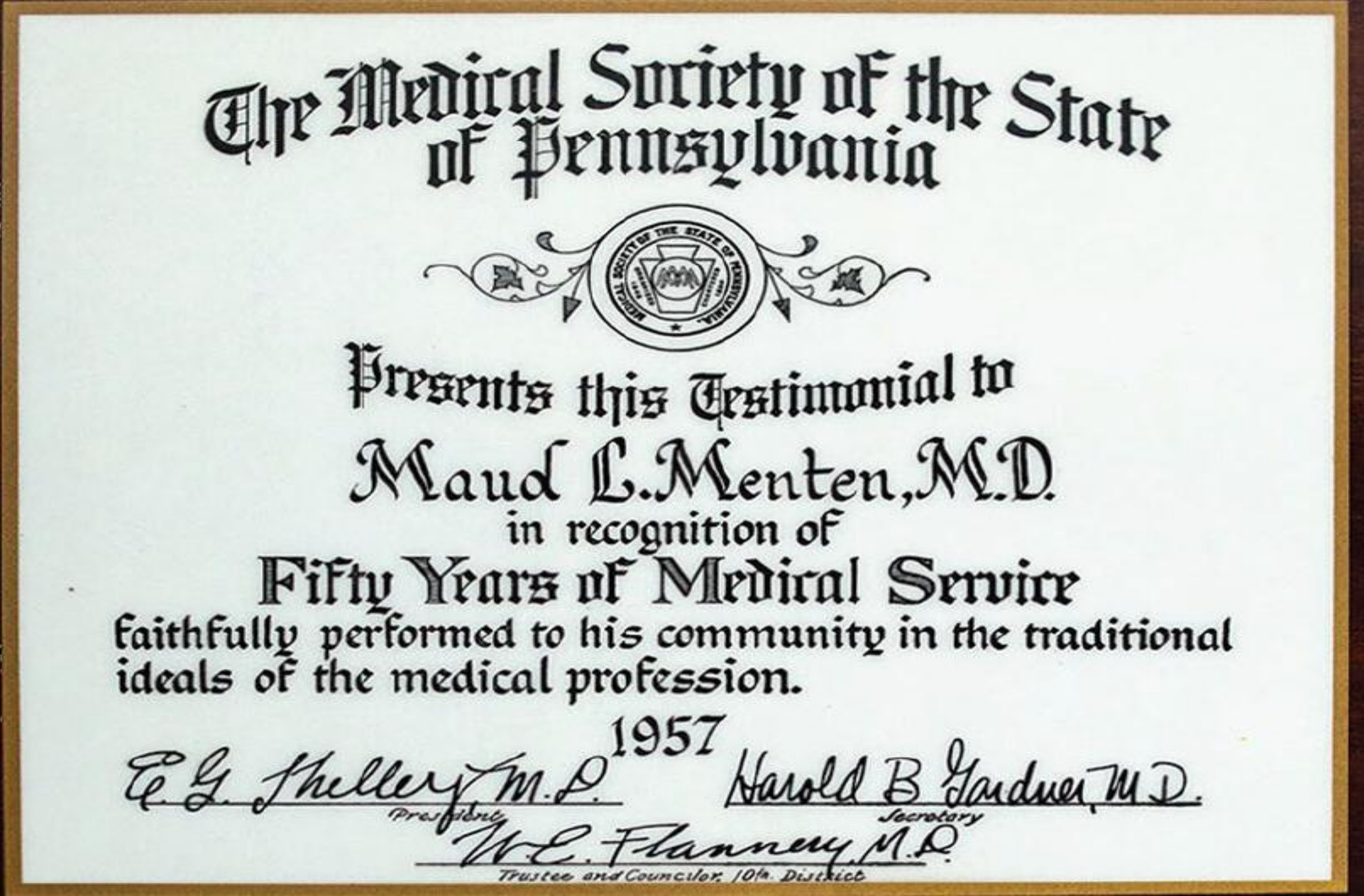


The Medical Society of the State of Pennsylvania

Presents this Testimonial to

Maud L. Menten, M.D.

in recognition of

Fifty Years of Medical Service

faithfully performed to his community in the traditional ideals of the medical profession.

1957

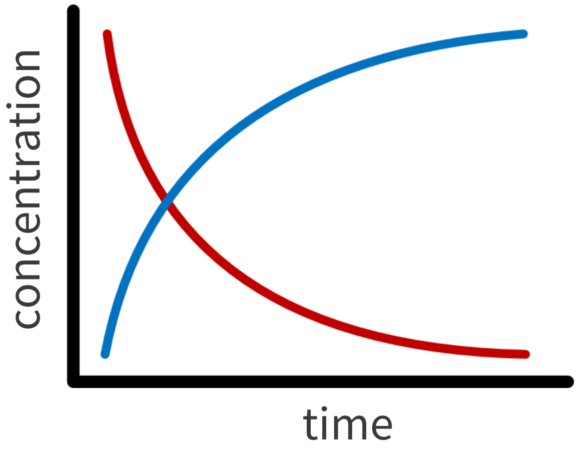
E. G. Shelley, M.D.
President

Harold B. Gardner, M.D.
Secretary

W. E. Flannery, M.D.
Trustee and Councilor, 10th District

Previously on Chemical Kinetics...

We need a function that depends only on the concentration of the reactants to describe how the rate changes with time



⚠

$$\boxed{r = -\frac{1}{\xi_R}\frac{d[\mathrm{Reactant}]}{dt} = k[\mathrm{A}]^{\alpha}[\mathrm{B}]^{\beta}}$$

$$k(T, pH, I, etc...)$$

α, β ≡ orders with respect to substances A and B
α + β ≡ overall order

Order 0

$$\frac{r}{[\mathrm{A}]^0} = k \quad (\mathrm{M\,s^{-1}})$$

Order 1

$$\frac{r}{[\mathrm{A}]} = k \quad (\mathrm{s^{-1}})$$

Order 2

$$\frac{r}{[\mathrm{A}][\mathrm{B}]} = k \quad (\mathrm{M^{-1}\,s^{-1}})$$

Order 3

$$\frac{r}{[\mathrm{A}][\mathrm{B}]^2} = k\,(\mathrm{M^{-2}\,s^{-1}})$$

Rate-determining step

Overall reaction

$$2\,NO_2(g) + F_2(g) \rightarrow 2\,NO_2F(g)$$

Elementary Steps

Slow 1. $NO_2 + F_2 \rightarrow NO_2F + F$ *Bimolecular: two molecules collide*

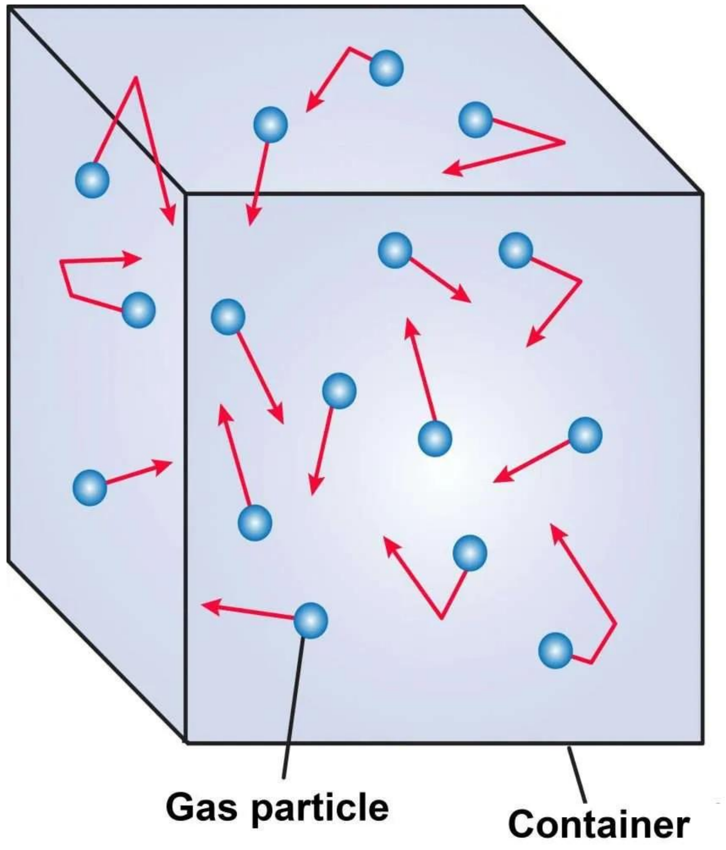
Fast 2. $NO_2 + F \rightarrow NO_2F$ *Bimolecular: uses the F atom produced in step 1*

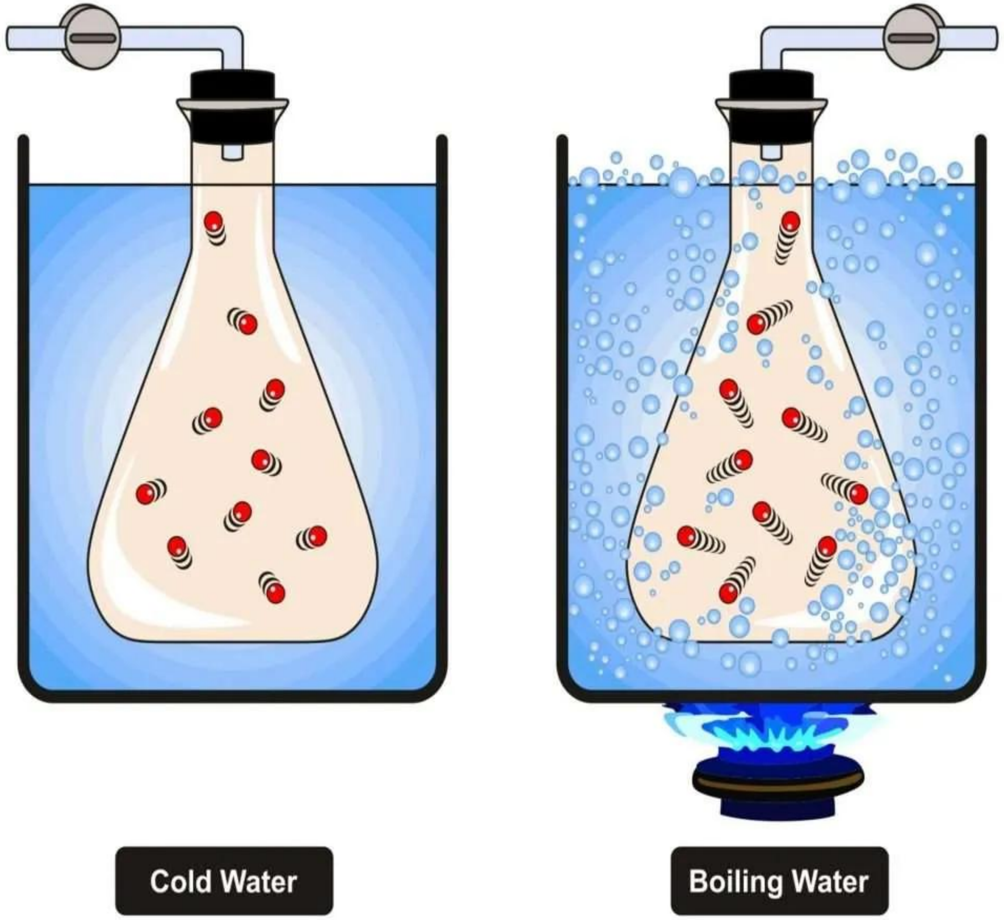
The rate-determining step is the slowest step in a reaction mechanism. It acts as a "bottleneck" that limits the overall reaction rate.

