CHEMICAL EQUILIBRIUM

The content in this topic is the basis for mastering Learning Objectives 6.1–6.10 as found in the Curriculum Framework.

When you finish reviewing this topic, be sure you are able to:

- Know how to write equilibrium and nonequilibrium expressions for K and Q
- Explain the reversibility of a chemical system under a specified set of conditions
- Predict how Q and K change when conditions change
- Calculate equilibrium constants using numerical or graphical data
- Use stoichiometry and the law of mass action to determine equilibrium concentrations and partial pressures
- Predict the relative concentrations of reactants and products from the magnitudes of equilibrium constants
- Use Le Châtelier's principle and kinetics to predict the relative rates of forward and reverse reactions
- Use Le Châtelier's principle to predict the direction a reaction will proceed as a result of a given change
- Use Le Châtelier's principle to explain the effect a change will have on Q or K
- Use Le Châtelier's principle to design a set of conditions that will optimize a desired result

The Concept of Equilibrium | Section 15.1

Chemical equilibrium occurs when two opposite reactions occur at the same rate. A chemical equilibrium is dynamic. That is, even though no macroscopic changes are observable, on the submicroscopic level, atoms, ions, and molecules continue to change as both a forward and a reverse reaction occur at the same rate.

Consider the reaction of the colorless gas dinitrogen tetroxide to form brown nitrogen dioxide gas in a clear container:

$$N_2O_4(g) \rightarrow 2NO_2(g)$$
colorless   brown
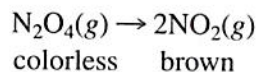
At the beginning of the reaction, only N_2O_4 is present so the contents of the container are colorless. Soon a brown color appears, which gets darker and darker with time. Finally, no further change of color is observed. At this point, spectroscopic evidence shows that the flask contains both N_2O_4 and NO_2 and the concentration of both gases remains constant. The system is at equilibrium:

$$N_2O_4(g) \rightleftharpoons 2NO_2(g)$$
colorless   brown
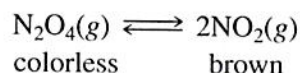
The " $\rightleftharpoons$ " denotes the equilibrium condition. That is, the forward and reverse reactions occur at the same rate. At equilibrium, there is no observable change in concentration, temperature, pressure, color, or any other property. Even so, the molecules continue to interconvert as forward and reverse reactions occur at the same rate.

Figure 15.1a shows what happens to the concentration of each gas as a function of time. Notice that at equilibrium, although not equal, the concentration of each gas remains constant.
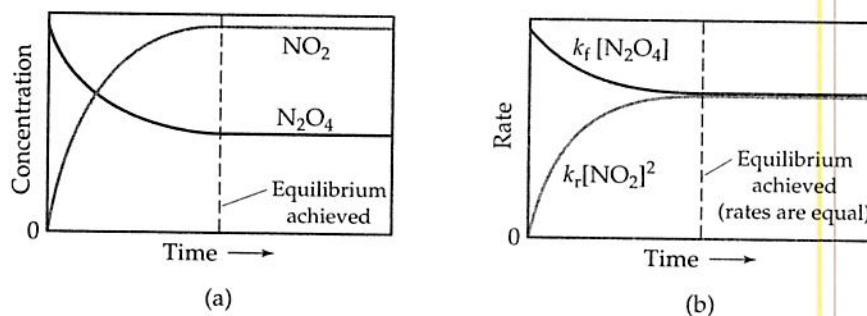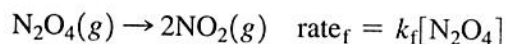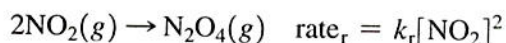

Figure 15.1 Achieving chemical equilibrium in the $N_2O_4(g) \rightleftharpoons 2NO_2(g)$ reaction. Equilibrium occurs when the rate of the forward reaction equals the rate of the reverse reaction.

Figure 15.1b illustrates the change in the rates of the forward and reverse reactions as the system approaches equilibrium. Notice that at equilibrium, the rates are equal.

For the forward reaction,

$$N_2O_4(g) \rightarrow 2NO_2(g) \quad \text{rate}_f = k_f[N_2O_4]$$

For the reverse reaction,

$$2NO_2(g) \rightarrow N_2O_4(g) \quad \text{rate}_r = k_r[NO_2]^2$$

At equilibrium, the rates are equal, so $k_f[N_2O_4] = k_r[NO_2]^2$.

