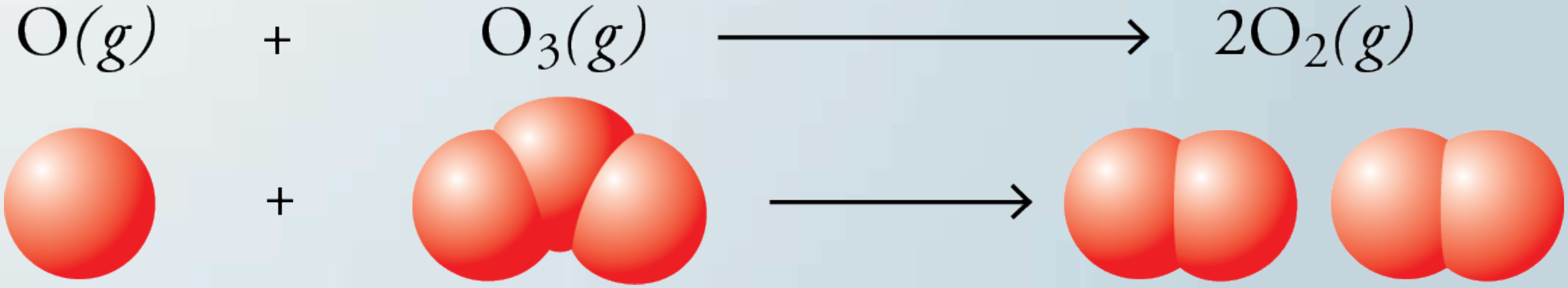
The Process of Chemical Reactions, Equilibrium, Strong and Weak Acids, and pH

IPOL 8512

Collision Theory

- Reactants must collide

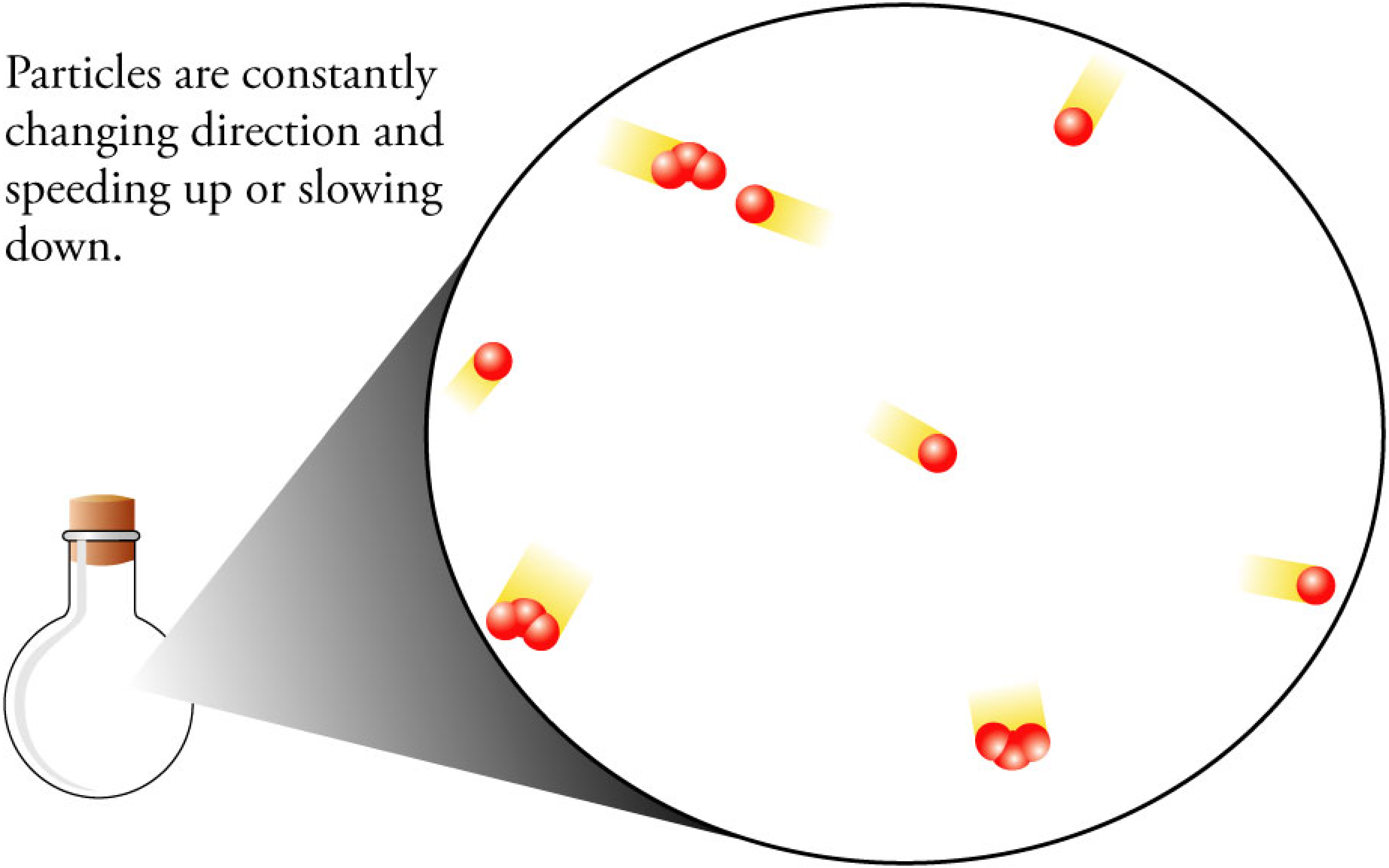


$$O(g) + O_3(g) \longrightarrow 2O_2(g)$$

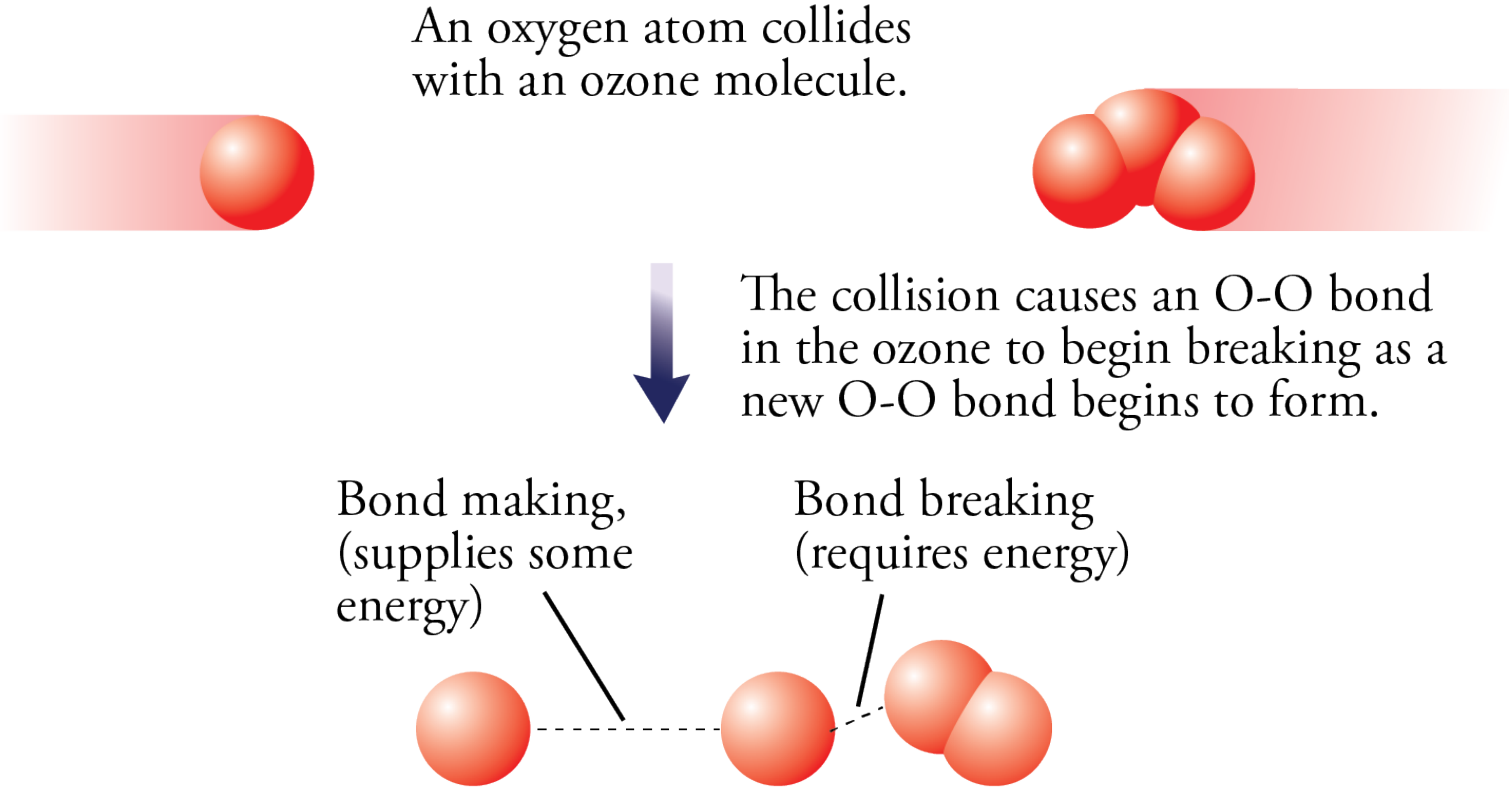
  - collision brings contact between reactants
  - collision provides energy to break bonds

$$O(g) + O_3(g) \rightarrow 2O_2(g)$$

Particles are constantly changing direction and speeding up or slowing down.



Bond Breaking and Making



An oxygen atom collides with an ozone molecule.

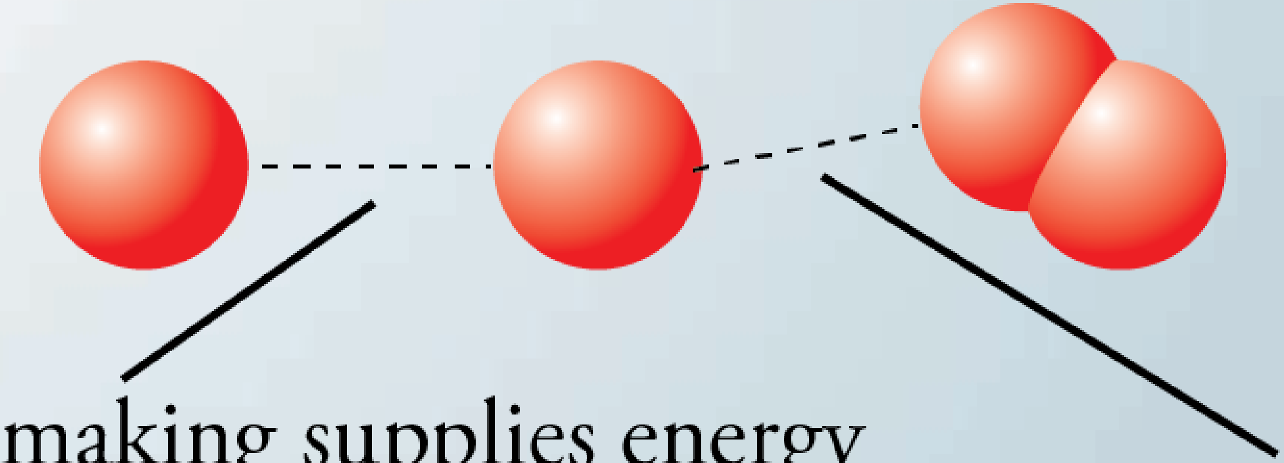
The collision causes an O-O bond in the ozone to begin breaking as a new O-O bond begins to form.