$$r = k[NO_2][F_2]$$

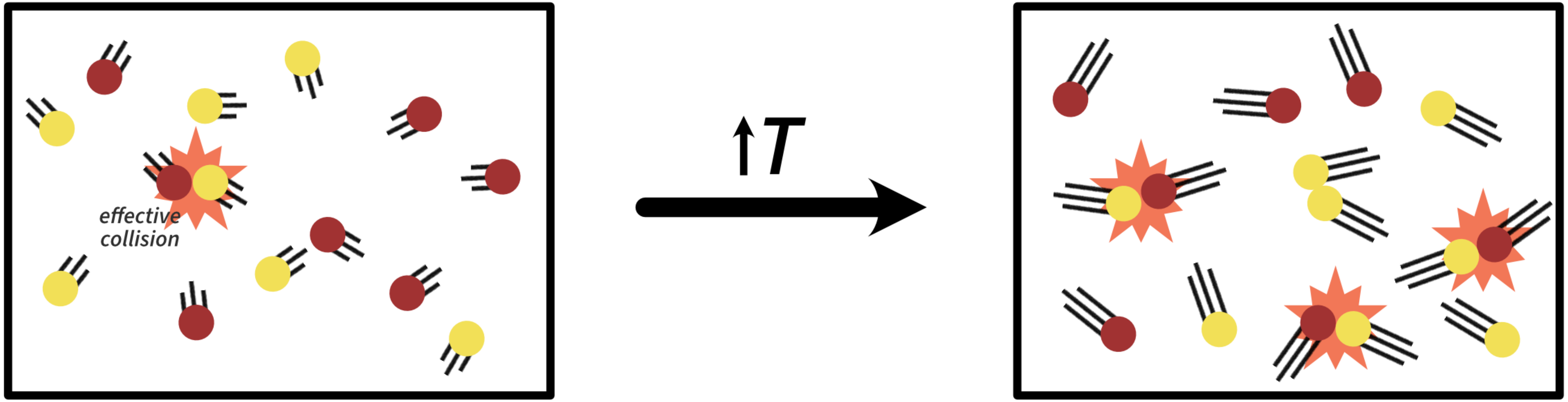
This is our proposed reaction mechanism. If we carry out the experiment and find that the reaction is first order with respect to NO_2 and first order with respect to F_2, then all we can conclude is that the rate law predicted by the mechanism is consistent with the experimental results.

