Ch 15. Chemical Equilibrium

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Reaction Rates: Kinetics

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Reaction Rate

- Reaction rate: the amount of a product that forms in a given period of time

- Reaction rate is explained by Collision Theory: Chemical reactions occur through collisions between molecules or atoms.

Reaction Rate

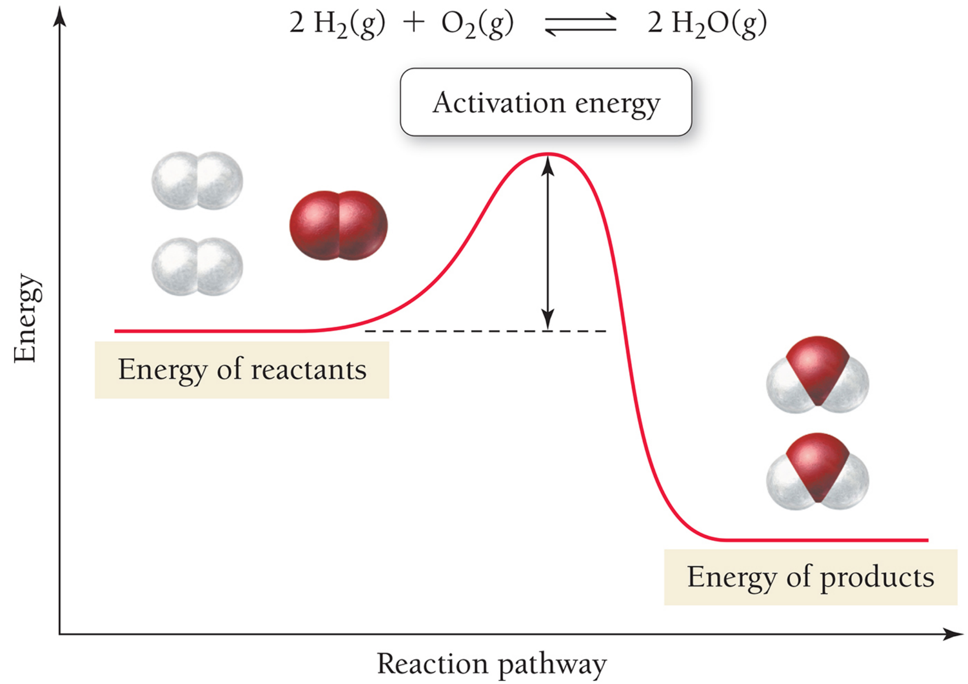
Reaction rate depends on:

1) the frequency of collisions <u>in the correct orientation,</u> and
2) the "forcefulness" of the collisions: whether collision occurs with enough energy (to go over energy barrier)

Eg. $O_3 + NO \rightarrow O_2 + NO_2$

Reaction Rates and Activation Energy

- Activation energy: the amount of energy necessary for reactants to surmount the energy barrier to reaction



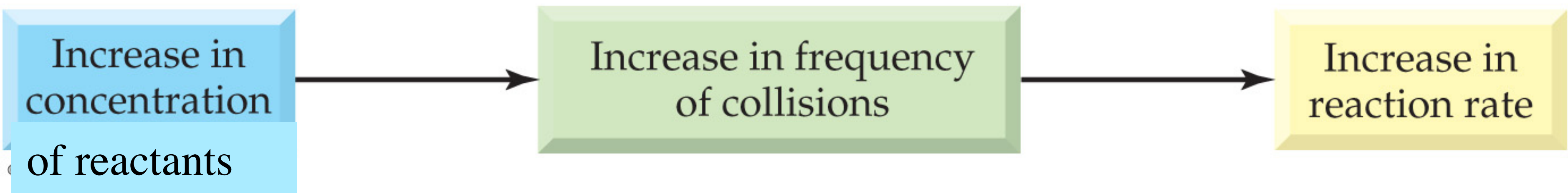
*At a given temp: higher the activation energy, the slower the reaction rate.

