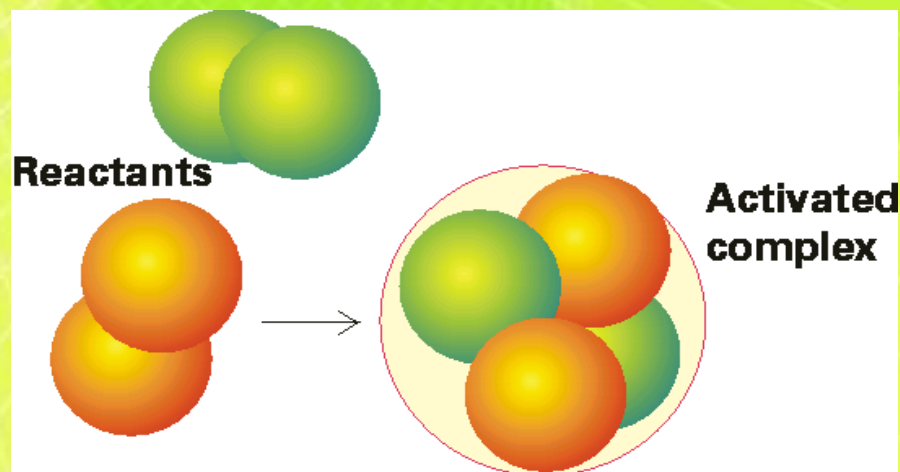
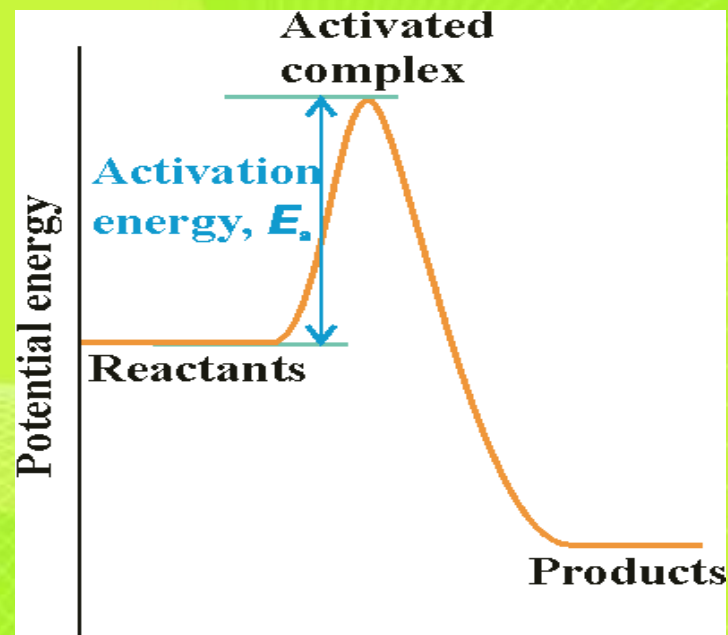


CHEMICAL KINETICS: 2

- Molecularity
- Elementary
- Reaction Mechanism
- Steady-state Approximation



Rate law for elementary reaction

- Law of Mass Action applies:
 - rate of rxn \propto product of active masses of reactants
 - “active mass” molar concentration raised to power of number of species
- Examples:
 - $A \rightarrow P + Q$ rate = $k_1 [A]^1$
 - $A + B \rightarrow C + D$ rate = $k_2 [A]^1 [B]^1$
 - $2A + B \rightarrow E + F + G$ rate = $k_3 [A]^2 [B]^1$

Molecularity of elementary reactions?

- Unimolecular (decay) $A \rightarrow P$

$$-\frac{d[A]}{dt} = k_1[A]$$

- Bimolecular (collision) $A + B \rightarrow P$

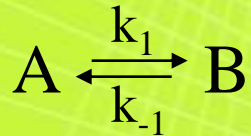
$$-\frac{d[A]}{dt} = k_2[A][B]$$

- Termolecular (collision) $A + B + C \rightarrow P$

$$-\frac{d[A]}{dt} = k_3[A][B][C]$$

- No other are feasible! *Statistically highly unlikely.*

Reversible reactions (small $\Delta_r G$)



Assume first order, elementary rxn in both directions

Rate:
$$-\frac{d[A]}{dt} = k_1[A] - k_{-1}[B]$$

Conservation of Mass:
$$[A]_0 + [B]_0 = [A] + [B]$$

$$[B] = [A]_0 + [B]_0 - [A]$$

$$-\frac{d[A]}{dt} = k_1[A] - k_{-1}([A]_0 + [B]_0 - [A])$$

Integrate:

$$\ln\left(\frac{k_1[A]_t - k_{-1}([A]_0 + [B]_0 - [A]_t)}{k_1[A]_0 - k_{-1}[B]_0}\right) = -(k_1 + k_{-1})t$$



$[A]_0$ $[B]_0$ initial

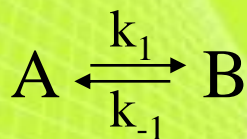
If $[B]_0 = 0$, so:

$$[A]_0 = [A] + [B]$$

If $[B]_0 \neq 0$, so:

$$[A]_0 + [B]_0 = [A] + [B]$$

At equilibrium



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

At equilibrium... $-\frac{d[A]}{dt} = 0 \longrightarrow k_1[A]_{eq} = k_{-1}[B]_{eq}$

The forward rate equals the reverse at equilibrium.

