

**Unit 2 – Day 5**

# **Kinetics**

**Catalysis**



# Last time

- Collision theory
- Sterics
- Reaction coordinate diagrams
- Transition state theory

# Lecture Topics

- Transition State Theory
- How Catalysts Work
- Industrial Catalysts
- Living Catalysts: Enzymes

# Transition state theory

Collision Theory has two major limitations:

1. It only applies to molecules in the gas phase.
2. It does not accurately account for sterics.

Transition State Theory is the more general theory that gives us a way to calculate the rate constant even when there are large steric requirements.

- It is usually applied to molecules in solution.

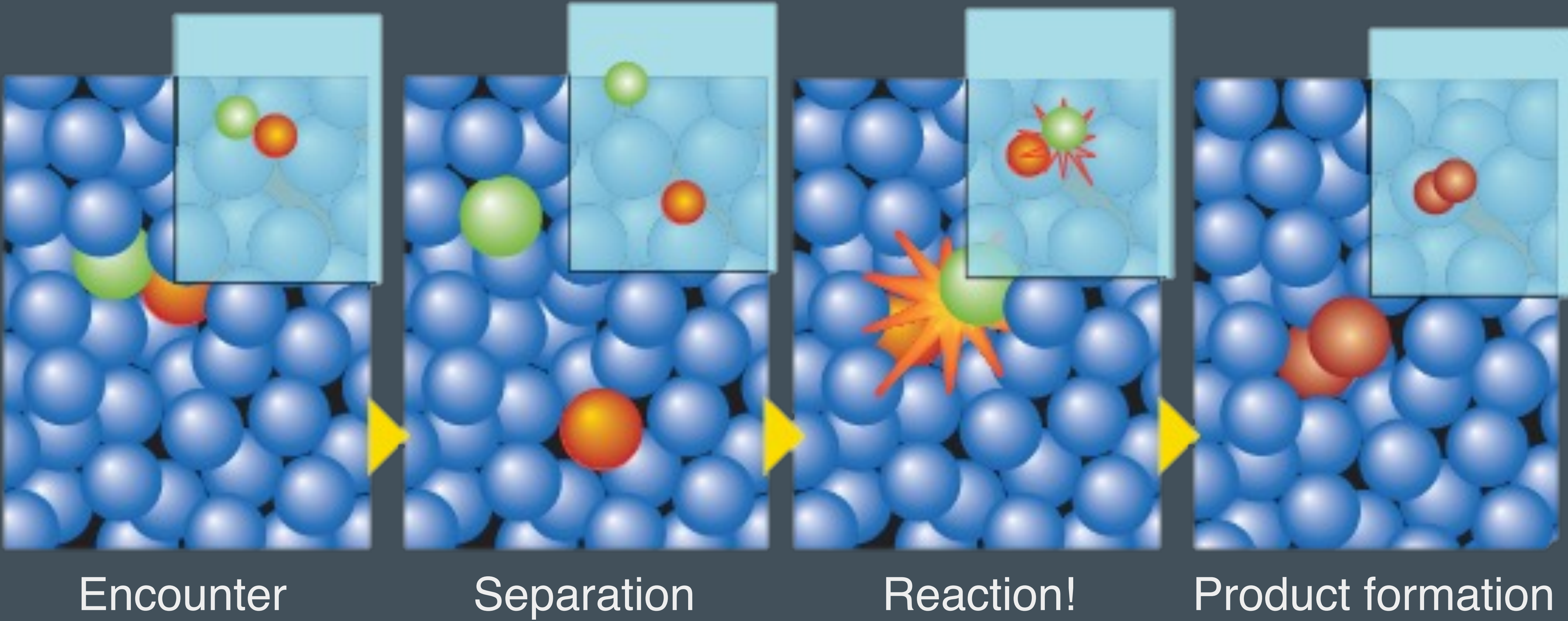
# Activated Complex theory

Transition State Theory is also referred to as Activated Complex Theory.

An **activated complex** is an arrangement of two molecules that can either go on to form products or fall apart again into the unchanged reactants.

- The original bonds have lengthened and weakened
- The new bonds are only partly formed

# Activated complex theory



# Potential Energy

In Transition State Theory, the activation energy is a measure of the energy of the activated complex relative to that of the reactants.

As the reactants approach each other, their potential energies initially drop (more stable) due to one factor:

1. Proton-electron attractions

As they get closer (Van der Waals, dipolar, ... IMFs) also decrease potential energy (more stable)

# Potential Energy

For a reaction to occur, molecules must get “too close”.

This causes their potential energies to increase due to two factors:

1. Proton-proton repulsions
2. Electron-electron repulsions (i.e. bond distortions)

For a reaction to happen, there must be enough kinetic energy to overcome these repulsions!



# Activation Barrier

If  $KE_{reactants} < E_A$ , then...

1. No reaction will occur.

$KE_{reactants} \geq E_A$ , the reactants will...

1. Form the activated complex
2. Has a probability (*i.e.* steric factor) of crossing through a transition state at the top of the potential energy barrier
3. Descend down the energy barrier and separate as products

# Example: Tracking the progress of a reaction

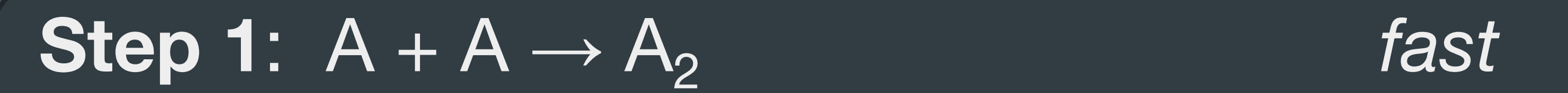
1. Start with reactants
2. Form the activated complex ( $\uparrow G$ )
3. Cross through a transition state at the top of the potential energy barrier
4. Roll down the energy barrier and separate as products ( $\downarrow G$ )
5. End with products



Energy

Progress of Reaction

# Example: Two step reaction



Energy

Progress of Reaction

# Question

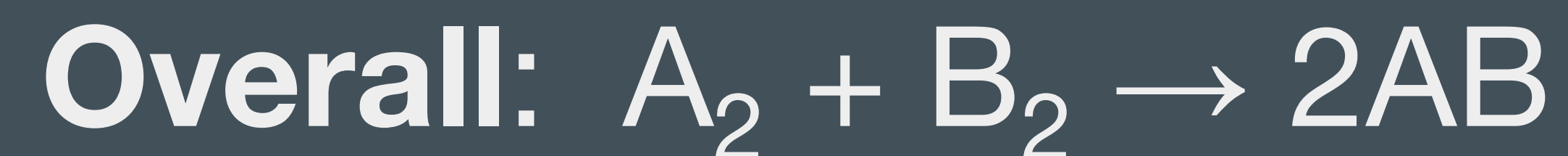
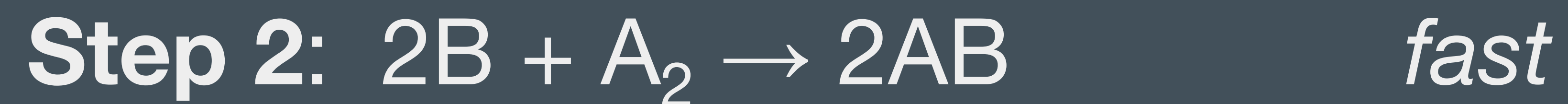
Use transition state theory to predict the mechanism for an unknown chemical reaction.

1. How many steps does it have?
2. How many intermediates does it have?
3. What is the rate determining step?
4. Is the reaction endothermic?
5. What is the activated complex for step 3?



# Slow reactions

Previously, we calculated the rate law for the below mechanism.



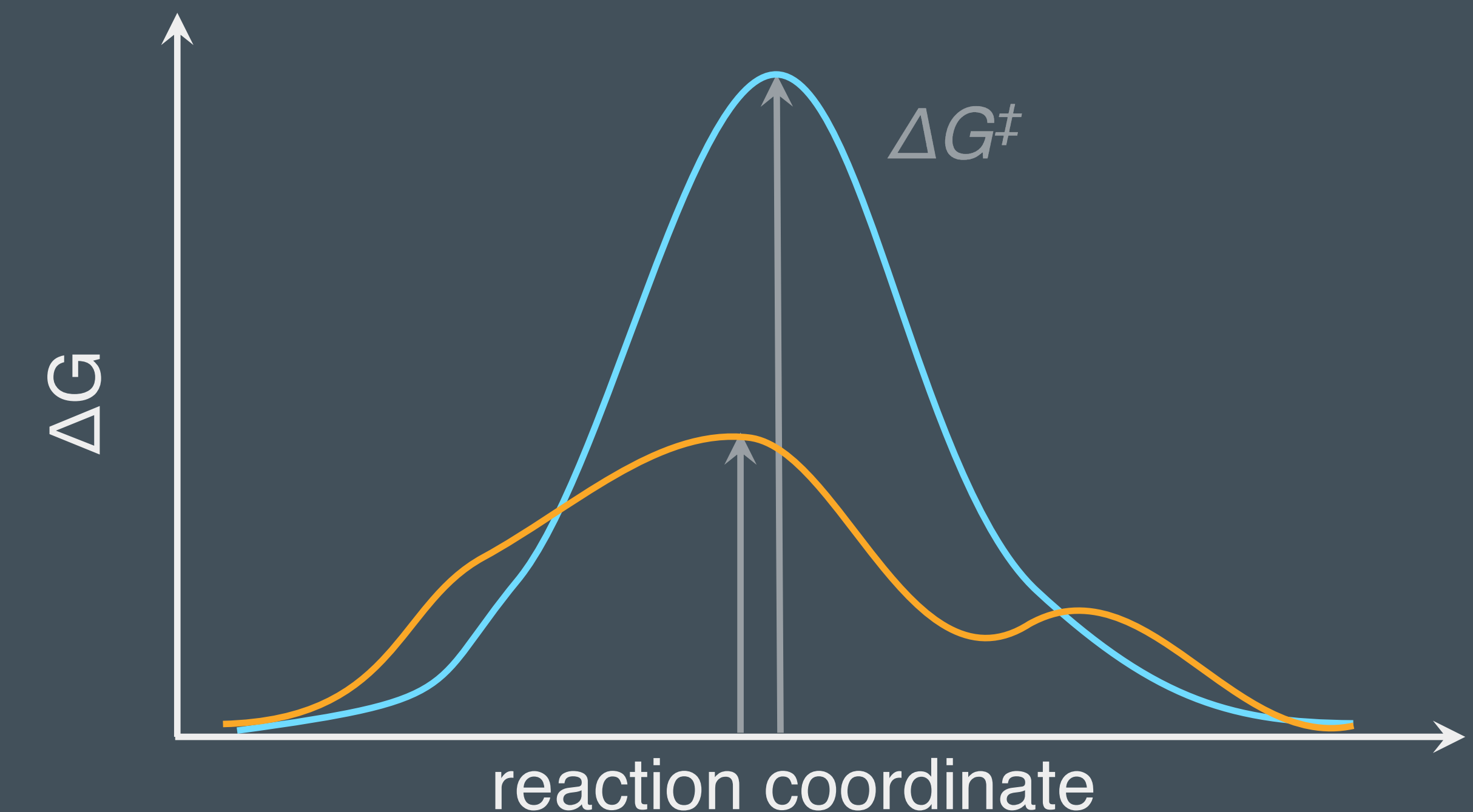
Is there a way to increase the speed of the reaction?

