Chapter 15

Chemical Equilibrium

Based on slides provided with Introductory Chemistry, Fifth Edition
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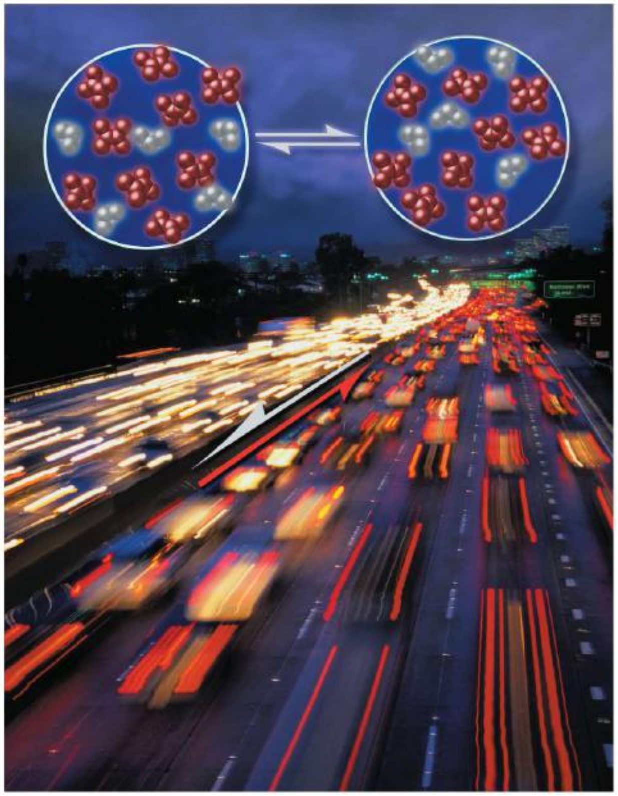
Dynamic Equilibrium

- Dynamic equilibrium involves two opposing processes occurring at the same rate.
- This image draws an analogy between a chemical equilibrium,

$$N_2O_4 \rightleftharpoons 2NO_2$$

in which the two opposing reactions occur at the same rate, and a freeway with traffic moving in opposing directions at the same rate.



Equilibrium Involves Sameness and Constancy

- We can think of equilibrium as *sameness* and *constancy*.
- When an object is in equilibrium with its surroundings, some property of the object has reached sameness with the surroundings and is no longer changing.

Equilibrium Involves Sameness and Constancy

- A cup of hot water is not in equilibrium with its surroundings with respect to temperature.
- If left undisturbed, the cup of hot water will slowly cool until it reaches equilibrium with its surroundings.
- At that point, the temperature of the water is the *same as* that of the surroundings (sameness) and *no longer changes* (constancy).

The Rate of a Chemical Reaction

- We examine the concept of equilibrium, especially chemical equilibrium—the state that involves sameness and constancy.
- Reaction rates are related to chemical equilibrium because a chemical system is at equilibrium when the rate of the forward reaction equals the rate of the reverse reaction.

The Rate of a Chemical Reaction

- The **rate of a chemical reaction**—a measure of how fast the reaction proceeds—is defined as the amount of reactant that changes to product in a given period of time.
- In a reaction with a fast rate, the reactants react to form products in a short period of time.
- In a reaction with a slow rate, the reactants react to form products over a long period of time.
- Reaction rates can be controlled if we understand the factors that influence them.

Collision Theory of Chemical Reactions

- Chemical reactions occur through collisions between molecules or atoms.
- If the collision occurs with enough energy—that is, if the colliding molecules are moving fast enough—the reaction can proceed to form the products.
  - Provided they approach each other in the right orientation
- If the collision occurs with insufficient energy, the reactant molecules bounce off one another without reacting.

Collision Theory of Chemical Reactions

- Since molecules have a wide distribution of velocities, collisions occur with a wide distribution of energies.
- High-energy collisions lead to products; low-energy collisions do not.

Collision Theory of Chemical Reactions

- Higher-energy collisions are more likely to lead to products because most chemical reactions have an *activation energy*.
- Activation energy is an energy barrier that must be overcome for the reaction to proceed.
- The activation energy may be the energy required to begin to break the bonds of the reactants.
  - Or it may include the energy needed to form a high-energy intermediate structure

Collision Theory of Chemical Reactions

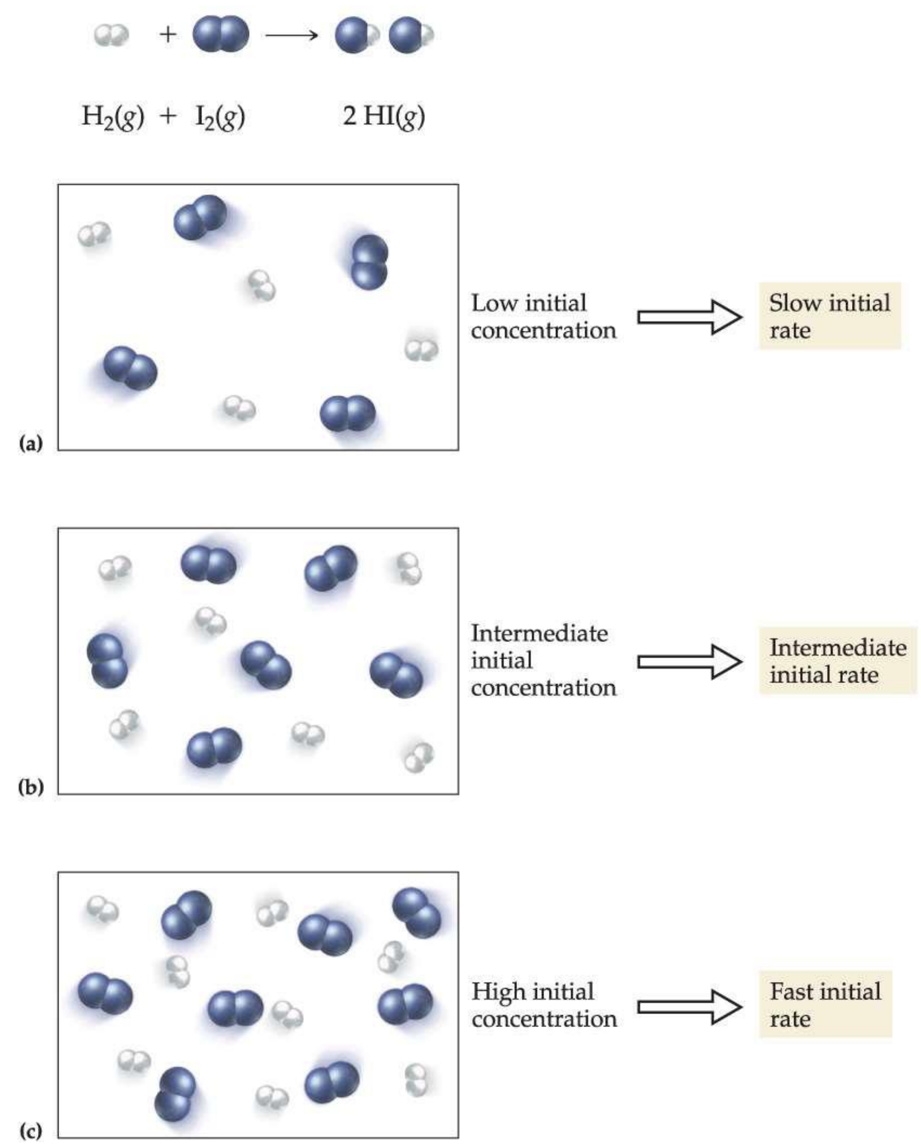
If molecules react via high-energy collisions, then the factors that influence the rate of a reaction must be the same factors that affect the number of high-energy collisions that occur per unit time.

The two most important factors are:

- the *concentration* of the reacting molecules
- the *temperature* of the reaction mixture.