What is the equilibrium constant for this reaction?

$$K_{eq} = \frac{[B]_{eq}}{[A]_{eq}}$$

In terms of rate constants?

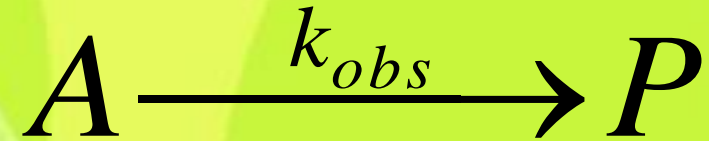
$$K_{eq} = \frac{k_1}{k_{-1}}$$

Reaction Mechanisms

Always remember....

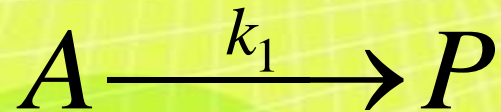
- One can never prove a reaction mechanism, although evidence may disprove a mechanism.
- Verifying proposed mechanisms requires extensive experimental verification of each proposed step!

Let's examine a reaction ...



Reaction could progress in multiple ways... How can we distinguish?

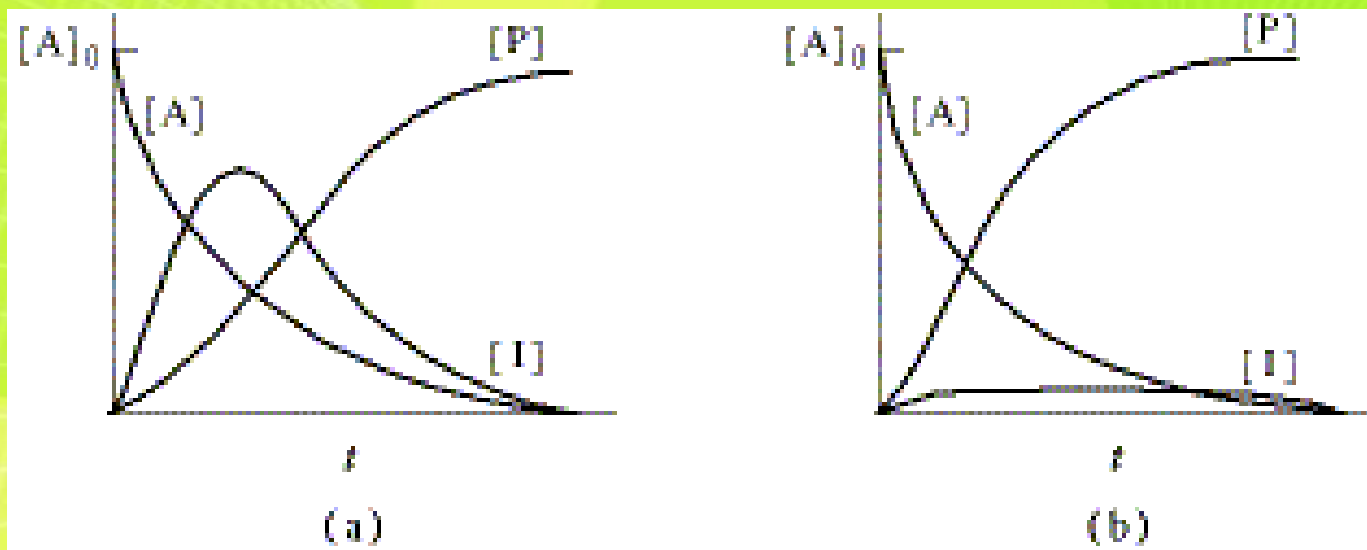
Case 1: One elementary step



Case 2: Two step reaction



let's focus on the intermediate...



How do k_1 and k_2 relate in case a? in case b?

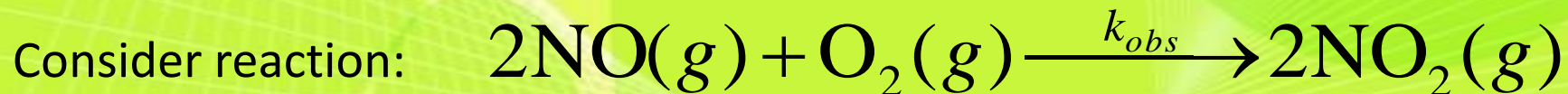
(a) I forms quickly but decays slowly... k_1 is fast relative to k_2 .

