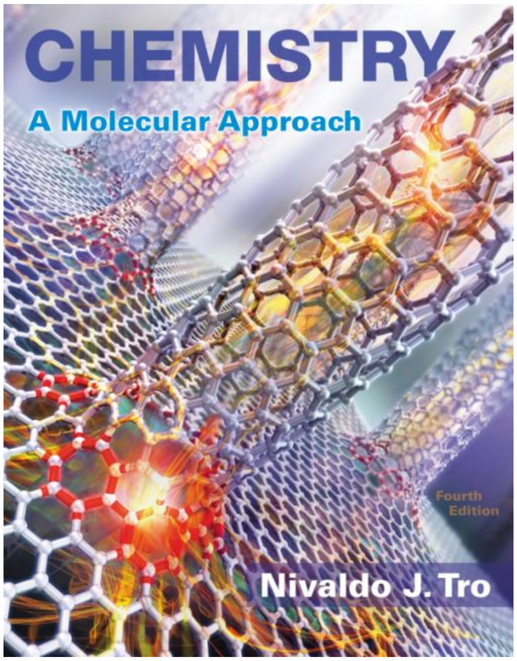


Lecture Presentation

Chapter 15

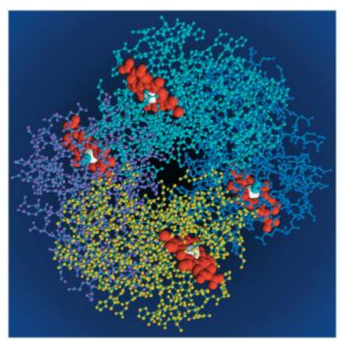
Chemical Equilibrium

Hemoglobin

- Hemoglobin is a protein (Hb) found in red blood cells that reacts with O_2.
  - It enhances the amount of O_2 that can be carried through the bloodstream.

$$Hb + O_2 \rightleftharpoons HbO_2$$

  - The $\rightleftharpoons$ is used to describe a process that is in **dynamic equilibrium**.

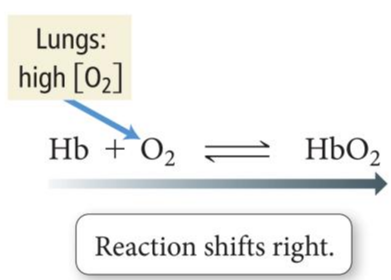


Hemoglobin Equilibrium System
$Hb + O_2 \rightleftharpoons HbO_2$

- The concentrations of Hb, O_2, and HbO_2 are all interdependent.
- The relative amounts of Hb, O_2, and HbO_2 at equilibrium are related to a constant called the **equilibrium constant, *K*.**
  - A large value of *K* indicates a high concentration of products at equilibrium.
- Changing the concentration of any one of these necessitates changes to the other concentrations to restore equilibrium.

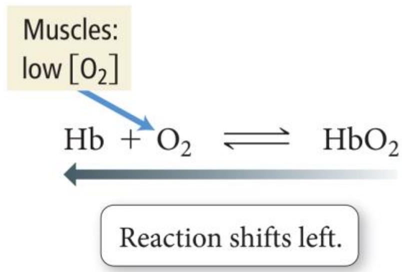
O_2 Transport

- In the lungs:
  - High concentration of O_2
  - The equilibrium shifts to the right.
  - Hb and O_2 combine to make more HbO_2.



O_2 Transport

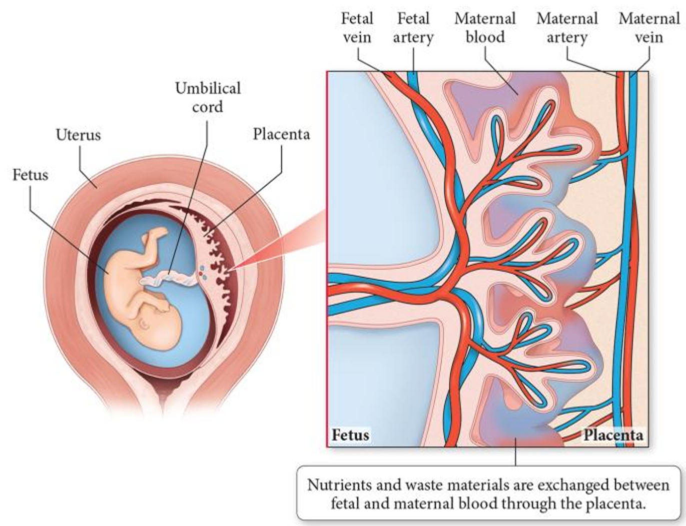
- In the muscles:
  - Low concentration of O_2
  - The equilibrium shifts to the right.
  - HbO_2 breaks down (dissociates), increasing the amount of free O_2.



Fetal Hemoglobin

- Fetal hemoglobin's equilibrium constant is larger than adult hemoglobin's constant.
- Fetal hemoglobin is more efficient at binding O_2.
- O_2 is transferred to the fetal hemoglobin from the mother's hemoglobin in the placenta.

