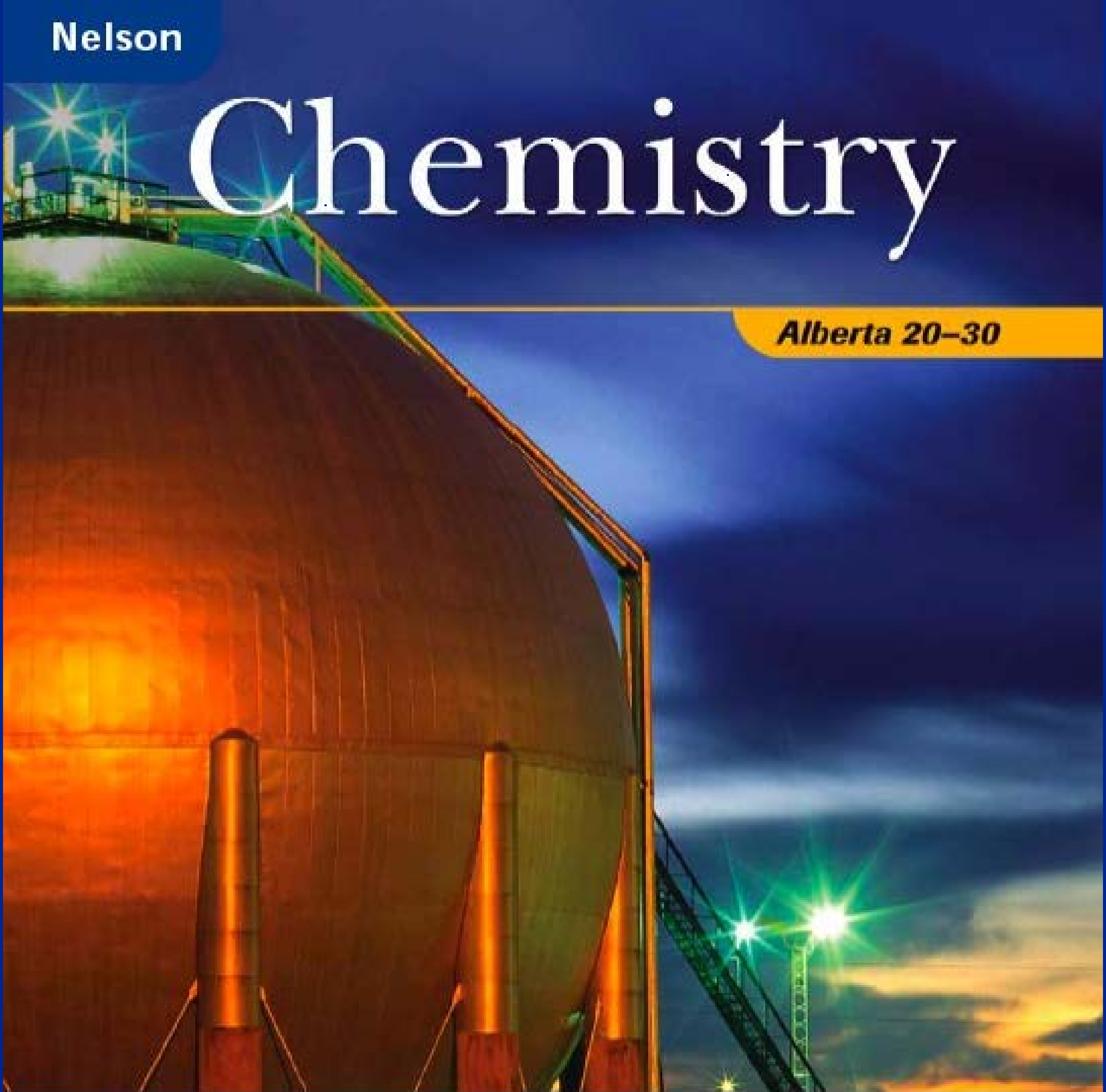
Nelson

Chemistry

Alberta 20–30



Chapter 12 Explaining Chemical Changes

Reaction Progress

Some reactions do not proceed spontaneously at room temperature unless additional energy is added to start them off.

Why is this initiating energy source necessary to cause the reaction?

From your experience, you may also have noticed that different reactants appear to react at different rates.

For example, different metals in contact with the same acid react at varying rates, and the same metal in contact with different acids reacts at varying rates.

Collision–Reaction Theory

Chemists created the collision–reaction theory to describe, explain, and predict characteristics of chemical reactions. Some of the main ideas of the collision–reaction theory are the following: (p525)

- A chemical sample consists of entities that are in constant random motion at various speeds, rebounding elastically from collisions with each other. (Kinetic energy is conserved during elastic collisions.)
- A chemical reaction must involve collisions of reactant entities.
- An effective collision requires sufficient energy. Collisions with the required minimum energy have the potential to react.
- An effective collision also requires the correct orientation (positioning) of the colliding entities so that bonds can be broken and new bonds formed.
- Ineffective collisions involve entities that rebound elastically from the collision.

Collision–Reaction Theory

According to collision–reaction theory, reactions can only take place when entities collide, but not all collisions result in a reaction. If the orientation is correct and the energy is sufficient, then a reaction can occur (**Figure 1**).

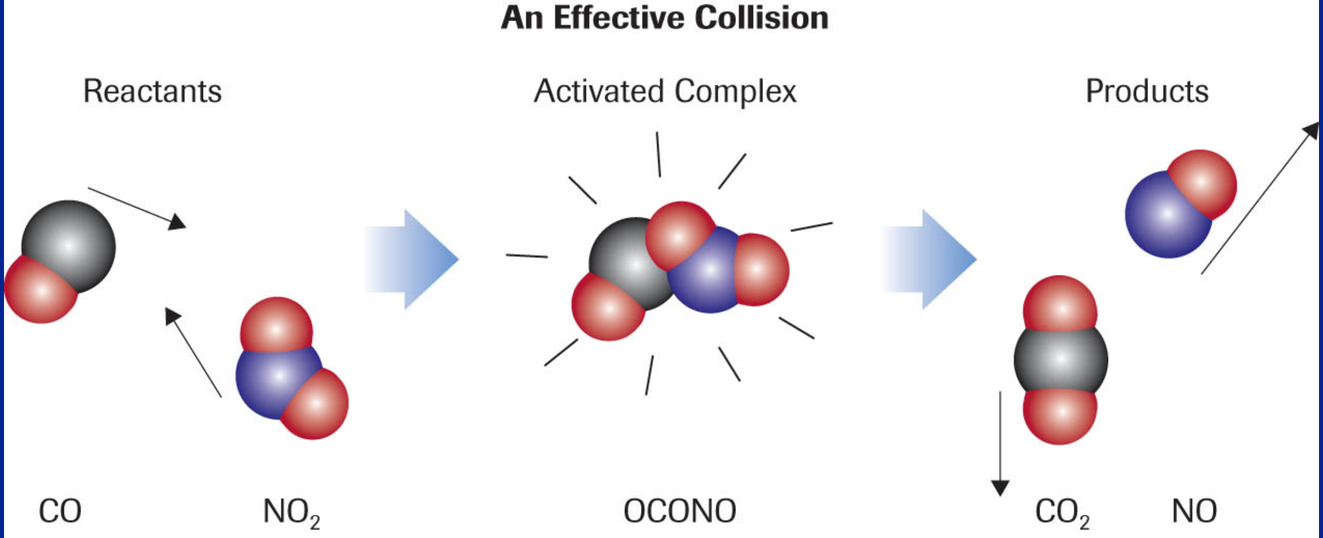


Figure 1
These molecules have both the correct orientation and sufficient energy, so the collision is effective: the atoms are rearranged and products are formed.

Collision–Reaction Theory

In other reactions, however, the collisions of reactant entities may involve insufficient energy or the collision may not have the correct orientation (**Figure 2**).