# Rate of Reaction: Catalysis

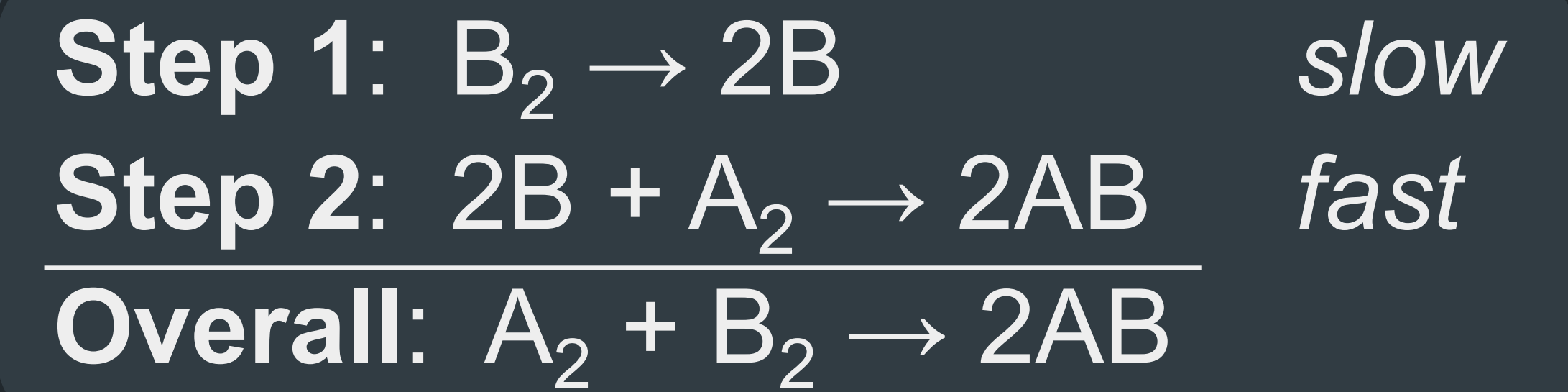
There are 4 chemical factors that affect the speed of a reaction:  
(concentrations, temperature, surface area)

## #4 Catalysts

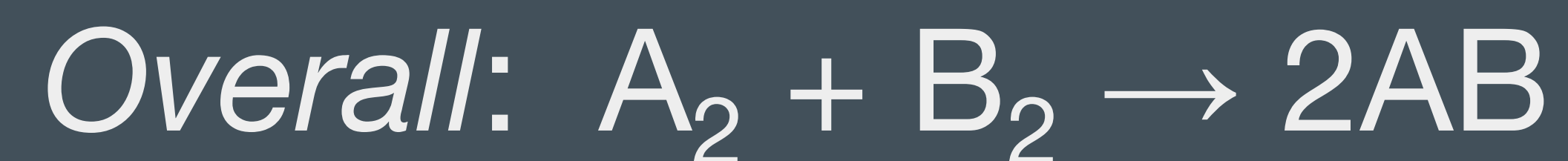
speed up the rate of a reaction by providing an alternate mechanism for the reaction. They are not used up in the reaction.



# Catalysts



Suppose you could speed up a reaction by adding some **C**:



**C** is a catalyst – it is consumed early in the reaction and regenerated as a product later. It does not appear in the overall reaction.



# (Virtual) Demonstration

Decomposition of hydrogen peroxide



This reaction is very slow at room temperature, thus you can purchase a bottle of  $\text{H}_2\text{O}_2$  at the store. However, potassium iodide speeds up the reaction.

# Catalysts

A **catalyst** is a compound or material that **provides a new reaction pathway** (a new mechanism) for the reactants to become products.

- The **new pathway has a lower transition state energy** than the original pathway.
- The new pathway might have the same number of elementary steps or it might have more or fewer.

The catalyst is not consumed and therefore will not appear in the net reaction.

**The catalyst is the only factor that lowers the activation energy.**

# Reaction profile



# Question

A diabolical super-villain invents an anti-catalyst which creates an alternative, *higher-energy* pathway for a chemical reaction to take. When he adds his anti-catalyst to the city's reagent supply, what will happen to the speed of the reaction?

- A. The reaction will slow down
- B. The reaction will speed up
- C. There will be no change in the reaction speed

# Types of Catalysts

**Homogenous catalyst:** catalyst is in the same phase as the reactants

**Heterogenous catalyst:** catalyst is in a phase different from the reactants

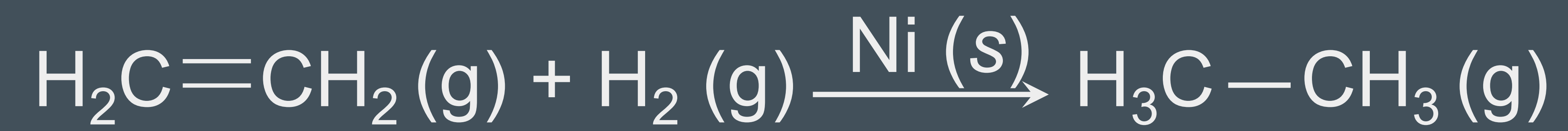
# Example

What type of catalyst is  $\text{Br}_2$ ?



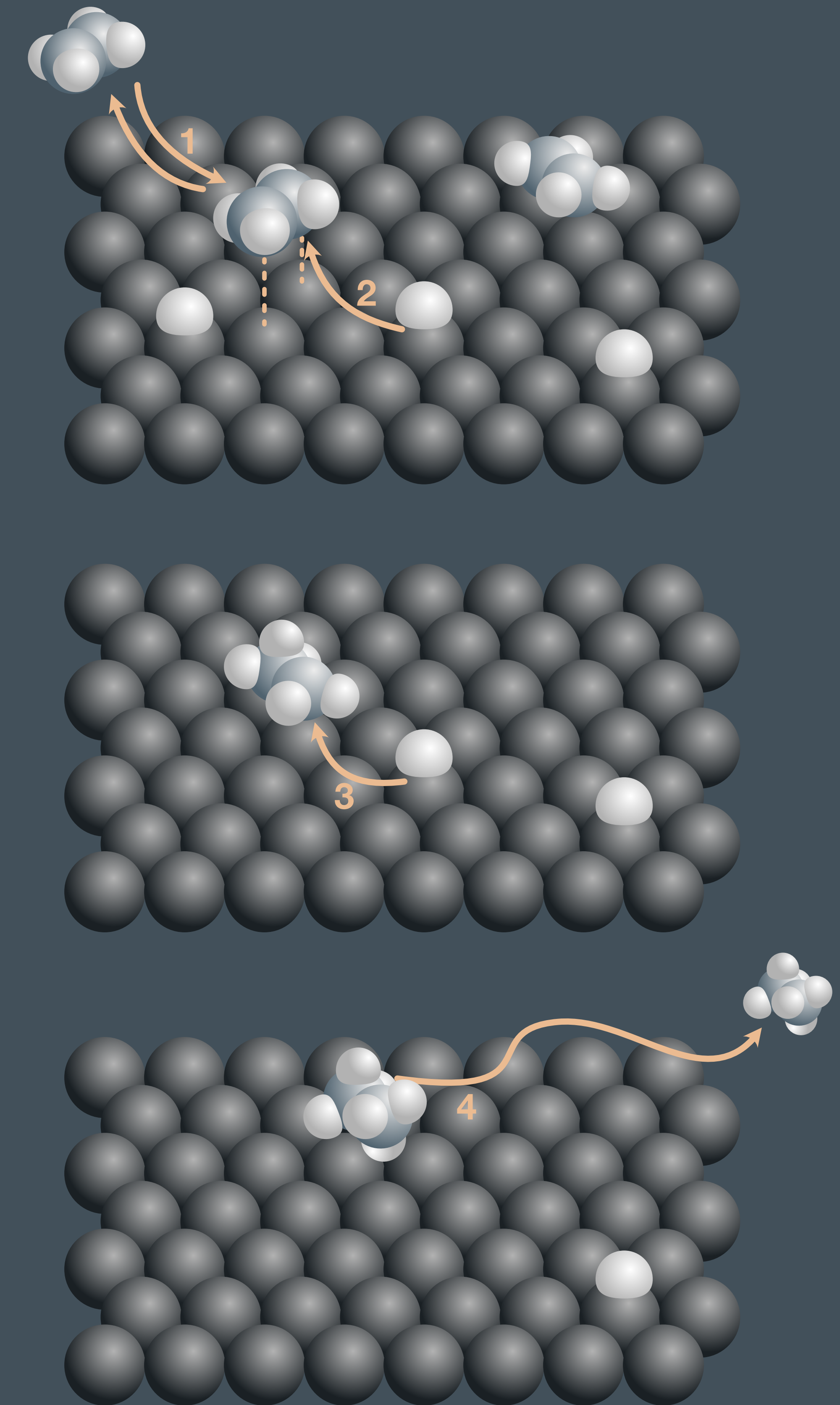
# Example

What type of catalyst is Ni?



# The mechanism of Ni catalyzed hydrogenation

What type of catalyst is Ni?





# Examples of Everyday Catalysts

**Water** increases the rate of iron reacting with oxygen to form rust. Salt water increases the rusting rate even further.