Oxygen Exchange between Mother and Fetus



Reaction Dynamics

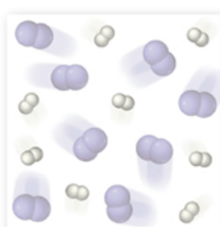
- When a reaction starts, the reactants are consumed and products are made.
  - The reactant concentrations decrease, and the product concentrations increase.
  - As reactant concentration decreases, the forward reaction rate decreases.
- Eventually, the products can react to re-form some of the reactants, assuming the products are not allowed to escape.
  - As product concentration increases, the reverse reaction rate increases.
- Processes that proceed in both the forward and reverse directions are said to be **reversible**.

$$\text{reactants} \rightleftharpoons \text{products}$$

Dynamic Equilibrium

- As the forward reaction slows and the reverse reaction accelerates, eventually they reach the same rate.
- **Dynamic equilibrium** is the condition wherein the rates of the forward and reverse reactions are equal.
- Once the reaction reaches equilibrium, the concentrations of all the chemicals remain constant because the chemicals are being consumed and made at the same rate.

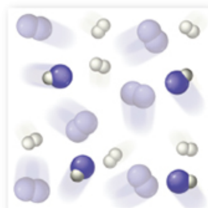
$H_2(g) + I_2(g) \rightleftharpoons 2\ HI(g)$



At time 0, there are only reactants in the mixture, so only the forward reaction can take place.

$[H_2] = 8, [I_2] = 8, [HI] = 0$

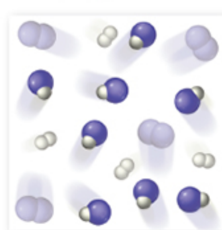
$H_2(g) + I_2(g) \rightleftharpoons 2\ HI(g)$



At time 16, there are both reactants and products in the mixture, so both the forward reaction and reverse reaction can take place.

$[H_2] = 6$, $[I_2] = 6$, $[HI] = 4$

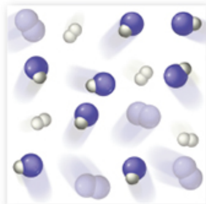
$H_2(g) + I_2(g) \rightleftharpoons 2\ HI(g)$



At time 32, there are now more products than reactants in the mixture, the forward reaction has slowed down as the reactants run out, and the reverse reaction accelerated.

$[H_2] = 4$, $[I_2] = 4$, $[HI] = 8$

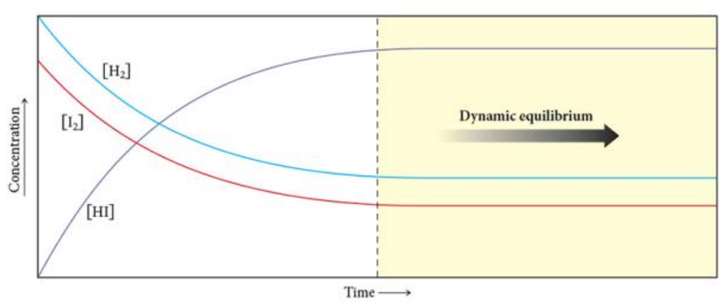
$H_2(g) + I_2(g) \rightleftharpoons 2\ HI(g)$



At time 48, the amounts of products and reactants in the mixture haven't changed; the forward and reverse reactions are proceeding at the same rate. It has reached equilibrium.

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

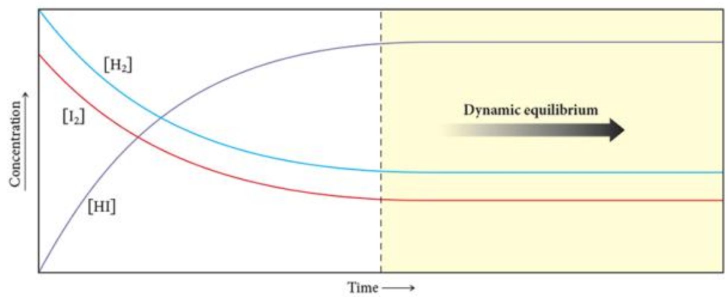
As the concentration of product increases and the concentrations of reactants decrease, the rate of the forward reaction slows down, and the rate of the reverse reaction speeds up.



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

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

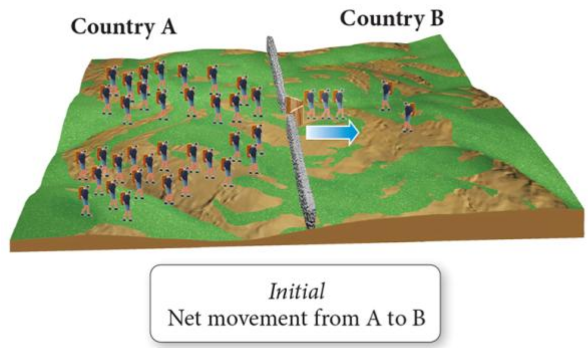
The concentrations of reactants and products no longer change.



Equilibrium ≠ Equal

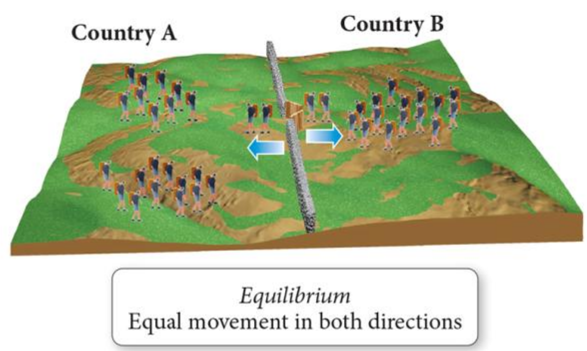
- The rates of the forward and reverse reactions are equal at equilibrium.
- But that does not mean the concentrations of reactants and products are equal.
- Some reactions reach equilibrium only after almost all the reactant molecules are consumed; we say the position of equilibrium favors the products.
- Other reactions reach equilibrium when only a small percentage of the reactant molecules are consumed; we say the position of equilibrium favors the reactants.