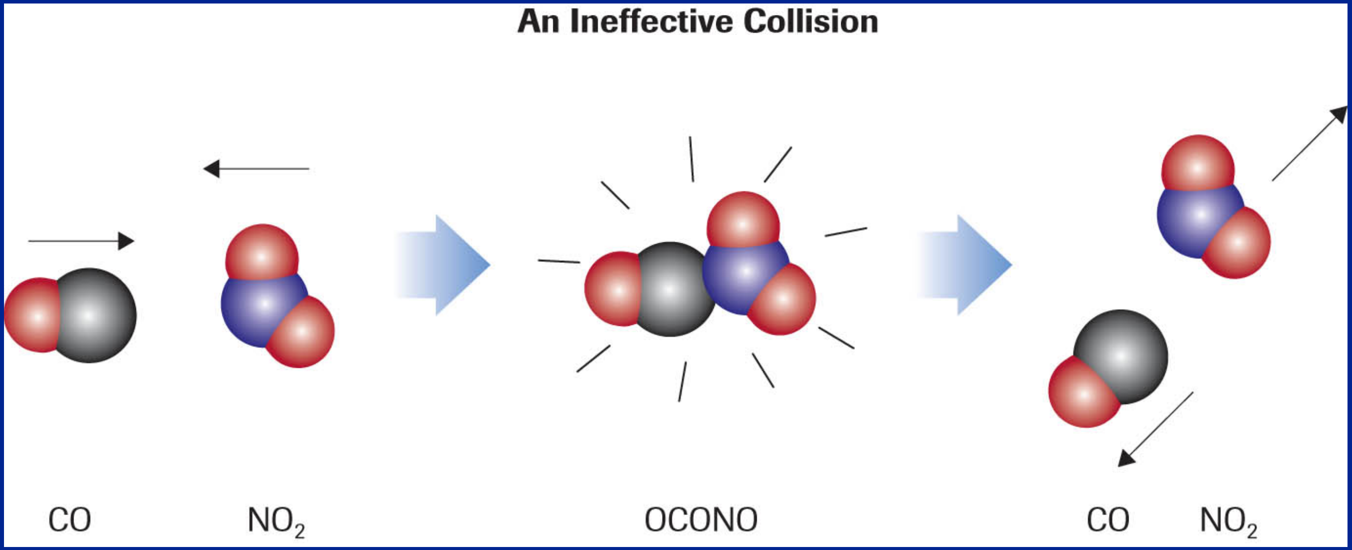


Figure 2
These molecules collide with a "wrong" orientation, so the bonds do not rearrange and no new substances form. The collision is ineffective.

Collision–Reaction Theory

There are two sources of evidence that need explaining.

First, why do some chemicals react faster than others, when all other variables except the type of chemical are controlled?

For example, why does magnesium react faster than zinc with hydrochloric acid?

Second, why do some reactions require an initial input of external energy to react?

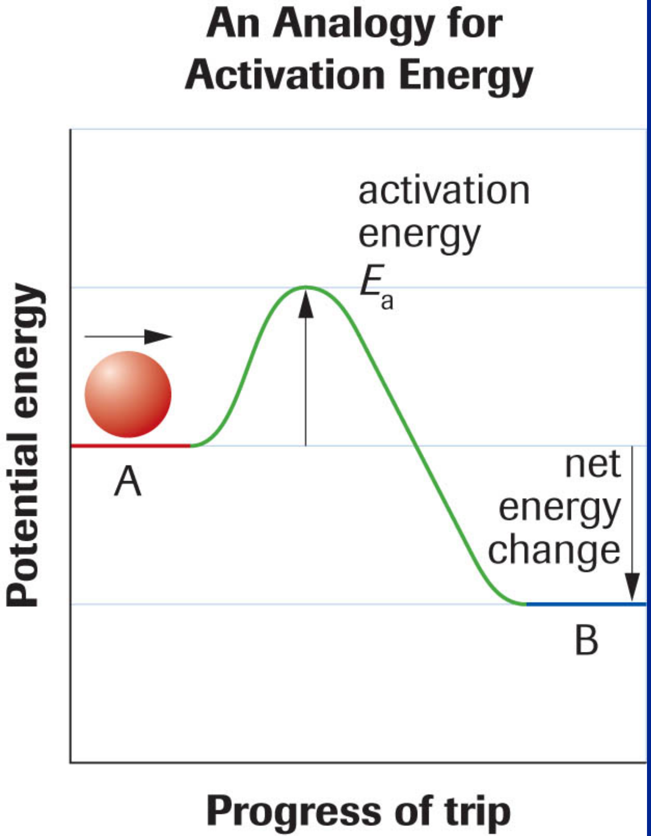
For example, why is a match needed to start the combustion of a hydrocarbon?

Activation Energy of a Reaction

Activation energy - an energy barrier that must be overcome for a chemical reaction to occur.

Entities must reach this minimum energy before they can react. The input energy (which supplies the activation energy) may be in the form of heat, light, or electricity.

Activation Energy of a Reaction



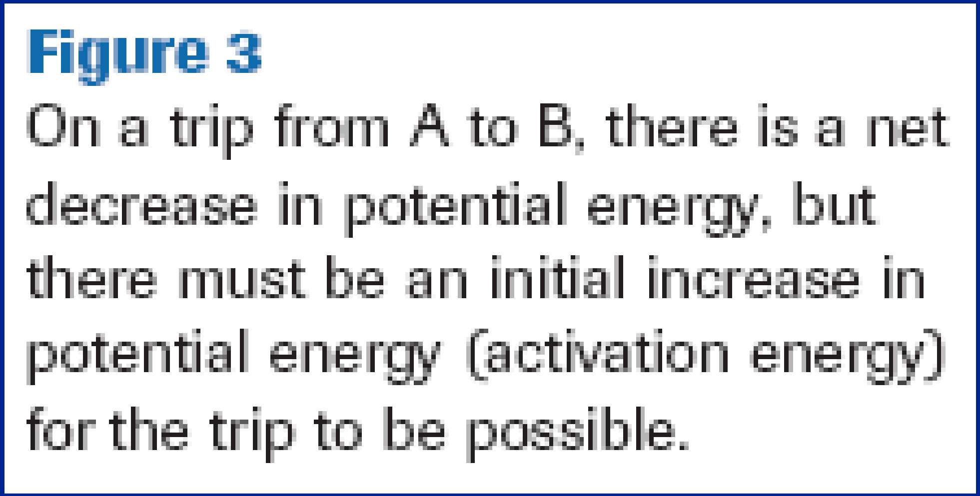


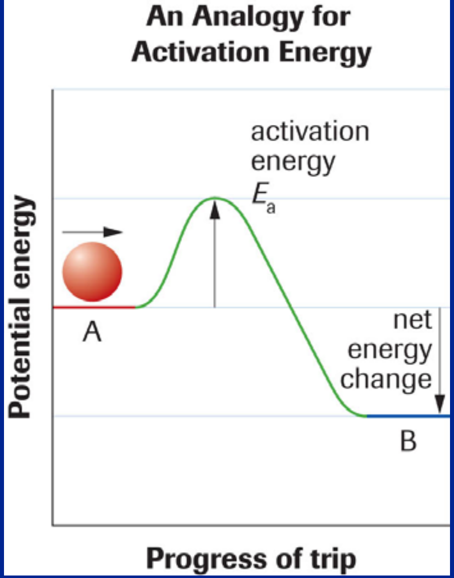
Figure 3
On a trip from A to B, there is a net decrease in potential energy, but there must be an initial increase in potential energy (activation energy) for the trip to be possible.

Activation Energy of a Reaction

Consider the analogy of a billiard ball rolling on a smooth track shaped as shown in **Figure 3**.

The ball can only successfully overcome the rise of the track to reach point B if it has a large enough initial speed (kinetic energy).

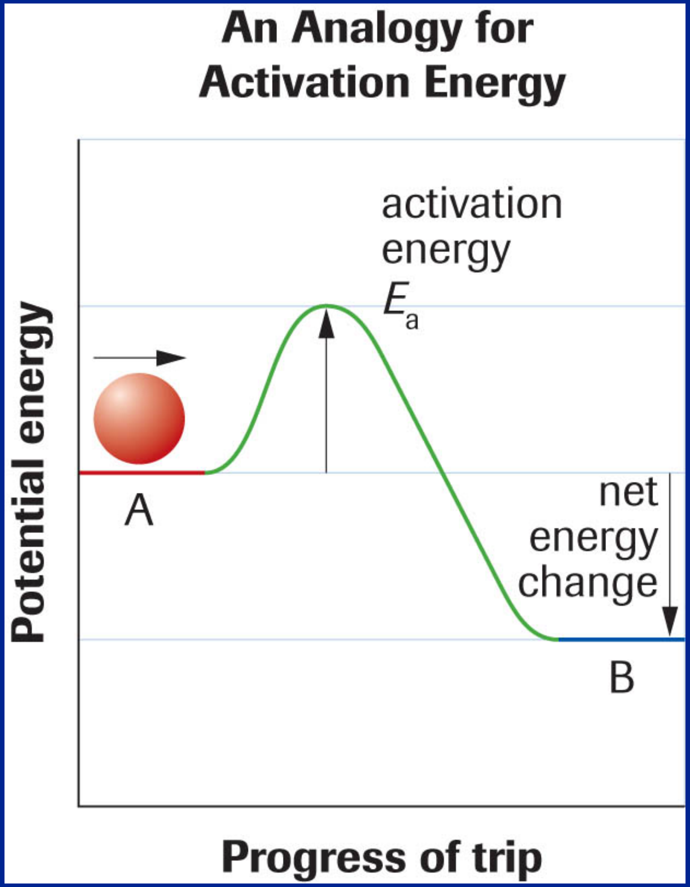
We could call this situation an ***effective*** trip.