Effects of Three Conditions on Reaction Rates

1. Concentration
2. Temperature
3. Catalysts

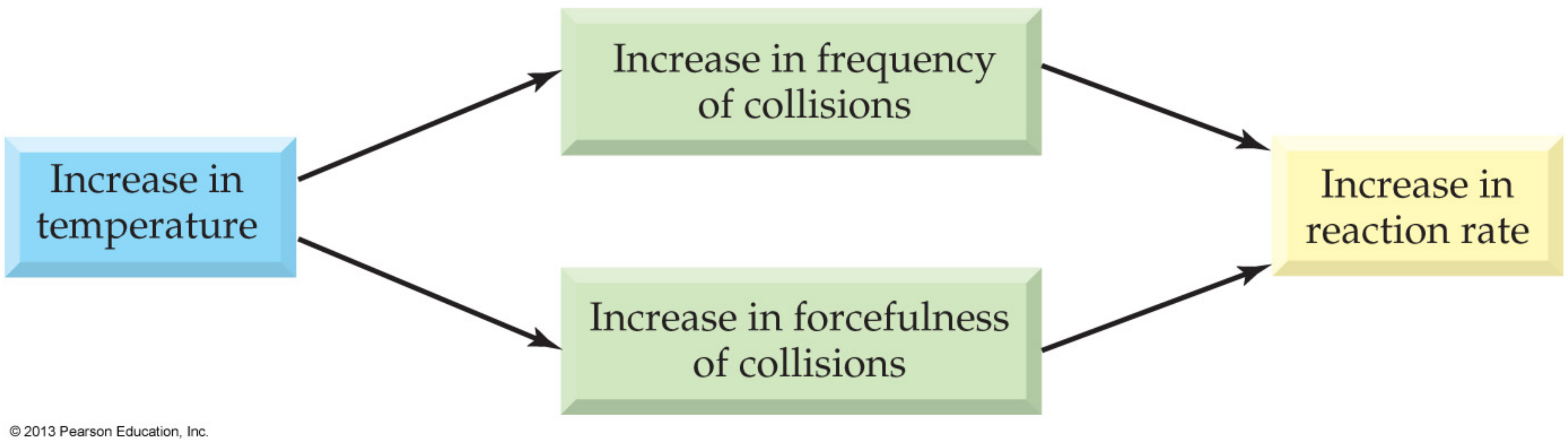
Effect of Concentration on Reaction Rates

Reaction rate generally increases with increasing reactant concentration.



Effect of Temperature on Reaction Rates

Reaction rate generally increases with increasing temperature of reaction mixture.