**A catalytic converter** turns some of the CO and unburned hydrocarbons in car exhaust to less toxic CO<sub>2</sub>.

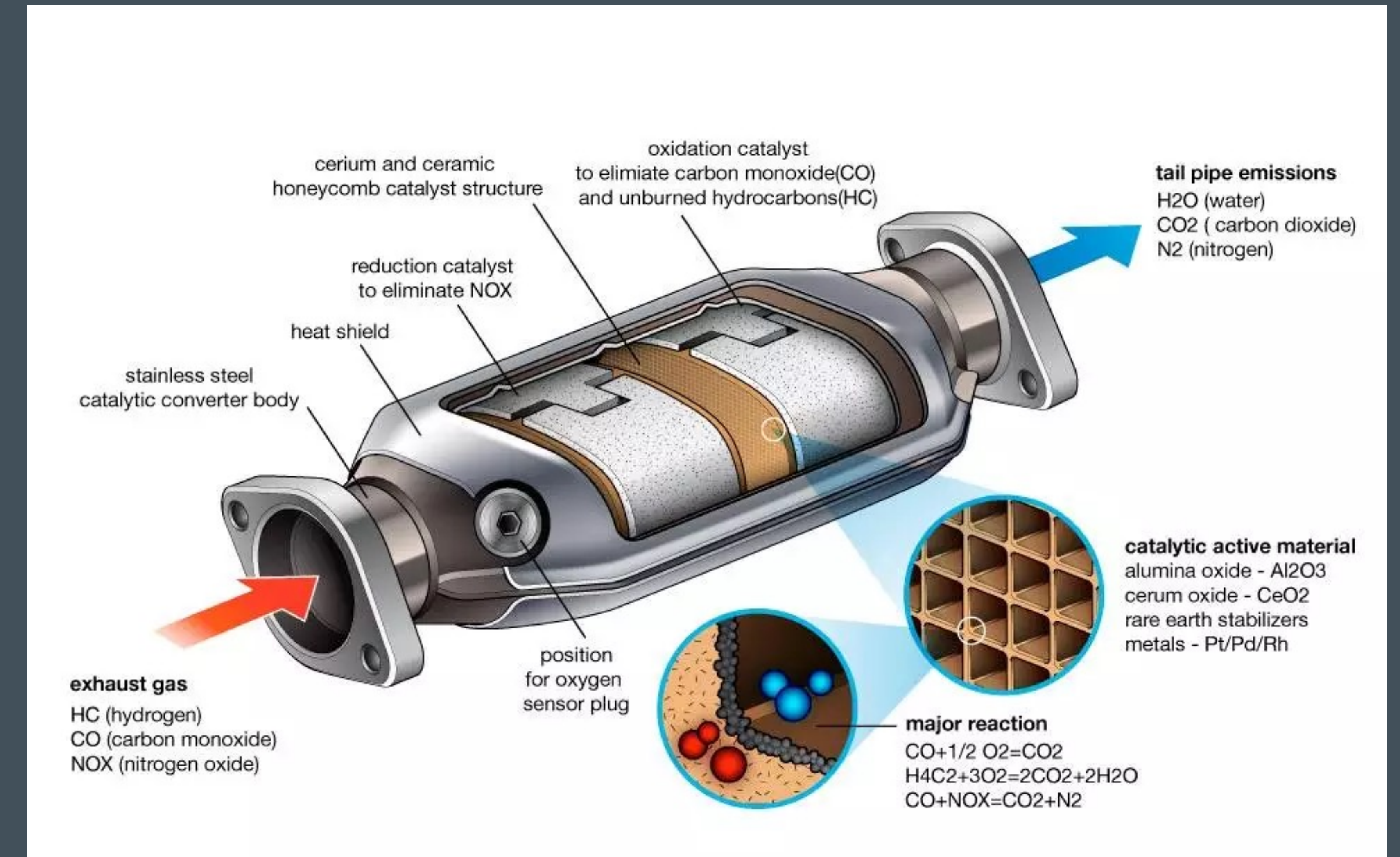
**Enzymes** speed up all sorts of biological reactions, including respiration that allow life to exist.

# Catalytic converters

The mixture of gases leaving an engine includes not only carbon dioxide and water, but also carbon monoxide, unburned hydrocarbons, and the nitrogen oxides collectively referred to as  $\text{NO}_x$ .

Air pollution is decreased if the carbon compounds are oxidized to  $\text{CO}_2$  and the  $\text{NO}_x$  species are reduced to nitrogen.

We use a special category of heterogeneous catalysts called **microporous catalysts** that have large surface areas and reaction specificity.



Pt reduction catalyst

Rh oxidation catalyst

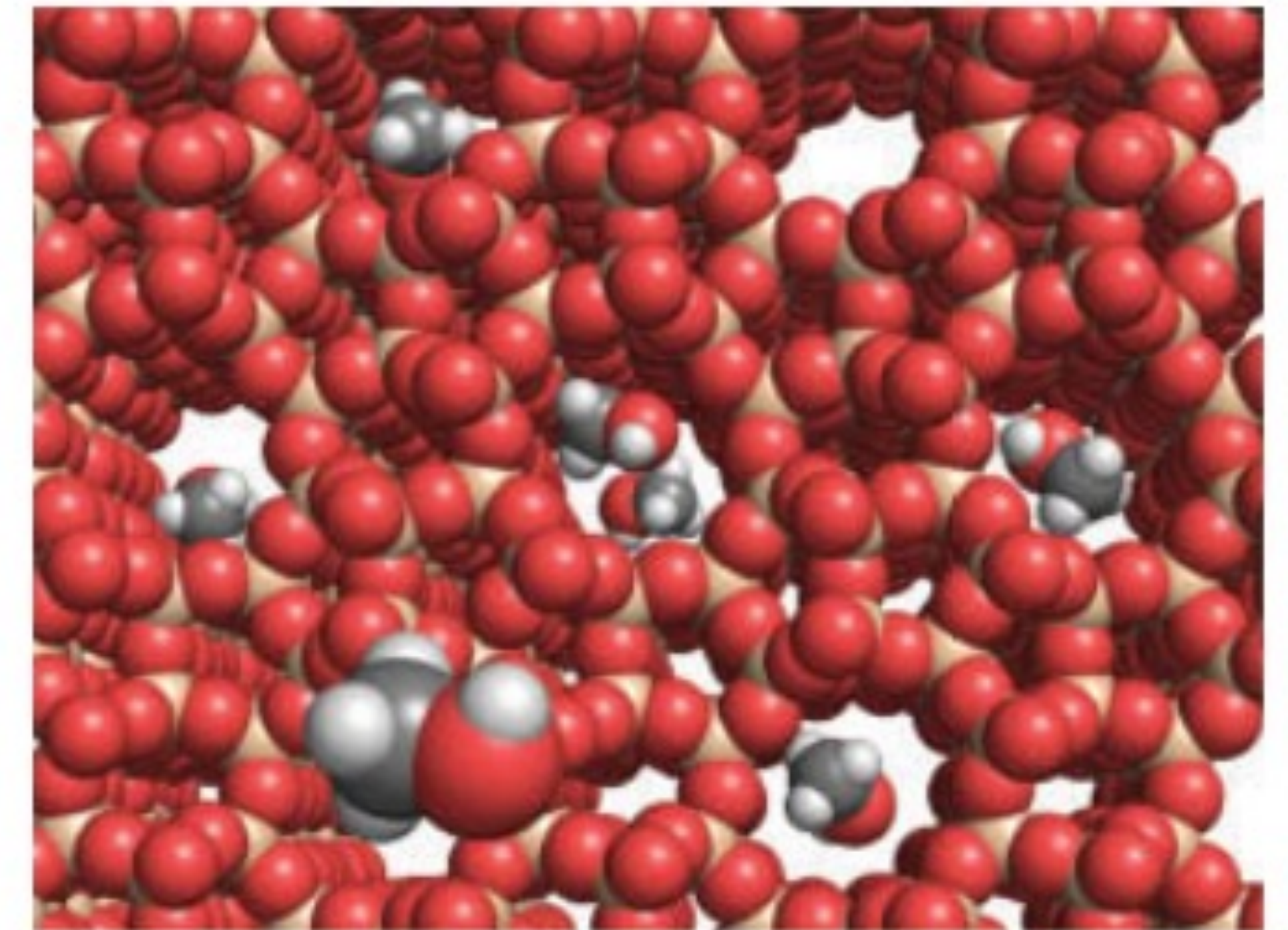
# Zeolites

Catalytic converters use microporous materials called Zeolites

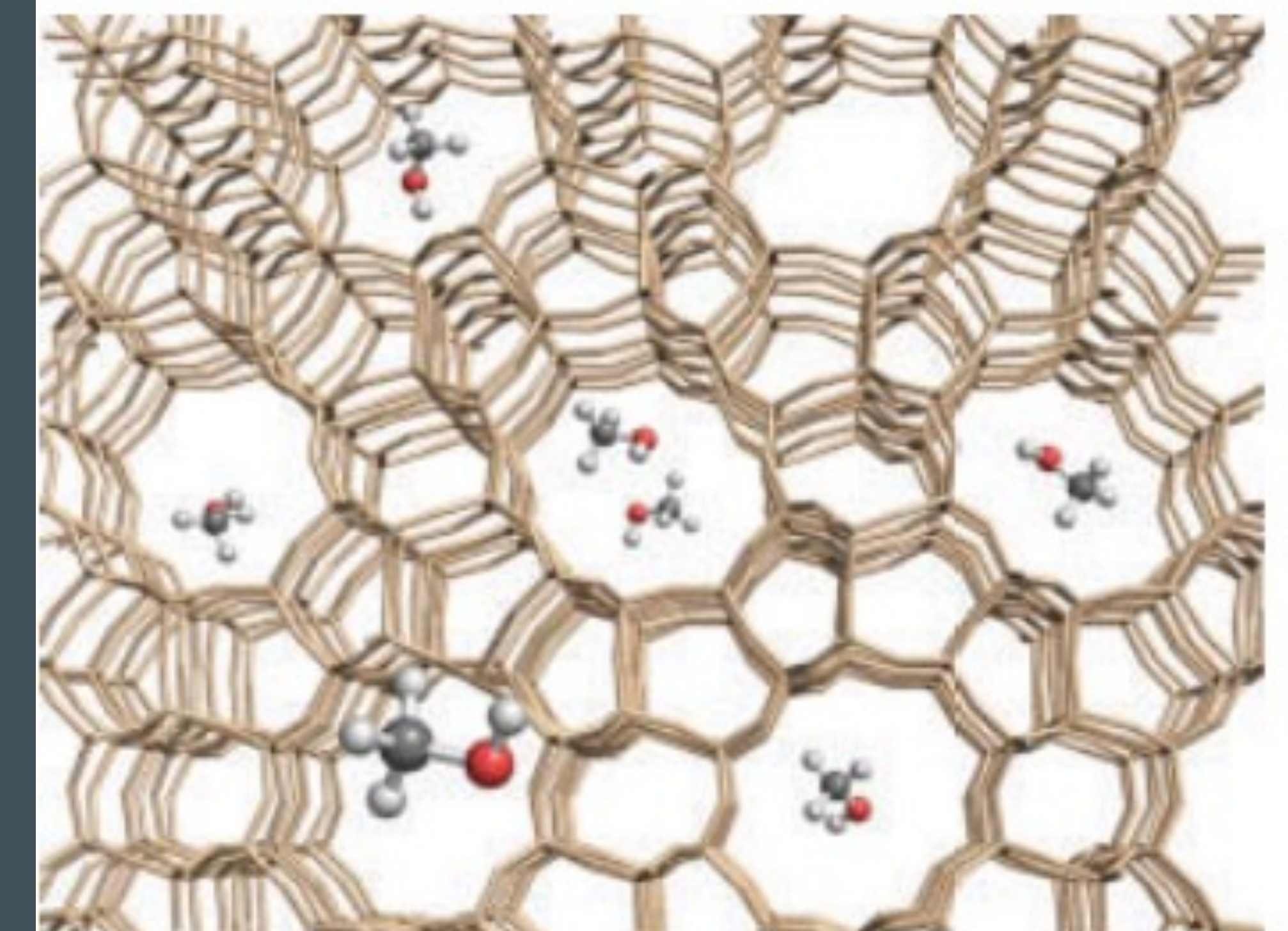
Zeolites are just aluminosilicates that have 3-D structures riddled with hexagonal channels connected by tunnels

- **Reminder:** silicate structures are based on  $\text{SiO}_4$  tetrahedral units with different negative charges and different numbers of shared O atoms

They trap nitrogen oxides so that they can be reduced to harmless nitrogen gas.