Statistical mechanics

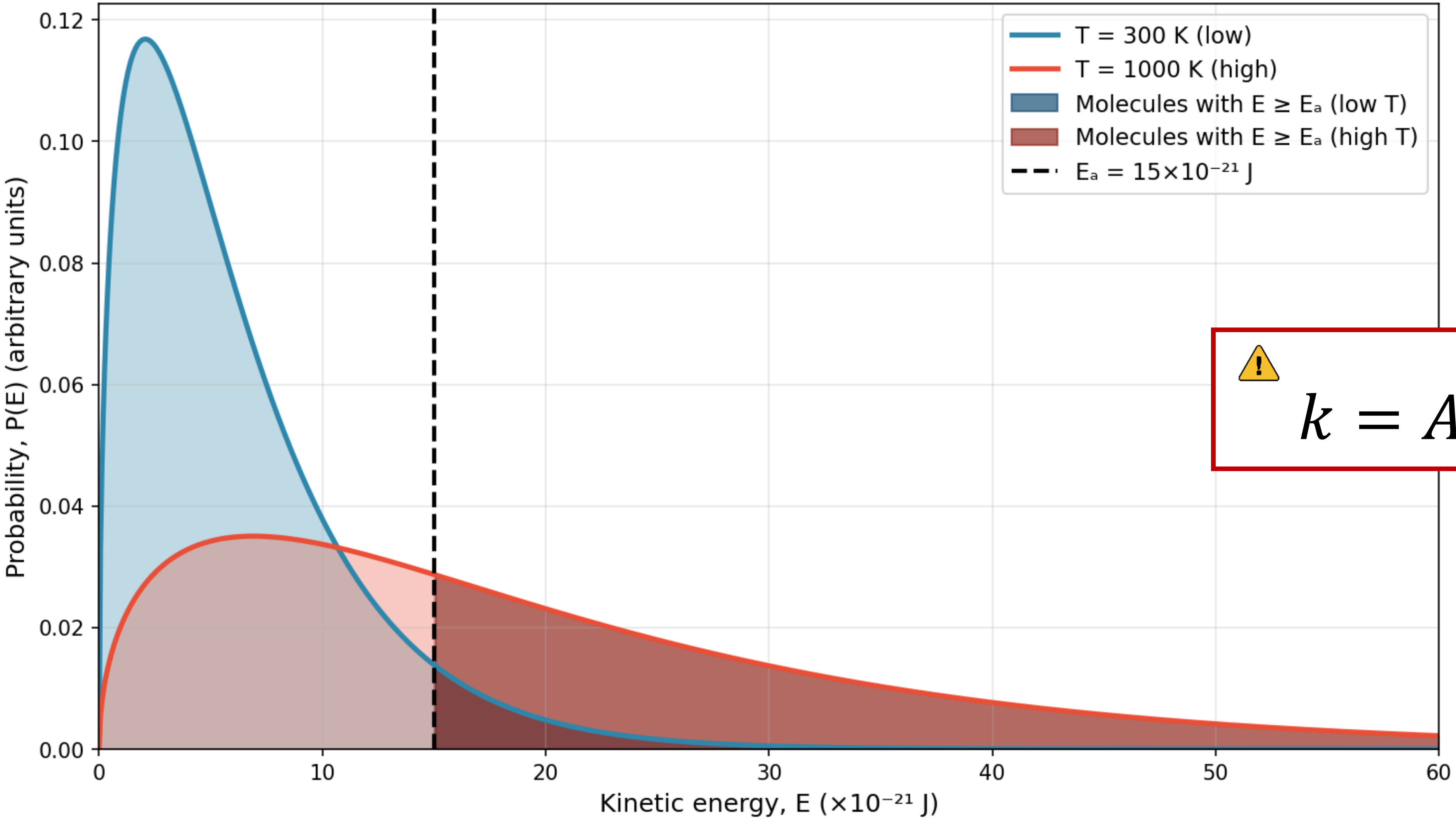




Collision theory of chemical reactions



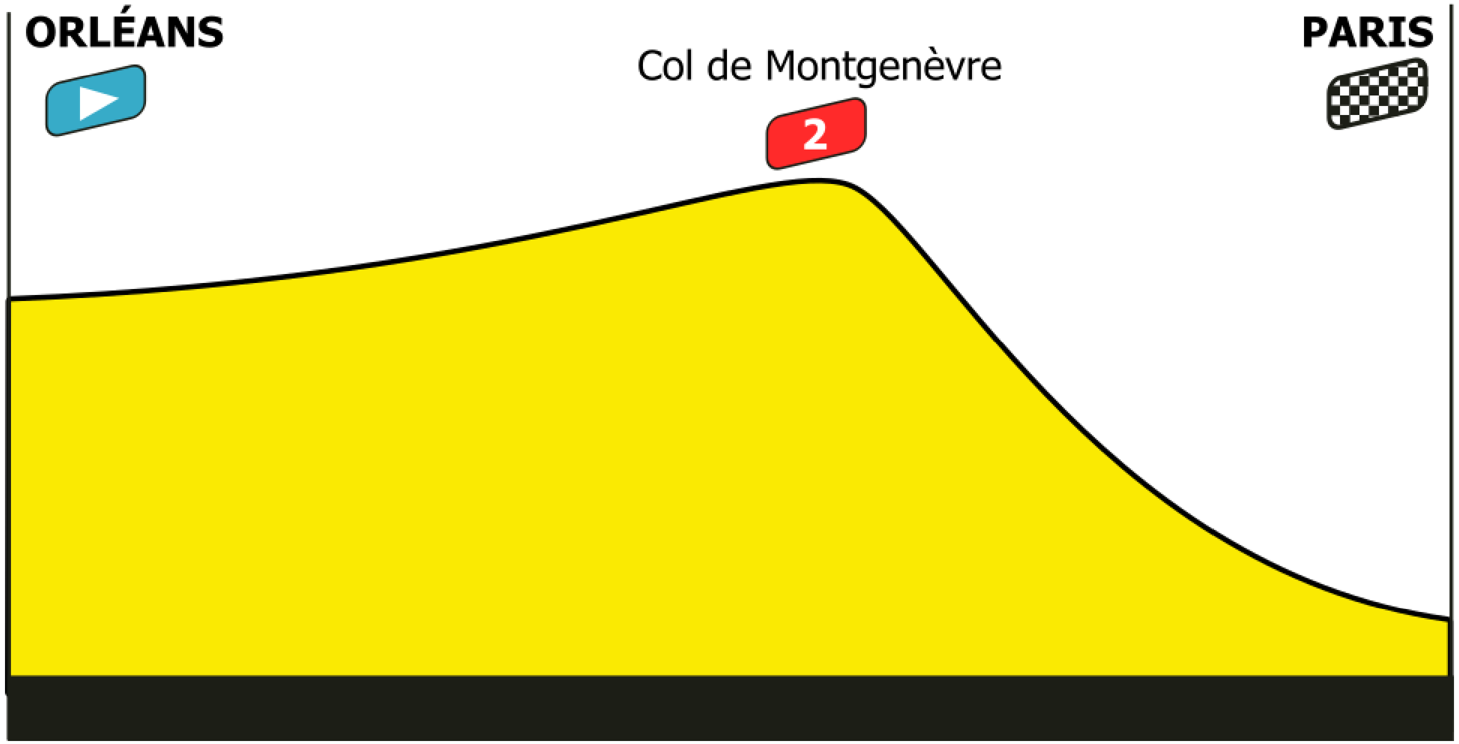
Activation Energy: Arrhenius equation



⚠

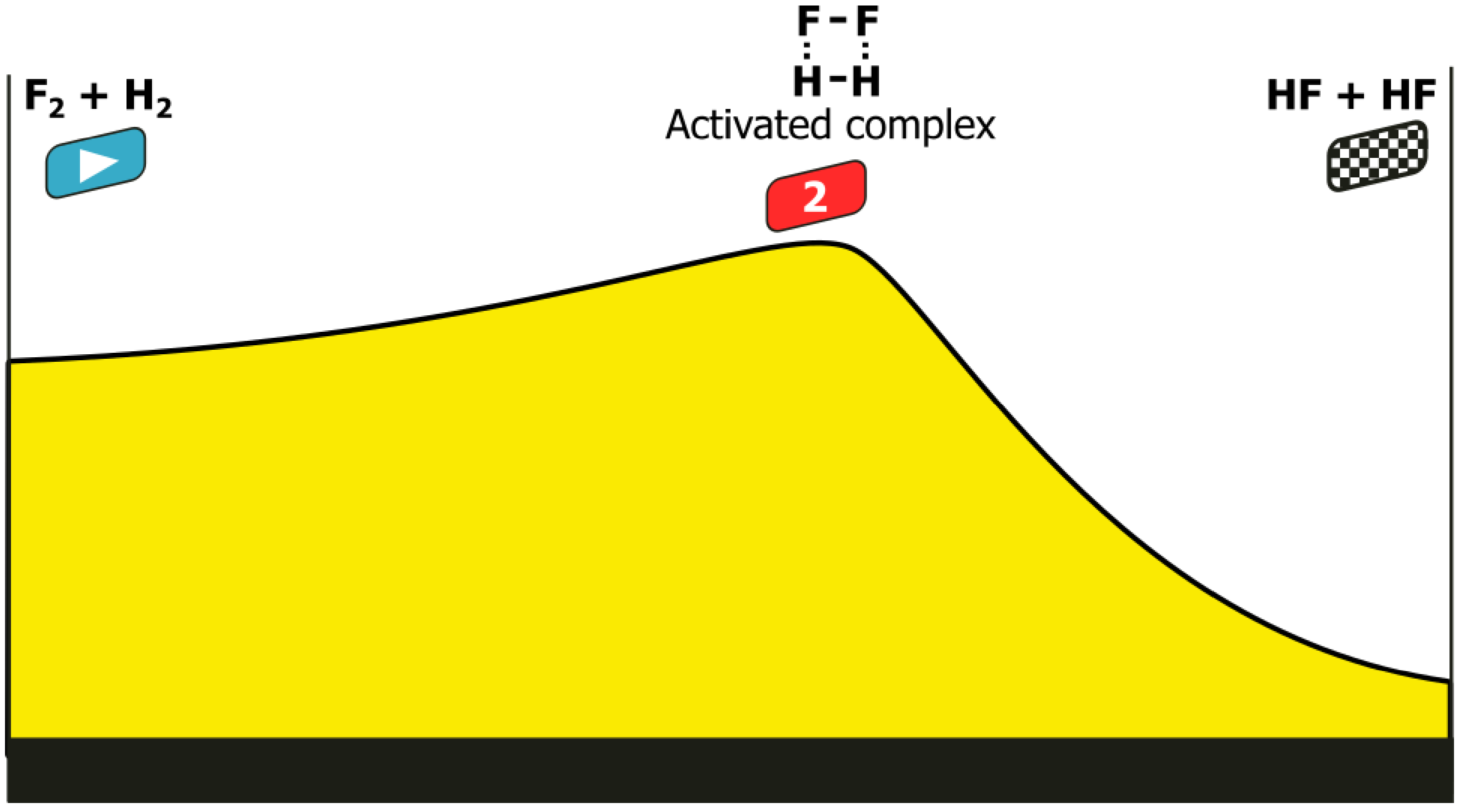
$$k = Ae^{-\frac{E_a}{RT}}$$

Understanding the activation energy



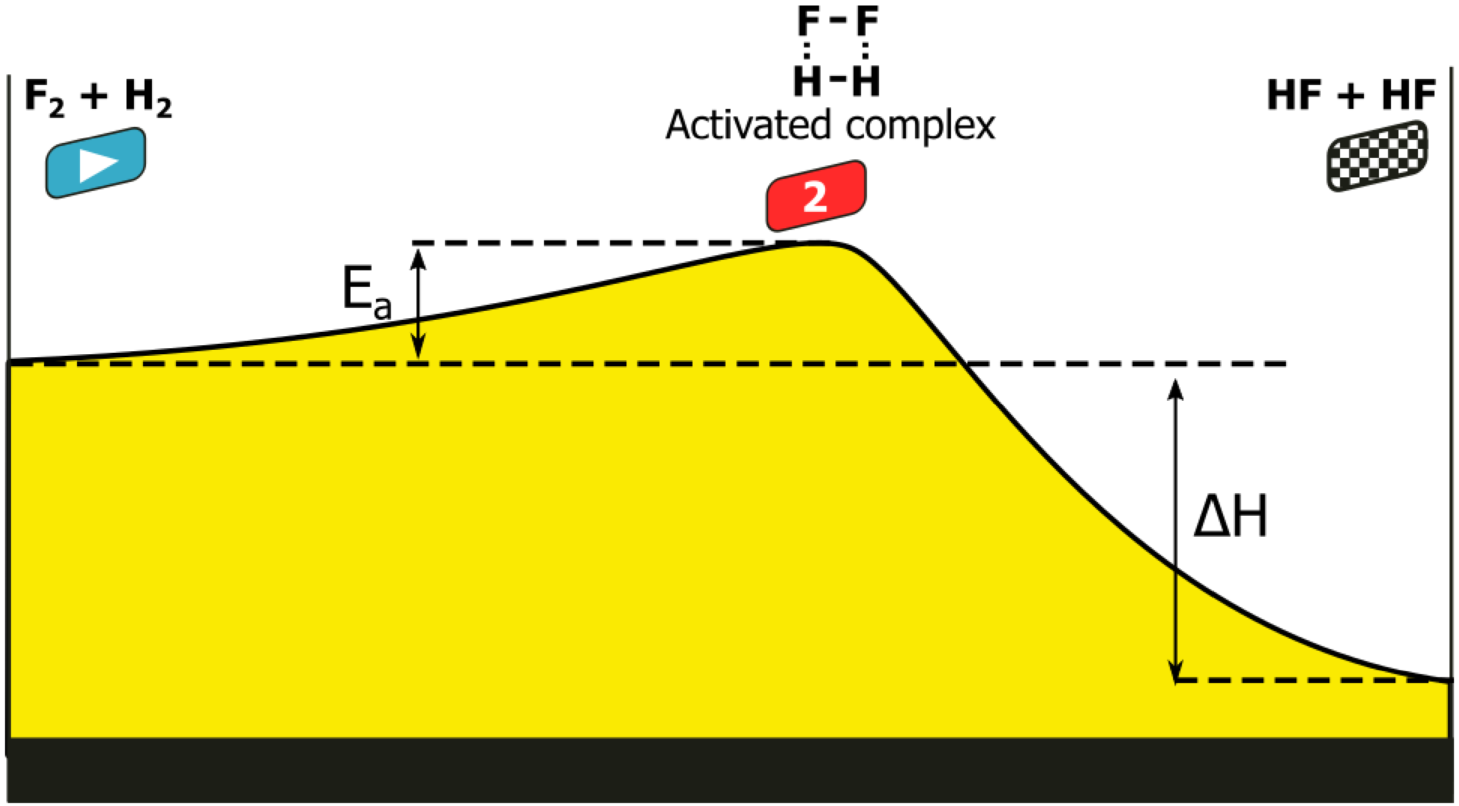
Elevation Profile and Potential Energy of a Tour of France Stage

Understanding the activation energy



Reaction Coordinate Diagram for HF Formation

Understanding the activation energy



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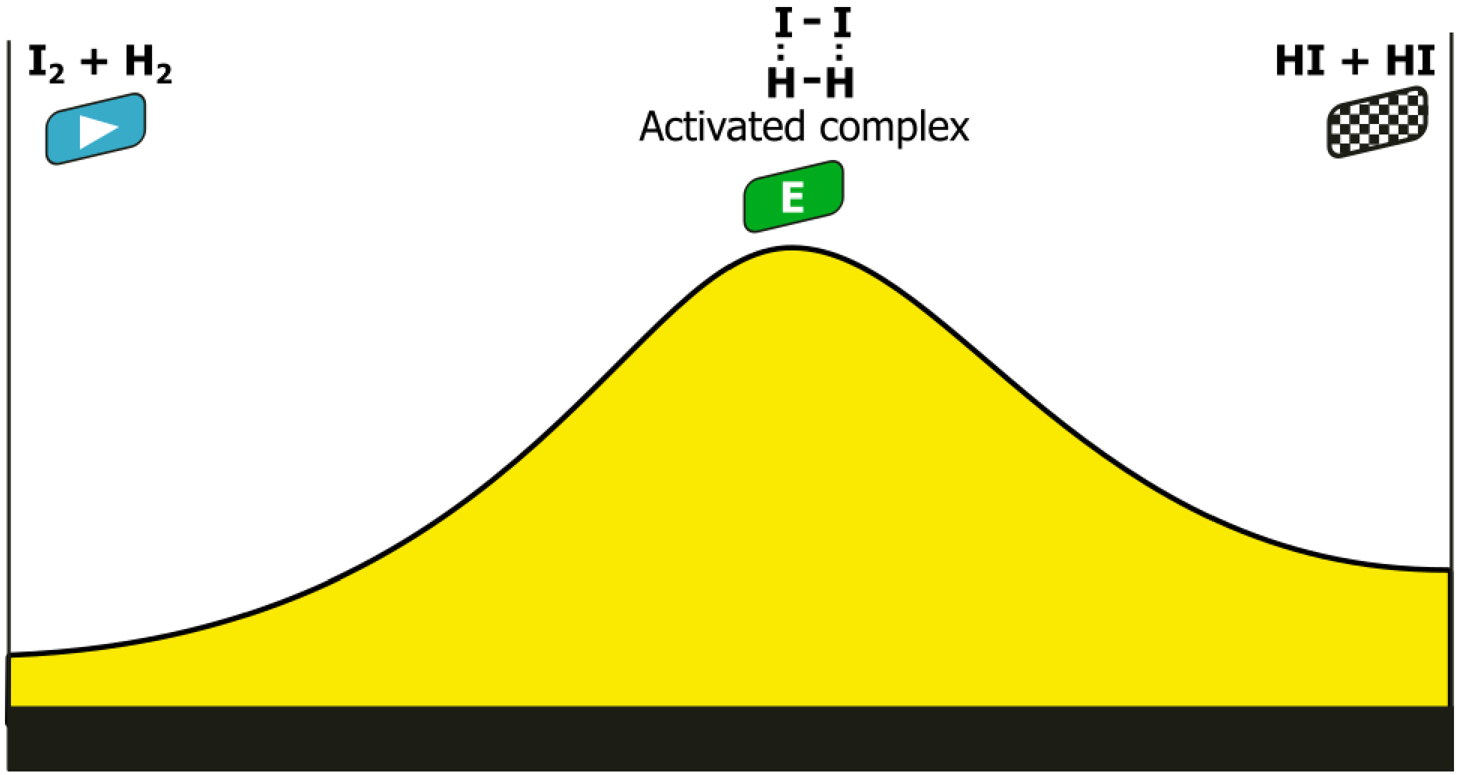