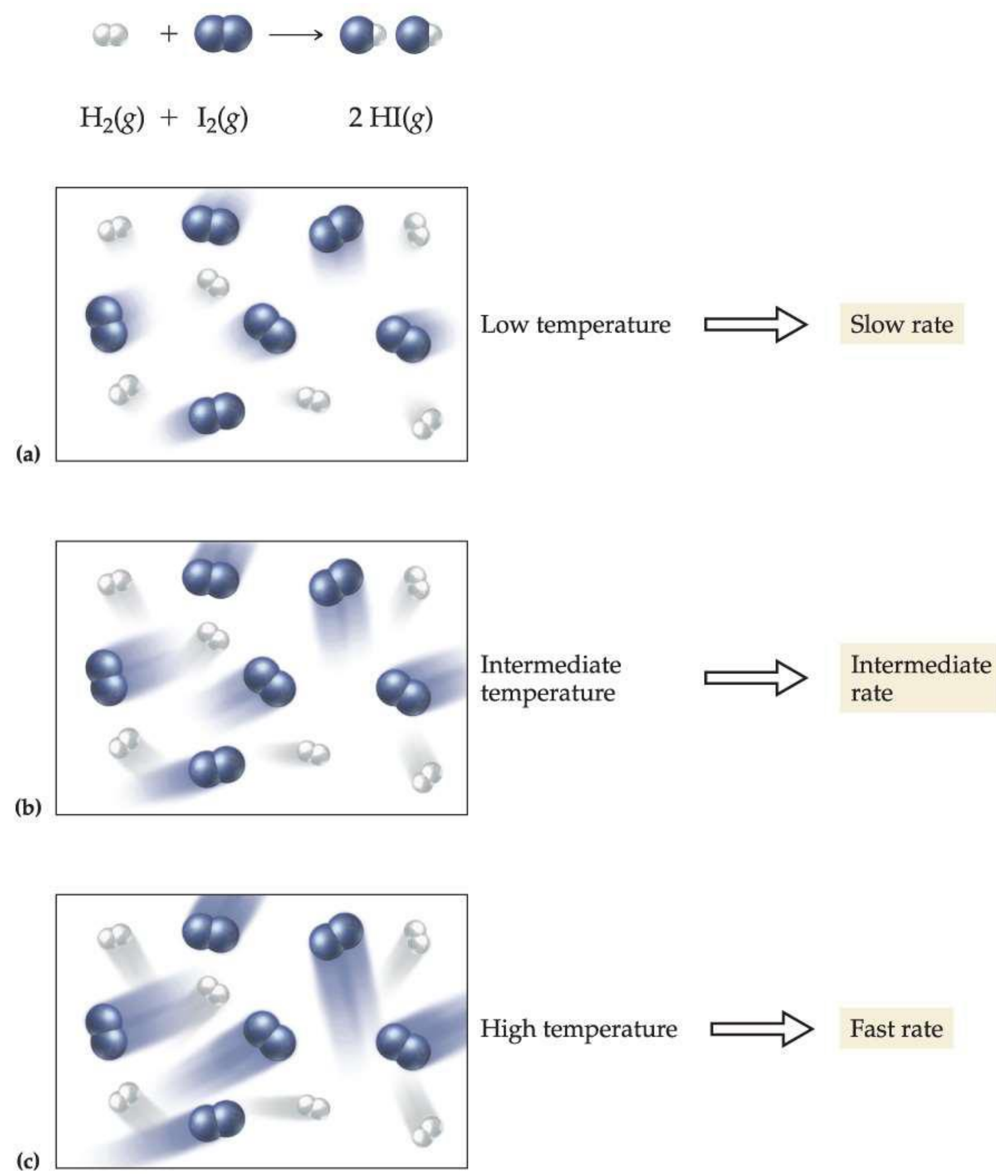
How Concentration Affects the Rate of a Reaction

- The rate of a chemical reaction generally increases with increasing concentration of the reactants.
- The exact relationship between increases in concentration and increases in reaction rate varies for different reactions and is the subject of studies in chemical kinetics.



How Temperature Affects the Rate of a Reaction

- Raising the temperature makes the molecules move faster.
- More collisions occur per unit time, resulting in a faster reaction rate.
- A higher temperature results in more collisions that are of higher energy.
- Since it is the high-energy collisions that result in products, this also produces a faster rate.



Collision Theory of Chemical Reactions

To summarize:

- Reaction rates generally increase with increasing reactant concentration.
- Reaction rates generally increase with increasing temperature.
- Reaction rates generally decrease as a reaction proceeds.
  -- Because the reactant concentrations decrease as they are depleted

The Idea of Dynamic Chemical Equilibrium

- A reaction that can proceed in both the forward and reverse directions is a **reversible reaction.**
- In a chemical reaction, the condition in which the rate of the forward reaction equals the rate of the reverse reaction is called **dynamic equilibrium.**
- This condition is not static—it is dynamic because the forward and reverse reactions are still occurring but at the same constant rate.

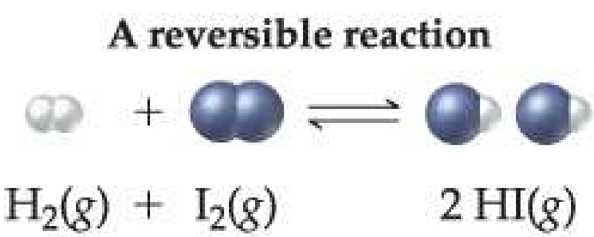
The Idea of Dynamic Chemical Equilibrium

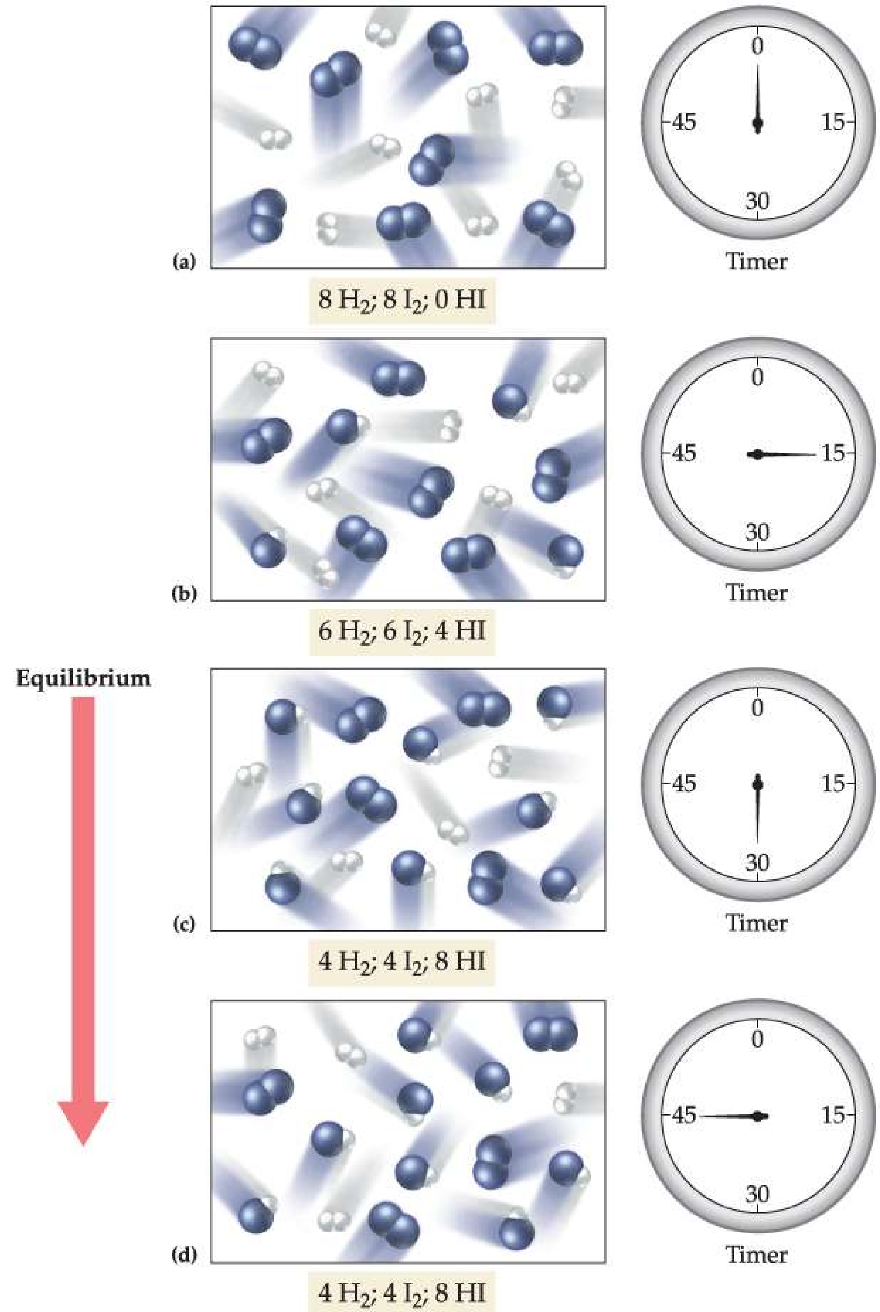
- When dynamic equilibrium is reached, the concentrations of reactants and products no longer change.
- The reactants and products are being depleted at the same rate at which they are being formed.

Equilibrium

When the concentrations of the reactants and products no longer change, equilibrium has been reached.

