Collision Theory

- **The reactant particles must collide.**
  - The collision brings the reactants together, and the kinetic energy of the particles provides the energy necessary for the reaction to proceed.

Collision Theory

- **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.

Collision Theory

- **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.

Factors that Affect Rates of Chemical Reactions

- Temperature
  - Increased temperature means increased average velocity of particles and thus increased rate of collisions between particles.
  - Increased temperature means increased average kinetic energy of collisions and thus increased percentage of collisions with the minimum energy necessary to react.

Factors that Affect Rates of Chemical Reactions

- Temperature
  - Decreased temperature means decreased average velocity of particles and thus decreased rate of collisions between particles.
  - Decreased temperature means decreased average kinetic energy of collisions and thus decreased percentage of collisions with the minimum energy necessary to react.

Factors that Affect Rates of Chemical Reactions

- Concentrations of reactants
  - Increased concentration of a reactant increases the rate of collisions between reactant particles and thus increases the rate of the reaction.
  - Decreased concentration of a reactant decreases the rate of collisions between reactant particles and thus decreases the rate of the reaction.

Factors that Affect Rates of Chemical Reactions

- Catalysts
  - Catalysts provide a different pathway between reactants and products that has a lower activation energy, making it so a greater percentage of collisions between reactant particles have the minimum energy necessary to react.
  - This increases the rate of reaction.

Dynamic Equilibrium

$$CO(g) + H_2O(g) \underset{}{\overset{870\ °C}{\rightleftharpoons}} CO_2(g) + H_2(g)$$

- This reaction is significantly reversible.
- When CO(g) and H_2O(g) are combined, they begin to form CO_2(g) and H_2(g).
- The CO_2(g) and H_2(g) react to reform CO(g) and H_2O(g).
- Very quickly, the system comes to a point where although the forward and reverse reactions continue, the rates of these two reactions are equal, so there is no net change in the concentration of CO(g), H_2O(g), CO_2(g), and H_2(g).
- This is called a dynamic equilibrium.

Three Factors that Affect Equilibrium Reactions

- Changing concentrations of reactants and products
- Changing temperature
- The addition of a catalyst

Effect of Increased Concentration of Reactant on Equilibrium

Increased concentration of reactant for a system at equilibrium with $Rate_{forward} = Rate_{reverse}$

↓

Increased $Rate_{forward}$

↓

$Rate_{forward} > Rate_{reverse}$

↓

System shifts toward products

$$CO(g) + H_2O(g) \underset{}{\overset{870\ °C}{\rightleftharpoons}} CO_2(g) + H_2(g)$$

- Increasing the concentration of CO(g) and/or H_2O(g) will increase the forward reaction rate, making the rate of the forward reaction greater than the rate of the reverse reaction, shifting the reaction to the right to products.

Effect of Increased Concentration of Product on Equilibrium

Increased concentration of product for a system at equilibrium with $Rate_{forward} = Rate_{reverse}$

↓

Increased $Rate_{reverse}$

↓

$Rate_{reverse} > Rate_{forward}$

↓

System shifts toward reactants

$$CO(g) + H_2O(g) \underset{}{\overset{870\ °C}{\rightleftharpoons}} CO_2(g) + H_2(g)$$

- Increasing the concentration of CO_2(g) and/or H_2(g) will increase the reverse reaction rate, making the rate of the reverse reaction greater than the rate of the forward reaction, shifting the reaction to the left to reactants.

Effect of Decreased Concentration of Reactant on Equilibrium

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

↓

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

↓

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

↓

System shifts toward reactants

$$CO(g) + H_2O(g) \underset{}{\overset{870\ °C}{\rightleftharpoons}} CO_2(g) + H_2(g)$$

- Decreasing the concentration of CO(g) and/or H_2O(g) will decrease the forward reaction rate, making the rate of the forward reaction less than the rate of the reverse reaction, shifting the reaction to the left to reactants.

