12.3 - Catalysis and Reaction Rates

A. Empirical Effect of Catalysts

- A catalyzed reaction produces a greater yield in the same period of time (even at a lower temperature) than an uncatalyzed reaction.
- The use of a catalyst does not alter the net enthalpy change for a chemical reaction.
- In green plants, the process of photosynthesis can take place only in the presence of the catalyst chlorophyll.
- Most catalysts significantly accelerate reactions, even when present in very tiny amounts compared with the amount of reactants present.
- Metals prepared with a large surface area (powder or shavings) catalyze many reactions.

A **common consumer example** of catalysis today is the use of platinum, palladium, and rhodium in catalytic converters in car exhaust systems.

- These catalysts speed the combustion of the exhaust gases so that a higher proportion of the exhaust will be the relatively harmless, completely oxidized products.

Catalysts allow the use of lower temperatures. This not only reduces energy consumption but also prevents the decomposition of reactants and products and decreases unwanted side reactions. The result is an increase in the efficiency and economic benefits of many industrial reactions.

Catalysts in Living Systems

Compounds that act as catalysts in living systems are called **enzymes**. Enzymes are usually extremely complex molecules (proteins).

A lot of physiological reactions, such as metabolism, are actually controlled by the amount of enzyme present.

Enzymes are also of great importance for catalyzing reactions in the food, beverage, cleaner, and pharmaceutical industries.

B. Theoretical Explanation of Catalysis

Catalysts accelerate a reaction by providing an **alternative lower energy pathway** from reactants to products. That is, a catalyst allows the reaction to occur by a different activated complex, but resulting in the same products overall. If the new pathway has a lower activation energy, a greater fraction of molecules possess the minimum required energy and the reaction rate increases.

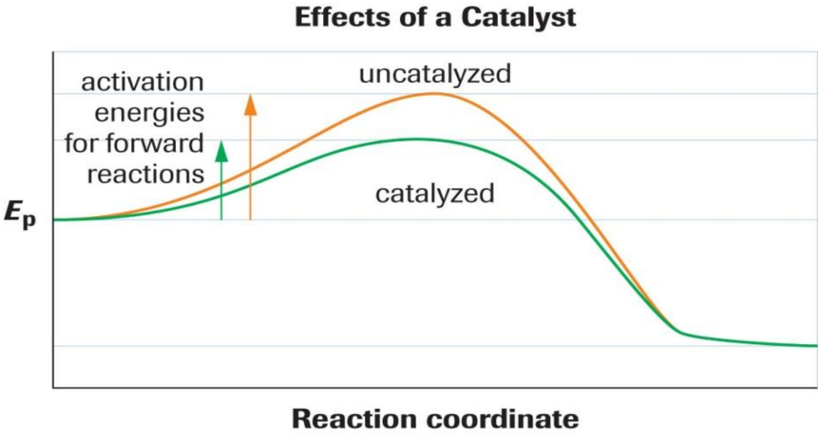
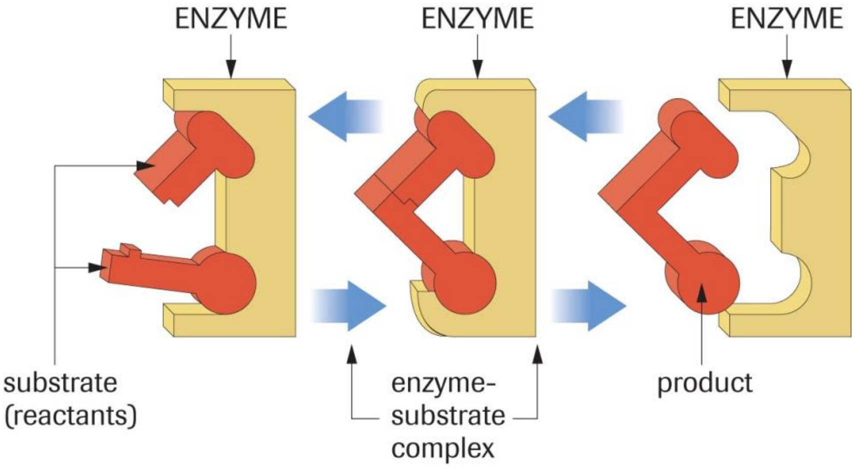


Figure 4
The catalyzed pathway has a lower activation energy, so more collisions lead to a successful reaction.

Scientists do not really understand the actual mechanism by which catalysis occurs for most reactions, and discovering effective catalysts has traditionally been an empirical process involving trial-and-error.

Most of the catalysts (enzymes) for biological reactions work by shape and orientation. They fit substrate proteins into locations on the enzyme as a key fits into a lock, enabling only specific molecules to link or detach on the enzyme, as shown below.



