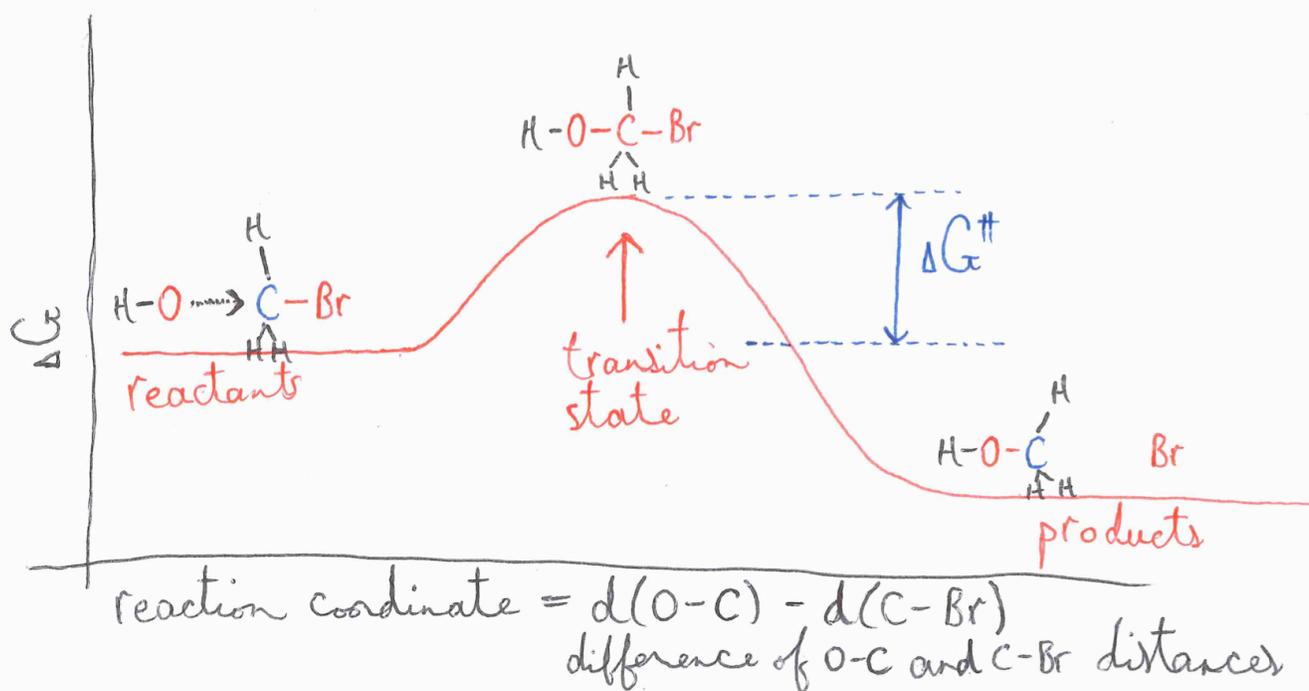
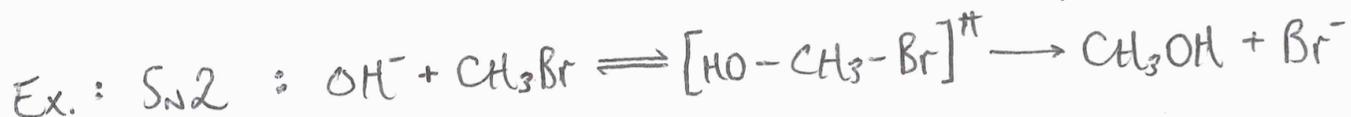


Transition state theory (TST), also known as Activated Complex Theory, has two main assumptions

- 1) The transition state is in equilibrium with the reactions.
- 2) One (special) vibrational motion results in the breakup of the transition state into the products.



The transition state (activated complex) is a transient species of high energy that falls apart to generate the products of the reaction.

