TOPIC

15

CHEMICAL EQUILIBRIUM

Quantitative chemical equilibrium for gaseous reactions as described in Chapter 15 of *Chemistry the Central Science* is often the topic of Question 1 in the free response section of the AP exam in chemistry. Qualitative concepts of chemical equilibrium, especially those involving Le Châtelier's principle, are often the topic of one of the required essay questions of the free response section of the exam. Both quantitative and qualitative questions appear in the multiple choice section. Students should be able to write equilibrium expressions, interconvert Kp and Kc equilibrium constants, calculate equilibrium constants and concentrations from given data, and apply Le Châtelier's principle to equilibrium systems.

The Concept of Equilibrium

Section 15.1

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

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

colorless brown

The "$\leftrightarrows$" denotes that the system is at equilibrium. That is, the forward and reverse reactions occur at the same rate. Even though at equilibrium there is no observable change in temperature, pressure, color or any other property, the molecules continue to interconvert.

The Equilibrium Constant

Section 15.2 and 15.4

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 reactants divided by those of products.

For example, for the reaction:

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

The equilibrium constant expression is:

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

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

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

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

$$Kp = P^2_{NO_2}/P_{N_2O_4}$$

The "p" in Kp 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 Kc and Kp is given:

$$Kp = Kc(RT)^{\Delta n}$$

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 as reactants become products.

In the example, $N_2O_4(g) \leftrightarrows 2NO_2(g)$, $\Delta n = +1$ 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:

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

does not include the solid AgCl(s).

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

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

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

Your Turn 15.1

Write the equilibrium constant expressions, Kc and Kp for the following reaction:
$CaCO_3(s) \leftrightharpoons CaO(s) + CO_2(g)$
Write your answer in the space provided.

Interpreting 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 gives an indication 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" with products predominating. For example:

$$2NO(g) + O_2(g) \leftrightharpoons 2NO_2(g), Kc = 5.0 \times 10^{12}.$$

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

$$2HBr(g) \rightleftharpoons H_2(g) + Br_2(g), Kc = 5.8 \times 10^{-18}.$$

When a reaction is written in reverse, the equilibrium expression for the reverse reaction is the reciprocal of that of the forward reaction.

Example:

Kc for $AgCl(s) \leftrightharpoons Ag^+(aq) + Cl^-(aq)$ is 1.8×10^{-10}.

What is Kc for $Ag^+(aq) + Cl^-(aq) \leftrightharpoons AgCl(s)$?

Solution:

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

Your Turn 15.2

For which reaction given 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 $SO_2(g) + 1/2\ O_2(g) \leftrightarrows SO_3(g)$, $Kp = 1.85$.

What is Kp at 1000 K for $2SO_2(g) + O_2(g) \leftrightarrows 2SO_3(g)$?

Solution:

For $SO_2(g) + 1/2O_2(g) \leftrightarrows SO_3(g)$, $Kp = Pso_3/Pso_2 \cdot Po_2{}^{1/2} = 1.85$

For $2SO_2(g) + O_2(g) \leftrightarrows 2SO_3(g)$, $Kp = Pso_3{}^2/Pso_2{}^2 \cdot Po_2$

$= (1.85)^2 = 3.42$

Section 15.5 Calculating Equilibrium Constants

Calculations of equilibrium constants from initial and equilibrium concentrations and/or pressures are perhaps the most 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, Kc, for the reaction.

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

Solution:

We first need to 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 one mole of nitrogen that reacts, three moles 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 is +2x.

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

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

An equilibrium concentration of ammonia of 0.14 M is given in the problem. 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:

$Kc = [NH_3]^2/[N_2][H_2]^3 = (0.140\ M)^2/(0.13\ M)(0.27\ M)^3 = 7.66$

(Note: The units for equilibrium constants are not included.)

Applications of Equilibrium Constants

Section 15.6

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, non-equilibrium 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 proceed to achieve equilibrium.

To determine the direction the reaction will proceed toward equilibrium, compare the value of Q to the value of Kc (or Kp).

If Kc = Q, the system is already at equilibrium.

If Kc < Q, the system will proceed to the left to achieve equilbrium.

If Kc > Q, the system will proceed to the right to achieve equilbrium.