(b) I builds up to a constant, nearly negligible, concentration until near end of reaction. ... k_1 is slow relative to k_2 .

$$\frac{d[I]}{dt} \approx 0$$

Steady state approximation... Valid only if $k_2 > k_1$.

Rate Laws do not yield unique mechanisms
An empirically determined rate law does not imply a
unique reaction mechanism!



Experimentally, it was determined that the rate is given by:

$$v(t) = k_{obs}[\text{NO}]^2[\text{O}_2]$$

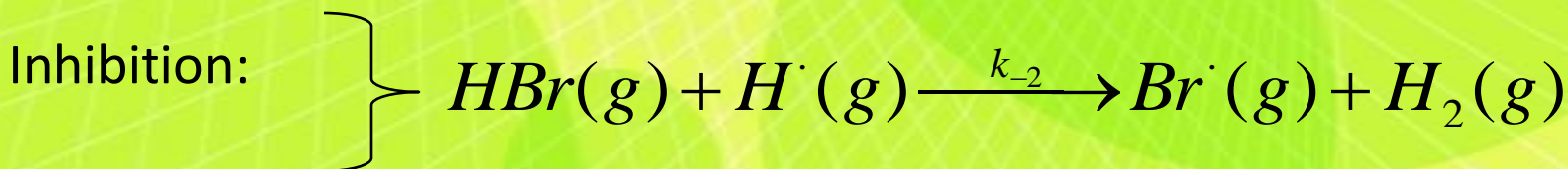
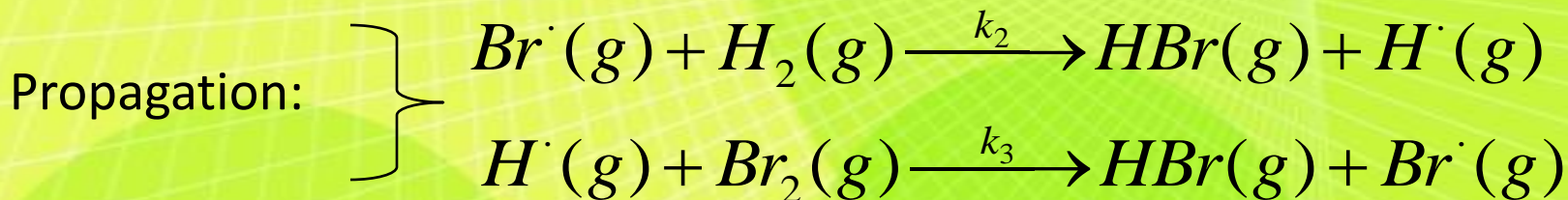
Researchers proposed two possible mechanisms. They need to
determine if one of them is correct.

So how would researchers distinguish between the mechanisms?

Remember the Chain Rxn from CK-6?



Proposed Mechanism



Elementary Reactions and Mechanism

Elementary reactions are steps of molecular events showing how reactions proceed. This type of description is a **mechanism**.

The mechanism for the reaction between CO and NO₂ is proposed to be



Add these two equations led to the overall reaction



A mechanism is a proposal to explain the rate law, and it has to satisfy the rate law. A satisfactory explanation is **not a proof**.

Explain terms in **red**

Molecularity of Elementary Reactions

The total order of rate law in an elementary reaction is **molecularity**.

The rate law of elementary reaction is derived from the equation. The order is the number of reacting molecules because they must collide to react.

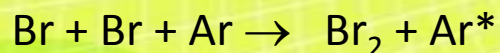
A molecule decomposes by itself is a **unimolecular** reaction (step); two molecules collide and react is a **bimolecular** reaction (step); & three molecules collide and react is a **termolecular** reaction (step).



$$\text{rate} = k [\text{O}_3]$$



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

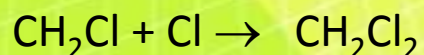
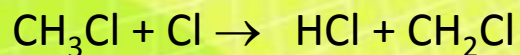
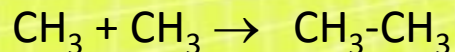
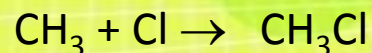
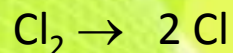


$$\text{rate} = k [\text{Br}]^2[\text{Ar}]$$

Caution: Derive rate laws this way **only** for **elementary** reactions.

