10

Equilibrium

HOW OFTEN DOES EQUILIBRIUM APPEAR ON THE EXAM?

In the Multiple-Choice section, this topic appears in about 4 out of 75 questions.

In the Free-Response section, this topic appears every year.

THE EQUILIBRIUM CONSTANT, K_{eq}

Most chemical processes are reversible. That is, reactants react to form products, but those products can also react to form reactants.

A reaction is at equilibrium when the rate of the forward reaction is equal to the rate of the reverse reaction.

The relationship between the concentrations of reactants and products in a reaction at equilibrium is given by the equilibrium expression, also called the **law of mass action.**

The Equilibrium Expression
For the reaction $aA + bB \rightleftharpoons cC + dD$ $K_{eq} = \frac{[C]^c[D]^d}{[A]^a[B]^b}$ 1. [*A*], [*B*], [*C*], and [*D*] are molar concentrations or partial pressures at equilibrium. 2. Products are in the numerator, and reactants are in the denominator. 3. Coefficients in the balanced equation become exponents in the equilibrium expression. 4. Solids and pure liquids are not included in the equilibrium expression—only aqueous reactants and products are included. 5. Units are not given for K_{eq}.

Let's look at a few examples:

1. $HC_2H_3O_2(aq) \rightleftharpoons H^+(aq) + C_2H_3O_2^-(aq)$

$$K_{eq} = K_a = \frac{[H^+][C_2H_3O_2^-]}{[HC_2H_3O_2]}$$

This reaction shows the dissociation of acetic acid in water. All of the reactants and products are aqueous particles, so they are all included in the equilibrium expression. None of the reactants or products have coefficients, so there are no exponents in the equilibrium expression. This is the standard form of K_a, the acid dissociation constant.

2. $2H_2S(g) + 3O_2(g) \rightleftharpoons 2H_2O(g) + 2SO_2(g)$

$$K_{eq} = K_c = \frac{[H_2O]^2[SO_2]^2}{[H_2S]^2[O_2]^3}$$

$$K_{eq} = K_p = \frac{P^2_{H_2O}P^2_{SO_2}}{P^2_{H_2S}P^3_{O_2}}$$

All of the reactants and products in this reaction are gases, so K_{eq} can be expressed in terms of concentration (K_c, moles/liter or molarity) or in terms of partial pressure (K_p, atmospheres). In the next section, we'll see how these two different ways of looking at the same equilibrium situation are related. All of the reactants and products are included here, and the coefficients in the reaction become exponents in the equilibrium expression.

3. $CaF_2(s) \rightleftharpoons Ca^{2+}(aq) + 2\,F^-(aq)$

$$K_{eq} = K_{sp} = [Ca^{2+}][F^-]^2$$

This reaction shows the dissociation of a slightly soluble salt. There is no denominator in this equilibrium expression because the reactant is a solid. Solids are left out of the equilibrium expression because the concentration of a solid is constant. There must be some solid present for equilibrium to

exist, but you do not need to include it in your calculations. This form of K_{eq} is called the solubility product, K_{sp}, which we already saw in Chapter 9.

4. $NH_3(aq) + H_2O(l) \rightleftharpoons NH_4^+(aq) + OH^-(aq)$

$$K_{eq} = K_b = \frac{[NH_4^+][OH^-]}{[NH_3]}$$

This is the acid-base reaction between ammonia and water. We can leave water out of the equilibrium expression because it is a pure liquid. By pure liquid, we mean that the concentration of water is so large (about 50 molar) that nothing that happens in the reaction is going to change it significantly, so we can consider it to be constant. This is the standard form for K_b, the base dissociation constant.

Here is a roundup of the equilibrium constants you need to be familiar with for the test.

- K_c is the constant for molar concentrations.
- K_p is the constant for partial pressures.
- K_{sp} is the solubility product, which has no denominator because the reactants are solids.
- K_a is the acid dissociation constant for weak acids.
- K_b is the base dissociation constant for weak bases.
- K_w describes the ionization of water ($K_w = 1 \times 10^{-14}$).

The equilibrium constant has a lot of aliases, but they all take the same form and tell you the same thing. The **equilibrium constant** tells you the relative amounts of products and reactants at equilibrium.