Bond making, (supplies some energy)

Bond breaking (requires energy)

Initially, the energy required for bond breaking is greater than the energy supplied from bond making. The extra energy necessary for the reaction comes from the kinetic energy of the colliding particles.

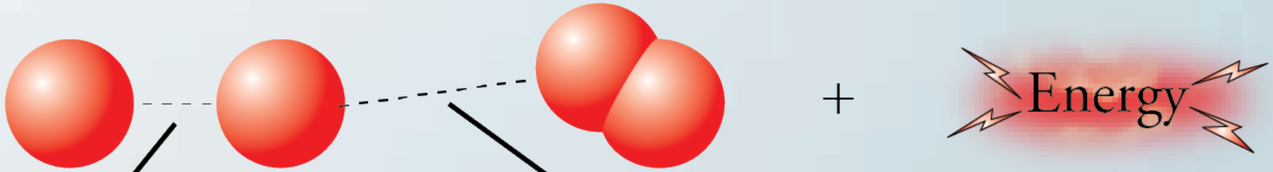
Formation of Activated Complex



Bond making supplies energy
equal to the energy required for bond breaking.

Formation of Product

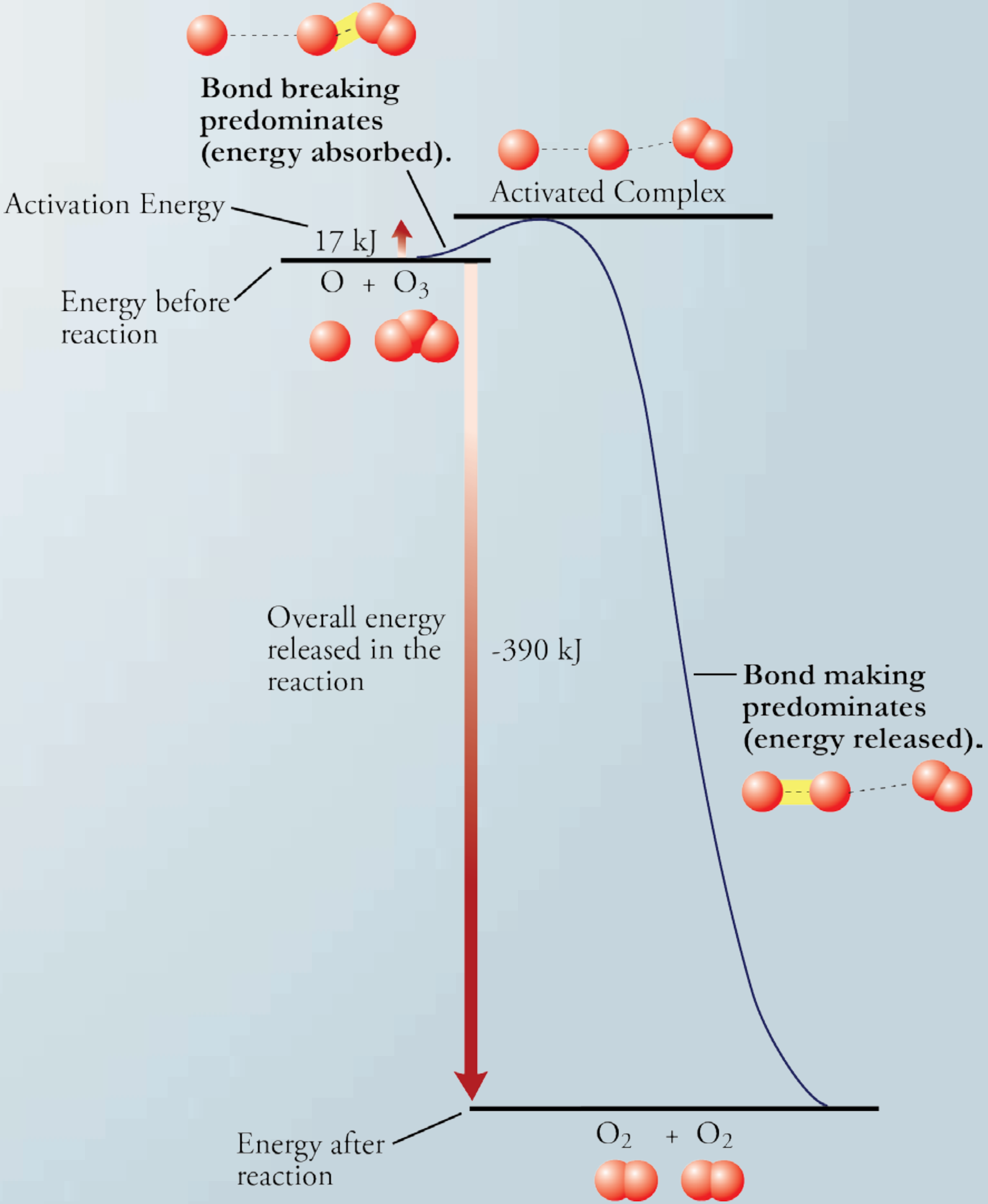
Beyond some point in the reaction, bond making predominates over bond breaking.



Bond making supplies more energy than is necessary for bond breaking...

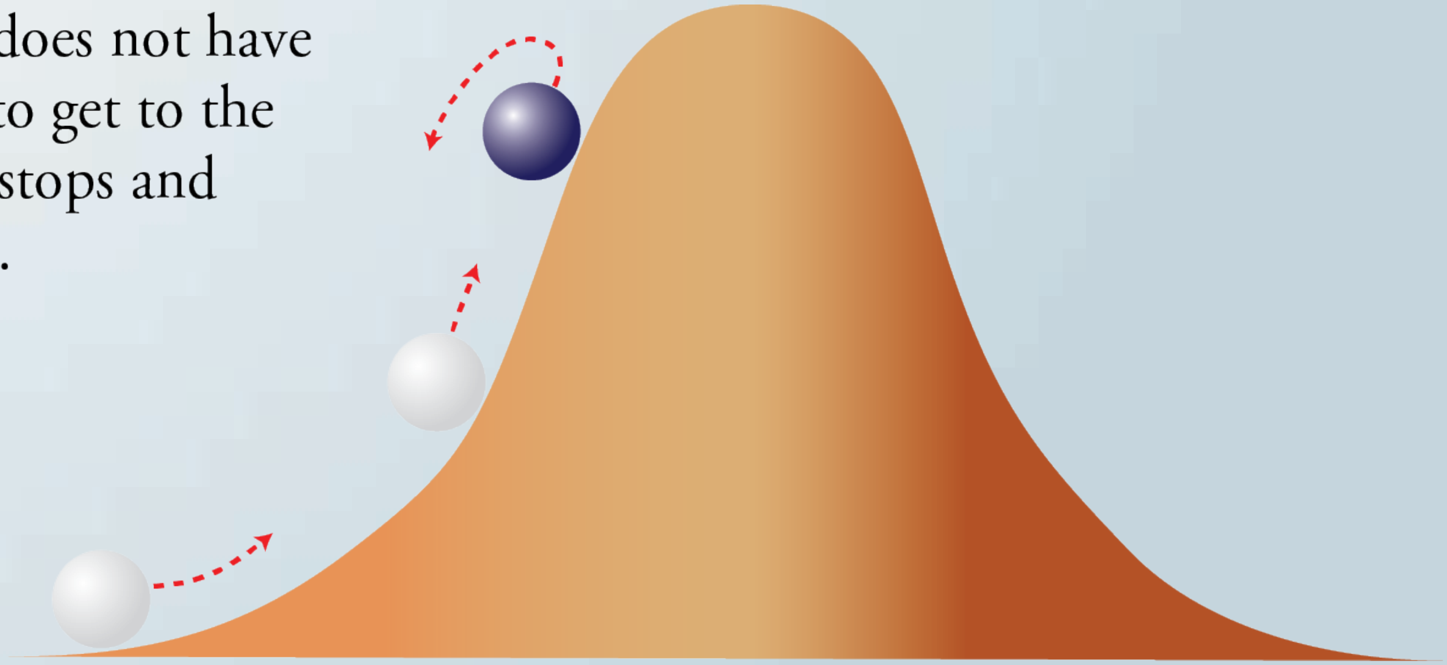
so energy is released

Energy Diagram for O/O_3 Reaction

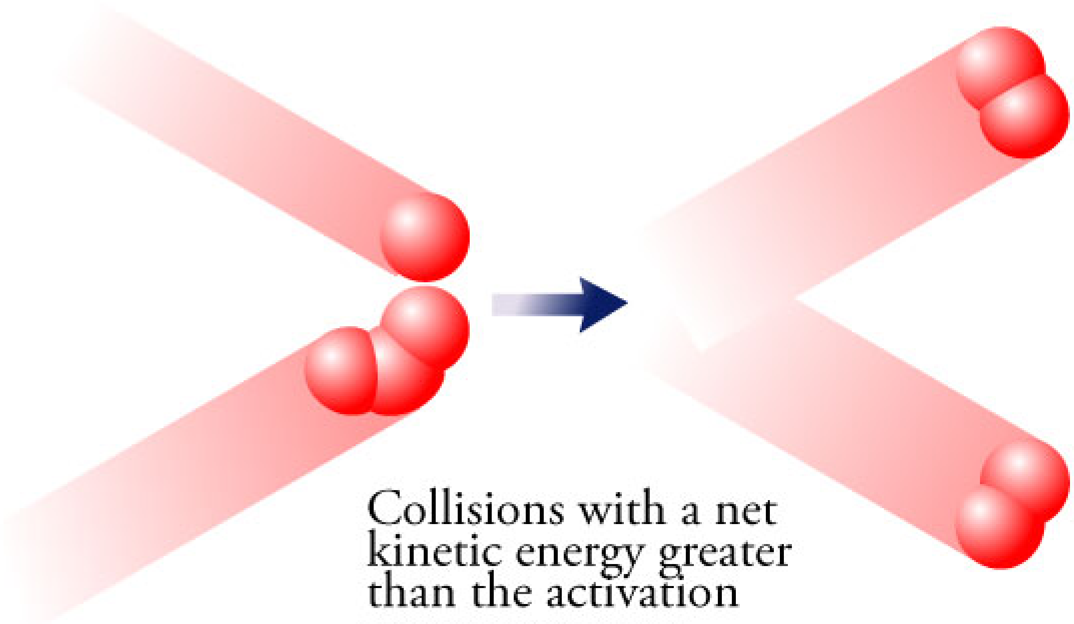


Reactions must have a minimum activation energy…if too little, no change

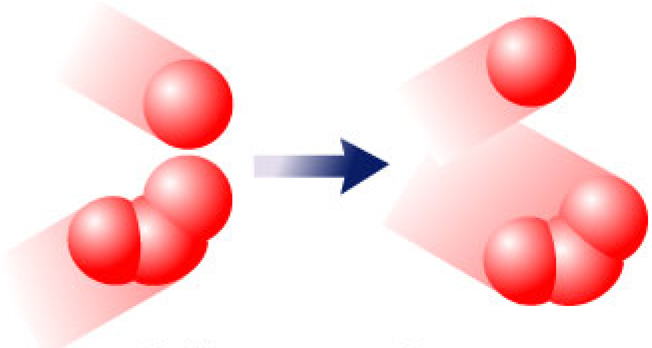
If a rolling ball does not have enough energy to get to the top of a hill, it stops and rolls back down.



