Chapter 12

Reaction Rates and Chemical Equilibrium

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Many Chemical Reactions Occur in Our Atmosphere

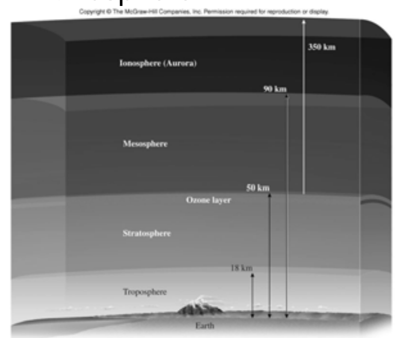

Figure 12.1

Introduction

- What factors effect how fast a reaction goes?
- How do we describe a reaction that does not go to completion?

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Chapter 12 Topics

1. Reaction rates
2. Collision theory
3. Conditions that effect reaction rates
4. Chemical equilibrium
5. The Equilibrium constant
6. Le Chatelier's principle

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12.1 Reaction Rates

- Reaction rate is a measure of how fast a reaction occurs.
- Some reactions are inherently fast and some are slow:

Figure 12.2

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Effect of Concentration

Grill
Mg/HCl

- Changing the concentration of a reactant can change the reaction rate:

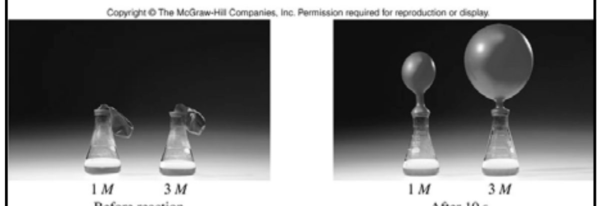

Figure 12.3

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Effect of Surface Area

Sugar
Lycopodium

Figure 12.4

A Iron Nail B Steel wool

Catalysis

MnO_2/H_2O_2

- The catalyst called catalase in this piece of liver causes the decomposition of H_2O_2 to occur faster.

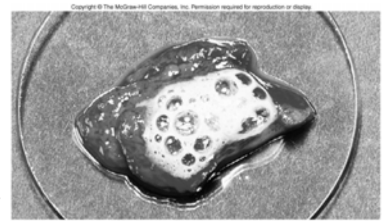


Figure 12.5

12.2 Collision Theory

- In order for a reaction to occur, reactant molecules must collide
  - with proper orientation
  - with enough energy
- Only a small fraction of the collisions that do occur meet these requirements.

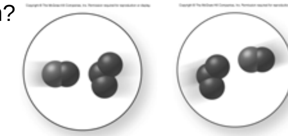
Collision Theory Orientation

collisions

- Consider the following reaction that occurs in smog:

$$NO(g) + O_3(g) \rightarrow O_2(g) + NO_2(g)$$

- Which of the following collisions has a proper orientation?



Collision Theory Energy Diagrams (Before and After)

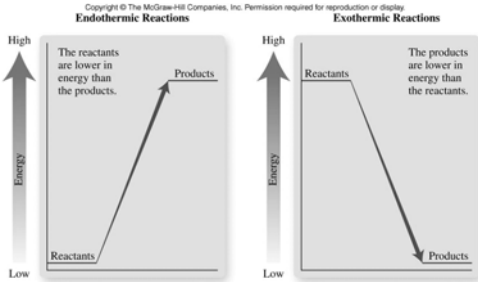


Figure 12.6

Collision Theory Energy Diagram (During)

Energy diagram

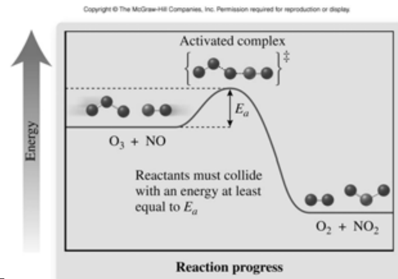


Figure 12.7

Collision Theory Energy Requirements

- In order for reactants to convert to products, an energy barrier called the activation energy, E_a, must be overcome.
- Collisions that have the proper orientation and have at least the minimum E_a can convert to products.
- The activation energy needed is related to the amount of energy needed to break bonds.