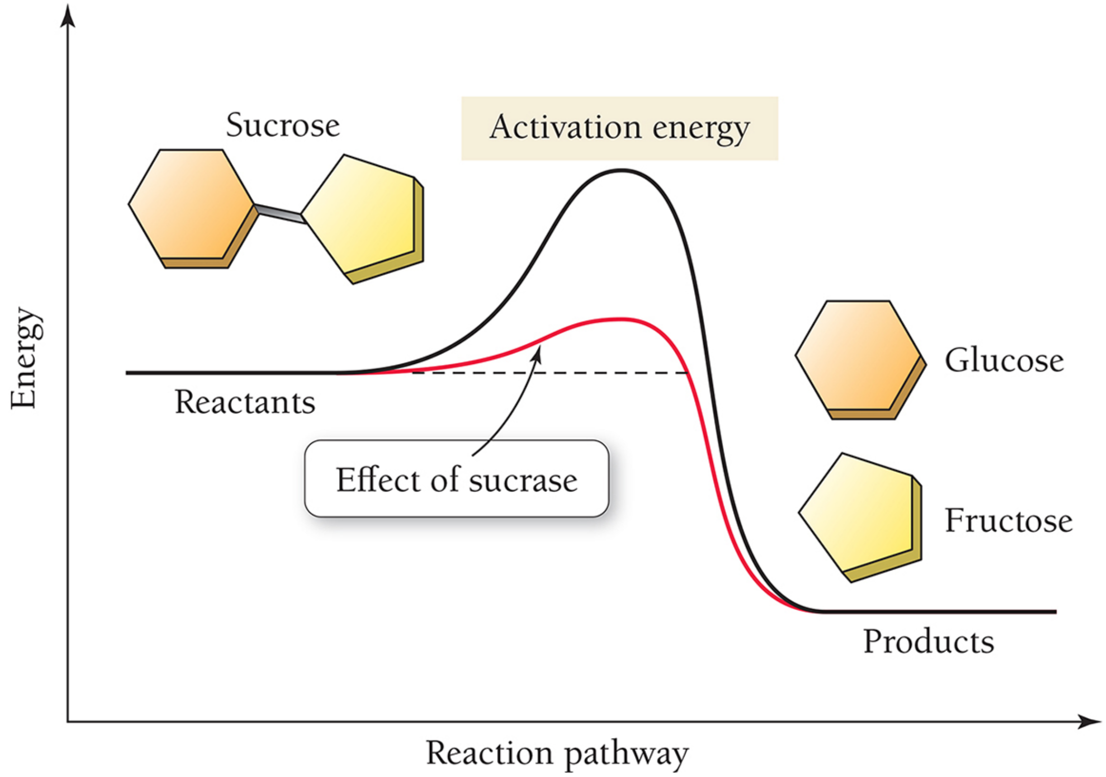


Effect of Catalyst on Reaction Rates

- Catalyst: A substance that increases the rate of a chemical reaction but is not consumed by the reaction.

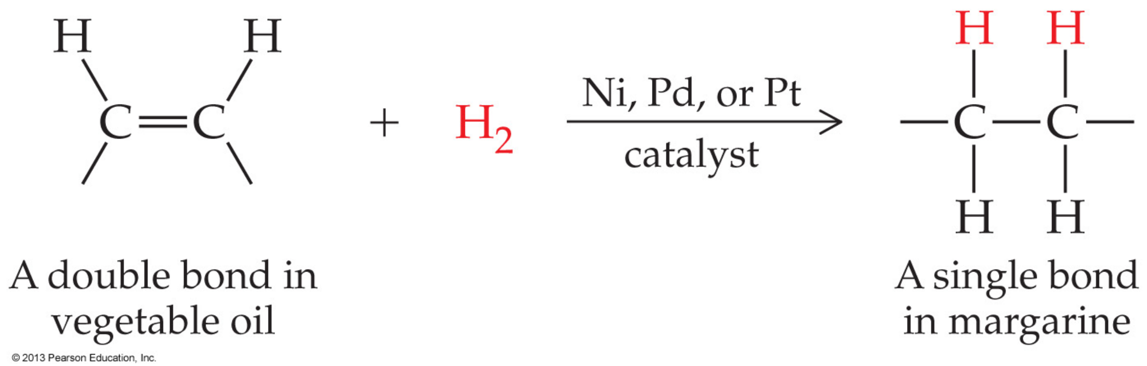
Catalyst

- A catalyst increases reaction rate by allowing the reaction to take place by an alternative chemical pathway with a lower energy barrier.

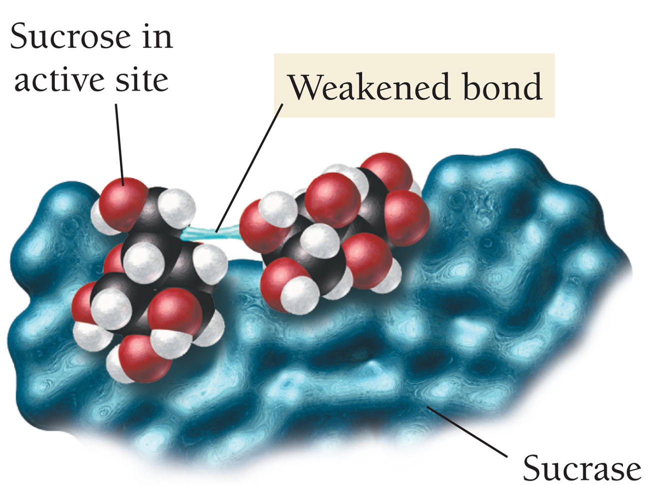


Examples of Catalysts

- Non-enzymatic catalysts



- Enzyme catalysts



Ex Probs

Summary: Effects of Conc, Temp, Catalyst on Rxn Rates

TABLE 7.3 Effects of Changes in Reaction Conditions on Reaction Rates

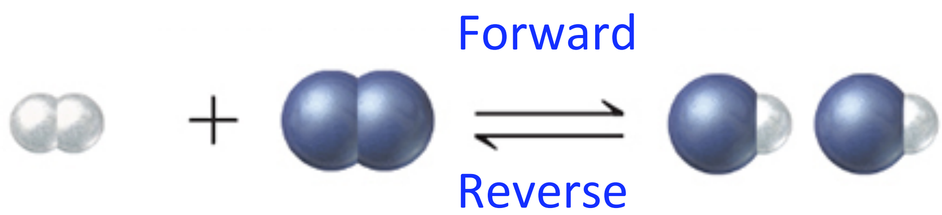
Change	Effect
Concentration	Increase in reactant concentration increases rate. Decrease in reactant concentration decreases rate.
Temperature	Increase in temperature increases rate. Decrease in temperature decreases rate.
Catalyst added	Increases reaction rate.