Molecularity of elementary reactions - Example

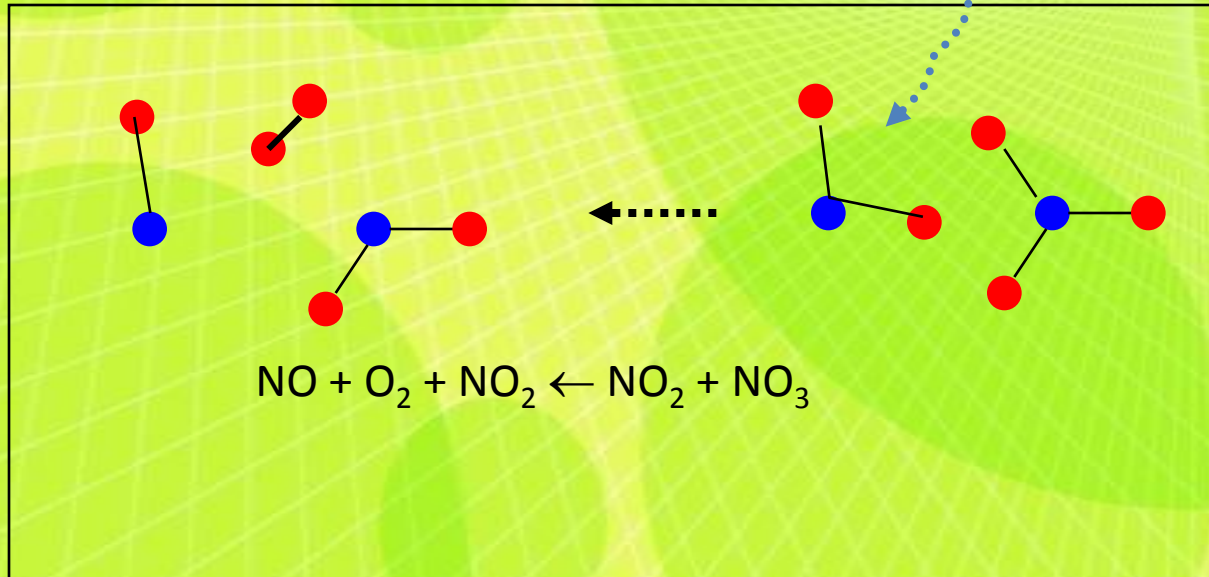
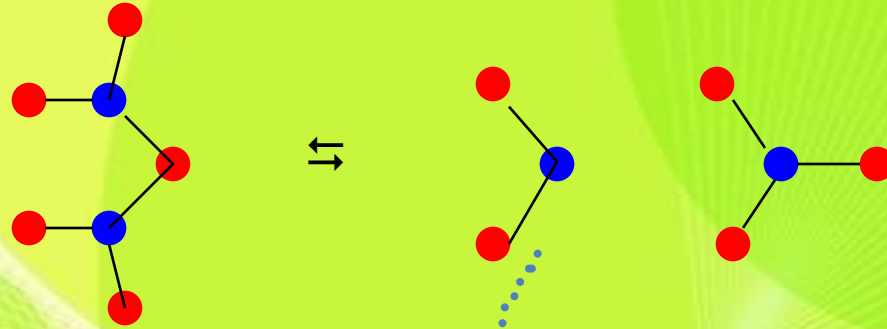
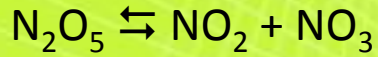
Some elementary reactions for the reaction between CH_4 and Cl_2 are



* * * (more)

Write down the rate laws and describe them as uni- bi- or ter-molecular steps yourself, please.

Elementary Reactions are Molecular Events



Explain differences between elementary and over reaction equations

Rate Laws and Mechanisms

A **mechanism** is a collection of elementary steps devised to explain the reaction in view of the observed rate law. You need the skill to derive a rate law from a mechanism, but proposing a mechanism is a task after you have learned more chemistry.

For the reaction, $2 \text{NO}_2 (\text{g}) + \text{F}_2 (\text{g}) \rightarrow 2 \text{NO}_2\text{F} (\text{g})$, the rate law is,

$$\text{rate} = k [\text{NO}_2] [\text{F}_2].$$

Can the elementary reaction be the same as the overall reaction?

If they were the same the rate law would have been

$$\text{rate} = k [\text{NO}_2]^2 [\text{F}_2],$$

Therefore, the overall reaction is not an elementary reaction. Its mechanism is proposed next.

Rate-determining Step in a Mechanism

The **rate determining step** is the slowest elementary step in a mechanism, and the rate law for this step is the rate law for the overall reaction.

The (determined) rate law is, $rate = k [NO_2] [F_2]$,
for the reaction, $2 NO_2 (g) + F_2 (g) \rightarrow 2 NO_2F (g)$,
and a two-step mechanism is proposed:

- i $NO_2 (g) + F_2 (g) \rightarrow NO_2F (g) + F (g)$
- ii $NO_2 (g) + F (g) \rightarrow NO_2F (g)$

Which is the rate determining step?