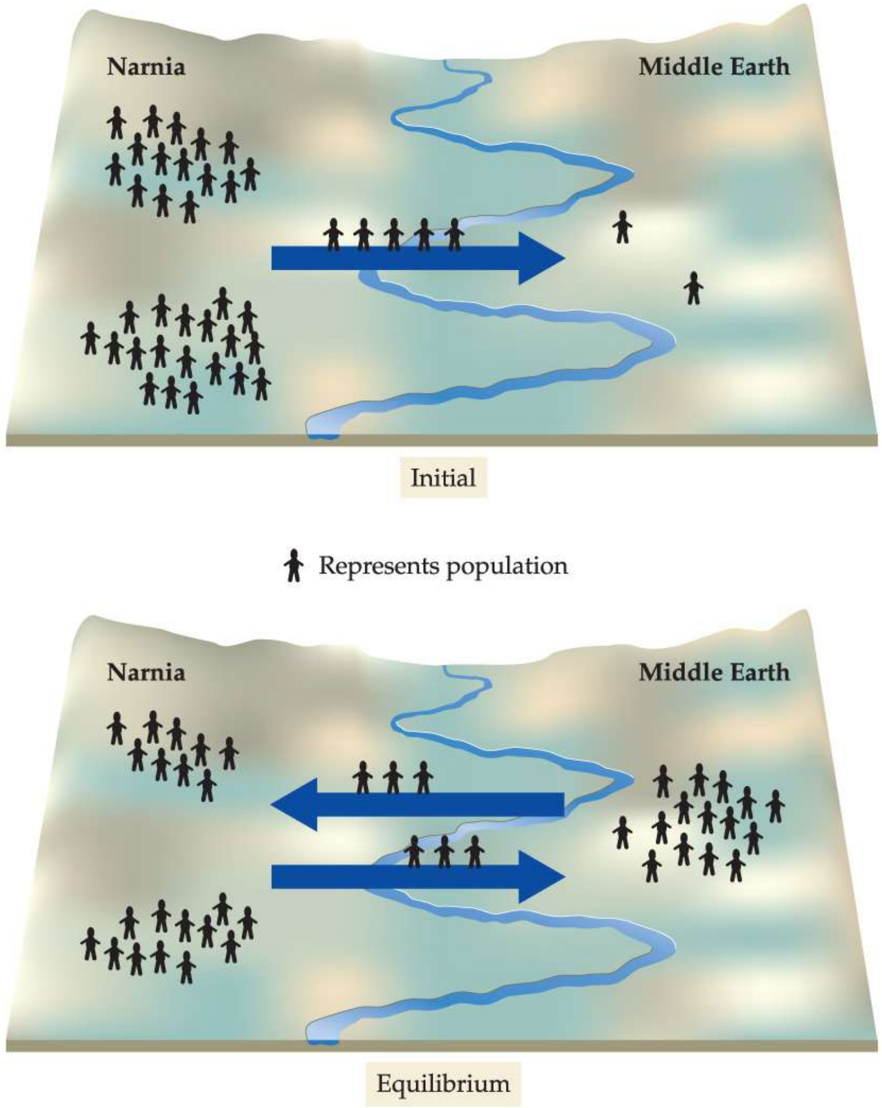
- Assuming a closed system where products are not leaving





Population Analogy for a Chemical Reaction Proceeding to Equilibrium

- Eventually, the *rate* of people moving out of Narnia (which has been slowing down as people leave) equals the *rate* of people moving back to Narnia (which has been increasing as Middle Earth gets more crowded).
- Dynamic equilibrium has been reached.



The Equilibrium Constant K_{eq}

A way to quantify the relative concentrations of the reactants and products at equilibrium

- When dynamic equilibrium is reached, the forward reaction rate is the same as the reverse reaction rate (sameness).
- Because the reaction rates are the same, the concentrations of the reactants and products no longer change (constancy).
- The constancy does ***not*** imply that the concentrations of reactants and products are *equal* to one another at equilibrium. In general, they are not equal.

The Equilibrium Constant K_{eq}

- Some reactions reach equilibrium only after most of the reactants have formed products.
- Other reactions reach equilibrium when only a small fraction of the reactants have formed products.
- The amounts of reactants and products **when equilibrium is reached** depend on the reaction and can be expressed numerically by the equilibrium constant $\boldsymbol{K_{eq}}$.

The Equilibrium Constant K_{eq}

- Consider the generic chemical reaction

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

  where A and B are reactants, C and D are products, and *a*, *b*, *c*, and *d* are the respective stoichiometric coefficients in the chemical equation.

- The **equilibrium constant** for the reaction is defined as the ratio—at equilibrium—of the concentrations of the products raised to their stoichiometric coefficients divided by the concentrations of the reactants raised to their stoichiometric coefficients.

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

Products

Reactants

Writing Equilibrium Expressions for Chemical Reactions

- Write an equilibrium expression for the reaction

$$\boxed{2}\,N_2O_5(g) \rightleftharpoons \boxed{4}\,NO_2(g) + \boxed{}\,O_2(g)$$

Implied 1

$$K_{eq} = \frac{[NO_2]^{\boxed{4}}\,[O_2]^{\boxed{}}}{[N_2O_5]^{\boxed{2}}}$$

- Notice that the *coefficients* in the chemical equation become the *exponents* in the equilibrium expression.

The Significance of the Equilibrium Constant

- K_{eq} is large:

$$H_2(g) + Br_2(g) \rightleftharpoons 2\,HBr(g) \quad K_{eq} = 1.9 \times 10^{19} \text{ at } 25\ °C$$

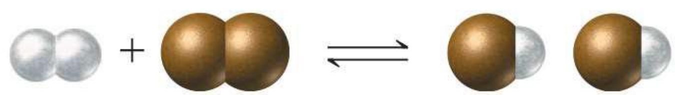
- K_{eq} is small:

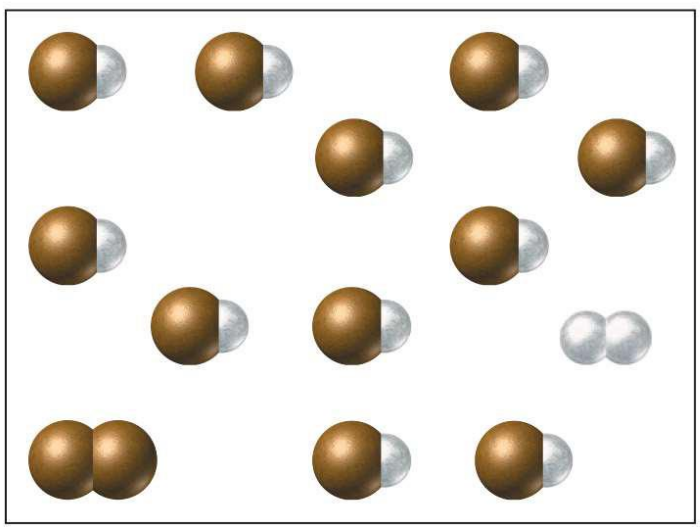
$$N_2(g) + O_2(g) \rightleftharpoons 2\,NO(g) \quad K_{eq} = 4.1 \times 10^{-31} \text{ at } 25\ °C$$

The Meaning of a Large Equilibrium Constant

There will be a high concentration of *products* and a low concentration of reactants at equilibrium.

$$H_2(g) + Br_2(g) \rightleftharpoons 2\,HBr(g)$$



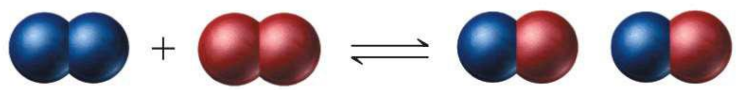


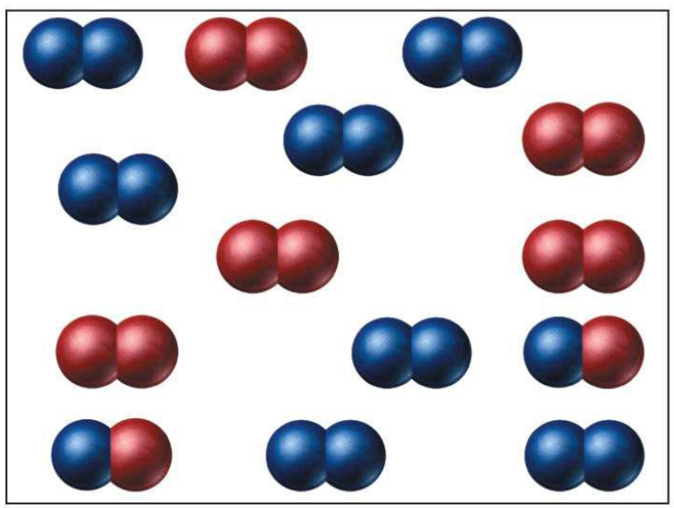
$$K_{eq} = \frac{[HBr]^2}{[H_2][Br_2]} = \textbf{Large Number}$$

The Meaning of a Small Equilibrium Constant

There will be a high concentration of *reactants* and a low concentration of products at equilibrium.

$$N_2(g) + O_2(g) \rightleftharpoons 2\,NO(g)$$





$$K_{eq} = \frac{[NO]^2}{[N_2][O_2]} = \textbf{Small Number}$$

Practice
Check your answer on the next slide

Write the equilibrium constant expressions, *K*, and predict the position of equilibrium for the following

$2\,SO_2(g) + O_2(g) \rightleftarrows 2\,SO_3(g)$ $\qquad K = 8 \times 10^{25}$

$N_2(g) + 2\,O_2(g) \rightleftarrows 2\,NO_2(g)$ $\qquad K = 3 \times 10^{-17}$

Practice

Write the equilibrium constant expressions, *K*, and predict the position of equilibrium for the following

$2\ SO_2(g) + O_2(g) \rightleftarrows 2\ SO_3(g)$ $K = 8 \times 10^{25}$

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

favors products

$N_2(g) + 2\ O_2(g) \rightleftarrows 2\ NO_2(g)$ $K = 3 \times 10^{-17}$

$$K = \frac{[NO_2]^2}{[N_2]\ [O_2]^2}$$

favors reactants

What Does an Equilibrium Constant Imply about a Reaction?