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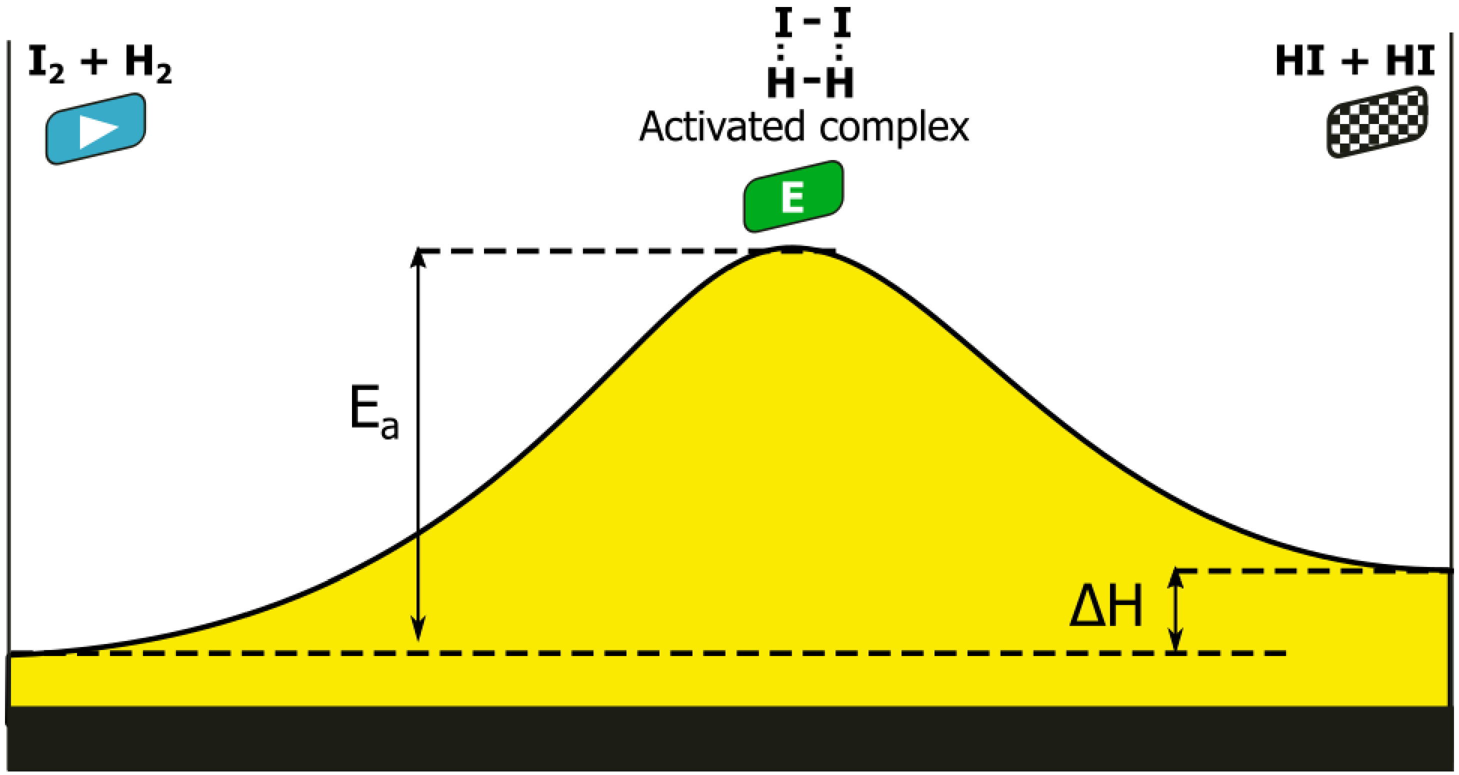


Reaction Coordinate Diagram for HI Formation

Challenge question

For the reaction of formation of hydrogen iodide from its elements at 400 °C, the activation energy is 172 kJ mol^{-1}. Calculate the increase in the reaction rate when the temperature is raised from 400 °C to 500 °C.

⚠

$$\boxed{k = Ae^{-\frac{E_a}{RT}}}$$

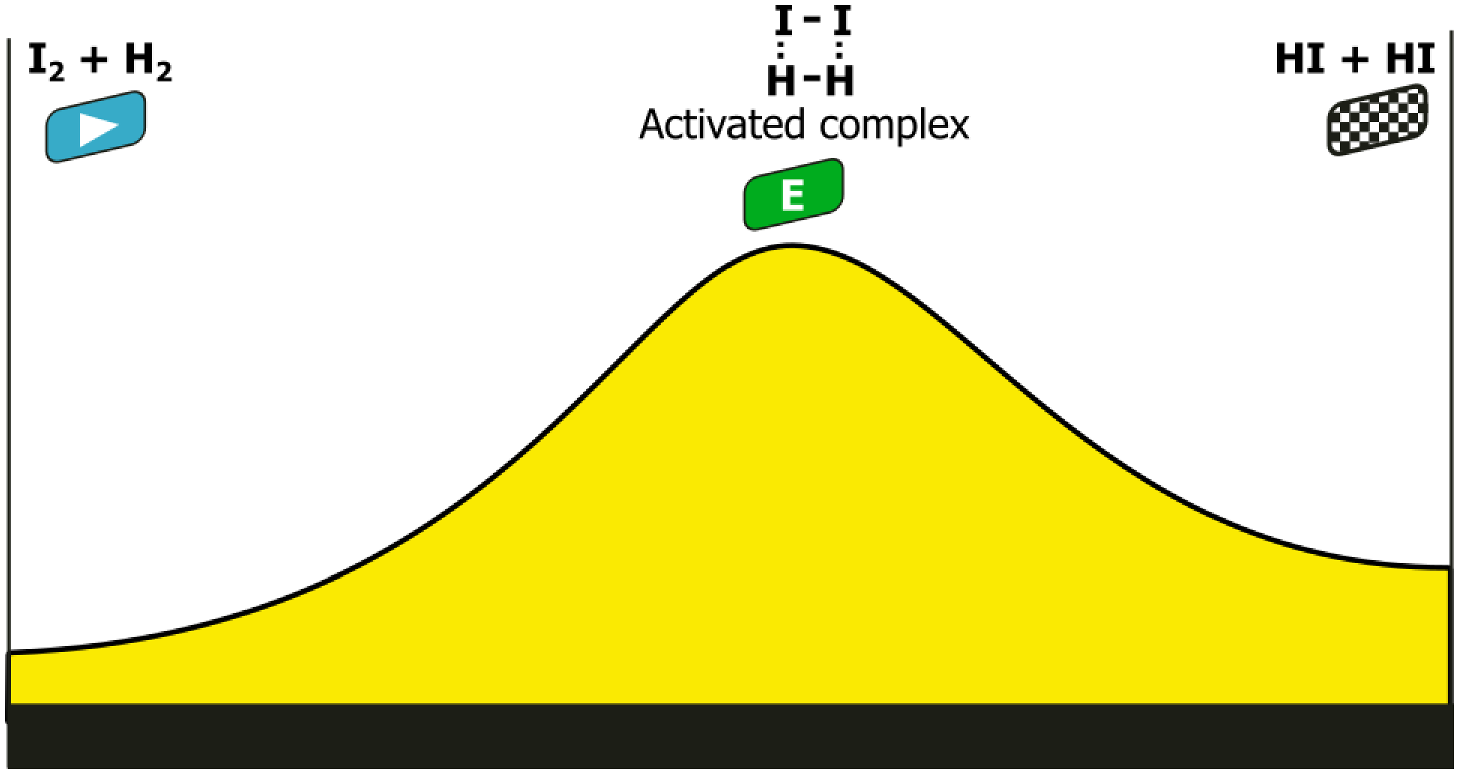
$$\ln\left(\frac{k_2}{k_1}\right) = \frac{E_a}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)$$

$$\ln\left(\frac{k_2}{k_1}\right) = \frac{172000}{8.314}\left(\frac{1}{673.15} - \frac{1}{773.15}\right)$$

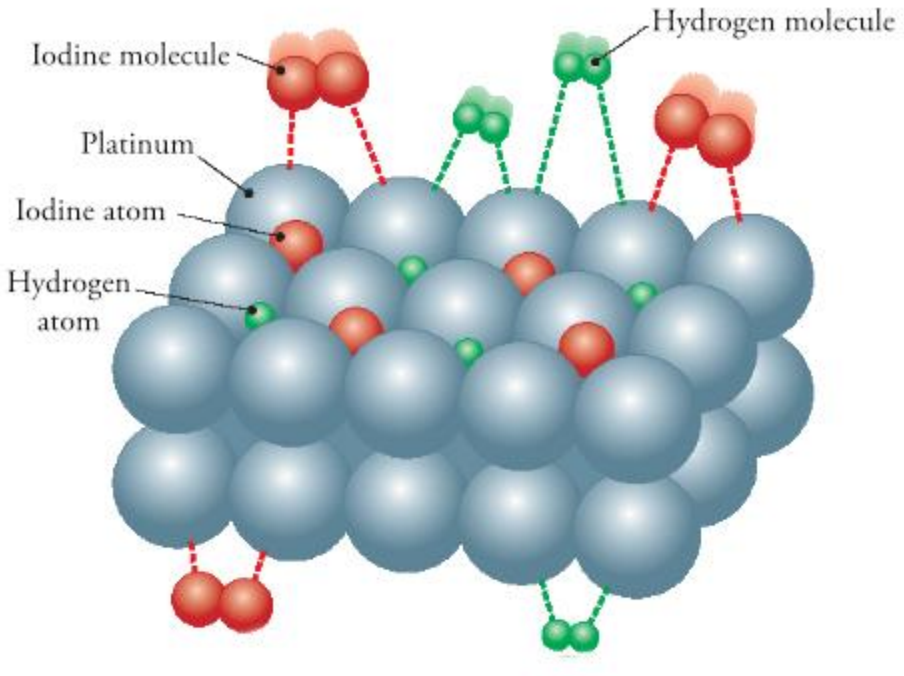
$$\ln\left(\frac{k_2}{k_1}\right) = 20687.5 \times 1.922 \times 10^{-4} = 3.976$$

$$\boxed{\frac{k_2}{k_1} = e^{3.976} \approx 53.3}$$

Catalysis: A Different Route to Faster Reactions



Surface Catalysis through adsorption



H_2 and I_2 molecules a**D**sorb onto the platinum surface, where their bonds weaken and dissociate into atoms. The adsorbed H and I atoms then migrate across the surface, react to form HI and desorb from the surface as HI molecules.