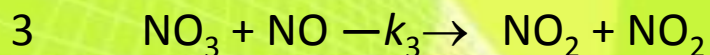
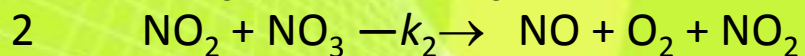
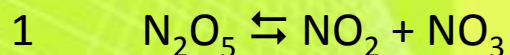
Answer:

The rate for step i is $rate = k [NO_2] [F_2]$, which is the rate law, this suggests that step i is the rate-determining or the s-l-o-w step.

Explain rate determining step in a mechanism and use it to derive the rate law.

Deriving a rate law from a mechanism - 3

The decomposition of N_2O_5 follows the mechanism:



fast equilibrium

slow

fast

Derive the rate law.

Solution:

The slow step determines the rate,

$$\text{rate} = k_2 [\text{NO}_2] [\text{NO}_3]$$

From 1, we have

$$\frac{[\text{NO}_2] [\text{NO}_3]}{[\text{N}_2\text{O}_5]} = K$$

Thus, rate = $K k_2 [\text{N}_2\text{O}_5]$

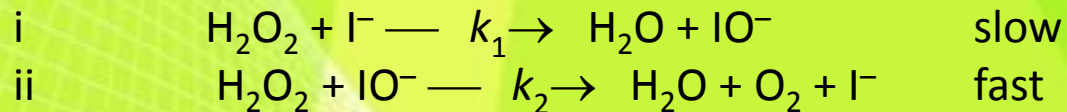
NO_2 & NO_3 are **intermediate**

K , **equilibrium constant**

K differ from k

Deriving a Rate Law From a Mechanism - 0

The decomposition of H_2O_2 in the presence of I^- follow this mechanism,



What is the rate law?

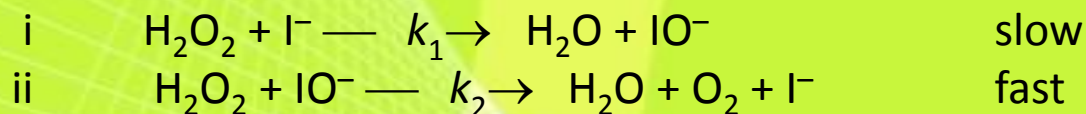
Energy



Solve the problem

Deriving a rate law from a mechanism - 1

The decomposition of H_2O_2 in the presence of I^- follow this mechanism,



What is the rate law?

Solution

The slow step determines the rate, and the rate law is:

$$\text{rate} = k_1 [\text{H}_2\text{O}_2] [\text{I}^-]$$

Since both $[\text{H}_2\text{O}_2]$ and $[\text{I}^-]$ are measurable in the system, this is the rate law.

Deriving a rate law from a mechanism - 2

Derive the rate law for the reaction, $\text{H}_2 + \text{Br}_2 = 2 \text{HBr}$,

from the proposed mechanism:

- i $\text{Br}_2 \rightleftharpoons 2 \text{Br}$
- ii $\text{H}_2 + \text{Br} \xrightarrow{k_2} \text{HBr} + \text{H}$
- iii $\text{H} + \text{Br} \xrightarrow{k_3} \text{HBr}$

Solution:

The fast equilibrium condition simply says that

$$k_1 [\text{Br}_2] = k_{-1} [\text{Br}]^2$$

and $[\text{Br}] = (k_1/k_{-1} [\text{Br}_2])^{1/2}$

The slow step determines the rate law,

$$\begin{aligned} \text{rate} &= k_2 [\text{H}_2] [\text{Br}] \\ &= k_2 [\text{H}_2] (k_1/k_{-1} [\text{Br}_2])^{1/2} \\ &= k [\text{H}_2] [\text{Br}_2]^{1/2}; \end{aligned}$$

total order 1.5

fast equilibrium (k_1, k_{-1})

