Endothermic: A process or reaction that absorbs heat and has a positive ΔH.

Exothermic: A process or reaction that releases heat and has a negative ΔH.

Law of conservation of energy: Energy can be neither created nor destroyed in any physical or chemical change.

Heat of reaction: Represented by ΔH, is the difference between the energy absorbed in breaking bonds and that released in forming bonds. ΔH is also known as enthalpy change.

7.2 Exothermic and Endothermic Reactions

When the total strength of the bonds formed in the products is greater than the total strength of the bonds broken in the reactants, energy is released and a reaction is *exothermic*. All combustion reactions are exothermic.

An exothermic reaction—negative ΔH

Heat is a product.

$$CH_4(g) + 2\,O_2(g) \longrightarrow CO_2(g) + 2\,H_2O(l) + 213\ \text{kcal}$$

or

$$CH_4(g) + 2\,O_2(g) \longrightarrow CO_2(g) + 2\,H_2O(l) \qquad \Delta H = -213\ \text{kcal/mol}$$

When the total energy of the bonds formed in the products is less than the total energy of the bonds broken in the reactants, energy is absorbed and the reaction is endothermic.

An endothermic reaction—positive ΔH

Heat is a reactant.

$$N_2(g) + O_2(g) + 43\text{ kcal} \longrightarrow 2\,NO(g)$$

or

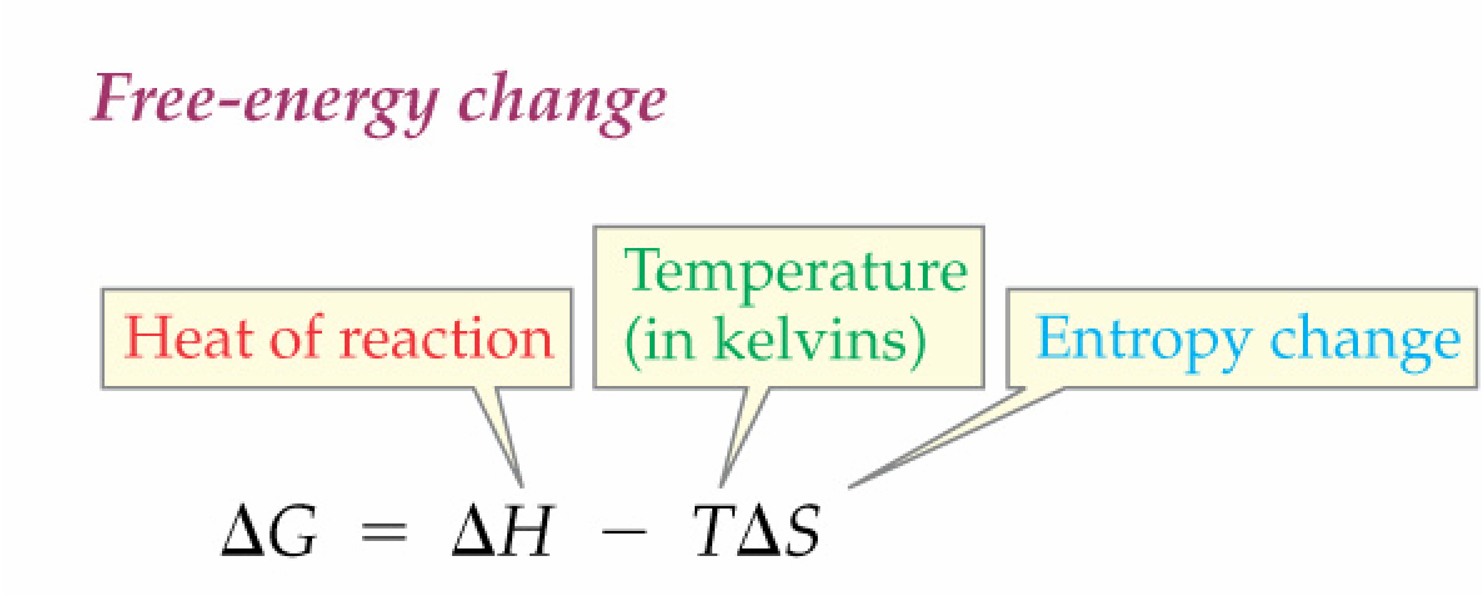
$$N_2(g) + O_2(g) \longrightarrow 2\,NO(g) \qquad \Delta H = +43\text{ kcal/mol}$$

7.3 Why Do Chemical Reactions Occur: Free Energy

Spontaneous process: A process or reaction that, once started, proceeds on its own without any external influence.

Entropy: A measure of the amount of molecular disorder in a system. Symbol *S* is used for entropy and it has the unit of calories per mole Kelvin. The greater the disorder or randomness of the particles in a substance or mixture, the larger the value of *S*.