Rearranging: $[NO_2]^2/[N_2O_4] = k_f/k_r$.

The constant k_f/k_r is called the equilibrium constant, K.

Your Turn 15.1

A drop of water is placed in the center of a plastic petri dish in a dry environment and the mass of the system is determined. The mass of the lid is determined and then placed on the petri dish. An ice chip is placed on top of the lid. Momentarily, a fog appears on the underside of the lid just below the ice chip. The ice chip is removed and the outside top of the lid is dried and weighed. The bottom of the petri dish is weighed. Answer the following questions about this system.

a. *What happens to the drop of water in the petri dish as time elapses?*
b. *What is the fog on the underside of the lid?*
c. *Write an equation describing what happens to the water in the system.*
d. *What observation might support the supposition that equilibrium is eventually established?*
e. *What observation might support the supposition that the process represented by the equation in Answer c is reversible?*

Write your answers in the space provided.

The Equilibrium Constant

Section 15.2

The **equilibrium-constant expression**, also called the **law of mass action**, for any reaction takes the form of a ratio of the molar concentrations of products divided by those of reactants.

For example, for the reaction:

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

the equilibrium-constant expression is:

$$K_c = [NO_2]^2/[N_2O_4]$$

Each molar concentration is raised to the power of the respective coefficient in the balanced chemical equation.

The "c" in K_c denotes that the amounts of reactants and products are expressed in the molar concentration unit, M, moles per liter.

If the reactants and products are expressed in partial pressures in a gaseous reaction, the equilibrium-constant expression is written:

$$K_p = P_{NO_2}^2 / P_{N_2O_4}$$

The "p" in K_p denotes that all the reactants and products are expressed as partial pressures, in atmospheres. The exponents are the coefficients in the balanced equation.

The relationship between K_c and K_p is given:

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

where R, the universal gas constant $= 0.0821$ L atm/mol K

T is the absolute temperature in K

Δn is the change in number of moles of gas (gaseous products minus gaseous reactants)

In the example, $N_2O_4(g) \rightleftharpoons 2NO_2(g)$, $\Delta n = +1$ because one mole of gaseous reactants becomes two moles of gaseous products, which is a net gain of one mole.

Whenever a pure solid and/or a pure liquid appears in the equilibrium reaction, its concentration is not included in the equilibrium expression.

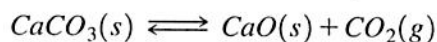For example, the equilibrium expression for the reaction:

$$AgCl(s) \rightleftharpoons Ag^+(aq) + Cl^-(aq)$$

does not include the solid $AgCl(s)$.

$$K_c = [Ag^+][Cl^-]$$

Similarly, for $2H_2O(l) \rightleftharpoons H_3O^+(aq) + OH^-(aq)$, the equilibrium expression is:

$$K_c = [H_3O^+][OH^-]$$

Write the equilibrium-constant expressions, K_c and K_p, for the following reaction:

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

Write your answer in the space provided.

## Understanding and Working with Equilibrium Constants

Section 15.3

The magnitude of the equilibrium constant for a given reaction roughly reflects the ratio of products to reactants and suggests whether products or reactants predominate at equilibrium.

A very large value of an equilibrium constant means that products predominate, and the equilibrium reaction is said to "lie to the right". For example:

$$2NO(g) + O_2(g) \rightleftharpoons 2NO_2(g), \quad K_c = 5.0 \times 10^{12}$$

A very small value of an equilibrium constant means that reactants predominate, and the reaction "lies to the left." For example:

$$2HBr(g) \rightleftharpoons H_2(g) + Br_2(g), \quad K_c = 5.8 \times 10^{-18}$$
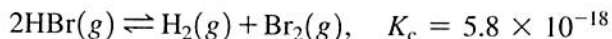
When a reaction is written in reverse, the equilibrium expression for the reverse reaction is the reciprocal of that of the forward reaction.

Example:

K_c *for* $AgCl(s) \rightleftharpoons Ag^+(aq) + Cl^-(aq)$ *is* 1.8×10^{-10}.
What is K_c *for* $Ag^+(aq) + Cl^-(aq) \rightleftharpoons AgCl(s)$?