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

Example:

Consider the interaction of dinitrogen tetroxide and nitrogen dioxide:

$N_2O_4(g) \leftrightarrows 2NO_2(g)$ *at* $100°C$, $Kc = 0.211$

Which direction will the reaction proceed 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 Kc.

$$Q = [NO_2]^2/[N_2O_4] = (0.50)^2/(1.0) = 0.25$$

$$Kc = 0.211 < 0.25 = Q$$

The reaction proceeds 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 proceeds toward* $N_2O_4(g)$ *to achieve equilibrium.*

Section 15.7 Le Châtelier's Principle

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:

1. Change in concentrations of reactants or products.

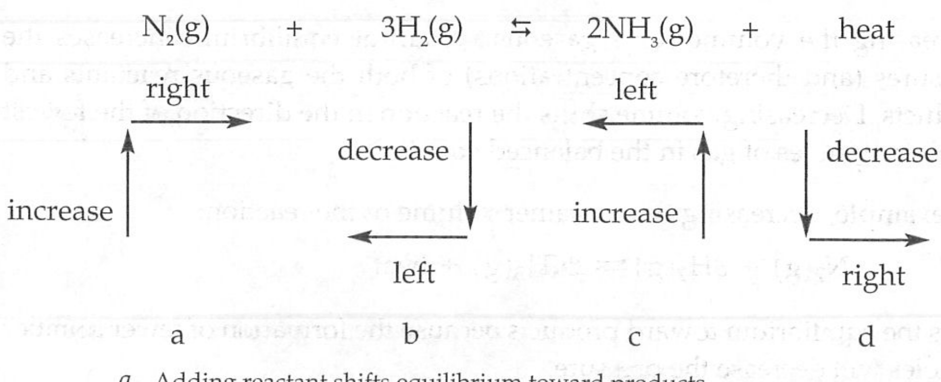
Adding a reactant shifts the equilibrium toward products. The increased concentration of the reactant makes the forward reaction faster than the reverse reaction, causing the reaction to shift toward products. (Recall that increasing the concentration of a reactant increases the rate of the forward reaction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

Removing a reactant shifts the equilibrium toward reactants. A decreased concentration of a reactant slows the forward reaction, making the reverse reaction faster than the forward 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 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 15.1 summarizes the effect of changing the concentrations of reactants or products on a system at equilibrium.



a. Adding reactant shifts equilibrium toward products.
b. Removing reactants shifts equilibrium toward reactants.
c. Adding products shifts equilibrium toward reactants.
d. Removing products shifts equilibrium toward products.

Figure 15.1. The effect of adding or removing reactants or products on a system at equilibrium.

Common misconception: Figure 15.1, 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 and how that change affects the equilibrium position.

Your Turn 15.3

How will decreasing the concentration of hydrogen gas affect the amount of hydrogen iodide present at equilibrium? Explain.

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

Write your answer in the space provided.

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 fewest number of moles of gas in the balanced equation.

For example, decreasing the container volume of the reaction:

$$N_2(g) + 3H_2(g) \leftrightarrows 2NH_3(g) + \text{heat}$$

shifts the equilibrium toward products because the formation of fewer 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, Kp, 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 Kp a constant.

$$Kp = P^2_{NH_3}/P_{N_2}P^3_{H_2}$$

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 15.4

What is the effect on the equilibrium between ozone and oxygen when the volume of the container is increased? Explain your answer on the basis of rates of reaction.

$2O_3(g) \leftrightarrows 3O_2(g)$

Write your answer in the space provided

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3. Change in temperature

Increasing temperature favors the endothermic reaction. The rate of both the forward and the reverse reactions are increased due to 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, a sufficient number of exothermic reactants already have enough 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. As increasing temperature increases the energy of both reactants and products, it 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, a sufficient number of exothermic reactants still have enough energy to surmount the energy barrier and react.

Changing temperature changes the equilibrium constant. In contrast, changes in concentration, volume, or pressure alter the position of an equilibrium without changing the equilibrium constant. Figure 15.1 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 by equal amounts the activation energies of both the forward and reverse reactions. (See Figure 15.2.)