An Analogy: Population Changes



When Country A citizens feel overcrowded, some will emigrate to Country B .

An Analogy: Population Changes



However, after a time, emigration will occur in both directions at the same rate, leading to populations in Country A and Country B that are constant but not necessarily equal.

Equilibrium Constant

- Even though the concentrations of reactants and products are not equal at equilibrium, there is a relationship between them.

- The relationship between the chemical equation and the concentrations of reactants and products is called the **law of mass action**.

Equilibrium Constant

- For the general equation $aA + bB \rightleftharpoons cC + dD$, the law of mass action gives the relationship below.
  - The lowercase letters represent the coefficients of the balanced chemical equation.
  - Always products over reactants

- ***K*** is called the **equilibrium constant**.
  - Unitless

$$K = \frac{\overbrace{[C]^c[D]^d}^{\text{Products}}}{\underbrace{[A]^a[B]^b}_{\text{Reactants}}} \qquad \boxed{\text{The Law of Mass Action}}$$

Writing Equilibrium Constant Expressions

- So, for the reaction

  $2\ N_2O_5(g) \rightleftharpoons 4\ NO_2(g) + O_2(g)$

  the equilibrium constant expression is as follows:

$$K = \frac{[NO_2]^4[O_2]}{[N_2O_5]^2}$$

What Does the Value of K_{eq} Imply?

- When the value of $K_{eq} >> 1$, the reaction reaches equilibrium where there will be many more product molecules present than reactant molecules.

- The position of equilibrium favors products.

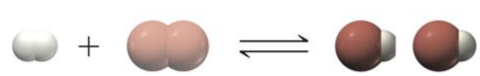
What Does the Value of K_{eq} Imply?

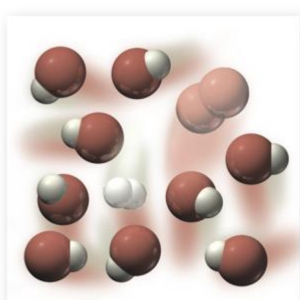
- When the value of K_{eq} << 1, the reaction reaches equilibrium where there will be many more reactant molecules present than product molecules.

- The position of equilibrium favors reactants.

A Large Equilibrium Constant

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

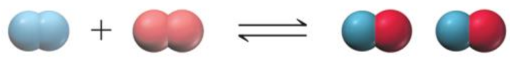


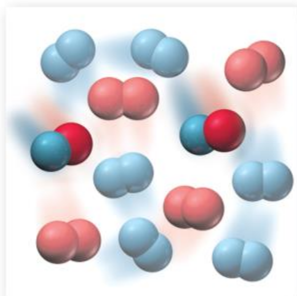


$$K = \frac{[HBr]^2}{[H_2][Br_2]} = \text{large number}$$

A Small Equilibrium Constant

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





$$K = \frac{[NO]^2}{[N_2][O_2]} = \text{small number}$$

Relationships between *K* and Chemical Equations

- When the reaction is written backward, the equilibrium constant is inverted.

For the reaction $aA + bB \rightleftharpoons cC + dD$, the equilibrium constant expression is as follows:

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

For the reaction $cC + dD \rightleftharpoons aA + bB$, the equilibrium constant expression is as follows:

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

$$\therefore\ K_{backward} = \frac{1}{K_{forward}}$$

Relationships between *K* and Chemical Equations

- When the coefficients of an equation are multiplied by a factor, the equilibrium constant is raised to that factor.

For the reaction $aA + bB \rightleftharpoons cC$, the equilibrium constant expression is as follows:

$$K_{original} = \frac{[C]^c}{[A]^a \times [B]^b}$$

For the reaction $2aA + 2bB \rightleftharpoons 2cC$, the equilibrium constant expression is as follows:

$$K_{new} = \frac{[C]^{2c}}{[A]^{2a} \times [B]^{2b}}$$

$$= \left(\frac{[C]^c}{[A]^a \times [B]^b}\right)^2$$

$$\therefore\ K_{new} = K^n_{original}$$

Relationships between *K* and Chemical Equations

- When you add equations to get a new equation, the equilibrium constant of the new equation is the product of the equilibrium constants of the old equations.