A large value for K_{eq} means that products are favored over reactants at equilibrium, while a small value for K_{eq} means that reactants are favored over products at equilibrium.

K_{eq} AND GASES

As we saw in the example above, the equilibrium constant for a gas phase reaction can be written in terms of molar concentrations, K_c, or partial pressures, K_p. These two forms of K can be related by the following equation, which is derived from the ideal gas law.

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

K_p = partial pressure constant (using atmospheres as units)
K_c = molar concentration constant (using molarities as units)
R = the ideal gas constant, 0.0821 (L-atm)/(mol-K)
T = absolute temperature (K)
Δn = (Moles of product gas – moles of reactant gas)

THE REACTION QUOTIENT, *Q*

The reaction quotient is determined in exactly the same way as the equilibrium constant, but initial conditions are used in place of equilibrium conditions. The reaction quotient can be used to predict the direction in which a reaction will proceed from a given set of initial conditions.

The Reaction Quotient

For the reaction

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

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

$[A]$, $[B]$, $[C]$, and $[D]$ are initial molar concentrations or partial pressures.

- If Q is less than the calculated K for the reaction, the reaction proceeds forward, generating products.
- If Q is greater than K, the reaction proceeds backward, generating reactants.
- If $Q = K$, the reaction is already at equilibrium.

K_{eq} AND MULTISTEP PROCESSES

There is a simple relationship between the equilibrium constants for the steps of a multistep reaction and the equilibrium constant for the overall reaction.

If two reactions can be added together to create a third reaction, then the K_{eq} for the two reactions can be multiplied together to get the K_{eq} for the third reaction.

If	$A + B \rightleftharpoons C$	$K_{eq} = K_1$
and	$C \rightleftharpoons D + E$	$K_{eq} = K_2$
then	$A + B \rightleftharpoons D + E$	$K_{eq} = K_1K_2$

LE CHATELIER'S LAW

Le Chatelier's law says that whenever a stress is placed on a situation at equilibrium, the equilibrium will shift to relieve that stress.

Let's use the **Haber process,** which is used in the industrial preparation of ammonia, as an example.

$$N_2(g) + 3\,H_2(g) \rightleftharpoons 2\,NH_3(g) \qquad \Delta H° = -92.6\text{ kJ}$$

Concentration

- When the concentration of a reactant or product is increased, the reaction will proceed in the direction that will use up the added substance.

If N_2 or H_2 is added, the reaction proceeds in the forward direction. If NH_3 is added, the reaction proceeds in the reverse direction.

- When the concentration of a reactant or product is decreased, the reaction will proceed in the direction that will produce more of the substance that has been removed.

If N_2 or H_2 is removed, the reaction will proceed in the reverse direction. If NH_3 is removed, the reaction will proceed in the forward direction.

Volume

- When the volume in which a reaction takes place is increased, the reaction will proceed in the direction that produces more moles of gas.

When the volume for the Haber process is increased, the reaction proceeds in the reverse direction because the reactants have more moles of gas (4) than the products (2).

- When the volume in which a reaction takes place is decreased, the reaction will proceed in the direction that produces fewer moles of gas.

When the volume for the Haber process is decreased, the reaction proceeds in the forward direction because the products have fewer moles of gas (2) than the reactants (4).

- If there is no gas involved in the reaction, or if the reactants and products have the same number of moles of gas, then volume changes have no effect on the equilibrium.

Temperature

- When temperature is increased, the reaction will proceed in the endothermic direction.

When the temperature for the Haber process is increased, the reaction proceeds in the reverse direction because the reverse reaction is endothermic ($\Delta H°$ is positive).

- When temperature is decreased, the reaction will proceed in the exothermic direction.

When the temperature for the Haber process is decreased, the reaction proceeds in the forward direction because the forward reaction is exothermic ($\Delta H°$ is negative).