- To decide whether a process is spontaneous, both the enthalpy change and the entropy change must be taken into account.
- When ΔH and ΔS are both favorable, a process is ***spontaneous***; when both are unfavorable, a process is ***nonspontaneous***.
- ***Free energy change (ΔG):*** Free energy change is used to describe spontaneity of a process. It takes both ΔH and ΔS into account.



The value of the free-energy change (ΔG) determines spontaneity.

- ΔG is negative; free energy is released; process is exothermic or exergonic.
- ΔG is positive; free energy is added; process is endothermic or endergonic.

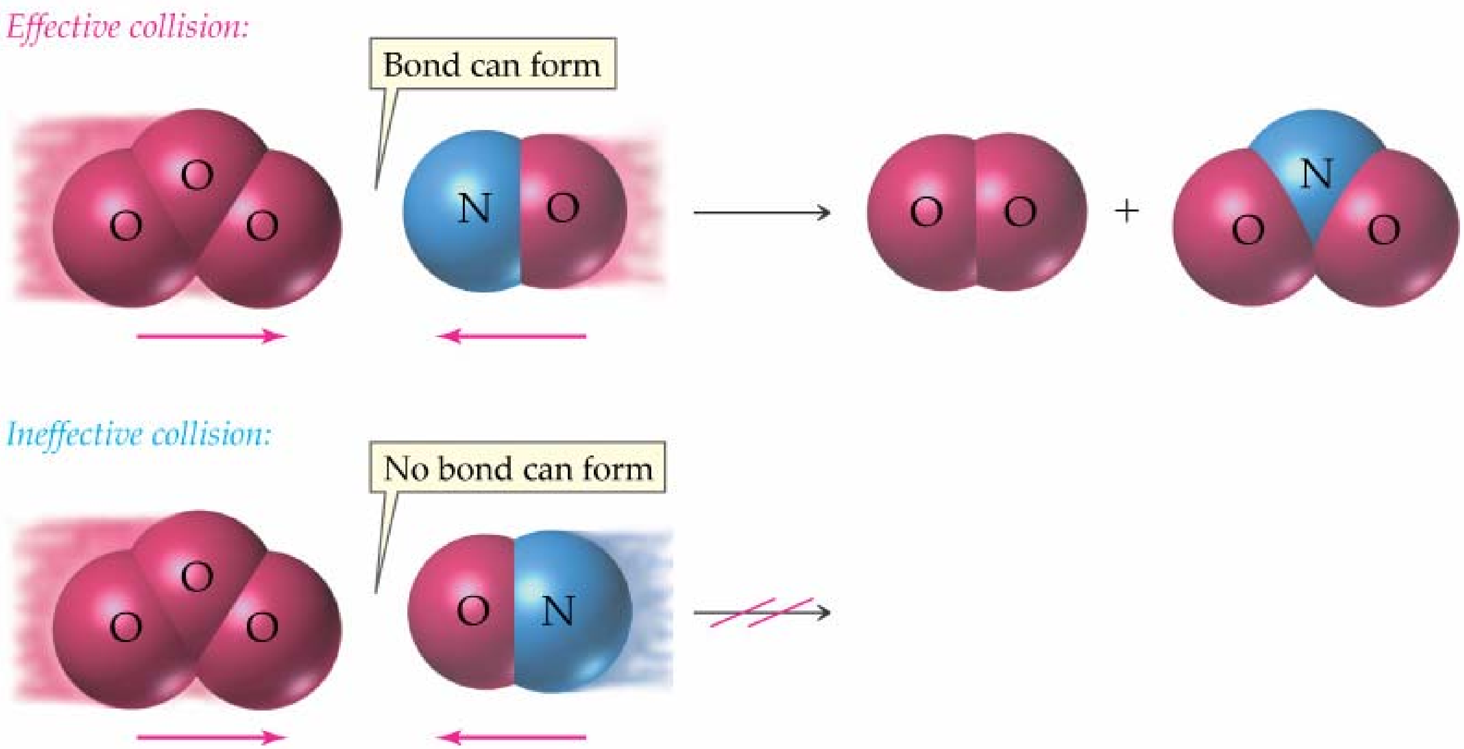
7.4 How Do Chemical Reactions Occur: Reaction Rates

The value of ΔG indicates whether a reaction will occur but it does not say anything about how fast the reaction will occur or about the details of the molecular changes that takes place during the reaction.