The minimum kinetic energy required is analogous to the ***activation energy*** for a reaction. If the ball does not have enough kinetic energy, it will not reach the top of the track and will just roll back to point A. This is like two molecules colliding without enough energy to rearrange their bonds - they just rebound elastically.

Activation Energy of a Reaction

A ball that returns to point A will have the same kinetic energy it began with, but a ball that makes it to point B will have more kinetic energy (but less potential energy) because it will be moving faster.



Activation Energy of a Reaction

The example above is also analogous to the enthalpy change for an exothermic reaction. The enthalpy change (net chemical energy change) results in energy being immediately released to neighbouring entities.

These entities then move faster, collide with more energy, and are more likely to react.

Activation Energy of a Reaction

The energy released when the first few molecules of hydrogen and oxygen react (initiated by a spark or flame) is quickly transferred to other molecules, allowing the reaction to proceed unaided by external sources of energy (**Figure 4**).

The reaction, once begun, is self-sustaining as long as enough reactants remain to make collisions likely.

Exothermic reactions, once begun, often drive themselves.

Activation Energy of a Reaction

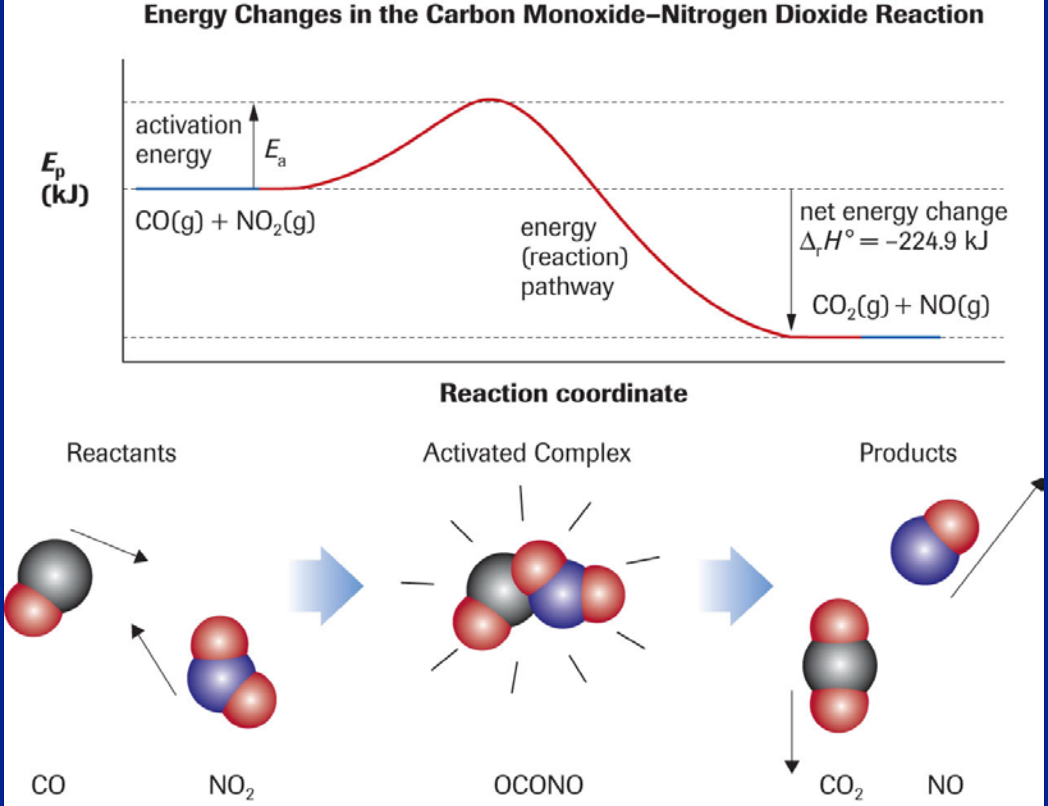
Consider the reaction of carbon monoxide with nitrogen dioxide, plotted as potential energy of the molecules versus progress of reaction.

$$CO(g) + NO_2(g) \rightarrow CO_2(g) + NO(g) \qquad \Delta_r H^\circ = -224.9\ \text{kJ}$$

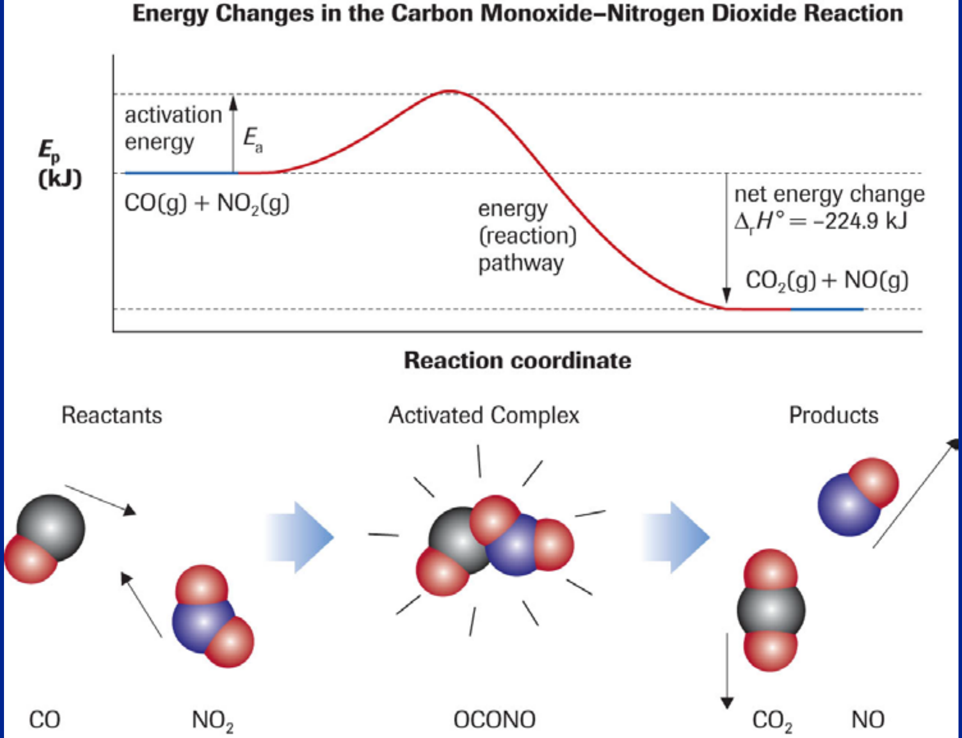
Activation Energy of a Reaction

The molecular collision follows an energy (or reaction) pathway along the plot from left to right.

The *energy pathway* is the relative potential energy of the chemical system as it moves from reactants through activated complex to products.



Activation Energy of a Reaction



Energy Changes in the Carbon Monoxide–Nitrogen Dioxide Reaction

The *activated complex* is the chemical entity containing the collided reactants.
As the molecules approach each other, they are affected by repulsion forces and begin to slow down.
If the molecules have enough kinetic energy, meaning more energy than is required to get to the energy level of the activated complex - they can approach closely enough for their bond structure to rearrange.
Repulsion forces push the product molecules apart, converting E_P to E_K.