Chemical Equilibrium

Chemical Equilibrium

Reversible Reactions

- Reversible Reaction: a reaction that can go in either direction, from products to reactants or reactants to products



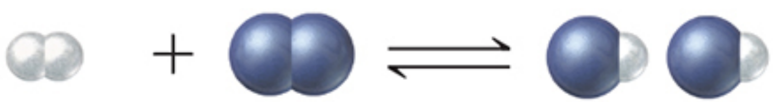
$$H_2(g) + I_2(g) \rightleftharpoons 2\,HI(g)$$

- Both reactants and products have approximately equal stability.

Chemical Equilibrium

- Chemical equilibrium: A state in which the forward rate and reverse rate of the reaction are the same, so the concentrations of reactants and products remain constant

A reversible reaction



$H_2(g) + I_2(g) \qquad 2\,HI(g)$

Equilibrium

- Equilibrium is characterized by sameness and constancy (“stable state”).
- Equilibrium is important in explaining many natural phenomena.
- Living things are not in equilibrium with their surroundings.

Dynamic Equilibrium

- Chemical equilibrium is a dynamic state: Each substance is being continuously made and broken down (although at the same rate so its concentration remain constant).

Equilibrium

- Equilibrium does not mean that the concentrations of reactants and products are equal at equilibrium (only that they don't change).

Equilibrium Constant and Equilibrium Constant Expression

$$aA + bB \rightleftharpoons cC + dD$$

Products

$$K_{eq} = \frac{[C]^c\,[D]^d}{[A]^a\,[B]^b}$$

Reactants

$$2\,SO_2\,(g) + O_2\,(g) \rightleftharpoons 2\,SO_3\,(g)$$

$$K = \frac{[SO_3]^2}{[SO_2]^2\,[O_2]}$$

Coefficients in chemical equation become exponents in equilibrium expression.

Concentrations

- The concentrations in an equilibrium expression should always be in units of molarity (M), but the units themselves are dropped.
- Concentrations of pure solids and liquids are omitted from equilibrium constant expression.

Why is K_{eq} Useful?

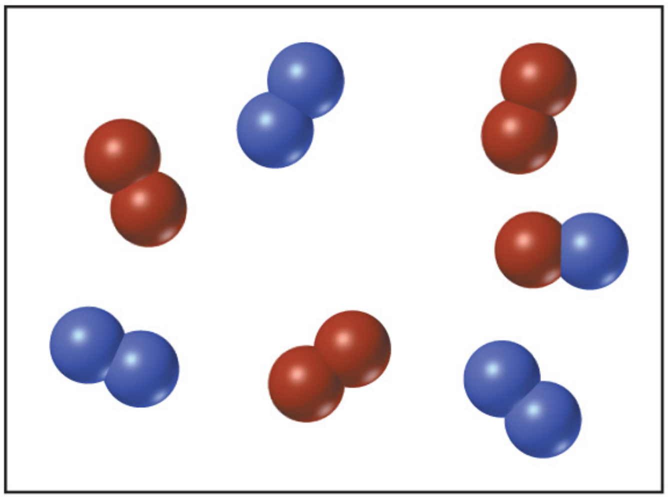
K Tells Extent of a Reaction at Equilibrium.