slow

fast

explain

Br is an intermediate

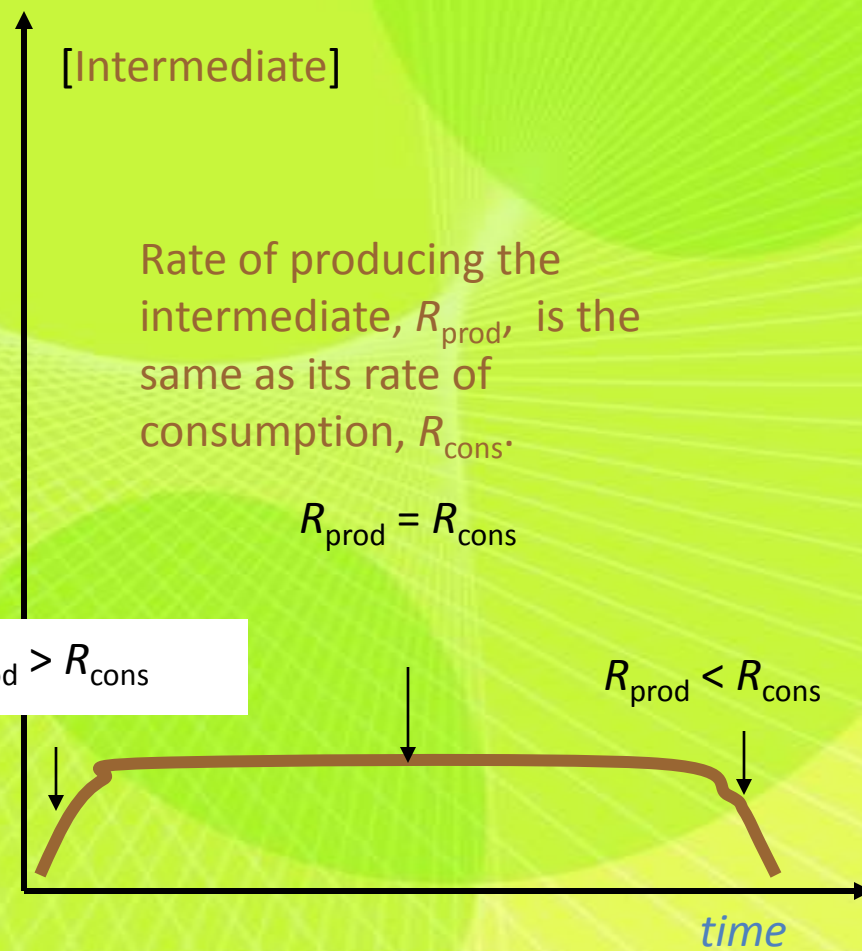
$$k = k_2 (k_1/k_{-1})^{1/2} \text{ M}^{-1/2} \text{ s}^{-1}$$

Deriving rate laws from mechanisms – steady-state approximation

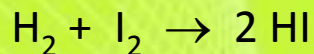
The steady-state approximation is a general method for deriving rate laws when the relative speed cannot be identified.

It is based on the assumption that the concentration of the intermediate is constant.

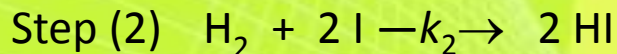
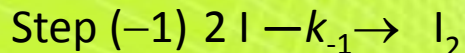
Be able to apply the steady-state approximation to derive rate laws



Let's assume the mechanism for the reaction.



as follows.



Derive the rate law.

Derivation:

$$\text{rate} = k_2 [\text{H}_2] [\text{I}]^2 \text{ ('cause this step gives products)}$$

but I is an **intermediate**, this is not a rate law yet.

$$\begin{aligned} \text{Since} \quad k_1 [\text{I}_2] & \quad (= \text{rate of producing I}) \\ & = k_{-1} [\text{I}]^2 + k_2 [\text{H}_2] [\text{I}]^2 \quad (= \text{rate of consuming I}) \end{aligned}$$

$$\begin{aligned} \text{Thus,} \\ [\text{I}]^2 & = \frac{k_1 [\text{I}_2]}{k_{-1} + k_2 [\text{H}_2]} \end{aligned}$$

$$\therefore \text{rate} = k_1 k_2 [\text{H}_2] [\text{I}_2] / \{k_{-1} + k_2 [\text{H}_2]\}$$

Steady-state approximation -

2

Steady state

Steady-state approximation - 3

From the previous result:

$$\text{rate} = \frac{k_1 k_2 [\text{H}_2] [\text{I}_2]}{\{k_{-1} + k_2 [\text{H}_2]\}}$$

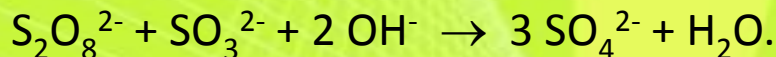
Discussion:

(i) If $k_{-1} \ll k_2 [\text{H}_2]$ then $\{k_{-1} + k_2 [\text{H}_2]\} = k_2 [\text{H}_2]$,
then $\text{rate} = k_1 k_2 [\text{H}_2] [\text{I}_2] / \{k_2 [\text{H}_2]\} = k_1 [\text{I}_2]$ (pseudo 1st order wrt I_2)
using large concentration of H_2 or step 2 is fast (will meet this condition).

(ii) If step (2) is slow, then $k_2 \ll k_{-1}$,
and if $[\text{H}_2]$ is not large, we have $\{k_{-1} + k_2 [\text{H}_2]\} = k_{-1}$
and $\text{rate} = k_1 k_2 [\text{H}_2] [\text{I}_2] / k_{-1} = k_2 [\text{H}_2] [\text{I}_2]$

Steady-state approximation - 4

In an alkaline solution, peroxydisulfate oxidizes sulfite to yield sulfate,



The following mechanism has been proposed:

- i $\text{S}_2\text{O}_8^{2-} + \text{SO}_3^{2-} \xrightarrow{-k_1} \text{S}_2\text{O}_7^{2-} + \text{SO}_4^{2-}$
- ii $\text{S}_2\text{O}_7^{2-} + \text{H}_2\text{O} \xrightarrow{-k_2} 2 \text{SO}_4^{2-} + 2 \text{H}^+$
- iii $\text{H}^+ + \text{OH}^- \xrightarrow{-k_3} \text{H}_2\text{O}$ (fast equilibrium to be discussed)

Steady-state approximation follows these steps:

What is or are the intermediates I?