Solution:

For the first reaction, $K_c = 1.8 \times 10^{-10} = [Ag^+][Cl^-]$

For the reaction in question, $K_c = 1/[Ag^+][Cl^-] = 1/1.8 \times 10^{-10}$
$$= 5.6 \times 10^{+9}$$

Your Turn 15.3

For which reaction in the above example do products predominate? Which reaction lies to the left? Explain. Write your answer in the space provided.

When a reaction is balanced by doubling the coefficients, then the equilibrium constant for the reaction balanced with the doubled coefficients is the square of the equilibrium constant of the original reaction.

Example:

At 1000 K for $SO_2(g) + \frac{1}{2}O_2(g) \rightleftharpoons SO_3(g)$, $K_p = 1.85$.
What is K_p at 1000 K for $2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g)$?

Solution:

For $SO_2(g) + \frac{1}{2}O_2(g) \rightleftharpoons SO_3(g)$,

$K_p = P_{SO_3}/(P_{O_2})^{1/2}(P_{SO_2}) = 1.85$

For $2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g)$, $K_p = (P_{SO_3})^2/(P_{O_2})(P_{SO_2})^2$
$= (1.85)^2 = 3.42$

Your Turn 15.4

The equilibrium constant at 25 °C for the reaction, $N_2(g) + O_2(g) \rightleftharpoons 2NO(g)$ is 1×10^{-30}. Calculate the equilibrium constants for the following reactions:

a. $\frac{1}{2}N_2(g) + \frac{1}{2}O_2(g) \rightleftharpoons NO(g)$

b. $2NO(g) \rightleftharpoons N_2(g) + O_2(g)$
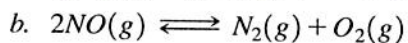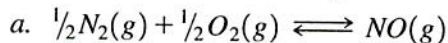
Justify your answers. Write your answers in the space provided.

Calculating Equilibrium Constants

Calculations of equilibrium constants from initial and equilibrium concentrations and/or pressures are important calculations required for mastery of the Advanced Placement exam in chemistry. Often an ICE table is used to analyze and manipulate the data. ICE stands for "initial," "change," and "equilibrium."

Example:

Initially, 0.40 mol of nitrogen and 0.96 mol of hydrogen are placed in a 2.0 L container at constant temperature. The mixture is allowed to react, and at equilibrium, the molar concentration of ammonia is found to be 0.14 M. Calculate the equilibrium constant, K_c, for the reaction:

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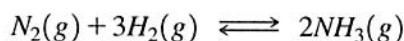
Solution:

First, calculate the initial concentrations of the reactants from the initial amounts and the volume of the container.

$[N_2] = 0.40\ mol/2.0\ L = 0.20\ M = $ *"I" (initial concentration) for N_2.*
$[H_2] = 0.96\ mol/2.0\ L = 0.48\ M = $ *"I" (initial concentration) for H_2.*

Assume the molar concentration of nitrogen that reacts is "x." Then, the molar concentration of hydrogen that reacts is 3x, because the balanced chemical equation tells us that for each 1 mol of nitrogen that reacts, 3 mol of hydrogen react. By similar reasoning, the molar concentration of ammonia formed is 2x. Therefore,

"C" (change) for nitrogen $= -x$
"C" (change) for hydrogen $= -3x$
"C" (change) for ammonia $= +2x$

Next, set up an ICE table as follows, and add "I" + "C" for each quantity to obtain "E," the corresponding equilibrium quantity:

	$N_2(g)$	$+3H_2(g)$	$\rightleftharpoons 2NH_3(g)$
I	0.20 M	0.48 M	0 M
C	$-x$	$-3x$	$+2x$
E	$0.20 - x$	$0.48 - 3x$	$2x$

The equilibrium concentration of ammonia is given in the problem as 0.14 M NH_3.
So, $2x = 0.14\ M$ and $x = 0.070\ M$.
At equilibrium, $[N_2] = 0.20 - x = 0.20 - 0.070 = 0.13\ M$.
At equilibrium, $[H_2] = 0.48 - 3x = 0.48 - 3(0.070) = 0.27\ M$.