Collision Energy and Activation Energy

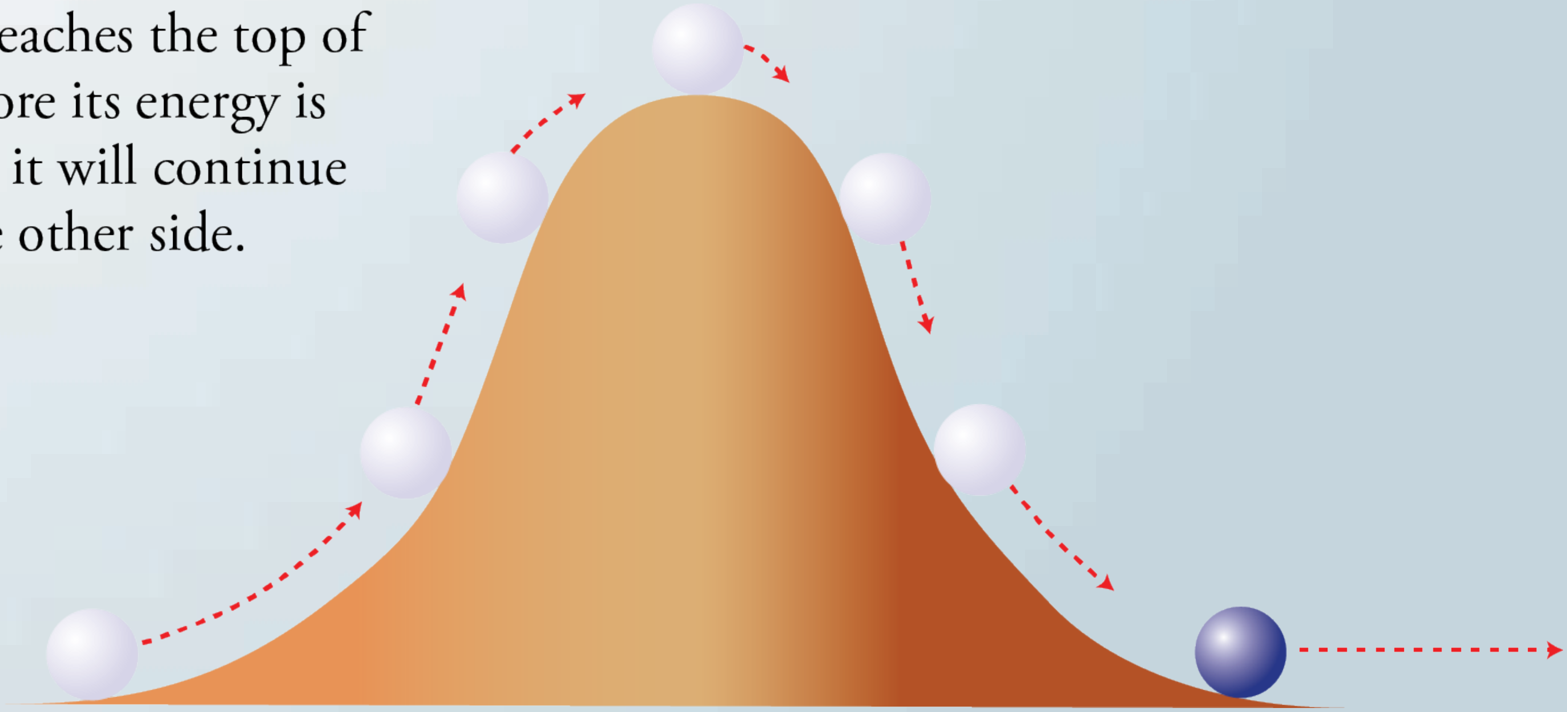


Collisions with a net kinetic energy greater than the activation energy can react.



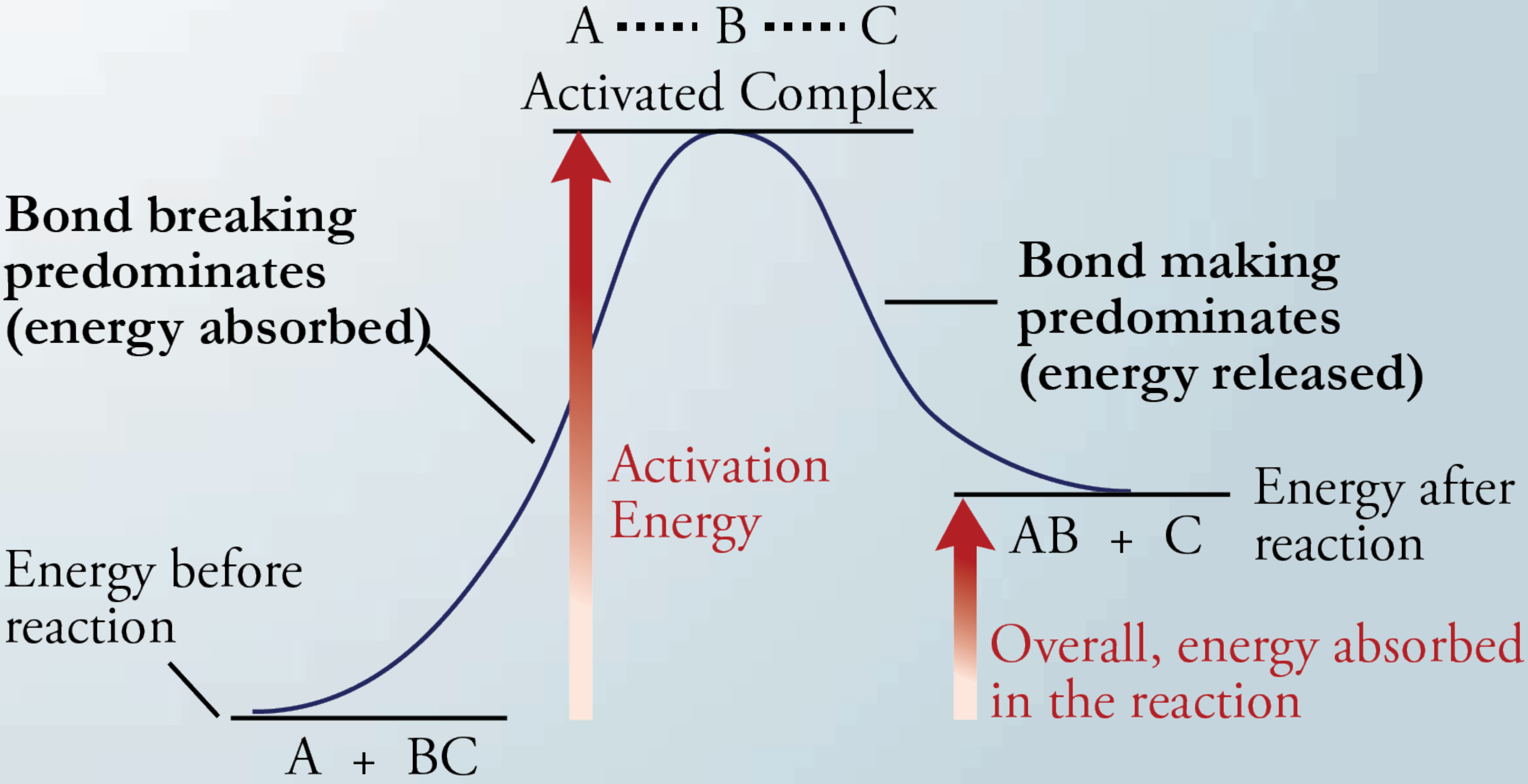
Collisions with a net kinetic energy less than the activation energy cannot react.

Reactions must have a minimum activation energy…if enough, change



If a ball reaches the top of a hill before its energy is depleted, it will continue down the other side.

Endergonic Reactions



A ····· B ····· C
Activated Complex

Bond breaking predominates (energy absorbed)

Bond making predominates (energy released)