To summarize:

$K_{eq} << 1$	Reverse reaction is favored; forward reaction does not proceed very far.
$K_{eq} \approx 1$	Neither direction is favored; forward reaction proceeds about halfway (significant amounts of both reactants and products are present at equilibrium).
$K_{eq} >> 1$	Forward reaction is favored; forward reaction proceeds virtually to completion.

Heterogeneous Equilibria: The Equilibrium Expression for Reactions Involving a Solid or a Liquid

- A solid or a liquid stays apart from the solution
  - It only reacts through its surface
  - Surface area doesn't affect equilibrium
- Its "concentration" cannot change
- Having more or less of the solid or liquid does not change the equilibrium constant

Heterogeneous Equilibria: The Equilibrium Expression for Reactions Involving a Solid or a Liquid

If the liquid participating in the reaction is also the solvent, and the concentrations of the other reactants or products are relatively low, we still treat the solvent as “pure” and don’t include it in the Keq, since its concentration will not change significantly. For example:

- Water, when involved in a reaction happening in aqueous solution.

Heterogeneous Equilibria: The Equilibrium Expression for Reactions Involving a Solid or a Liquid

- The concentrations of pure solids and pure liquids are excluded from equilibrium expressions because they are constant.

$$CaCO_3(s) \rightleftharpoons CaO(s) + CO_2(g)$$

$$K_{eq} = [CO_2]$$

- Since $CaCO_3(s)$ and $CaO(s)$ are both solids, they are omitted from the equilibrium expression.

Calculating Equilibrium Constants

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

- GIVEN:

  $[H_2] = 0.11$ M

  $[I_2] = 0.11$ M

  $[HI] = 0.78$ M
- FIND: K_{eq}

$$K_{eq} = \frac{[HI]^2}{[H_2][I_2]} = \frac{[0.78]^2}{[0.11][0.11]} = 5.0 \times 10^1$$

Using Equilibrium Constants in Calculations

$$2\,COF_2(g) \rightleftharpoons CO_2(g) + CF_4(g) \qquad K_{eq} = 2.00 \text{ at } 1000\ ^\circ C$$

- GIVEN:

  $[COF_2] = 0.255$ M

  $[CF_4] = 0.118$ M

  $K_{eq} = 2.00$
- FIND: $[CO_2]$

$$K_{eq} = \frac{[CO_2][CF_4]}{[COF_2]^2}$$

$$[CO_2] = K_{eq}\frac{[COF_2]^2}{[CF_4]}$$

$$[CO_2] = 2.00\frac{[0.255]^2}{[0.118]}$$

$$= 1.10\text{ M}$$

Disturbing a Reaction at Equilibrium: Le Châtelier's Principle

When a chemical system at equilibrium is disturbed, the **system shifts in a direction that minimizes the disturbance**.

It is an intuitive way of thinking about shifts in equilibrium systems

- Increase a reactant concentration:
  - Equilibrium "shifts to the right"
  - Some of the added reactant is consumed

- Decrease a reactant concentration:
  - Equilibrium "shifts to the left"
  - Some of the removed reactant is generated by the <u>reverse reaction</u> of the products going back to reactants

- Increase a product concentration:
  - Equilibrium "shifts to the left"
  - Some of the added product is removed by the <u>reverse reaction</u> going back to reactants

- Decrease a product concentration:
  - Equilibrium "shifts to the right"
  - Some of the removed product is replenished by the forward reaction

If forward reaction is endothermic

- Increase temperature (more thermal energy):
  - Equilibrium "shifts to the right"
  - Some of the extra thermal energy is consumed

- Decrease temperature (less thermal energy):
  - Equilibrium "shifts to the left"
  - Thermal energy is produced by the reverse reaction

If forward reaction is exothermic

- ➢ Changes are in the opposite direction as when the forward reaction is endothermic

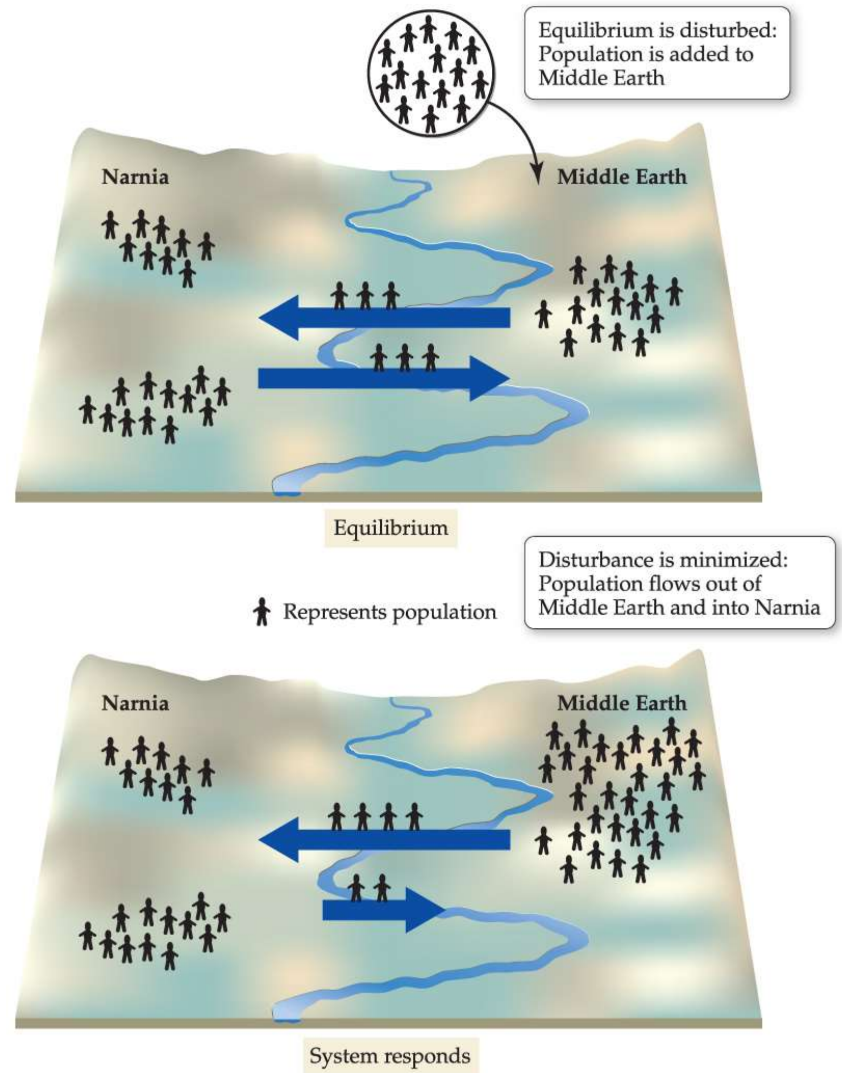
- Increase temperature (more thermal energy):
  - Equilibrium "shifts to the left"
  - Some of the extra thermal energy is consumed by the reverse reaction
- Decrease temperature (less thermal energy):
  - Equilibrium "shifts to the right"
  - Thermal energy is produced by the forward reaction

Be careful in applying Le Châtelier's Principle

- At a given temperature, it is just an intuitive way of describing the effect of concentration changes
  - Disturbances that don't change concentrations do nothing
  - A carelessly stated problem may not have a definite answer
- For temperature changes, it's reliable only when the temperature change doesn't cause a change in concentration
  - Such as when gases are involved, where volume may change with temperature

Population Analogy for Le Châtelier's Principle

When a system at equilibrium is disturbed, it shifts to minimize the disturbance. In this case, adding population to Middle Earth (the disturbance) causes population to move out of Middle Earth (minimizing the disturbance).