(a)

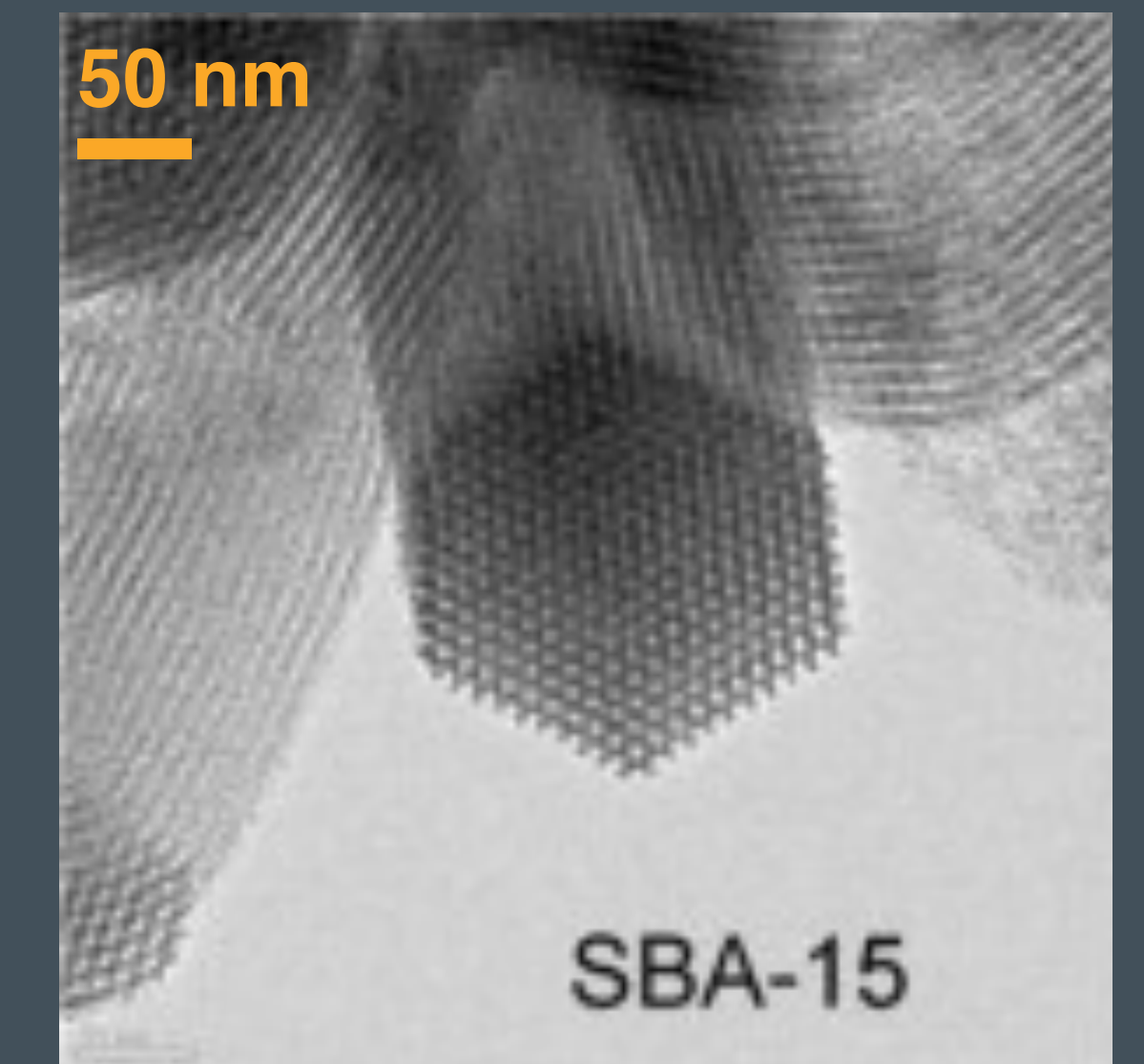


(b)

# Porous Materials

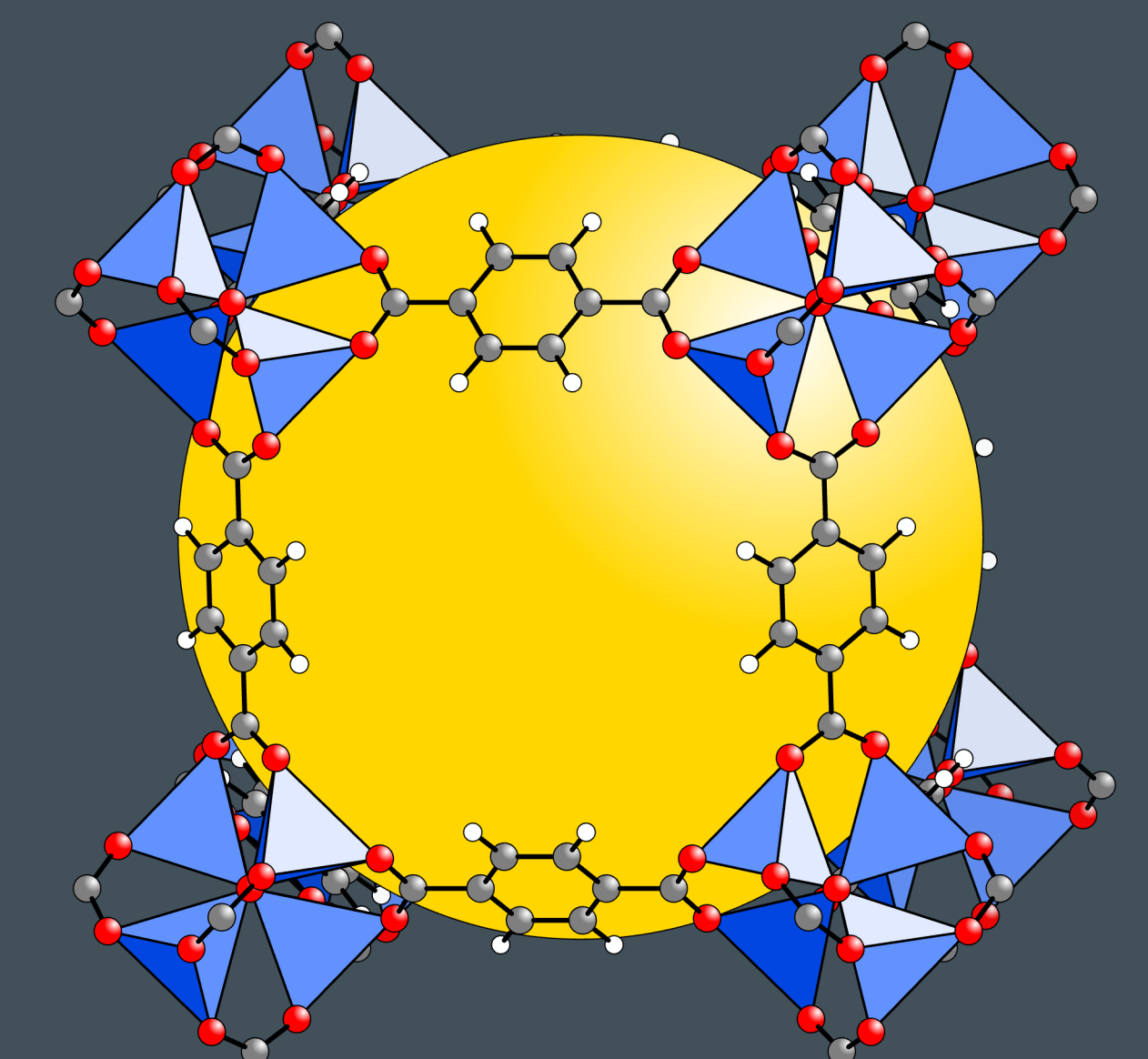
Mesoporous: a material with pores that are 2-50 nm in diameter