Activation Energy

Energy before reaction

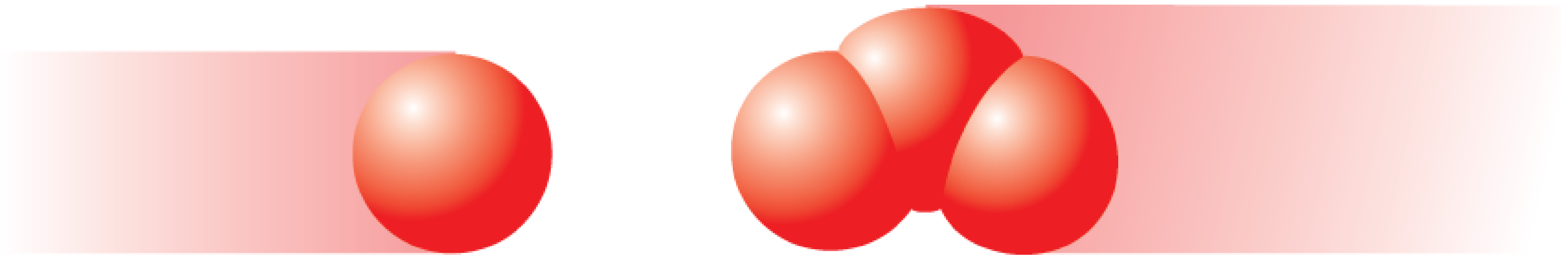
A + BC

Energy after reaction

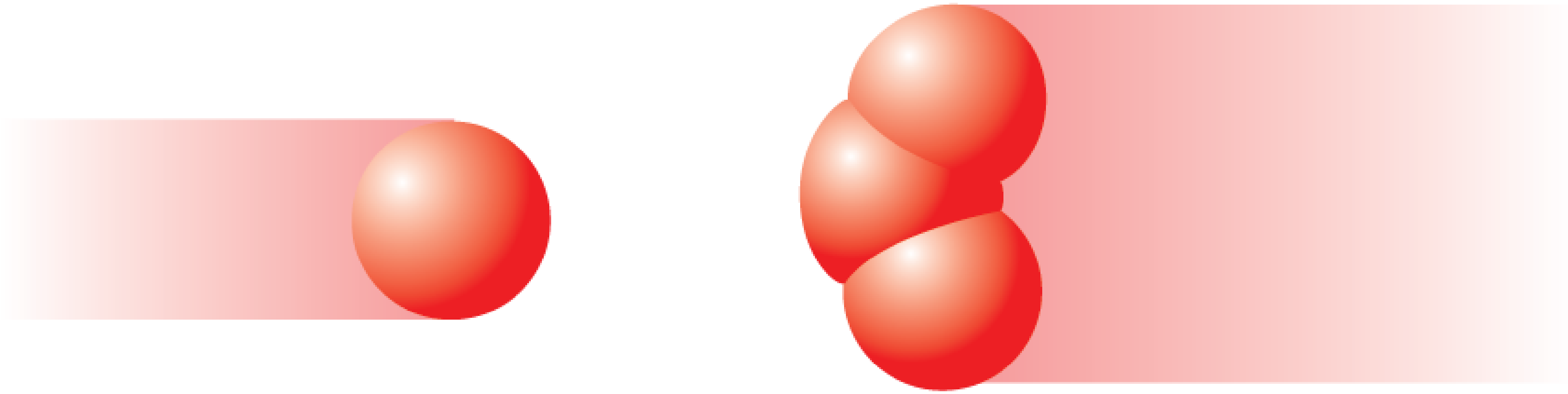
AB + C

Overall, energy absorbed in the reaction

Orientation



One favorable orientation



One unfavorable orientation

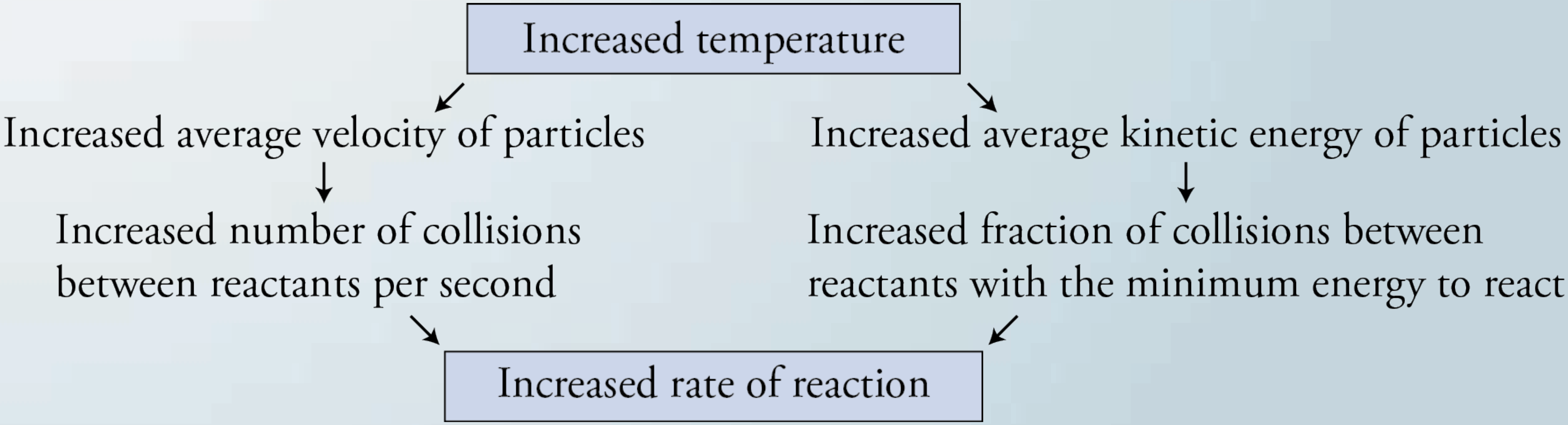
Summary

- **The reactant particles must collide.**
  - The collision brings together the atoms that will form the new bonds, and the kinetic energy of the particles provides energy for the reaction to proceed.
- **The collision must provide at least the minimum energy necessary to produce the activated complex.**
  - It takes energy to initiate the reaction by converting the reactants into the activated complex. If the collision does not provide this energy, products cannot form.

Summary (part 3)

- **The orientation of the colliding particles must favor the formation of the activated complex, in which the new bond or bonds are able to form as the old bond or bonds break.**
  - Because the formation of the new bonds provides some of the energy necessary to break the old bonds, the making and breaking of bonds must occur more or less simultaneously. This is only possible when the particles collide in such a way that the bond-forming atoms are close to each other.

Temperature and Rate of Reaction



Increased temperature

Increased average velocity of particles

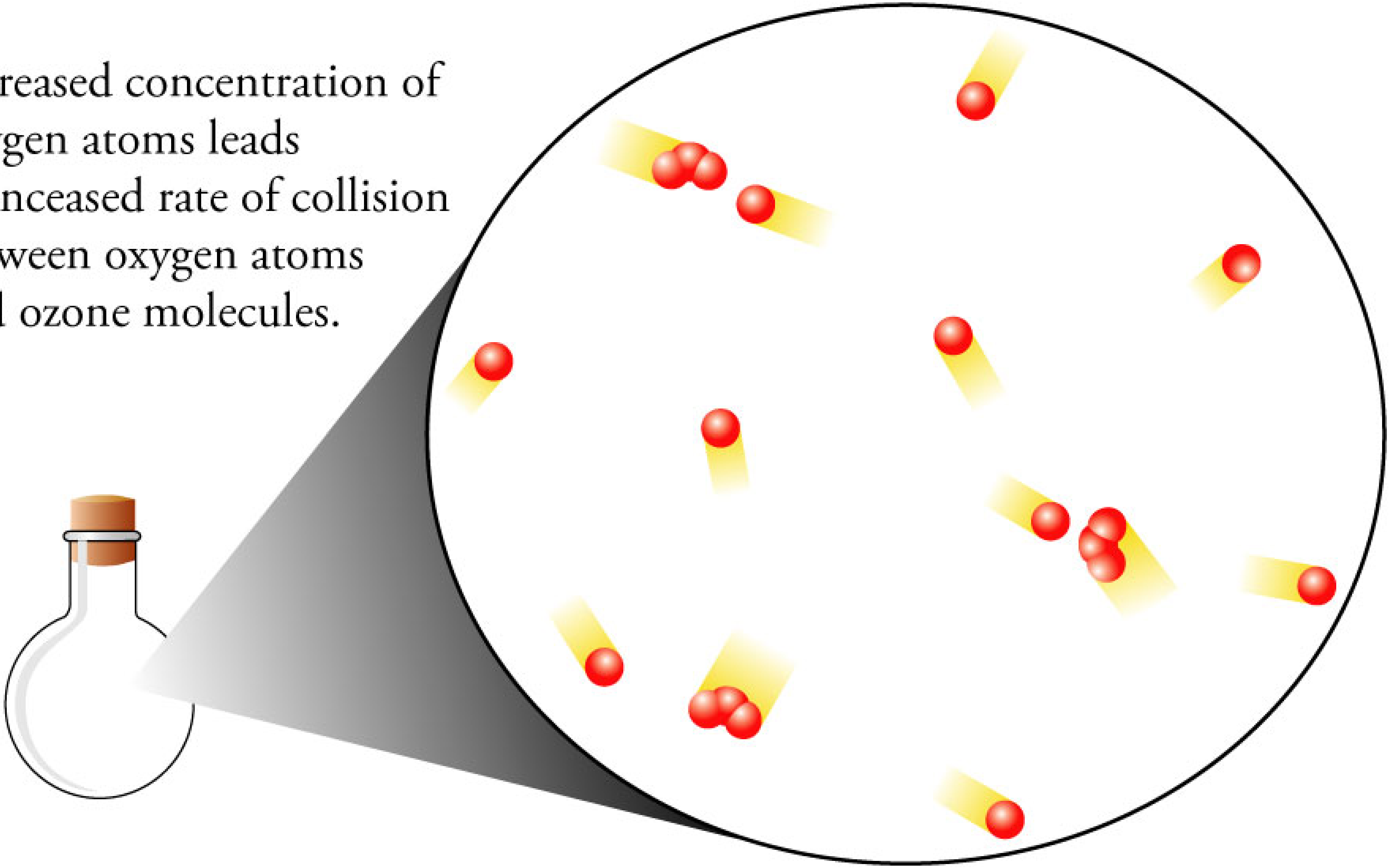
Increased number of collisions between reactants per second

Increased average kinetic energy of particles

Increased fraction of collisions between reactants with the minimum energy to react

Increased rate of reaction

Increased Concentration of One Reactant



Increased concentration of oxygen atoms leads to inceased rate of collision between oxygen atoms and ozone molecules.

Concentration and Rates of Reaction

Increased concentration of reactant
(Increased number of particles per unit volume)

↓

Decreased average distance between particles and decreased volume available in which to move without colliding

↓

Increased number of collisions between reactants per liter per second

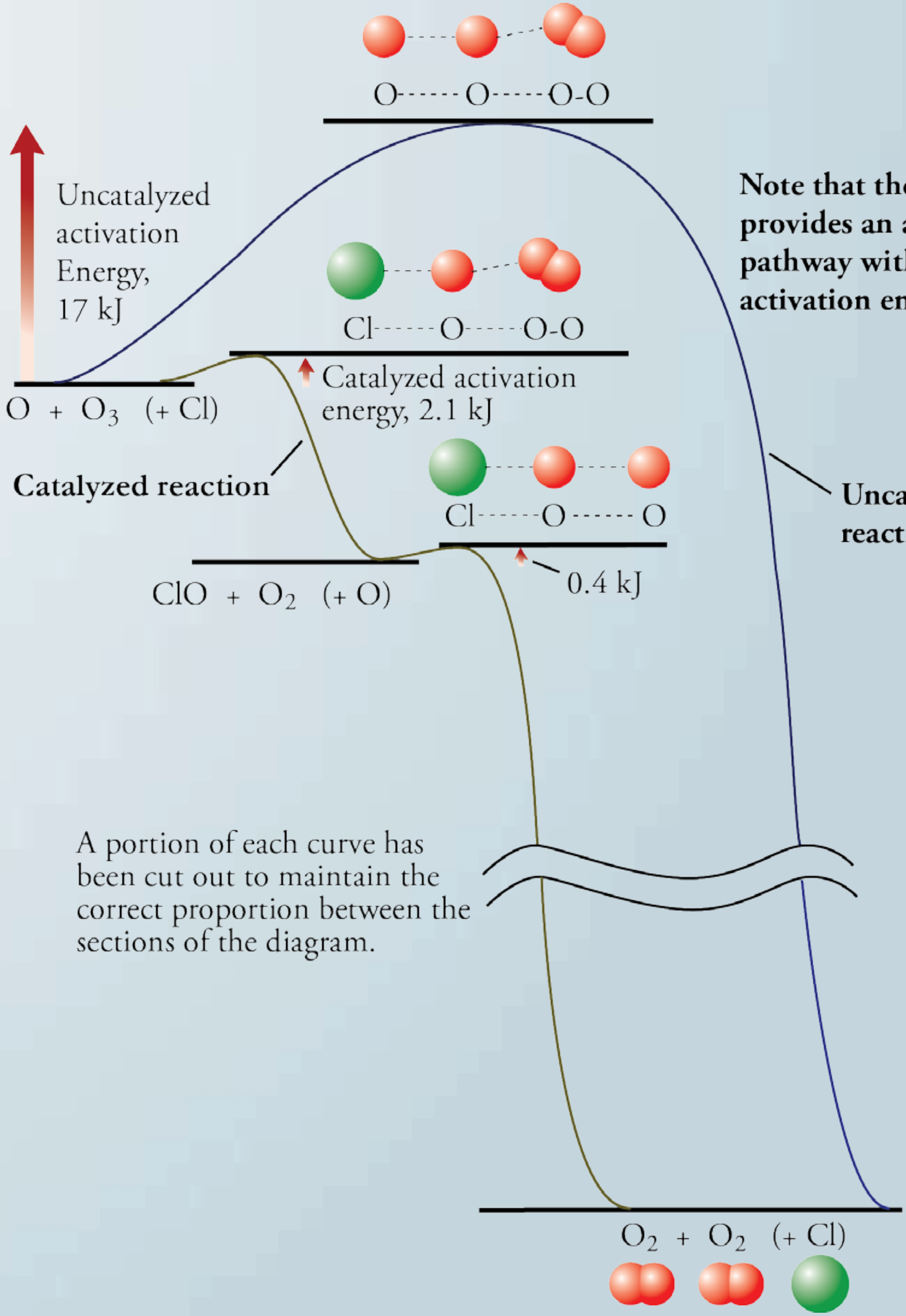
↓

Increased number of particles fulfilling the requirements for reaction

↓

Increased rate of reaction

Catalyzed O/O_3 Reaction



Note that the catalyst provides an alternate pathway with a lower activation energy.