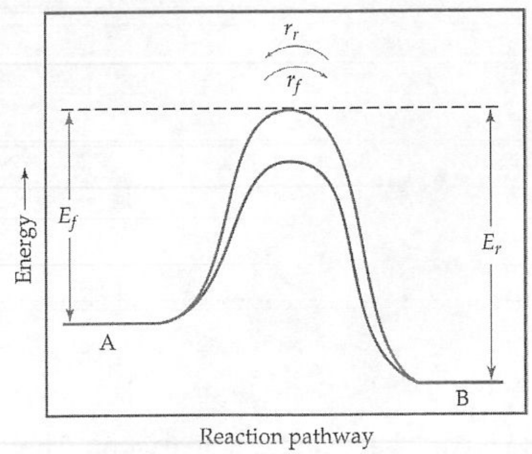

Figure 15.2. A catalyst works by providing a different pathway from reactants to products. The activation energy of both the forward and reverse reactions is lower. A catalyst does not affect the position of the equilibrium.

Multiple Choice Questions

1. $3H_2(g) + N_2(g) = 2NH_3(g) \quad \Delta H = -92.2\ kJ$
The number of moles of $H_2(g)$ are decreased by:
   A) *decreasing container size.*
   B) *adding NH_3.*
   C) *increasing temperature.*
   D) *removing N_2.*
   E) *adding a catalyst.*

2. *Which factor will affect both the value of the equilibrium constant and the position of equilibrium for the formation of calcium carbonate?*
$CaO(s) + CO_2(g) \leftrightarrows CaCO_3(s) + heat$
   A) *increasing the volume of the container*
   B) *adding CO_2*
   C) *removing CaO(s)*
   D) *raising the temperature*
   E) *adding a catalyst*

3. *Consider a reaction $3A(g) + B(s) \leftrightarrows 2C(g)$. 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

4. *Consider the following reaction:*
$2SO_2(g) + O_2(g) \leftrightarrows 2SO_3(g)$ $Kp = 9.0$ *at a certain temperature.*
At the same temperature, what is Kp for $SO_2(g) + 1/2O_2(g) \leftrightarrows SO_3(g)$?
   A) 9.0
   B) 4.5
   C) 3.0
   D) 18
   E) 2.3

5. *For the chemical reaction,* $PCl_3(g) + Cl_2(g) \leftrightarrows PCl_5(g)$, $\Delta H^{\circ}_{rxn} = -92.6\ kJ$. *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*

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

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

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

   C) $Kc = 1.0$

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

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

7. *What is the equilibrium expression for the decomposition of ammonium carbonate,* $(NH_4)_2CO_3$, *according to the following equation?*

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

   A) $Kc = [NH_3][CO_2][H_2O]$

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

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

   D) $Kc = (NH_4)_2[CO_3]/[NH_3]^2[CO_2][H_2O]$

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

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

   $2SO_2(g) + O_2(g) \leftrightarrows 2SO_3(g)$

   When 2.00 mol of O_2 *and 2.00 mol of* SO_2 *are placed in a one liter 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*

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

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

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, Kp?

A) 0.333

B) 27

C) 3.00

D) 0.25

E) 0.50

10. *Consider the chemical equilibrium: $Na_2CO_3(s) \leftrightarrows CO_2(g) + Na_2O(s)$ in a closed container at a certain temperature. 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.*

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:*

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

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

a. *Write the Kp equilibrium constant expression for the reaction.*

b. *Calculate Kc 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:*

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

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:

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.*

Additional Practice in *Chemistry the Central Science*

For more practice working kinetics problems in preparation for the Advanced Placement examination, try these problems in Chapter 15 of Chemistry the Central Science:

Additional Exercises: 15.57, 15.60, 15.63, 15.65, 15.66, 15.67, 15.68, 15.69, 15.74, 15.76.

Integrated Exercises: 15.81, 15.82, 15.85, 15.86, 15.87, 15.88.