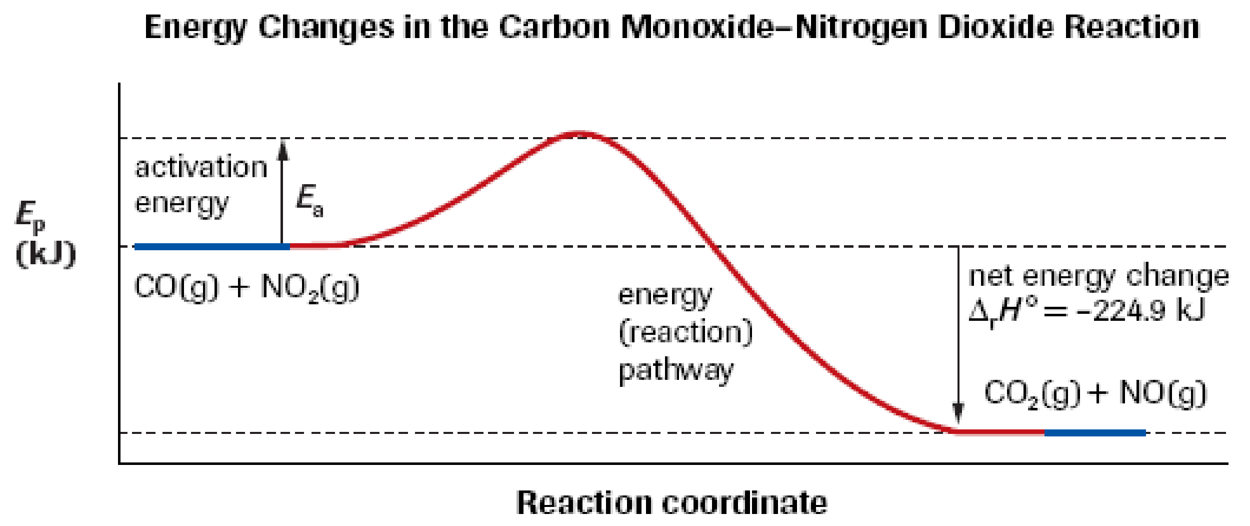
Activation Energy of a Reaction

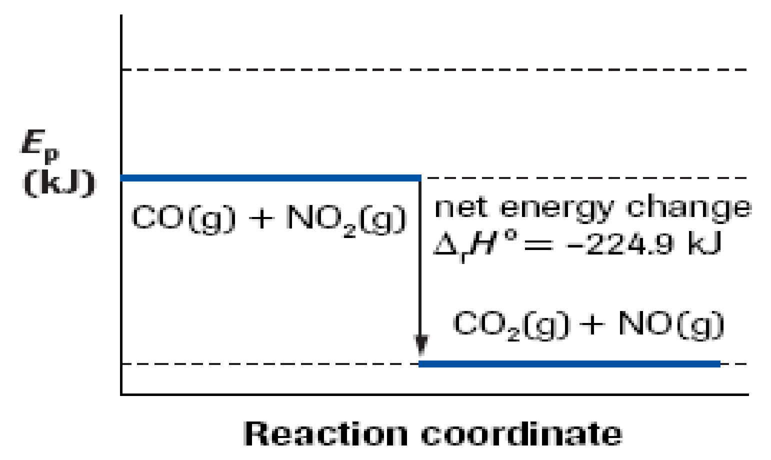
If a large quantity of energy is needed to start a reaction and if the reaction progresses relatively slowly, then the activation energy is large.

A spontaneous reaction at room temperature and a higher rate of reaction is interpreted as a relatively small activation energy.

You can think of the new energy pathway diagrams as being an expanded form of chemical potential energy diagram, with the approximate energy of the activated complex also represented. This is shown on the next slide.