A portion of each curve has been cut out to maintain the correct proportion between the sections of the diagram.

Catalysts and Rate of Reactions

The catalyst provides an alternate pathway with a lower activation energy.

↓

A greater fraction of collisions have the activation energy.

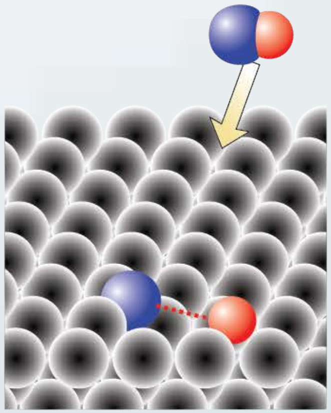
↓

A greater fraction of collisions lead to products.

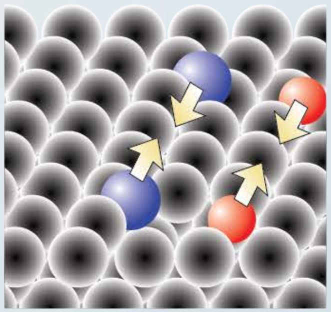
↓

Increased rate of reaction

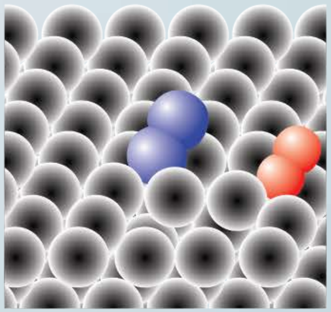
Heterogeneous Catalysis



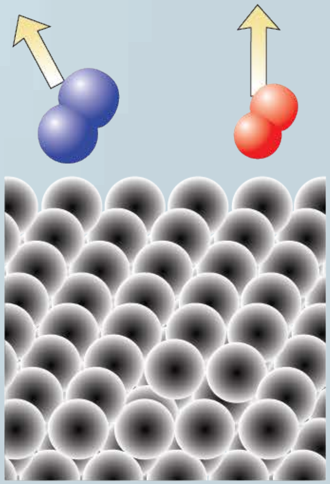
Step 1 - The reactant molecules are adsorbed, and the bonds are weakened.



Step 2 - The atoms migrate across the catalyst.



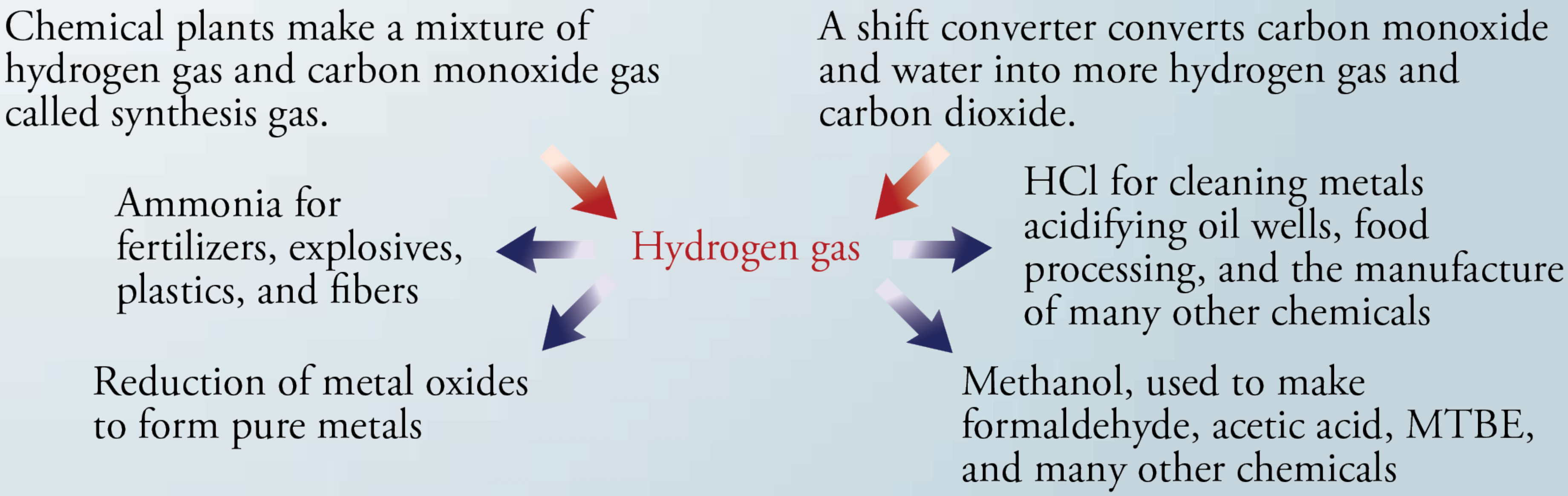
Step 3 - New bonds form.



Step 4 - The products leave the catalyst.

Production and Uses of Hydrogen Gas

$$CH_4(g) + H_2O(g) \rightleftharpoons CO(g) + 3H_2(g)$$



Chemical plants make a mixture of hydrogen gas and carbon monoxide gas called synthesis gas.

A shift converter converts carbon monoxide and water into more hydrogen gas and carbon dioxide.

Hydrogen gas

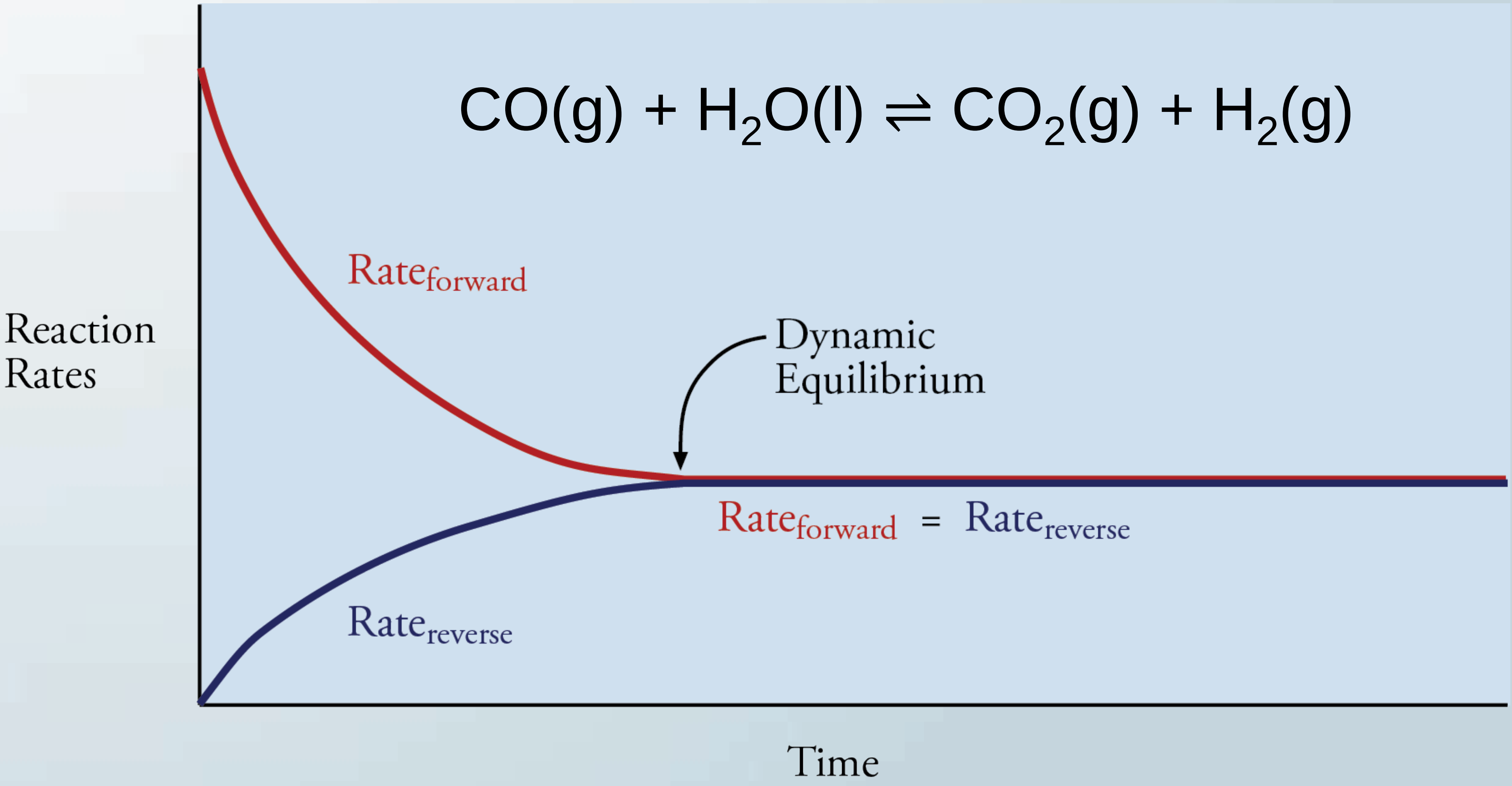
Ammonia for fertilizers, explosives, plastics, and fibers

HCl for cleaning metals acidifying oil wells, food processing, and the manufacture of many other chemicals

Reduction of metal oxides to form pure metals

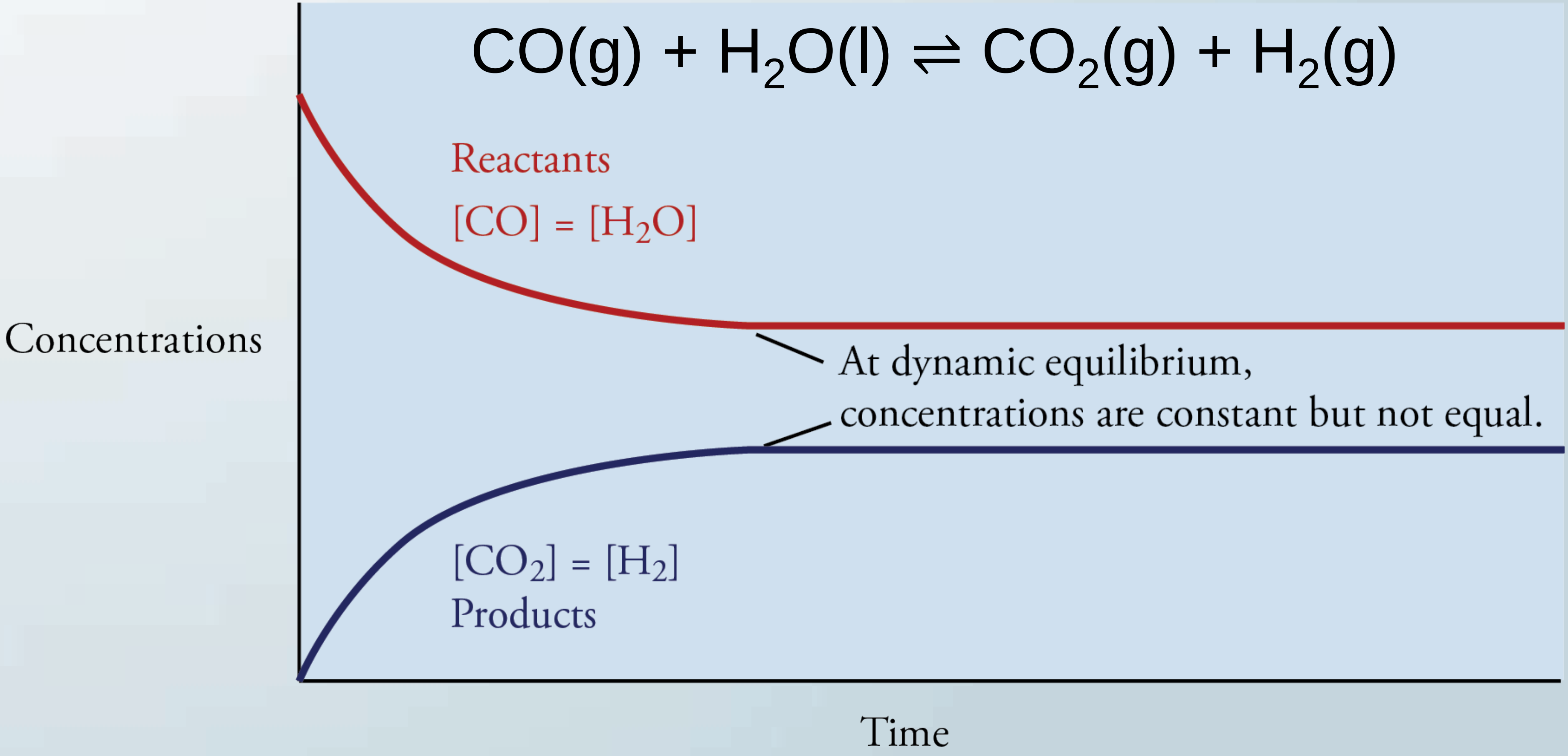
Methanol, used to make formaldehyde, acetic acid, MTBE, and many other chemicals