Substituting into the equilibrium-constant expression for the reaction:
$K_c = [NH_3]^2/[N_2][H_2]^3 = (0.140\ M)^2/(0.13\ M)(0.27\ M)^3 = 7.66$

(Note: The units for equilibrium constants are rarely included.)

Section 15.6   **Applications of Equilibrium Constants**

The **reaction quotient expression**, Q, for any chemical reaction is defined in the same way as the equilibrium-constant expression. However, unlike the equilibrium-constant expression, nonequilibrium values for concentrations or partial pressures may be substituted into the reaction quotient expression.

The reaction quotient, Q, is useful in determining the direction (forward or reverse) a chemical reaction will go to achieve equilibrium.

To determine the direction the reaction will go toward equilibrium, compare the value of Q to the value of K_c (or K_p).

If $K_c = Q$, the system is already at equilibrium.

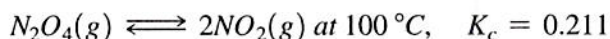If $K_c < Q$, the system will go to the left to achieve equilibrium.

If $K_c > Q$, the system will go to the right to achieve equilibrium.

(Notice that if K_c and Q are placed in alphabetical order, the $=$, $<$, and $>$ signs point the direction the reaction will go toward equilibrium.)

> **Examples:**
>
> *Consider the interaction of dinitrogen tetroxide and nitrogen dioxide:*
>
> $N_2O_4(g) \rightleftharpoons 2NO_2(g)$ *at* $100\,°C$, $\quad K_c = 0.211$
>
> *Which direction will the reaction go if* $[N_2O_4] = 1.0\ M$ *and* $[NO_2] = 0.5\ M$?
>
> **Solution:**
>
> *Substitute the given initial concentrations into the expression for Q, which is the same as the expression for K_c.*
>
> $Q = [NO_2]^2/[N_2O_4] = (0.50)^2/(1.0) = 0.25$
>
> $K_c = 0.211 < 0.25 = Q$
>
> *The reaction goes from right to left toward reactants to establish equilibrium. Notice that at the given concentrations, there is too much $NO_2(g)$, and not enough $N_2O_4(g)$. The reaction goes toward $N_2O_4(g)$ to achieve equilibrium. Notice that if Q is greater than K, there are more products present than there will be at equilibrium. More molecules of product will cause higher molecular collisions between product molecules and increase the rate of the reverse reaction. This will drive the net reaction toward more reactants (to the left) until equilibrium is reestablished.*

Le Châtelier's Principle   Section 15.7

Le Châtelier's principle summarizes the behavior of a chemical reaction at equilibrium when a stress is imposed on the reaction. It states that if a change is applied to a system at equilibrium, the system will move in a direction that minimizes the change.

To understand Le Châtelier's principle and why changes affect equilibria, it is important to remember that the equilibrium condition is when the rates of the forward and reverse reactions of a chemical system are equal. By a change to a system at equilibrium, we mean a change that alters the rate of either the forward or reverse reaction so the system is no longer at equilibrium. The system responds to move in a direction that reestablishes equilibrium. The system is said to "shift right" (toward products) or "shift left" (toward reactants) depending on the change that disturbs the equilibrium.

Changes that affect equilibria are the following:

1. Change in concentrations of reactants or products.

Adding a reactant shifts the equilibrium toward products. The increased concentration of the reactant makes the forward reaction faster than the reverse reaction, causing the reaction to shift toward products. (Recall that increasing the concentration of a reactant increases the rate of the forward reaction because, at higher concentrations, collisions are more frequent.)

Removing a reactant shifts the equilibrium toward reactants. A decreased concentration of a reactant decreases the molecular collisions between reactants. This slows the forward reaction, making it slower than the reverse reaction, causing the reaction to shift toward reactants.

Adding a product shifts the equilibrium toward reactants. An increased concentration of product speeds the reverse reaction by increasing molecular collisions and shifting the reaction toward reactants.

Removing a product shifts the equilibrium toward products. Decreased product concentration slows the reverse reaction, causing the reaction to favor products.