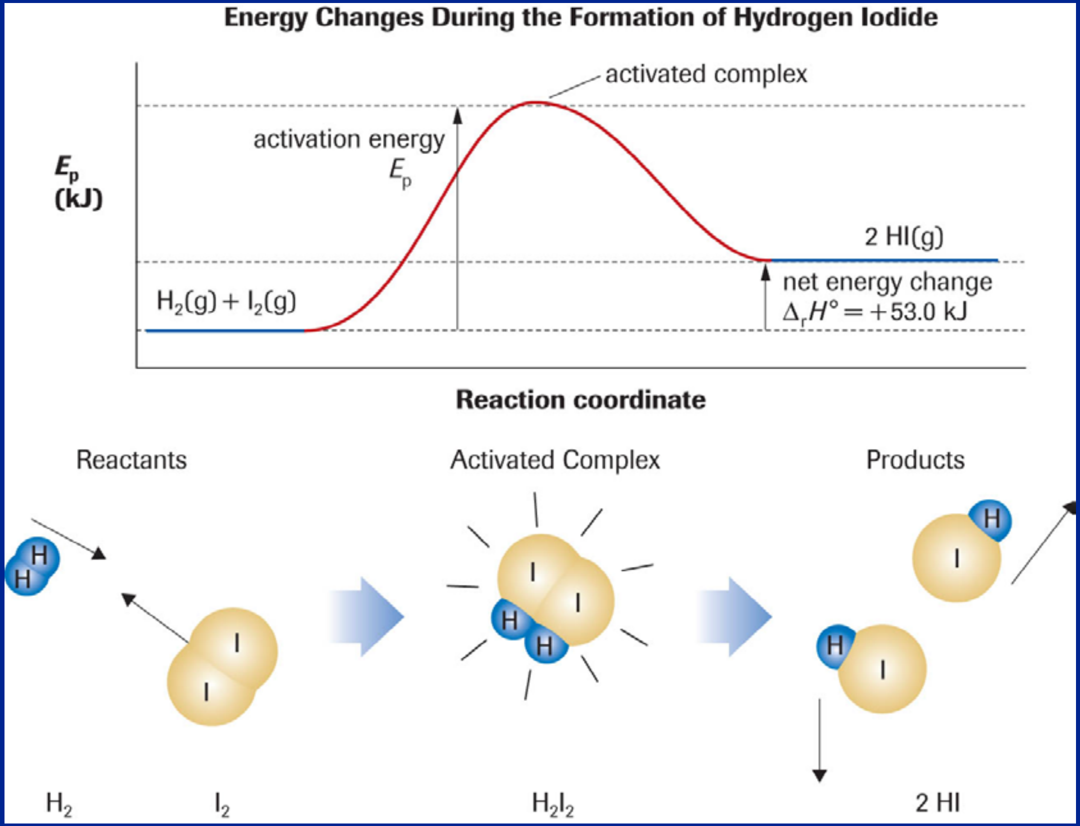
Activation Energy of a Reaction





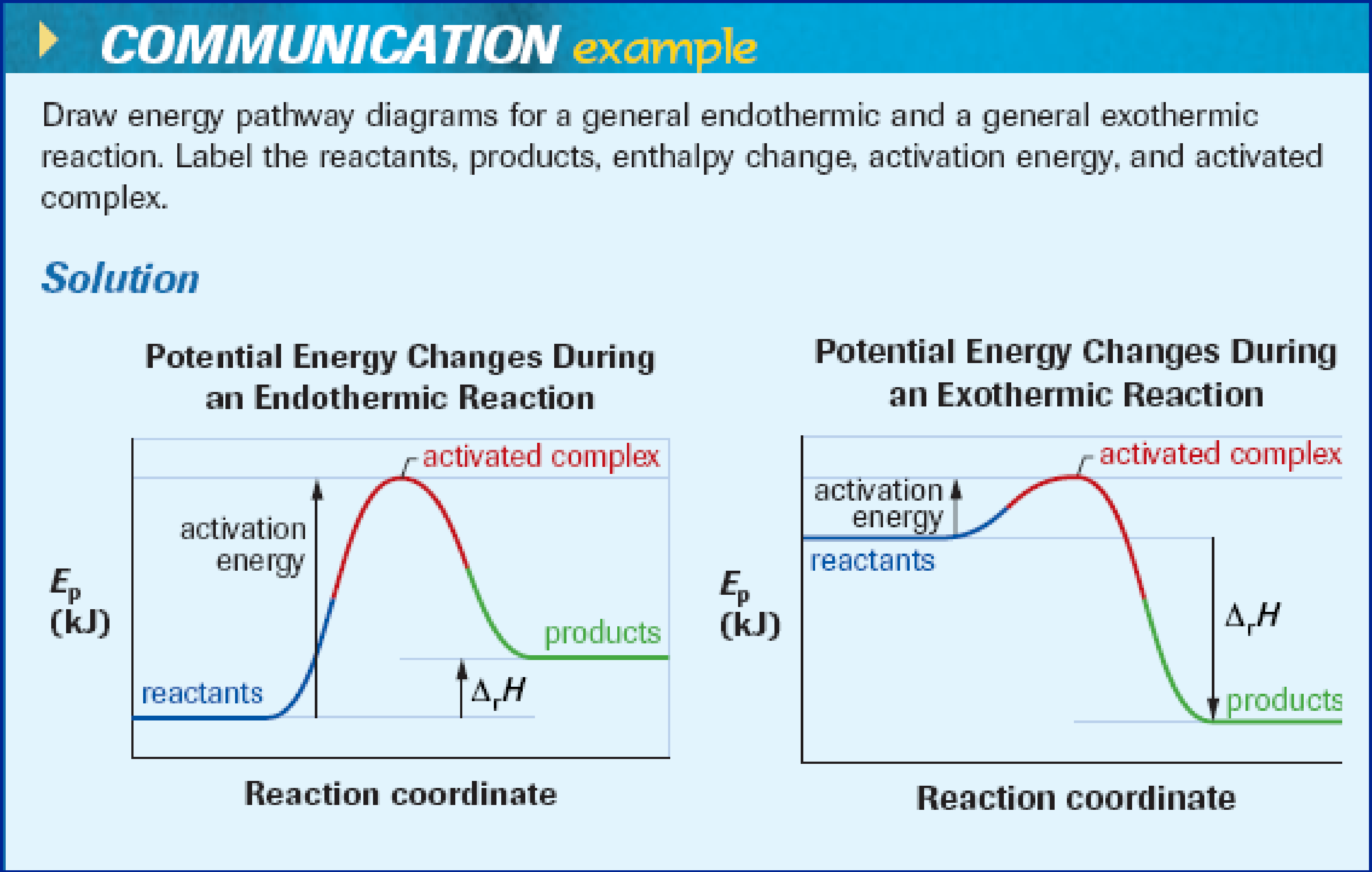
Activation Energy of a Reaction

If the potential energy of the products were greater than that of the reactants - the reaction would be endothermic.


Energy Changes During the Formation of Hydrogen Iodide

A continuous input of energy, usually heat, would be needed to keep the reaction going, and the enthalpy change would be positive (**Figure 7**).

Activation Energy of a Reaction



COMMUNICATION *example*

Draw energy pathway diagrams for a general endothermic and a general exothermic reaction. Label the reactants, products, enthalpy change, activation energy, and activated complex.

Solution

Potential Energy Changes During an Endothermic Reaction

Potential Energy Changes During an Exothermic Reaction

12.2 Bond Energy and Reactions

Electrical forces hold atoms together.

If atoms or ions are bonded together, energy (in the form of heat, light, or electricity) is required to separate them.

In other words, bond breaking requires energy.

bonded particles + energy → separated particles

In contrast, bond making releases energy.

separated particles → bonded particles + energy

12.2 Bond Energy and Reactions

The stronger the bond holding the particles together, the greater the quantity of energy required to separate them.

Bond energy is the energy required to break a chemical bond. It is also the energy released when a bond is formed.

Even the simplest of chemical reactions involves the breaking and forming of several individual bonds.

12.2 Bond Energy and Reactions

Endothermic Reactions:
Consider the decomposition of water:

$$2\,H_2O(l) \rightarrow 2\,H_2(g) + O_2(g) \qquad \Delta_r H^\circ = +571.6\ \text{kJ}$$

Hydrogen–oxygen bonds in the water molecules must be broken, and the hydrogen–hydrogen and oxygen–oxygen bonds must be formed.

Since the overall change is endothermic, the energy required to break the O—H bonds must be greater than the energy released when the H—H and O=O bonds form.

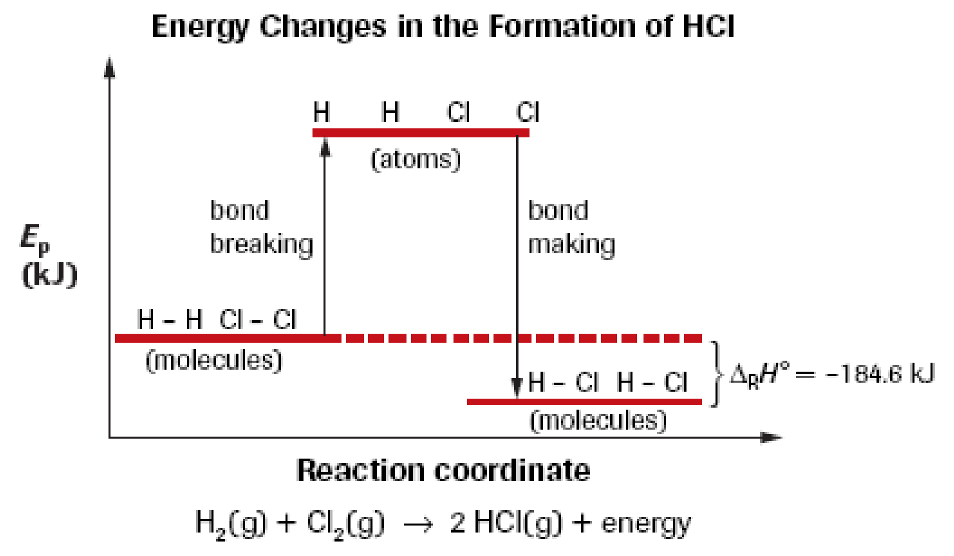
In any endothermic reaction, more energy is needed to break bonds in the reactants than is released by bonds formed in the products.

12.2 Bond Energy and Reactions

Exothermic Reactions:

For exothermic reactions more energy is released by bonds formed in the products than is needed to break bonds in the reactants.

The reaction between hydrogen and chlorine (**Figure 3**) illustrates the energy of bond breaking and bond making.

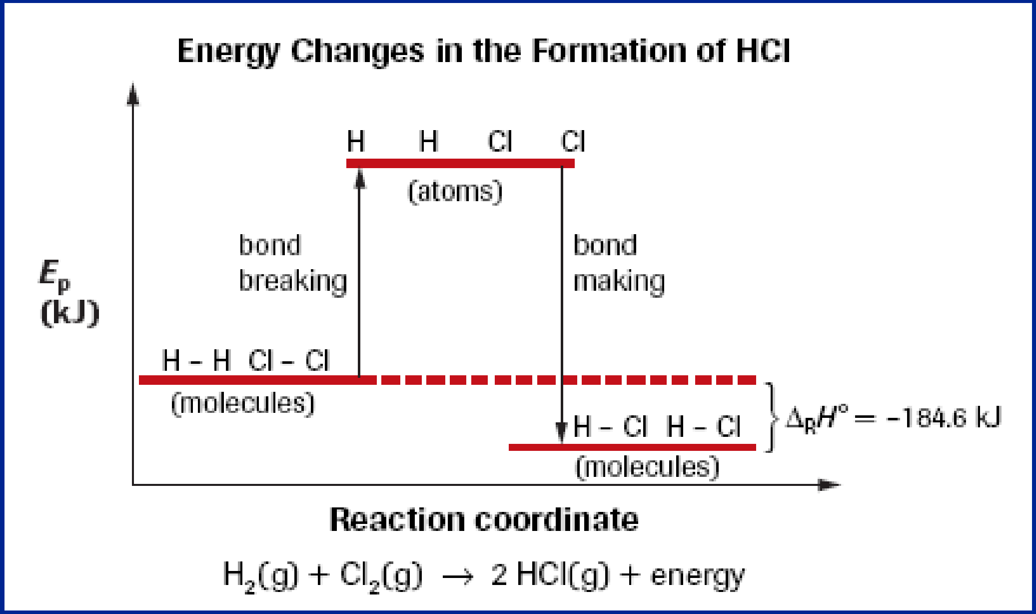


12.2 Bond Energy and Reactions

Energy is required to break the bonds in hydrogen molecules (H_2) to create hydrogen atoms (H), each having higher chemical potential energy than a hydrogen molecule.

The chlorine atoms have higher potential energy than the chlorine molecules. When the hydrogen and chlorine atoms make bonds to create hydrogen chloride molecules, energy is released.

This reaction is **exothermic**, more energy is released by bond making than is required for bond breaking.