Dependence of Reaction Rate on Temperature

Reactions almost always occur faster at higher temperature. Quantified by the Arrhenius Equation for the rate constant

$$k = Ae^{-E_a/RT}$$

A = frequency factor

E_a = activation energy

R = gas constant = $8.314 \text{ J K}^{-1} \text{ mol}^{-1}$

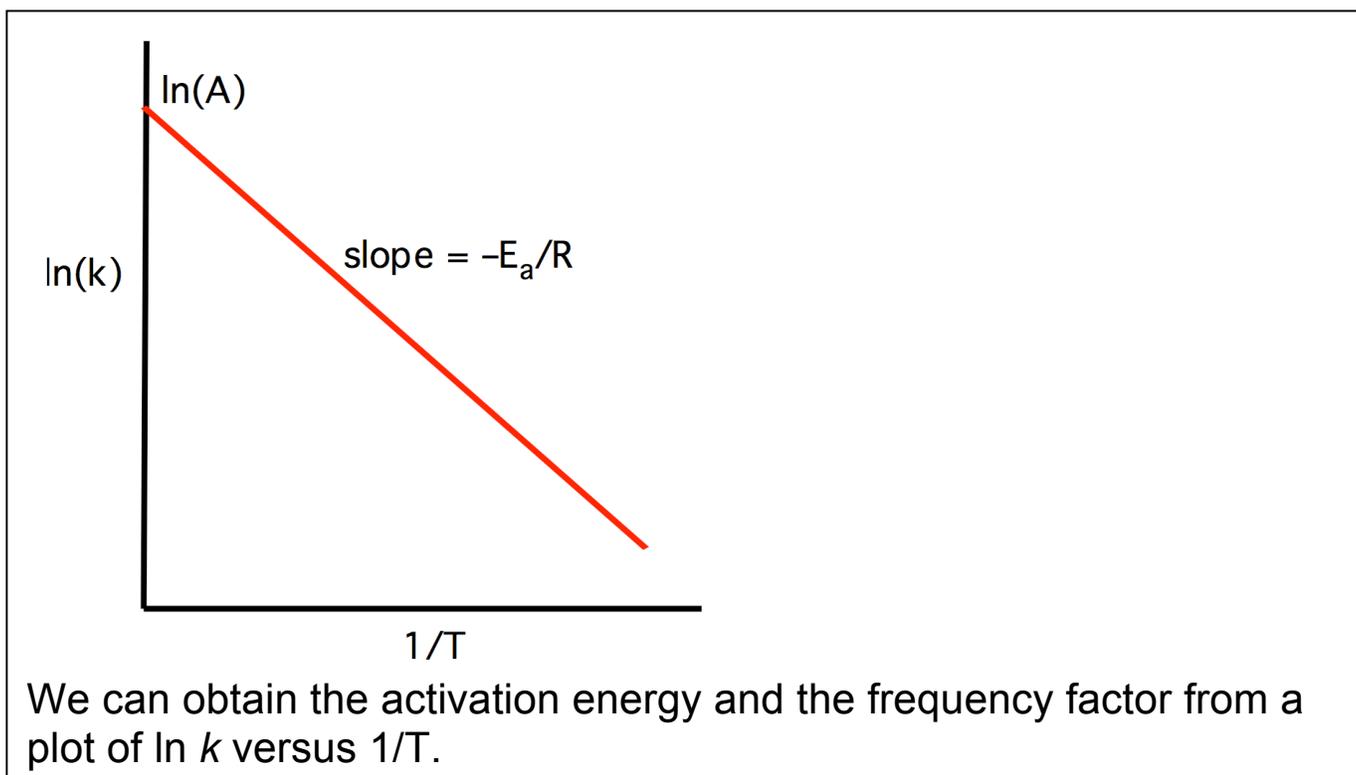
T = temperature (in K)

Increase E_a : decrease k

Increase T : increase k

Take the logarithm of the Arrhenius Equation:

$$\ln k = \ln A - \frac{E_a}{RT} \quad (\text{used } \ln xy = \ln x + \ln y)$$



Reaction Mechanisms

- Most reactions occur in a series of steps
- The balanced equation does not tell us how the reaction occurs!
- The series of steps is the reaction mechanism