Disturb a System by Adding Products

$$N_2O_4(g) \rightleftharpoons 2\,NO_2(g)$$

Reaction shifts left

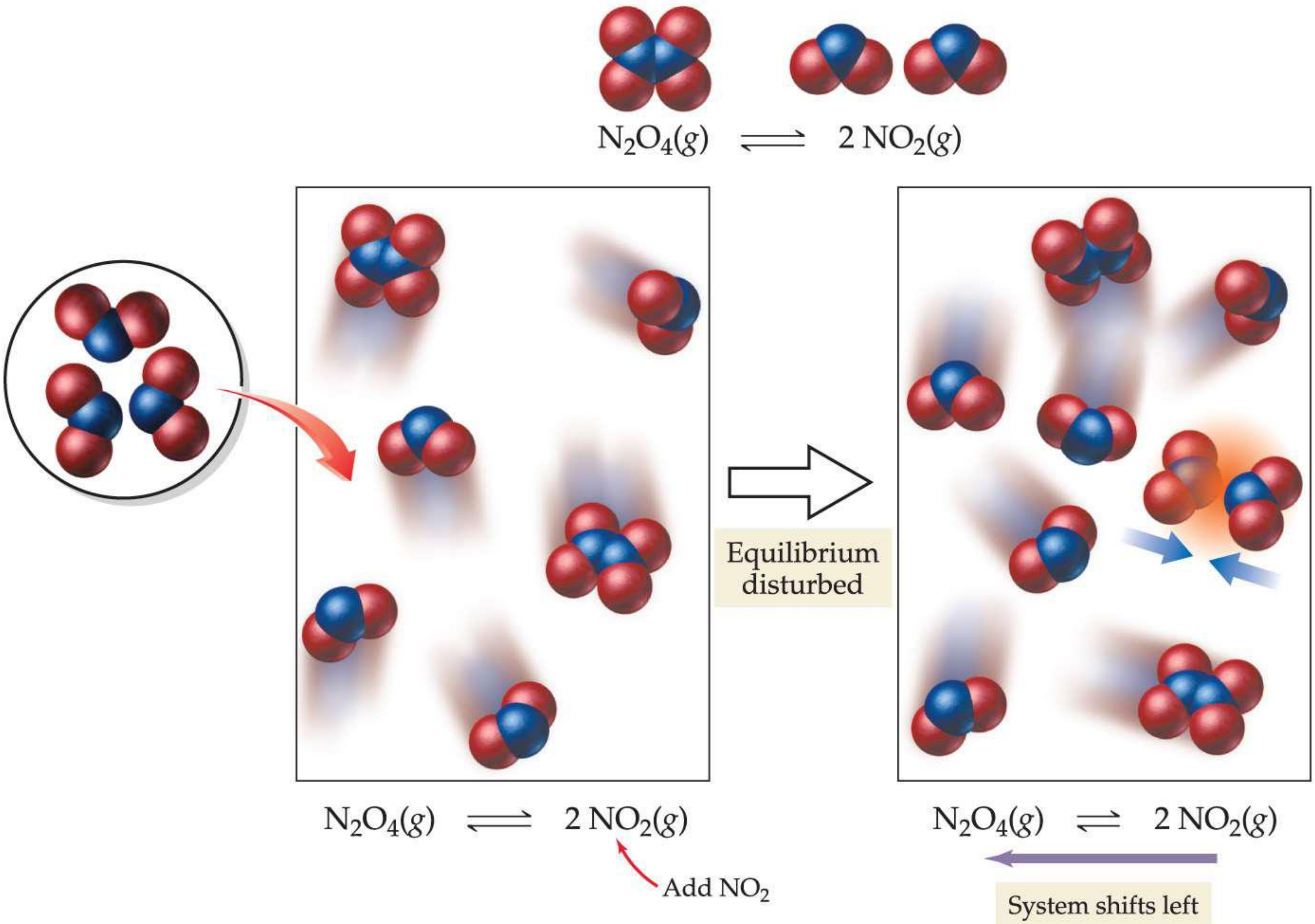
Add NO_2

@ constant V

Le Châtelier's principle in action I:
When a system at equilibrium is disturbed, it changes to minimize the disturbance: Adding NO_2 (the disturbance) causes the reaction to shift left, consuming NO_2 by forming more N_2O_4.

Caution:
If we don't add NO_2 at constant volume, we cannot reliably use the Le Chatelier Principle here

Disturb a System by Adding Products



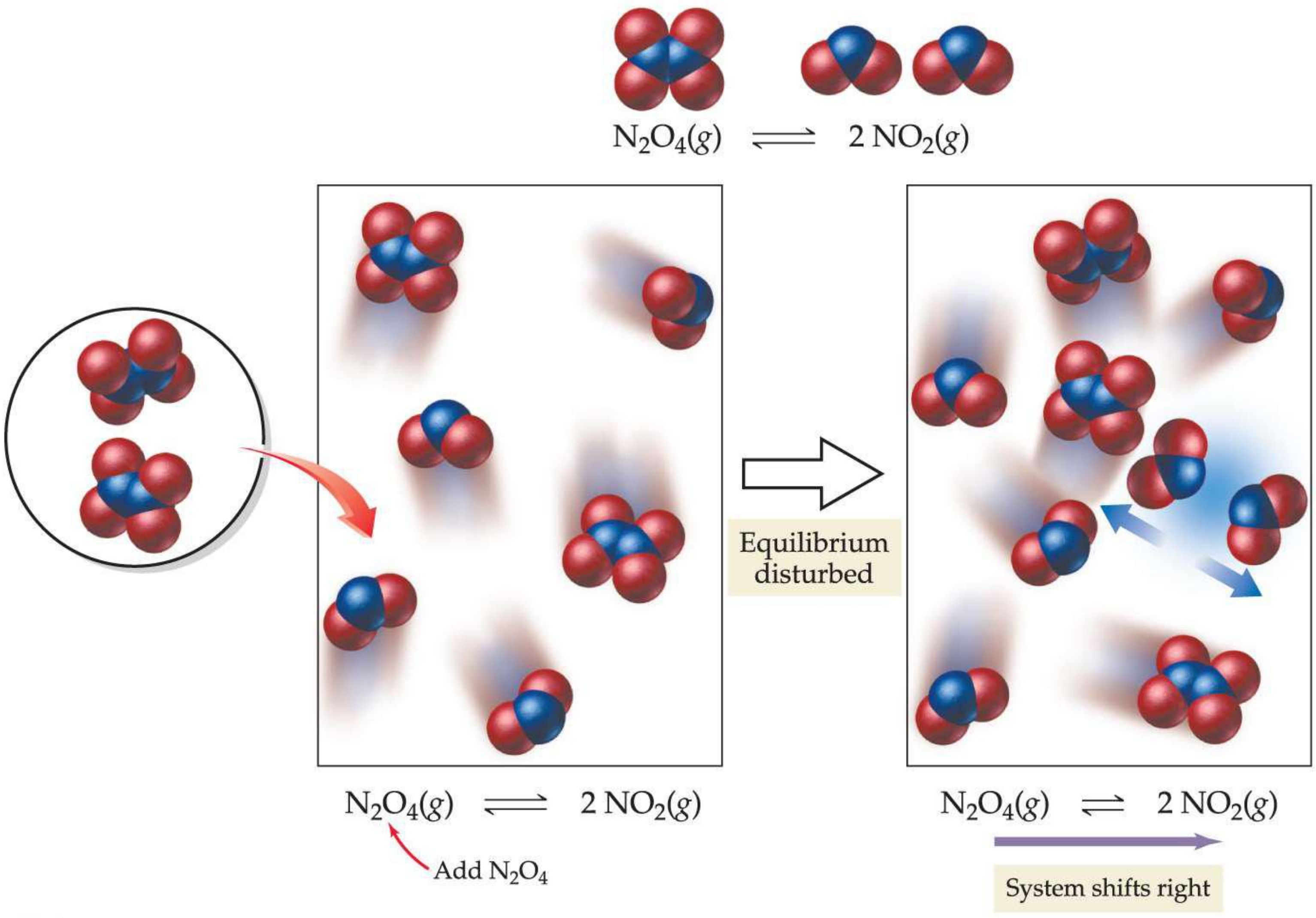
Disturb a System by Adding Reactants

Le Châtelier's principle in action II:

When a system at equilibrium is disturbed, it changes to minimize the disturbance:

Adding N_2O_4 (the disturbance) causes the reaction to shift right, consuming N_2O_4 by producing more NO_2.

Disturb a System by Adding Reactants



The Effect of a Volume Change on Equilibrium

- Changing the volume of a gas (or a gas mixture) results in a change in pressure.
- A *decrease* in volume causes an *increase* in pressure, and an *increase* in volume causes a *decrease* in pressure. (@ const. V)
- From the ideal gas law, $PV = nRT$, we can see that lowering the number of moles of a gas (n) results in a lower pressure (P) at constant temperature and volume.
- A system can respond to a disturbance by changing the moles of gas present to relieve a pressure change.