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12.3 Conditions that Effect Reaction Rates

- Increasing the concentration (or surface area) of reactants or the reaction temperature increases reaction rate by increasing the number of effective collisions.

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Conditions that Effect Reaction Rates

- Increasing the concentration or surface area of one or more reactants increases the number of effective collisions by increasing the total number of collisions (fraction remains the same).

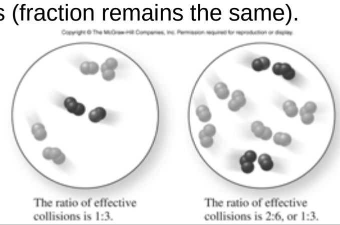

Figure 12.8

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Conditions that Effect Reaction Rates

- Increasing the temperature of the reaction increases the number of effective collisions by both increasing the total number of collisions and increasing the fraction of collisions that are effective.

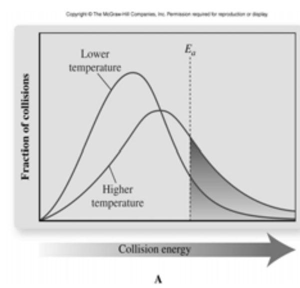

Figure 12.9

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Effect of temperature on fraction of effective collisions:

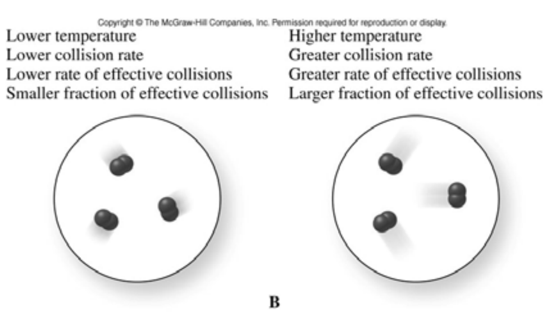

Figure 12.9

Conditions that Effect Reaction Rates

- Adding an appropriate catalyst increases the number of effective collisions by lowering the activation energy. This also increases the fraction of collisions that are effective.

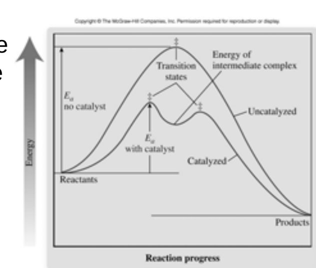

Figure 12.10

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Catalysis

- Catalytic converters dramatically speed of the reactions of toxic gases to form harmless products:
  - CO to CO_2
  - NO to N_2 and O_2

CO anim
NO anim

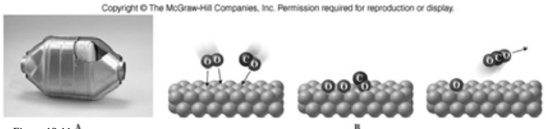

Figure 12.11 Catalyst is a palladium/platinum metal surface

Catalysis

- A catalyst is not a reactant or product. It interacts with the reactants, but is not permanently changed during the reaction.
- Since catalysts are "recycled," small amounts are needed and last a long time.

The thousands of enzymes in our bodies act to catalyze specific biological processes.

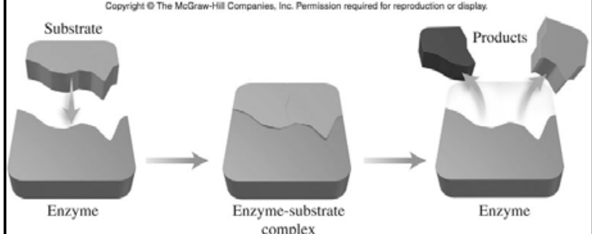

Figure 12.12

The enzyme sucrase catalyzes the decomposition of sucrose by making bond-breaking easier:

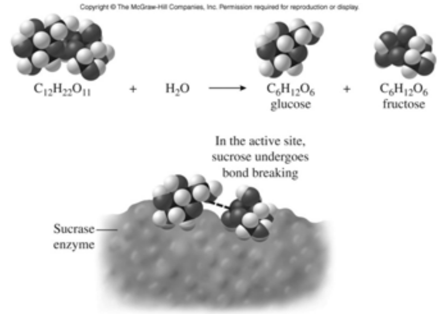

Figure 12.13

Destruction of Ozone in the Stratosphere

- Chlorine atoms from CF_2Cl_2 catalyze the decomposition of ozone in the stratosphere:

$$O_3(g) + Cl(g) \rightarrow ClO(g) + O_2(g)$$
$$ClO(g) + O_3(g) \rightarrow Cl(g) + 2O_2(g)$$

Destruction of Ozone in the Stratosphere

- Chlorine atoms from CF_2Cl_2 catalyze the decomposition of ozone in the stratosphere:

$$O_3(g) + Cl(g) \rightarrow ClO(g) + O_2(g)$$
$$ClO(g) + O_3(g) \rightarrow Cl(g) + 2O_2(g)$$

- The ClO(g) formed in step 1 is an intermediate that is formed temporarily.

Energy Diagram of Catalyzed Reaction

- This catalyzed reaction has a two transition states, and a lowered energy for the intermediate.

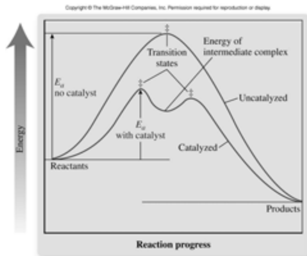

Figure 12.10

12.4 Chemical Equilibrium

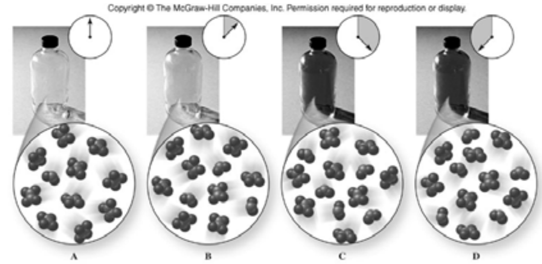

Figure 12.14

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

Chemical Equilibrium

- When a chemical reaction reaches a state where the concentrations of reactants and products remain constant, a chemical equilibrium has been established.

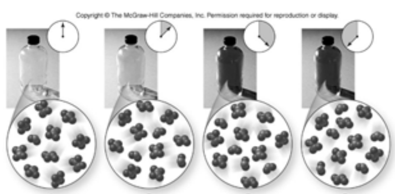

Figure 12.14

Chemical Equilibrium

- At equilibrium, the rate of the forward reaction is equal to the rate of the reverse reaction:

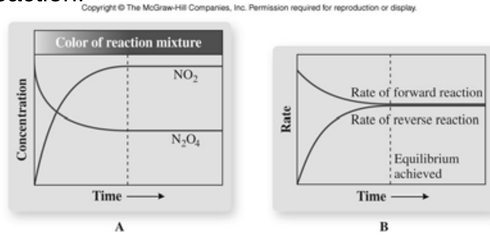

Figure 12.15

Chemical Equilibrium

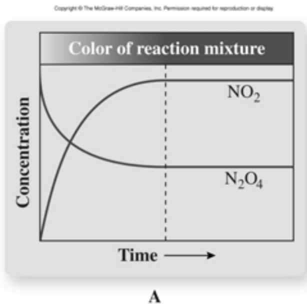

Figure 12.15

Dynamic equilibrium

Chemical Equilibrium

- At equilibrium, the **rate** of the forward reaction is equal to the rate of the reverse reaction.