Figure 15.2 summarizes the effect of changing the concentrations of reactants or products on a system at equilibrium.
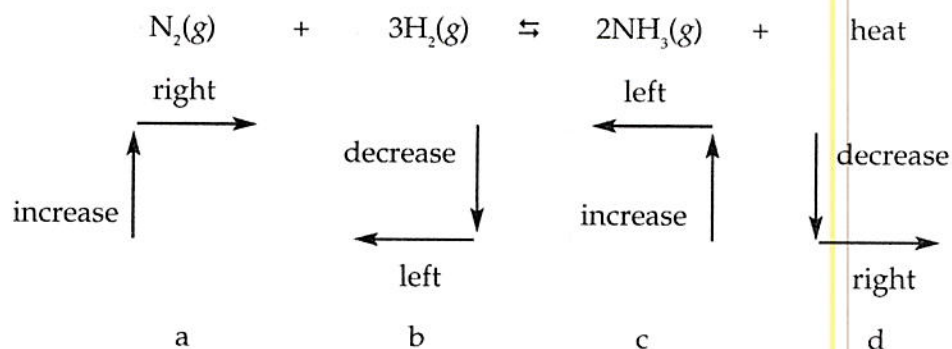
$$N_2(g) \quad + \quad 3H_2(g) \quad \leftrightarrows \quad 2NH_3(g) \quad + \quad \text{heat}$$

Figure 15.2 The effect of adding or removing reactants or products on a system at equilibrium.

a. Adding reactants shifts equilibrium toward products because increased molecular collisions between reactants speed the forward reaction.
b. Removing reactants shifts equilibrium toward reactants because fewer molecular collisions slow the forward reaction.
c. Adding products increases the collisions between product molecules, increases the reverse reaction, and shifts equilibrium toward reactants.
d. Removing products slows the reverse reaction and shifts equilibrium toward products.

Common misconception: Figure 15.2 tells *what direction* a system at equilibrium will shift under a given set of conditions. However, questions on the Advanced Placement exam often ask *why* a system behaves as it does. Be sure to study the discussion of why the rate of the forward or reverse reaction changes (the frequency of molecular collisions changes) and how that change affects the equilibrium position.

Your Turn 15.5

How will decreasing the concentration of hydrogen gas affect the amount of hydrogen iodide present at equilibrium? Explain. Write your answer in the space provided.

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

2. Change in volume (affects gaseous equilibria only).

Decreasing the volume for a gaseous system at equilibrium increases the pressures (and, therefore, concentrations) of both the gaseous reactants and products. Decreasing volume shifts the reaction in the direction of the least number of moles of gas in the balanced equation.

For example, decreasing the container volume of the reaction:

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

causes the equilibrium to move toward products because the formation of lesser number of moles will decrease the pressure.

Decreasing the volume increases the total pressure. The system responds by moving in a direction that will reduce the total pressure. In this case, the reaction shifts toward NH_3, because the number of moles in the system will decrease and the pressure will decrease. Another way to say this is that when the total pressure increases, the equilibrium shifts in a direction that reduces the number of moles of gas, in this case, to the right.

For example, if the volume of the container is halved, the pressures of each gas will double. However, the equilibrium constant, K_p, is defined in terms of the stoichiometry of the reaction and doubling all pressures increases the numerator (a squared term) less than the denominator (the combination of terms raised to the third and first powers). Thus, the equilibrium is out of balance and adjusts to the right to rebalance the mixture keeping K_p a constant.

$$K_p = P_{NH_3}^2 / P_{N_2} P_{H_2}^3$$

On a molecular level, consider that an increase in pressure increases the rates of both the forward and reverse reactions because the number of collisions for both reactants and products are more frequent. However, the rates of the forward and reverse reactions are not increased equally. The rate of the forward reaction, because it has more moles of gas, increases more than the rate of the reverse reaction. The reaction shifts right consuming enough reactants to again make the rates equal.

Your Turn 15.6

What is the effect on the equilibrium between ozone, O_3, and oxygen, O_2, when the volume of the container is increased? Explain your answer discussing changes in the relative rates of reaction. Write your answer in the space provided.

$$2O_3(g) \rightleftharpoons 3O_2(g)$$
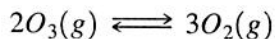
3. Change in temperature.