Consider the reaction $2 \text{NO}(g) + \text{O}_2(g) \rightarrow 2 \text{NO}_2(g)$

This reaction cannot occur as written because

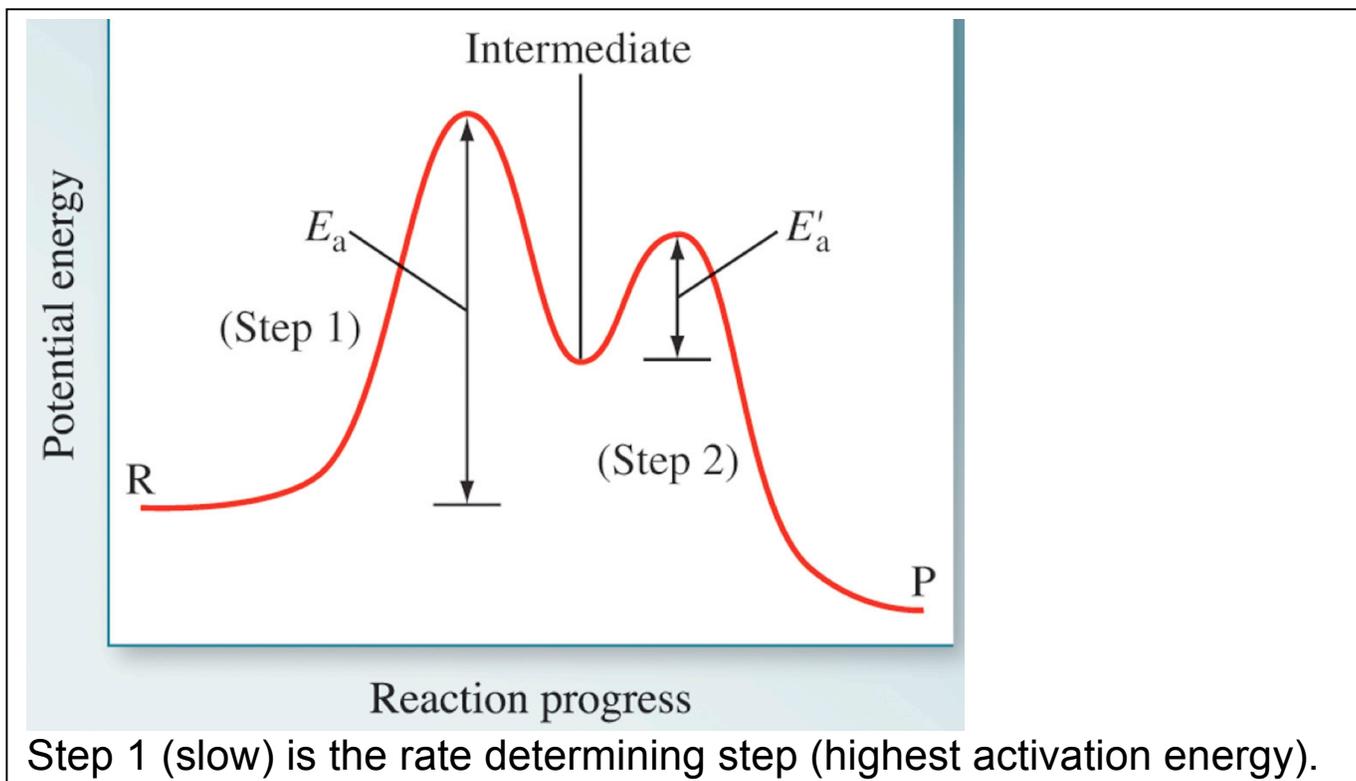
1. The simultaneous collision of 3 molecules is unlikely
2. N_2O_2 is detected during the course of the reaction

Possible mechanism:



The elementary reactions must add up to give the overall rxn.