12.2 Bond Energy and Reactions

Bond energies are the fourth method that you have encountered for predicting or explaining a change in enthalpy for a chemical reaction.

The methods that you have studied for predicting and/or explaining a change in enthalpy are the following:

1. calorimetry: the change in enthalpy equals the change in thermal energy
2. Hess’ law: the change in enthalpy equals the sum of component enthalpy changes
3. molar enthalpies of formation: the change in enthalpy equals the enthalpies of formation of the products minus the enthalpies of formation of the reactants
4. bond energies: the change in enthalpy equals the energy released from bond

12.2 Summary: Bond Energy and Enthalpy Changes

- Bond energy is the energy required to break a chemical bond; it is also the energy released when a bond is formed.
- The change in enthalpy represents the net effect from breaking and making bonds.
  $\Delta_r H$ = energy released from bond making – energy required for bond breaking
  Exothermic reaction: making > breaking ($\Delta_r H$ is negative.)
  Endothermic reaction: breaking > making ($\Delta_r H$ is positive.)

Empirical Effect of Catalysis

Catalysis deals with the properties and development of catalysts, and the effects of catalysts on the rates of reaction.

A **catalyst** is a substance that increases the rate of a chemical reaction without being consumed itself in the overall process.

- The chemical composition and amount of a catalyst are identical at the start and at the end of a reaction.

A catalyst reduces the quantity of energy required to start the reaction.

Empirical Effect of Catalysis

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.

Empirical Effect of Catalysis

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.

Empirical Effect of Catalysis

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.

Empirical Effect of Catalysis

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.

Theoretical Explanation of Catalysis

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.

Theoretical Explanation of Catalysis

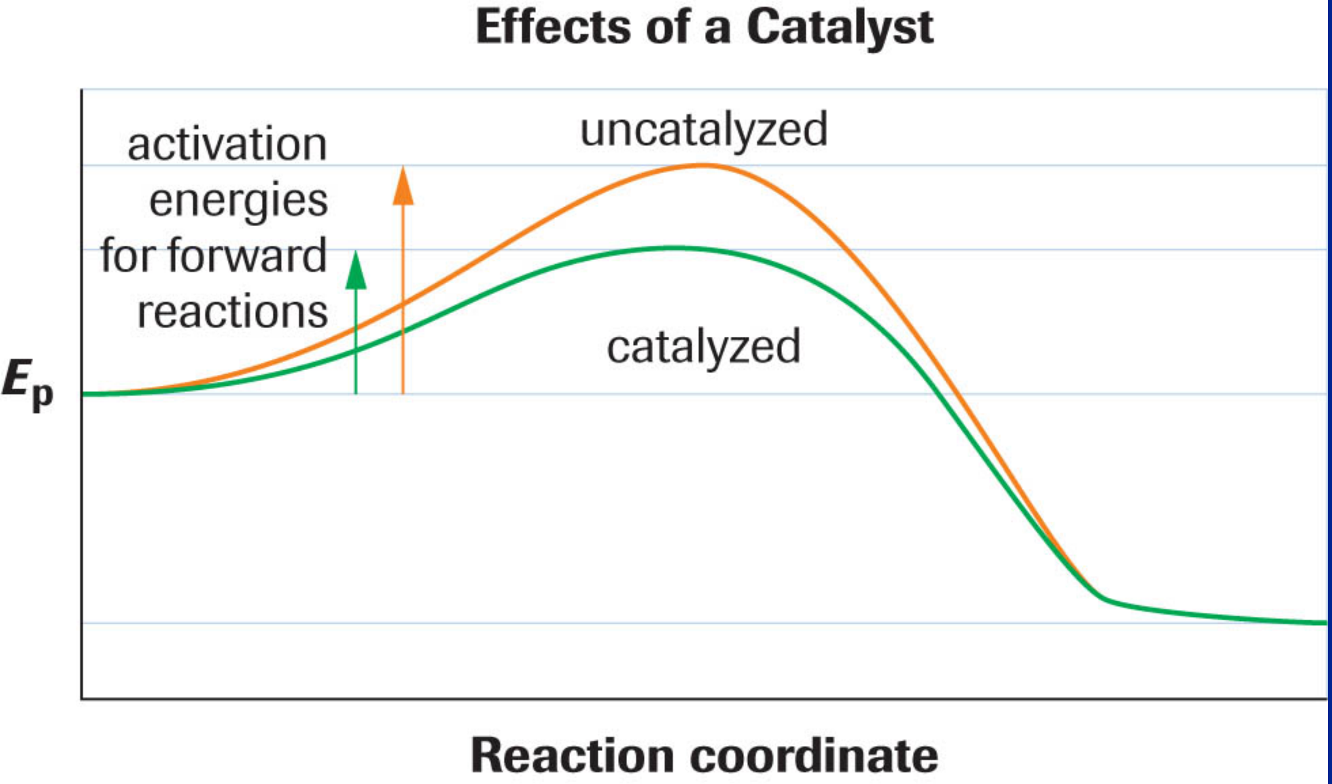
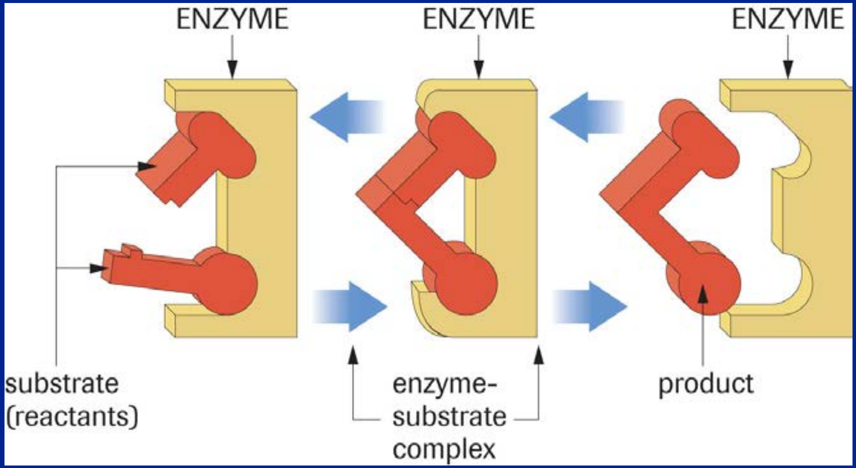


Figure 4
The catalyzed pathway has a lower activation energy, so more collisions lead to a successful reaction.

Theoretical Explanation of Catalysis

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 in **Figure 5**.



Theoretical Explanation of Catalysis

Catalysis and the Nature of Science

The practice of science uses two important kinds of reasonig:

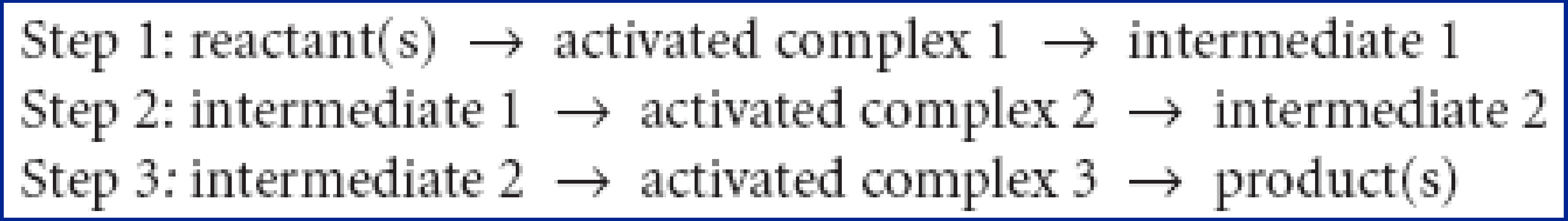
1. *Inductive reasoning* involves extending specific examples to obtain a general statement; for example, using the evidence from an experiment to form a hypothesis.

2. *Deductive reasoning* involves applying a general concept such as a theory, law, or generalization to obtain (deduce) a specific instance.

Theoretical Explanation of Catalysis

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.


Step 1: reactant(s) → activated complex 1 → intermediate 1
Step 2: intermediate 1 → activated complex 2 → intermediate 2
Step 3: intermediate 2 → activated complex 3 → product(s)

Theoretical Explanation of Catalysis

The inductive reasoning of using the evidence from an experiment to hypothesize a reaction mechanism is usually accompanied by deductive reasoning to test the logic of the mechanism.