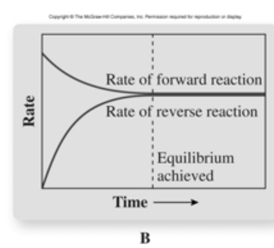

Figure 12.15

12.5 The Equilibrium Constant

- How can we describe a reaction that reaches equilibrium?
  - Some have similar amounts of reactants and products at equilibrium.
  - Some are reactant favored.
  - Some are product favored.

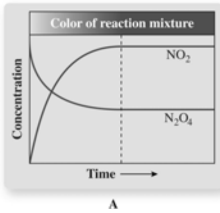

Figure 12.15

The Equilibrium Constant

- The position of equilibrium is a constant for a reaction at a specific temperature.
  - The relative amount of reactants and products is the same.
  - How do we determine what the “constant” is?

The Equilibrium Constant

- Consider the following reaction run at a specific temperature:

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

TABLE 12.1 Equilibrium Concentrations at Constant Temperature: $2HI(g) \rightleftharpoons H_2(g) + I_2(g)$

Experiment	Equilibrium [HI]	Equilibrium $[H_2]$	Equilibrium $[I_2]$	$\frac{[H_2][I_2]}{[HI]}$	$\frac{[H_2]+[I_2]}{[HI]}$	$\frac{[H_2][I_2]}{[HI]^2}$
1	0.704 *M*	0.180 *M*	0.550 *M*	0.141	1.04	0.200
2	1.44 *M*	0.757 *M*	0.550 *M*	0.186	0.903	0.201
3	0.634 *M*	0.283 *M*	0.283 *M*	0.126	0.893	0.199

The Equilibrium Constant

- Which expression gives the same value for all three experiments?
  - How can we generalize this expression?

TABLE 12.1 Equilibrium Concentrations at Constant Temperature: $2HI(g) \rightleftharpoons H_2(g) + I_2(g)$

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1	0.704 *M*	0.180 *M*	0.550 *M*	0.141	1.04	0.200
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The Equilibrium Constant (K_{eq})

- In general, for a reaction with the general form

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

the **equilibrium constant expression** is

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

- The brackets [C] mean “the concentration of” C.

$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$

- What is the equilibrium constant expression?
- What is the value of the equilibrium constant?

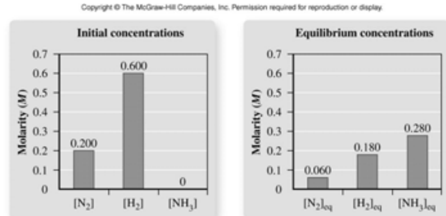

Figure 12.16

$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$

- Is this reaction reactant favored or product favored?

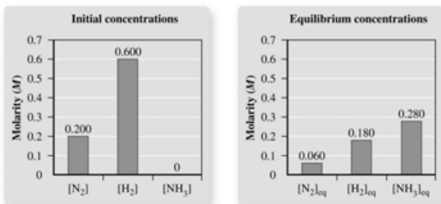

Figure 12.16

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K_{eq} and the Position of Equilibrium

TABLE 12.2 Meaning of the Value of K_{eq}

Value of the Equilibrium Constant K_{eq}	Position of Equilibrium
$K_{eq} >> 1$	Lies to the right. Products favored.
$K_{eq} << 1$	Lies to the left. Reactants favored.
$K_{eq} \approx 1$	Lies in the middle. Similar amounts of reactants and products.

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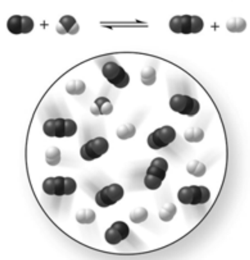
Predicting the Direction of Equilibrium

- Is this mixture of reactants and products at equilibrium?
- If not which direction will the reaction proceed?
  - In this example we can substitute number of molecules for concentration because the number of reactants and products in the balanced equation are the same – volume units of molarity would cancel out.