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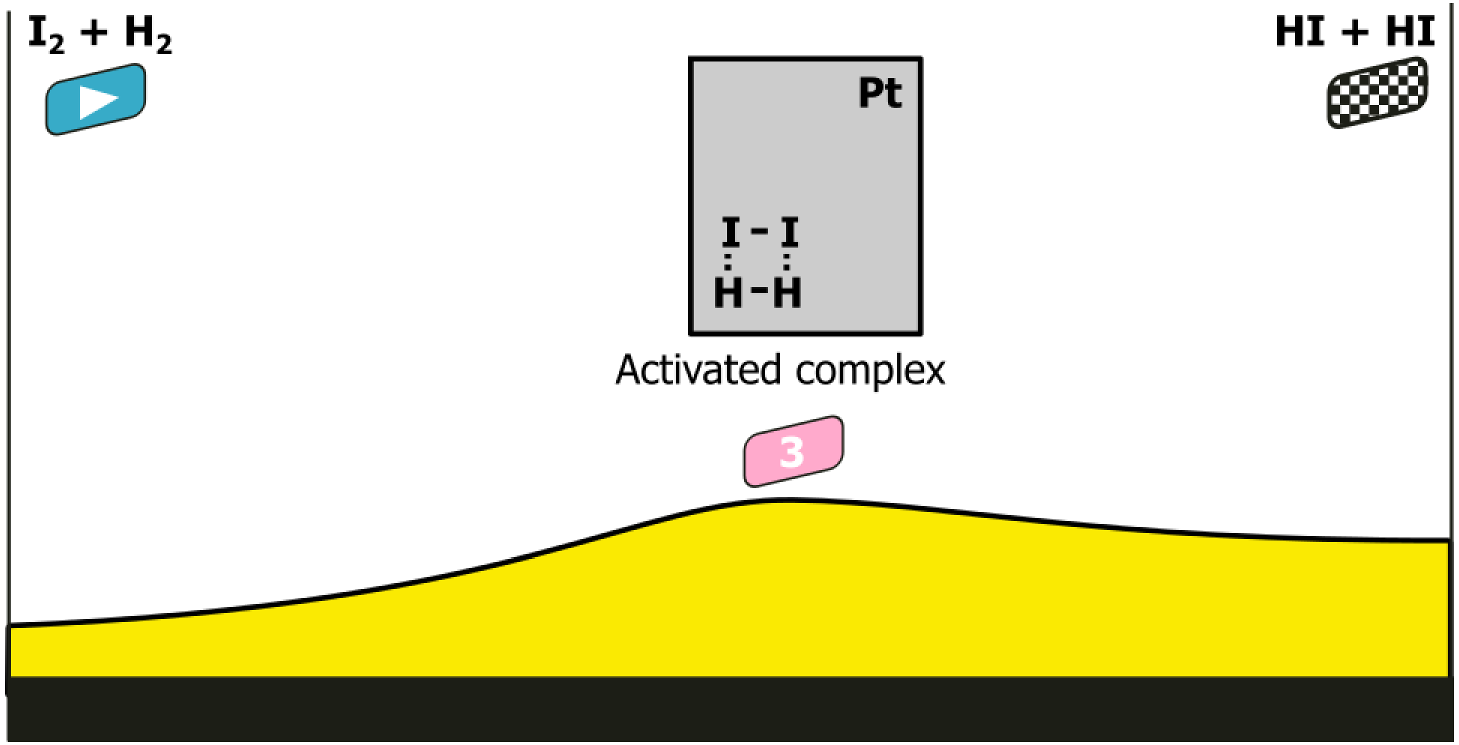
Catalysis lowers the activation energy of a reaction



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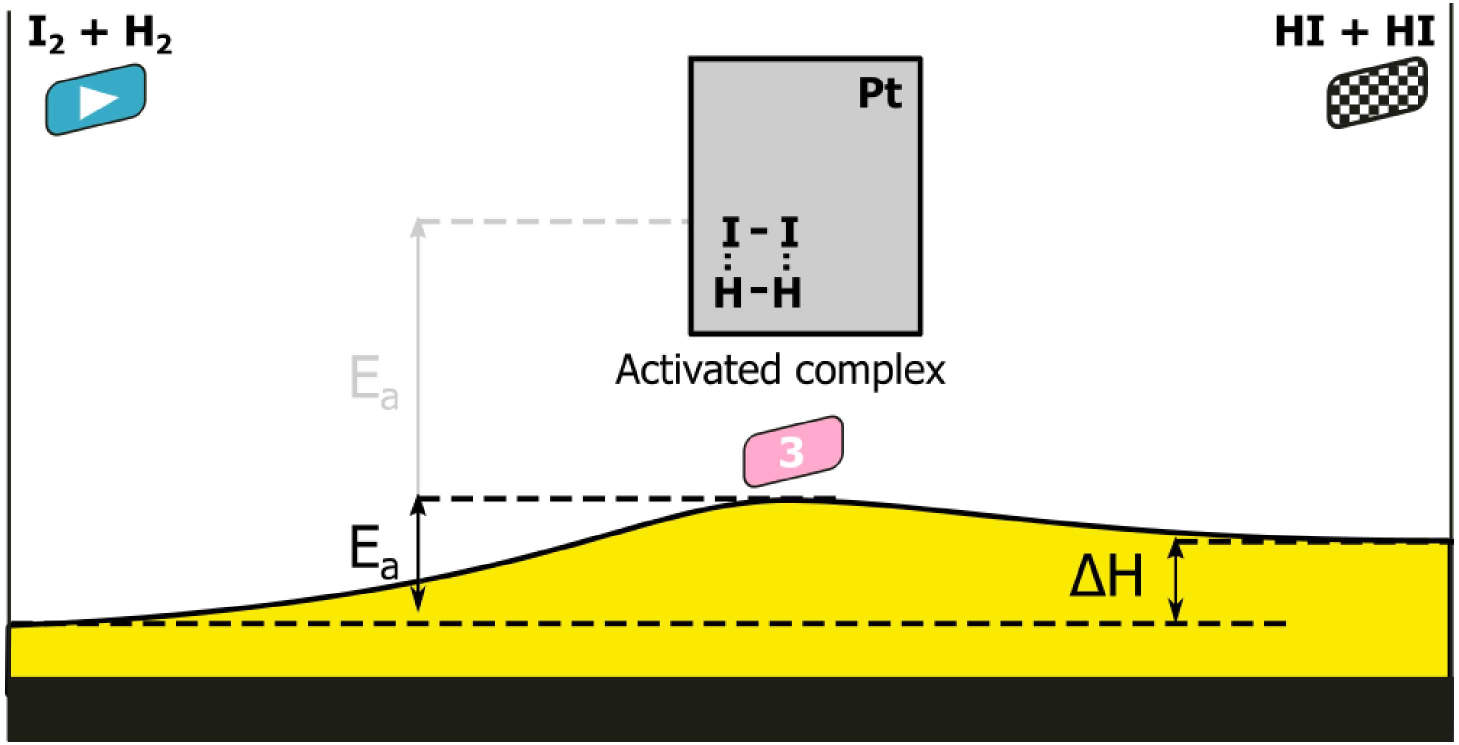
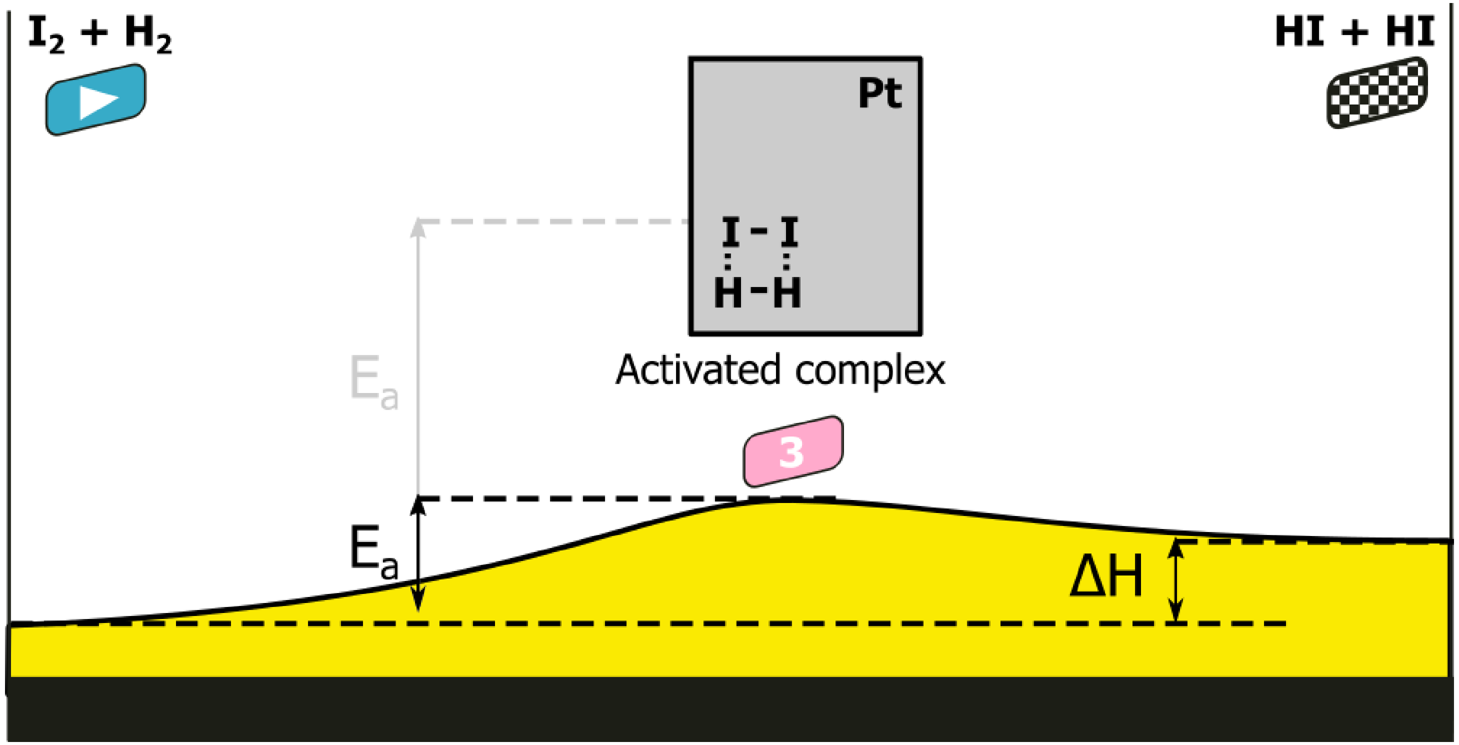


The platinum acts as a catalyst by lowering the activation energy through adsorption, bond breaking, and surface-mediated recombination

Catalysis lowers the activation energy of a reaction



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From Lesson 1: The Haber-Bosch Process

Fritz Haber (1868 –1934)

$$3\,H_2 + N_2 \nrightarrow 2\,NH_3$$

This reaction does not proceed because the molecules lack sufficient energy to break the N≡N triple bond

$$3\,H_2 + N_2 \xrightarrow{500\,°\mathrm{C},\ \mathrm{Fe}} 2\,NH_3$$

This reaction proceeds in seconds

Carl Bosch (1874-1940)

🍎 **Resource in moodle:** Fritz Haber, the chemist of life and dead

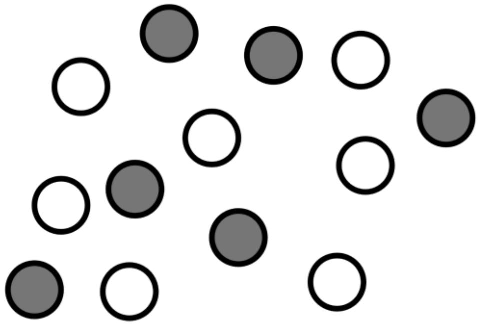
Types of catalysis

Homogeneous *(same phase)*

Catalyst and reactants exist in the same phase (typically all in solution or all in gas phase).