Use which step to give the rate law that may involve [I]?

Express the *rates* of producing and consuming intermediate(s)

Express [I] of intermediate(s) in terms of [Reactants]

Derive the rate law in terms of [Reactants]

Discuss

See page 607 PHH Text

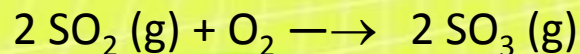
Catalysis

A **catalyst** is a substance that changes the *rate of a reaction* by lowering the activation energy, E_a . It participates a reaction in forming an intermediate, but is regenerated.

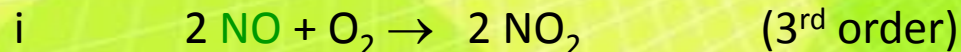
Enzymes are marvelously **selective catalysts**.

A catalyzed reaction,

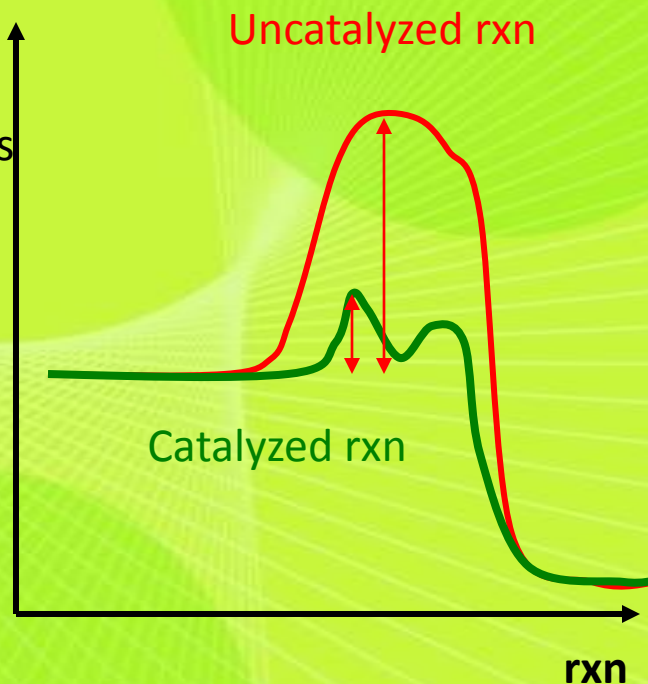
NO (catalyst)



via the mechanism



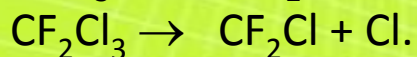
Energy



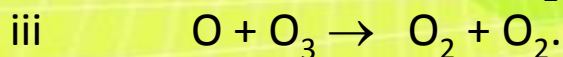
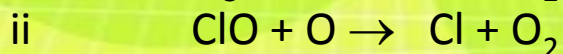
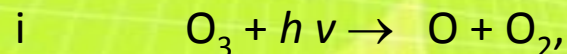
Catalyzed decomposition of ozone

R.J. Plunkett in DuPont discovered carbon fluorine chlorine compounds.

The CFC decomposes in the atmosphere:



The Cl catalyzes the reaction via the mechanism:



The net result or reaction is



Scientists sound the alarm, and the CFC is banned now.

Homogenous vs. heterogeneous catalysts

A catalyst in the same phase (gases and solutions) as the reactants is a **homogeneous catalyst**. It is effective, but recovery is difficult.

When the catalyst is in a different phase than reactants (and products), the process involves **heterogeneous catalysis**. Chemisorption, absorption, and adsorption cause reactions to take place via different pathways.

Platinum is often used to catalyze hydrogenation

Catalytic converters reduce CO and NO emission.

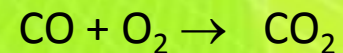
Heterogeneous catalysts

Ceryx's vision is to design, produce, and commercialize advanced systems that balance Cost, Performance, Emissions Reduction, and Fuel Penalty to make the economics of pollution control viable.

We explore new ways to look at the air quality challenges faced by industry and search for potential solutions by combining proven technologies with state-of-the-art science.