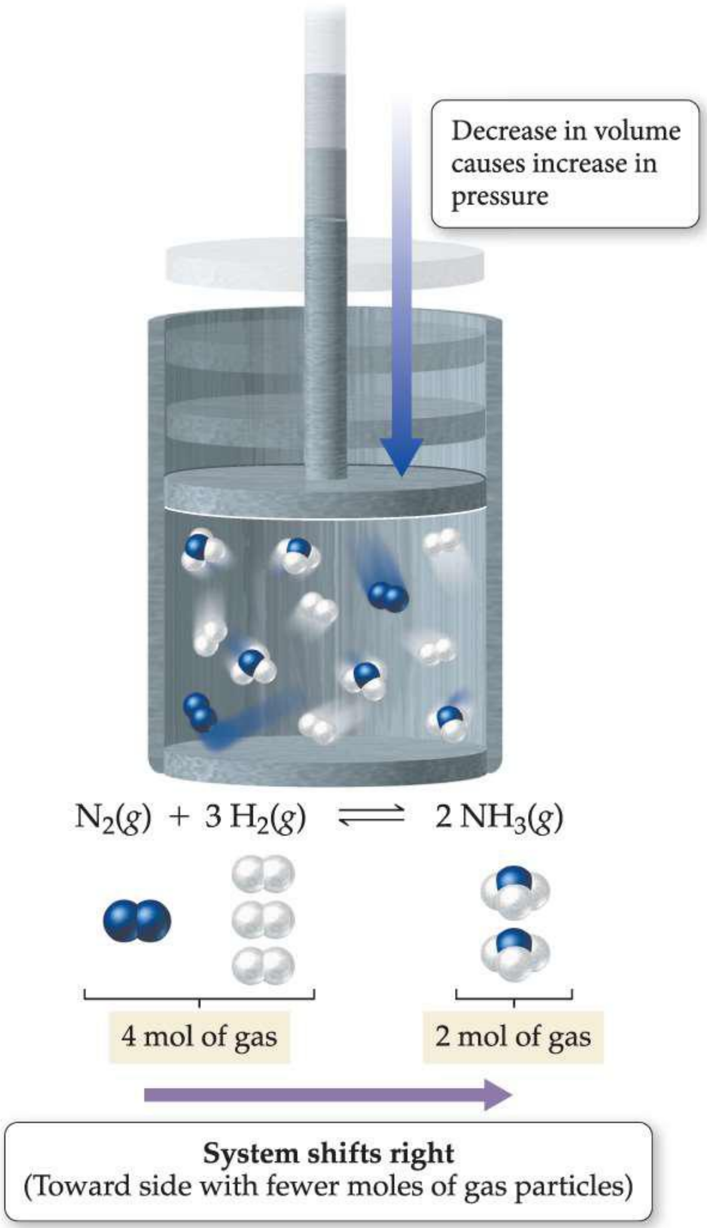
The Effect of a Volume Change on Equilibrium

Caution:

- We can only apply Le Chatelier if the pressure changes <u>involve changes in reactant and product concentrations</u>
- If we just inject a nonreactive gas and change the total pressure that way (but keep T and V the same), nothing will happen.

Effect of Volume Decrease on Equilibrium

When the volume of an equilibrium mixture decreases, the pressure increases. The system responds (to bring the pressure back down) by shifting to the right, the side of the reaction with the fewer moles of gas particles.



Effect of Volume Decrease on Equilibrium: Looking under the hood of Le Chatelier Principle

$$N_2(g) + 3\,H_2(g) \rightleftharpoons 2\,NH_3(g) \qquad K_{eq} = \frac{[N_2][H_2]^3}{[NH_3]^2}$$

Decreasing V increases all concentrations by the same factor

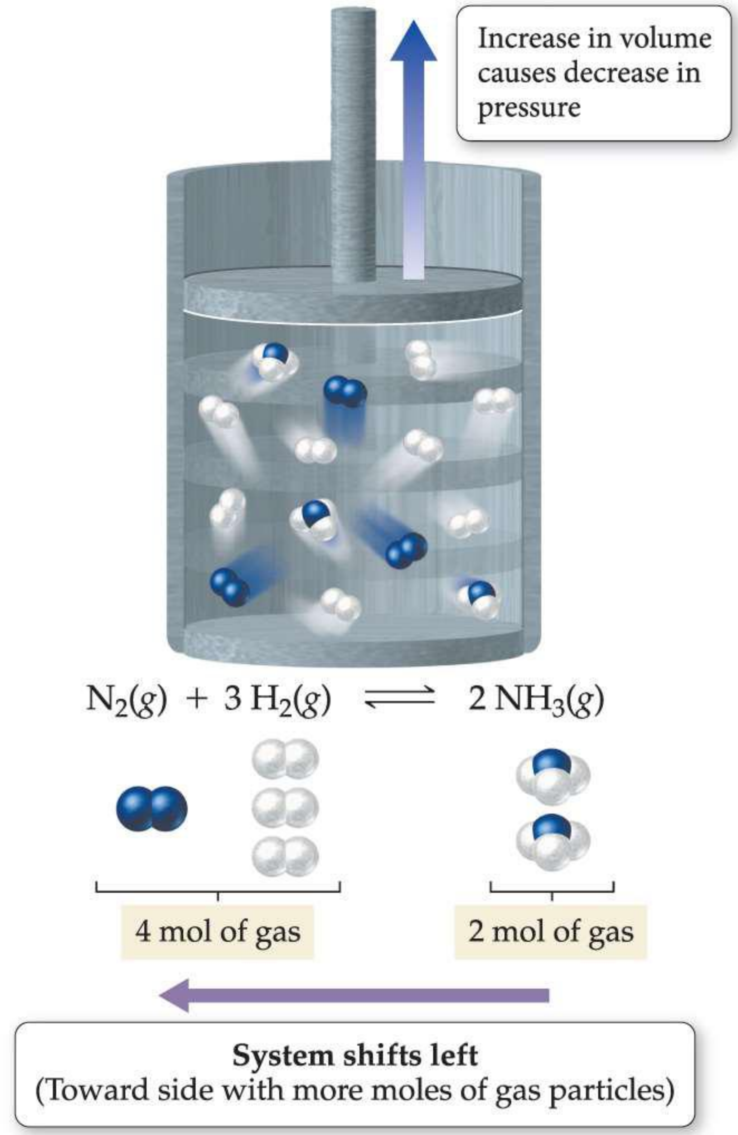
The reactants *here* have larger exponents in K_{eq} than the products, and $[N_2][H_2]^3$ increases more than $[NH_3]^2$

e.g. If volume is halved:

- $[N_2][H_2]^3$ would increase by a factor of $2 \cdot 2^3 = 16$
- $[NH_3]^2$ would increase by a factor of $2^2 = 4$
- K_{eq} must stay the same, so $[N_2]$ and $[H_2]$ must decrease
- Reaction shifts to the right

Effect of Volume Increase on Equilibrium

When the volume of an equilibrium mixture increases, the pressure decreases. The system responds (to raise the pressure) by shifting to the left, the side of the reaction with more moles of gas particles.



The Effect of a Volume Change on Equilibrium

Effects of volume change — summary:

- Decreasing the volume causes the reaction to shift in the direction that has fewer moles of gas particles.
- Increasing the volume causes the reaction to shift in the direction that has more moles of gas particles.
- Notice that if a chemical reaction has an equal number of moles of gas particles on both sides of the chemical equation, a change in volume has no effect.

The Effect of a Temperature Change on Equilibrium

- In an ***exothermic*** reaction, we can think of thermal energy as a product. Raising the temperature of an exothermic reaction—think of this as adding thermal energy to the product side—causes the reaction to shift left.
- In an ***endothermic*** reaction, we can think of thermal energy as a reactant. Raising the temperature of an endothermic reaction—think of this as adding thermal energy to the reactant side—causes the reaction to shift right.

In an Exothermic Reaction, We Can Think of Heat as a Product

$$\textbf{Exothermic reaction:}\quad A + B \rightleftharpoons C + D + \text{Heat}$$

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

2) Reaction shifts left

1) Add heat

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

2) Reaction shifts right

1) Remove heat

In an Endothermic Reaction, We Can Think of Heat as a Reactant

Endothermic reaction: $A + B + \text{Heat} \rightleftharpoons C + D$

Colorless Brown

$$N_2O_4(g) + \text{Heat} \rightleftharpoons 2\,NO_2(g)$$

1) Add heat 2) Reaction shifts right

Colorless Brown

$$N_2O_4(g) + \text{Heat} \rightleftharpoons 2\,NO_2(g)$$

1) Remove heat 2) Reaction shifts left

Be careful in applying Le Châtelier's Principle

- We need to be careful in applying Le Chatelier's Principle
- For temperature changes, it's reliable only when the temperature change doesn't cause a change in concentration
  - Such as when gases are involved, where volume would change with temperature at constant pressure
  - When gaseous reactants or products are involved, heating/cooling at constant volume ensures that we are only observing the effect of the heat of reaction

Applying Le Chatelier's Principle is much easier and more intuitive than using concentrations and K_{eq}

But:
Careless application will result in wrong predictions

Make sure that:

- Pressure/volume effects for gases are working through changing concentrations of reactants and products
- Temperature changes are not affecting volumes (therefore concentrations) before using exothermic/endothermic heat of reaction to predict the direction of change

Not Changing the Position of Equilibrium: The Effect of Catalysts

- Catalysts provide an alternative, more efficient mechanism
- Catalysts work for both forward and reverse reactions
- Catalysts affect the rate of the forward and reverse reactions by the same factor
- Therefore, **catalysts do not affect the position of equilibrium**

Equilibrium as a Function of Temperature

Since the reaction is endothermic, warm temperatures (a) cause a shift to the right, toward the production of brown NO_2. Cool temperatures (b) cause a shift to the left, to colorless N_2O_4.