Examples:

- Acid-catalysed esterification (H_2SO_4 in liquid phase)
- Ozone depletion by Cl radicals (gas phase)
- Enzyme catalysis in solution

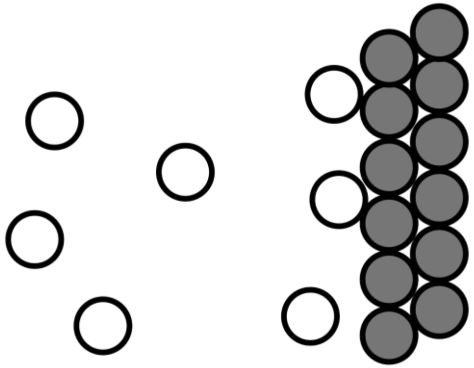


Heterogeneous *(different phases)*

Catalyst and reactants exist in different phases (typically a solid catalyst with liquid or gas reactants).

Examples:

- Haber process (Fe catalyst, gas reactants)
- Catalytic converters (Pt/Pd/Rh on exhaust gases)
- Hydrogenation with Ni or Pd catalyst



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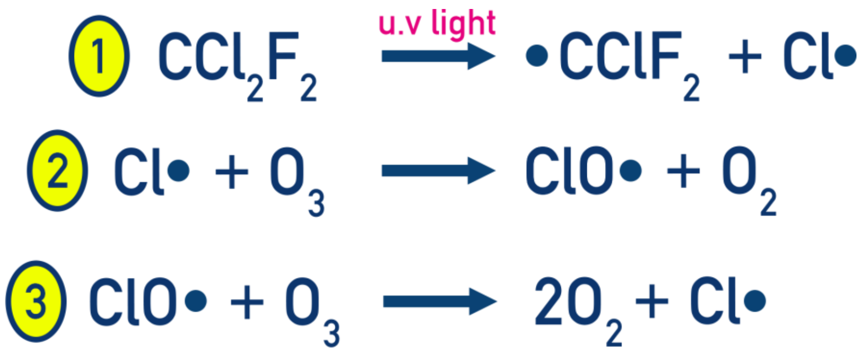

$$① \; CCl_2F_2 \xrightarrow{\text{u.v light}} \bullet CClF_2 + Cl\bullet$$

$$② \; Cl\bullet + O_3 \longrightarrow ClO\bullet + O_2$$

$$③ \; ClO\bullet + O_3 \longrightarrow 2O_2 + Cl\bullet$$

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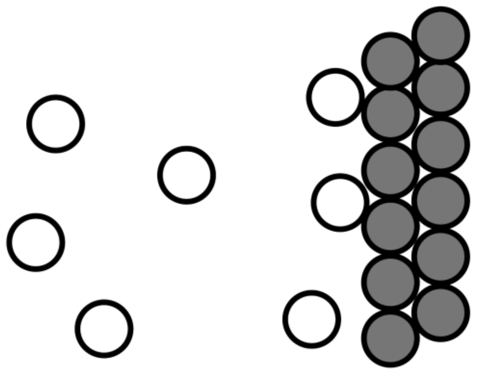

Types of catalysis

Homogeneous *(same phase)*

Ca
al

Ex

LA CAPA DE OZONO SUCUMBE ANTE LA INDUSTRIA QUIMICA

José Luis García Ortega

Una gran pancarta bloquea la entrada a la reunión del Protocolo de Montreal en Viena. © Greenpeace/Geier

El pasado mes de diciembre tuvo lugar en Viena la gran cumbre de la capa de ozono. El objetivo: reformar el Protocolo de Montreal para restringir, aún más, los compuestos químicos que destruyen el ozono. El resultado, sin embargo, ha sido absolutamente dejarla en la práctica como estaba. Además, en los países en desarrollo, su producción podrá aumentar sin restricciones durante 20 años.

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El Gobierno español fue uno de los principales obstáculos para lograr incluso esos tímidos acuerdos, abu-

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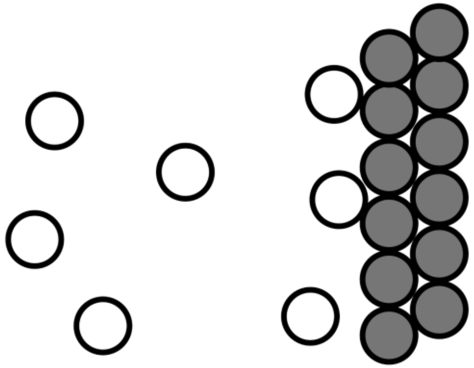

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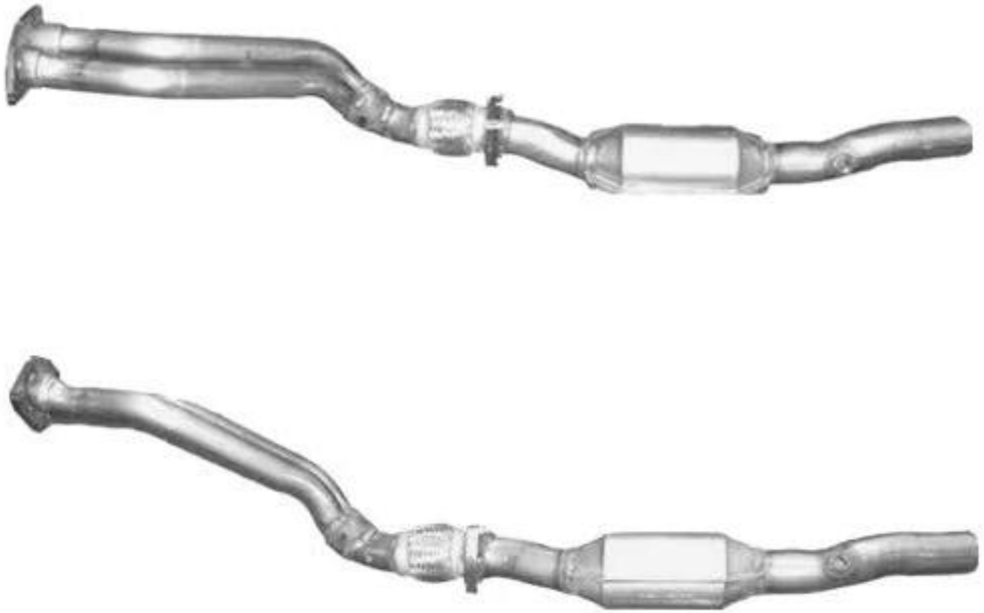

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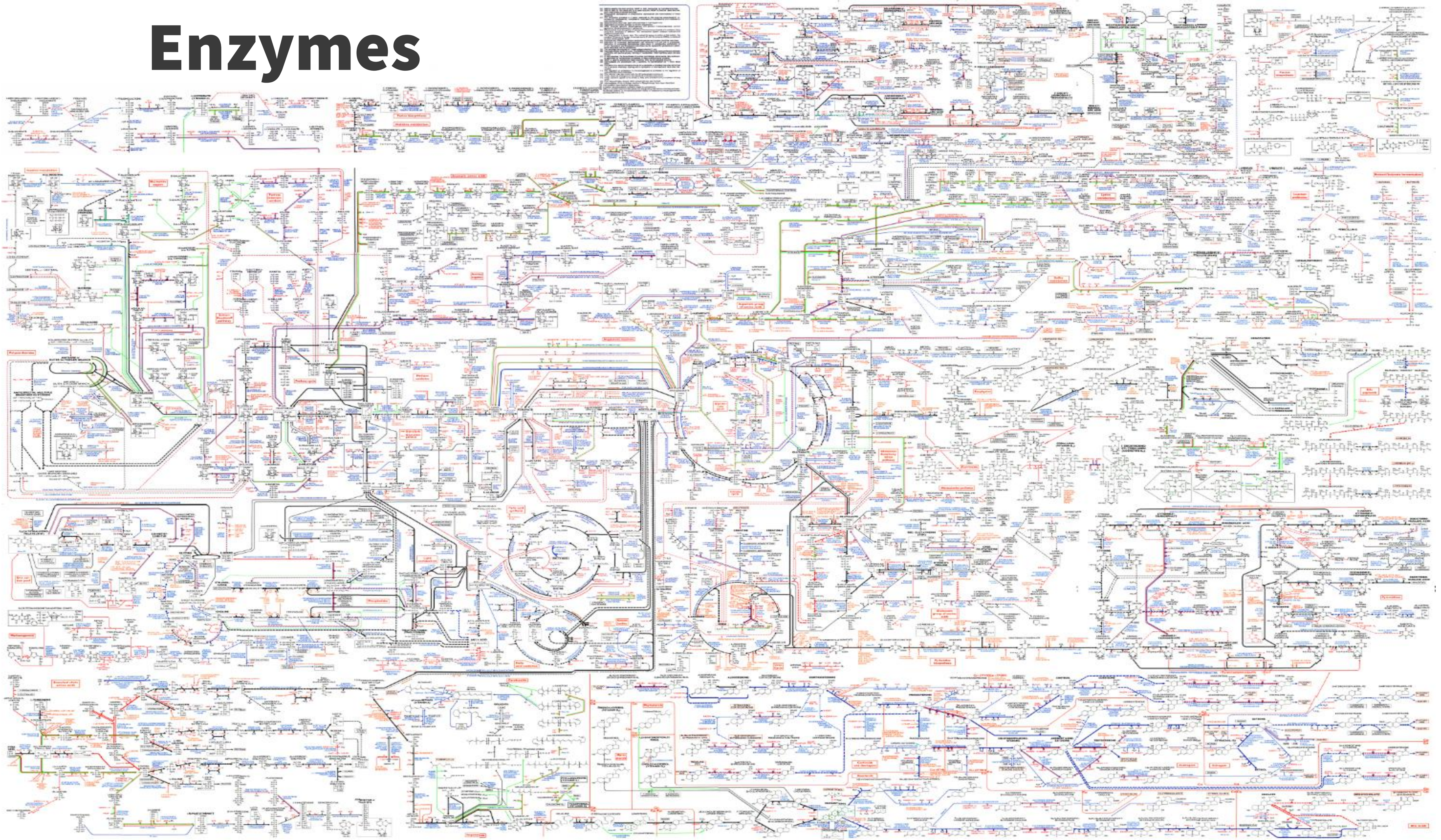
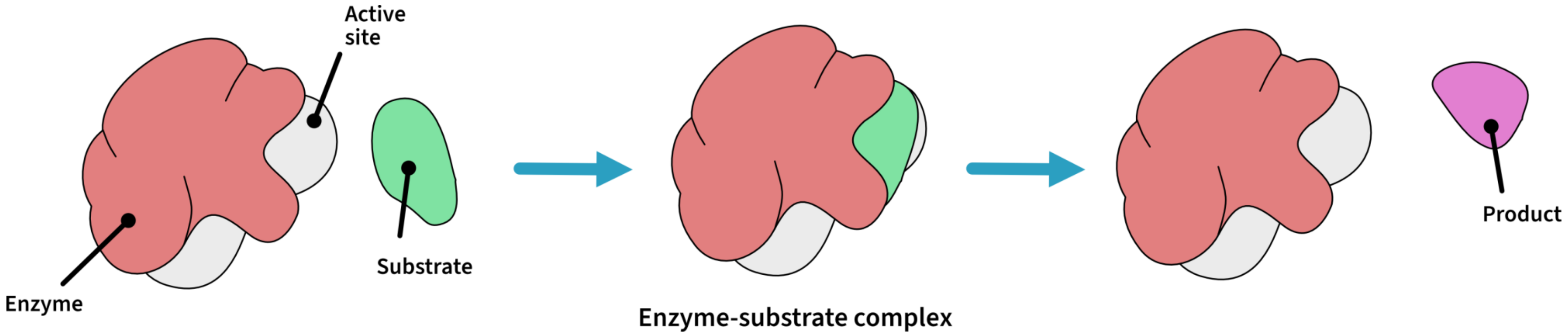
Enzymes