Multiple Choice Answers and Explanations

1. *A. According to Boyles law, decreasing the container size will increase the partial pressures of all three gases and hence the total pressure. Because there are more moles of gaseous reactants (4) than gaseous products (2), reactant molecules will tend to collide more frequently than product molecules. The forward reaction rate will increase more than the reverse reaction rate. The system will shift toward products decreasing the number of moles of $H_2(g)$. A catalyst does not change the position of the equilibrium. All the other choices increase the number of moles of $H_2(g)$.*

2. *D. Temperature is the only variable that will change the equilibrium constant. Increasing the temperature will favor the endothermic (in this case, the reverse) reaction, causing the equilibrium to shift to the left increasing the partial pressure of CO_2 and decreasing Kp.*

3. *E. $Kc = [C]^2/[A]^3 = (2.0\ M)^2/(2.0\ M)^3 = 0.50$*
(Note that calculators are not allowed on the multiple choice section so complex numeric problems such as this one require relatively simple arithmetic.)

4. *C. The reaction in question is the same as the given reaction except that it is balanced with coefficients half the value of the given reaction. Since coefficients are exponents in equilibrium constant expressions, kp for the second reaction is the square root of Kp for the given reaction:* $(9.0)^{1/2} = 3.0$.

5. *B. The reaction is exothermic so low temperature will favor products. Additionally, high pressure will shift the reaction toward products because compressing the gases will cause the forward reaction to become faster than the reverse reaction. This is because at higher pressures more molecular collisions are likely to take place. The two moles of gas on the left will become one mole of gas on the right, lowering the pressure.*

6. *E. "Nearly to completion" means that by the time the system reaches equilibrium, most of the reactants have become products. Kc is the ratio of products to reactants, so the larger the Kc, the larger the quantity of products at equilibrium.*

7. *B. The equilibrium constant, Kc, equals the ratio of the concentrations of products to reactants, each raised to the power of the coefficient that balances the equation. Equilibrium constants do not include reactants or products that are pure solids or liquids.*

8. *C. An "ICE" table would look like this:*

	$2SO_2(g)$	$+\ O_2(g)$	$=\ 2SO_3(g)$
I	2.00	2.00	0
C	$-2x$	$-x$	$+2x$
E	$2.00-2x$	$2.00-x$	$2x$

$2x = 1.00$ *mol/L*, $x = 0.50$ *mol/L*, $2.00 - x = 1.50$ *mol/L*
$= 1.50$ *mol.*

9. *A. An "ICE" table would look like this:*

	$3H_2(g)+$	$N_2(g)$	$=\ 2NH_3(g)$
I	0	0	
C	$+3x$	$+x$	$-2x$
E	$3x$	x	3.00

$x = 1.00,\ 3x = 3.00$

$kp = (P_{NH_3})^2/(P_{H_2})^3(P_{N_2}) = (3.00)^2/(3.00)^3(1.00) = 0.333$

10. B. $Kp = P_{CO_2}$. *The partial pressure of the* CO_2 *at equilibrium is equal to the equilibrium constant, Kp. Equilibrium constants do not include reactants or products that are pure solids or liquids.*

Free Response Answers

a. $Kp = P^2_{NH_3}P_{H_2O}P_{CO_2}$. *The Kp expression is the product of the partial pressures of products raised to the power of the coefficients that balance the equation. Pure solids and liquids are excluded from any equilibrium expression.*

b. $Kc = Kp/(RT)^{\Delta n}$ *where* $R = 0.0821$ *L atm/mol K, T is the absolute temperature in Kelvin, and* Δn *is the change in number of moles of gas as the reaction proceeds left to right. In this case* $\Delta n = +4$ *because four moles of gas are produced from zero moles of gas.*

$$Kc = Kp/(RT)^{\Delta n} = 0.295/[(0.0821)(400 + 273)]^4$$
$$= 3.17 \times 10^{-8}.$$

c. *If x equals the partial pressure of* H_2O *formed in the reaction, an ICE table will look like this:*

$(NH_4)_2CO_3(s)$ =	$2NH_3(g)+$	$H_2O(g)+$	$CO_2(g)$
I	0	0	0
C	$+2x$	$+x$	$+x$
E	$2x$	x	x

(Note: It is not important to know how much solid is present initially or at equilibrium.)