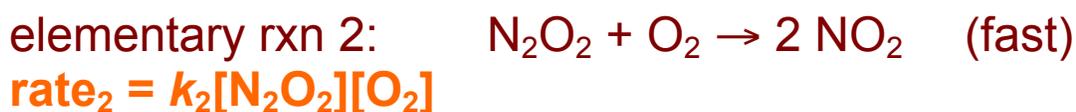
Rate determining step: slowest step in the rxn mechanism
(elementary step with the largest activation energy)



N_2O_2 is called an *intermediate* because

1. It appears in the mechanism but not in the balanced Eq.
2. It is produced in one step and consumed in a later step.

For each elementary reaction, the rate law is given by the stoichiometry coefficients:



The rate law of the rate-determining step must be equal to the overall reaction rate law.

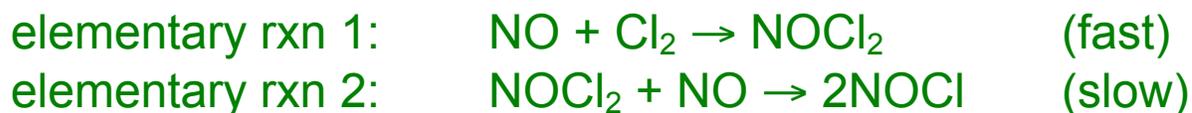
For $2 \text{NO}(g) + \text{O}_2(g) \rightarrow 2 \text{NO}_2(g)$ this is: $\text{rate} = k[\text{NO}]^2$

Mechanisms with a Fast First Step

Consider the reaction $2\text{NO}(g) + \text{Cl}_2(g) \rightarrow 2\text{NOCl}(g)$
with experimentally determined rate = $k[\text{NO}]^2[\text{Cl}_2]$.

One possibility is that this reaction *is* an elementary step. But this is unlikely because it would require 3 molecules simultaneously colliding.

A more plausible mechanism is

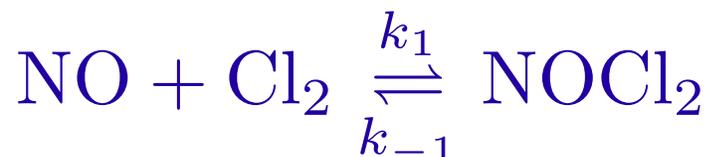


The overall rate law is given by the rate-determining step, which gives $\text{rate} = k[\text{NOCl}_2][\text{NO}]$

But this rate expression contains an *intermediate*, NOCl_2 . We need an expression that only contains the reactants, or else we can't compare to the experimental rate law.

Since NOCl_2 is produced quickly and consumed slowly, it reaches a *steady state* concentration, and the first (fast) step establishes a dynamic equilibrium (forward = backward rate).

We express this as:



The dynamic equilibrium is

$$k_1 [\text{NO}][\text{Cl}_2] = k_{-1} [\text{NOCl}_2]$$

which lets us express

$$[\text{NOCl}_2] = \frac{k_1}{k_{-1}} [\text{NO}][\text{Cl}_2]$$

The rate law is then:

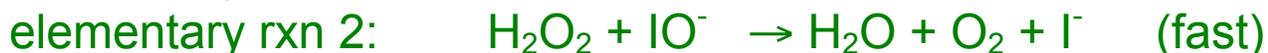
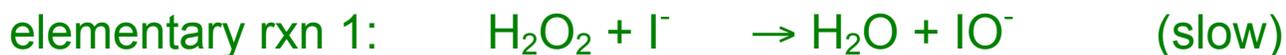
$$\text{rate} = k_2 [\text{NOCl}_2][\text{NO}] = \frac{k_2 k_1}{k_{-1}} [\text{NO}]^2 [\text{Cl}_2]$$

Catalyst:

In the presence of iodide ions (I^-), the decomposition of hydrogen peroxide *speeds up*.