For the reactions (1) $aA \rightleftharpoons bB$ and (2) $bB \rightleftharpoons cC$, the equilibrium constant expressions are as follows:

$$K_1 = \frac{[B]^b}{[A]^a} \quad K_2 = \frac{[C]^c}{[B]^b}$$

For the reaction $aA \rightleftharpoons cC$, the equilibrium constant expression is as follows:

$$K_{new} = \frac{[C]^c}{[A]^a}$$

$$= \frac{\cancel{[B]^b}}{[A]^a} \times \frac{[C]^c}{\cancel{[B]^b}}$$

$$\therefore\ K_{new} = K_1 \times K_2$$

Equilibrium Constants for Reactions Involving Gases

- The concentration of a gas in a mixture is proportional to its partial pressure.
- Therefore, the equilibrium constant can be expressed as the ratio of the partial pressures of the gases.
- For $a\text{A}(g) + b\text{B}(g) \rightleftharpoons c\text{C}(g) + d\text{D}(g)$, the equilibrium constant expressions are as follows:

$$K_c = \frac{[\text{C}]^c \times [\text{D}]^d}{[\text{A}]^a \times [\text{B}]^b} \quad \text{or} \quad K_p = \frac{P_\text{C}{}^c \times P_\text{D}{}^d}{P_\text{A}{}^a \times P_\text{B}{}^b}$$

K_c and K_p

- In calculating K_p, the partial pressures are always in atm.
- The values of K_p and K_c are not necessarily the same because of the difference in units.

$$K_p = K_c(RT)^{\Delta n}$$

  - Δn is the difference between the number of moles of reactants and moles of products.
  - $K_p = K_c$ when $\Delta n = 0$

Deriving the Relationship between K_p and K_c

$$[A] = \frac{n_A}{V},\ n_A = \text{moles of A},\ V = \text{volume of gas}$$

$$P_A V = n_A RT, \text{ from the Ideal Gas Law}$$

$$\textit{substituting} \quad P_A = \frac{n_A}{V} RT = [A]RT$$

$$\therefore \quad [A] = \frac{P_A}{RT}$$

Deriving the Relationship between K_p and K_c

$$[X] = \frac{P_X}{RT}$$

for $aA(g) + bB(g) \rightleftharpoons cC(g) + dD(g)$

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

$$K_p = \frac{P_C{}^c \times P_D{}^d}{P_A{}^a \times P_B{}^b}$$

substituting

$$K_c = \frac{\left(\frac{P_C}{RT}\right)^c \times \left(\frac{P_D}{RT}\right)^d}{\left(\frac{P_A}{RT}\right)^a \times \left(\frac{P_B}{RT}\right)^b} = \frac{P_C{}^c P_D{}^d \left(\frac{1}{RT}\right)^{c+d}}{P_A{}^a P_B{}^b \left(\frac{1}{RT}\right)^{a+b}} = K_p \left(\frac{1}{RT}\right)^{(c+d)-(a+b)}$$

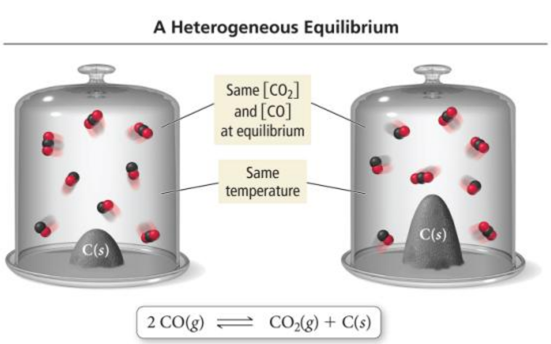
$$\text{rearranging} \quad K_p = K_c (RT)^{(c+d)-(a+b)} = K_c (RT)^{\Delta n}$$

Heterogeneous Equilibria

- The concentrations of pure solids and pure liquids do not change during the course of a reaction.
- Because their concentration doesn't change, solids and liquids are not included in the equilibrium constant expression.
- For the reaction $CO_2(g) + H_2O(\ell) \rightleftharpoons H^+(aq) + HCO_3^-(aq)$ the equilibrium constant expression is as follows:

$$K_c = \frac{[H^+][HCO_3^-]}{[CO_2]}$$

Heterogeneous Equilibria



The amount of C is different, but the amounts of CO and CO_2 remain the same. Therefore, the amount of C has no effect on the position of equilibrium.

Calculating Equilibrium Constants from Measured Equilibrium Concentrations

- The most direct way of finding the equilibrium constant is to measure the amounts of reactants and products in a mixture at equilibrium.
- The equilibrium mixture may have different amounts of reactants and products, but the value of the equilibrium constant will always be the same, as long as the temperature is kept constant.
  - The value of the equilibrium constant is independent of the initial amounts of reactants and products.

Initial and Equilibrium Concentrations for $H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$ at 445 ° C

TABLE 15.1 Initial and Equilibrium Concentrations for the Reaction $H_2(g) + I_2(g) \rightleftharpoons 2\,HI(g)$ at 445 °C

Initial Concentrations			Equilibrium Concentrations			Equilibrium Constant
$[H_2]$	$[I_2]$	$[HI]$	$[H_2]$	$[I_2]$	$[HI]$	$K_c = \frac{[HI^2]}{[H_2][I_2]}$
0.50	0.50	0.0	0.11	0.11	0.78	$\frac{(0.78)^2}{(0.11)(0.11)} = 50$
0.0	0.0	0.50	0.055	0.055	0.39	$\frac{(0.39)^2}{(0.055)(0.055)} = 50$
0.50	0.50	0.50	0.165	0.165	1.17	$\frac{(1.17)^2}{(0.165)(0.165)} = 50$
1.0	0.50	0.0	0.53	0.033	0.934	$\frac{(0.934)^2}{(0.53)(0.033)} = 50$
0.50	1.0	0.0	0.033	0.53	0.934	$\frac{(0.934)^2}{(0.033)(0.53)} = 50$

Calculating Equilibrium Concentrations

- Stoichiometry can be used to determine the equilibrium concentrations of all reactants and products if you know initial concentrations and one equilibrium concentration.
- Set up an ICE table based on the information provided.
- Use the change in the concentration of the substance you know to determine the change in the other chemicals in the reaction.