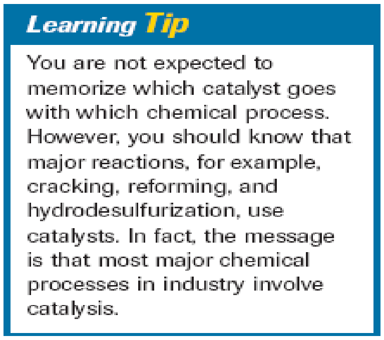
Catalysis and the Nature of Science

- A ***reaction mechanism*** describes the individual reaction steps and the intermediates formed during the reaction, starting with reactants and finishing with products.
- **Intermediates** are chemical entities that form with varying stability at the end of a step in a reaction mechanism.

The intermediate then reacts in a subsequent step and does not appear in the final reaction mixture.

C. Uses of Catalysts

1. The oil industry uses catalysts in the cracking and reforming of crude oil and bitumen to produce more marketable fractions (such as gasoline).
    - Catalysts increase the rate of the reaction while decreasing the energy (which often means decreasing the temperature) required for the chemical process.



Learning *Tip*

You are not expected to memorize which catalyst goes with which chemical process. However, you should know that major reactions, for example, cracking, reforming, and hydrodesulfurization, use catalysts. In fact, the message is that most major chemical processes in industry involve catalysis.

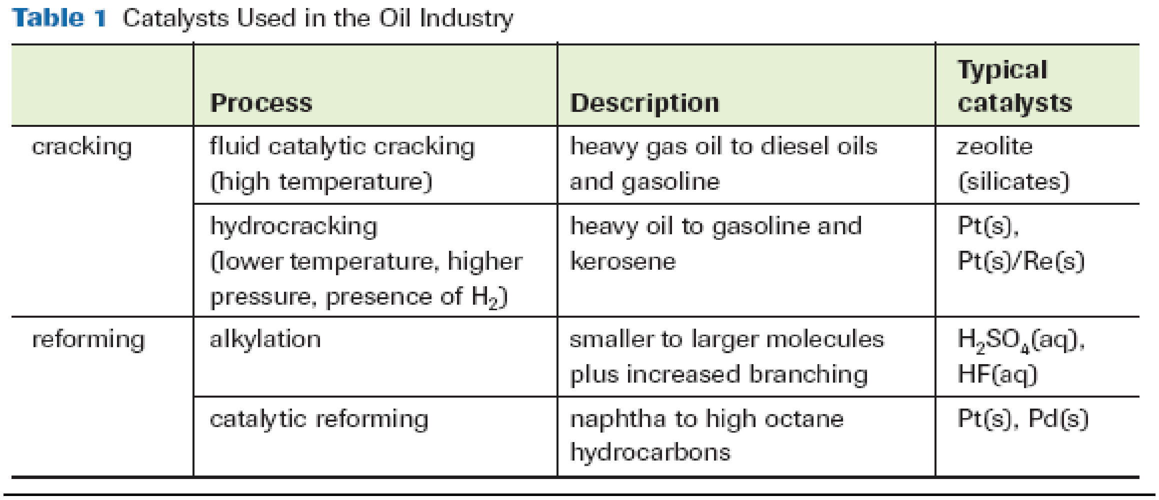


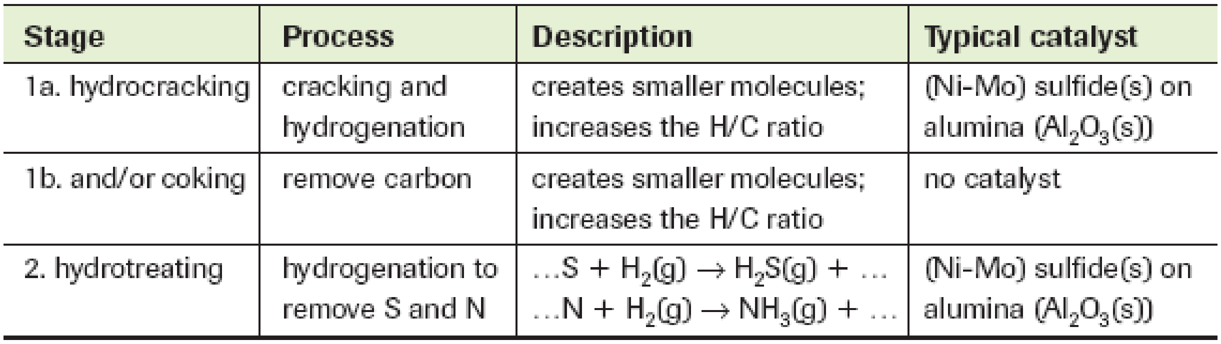
Table 1 Catalysts Used in the Oil Industry

	Process	Description	Typical catalysts
cracking	fluid catalytic cracking (high temperature)	heavy gas oil to diesel oils and gasoline	zeolite (silicates)
	hydrocracking (lower temperature, higher pressure, presence of H_2)	heavy oil to gasoline and kerosene	Pt(s), Pt(s)/Re(s)
reforming	alkylation	smaller to larger molecules plus increased branching	H_2SO_4(aq), HF(aq)
	catalytic reforming	naphtha to high octane hydrocarbons	Pt(s), Pd(s)

<u>Upgrading of Bitumen from Oil Sands</u>

Oil sand is about 84% bitumen, over 90% of which is recovered from the sand.