Increasing temperature favors the endothermic reaction. The rate of both the forward and reverse reactions is increased because of faster moving particles, more frequent collisions, and more effective collisions. However, the rate of the endothermic reaction increases more than does the rate of the exothermic reaction. This is because the activation energy of the endothermic reaction is always greater than that of the exothermic reaction. At low temperatures, enough exothermic reactants already have sufficient energy to overcome the relatively low activation barrier. At low temperature, very few endothermic reactants have the requisite energy to go over the relatively high activation barrier. Increasing temperature increases the energy of both reactants and products. However, high temperature aids the lower-energy endothermic reactants more than the higher-energy exothermic reactants. Thus, increasing temperature increases the rate of the endothermic reaction more than it increases the rate of the exothermic reaction.

Decreasing temperature favors the exothermic reaction. A lower temperature slows the rate of both forward and reverse reactions. However, at low temperatures, enough exothermic reactants still have sufficient energy to surmount the energy barrier and react.

Changing temperature changes the equilibrium constant. In contrast, changes in concentration, volume, or pressure change the position of an equilibrium without changing the equilibrium constant. Figure 15.2 shows that you can deduce the effect of temperature on the direction of change of an equilibrium system if you treat temperature as a reactant (in an endothermic reaction) or a product (in an exothermic reaction).

The Effect of a Catalyst

A catalyst does not affect the position of the equilibrium, but it does increase the rate at which equilibrium is established. A catalyst increases the rate of a reaction by lowering the activation energy. However, a catalyst lowers the activation energies of both the forward and reverse reactions by equal amounts (see Figure 15.3).
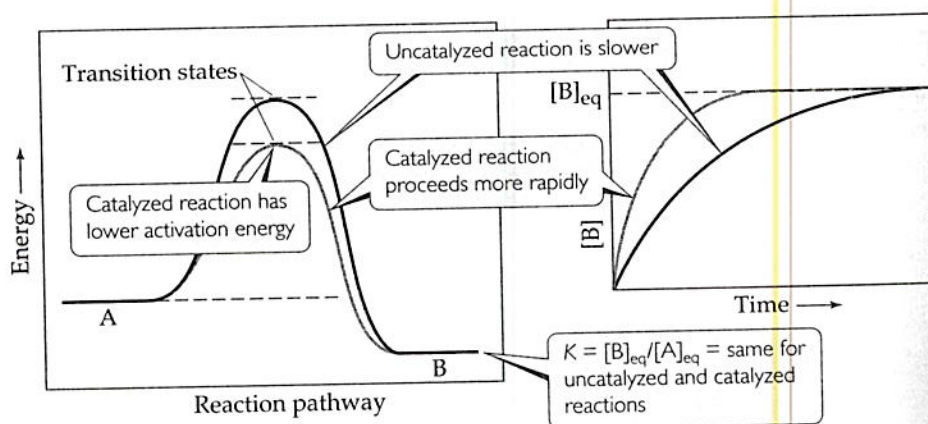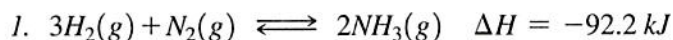

Figure 15.3 A catalyst works by providing a different pathway from reactants to products. The activation energy of both the forward and reverse reactions is low. A catalyst does not affect the position of the equilibrium.

Multiple Choice Questions

1. $3H_2(g) + N_2(g) \rightleftharpoons 2NH_3(g) \quad \Delta H = -92.2 \, kJ$

   The number of moles of $H_2(g)$ are decreased by

   A) decreasing the container size.

   B) adding NH_3.

   C) increasing the temperature.

   D) removing N_2.

   E) adding a catalyst.

2. Consider a reaction: $3A(g) + B(s) \rightleftharpoons 2C(g)$. If 2.0 mol A, 3.0 mol B, and 2.0 mol C are present in a 1.0 L flask at equilibrium, what is the value of K_c?

   A) 4.0

   B) 1.0

   C) 2.0

   D) 0.25

   E) 0.50

3. Consider the following reaction:

   $2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g) \, K_p = 9.0$ at a certain temperature.

   At the same temperature, what is K_p for $SO_2(g) + \frac{1}{2}O_2(g) \rightleftharpoons SO_3(g)$?