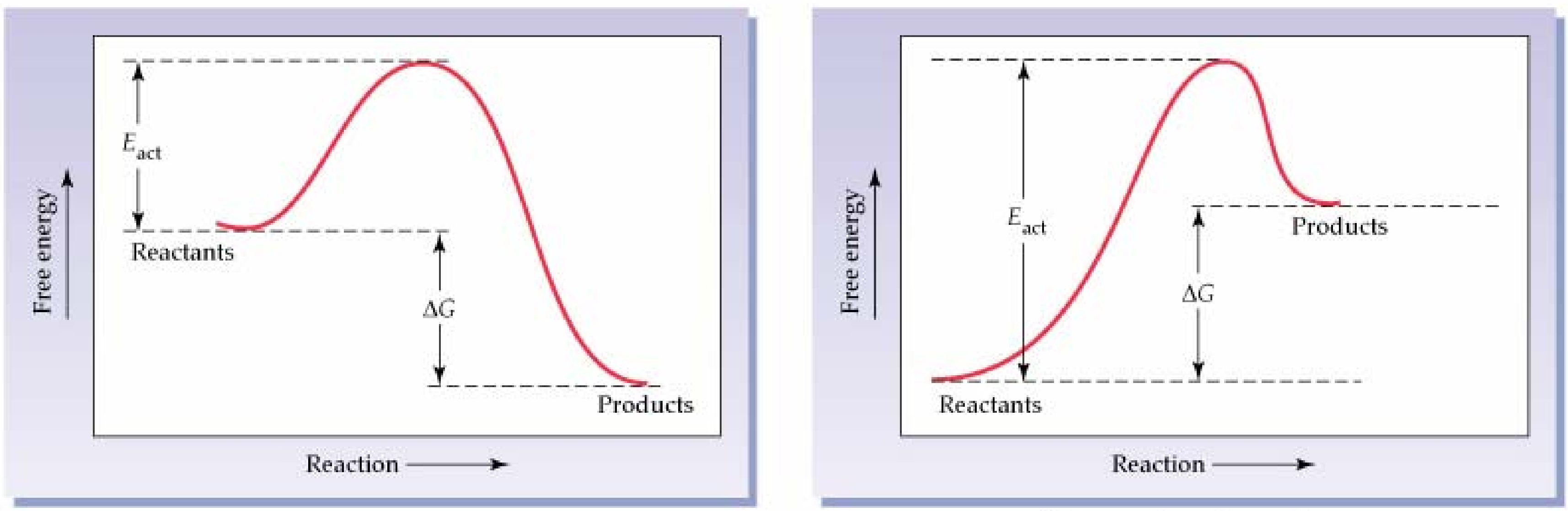
For a chemical reaction to occur:

- Reactant particle must collide.
- Some chemical bonds have to break.

- Some chemical bonds have to form.
- Not all collision leads to product; only the colliding molecules approaching with right orientation will form bond.



The energy change that occurs during the course of a chemical reaction can be visualized in an energy diagram as shown in the following Fig. 7.3.