$$K = \frac{[M]^m[N]^n \cdots}{[A]^a[B]^b \cdots}$$

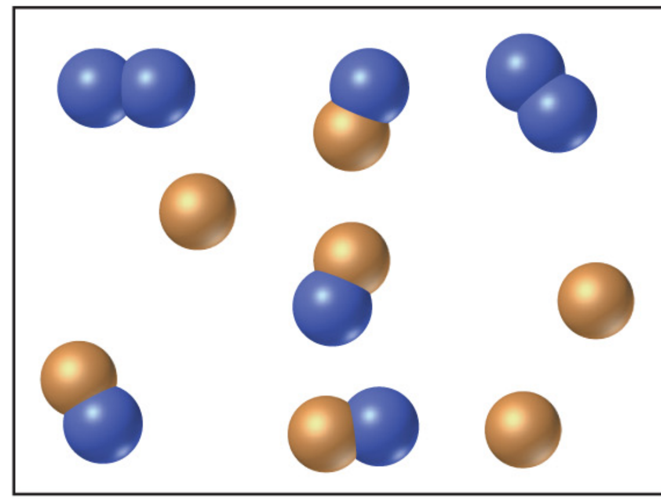
- If K >>1, there are more products than reactants at equilibrium → Forward rxn is close to completion (Forward rxn is favored).
- If K <<1, there are more reactants than products at equilibrium → Forward rxn hardly proceeds (Reverse rxn is favored).
- If K~1, significant amounts of both reactants and products are present at equilibrium (Neither direction is favored.)

Ex Problem: Equilibrium

The following pictures represent two different reactions that have reached equilibrium, followed by the reaction equation for each reaction.



$A_2 + B_2 \longrightarrow 2\,AB$



$A_2 + 2B \longrightarrow 2\,AB$

- For each reaction, write the expression for K and calculate the value of K.

Equilibrium: Le Chatlier’s Principle

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Le Chatlier's Principle

- What happens when a change in reaction conditions is imposed on the equilibrium?
- Le Chatlier's Principle: When a system at equilibrium is disturbed, the system shifts in a direction to counteract the effect of disturbance.
- Disturbance: change in concentration, pressure/ volume, temperature
- Equilibrium shift: Concentrations of products and reactants change to new, constant values (a new equilibrium state is reached).

Effect of Concentration Change on Equilibrium

1. Allow the following reaction to reach equilibrium:

   $CO(g) + 2H_2(g) \rightleftharpoons CH_3OH(g)$

2. Then add more CO (reactant). What happens?

Le Chatlier's principle: Reaction gets rid of the CO by using it up. Reaction shifts to right (conc of P ↑).

$$CO(g) + 2\,H_2(g) \rightleftharpoons CH_3OH(g)$$

$$K = \frac{[CH_3OH]}{[CO]\,[H_2]^2}$$

- New equilibrium state is reached (new concs): greater [CO], smaller [H_2], greater [CH_3OH], <u>but same K</u>

Effect of Concentration Change on Equilibrium

1. Allow the following reaction to reach equilibrium:

   $CO(g) + 2H_2(g) \rightleftharpoons CH_3OH(g)$

2. Then add more CH_3OH. Effect?

Le Chatlier's principle: Reaction gets rid of CH_3OH by using it up. Reaction shifts to left (conc of R $\uparrow$).

$$CO(g) + 2\,H_2(g) \rightleftharpoons CH_3OH(g)$$

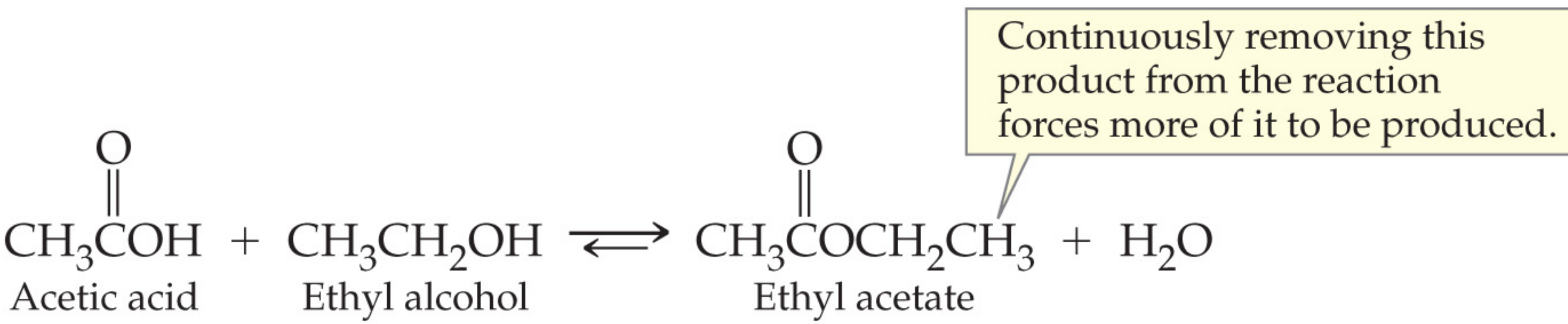
$$K = \frac{[CH_3OH]}{[CO]\,[H_2]^2}$$

- New equilibrium state is reached (new concs): greater $[CH_3OH]$, greater $[H_2]$, greater [CO], <u>but same K</u>

Effect of Concentration Change on Equilibrium

1. Allow the reaction below to reach equilibrium.
2. Then continually remove ethyl acetate product. Effect?

Le Chatlier's principle: Reaction tries to make more ethyl acetate. Reaction tries to shift to right.