   A) 9.0

   B) 4.5

   C) 3.0

   D) 18

   E) 2.3

4. For the chemical reaction, $PCl_3(g) + Cl_2(g) \rightleftharpoons PCl_5(g)$, $\Delta H^{\circ}_{rxn} = -92.6 \, kJ$, which conditions favor maximum conversion of the reactants to product?

   A) high pressure and high temperature

   B) high pressure and low temperature

   C) low pressure and low temperature

   D) low pressure and high temperature

   E) adding a catalyst

5. Which of the following equilibrium constants indicates that its corresponding reaction goes nearly to completion?

A) $K_c = 1.0 \times 10^{-2}$

B) $K_c = 1.0 \times 10^{-8}$

C) $K_c = 1.0$

D) $K_c = 1.0 \times 10^{+2}$

E) $K_c = 1.0 \times 10^{+8}$

6. Identify the equilibrium expression for the decomposition of ammonium carbonate, $(NH_4)_2CO_3$, according to the following equation.

$$(NH_4)_2CO_3(s) \rightleftharpoons 2NH_3(g) + CO_2(g) + H_2O(g)$$
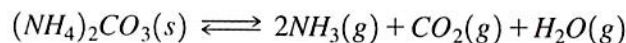
A) $K_c = [NH_3][CO_2][H_2O]$

B) $K_c = [NH_3]^2[CO_2][H_2O]$

C) $K_c = [NH_3]^2[CO_2][H_2O]/[(NH_4)_2CO_3]$

D) $K_c = [(NH_3)_2CO_3]/[NH_3]^2[CO_2][H_2O]$

E) $K_c = [NH_3][CO_2]$

7. In the presence of a catalyst, sulfur dioxide reacts with oxygen to form sulfur trioxide.

$$2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g)$$
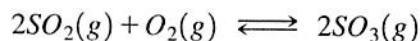
When 2.00 mol of O_2 and 2.00 mol of SO_2 are placed in a 1 L container, and allowed to come to equilibrium at a certain temperature, the mixture is found to contain 1.00 mol of SO_3. What is the amount of O_2 at equilibrium?

A) 0.00 mol

B) 1.00 mol

C) 1.50 mol

D) 0.50 mol

E) 0.75 mol

8. Ammonia is placed in a flask and allowed to come to equilibrium at a specified temperature according to the equation:

$$3H_2(g) + N_2(g) \rightleftharpoons 2NH_3(g)$$
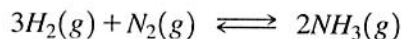
Analysis of the equilibrium mixture shows that it contains 3.00 atm NH_3 and 1.00 atm N_2. What is the value of the equilibrium constant, K_p?

A) 0.333

B) 27

C) 3.00

D) 0.25

E) 0.50

Questions 9–12 refer to the following system at equilibrium:

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

9. Which factor will affect both the value of the equilibrium constant AND the position of equilibrium for the formation of calcium carbonate?

   A) increasing the volume of the container

   B) adding CO_2

   C) removing $CaO(s)$

   D) raising the temperature

   E) adding a catalyst

10. The most convenient way to measure the equilibrium constant for the system is to measure

    A) the temperature of the reaction.

    B) the pressure of the CO_2 gas.

    C) the molar concentrations of all the reactants.

    D) the forward and reverse rate constants.

    E) the mass of the solid present.

11. For the reaction at a certain temperature, $K_p = 2.5$. If the partial pressure of CO_2 at that temperature is 1.5 atm, what are the relative values of Q and K and which direction will the reaction go to reestablish equilibrium?

    A) There is insufficient information to make a prediction.

    B) $K > Q$. The reaction goes to the right.

    C) $K < Q$. The reaction goes to the left.

    D) $K > Q$. The reaction goes to the left.

    E) $K < Q$. The reaction goes to the right.

12. What changes and corresponding observations would you be able to make to this system that might explain the reversibility of this reaction?

    A) If the volume of the container were doubled, the pressure would half.

    B) If the volume of the container were halved, the pressure would change, but not double.

    C) If $CaCO_3(s)$ were added to the container under the same conditions, no change in pressure would be observed.

    D) If $CaO(s)$ were added to the container under the same conditions, the pressure would decrease.

    E) If the system were heated, the pressure would decrease.

Refer to the following information to answer Questions 13–16.