Catalyzed reactions:

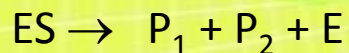




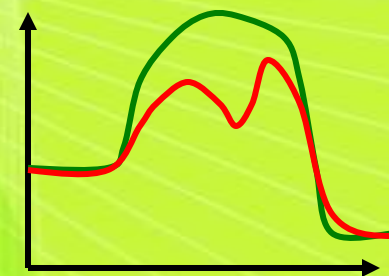
Enzymes – selective catalysts

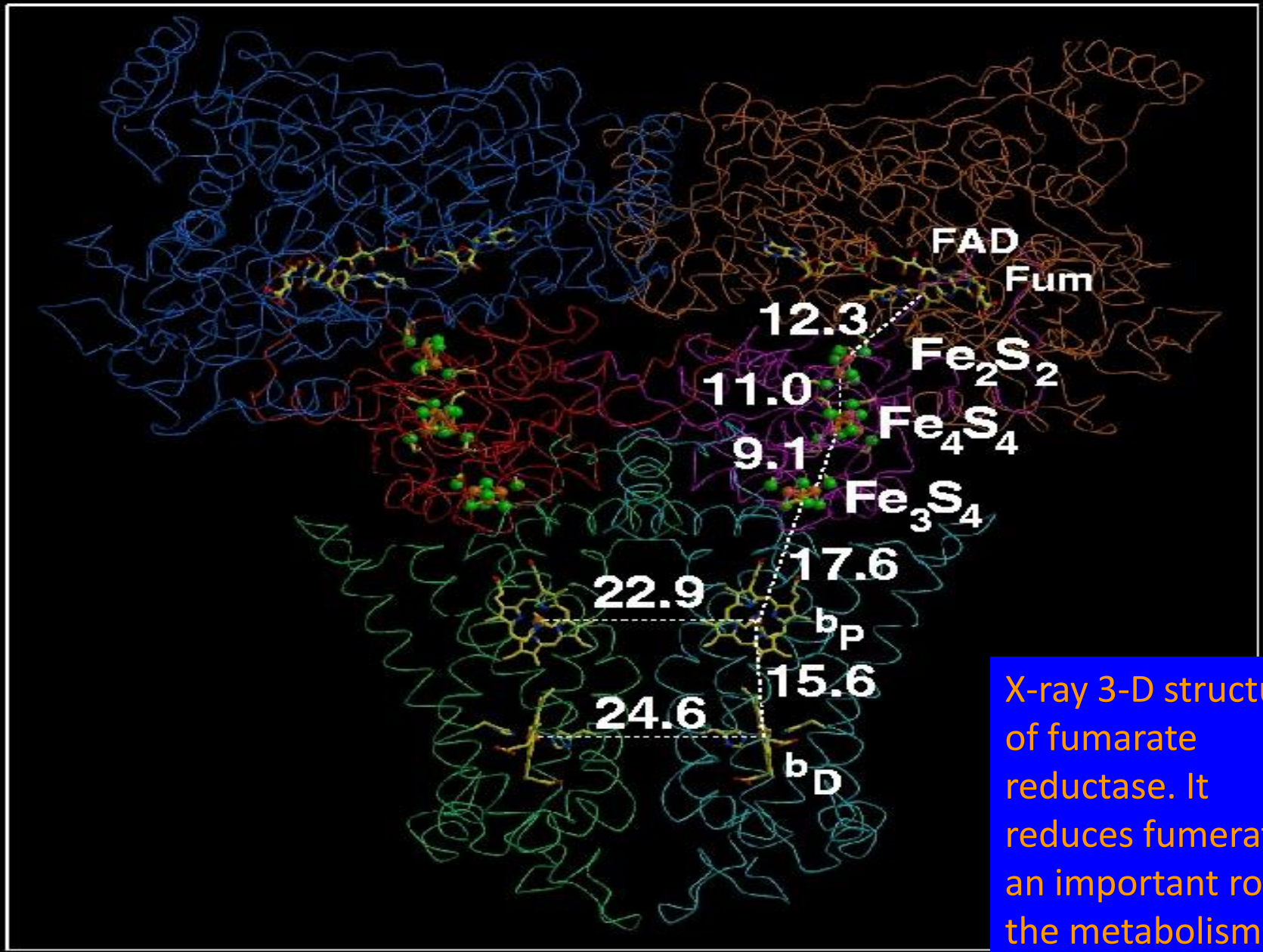
Enzymes are a long protein molecules that fold into balls. They often have a metal coordinated to the O and N sites.

Molecules catalyzed by enzymes are called **substrates**. They are held by various sites (together called the **active site**) of the enzyme molecules and just before and during the reaction. After having reacted, the products P_1 & P_2 are released.



Enzymes are biological catalysts for biological systems.





X-ray 3-D structure of fumarate reductase. It reduces fumarate, an important role in the metabolism of anaerobic bacteria,

Chemical Kinetics - Summary

Explain how the various factors affect reaction rates.

Define reaction rates, average rates, initial rates and rate constants.

Evaluate rate law from experiments

Properly apply 1st and 2nd differential rate laws and integrated rate laws.

Interpret elementary reactions and mechanisms. Derive rate laws from a given mechanism. Apply the steady-state method to derive the rate law of a given mechanism, and discuss the results.

Explain the action of catalysts in terms of chemistry and in terms of energy of activation.