The Reaction Quotient

- If a reaction mixture containing both reactants and products is not at equilibrium, how can we determine from which direction the reaction will reach equilibrium?
- The answer is to compare the current concentration ratios to the equilibrium constant.
- The non-equilibrium concentration ratio of the products (raised to the power of their coefficients) to the reactants (raised to the power of their coefficients) is called the **reaction quotient**, ***Q***.

The Reaction Quotient

For the gas phase reaction

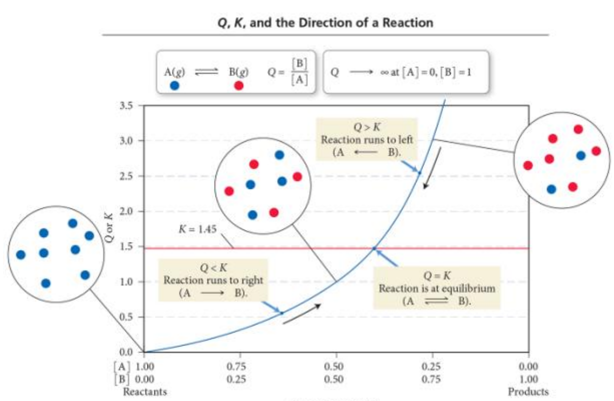
$$a\,\mathrm{A} + b\,\mathrm{B} \rightleftharpoons c\,\mathrm{C} + d\,\mathrm{D}$$

the reaction quotient is as follows:

$$Q_c = \frac{[\mathrm{C}]^c[\mathrm{D}]^d}{[\mathrm{A}]^a[\mathrm{B}]^b} \qquad Q_p = \frac{P_\mathrm{C}^c P_\mathrm{D}^d}{P_\mathrm{A}^a P_\mathrm{B}^b}$$

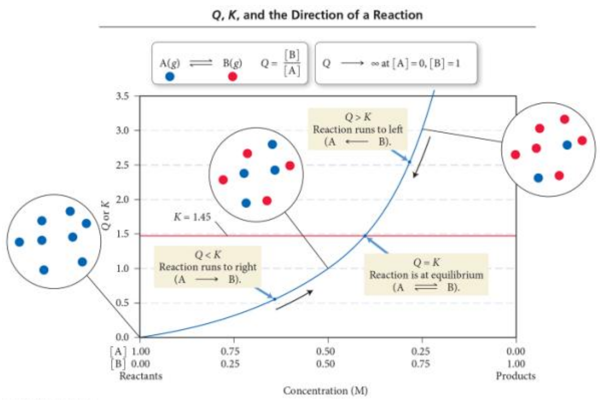
The Reaction Quotient: Predicting the Direction of Change

- If $Q > K$, the reaction will proceed fastest in the reverse direction.
  - The products will decrease, and reactants will increase.



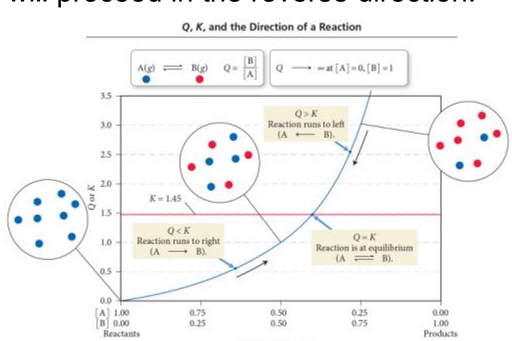
The Reaction Quotient: Predicting the Direction of Change

- If $Q < K$, the reaction will proceed fastest in the forward direction.
  - The products will increase, and reactants will decrease.



The Reaction Quotient: Predicting the Direction of Change

- If $Q = K$, the reaction is at equilibrium.
  - The products and reactants will not change.
- If a reaction mixture contains just reactants, then $Q = 0$, and the reaction will proceed in the forward direction.
- If a reaction mixture contains just products, then $Q = \infty$, and the reaction will proceed in the reverse direction.



Finding Equilibrium Concentrations When Given *K* and Initial Concentrations or Pressures

STEP 1: Prepare the ICE table.

STEP 2: Decide in which direction the reaction will proceed.

- Compare Q to K.

STEP 3: Define the changes of all substances in terms of x.

- Use the coefficient from the chemical equation as the coefficient of x.
- The x change is – for materials on the side the reaction is proceeding away from, + for substances on the side the reaction is proceeding toward.

STEP 4: Solve for x.

- For second-order equations, take square roots of both sides or use the quadratic formula.
- Simplify and approximate the answer for very large or small equilibrium constants, if possible.

Approximations to Simplify the Math

- When the equilibrium constant is very small, the position of equilibrium favors the reactants.
- For relatively large initial concentrations of reactants, the reactant concentration will not change significantly when it reaches equilibrium.
  - Assuming the reaction is proceeding forward

$$[x]_{\text{equilibrium}} = ([x]_{\text{initial}} - ax) \approx [x]_{\text{initial}}$$

- We are approximating the equilibrium concentration of reactant to be the same as the initial concentration.