Figure 12.17

$$CO(g) + H_2O(g) \rightleftharpoons CO_2(g) + H_2(g) \quad K_{eq} = 16$$



EXAMPLE 12.7 Predicting the Direction of a Reaction

Consider this reaction and its equilibrium constant:

$$S_2Cl_2(g) + Cl_2(g) \rightleftharpoons 2SCl_2(g) \qquad K_{eq} = 4$$

The following molecular picture shows a mixture of reactants and products.

(a) Determine whether this system is at equilibrium. If it is not, predict the direction in which the reaction will proceed to reach equilibrium.
(b) What will happen to the concentration of Cl_2?

Heterogeneous Equilibrium

- Homogeneous equilibria –
  - reactants and products are in the same physical state
- Heterogeneous equilibria –
  - reactants and products are not all in the same physical state

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Heterogeneous Physical Equilibria

- Consider the evaporation of bromine in a closed container:
  $Br_2(l) \rightleftharpoons Br_2(g)$
- The concentration of bromine vapor, $[Br_2]$, at equilibrium is a constant, and is independent of the amount of bromine liquid.

Figure 12.18

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Heterogeneous Physical Equilibria

- Consider the evaporation of bromine in a closed container:
  $Br_2(l) \rightleftharpoons Br_2(g)$

$$K_{eq} = \frac{[Br_2(g)]}{\text{constant}}$$

$$K_{eq} = \frac{1}{\text{constant}} \times [Br_2(g)]$$

$$K'_{eq} = K_{eq} \times \text{constant} = [Br_2(g)]$$

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Heterogeneous Physical Equilibria

- Because the concentrations of liquids and solids are constant, they are left out of the equilibrium constant expression.
- Only gases and aqueous phase substances are included.

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Heterogeneous Equilibria

- What is the equilibrium constant expression for the decomposition of calcium carbonate?

Figure 12.19

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12.6 Le Chatelier's Principle

- If a reactant or product is added to the system at equilibrium, the system is no longer at equilibrium.
  - We say that the equilibrium is disrupted or stressed.
- Le Chatelier's principle helps us predict in which direction the reaction will proceed to reestablish equilibrium.

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Le Chatelier's Principle

- Ways to disrupt a chemical equilibrium:
  - Adding or removing a reactant or product
  - Changing the volume of the reaction container
  - Changing the temperature (changes K_{eq} value)

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Reactant or Product Concentration

- $Fe^{3+}(aq)$ + $NCS^{-}(aq) \rightleftharpoons FeNCS^{2+}(aq)$

Figure 12.20

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Reactant or Product Concentration

- $Fe^{3+}(aq)$ + $NCS^{-}(aq)$ $\rightleftharpoons$ $FeNCS^{2+}(aq)$
- What happens when we add more $Fe(NO_3)_3$ or KNCS?

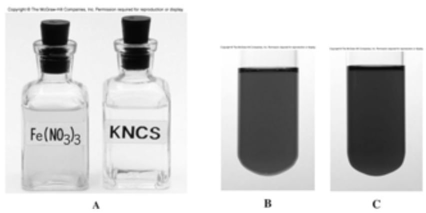

Figure 12.20

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Reactant or Product Concentration

- When the concentration of a reactant or product concentration is increased, the equilibrium will shift away from it to consume most of the added substance.
- When the concentration of a reactant or product concentration is decreased, the equilibrium will shift toward it to produce more of the removed substance.

TABLE 12.3 Equilibrium Shift Due to Concentration Changes

General Reaction	Add Reactant	Add Product	Remove Reactant	Remove Product
$A(g) + B(g) \rightleftharpoons C(g) + D(g)$	Shift right	Shift left	Shift left	Shift right

Volume of Reaction Container

- Which direction does the reaction proceed?

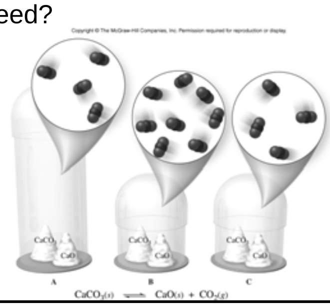

Figure 12.21

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Volume of Reaction Container

- Reducing the volume of the container makes the concentration of all gaseous substances to increase.
- The system shifts to reestablish equilibrium concentrations.