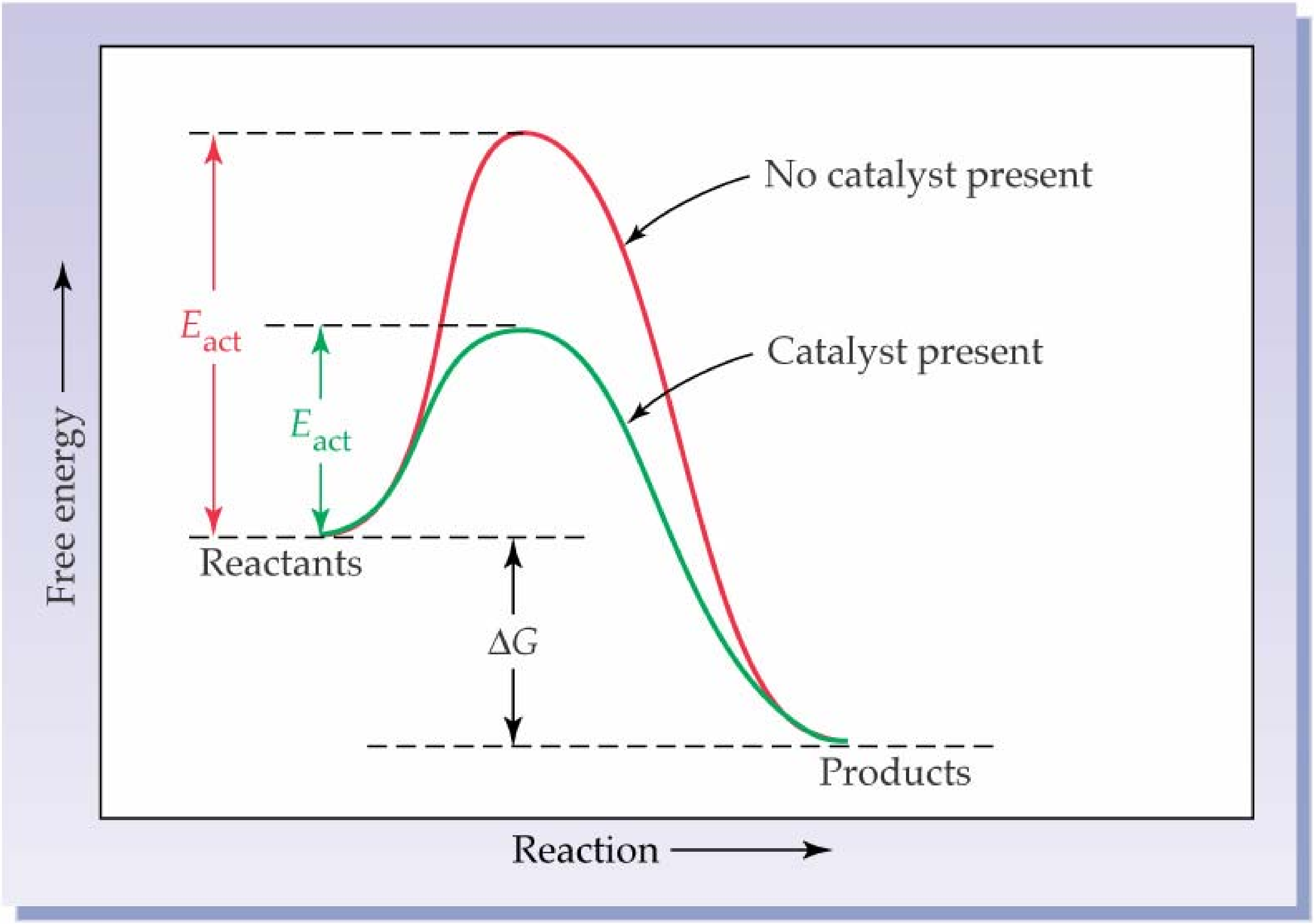


(a) An exergonic reaction

(b) An endergonic reaction

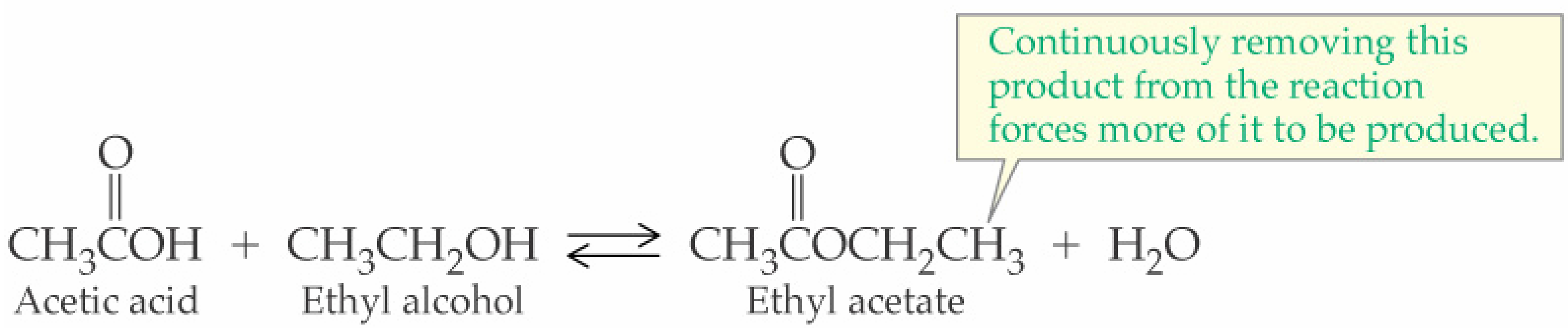
Activation energy **(E_a):** The amount of energy the colliding particles must have for productive collisions to occur. The size of the activation energy determines the reaction rate, or how fast the reaction occurs.

- The lower the activation energy, the greater the number of productive collisions in a given amount of time, and faster the reaction.
- Higher the activation energy, the lower the number of productive collisions , and slower the reaction.


No catalyst present
Catalyst present
E_{act}
E_{act}
Reactants
ΔG
Products
Free energy
Reaction

7.6 Reversible Reactions and Chemical Equilibrium

Reversible Reactions: A reaction that can go in either direction, from products to reactants or reactants to products. This is the situation that exists when the reactants and products are of approximately equal stability. This is the case, for example, in the reaction of acetic acid with ethyl alcohol to yield ethyl acetate.



The reaction vessel contains all four substances-acetic acid, ethyl alcohol, ethyl acetate, and water – and the reaction is said to be in a state of *Chemical Equilibrium*. It is not necessary for the concentrations of the reactants and products at equilibrium to be equal. The extent to which the forward or reverse reaction is favored over the other is a characteristic property of a given reaction under given reaction conditions.

7.8 Le Chatelier's Principle: The Effect of Changing Concentrations on Equilibria

Le Chatelier's Principle: When a stress is applied to a system at equilibrium, the equilibrium shifts to relieve the stress. The stress can be any change in concentration, pressure, volume, or temperature that disturbs original equilibrium.