Effect of Decreased Concentration of Product on Equilibrium

Decreased concentration of product for a system at equilibrium with $Rate_{forward} = Rate_{reverse}$

↓

Decreased $Rate_{reverse}$

↓

$Rate_{reverse} < Rate_{forward}$

↓

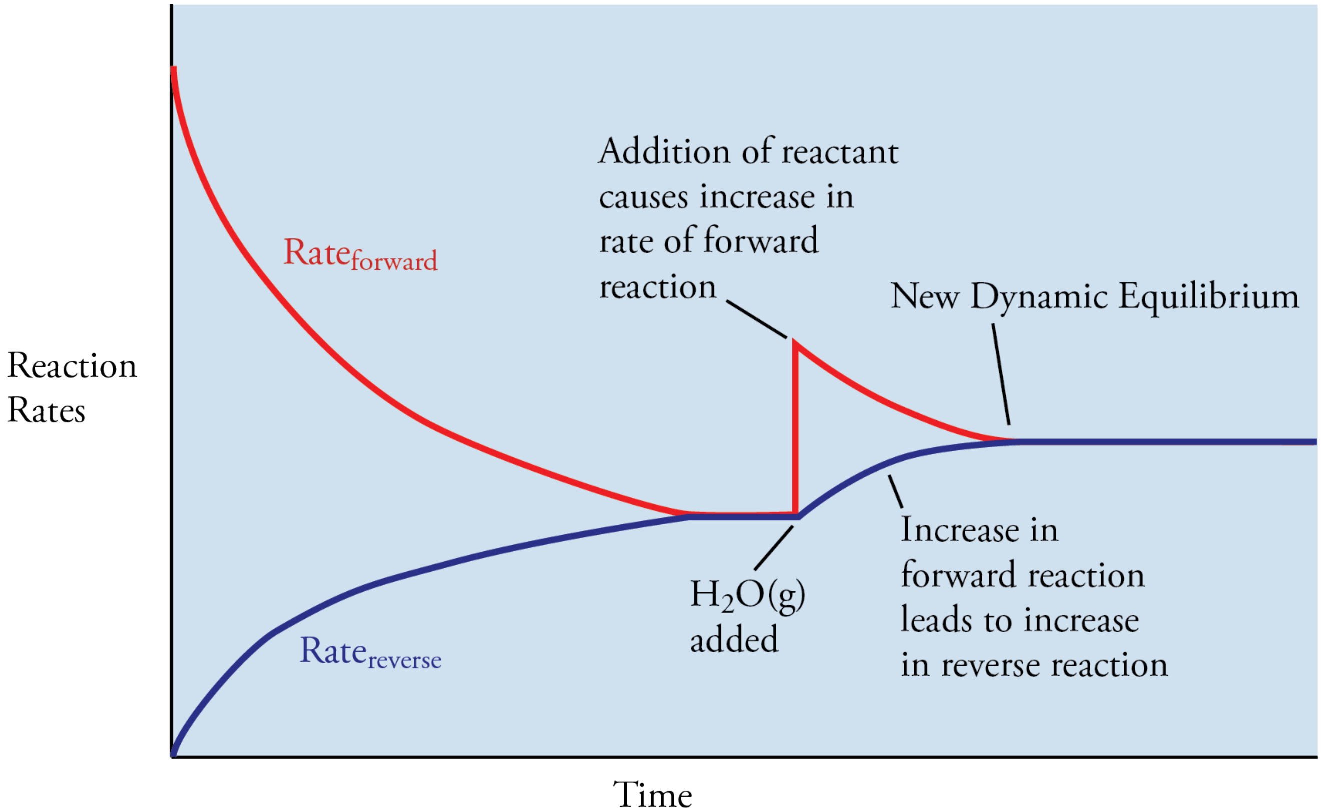
System shifts toward products