- Example: SBA-15

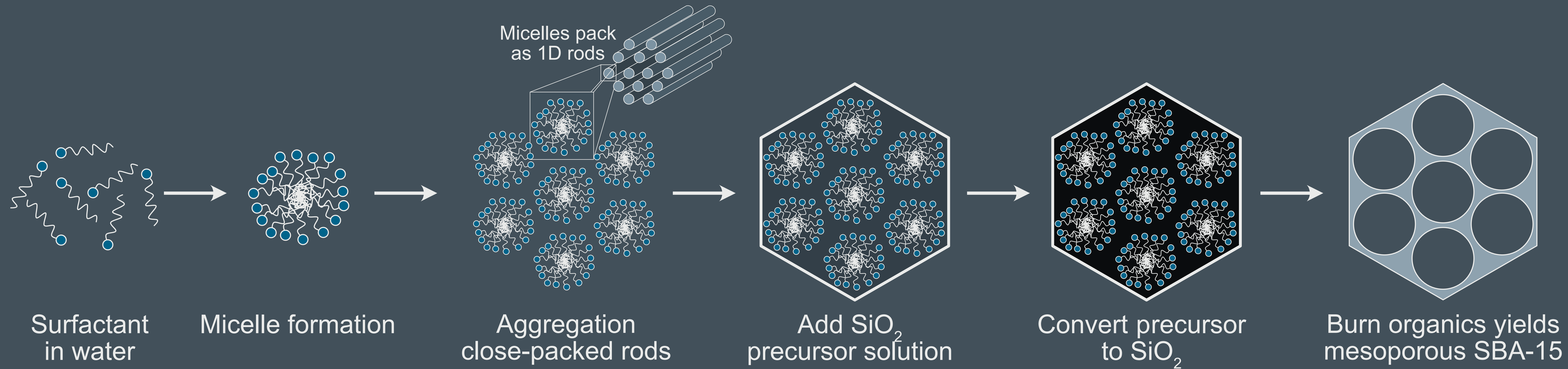


Microporous: a material with pores <2nm in diameter

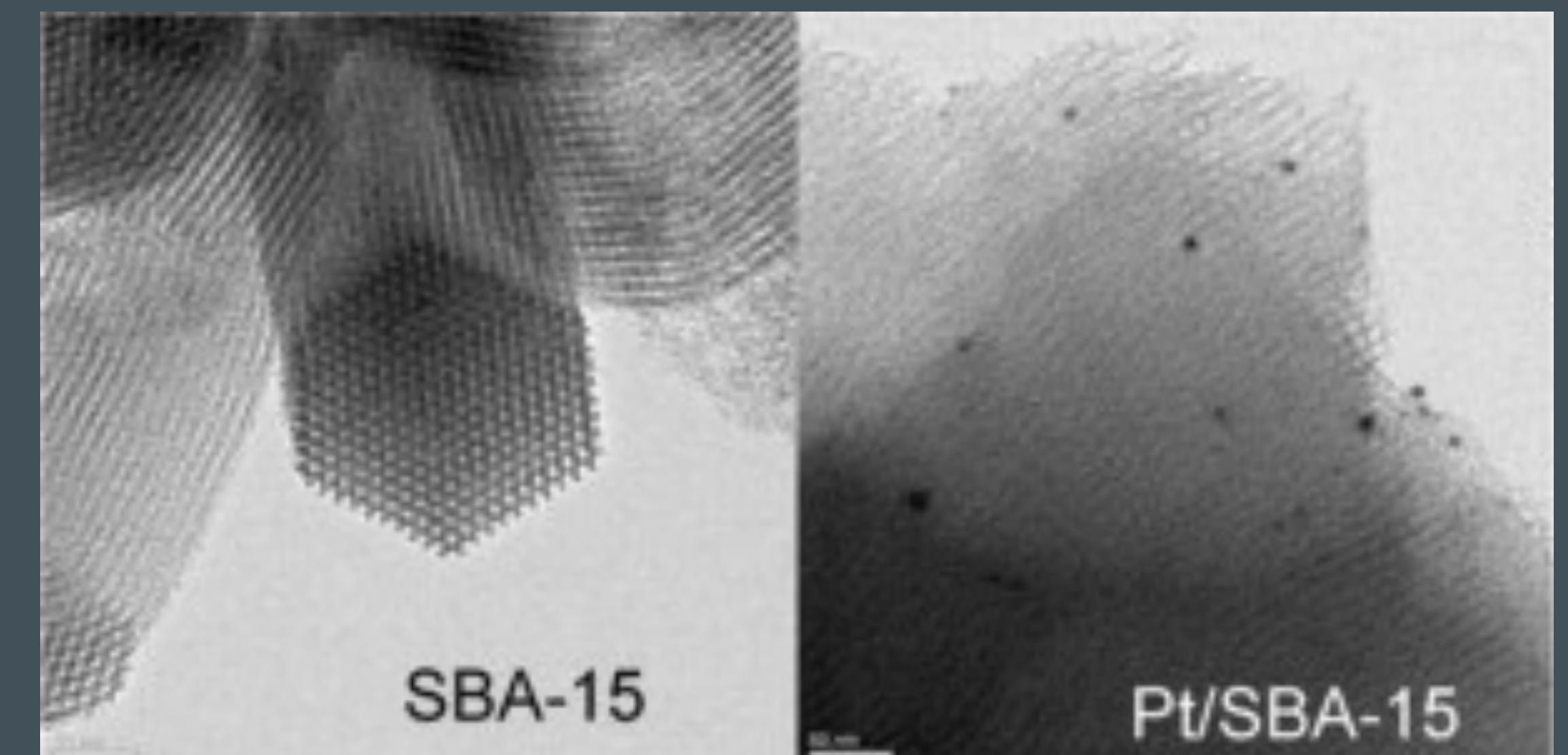
- Example: MOF-5



# Mesoporous: SBA-15



*A high surface area support for heterogenous catalyst nanoparticles*

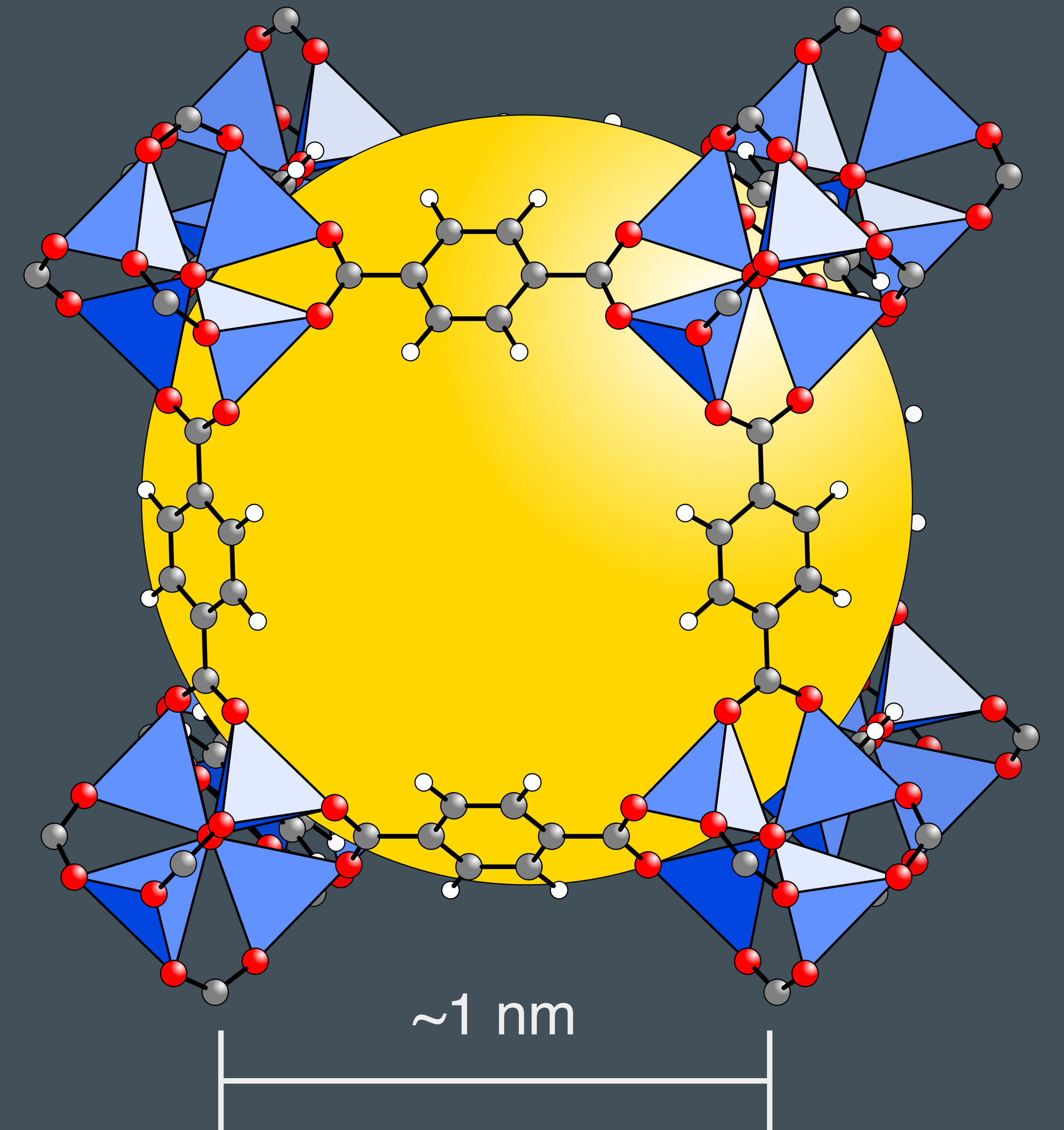


# Microporous: MOF-5



Dimethylformamide

(heat, solvent)



# Catalyst poisoning

Catalysts can be *poisoned* (deactivated).

A catalyst can adsorb a molecule so tightly that it prevents the catalyst from reacting with the target reactants.

Example: Lead is a common catalyst poison, which is one reason why lead-free gasoline must be used in engines fitted with catalytic converters.