$$Kp = P^2_{NH_3}P_{H_2O}P_{CO_2} = 0.295 = (2x)^2(x)(x) = 4x^4$$

$$x = 0.521$$

$$P_{NH_3} = 2x = 2\ (0.521) = 1.04\ atm$$

d. $x = P_{CO_2} = 0.521\ atm = P_{H_2O}$ *and* $2x$
$= P_{NH_3} = 2 \times 0.521 = 1.04\ atm$

$$P\ total = P_{CO_2} + P_{H_2O} + P_{NH_3} = 0.521 + 0.521 + 1.04$$
$$= 2.08\ atm.$$

e. *To calculate the number of grams of ammonium carbonate remaining at equilibrium, we must calculate the number of grams that reacted and subtract from the original 40.0 g. From the stoichiometry of the reaction, the moles of ammonium carbonate that reacted is equal to the number of moles of water found in the flask at equilibrium. The moles of water can be calculated from the partial pressure of water using the ideal gas equation.*

Moles of water at equilibrium $= PV/RT = (0.521\ atm)(3.00\ L)/(0.0821\ L\ atm/mol\ K)(400 + 273) = 0.0283\ mol\ H_2O$.

$0.283\ mol\ H_2O = 0.0283\ mol\ of\ (NH_4)2CO_3(s)$ *that reacted.*

The molar mass of $(NH_4)_2CO_3(s)$ *is 96.0 g/mol.*

The number of grams of $(NH_4)_2CO_3(s)$ *that reacted is 0.0283 mol x 96.0 g/mol = 2.72 g.*

The number of grams that remain is 40.0 g − 2.72 g = 37.3 g.

f. If 2.72 g react to establish equilibrium, then just slightly more than 2.72 grams of $(NH_4)_2CO_3(s)$ *must be present initially for equilibrium to be established because at equilibrium, some solid must remain.*

2. *a. Increasing or decreasing the amount of solid in an equilibrium mixture has no effect on the position of the equilibrium. S(s) does not appear in the equilibrium expression.*

b. The partial pressure of $H_2(g)$ *will increase. Additional* $H_2S(g)$ *added to the container increases the rate of the reverse reaction, causing more reactants to form as the equilibrium system rebalances.*

c. The mass of the solid sulfur remains the same. Increasing the volume of the container decreases the partial pressures of both gases, but because there is one mole of each gas on each side of the equilibrium equation, the equilibrium system does not change. If more moles of gas were on one side than the other, the equilibrium would shift toward the side with the greater number of moles of gas.

d. The mass of the solid sulfur will decrease. Heating a reaction increases the rate of both forward and reverse reactions because increasing temperature increases the speed with which the molecules move and the kinetic energy they have. Thus, at a higher temperature the collisions between molecules become more frequent. However, increasing temperature always increases the rate of the endothermic reaction more than the rate of the exothermic reaction because the higher temperature gives more molecules on the endothermic side the sufficient energy required to surmount the energy barrier.

Notice that this question can be tricky. Because pure solids are not included in the equilibrium expression, their relative amounts do not affect the position of the equilibrium. But their amounts are affected by changes in the equilibrium. Be sure to read each question carefully and answer the question directly.

e. *The final equilibrium position will not be affected even though the system will reach equilibrium faster. But catalysts increase the rates of both the forward and reverse reactions equally by lowering the activation energy.*

Your Turn Answers

15.1. $Kc = [CO_2]$. $Kp = P_{CO_2}$.

15.2. *In the reaction,* $Ag^+(aq) + Cl^-(aq) \leftrightarrows AgCl(s)$, *products predominate because the equilibrium constant,* $Kc = 5.6 \times 10^{+9}$, *is very large.*

The reaction, $AgCl(s) \leftrightarrows Ag^+(aq) + Cl^-(aq)$, *lies to the left where reactants predominate because the equilibrium constant,* $Kc = 1.8 \times 10^{-10}$ *is very small.*

15.3. *Decreasing* $[H_2]$ *will decrease the amount of HI present. The equilibrium will shift left, consuming HI, because the rate of the forward reaction will decrease due to more infrequent collisions.*

15.4. *Increasing the volume of the container decreases the pressure of both of the gases present. The equilibrium will shift in a direction to increase the pressure (to the right, toward oxygen.) Decreasing the pressure of both of the gases decreases their concentration, and decreases the rates of both the forward and reverse reactions. The rate of the forward reaction will decrease less than the rate of the reverse reaction, causing the equilibrium to shift toward products.*