CHAPTER 10 QUESTIONS

MULTIPLE-CHOICE QUESTIONS

Questions 1–4

(A) K_c
(B) K_p
(C) K_a
(D) K_w
(E) K_{sp}

1. This equilibrium constant uses partial pressures of gases as units.

2. This equilibrium constant always has a value of 1×10^{-14} at 25°C.

3. This equilibrium constant is used for the dissociation of an acid.

4. The equilibrium expression for this equilibrium constant does not contain a denominator.

5. For a particular salt, the solution process is endothermic. As the temperature at which the salt is dissolved increases, which of the following will occur?

   (A) K_{sp} will increase, and the salt will become more soluble.
   (B) K_{sp} will decrease, and the salt will become more soluble.
   (C) K_{sp} will increase, and the salt will become less soluble.
   (D) K_{sp} will decrease, and the salt will become less soluble.
   (E) K_{sp} will not change, and the salt will become more soluble.

6. $2\,HI(g) + Cl_2(g) \rightleftharpoons 2\,HCl(g) + I_2(g) + \text{energy}$

   A gaseous reaction occurs and comes to equilibrium as shown above. Which of the following changes to the system will serve to increase the number of moles of I_2 present at equilibrium?

   (A) Increasing the volume at constant temperature
   (B) Decreasing the volume at constant temperature
   (C) Adding a mole of inert gas at constant volume
   (D) Increasing the temperature at constant volume
   (E) Decreasing the temperature at constant volume

7. A sealed isothermal container initially contained 2 moles of CO gas and 3 moles of H_2 gas. The following reversible reaction occurred:

$$CO(g) + 2\,H_2(g) \rightleftharpoons CH_3OH(g)$$

At equilibrium, there was 1 mole of CH_3OH in the container. What was the total number of moles of gas present in the container at equilibrium?

(A) 1
(B) 2
(C) 3
(D) 4
(E) 5

8. $4\,NH_3(g) + 3\,O_2(g) \rightleftharpoons 2\,N_2(g) + 6\,H_2O(g) + \text{energy}$

Which of the following changes to the system at equilibrium shown above would cause the concentration of H_2O to increase?

(A) The volume of the system was decreased at constant temperature.
(B) The temperature of the system was increased at constant volume.
(C) NH_3 was removed from the system.
(D) N_2 was removed from the system.
(E) O_2 was removed from the system.

9. A sample of solid potassium nitrate is placed in water. The solid potassium nitrate comes to equilibrium with its dissolved ions by the endothermic process shown below.

$$KNO_3(s) + \text{energy} \rightleftharpoons K^+(aq) + NO_3^-(aq)$$

Which of the following changes to the system would increase the concentration of K^+ ions at equilibrium?

(A) The volume of the solution is increased.
(B) The volume of the solution is decreased.
(C) Additional solid KNO_3 is added to the solution.
(D) The temperature of the solution is increased.
(E) The temperature of the solution is decreased.

10. Citric acid, $H_3C_6H_5O_7$, can give up 3 hydrogen ions in solution. The 3 dissociation reactions are as follows:

$$H_3C_6H_5O_7 \rightleftharpoons H^+ + H_2C_6H_5O_7^- \qquad K_1 = x$$

$$H_2C_6H_5O_7^- \rightleftharpoons H^+ + HC_6H_5O_7^{2-} \qquad K_2 = y$$

$$HC_6H_5O_7^{2-} \rightleftharpoons H^+ + C_6H_5O_7^{3-} \qquad K_3 = z$$

Which of the following expressions gives the equilibrium constant for the reaction shown below?

$$H_3C_6H_5O_7 \rightleftharpoons 3\,H^+ + C_6H_5O_7^{3-}$$

(A) xyz
(B) $\frac{xy}{z}$
(C) $\frac{x}{yz}$
(D) $\frac{z}{xy}$
(E) $\frac{1}{xyz}$

11. $$H_2(g) + I_2(g) \rightleftharpoons 2\,HI(g)$$

At 450°C, the equilibrium constant, K_c, for the reaction shown above has a value of 50. Which of the following is true of the reaction at equilibrium?

(A) The rate of the forward reaction is greater than the rate of the reverse reaction.
(B) The rate of the forward reaction is less than the rate of the reverse reaction.
(C) The rate of the forward reaction is equal to the rate of the reverse reaction.
(D) An increase in the volume of the system will cause an increase in the value of K_c.
(E) A decrease in the volume of the system will cause an increase in the value of K_c.