Rates of Reaction for Reversible Reactions



$$CO(g) + H_2O(l) \rightleftharpoons CO_2(g) + H_2(g)$$

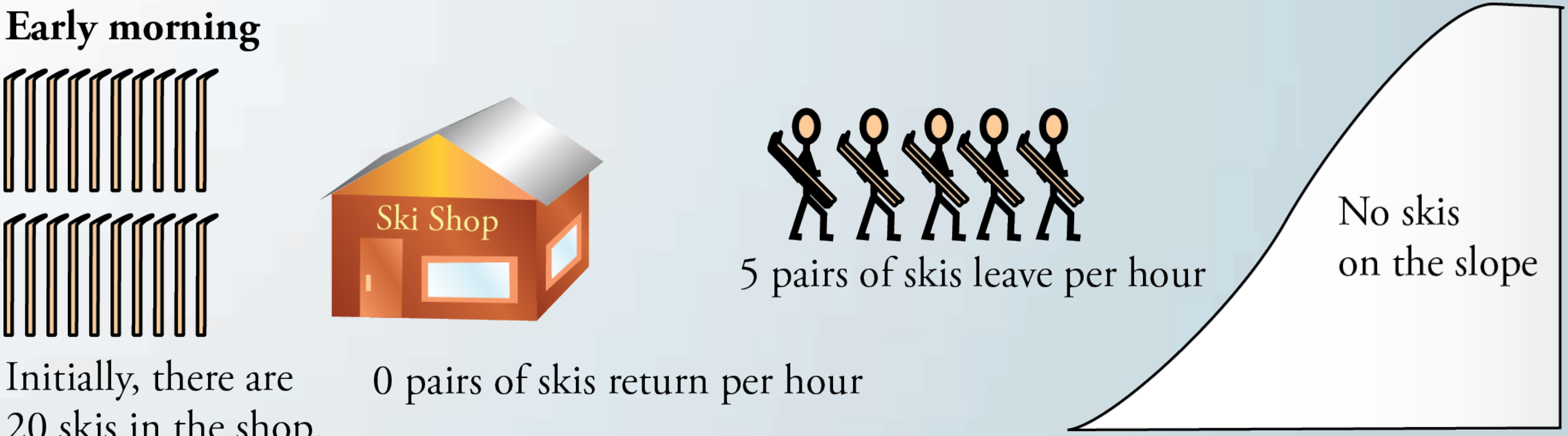
Changes in Concentrations for a Reversible Reaction



$$CO(g) + H_2O(l) \rightleftharpoons CO_2(g) + H_2(g)$$

Ski Shop Analogy for Equilibrium

Early morning



Initially, there are 20 skis in the shop.

0 pairs of skis return per hour

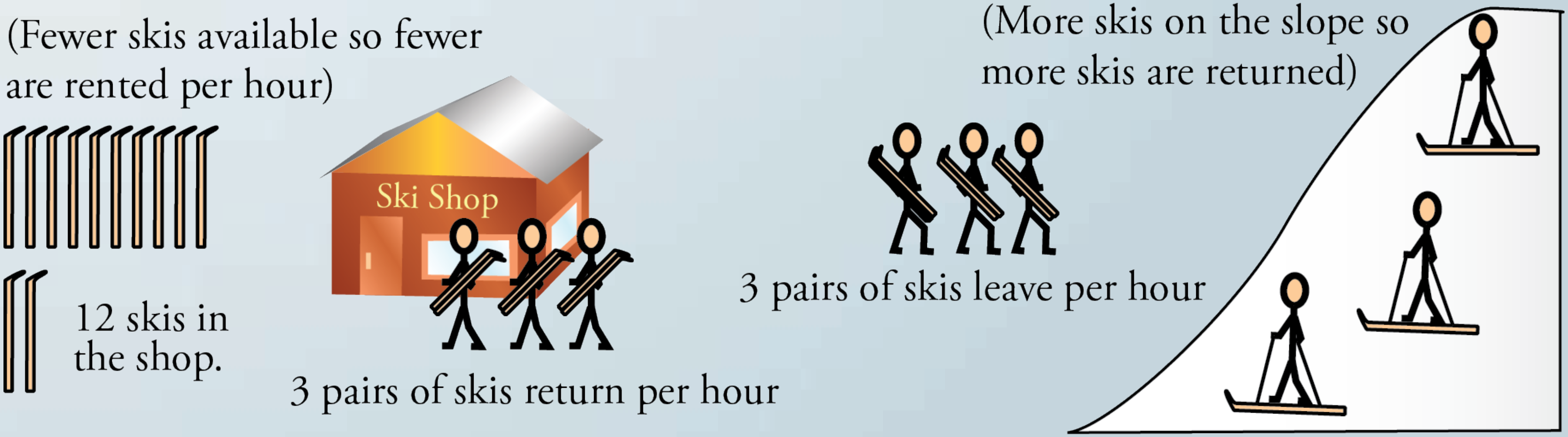
5 pairs of skis leave per hour

No skis on the slope

Later in the day

(Fewer skis available so fewer are rented per hour)

3 pairs of skis on the slope (More skis on the slope so more skis are returned)



12 skis in the shop.

3 pairs of skis leave per hour

3 pairs of skis return per hour

Equilibrium (No change in the number of skis in the shop and on the slope)

Equilibrium Constant Expression

$$CH_4(g) + H_2O(g) \rightleftharpoons CO(g) + 3H_2(g)$$

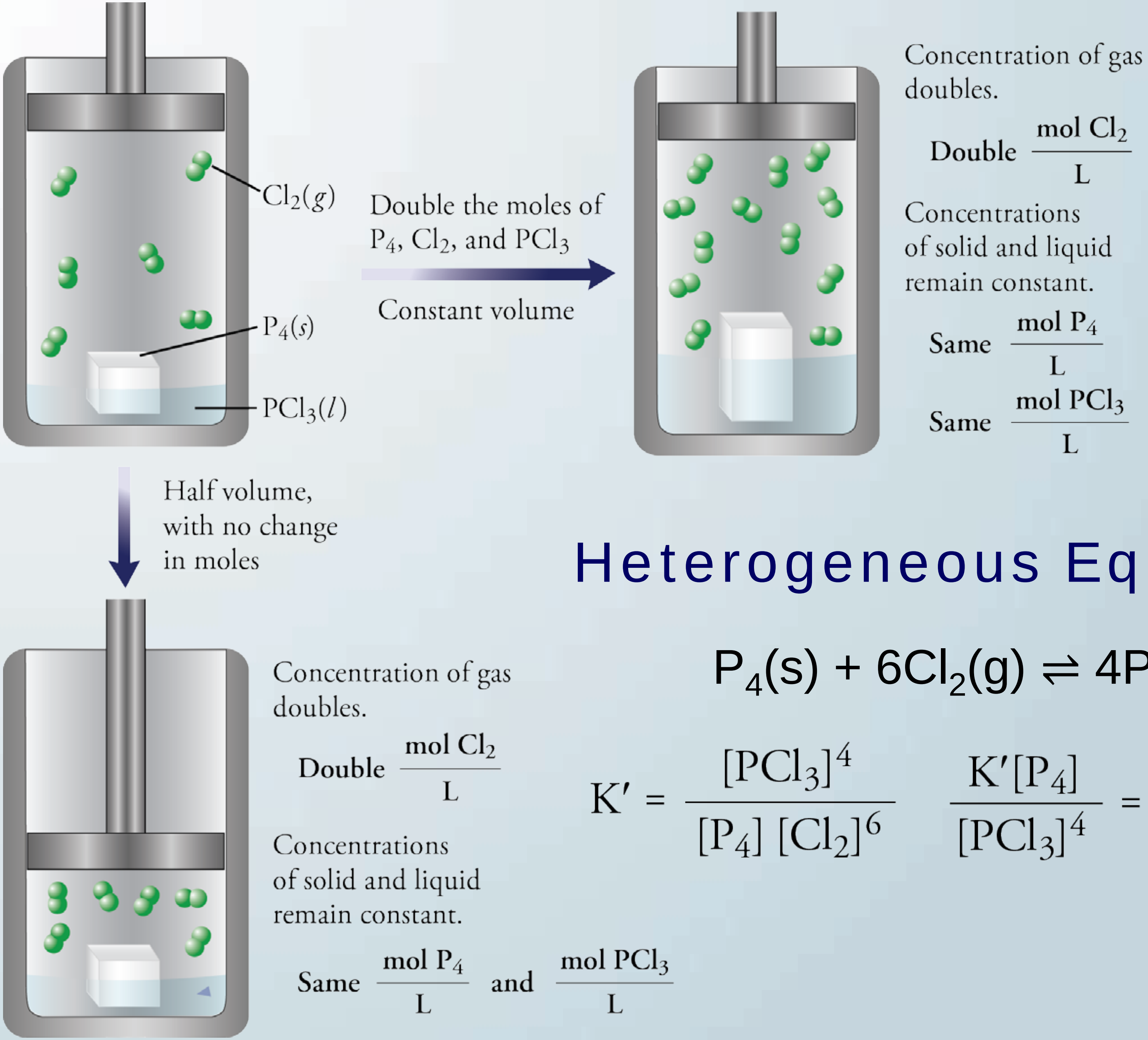
The coefficient before H_2 is 3, so we raise the concentration or pressure to the third power.

$$K_C = \frac{[CO]\,[H_2]^3}{[CH_4]\,[H_2O]} \qquad K_P = \frac{P_{CO}\,P_{H_2}^3}{P_{CH_4}\,P_{H_2O}}$$

[X] = moles X per liter

P_X = partial pressure X

pK = – log K



Double the moles of P$_4$, Cl$_2$, and PCl$_3$

Constant volume

Concentration of gas doubles.