(a) Warm: NO_2

(b) Cool: N_2O_4

The Effect of a Temperature Change on Equilibrium

To summarize:

In an ***exothermic*** chemical reaction, thermal energy is a product and the effects of temperature change are as follows:

- Increasing the temperature causes the reaction to shift left (in the direction of the reactants).
- Decreasing the temperature causes the reaction to shift right (in the direction of the products).

In an ***endothermic*** chemical reaction, thermal energy is a reactant and the effects of temperature change are as follows:

- Increasing the temperature causes the reaction to shift right (in the direction of the products).
- Decreasing the temperature causes the reaction to shift left (in the direction of the reactants).

Practice
Check your answer on the next slide

The reaction

$2\ SO_2(g) + O_2(g) \rightleftarrows 2\ SO_3(g)$ with $\Delta H° = -198$ kJ

is at equilibrium. How will each of the following changes affect the equilibrium concentrations of each gas once equilibrium is restored?

adding more O_2 to the container

condensing and removing SO_3

compressing the gases

cooling the mixture

doubling the volume of the container

warming the mixture

adding helium to the container

adding a catalyst to the mixture

Practice – Le Châtelier's Principle

The reaction

$2\ SO_2(g) + O_2(g) \rightleftarrows 2\ SO_3(g)$ with $\Delta H° = -198$ kJ

is at equilibrium. How will each of the following changes affect the equilibrium concentrations of each gas once equilibrium is restored?

adding more O_2 to the container	shift to SO_3
condensing and removing SO_3	shift to SO_3
compressing the gases	shift to SO_3
cooling the mixture	shift to SO_3
doubling the volume of the container	shift to SO_2
warming the mixture	shift to SO_2
adding helium to the container	no effect
adding a catalyst to the mixture	no effect

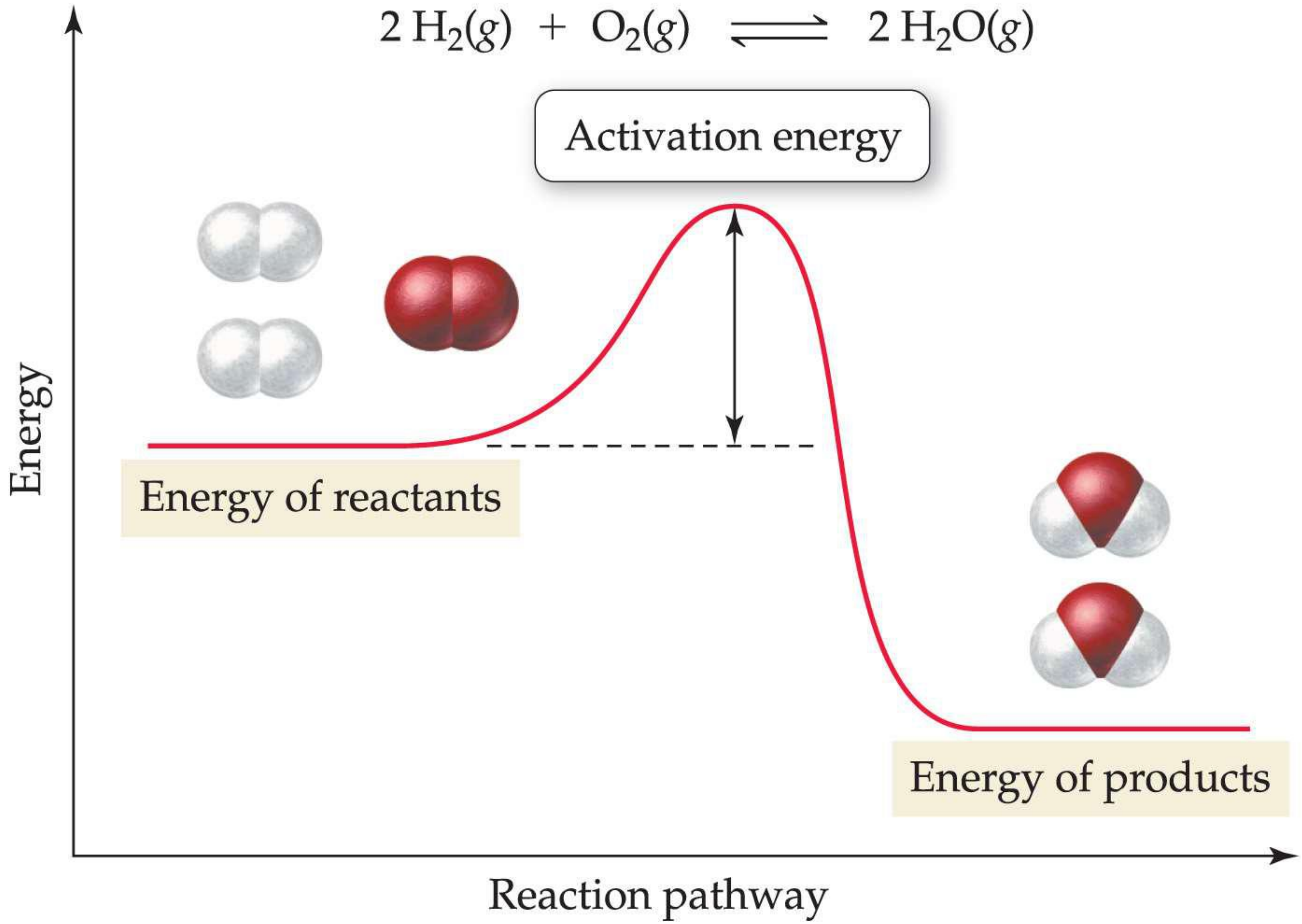
Everyday Chemistry: Hard Water

- Because of their relatively low solubility-product constants, water can easily become saturated with $CaCO_3$ and $MgCO_3$.
- A drop of water becomes saturated with $CaCO_3$ and $MgCO_3$ as the water evaporates.
- A saturated solution such as this precipitates some of its dissolved ions.
- These precipitates show up as scaly deposits on faucets, sinks, and cookware. Washing cars or dishes with hard water leaves spots of $CaCO_3$ and $MgCO_3$ as these solids precipitate out of drying drops of water.

The Path of a Reaction and the Effect of a Catalyst

- The equilibrium constant describes *how far* a chemical reaction will go. The reaction rate describes *how fast* it will get there.
- The **activation energy** (or activation barrier) for a reaction is the energy barrier that must be overcome in order for the reactants to be converted into products.
- Activation energies exist for most chemical reactions because the original bonds must begin to break before new bonds begin to form, and this requires energy.

How Activation Energies Affect Reaction Rates



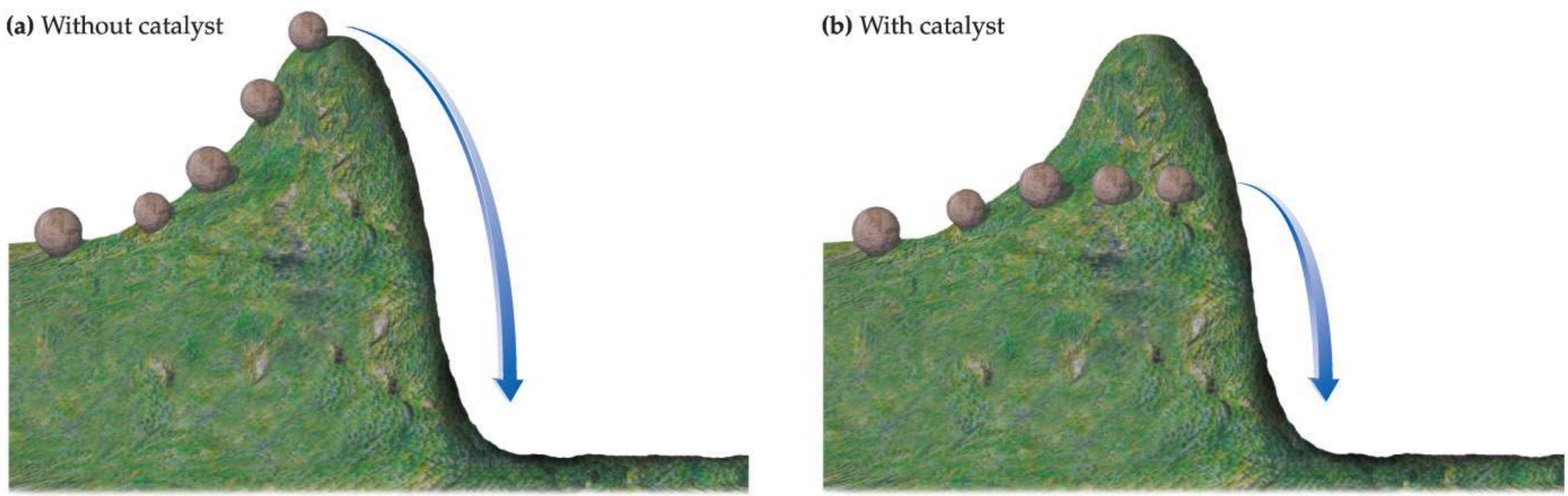
Are There Any Ways to Speed Up a Slow Reaction (One with a High Activation Barrier)?