Table 2 Catalysts Used during Bitumen Upgrading



Stage	Process	Description	Typical catalyst
1a. hydrocracking	cracking and hydrogenation	creates smaller molecules; increases the H/C ratio	(Ni-Mo) sulfide(s) on alumina ($Al_2O_3(s)$)
1b. and/or coking	remove carbon	creates smaller molecules; increases the H/C ratio	no catalyst
2. hydrotreating	hydrogenation to remove S and N	$\ldots S + H_2(g) \rightarrow H_2S(g) + \ldots$ $\ldots N + H_2(g) \rightarrow NH_3(g) + \ldots$	(Ni-Mo) sulfide(s) on alumina ($Al_2O_3(s)$)

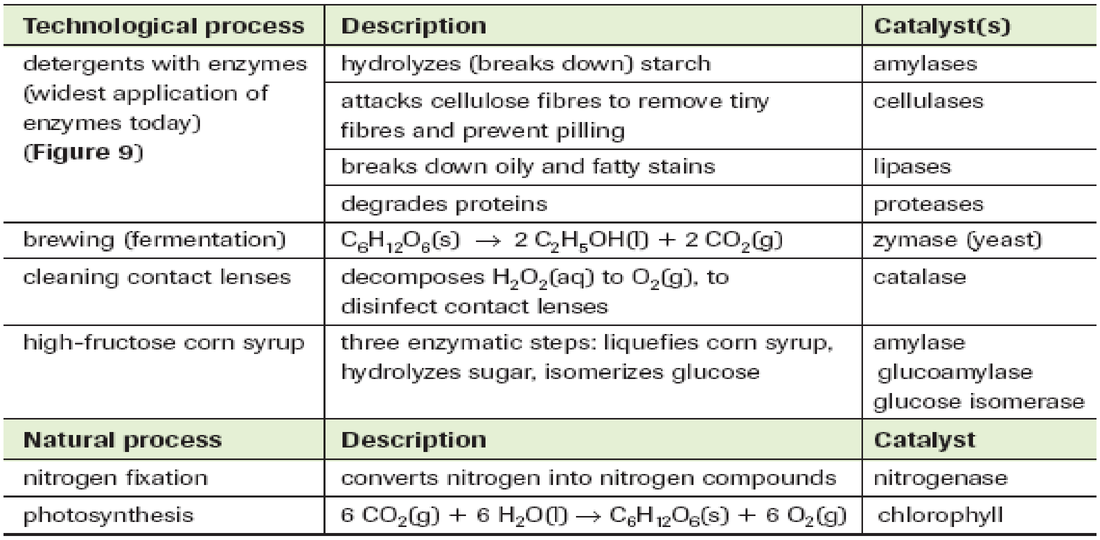
2. <u>Enzymes</u>

Natural product chemists have discovered many naturally occurring catalysts. Most of these catalysts are enzymes that increase the rate of specific reactions (**Table 4**).

Chemists are now using enzymes as catalysts for the production of chemicals not found in nature, such as pharmaceuticals and agricultural chemicals.

These enzymes are designed to be highly selective in the reaction each catalyzes, effective under ambient conditions, and convenient and safe to dispose.

Table 4 Natural Enzymes as Catalysts



Technological process	Description	Catalyst(s)
detergents with enzymes (widest application of enzymes today) (**Figure 9**)	hydrolyzes (breaks down) starch	amylases
	attacks cellulose fibres to remove tiny fibres and prevent pilling	cellulases
	breaks down oily and fatty stains	lipases
	degrades proteins	proteases
brewing (fermentation)	$C_6H_{12}O_6(s) \rightarrow 2\ C_2H_5OH(l) + 2\ CO_2(g)$	zymase (yeast)
cleaning contact lenses	decomposes $H_2O_2(aq)$ to $O_2(g)$, to disinfect contact lenses	catalase
high-fructose corn syrup	three enzymatic steps: liquefies corn syrup, hydrolyzes sugar, isomerizes glucose	amylase glucoamylase glucose isomerase
Natural process	**Description**	**Catalyst**
nitrogen fixation	converts nitrogen into nitrogen compounds	nitrogenase
photosynthesis	$6\ CO_2(g) + 6\ H_2O(l) \rightarrow C_6H_{12}O_6(s) + 6\ O_2(g)$	chlorophyll