Experimental rate law = $k[\text{H}_2\text{O}_2][\text{I}^-]$



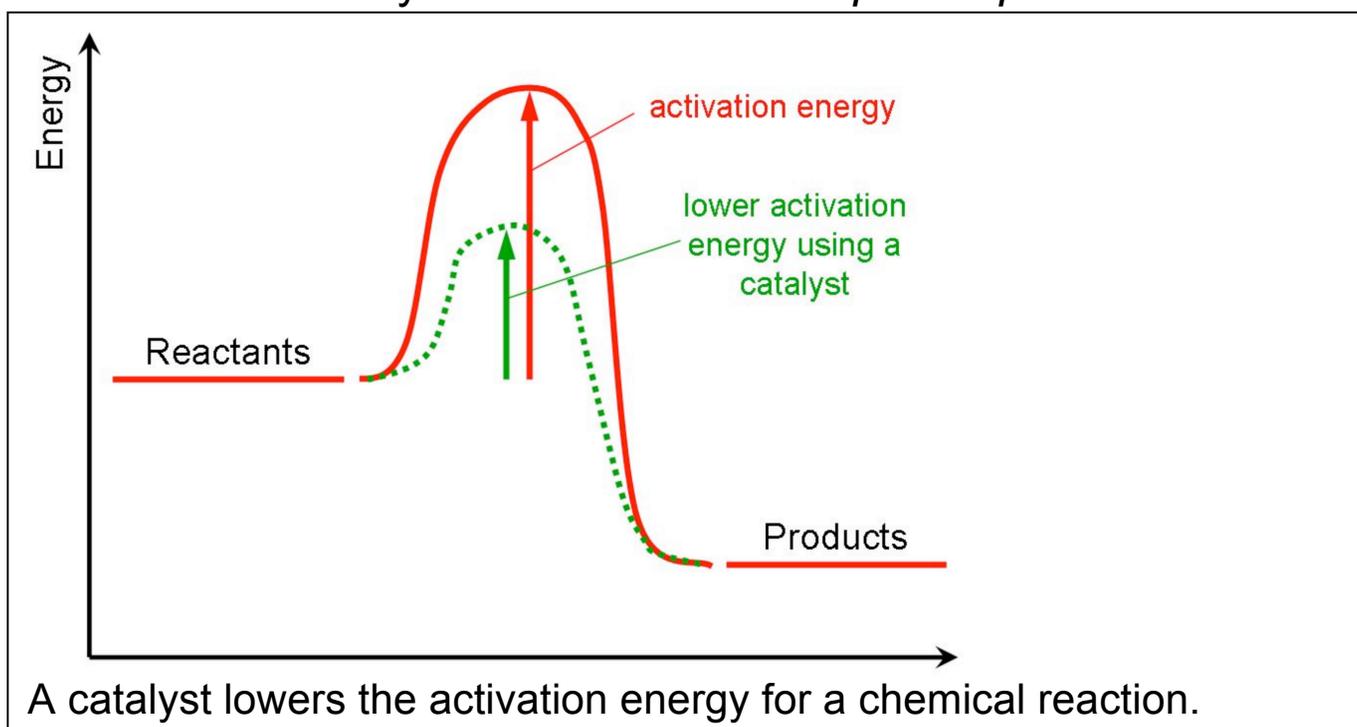
Recall that IO^- is called an *intermediate* because

1. It appears in the mechanism but not in the balanced Eq.
2. It is produced in one step and consumed in a later step.

What about the iodide ion?

1. It, also, does not appear in the balanced Eq.
2. It is consumed in one step and produced in a later step.

It is present at the start of the rxn, and it is present at the end. It is called a catalyst. Its function is to *speed up* the reaction.



Types of Catalysts

Heterogeneous catalysts: The reactants and catalyst are in different phases. The catalyst is often a solid (with a high surface area).

These are extremely important in industrial chemistry.

Homogeneous catalysts: The reactants and catalyst are in the same phase.

Enzyme catalysts: biological catalysts (in living cells)