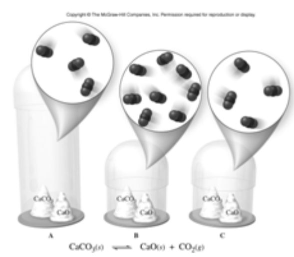

Figure 12. 21

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

Colorless Brown

- Which direction does the reaction proceed?

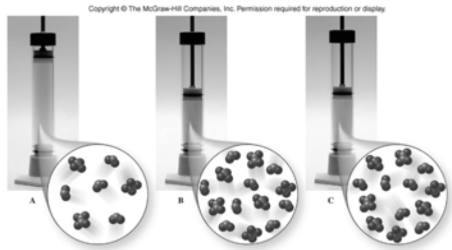

Figure 12.22

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

Colorless Brown

- The reaction proceeds in the direction that will make fewer gas particles.

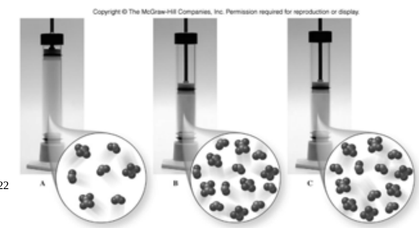

Figure 12.22

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Effect of Volume Changes

TABLE 12.4 Equilibrium Shifts Due to Volume Changes

Relative Number of Gaseous Molecules in Balanced Equation	Example	Increase Volume	Decrease Volume
reactants < products	$N_2O_4(g) \rightleftharpoons 2NO_2(g)$	Shift right	Shift left
reactants > products	$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$	Shift left	Shift right
reactants = products	$2NO(g) \rightleftharpoons N_2(g) + O_2(g)$	No shift	No shift

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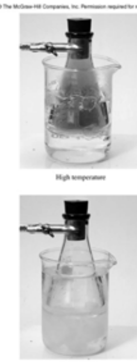
Temperature

- $N_2O_4(g) \rightleftharpoons 2NO_2(g)$
  Colorless Brown
- Which direction does the equilibrium when the temperature is
  - increased?
  - decreased?



High temperature

Low temperature

temperature

Figure 12.23

Temperature

- To predict the effect of temperature on the position of equilibrium, we must know whether a reaction is endothermic or exothermic.
- Endothermic:
  heat + $N_2O_4(g) \rightleftharpoons 2NO_2(g)$
- Exothermic:
  $2SO_2(g) + O_2(g) \rightleftharpoons 2SO_2(g)$ + heat

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Temperature

TABLE 12.5 Effect of Temperature Changes on the Position of Equilibrium

Type of Reaction	Equation	Increase Temperature	Decrease Temperature
Endothermic reaction	heat + A + B $\rightleftharpoons$ C + D	Shift right. K_{eq} increases.	Shift left. K_{eq} decreases.
Exothermic reaction	A + B $\rightleftharpoons$ C + D + heat	Shift left. K_{eq} decreases.	Shift right. K_{eq} increases.

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Catalysts

- A catalyst does not effect the position of equilibrium.
  – (It speeds up both the forward and the reverse reaction.)
- A catalyst only increases the rate at which equilibrium is reached.

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Increasing Product Yield

$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$ (exothermic)

Under which conditions of temperature and volume can the yield of NH_3 be maximized?

a) High or low temperatures?
b) Large or small volumes?

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Applying Le Chatelier's Principle

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

  Predict the direction the equilibrium will shift after each stress is applied:

a) Add CO (constant V)
b) Remove H_2O (constant V)
c) Increase volume
d) Increase temperature
e) Add a catalyst

$FeNCS^{2+}$

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Applying Le Chatelier's Principle

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

  The equilibrium constant is 1.0×10^{-6} at 1500 K and 6.2×10^{-4} at 2000 K.

- Is this reaction endothermic or exothermic?

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