Checking the Approximation and Refining as Necessary

- We can check our approximation by comparing the approximate value of *x* to the initial concentration.
- If the approximate value of *x* is less than 5% of the initial concentration, the approximation is valid.

$$\text{if } \frac{\text{approximate } x}{\text{initial concentration}} \times 100\% < 5\% \text{ the approximation is valid}$$

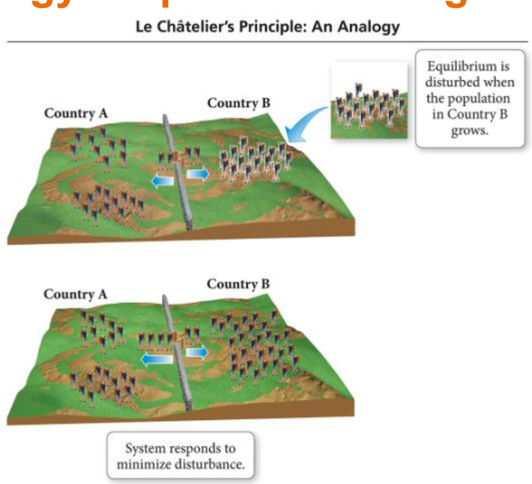
Disturbing and Restoring Equilibrium

- Once a reaction is at equilibrium, the concentrations of all the reactants and products remain constant.
- However, if the conditions are changed, the concentrations of all the chemicals will change until equilibrium is restored.
- The new concentrations will be different, but the equilibrium constant will be the same, unless there is a change in the temperature.

Le Châtelier’s Principle

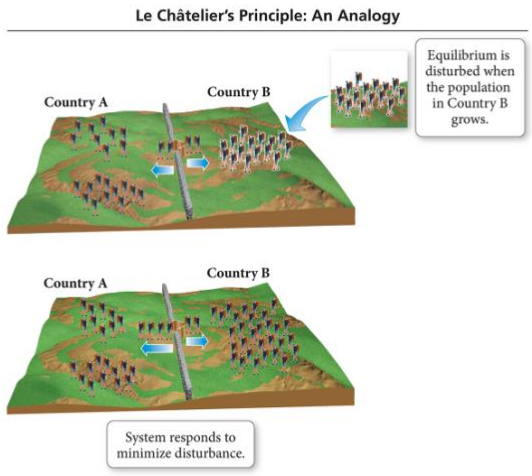
- Le Châtelier's principle guides us in predicting the effect various changes in conditions have on the position of equilibrium.
- It states that if a system at equilibrium is disturbed, the position of equilibrium will shift to minimize the disturbance.
- Disturbances include changing the concentration of a reactant or product, changing the volume or pressure, and changing the temperature.

An Analogy: Population Changes



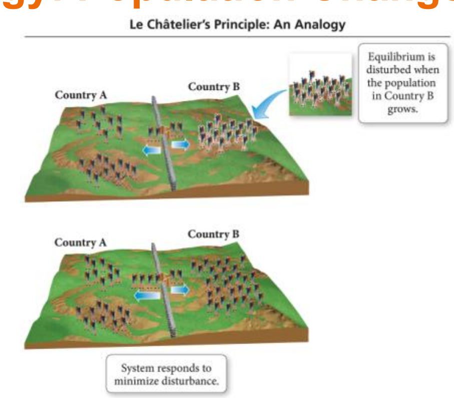
When the populations of Country A and Country B are in equilibrium, the emigration rates between the two countries are equal, so the populations stay constant.

An Analogy: Population Changes



When the birthrate in Country B increases, it disturbs the equilibrium established between Country A and Country B.

An Analogy: Population Changes



The result will be people moving from Country B into Country A faster than people moving from Country A into Country B.

This will continue until a new equilibrium between the populations is established; the new populations will have different numbers of people than the old ones.

Disturbing Equilibrium: Adding or Removing Reactants

- A reactant is added to a system at equilibrium, as long as the added reactant is included in the equilibrium constant expression:
  - That is, not a solid or liquid
    - How will this affect the rate of the forward reaction?
    - How will it affect the rate of the reverse reaction?
    - How will it affect the value of *K*?

Disturbing Equilibrium: Adding Reactants

- Adding a reactant initially increases the rate of the forward reaction but has no initial effect on the rate of the reverse reaction.
- The reaction proceeds to the right until equilibrium is restored.
- At the new equilibrium position, you will have more of the products than before, less of the non-added reactants than before, and less of the added reactant.
  - But you will not have as little of the added reactant as you had before the addition.
- At the new equilibrium position, the concentrations of reactants and products will be such that the value of the equilibrium constant is the same.

Disturbing Equilibrium: Adding or Removing Reactants

- A reactant is removed from a system at equilibrium, as long as the added reactant is included in the equilibrium constant expression.
  - That is, not a solid or liquid
- How will this affect the rate of the forward reaction?
- How will it affect the rate of the reverse reaction?
- How will it affect the value of *K*?