Resource in moodle: High resolution map

Enzymes

Enzyme is a protein that acts as a catalyst in living organisms which helps to speed up chemical reactions



Specificity
Each enzyme catalyses a specific reaction or set of closely related reactions

Mild conditions
Function at physiological temperature, pressure, and near-neutral pH

Efficiency
Rate enhancements of 10^6 to 10^{17} compared to uncatalysed reactions

ἐν + ζύμη = en zimo = in the yeast

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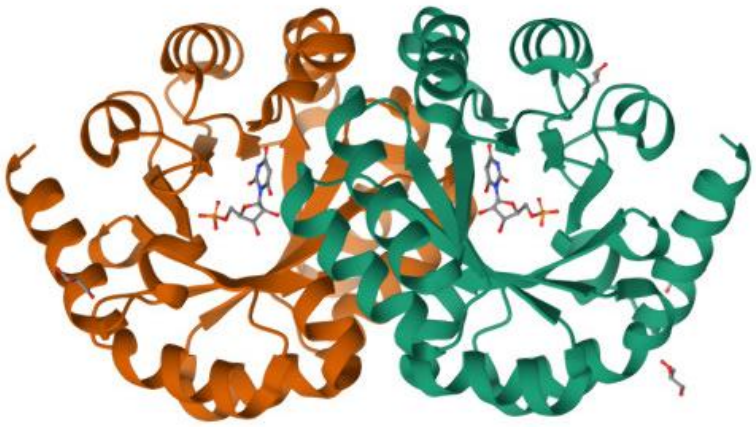

Orotidine 5′-phosphate decarboxylase

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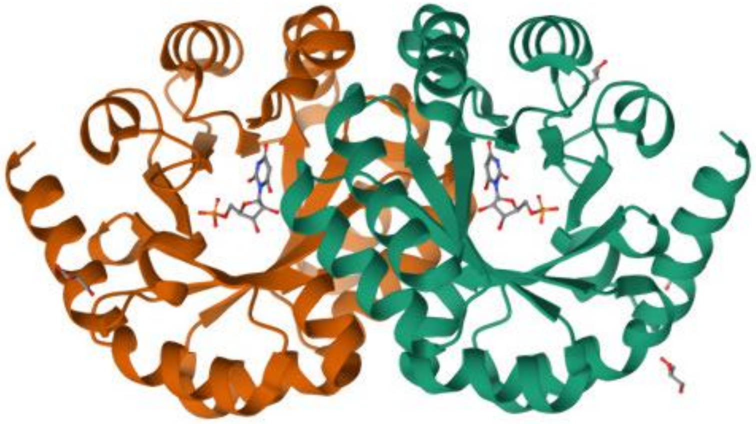

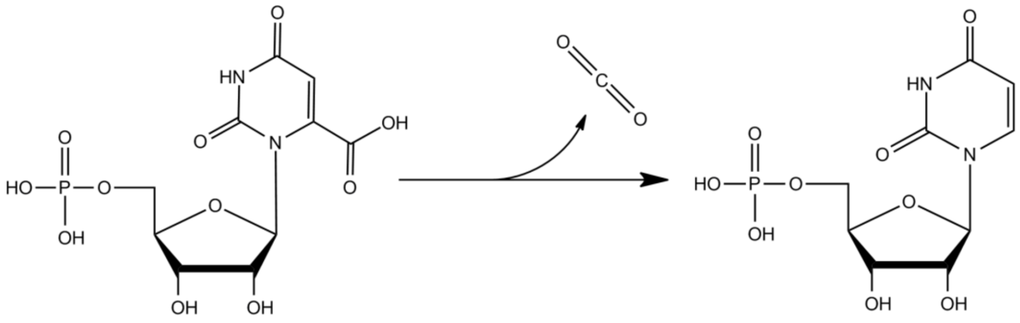

In a world without OPD: half-life: 78 million years
In a world with OPD: half-life: 18 ms (factor of 10^{17})

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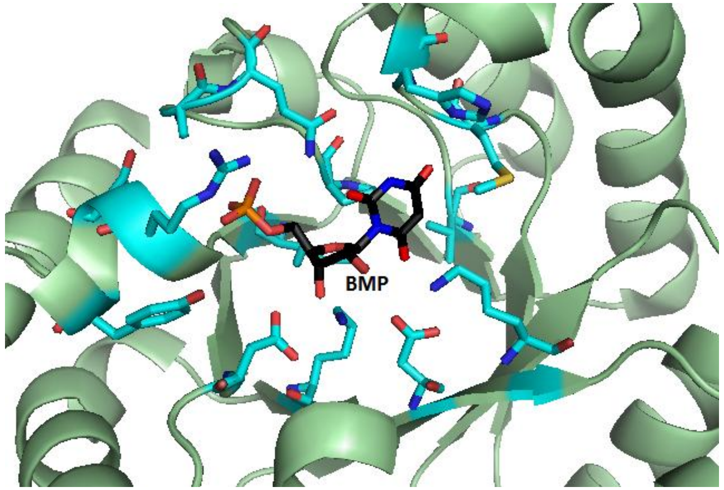
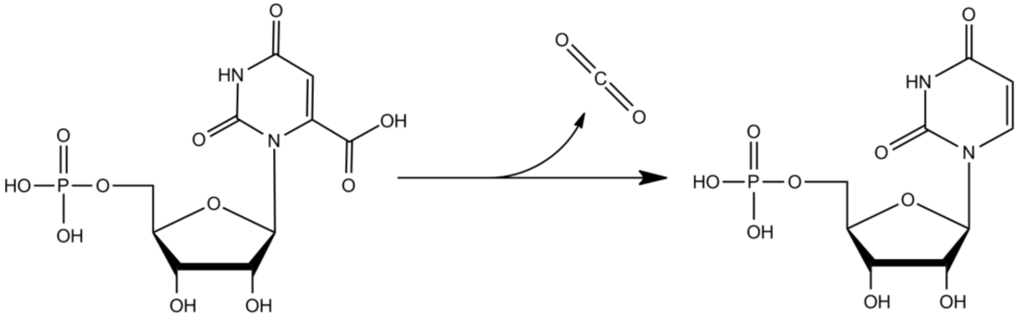


Orotidine 5′-phosphate decarboxylase (active site)



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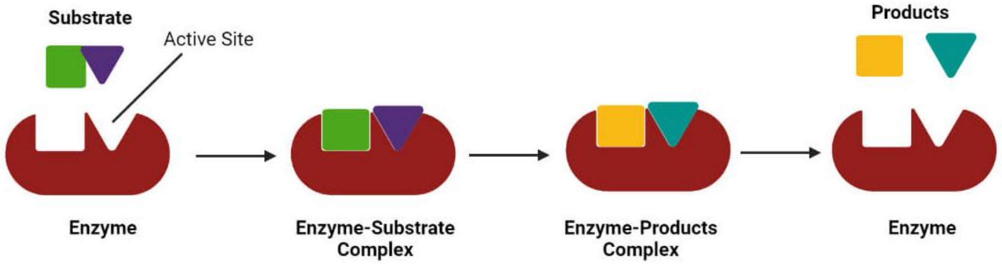
Enzyme–Substrate Binding Models

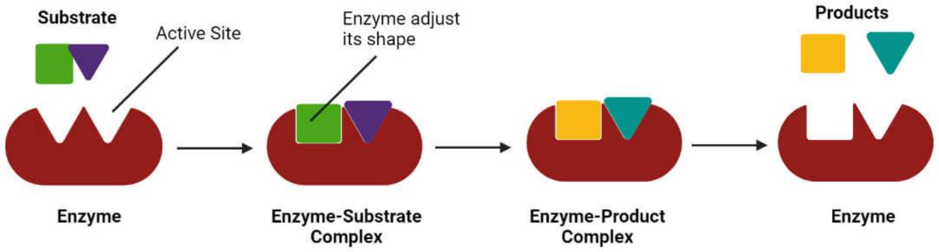
Lock-and-Key Model (1894)

The substrate fits exactly into the active site, like a key into a lock. The enzyme's shape is complementary to the substrate and does not change upon binding.