- For chemical reactions, the higher the activation energy, the fewer the number of reactant molecules that make it over the barrier, and the slower the reaction rate.
- In general: At a given temperature, the higher the activation energy for a chemical reaction, the slower the reaction rate.
- Are there any ways to speed up a slow reaction?
- Increase the concentrations of the reactants, which results in more collisions per unit time.
- Increase the temperature, which results in more collisions per unit time, and also in higher energy collisions.
- Use a *catalyst,* which lowers the activation energy barrier.

Hill Analogy for Effect of a Catalyst on Activation Energy

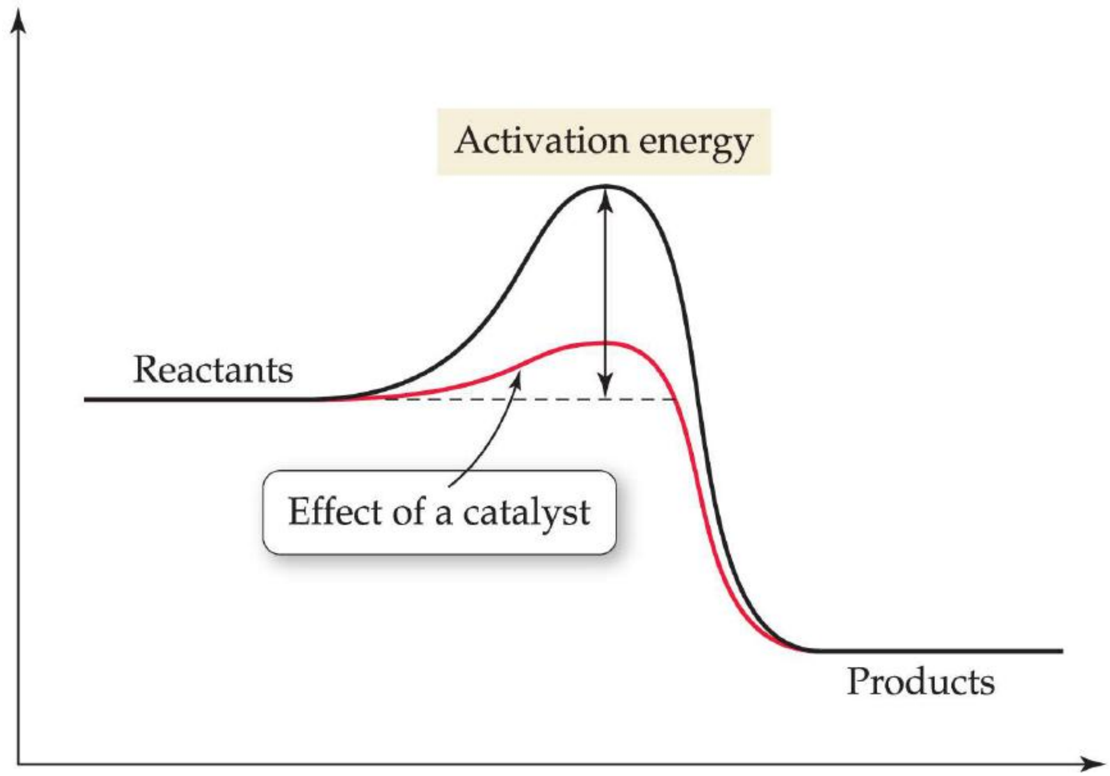
(a) One way to increase reaction rate is to push harder—this is analogous to an increase in temperature for a chemical reaction.

(b) Another way is to find a path that goes *around* the hill—this is analogous to the role of a catalyst for a chemical reaction.



Function of a Catalyst

A catalyst provides an alternative pathway with a lower activation energy barrier for the reaction.

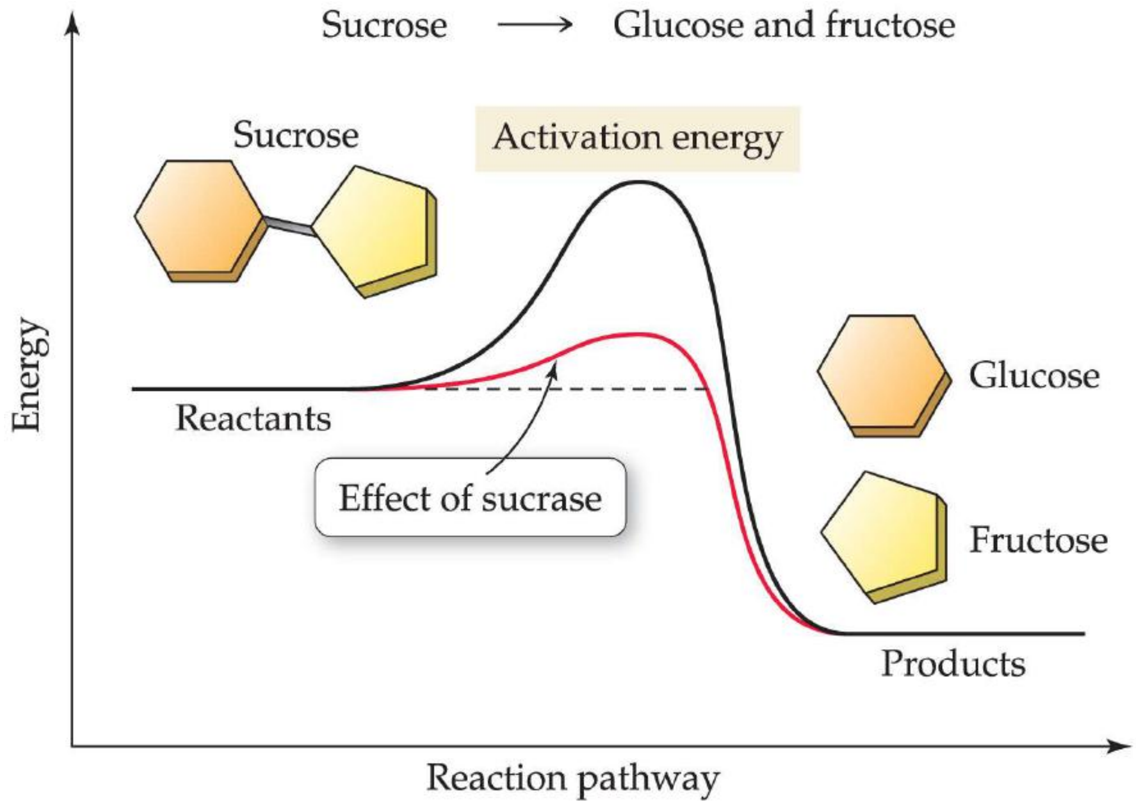


Enzymes: Biological Catalysts

- Many reactants are thermally sensitive—increasing the temperature often destroys them. The only way to carry out many reactions is to use catalysts.
- Most of the thousands of reactions that must occur for a living organism to survive would be too slow at normal temperatures. So living organisms use **enzymes,** biological catalysts that increase the rates of biochemical reactions.

FIGURE 15.17 An Enzyme Catalyst

The enzyme sucrase creates a pathway with a lower activation energy for the conversion of sucrose to glucose and fructose.



Chapter 15 in Review

- Equilibrium involves the ideas of sameness and constancy.
- The rate of a chemical reaction is the amount of reactant(s) that goes to product(s) in a given period of time.
- Dynamic chemical equilibrium occurs when the rate of the forward reaction equals the rate of the reverse reaction.
- In the equilibrium constant, K_{eq}, only the concentrations of gaseous or aqueous reactants and products are included—the concentrations of solid or liquid reactants or products are omitted.

Chapter 15 in Review

- Le Châtelier's principle states that when a chemical system at equilibrium is disturbed, the system shifts in a direction that minimizes the disturbance.
- The solubility-product constant, K_{sp}, describes the dissolving of an ionic compound.
- Most chemical reactions must overcome an *activation energy*. A catalyst—a substance that increases the rate of the reaction but is not consumed by it—lowers the activation energy.