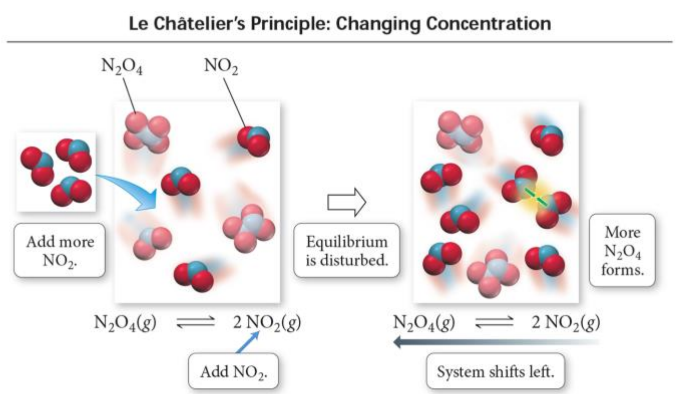
Disturbing Equilibrium: Removing Reactants

- Removing a reactant initially decreases the rate of the forward reaction but has no initial effect on the rate of the reverse reaction.
  - So, the reaction is going faster in reverse.
- The reaction proceeds to the *left* until equilibrium is restored.
- At the new equilibrium position, you will have less of the products than before, more of the non-removed reactants than before, and more of the removed reactant.
  - But, you will not have as much of the removed reactant as you had before the removal.
- At the new equilibrium position, the concentrations of reactants and products will be such that the value of the equilibrium constant is the same.

The Effect of Concentration Changes on Equilibrium

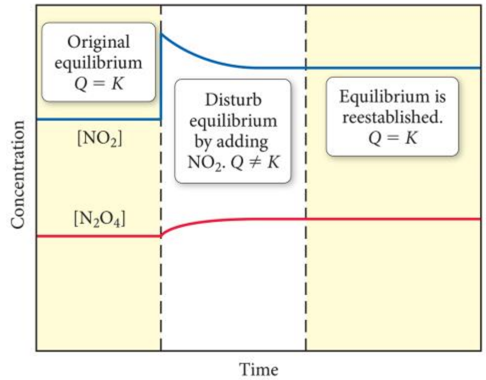
- Adding a reactant will decrease the amounts of the other reactants and increase the amount of the products until a new position of equilibrium is found that has the same *K*.
- Removing a product will increase the amounts of the other products and decrease the amounts of the reactants.
  - You can use this to drive a reaction to completion!
- **Equilibrium shifts away from the side with added chemicals or toward the side with removed chemicals.**
  - Remember, adding more of a solid or liquid does not change its concentration; therefore, it has no effect on the equilibrium.

The Effect of Concentration Changes on Equilibrium



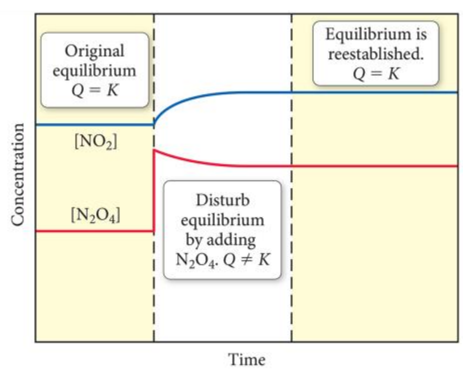
When NO_2 is added, some of it combines to make more N_2O_4.

The Effect of Concentration Changes on Equilibrium



When N_2O_4 is added, some of it decomposes to make more NO_2.

The Effect of Concentration Changes on Equilibrium



When N_2O_4 is added, some of it decomposes to make more NO_2.

Disturbing Equilibrium: Changing the Volume

- After equilibrium is established, the container volume is decreased.
- How will it affect the concentration of solids, liquids, solutions, and gases?
- How will this affect the total pressure of solids, liquids, and gases?
- How will it affect the value of *K*?

Effect of Volume Change on Equilibrium

- Decreasing the volume of the container increases the concentration of all the gases in the container.
  - It increases their partial pressures.
  - **It does not change the concentrations of solutions!**
- If their partial pressures increase, then the total pressure in the container will increase.
- According to Le Châtelier's principle, the equilibrium should shift to remove that pressure.
- The way the system reduces the pressure is to reduce the number of gas molecules in the container.
- **When the volume decreases, the equilibrium shifts to the side with fewer gas molecules.**

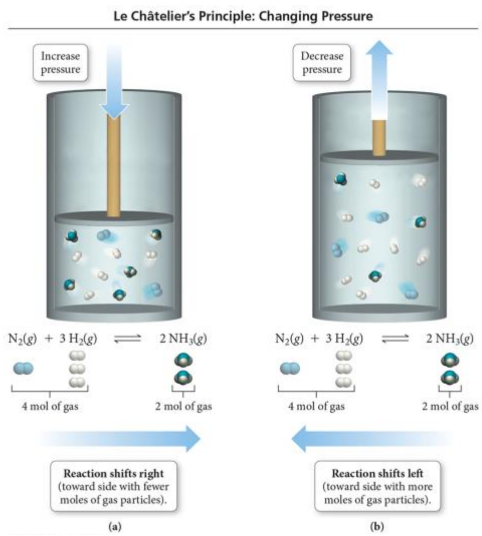
Disturbing Equilibrium: Reducing the Volume

- Decreasing the container volume will increase the total pressure.
  - Boyle's law
  - If the total pressure increases, the partial pressures of all the gases will increase—Dalton's law of partial pressures.
- Because the total pressure increases, the position of equilibrium will shift to decrease the pressure by removing gas molecules.
  - Shift toward the side with fewer gas molecules
- At the new equilibrium position, the partial pressures of gaseous reactants and products will be such that the value of the equilibrium constant is the same.