Induced Fit Model (1956)

The active site is flexible. Upon substrate binding, both enzyme and substrate undergo conformational changes to achieve optimal alignment for catalysis. Sometimes they need a co-factor



The enzyme–substrate interactions are strongest and most complementary in the transition state

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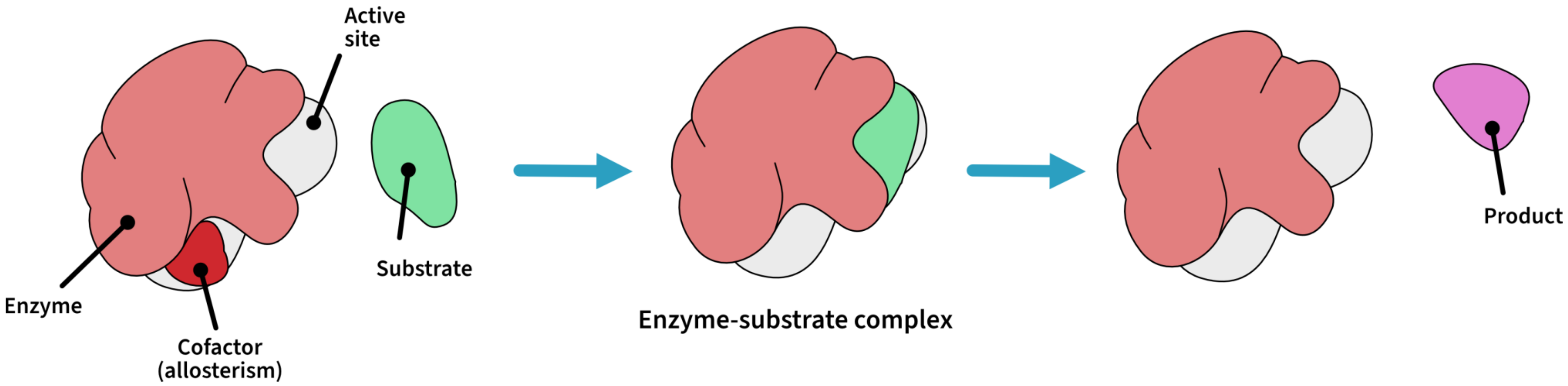

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The Michaelis-Menten model

Leonor Michaelis (1875 –1949)

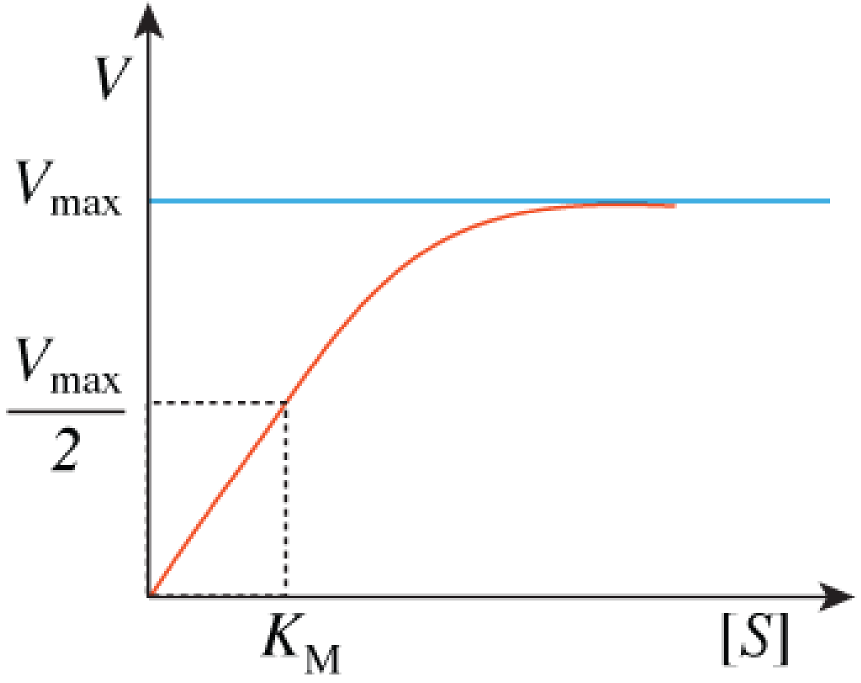
Maud Menten (1879-1960)

The Michaelis-Menten model

$$E+S \underset{k_{1r}}{\overset{k_1}{\rightleftharpoons}} ES \xrightarrow{k_2\,(k_{cat})} E+P$$

⚠

$$\boxed{V = \frac{V_{\max}[\mathrm{S}]}{K_M + [\mathrm{S}]}}$$



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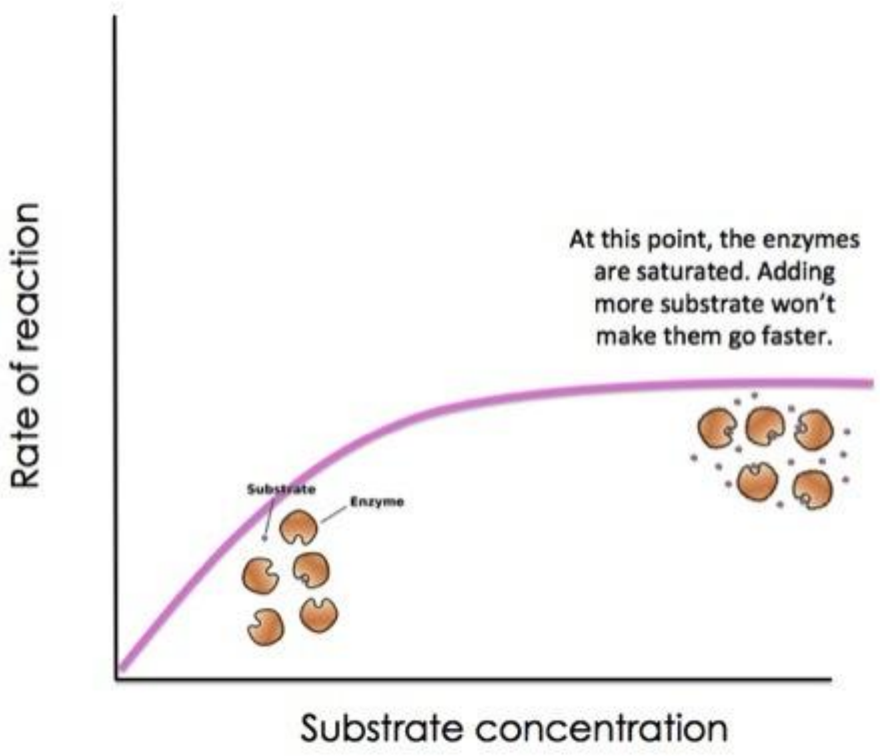
$$\mathrm{E+S} \underset{k_{1r}}{\overset{k_1}{\rightleftharpoons}} \mathrm{ES} \xrightarrow{k_2\,(k_{cat})} \mathrm{E+P}$$

⚠

$$\boxed{V = \frac{V_{\max}[\mathrm{S}]}{K_M + [\mathrm{S}]}}$$

V_{max} → Maximum catalytic capacity



At this point, the enzymes are saturated. Adding more substrate won't make them go faster.

The Michaelis-Menten model

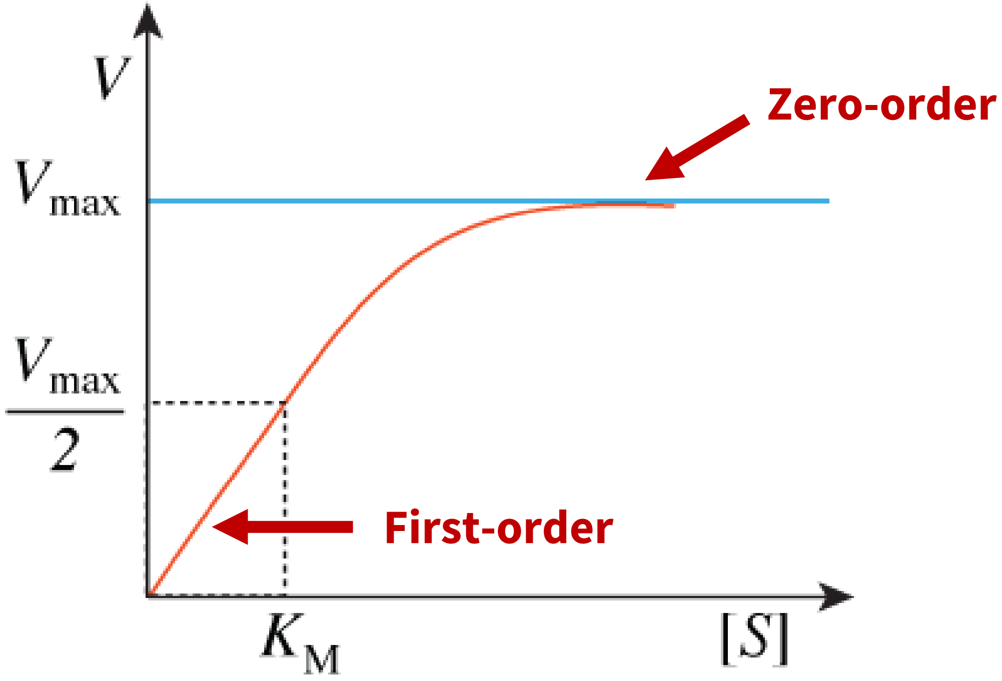
$$E+S \underset{k_{1r}}{\overset{k_1}{\rightleftharpoons}} ES \xrightarrow{k_2\,(k_{cat})} E+P$$

⚠

$$\boxed{V = \frac{V_{\max}[\mathrm{S}]}{K_M + [\mathrm{S}]}}$$

V_{max} → Maximum catalytic capacity
K_M → apparent affinity for the substrate

$$K_M = \frac{k_2 + k_{-1}}{k1}$$



Zero-order

First-order

Enzyme inhibitors

Competitive Inhibitors

Bind to the **active site** of the enzyme and compete directly with the substrate.

K_M **increases**, $V_{\max}$ **unchanged**.

Noncompetitive Inhibitors

Bind to a site different from the active site (allosteric site)

$V_{\max}$ **decreases**, K_M **unchanged**

Un-competitive Inhibitors

Bind only to the enzyme–substrate (ES) complex.

Both K_M **and** $V_{\max}$ **decrease**.

Irreversible Inhibitors

Form covalent or extremely tight bonds with the enzyme and permanently inactivate it.

Enzyme inhibitors

competitive non-competitive un-competitive

Competitive Inhibitors

Bind to the **active site** of the enzyme and compete directly with the substrate.

K_M increases, **$V_{\max}$ unchanged**.

The inhibitor competes with the substrate for the active site. Since this can be "overcome" by adding more substrate, Vmax remains unchanged (at infinite [S], all enzyme is saturated with substrate). But because it takes more substrate to saturate the enzyme, the apparent KM increases.

Noncompetitive Inhibitors

Bind to a site different from the active site (allosteric site)

$V_{\max}$ decreases, **K_M unchanged**

The inhibitor binds independently of the substrate, so no matter how much substrate you add, a fraction of the enzyme will always be inactive. That's why Vmax decreases. Since it doesn't affect substrate binding, KM remains unchanged.

Un-competitive Inhibitors

Bind only to the enzyme–substrate (ES) complex.

Both K_M and $V_{\max}$ decrease.

It only binds to the ES complex, which has a curious effect: by "sequestering" ES, it shifts the equilibrium toward forming more ES (by Le Chatelier), making the substrate appear to bind better (KM decreases). But since the ESI complex is unproductive, Vmax also decreases.