The diagrams below represent three systems at equilibrium, all in the same-size containers.
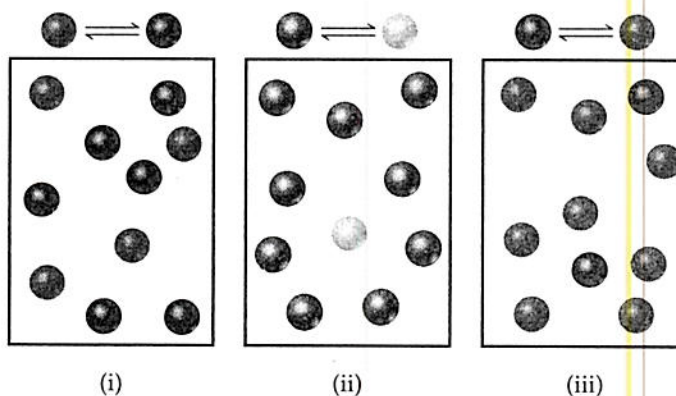
(i)   (ii)   (iii)

13. Rank the equilibrium constants in order of increasing magnitudes, lowest to highest.

    A) *i < ii < iii*

    B) *iii < i < ii*

    C) *ii < i < iii*

    D) *i < iii < ii*

    E) *iii < ii < i*

14. Assume each container is 100 L and each molecule represents 0.1 mol. What is the value of the equilibrium constant for System ii?

    A) 9

    B) 1/9

    C) 0.09

    D) 0.009

    E) 900

15. If more reactant were added to System i under the same conditions, what would be the result when equilibrium is reestablished?

    A) There would be no change in the amounts of reactants or products.

    B) More products would be produced because, until equilibrium is reestablished, the forward rate would exceed the reverse rate.

    C) Less products would be produced because, until equilibrium is reestablished, the forward rate would exceed the reverse rate.

    D) More products would be produced because, until equilibrium is reestablished, the reverse rate would exceed the forward rate.

    E) Less products would be produced because, until equilibrium is reestablished, the reverse rate would exceed the forward rate.

16. If product molecules were added to System iii under the same conditions at equilibrium, what would happen to the relative values of Q and K, before the addition, immediately after the addition, and upon the return to equilibrium?

    A) $Q = K$, throughout the process

    B) $Q = K, Q > K, Q = K$

    C) $Q < K, Q = K \, Q > K$

    D) $Q = K, Q < K, Q = K$

    E) There is not enough information to tell.

Free Response Questions

1. A 40.0 g sample of solid ammonium carbonate is placed in a closed, evacuated 3.00 L flask and heated to 400°C. It decomposes to produce ammonia, water, and carbon dioxide according to the equation:

$$(NH_4)_2CO_3(s) \rightleftharpoons 2NH_3(g) + H_2O(g) + CO_2(g)$$

The equilibrium constant, K_p, for the reaction is 0.295 at 400 °C.

    a. Write the K_p equilibrium-constant expression for the reaction.

    b. Calculate K_c at 400 °C.

    c. Calculate the partial pressure of $NH_3(g)$ at equilibrium at 400 °C.

    d. Calculate the total pressure inside the flask at equilibrium.

    e. Calculate the number of grams of solid ammonium carbonate in the flask at equilibrium.

    f. What is the minimum amount in grams of solid $(NH_4)_2CO_3$ that is necessary to be placed in the flask in order for the system to come to equilibrium?

2. Hydrogen gas reacts with solid sulfur to produce hydrogen sulfide gas.

$$H_2(g) + S(s) \rightleftharpoons H_2S(g) \quad \Delta H_{rxn} = -20.17 \, kJ/mol$$

An amount of solid S and an amount of gaseous H_2 are placed in an evacuated container at 25 °C. At equilibrium, some solid S remains in the container.

Predict and explain each of the following. In each case, predict what the stated change will have on the relative values of K and Q.

    a. the effect on the equilibrium partial pressure of H_2S gas when additional solid sulfur is introduced into the container

    b. the effect on the equilibrium partial pressure of H_2 gas when additional H_2S gas is introduced into the container

    c. the effect on the mass of solid sulfur present when the volume of the container is increased

    d. the effect on the mass of solid sulfur present when the temperature is decreased

    e. the effect of adding a catalyst to initial amounts of reactants