Effect of Pressure/Volume Change on Equilibrium

1. Allow rxn below to come to equilibrium.
2. Then increase pressure of reaction (decrease volume).

Le Chatlier's Principle: Reaction decreases pressure by moving in direction that produces fewer moles of gas. Equilibrium shifts to right.

$$\underbrace{N_2(g) + 3\,H_2(g)}_{\text{4 mol of gas}} \rightleftharpoons \underbrace{2\,NH_3(g)}_{\text{2 mol of gas}}$$

- Remember, pressure influences equilibrium only if gases are involved.
- Still same K.

Effect of Temperature Change on Equilibrium

1. Allow the exothermic rxn below to come to equilibrium.
2. Raise temp of reaction.

Le Chatlier's Principle: Rxn gets rid of heat by using it up. Reaction shifts to left.

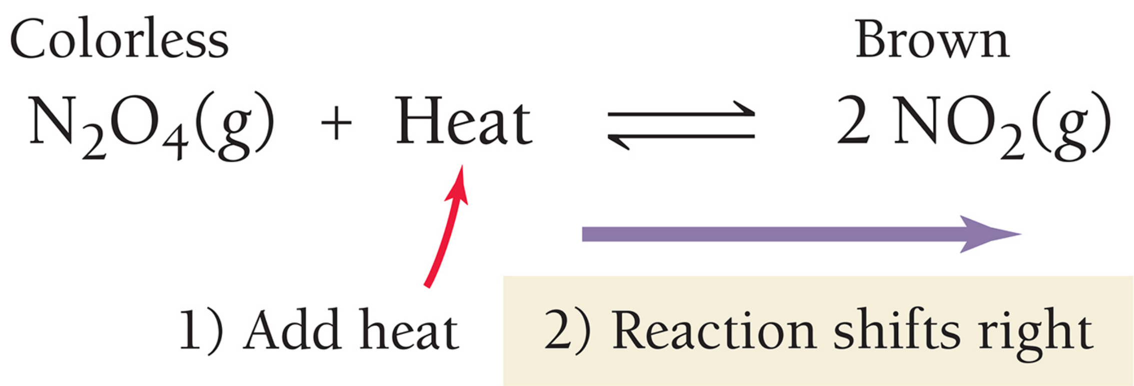
$$N_2(g) + 3\,H_2(g) \rightleftharpoons 2\,NH_3(g) + \text{Heat}$$

- If lower temp of exothermic reaction? Equil → R
- Change in temperature changes K.