$$CO(g) + H_2O(g) \overset{870\ °C}{\rightleftharpoons} CO_2(g) + H_2(g)$$

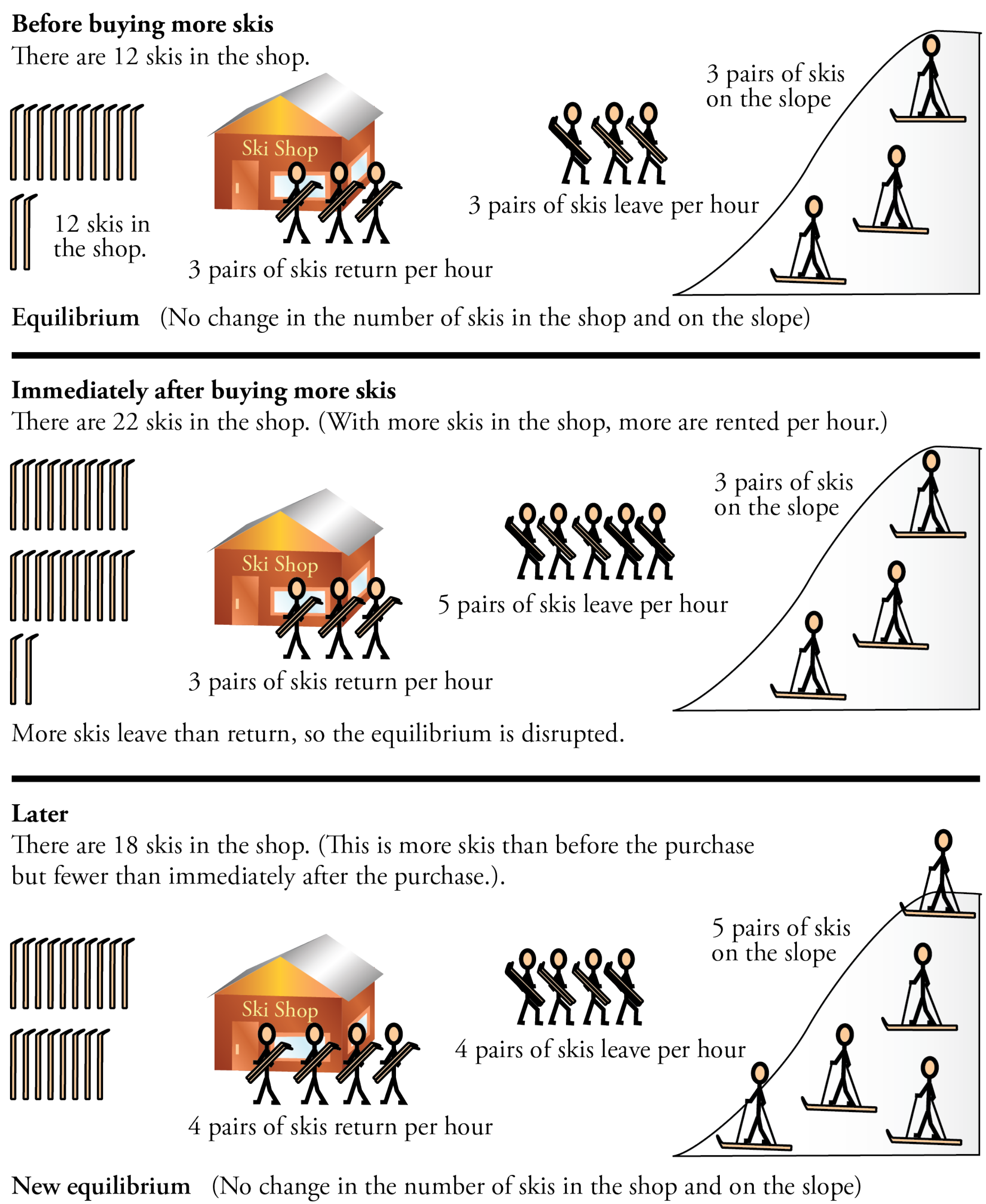
- Decreasing the concentration of CO_2(g) and/or H_2(g) will decrease the reverse reaction rate, making the rate of the reverse reaction less than the rate of the forward reaction, shifting the reaction to the right to products.