# Enzymes

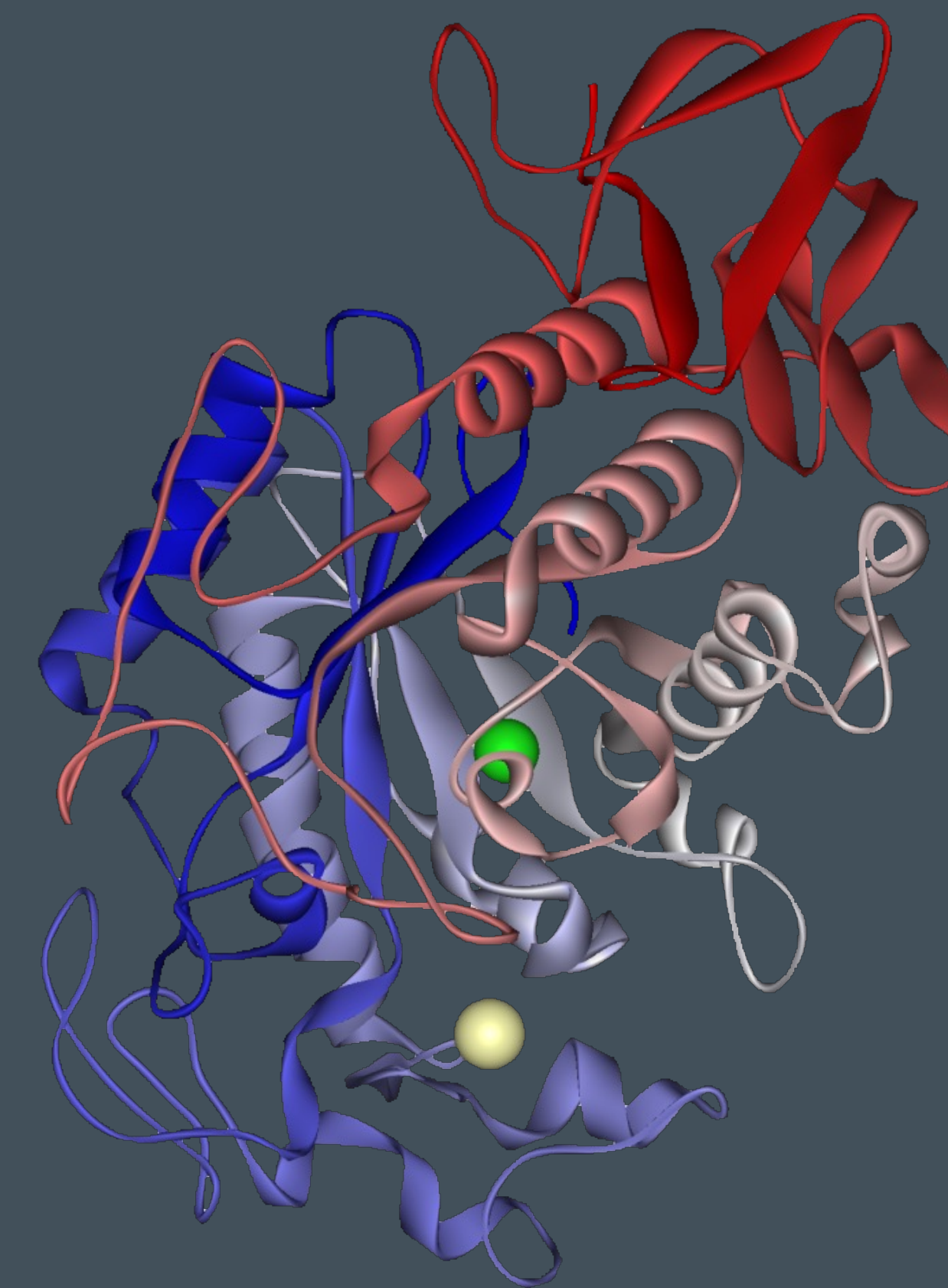
Enzymes are large molecules that have pocketlike active sites where chemical reactions take place

- **Enzyme:** the biology word for catalyst

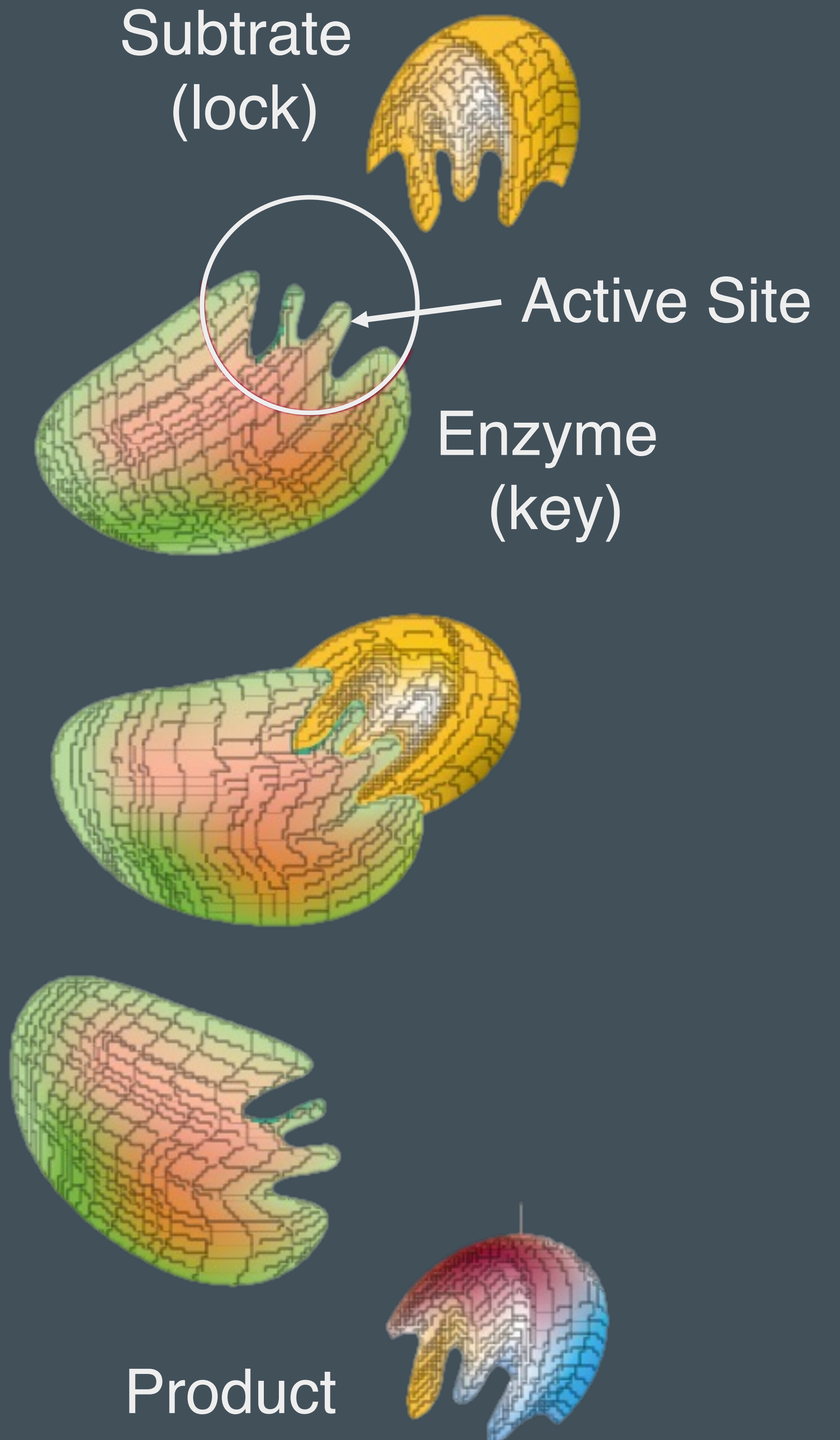
Some enzymes can distort upon substrate binding

- **Substrate:** the biology word for reactant

Once in the active site, the substrate undergoes reaction before releasing the product



Amylase



Product

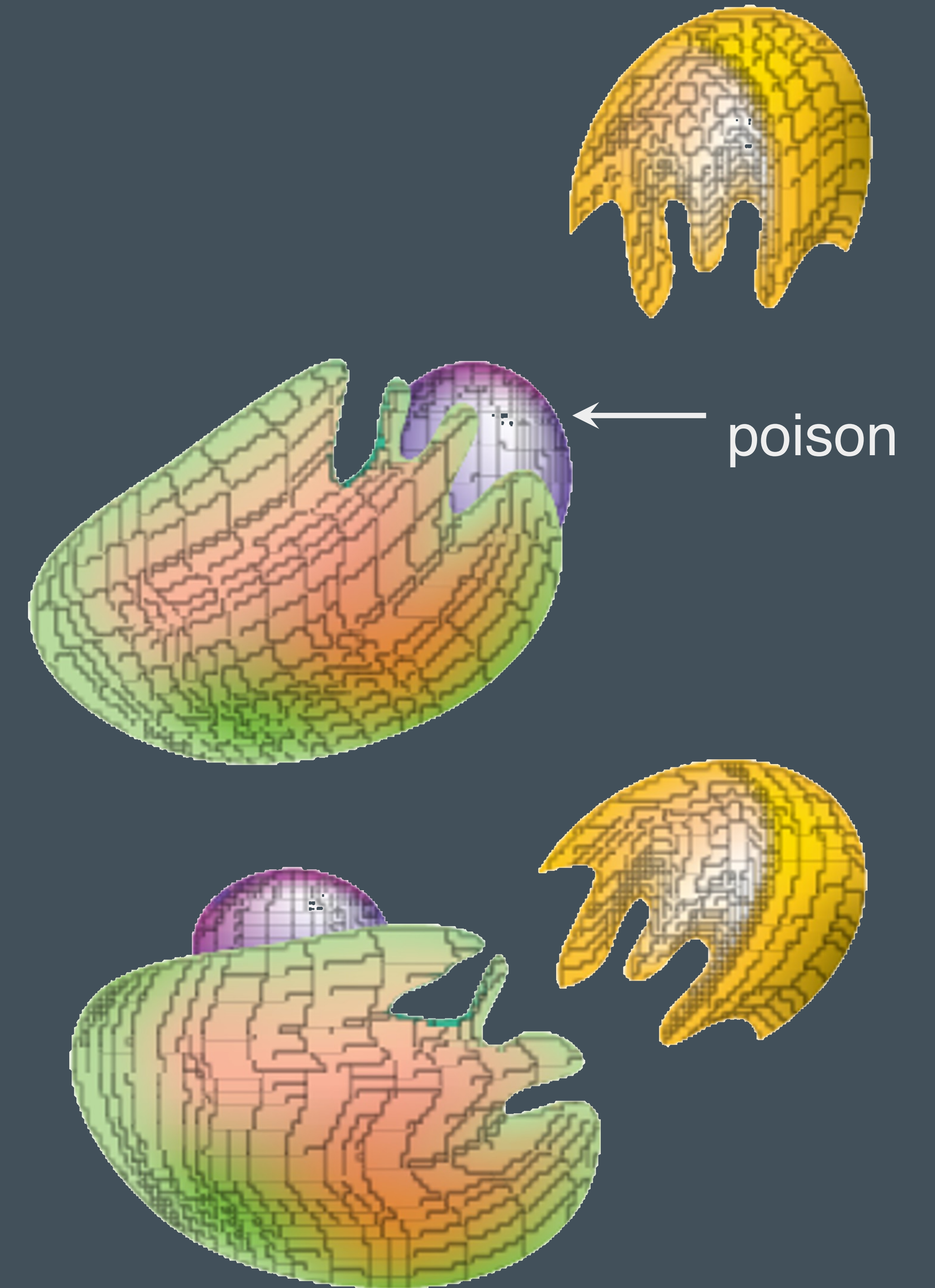


# Enzyme Poisoning

If an alien substrate attaches too strongly to the active site, the activity of the enzyme can be destroyed because the site is not available to bind the true substrate.