Effect of Temperature Change on Equilibrium

1. Allow the endothermic rxn below to come to equilibrium.
2. Raise temp of reaction.

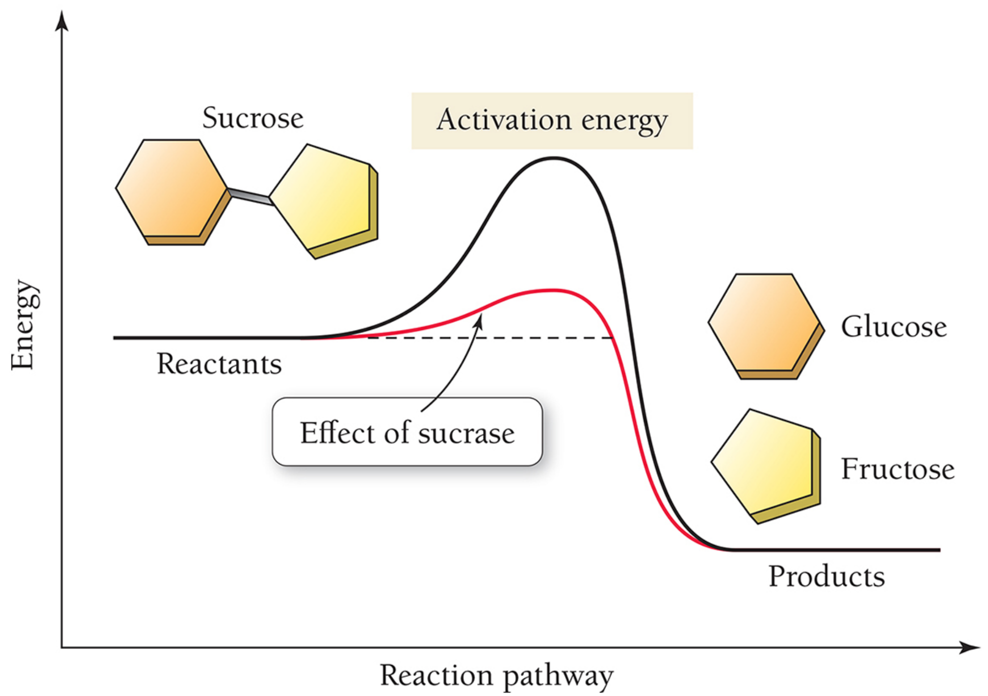
Le Chatlier's Principle: Rxn gets rid of heat by using it up. Reaction shifts to right.



- If lower temp of endothermic reaction? Equil → L

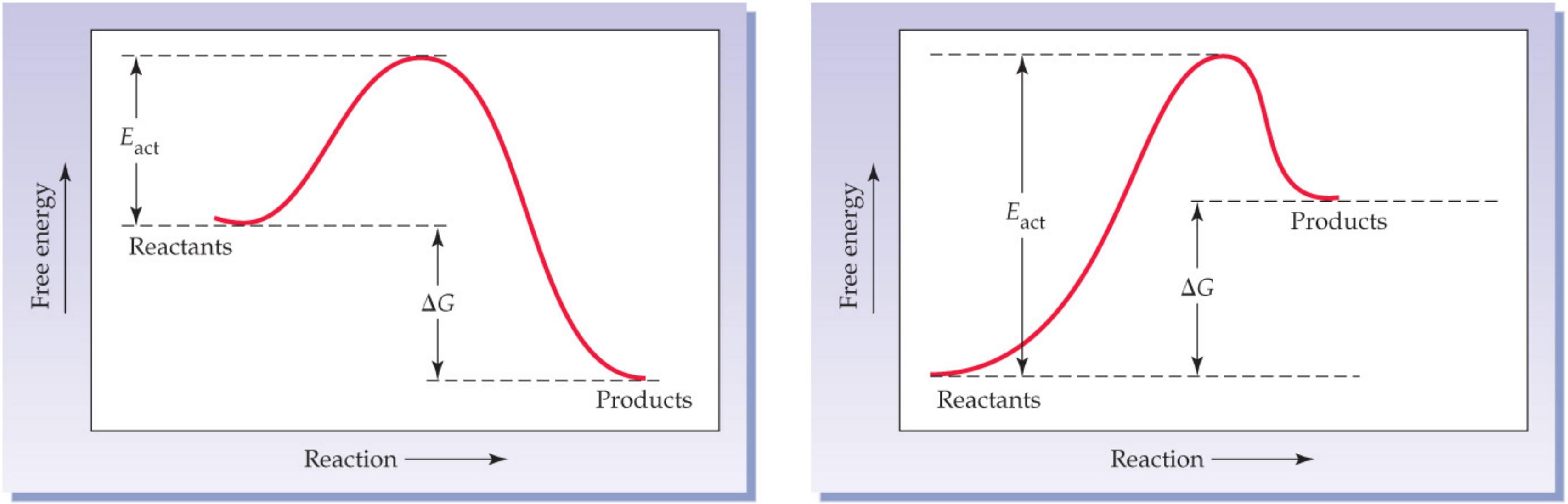
Effect of Catalyst on Equilibrium: NONE

- Catalysts do not affect equilibrium concentrations.
- Catalysts only speed up the reaction.



Ex Probs

Activation Energy and Free Energy



(a) An exergonic reaction

(b) An endergonic reaction

- Activation energy: Determines rate of reaction.
- Free energy change (ΔG): Determines whether reaction occurs or not without addition of energy (spontaneously)
- Enzyme only changes activation energy, not free energy change.