Double $\frac{\text{mol Cl}_2}{\text{L}}$

Concentrations of solid and liquid remain constant.

Same $\frac{\text{mol P}_4}{\text{L}}$

Same $\frac{\text{mol PCl}_3}{\text{L}}$

Half volume, with no change in moles

Concentration of gas doubles.

Double $\frac{\text{mol Cl}_2}{\text{L}}$

Concentrations of solid and liquid remain constant.

Same $\frac{\text{mol P}_4}{\text{L}}$ **and** $\frac{\text{mol PCl}_3}{\text{L}}$

Heterogeneous Equilibrium

$$P_4(s) + 6Cl_2(g) \rightleftharpoons 4PCl_3(l)$$

$$K' = \frac{[PCl_3]^4}{[P_4]\,[Cl_2]^6} \qquad \frac{K'[P_4]}{[PCl_3]^4} = \frac{1}{[Cl_2]^6} = K_C$$

Equilibrium Constant Expressions for Heterogeneous Equilibria

$$SO_2(g) + 2H_2S(g) \rightleftharpoons 3S(s) + H_2O(g)$$

The solid does not appear in the K_C and K_P expressions.

$$K_C = \frac{[H_2O]}{[SO_2]\,[H_2S]^2}$$

$$K_P = \frac{P_{H_2O}}{P_{SO_2}\,P_{H_2S}^2}$$

Effect of Increased Concentration on Equilibrium

$$CO(g) + H_2O(g) \rightleftharpoons CO_2(g) + H_2(g)$$

Increased concentration of reactant for a system at equilibrium with $\text{Rate}_{\text{forward}} = \text{Rate}_{\text{reverse}}$

↓

Increased $\text{Rate}_{\text{forward}}$

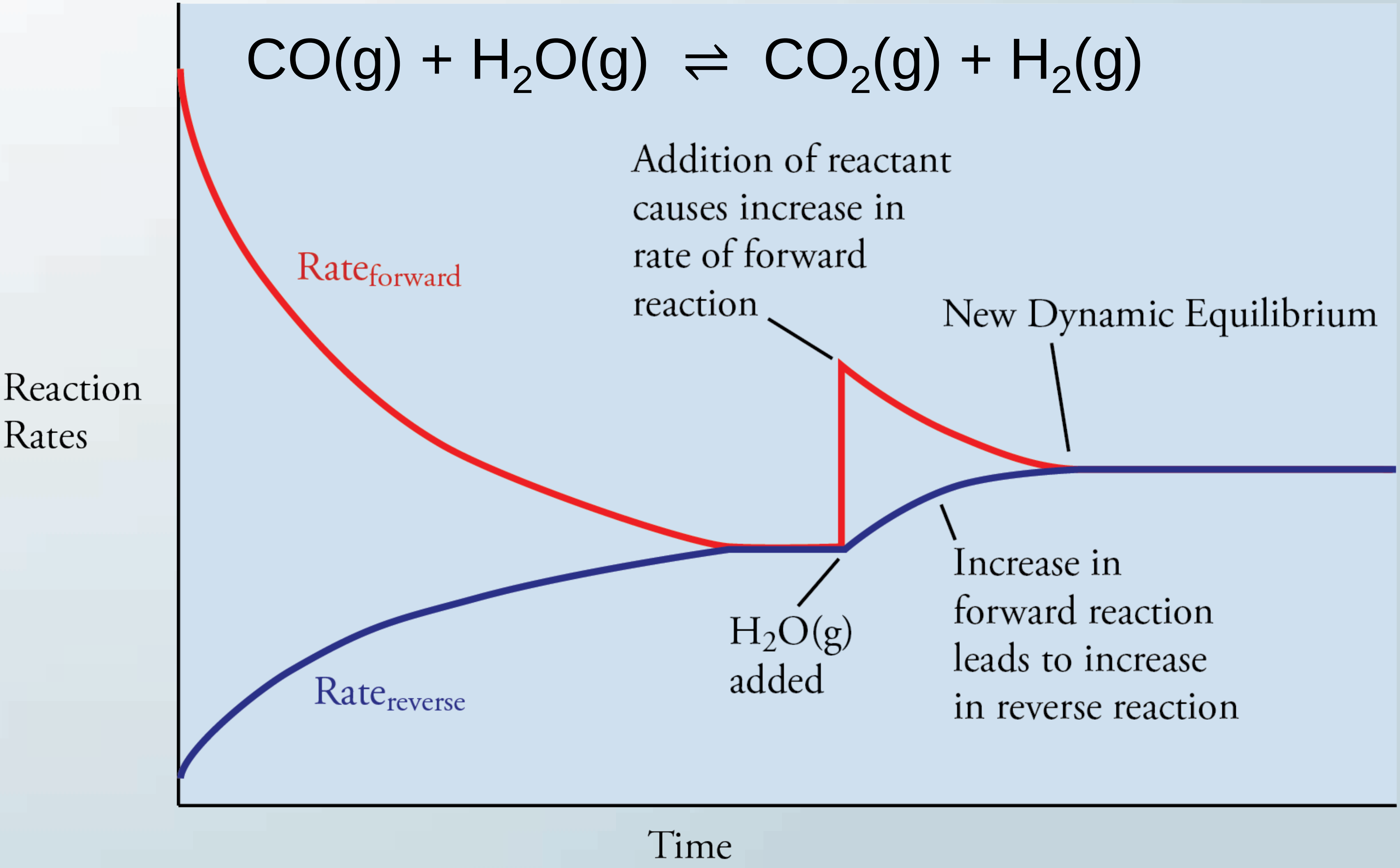
↓

$\text{Rate}_{\text{forward}} > \text{Rate}_{\text{reverse}}$

↓

System shifts toward products

Change in Rates When Reactant Added



$$CO(g) + H_2O(g) \rightleftharpoons CO_2(g) + H_2(g)$$

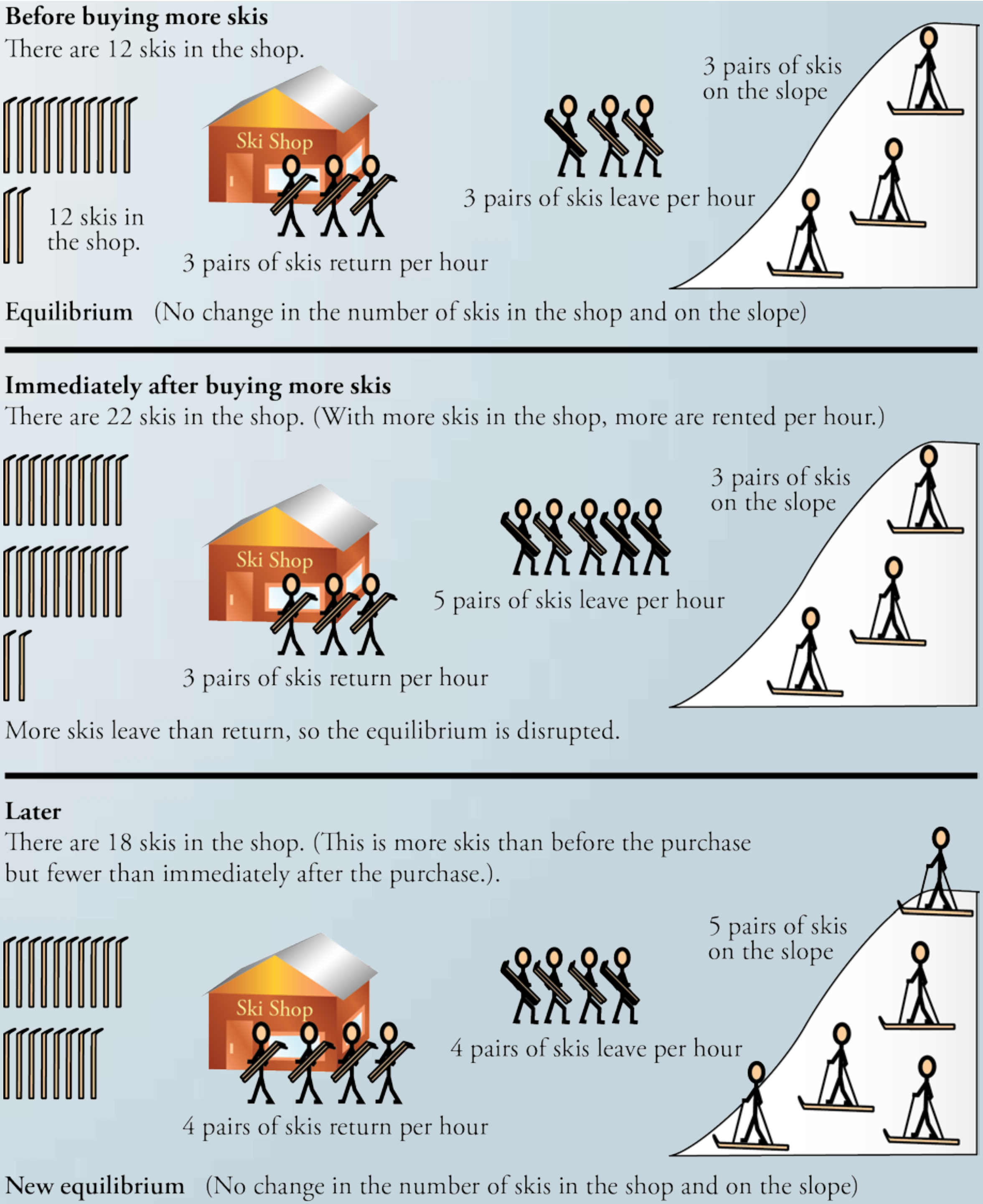
Addition of reactant causes increase in rate of forward reaction

New Dynamic Equilibrium

$H_2O(g)$ added

Increase in forward reaction leads to increase in reverse reaction

Ski Shop Analogy 2



Before buying more skis

There are 12 skis in the shop.

12 skis in the shop.

3 pairs of skis return per hour

3 pairs of skis leave per hour

3 pairs of skis on the slope

Equilibrium (No change in the number of skis in the shop and on the slope)

Immediately after buying more skis

There are 22 skis in the shop. (With more skis in the shop, more are rented per hour.)

3 pairs of skis return per hour

5 pairs of skis leave per hour

3 pairs of skis on the slope

More skis leave than return, so the equilibrium is disrupted.

Later

There are 18 skis in the shop. (This is more skis than before the purchase but fewer than immediately after the purchase.).