Chemists constantly ask themselves if a hypothesis makes sense based upon all the evidence they have collected and all of their chemical experience.

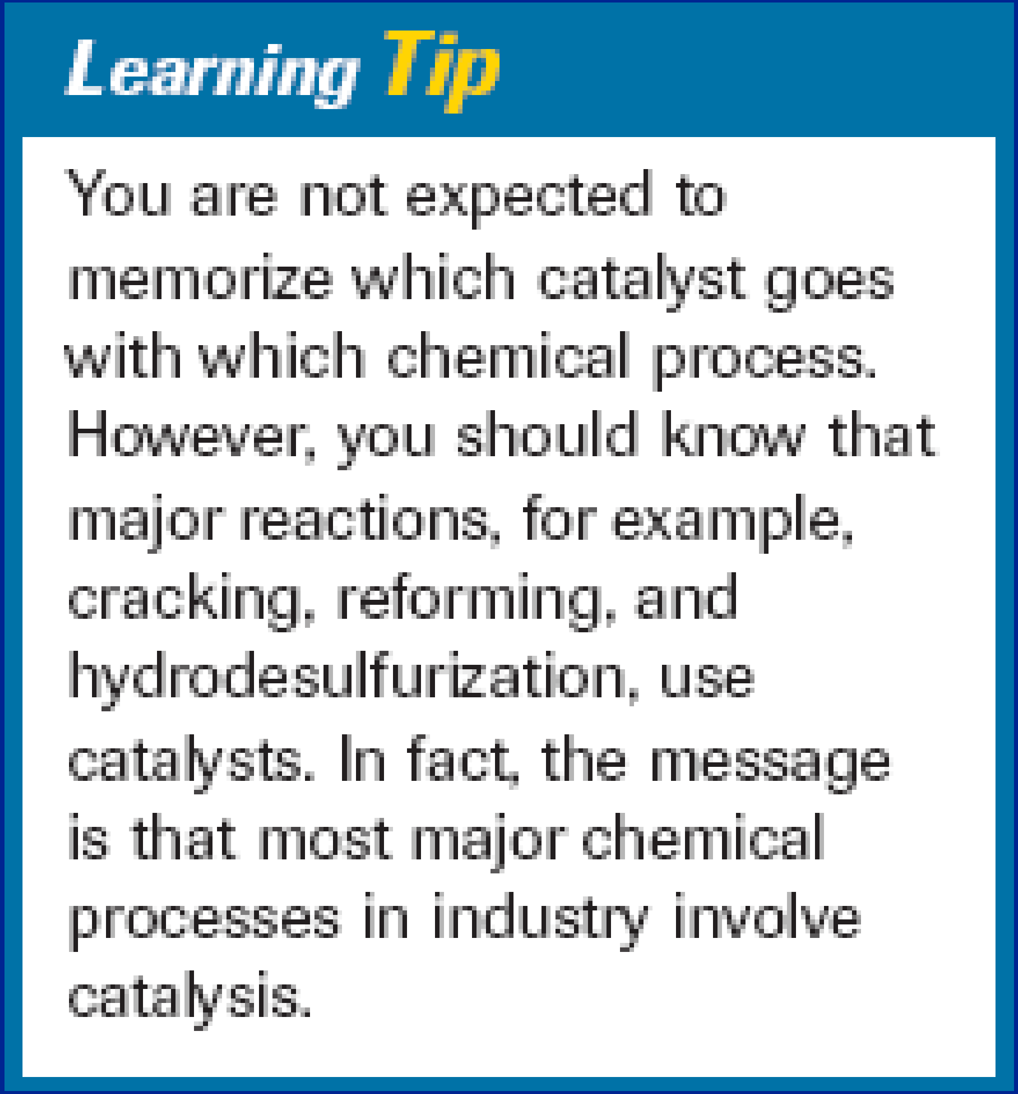
Uses of Catalysts

The Oil Industry

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.

Uses of Catalysts



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.

Uses of Catalysts

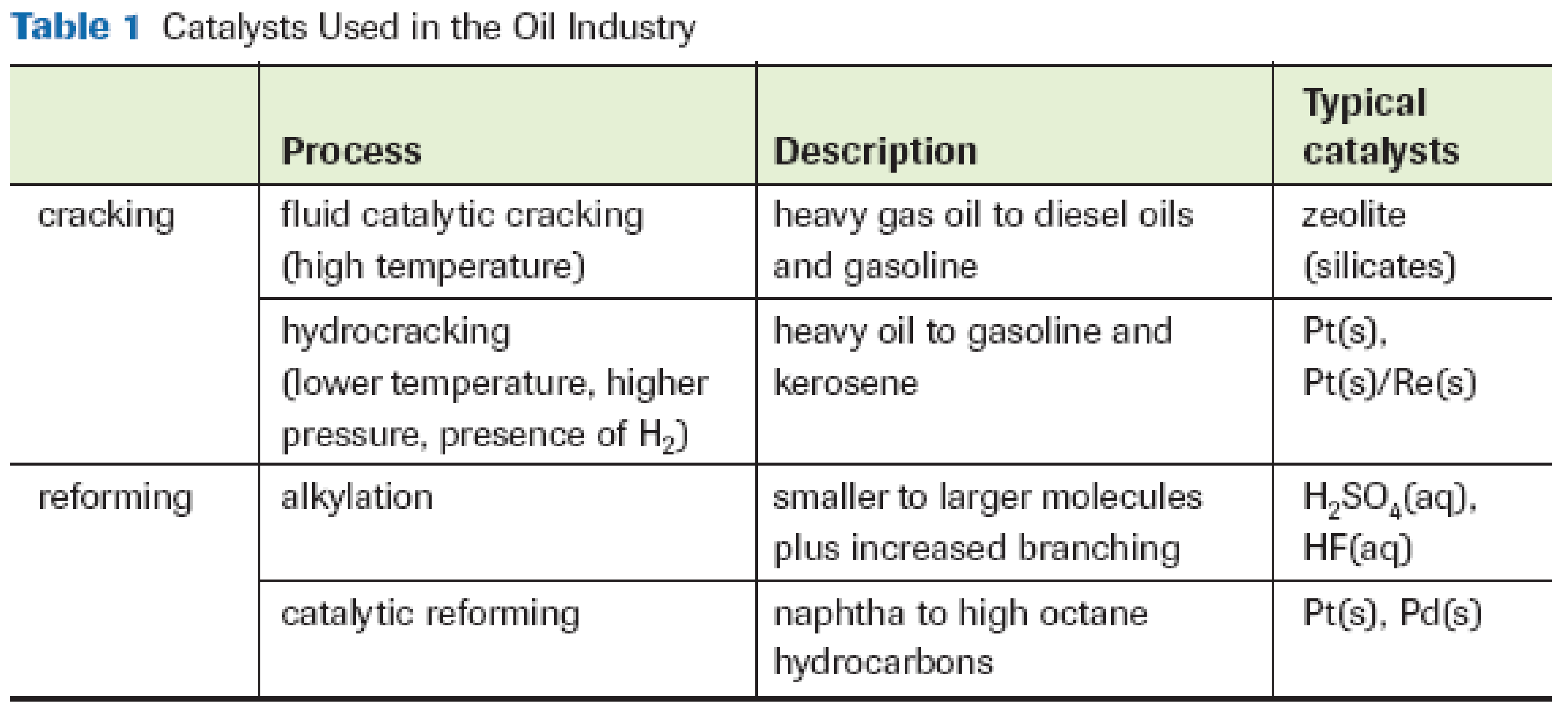


Table 1 Catalysts Used in the Oil Industry

	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)

