2$



Reaction mechanisms: steady-state approximation, pre-equilibria, unimolecular reactions

The rate-determining step



The reaction profile for a mechanism in which the first step (RDS) is rate-determining.

- The fig. on the left shows the reaction profile for a mechanism of a reaction in which the slowest step is the one with the highest activation energy or activation barrier. Once over the initial barrier, the intermediates cascade into products.
- A rate-determining step may also stem from the low concentration of a crucial reactant and need not correspond to the step with highest activation barrier.

Reaction mechanisms: steady-state approximation, pre-equilibria, unimolecular reactions

Reaction mechanisms: The rate-determining step

In these diagrams of reaction schemes, thick blue arrows represent fast steps and thin maroon arrows represent slow steps.

(a) The first step is rate-determining;

(b) the second step is rate-determining;

(c) although one step is slow, it is not rate-determining because there is a fast route that circumvents it.

- In general, the rate-determining step is the slowest step in a mechanism and controls the overall rate of the reaction.
- However, the rate-determining step is not just the slowest step: it must be slow and be a crucial gateway for the formation of products. If a faster reaction can also lead to products, then the slowest step is irrelevant because the slow reaction can then be side-stepped.

$$k_{slow} \ll k_{fast}$$