4 pairs of skis return per hour

4 pairs of skis leave per hour

5 pairs of skis on the slope

New equilibrium (No change in the number of skis in the shop and on the slope)

Effect of Decreased Concentration on Equilibrium

$$CO(g) + H_2O(g) \rightleftharpoons CO_2(g) + H_2(g)$$

Decreased concentration of one product for a system at equilibrium with $\text{Rate}_{\text{forward}} = \text{Rate}_{\text{reverse}}$

↓

Decreased $\text{Rate}_{\text{reverse}}$

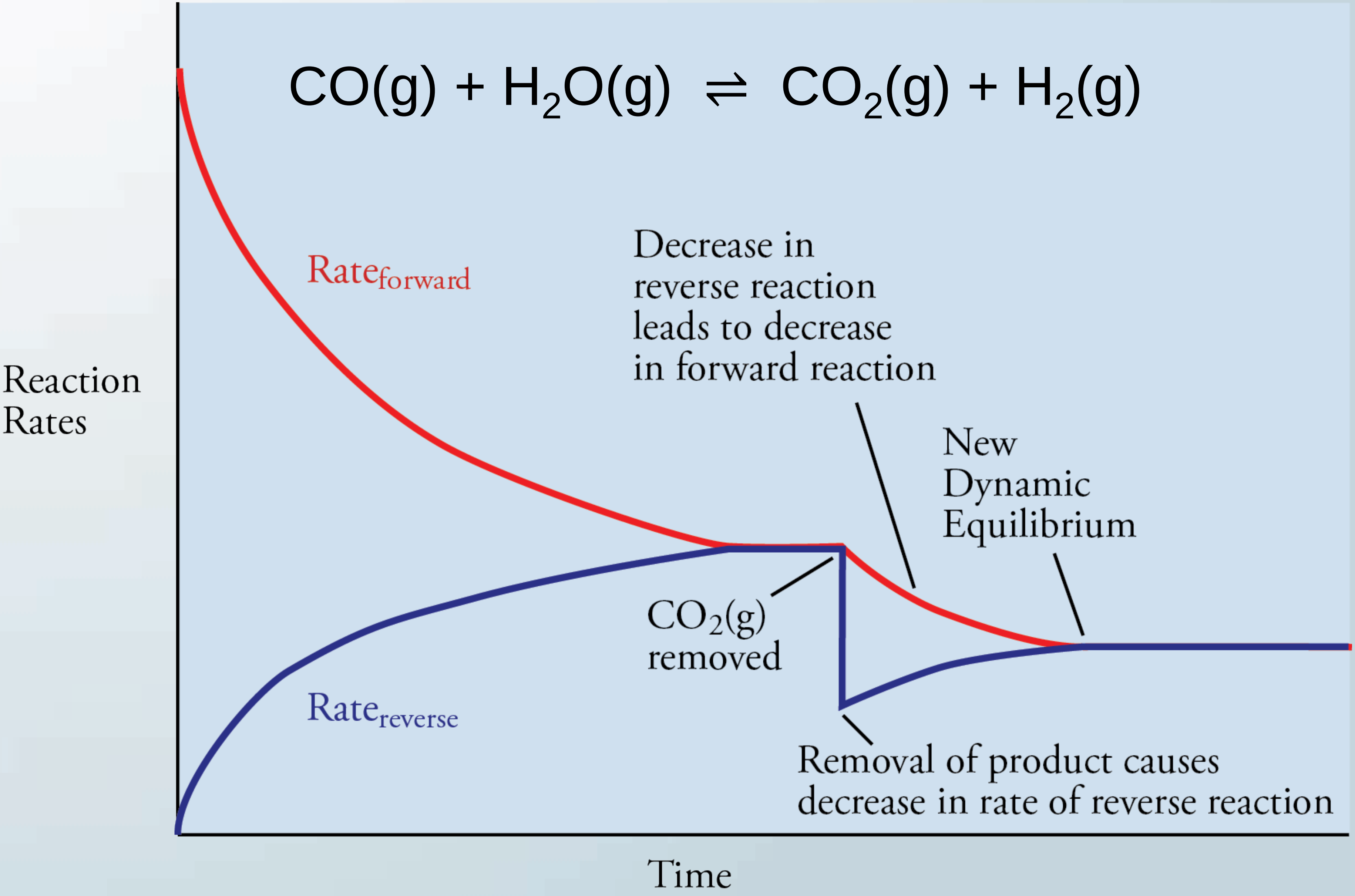
↓

$\text{Rate}_{\text{forward}} > \text{Rate}_{\text{reverse}}$

↓

System shifts toward products

Change in Rates When Product Removed



$$CO(g) + H_2O(g) \rightleftharpoons CO_2(g) + H_2(g)$$

Le Chatelier's Principle

- If a system at equilibrium is altered in a way that disrupts the equilibrium, the system will shift in such a way as to counter the change.

Chemical Equilibria in Aqueous Solutions

- Equilibrium concentrations important for many environmental problems
- There are also important non-equilibrium problems
  - ex. smog formation, stratospheric ozone depletion
  - chemical kinetics problems complicated
  - need to know reaction rates
  - involve many intermediate reactions and species.
- Equilibrium problems generally much easier to solve

Acid Dissociation Constant

- Weak acids have a reversible reaction with water to form hydronium ions (H_3O^+), which are often described as H^+.

$$HA(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + A^-(aq)$$

$$HA(aq) \rightleftharpoons H^+(aq) + A^-(aq)$$

- The equilibrium constant for this reactions is called the acid dissociation constant, K_a.

$$K_a = \frac{[H_3O^+][A^-]}{[HA]} \quad \text{or} \quad \frac{[H^+][A^-]}{[HA]}$$

- The can be described with pK_a.

$$pK_a = -\log K_a$$

$$K_a = 10^{-pKa}$$

Dissociation of Water

- Pure water undergoes a reversible reaction in which both H_3O^+ (H^+) and OH^- are generated.

$$2H_2O(l) \rightleftharpoons H_3O^+(aq) + OH^-(aq)$$

$$H_2O(l) \rightleftharpoons H^+(aq) + OH^-(aq)$$

- The equilibrium constant for this reaction is called the water dissociation constant.

$$K_w = [H^+][OH^-] = 1.01 \times 10^{-14} \quad \text{at } 25\ °\text{C}$$

- Because every H^+ (H_3O^+) ion that forms is accompanied by the formation of an OH^- ion, the concentrations of these ions in pure water are the same and can be calculated from K_w.

$$K_w = [H^+][OH^-] = (x)(x) = 1.01 \times 10^{-14}$$

$$x = [H^+] = [OH^-] = 1.01 \times 10^{-7}\ \text{M}$$

$(1.005 \times 10^{-7}$ M before rounding)

Acidic and Basic Solutions

$$K_w = [H^+][OH^-] = 1.01 \times 10^{-14} \text{ at } 25\ °C$$

- The equilibrium constant expression shows that the concentrations of H^+ and OH^- in water are linked. As one increases, the other must decrease to keep the product of the concentrations equal to 1.01×10^{-14}.
- If an acid, such as hydrochloric acid, is added to water, the concentration of the H^+ goes up, and the concentration of the OH^- goes down, but the product of those concentrations remains the same. An acidic solution can be defined as a solution in which the $[H^+] > [OH^-]$.
- If a base, such as sodium hydroxide, is added to water, the concentration of the OH^- goes up, and the concentration of the H^+ goes down. A basic solution can be defined as a solution in which the $[H^+] > [OH^-]$.

pH Calculations

- Acidity is measured with pH (from French "pouvoir hydrogene" or "power of hydrogen")

  $\mathrm{pH} = -\log[\mathrm{H}^+]$

  $[\mathrm{H}^+]$ = hydronium ion molarity = $10^{-\mathrm{pH}}$

  $K_w = [\mathrm{H}^+][\mathrm{OH}^-] \approx 10^{-14}$

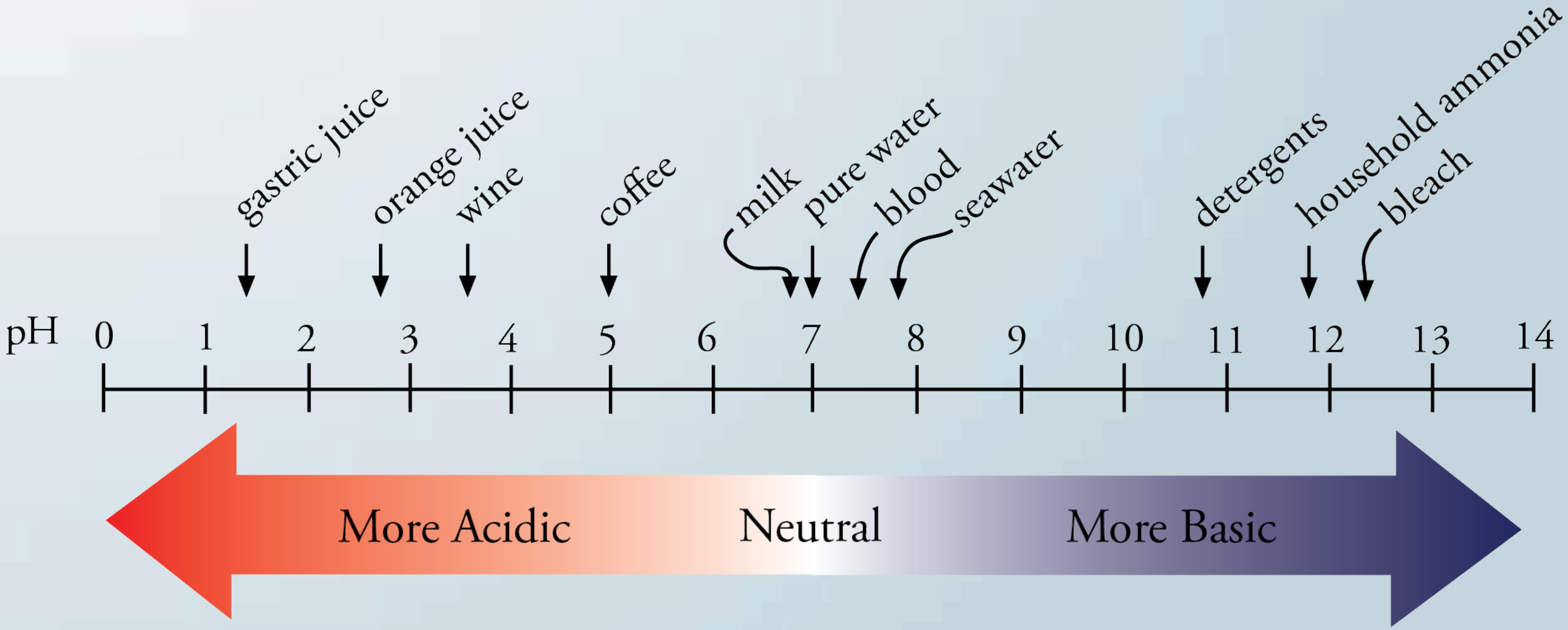
- Example: what is $[\mathrm{H}^+]$ and $[\mathrm{OH}^-]$ for a solution with a pH = 9?

  $[\mathrm{H}^+] = 10^{-\mathrm{pH}} = 10^{-9}\ \mathrm{M}$

  $[\mathrm{OH}^-] = K_w/[\mathrm{H}^+] = 10^{-14}/10^{-9} = 10^{-5}\ \mathrm{M\ OH}^-$

pH

- Acidic solutions have pH values less than 7, and the more acidic the solution is, the lower its pH.
- Basic solutions have pH values greater than 7, and the more basic the solution is, the higher its pH.



Acidic solutions have pH values less than 7.

Basic solutions have pH values greater than 7.

Strong Acid Calculation

Determine [H^+], [OH^-], and pH of a 0.025 M HNO_3 solution at 25 °C.

Solution:

$K_w = [H^+][OH^-] = 1.01 \times 10^{-14}$ at 25 °C

- We assume that nitric acid, $HNO_3(aq)$, like all strong acids, is completely ionized in water. Thus the concentration of H^+ is equal to the HNO_3 concentration.

[H^+] = **0.025 M H^+**

pH = -log pH = -log (0.025) = **1.60**

- When can use the K_w equation to calculate [OH^-].

$[OH^-] = K_w/[H^+] = 1.01 \times 10^{-14} / 0.025$

$= \mathbf{4.0 \times 10^{-13}}$ **M OH^-**

Note that the [OH^-] is not zero, even in a dilute acid solution.