Change in Rates When Reactant Added

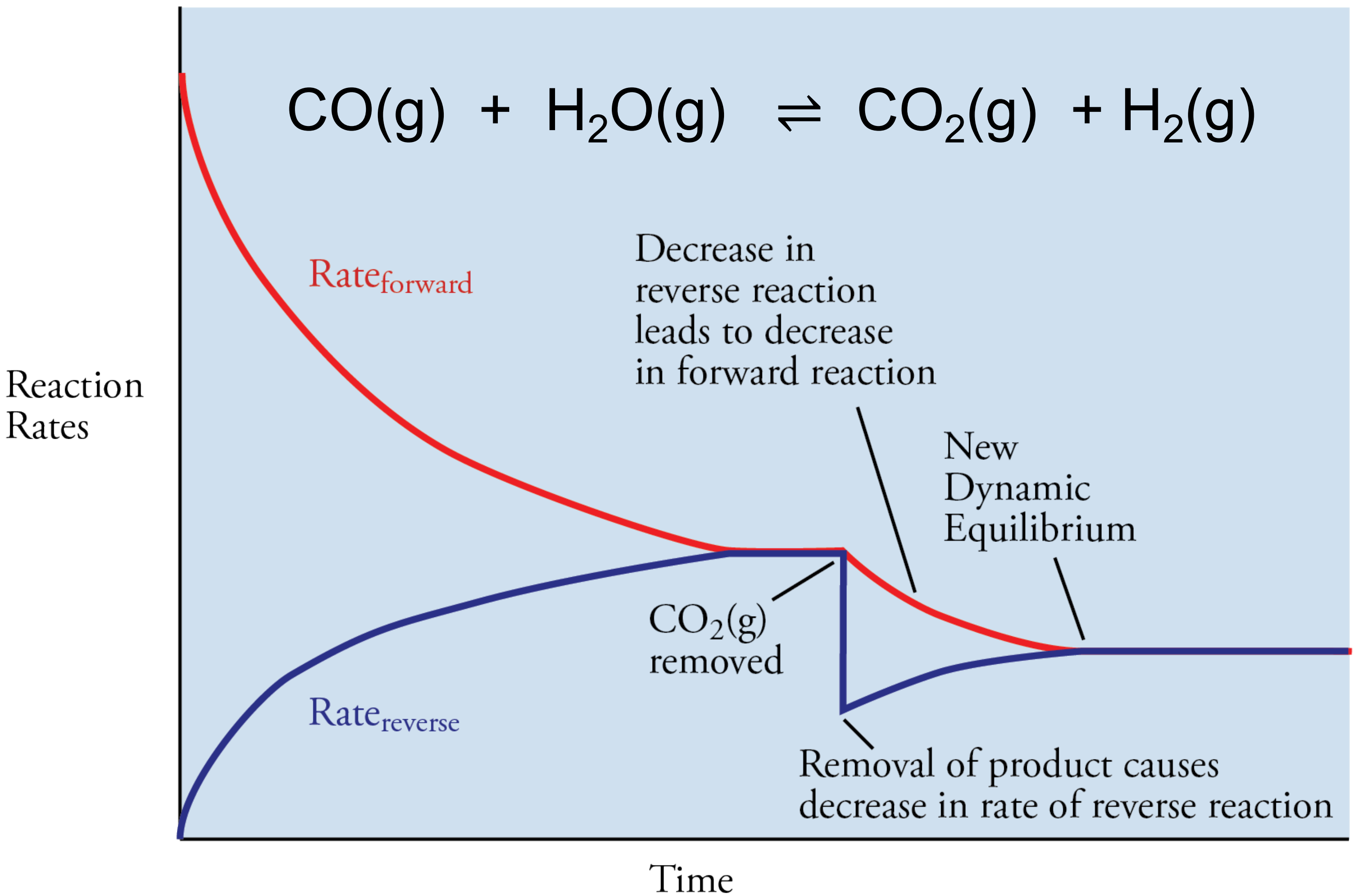
$$CO(g) + H_2O(g) \rightleftharpoons CO_2(g) + H_2(g)$$



Ski Shop Analogy 2



Change in Rates When Product Removed



Temperature and Dynamic Equilibrium

- Increased temperature increases the rates of both the forward and reverse reactions in an equilibrium system.
- Reversible chemical reactions are endothermic in one direction and exothermic in the other.
- Increased temperature increases the rate of the endothermic reaction more than the rate of the exothermic reaction, disrupting the equilibrium and making the endothermic reaction faster than the exothermic reaction.
- Therefore, increased temperature for a system at equilibrium, shifts the reaction in the endothermic direction.

Temperature and Dynamic Equilibrium

- For a system at equilibrium, decreased temperature decreases the rates of both the forward and reverse reactions.
- Decreased temperature decreases the rate of the endothermic reaction more than the rate of the exothermic reaction, so it disrupts the equilibrium and makes the endothermic reaction slower than the exothermic reaction.
- Therefore, decreased temperature for a system at equilibrium shifts the system in the exothermic direction.

Effect of Increased Temperature on Equilibrium

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

$K_w = [H^+][OH^-]$

Temperature	Kw
0 °C	1.14×10^{-15}
10 °C	2.92×10^{-15}
25 °C	1.01×10^{-14}
30 °C	1.47×10^{-14}
40 °C	2.92×10^{-14}
50 °C	5.47×10^{-14}
60 °C	9.61×10^{-14}

Catalysts and Dynamic Equilibrium

- Catalysts speed the forward and reverse reactions in an equilibrium system by the same amount, so they do not disrupt the equilibrium.
- Although catalysts do not shift equilibrium systems to reactants or products, they are often added to reversible reactions to get to equilibrium faster.

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.