Uses of Catalysts

Upgrading of Bitumen from Oil Sands

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

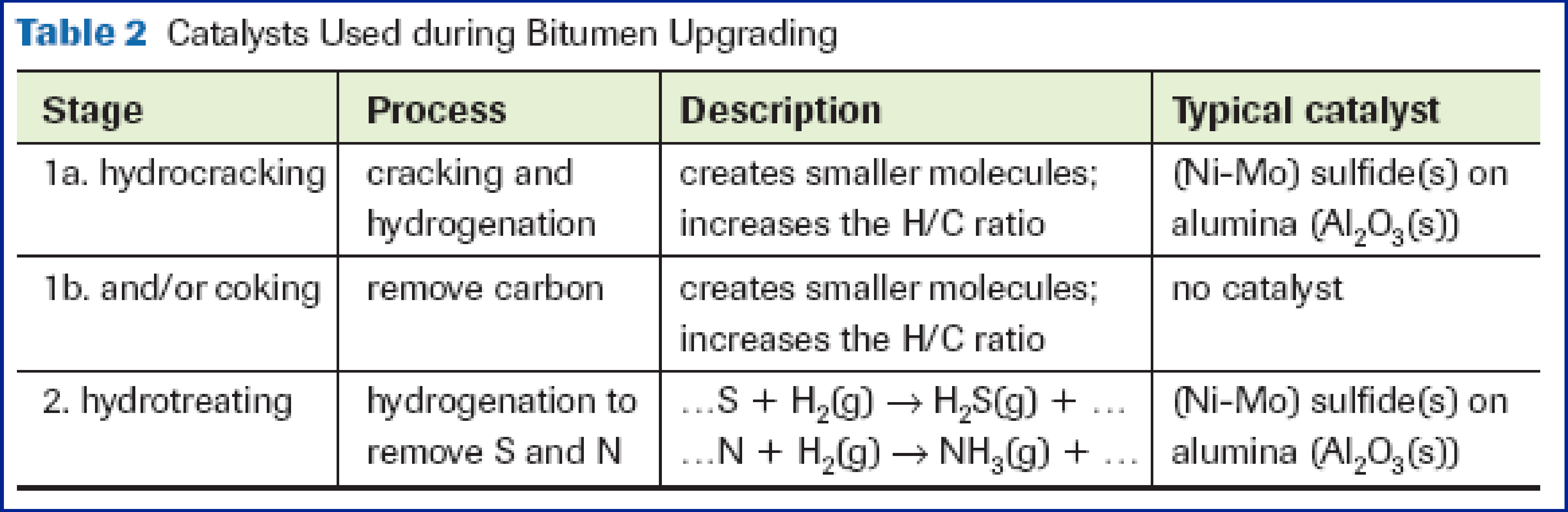


Table 2 Catalysts Used during Bitumen Upgrading

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))

Uses of Catalysts

Emissions Control

Emissions control is another use of catalysts.

These emissions may be nitrogen oxides (from power plants), sulfur (from gas plants), and chemicals that contribute to smog (from internal combustion engines).

Table 3 shows some of the emission control reactions and their catalysts. (You do not need to memorize these reactions and catalysts.)

Uses of Catalysts

Enzymes

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.

Uses of Catalysts

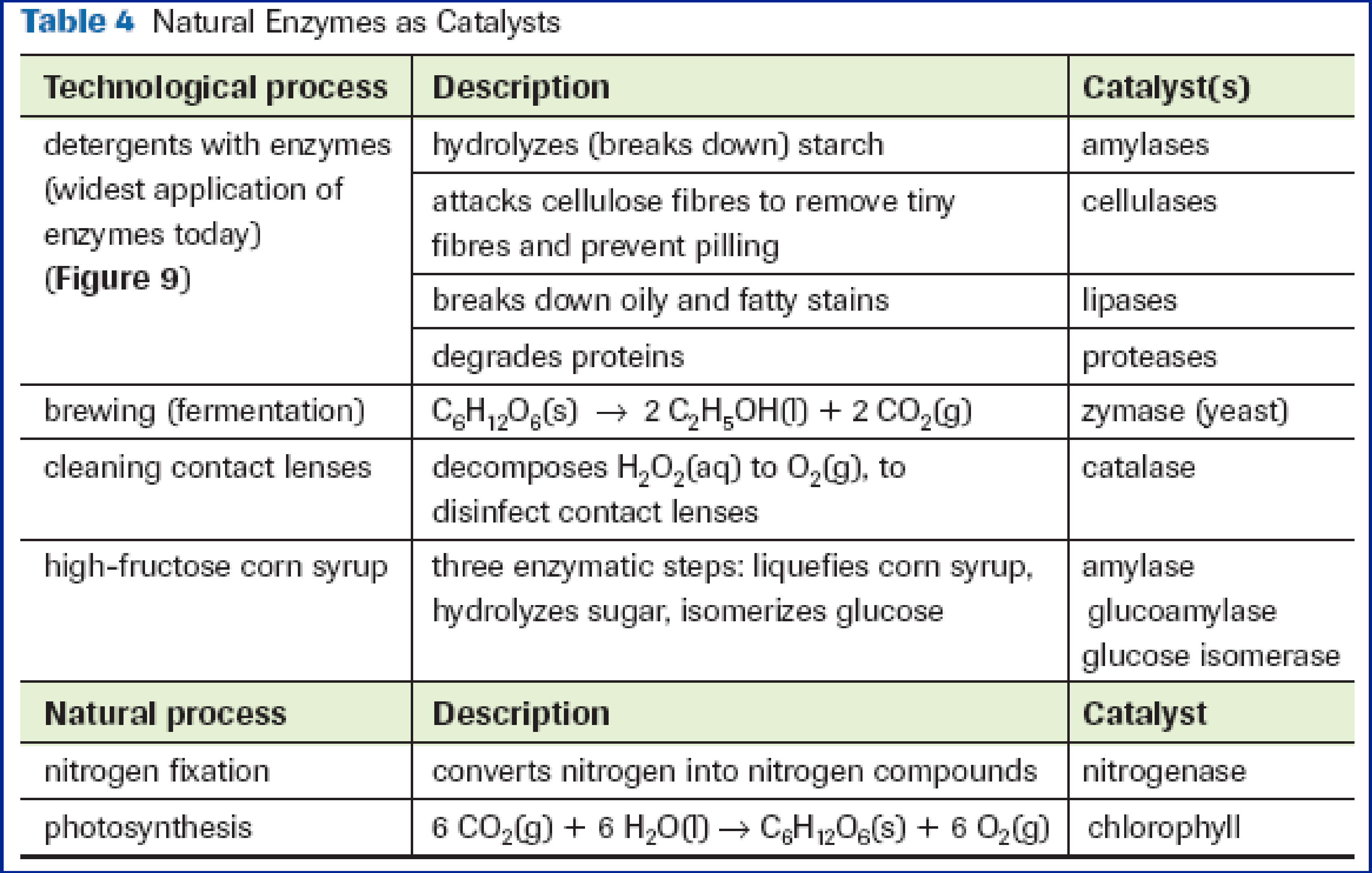


Table 4 Natural Enzymes as Catalysts

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

12.3 Summary

- **A catalyst is a substance that increases the rate of a reaction without being consumed in the overall process.**
- **According to theory, catalysts accelerate a reaction by providing an alternative pathway with a lower activation energy.**
- **A catalyst does not alter the net enthalpy change of a reaction. Both catalyzed and uncatalyzed versions of the same reaction have the same $\Delta_r H$.**
- **Catalysts are widely used in industry, consumer technologies, and biological processes.**

Chapter 12 Summary: Outcomes

Knowledge

- analyze and label energy diagrams for a chemical reaction, including reactants, products, enthalpy change, and activation energy (all sections)
- define activation energy as the energy barrier that must be overcome for a chemical reaction to occur (12.1)
- explain the energy changes that occur during chemical reactions referring to bonds breaking and forming and changes in potential and kinetic energy (12.2)
- explain that catalysts increase reaction rates by providing alternative pathways for changes without affecting the net energy involved (12.3)

Chapter 12 Summary: Outcomes

STS

- recognize the values and limitations of technological products and processes (12.1, 12.3)
- state that a goal of technology is to solve practical problems (12.2)
- evaluate technologies from a variety of perspectives (12.3)

Chapter 12 Summary: Outcomes

Skills

- initiating and planning: describe procedures for safe handling, storage, and disposal of materials used in the laboratory, with reference to WHMIS and consumer product labelling information (12.3)
- performing and recording: plot chemical potential energy diagrams, enthalpy diagrams, and energy pathway diagrams indicating changes in energy for chemical reactions (all sections);
- analyzing and interpreting: interpret energy diagrams for chemical reactions (all sections)
- communication and teamwork: work collaboratively in addressing problems and apply the skills and conventions of science in communicating information and ideas and in assessing results by using appropriate SI notation, and fundamental and derived units for calculating and communicating enthalpy changes (all sections)

Unit 6 General Outcomes

In this unit, you will

- determine and interpret energy changes in chemical reactions
- explain and communicate energy changes in chemical reactions