*Alien substrates are referred to as enzyme **poisons***

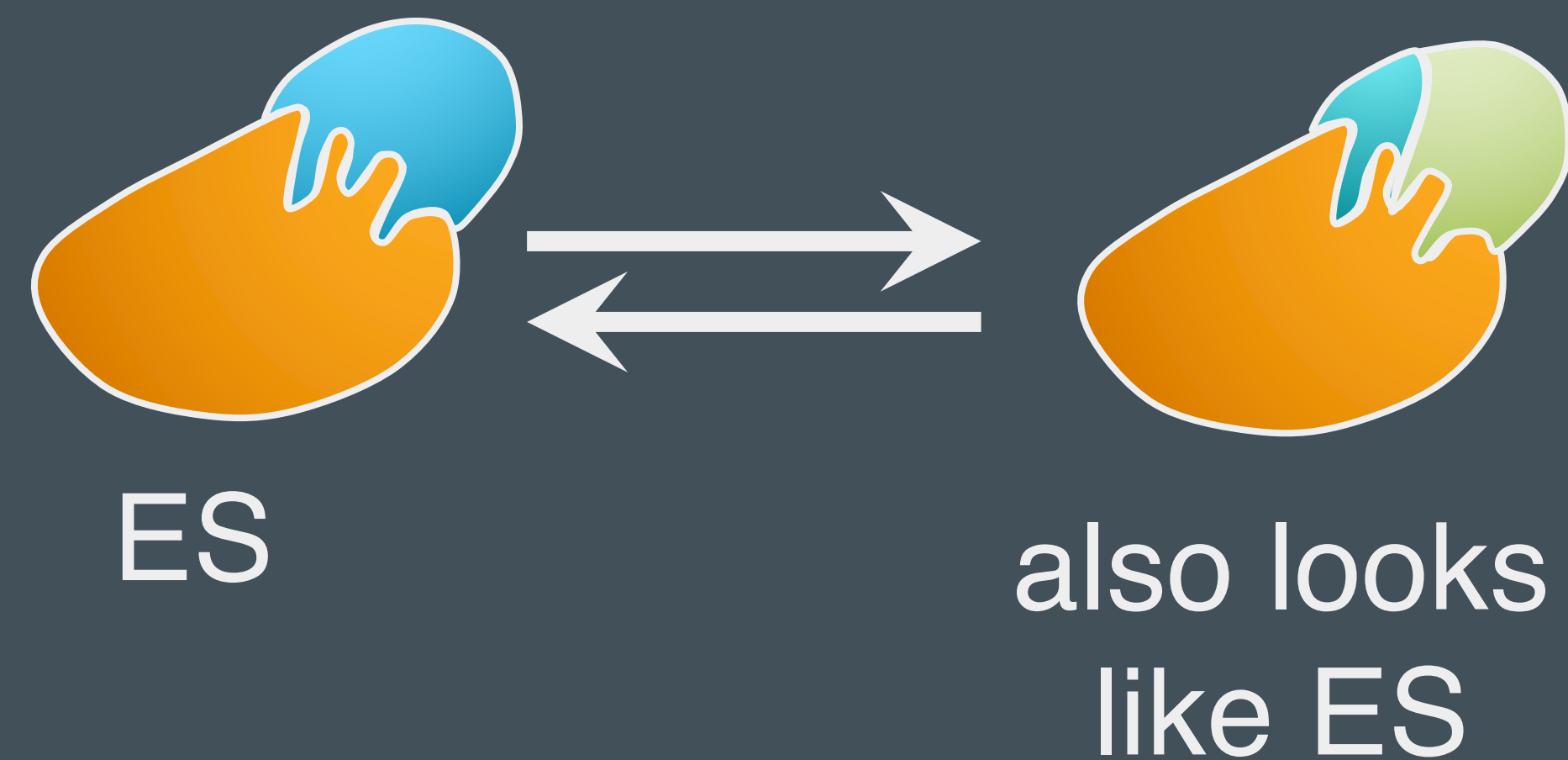
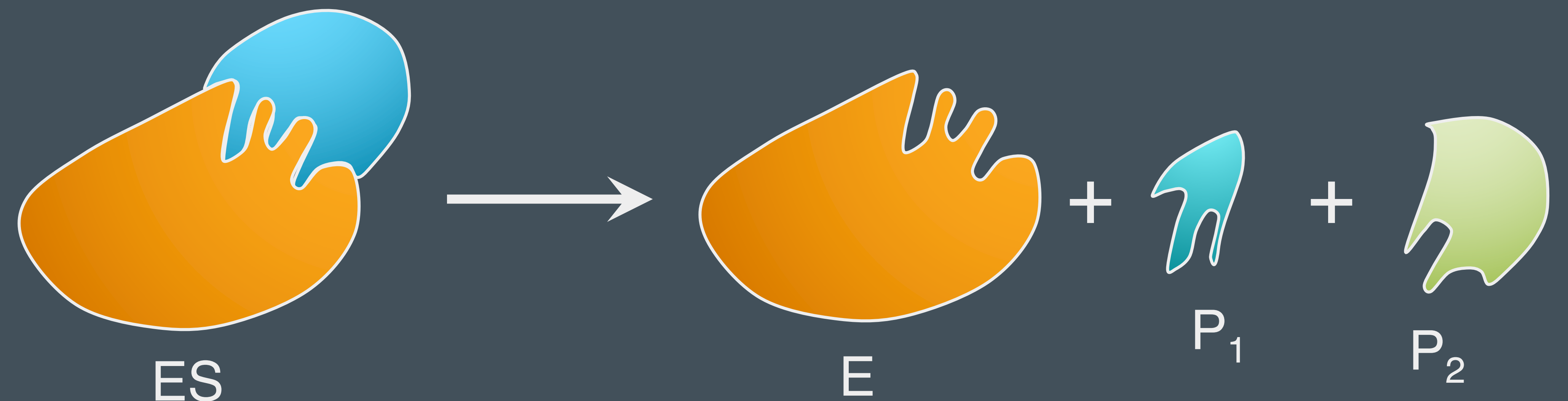
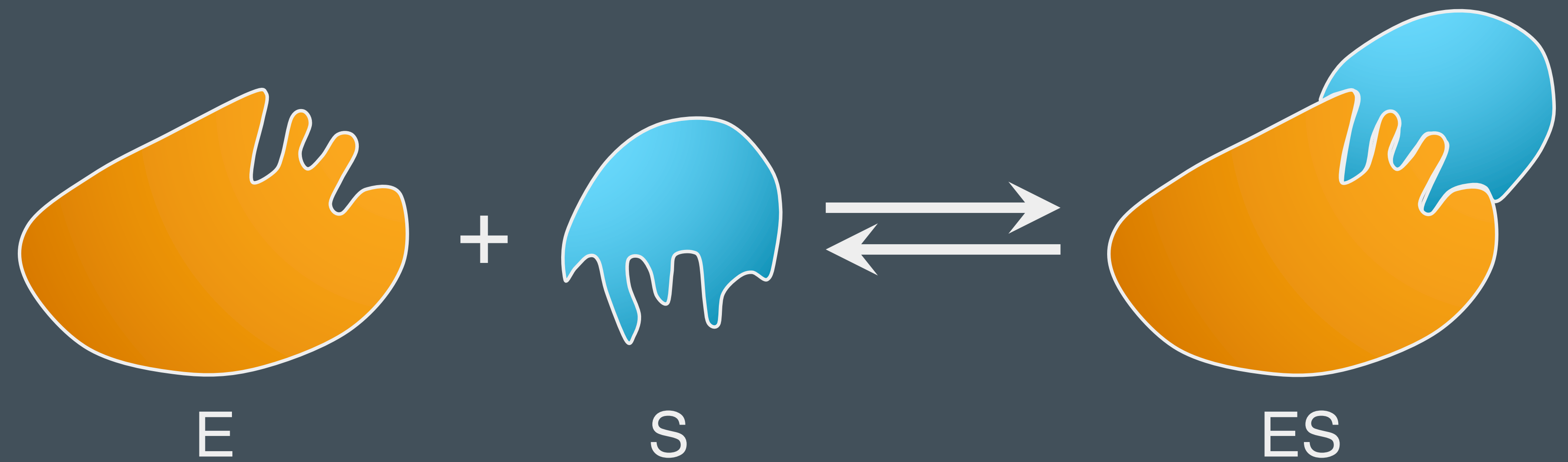
If the enzyme poison attaches to a different site other than the active site, the enzyme molecule can become distorted. This can change the shape of the active site such that the substrate no longer fits.



# Enzyme kinetics – Michaelis-Menten Kinetics

- Nothing new under the sun
- Derive using RDS and SSA approximation
- Experimentally measure:

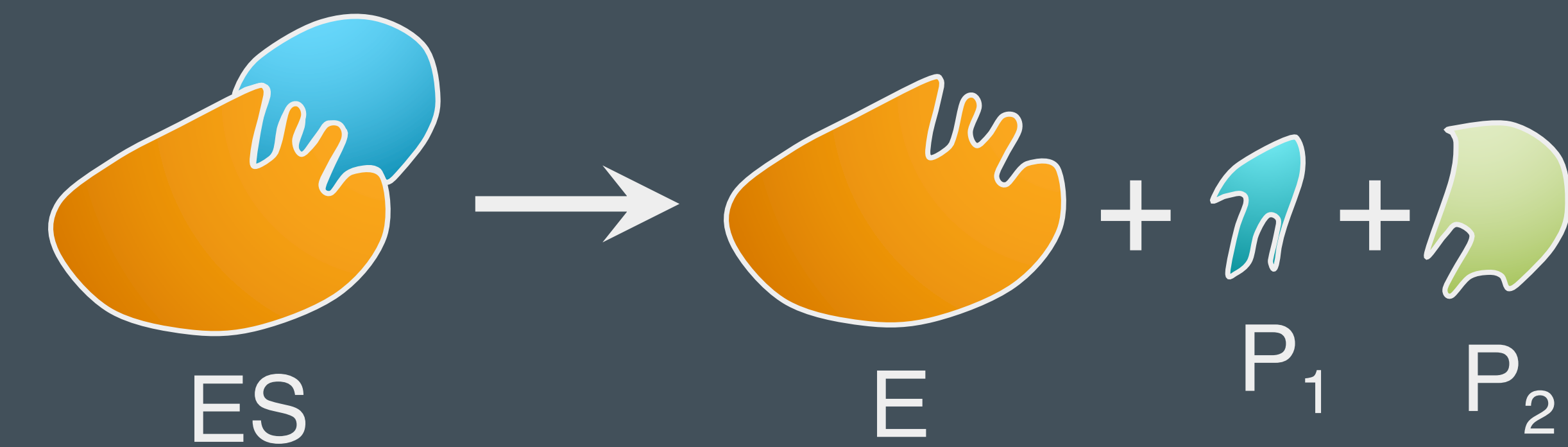
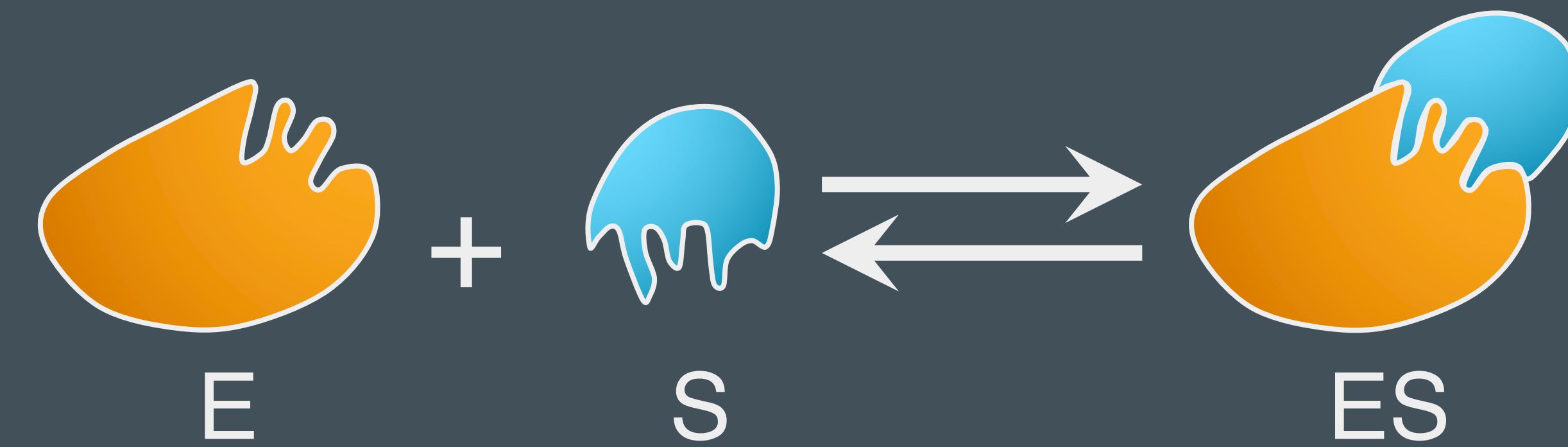
$$[E_0] = [E_{total}] = [E] + [ES]$$



# Enzyme kinetics – Michaelis-Menten Kinetics

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$$E_0 = E_{total} = E + ES$$



ES



Also could be ES

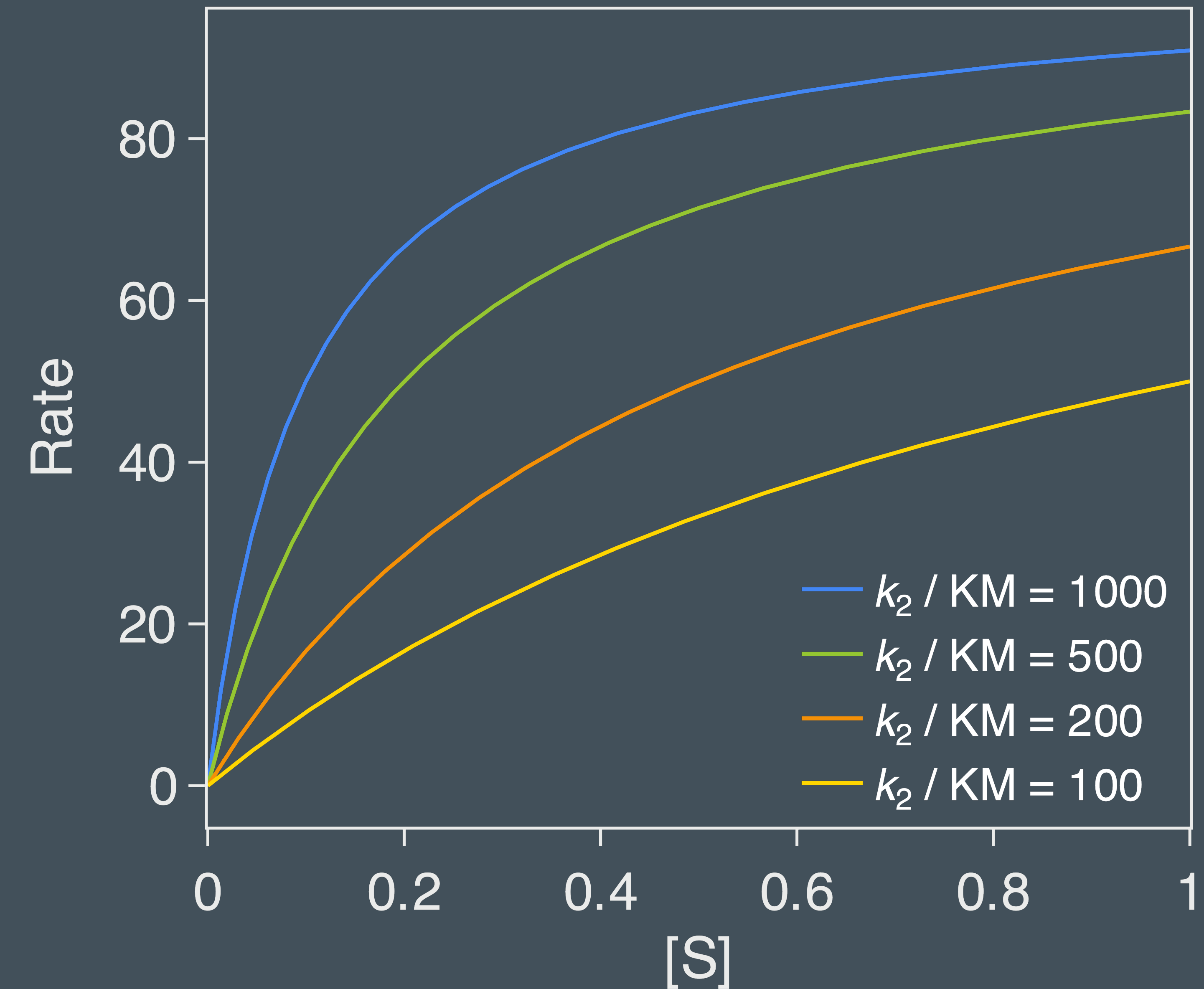
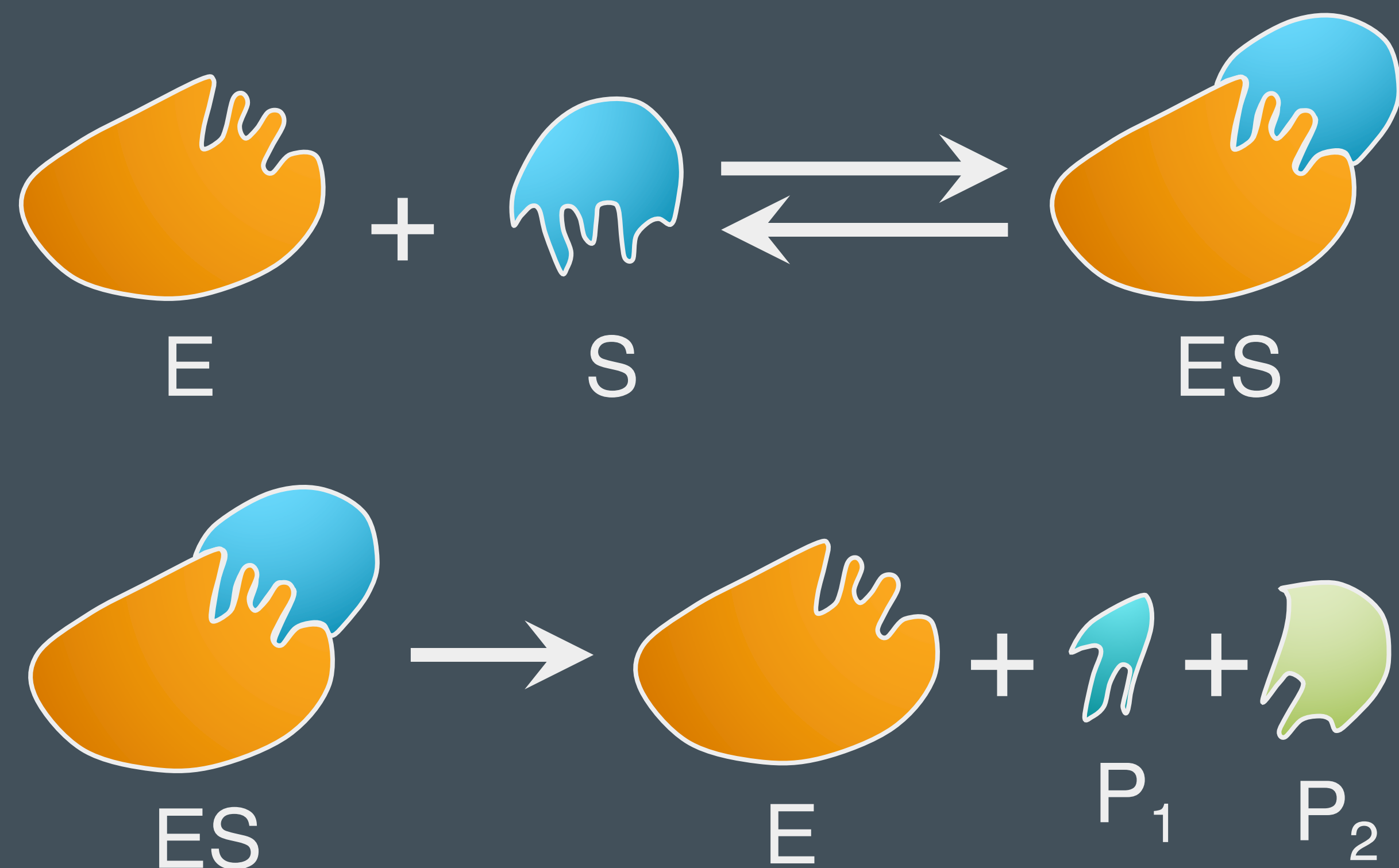
$$\text{rate of product formation} = \frac{k_2[S][E]_0}{K_m + [S]}$$

$$K_m = \frac{k_{-1} + k_2}{k_1}$$

# Enzyme kinetics – Michaelis-Menten Kinetics

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$$\text{rate of product formation} = \frac{k_2 [S] [E]_0}{K_m + [S]}$$

$$K_m = \frac{k_{-1} + k_2}{k_1}$$

“Catalytic efficiency” =  $k_2 / K_M$