Reaction	Cause of Disruption	To Counteract Change	Direction of Shift
All	Add reactant(s)	Decrease reactant(s)	To products
All	Add product(s)	Decrease product(s)	To reactants
All	Remove reactant(s)	Increase reactant(s)	To reactants
All	Remove product(s)	Increase products(s)	To products
Endothermic forward reaction	Increase temperature	Decrease temperature	To products
Endothermic forward reaction	Decrease temperature	Increase temperature	To reactants
Exothermic forward reaction	Increase temperature	Decrease temperature	To reactants
Exothermic forward reaction	Decrease temperature	Increase temperature	To products

Example

- Nitric acid can be made from the exothermic reaction of nitrogen dioxide gas and water vapor in the presence of a rhodium and platinum catalyst at 700-900 ºC and 5-8 atm.

$$3NO_2(g) + H_2O(g) \underset{\substack{750\text{-}920\ ^\circ C \\ 5\text{-}8\ \text{atm}}}{\overset{\text{Rh/Pt}}{\rightleftharpoons}} 2HNO_3(g) + NO(g) + 37.6\ \text{kJ}$$

Example

$$3NO_2(g) + H_2O(g) \underset{\substack{750\text{-}920\ ^\circ C \\ 5\text{-}8\ atm}}{\overset{Rh/Pt}{\rightleftharpoons}} 2HNO_3(g) + NO(g) + 37.6\ kJ$$

- Predict whether the changes in the equilibrium system that are described on the following slides will shift the system to more products, to more reactants, or neither. Explain each answer in two ways, (1) by applying Le Chatelier's principle and (2) by describing the effect of the change on the forward and reverse reaction rates.

Example Part (a)

$$3NO_2(g) + H_2O(g) \underset{\substack{750\text{-}920\ °C \\ 5\text{-}8\ atm}}{\overset{Rh/Pt}{\rightleftharpoons}} 2HNO_3(g) + NO(g) + 37.6\ kJ$$

- The concentration of H_2O gas is increased by the addition of more H_2O.
  - For Le Chatelier - $\uparrow H_2O$ so the system shifts to $\downarrow H_2O$ so shifts toward more products.
  - For rates - $\uparrow H_2O \rightarrow \uparrow R_f$ so $R_f > R_r$ and the system shifts to the right to more products.

$\uparrow$= increase $\downarrow$= decrease R_f = forward rate R_r = reverse rate

Example Part (b)

$$3NO_2(g) + H_2O(g) \underset{\substack{750\text{-}920\ °C \\ 5\text{-}8\ atm}}{\overset{Rh/Pt}{\rightleftharpoons}} 2HNO_3(g) + NO(g) + 37.6\ kJ$$

- The concentration of NO_2 is decreased.
  - For Le Chatelier - $\downarrow NO_2$ so system shifts to $\uparrow NO_2$ so shifts toward more reactants.
  - For rates - $\downarrow NO_2 \rightarrow \downarrow R_f$ so $R_f < R_r$ so the system shifts to the left to more reactants.

Example Part (c)

$$3NO_2(g) + H_2O(g) \underset{\substack{750\text{-}920\ °C \\ 5\text{-}8\ atm}}{\overset{Rh/Pt}{\rightleftharpoons}} 2HNO_3(g) + NO(g) + 37.6\ kJ$$

- The concentration of HNO_3 is decreased by removing the nitric acid as it forms.
  - For Le Chatelier - $\downarrow HNO_3$ so system shifts to $\uparrow HNO_3$ so shifts toward more products.
  - For rates - $\downarrow HNO_3 \rightarrow \downarrow R_r$ so $R_f > R_r$ so the system shifts to the right to more products.

Example Part (d)

$$3NO_2(g) + H_2O(g) \underset{\substack{750\text{-}920\ ^\circ C \\ 5\text{-}8\ atm}}{\overset{Rh/Pt}{\rightleftharpoons}} 2HNO_3(g) + NO(g) + 37.6\ kJ$$

- The temperature is decreased from 1000 ºC to 800 ºC.
  - For Le Chatelier - ↓T so system shifts to ↑T so shifts in the exothermic direction, which is toward more products.
  - For rates - ↓T → ↓R_f and ↓R_r , it ↓ the endothermic reaction more so $R_f > R_r$ so the system shifts to the right to more products.

Example Part (e)

$$3NO_2(g) + H_2O(g) \underset{\substack{750\text{-}920\ °C \\ 5\text{-}8\ atm}}{\overset{Rh/Pt}{\rightleftharpoons}} 2HNO_3(g) + NO(g) + 37.6\ kJ$$

- The Rh/Pt catalyst is added to the equilibrium system.
  - For Le Chatelier – just remember that catalysts do not shift reversible reactions in either direction.
  - For rates – add catalyst → ↑R_f and ↑R_r by the same amount, so the system does not shift to either reactants or products, but the system does get to equilibrium faster.