The Effect of Adding a Gas to a Gas-Phase Reaction at Equilibrium

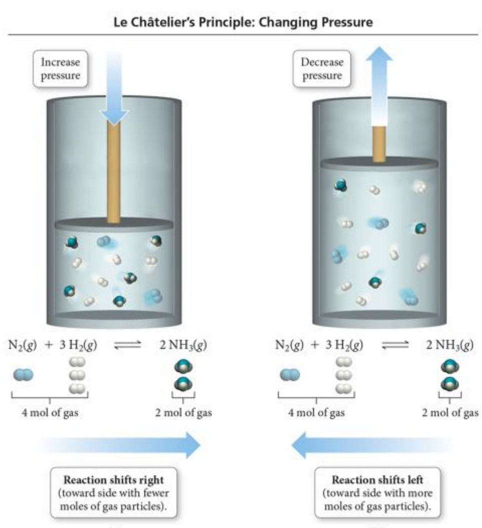
- Adding a gaseous reactant increases its partial pressure, causing the equilibrium to shift to the right.
  - Increasing its partial pressure increases its concentration.
  - It does not increase the partial pressure of the other gases in the mixture.
- Adding an inert gas to the mixture has no effect on the position of equilibrium.
  - It does not affect the partial pressures of the gases in the reaction.

The Effect of Volume Changes on Equilibrium



Because there are more gas molecules on the reactants' side of the reaction, when the pressure is increased, the position of equilibrium shifts toward the side with fewer molecules to decrease the pressure.

The Effect of Volume Changes on Equilibrium



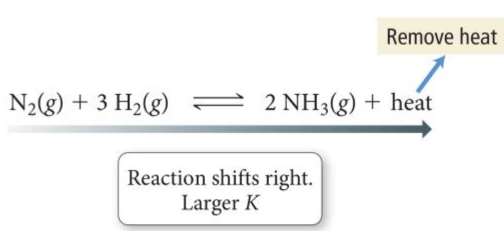
When the pressure is decreased by increasing the volume, the position of equilibrium shifts toward the side with the greater number of molecules—the reactant side.

The Effect of Temperature Changes on Equilibrium Position

- Exothermic reactions release energy, and endothermic reactions absorb energy
- Writing heat as part of the reaction helps us use Le Châtelier's principle to predict the effect of temperature changes, even though heat is not matter and is not written in a proper equation.

The Effect of Temperature Changes on Equilibrium for Exothermic Reactions

- For an exothermic reaction, heat is a product.
- Increasing the temperature is like adding heat.
- According to Le Châtelier's principle, the equilibrium will shift away from the added heat.

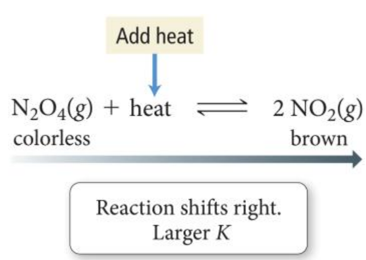


The Effect of Temperature Changes on Equilibrium for Exothermic Reactions

- **Adding heat to an exothermic reaction will decrease the concentrations of products and increase the concentrations of reactants.**
- **Adding heat to an exothermic reaction will decrease the value of *K*.**
- How will decreasing the temperature affect the system?

The Effect of Temperature Changes on Equilibrium for Endothermic Reactions

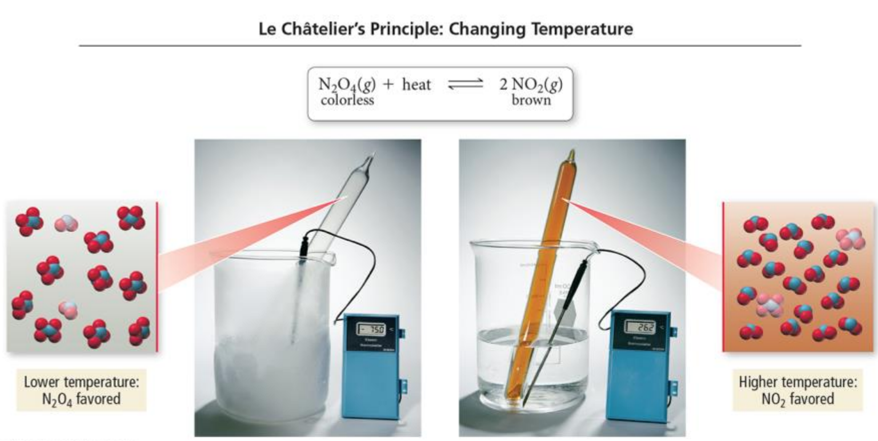
- For an endothermic reaction, heat is a reactant.
- Increasing the temperature is like adding heat.
- According to Le Châtelier's principle, the equilibrium will shift away from the added heat.



The Effect of Temperature Changes on Equilibrium for Endothermic Reactions

- Adding heat to an endothermic reaction will decrease the concentrations of reactants and increase the concentrations of products.
- Adding heat to an endothermic reaction will increase the value of *K*.

The Effect of Temperature Changes on Equilibrium



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.**