12. $2\ NOBr(g) \rightleftharpoons 2\ NO(g) + Br_2(g)$

The reaction above came to equilibrium at a temperature of 100°C. At equilibrium the partial pressure due to NOBr was 4 atmospheres, the partial pressure due to NO was 4 atmospheres, and the partial pressure due to Br_2 was 2 atmospheres. What is the equilibrium constant, K_p, for this reaction at 100°C?

(A) $\frac{1}{4}$

(B) $\frac{1}{2}$

(C) 1

(D) 2

(E) 4

13. $HCrO_4^- + Ca^{2+} \leftrightarrow H^+ + CaCrO_4$

If the acid dissociation constant for $HCrO_4^-$ is K_a and the solubility product for $CaCrO_4$ is K_{sp}, which of the following gives the equilibrium expression for the reaction above?

(A) $K_a K_{sp}$

(B) $\frac{K_a}{K_{sp}}$

(C) $\frac{K_{sp}}{K_a}$

(D) $\frac{1}{K_{sp} K_a}$

(E) $\frac{K_a K_{sp}}{2}$

14. $Br_2(g) + I_2(g) \leftrightarrow 2\ IBr(g)$

At 150°C, the equilibrium constant, K_c, for the reaction shown above has a value of 300. This reaction was allowed to reach equilibrium in a sealed container and the partial pressure due to $IBr(g)$ was found to be 3 atm. Which of the following could be the partial pressures due to $Br_2(g)$ and $I_2(g)$ in the container?

	$Br_2(g)$	$I_2(g)$
(A)	0.1 atm	0.3 atm
(B)	0.3 atm	1 atm
(C)	1 atm	1 atm
(D)	1 atm	3 atm
(E)	3 atm	3 atm

15. $H_2(g) + CO_2(g) \leftrightarrow H_2O(g) + CO(g)$

Initially, a sealed vessel contained only $H_2(g)$ with a partial pressure of 6 atm and $CO_2(g)$ with a partial pressure of 4 atm. The reaction above was allowed to come to equilibrium at a temperature of 700 K. At equilibrium, the partial pressure due to $CO(g)$ was found to be 2 atm. What is the value of the equilibrium constant K_p, for the reaction?

(A) $\frac{1}{24}$

(B) $\frac{1}{6}$

(C) $\frac{1}{4}$

(D) $\frac{1}{3}$

(E) $\frac{1}{2}$

PROBLEMS

1. $$BaF_2(s) \rightleftharpoons Ba^{2+}(aq) + 2\,F^-(aq)$$

The value of the solubility product, K_{sp}, for the reaction above is 1.0×10^{-6} at 25°C.

(a) Write the K_{sp} expression for BaF_2.

(b) What is the concentration of F^- ions in a saturated solution of BaF_2 at 25°C?

(c) 500 milliliters of a 0.0060-molar NaF solution is added to 400 ml of a 0.0060-molar $Ba(NO_3)_2$ solution. Will there be a precipitate?

(d) What is the value of $\Delta G°$ for the dissociation of BaF_2 at 25°C?

2. $$H_2CO_3 \rightleftharpoons H^+ + HCO_3^- \qquad K_1 = 4.3 \times 10^{-7}$$

$$HCO_3^- \rightleftharpoons H^+ + CO_3^{2-} \qquad K_2 = 5.6 \times 10^{-11}$$

The acid dissociation constants for the reactions above are given at 25°C.

(a) What is the pH of a 0.050-molar solution of H_2CO_3 at 25°C?

(b) What is the concentration of CO_3^{2-} ions in the solution in (a)?

(c) How would the addition of each of the following substances affect the pH of the solution in (a)?

(i) HCl

(ii) $NaHCO_3$

(iii) NaOH

(iv) NaCl

(d) What is the value of K_{eq} for the following reaction?

$$H_2CO_3 \rightleftharpoons 2\,H^+ + CO_3^{2-}$$

3. $$N_2(g) + 3\,H_2(g) \rightleftharpoons 2\,NH_3(g) \qquad \Delta H = -92.4\text{ kJ}$$

When the reaction above took place at a temperature of 570 K, the following equilibrium concentrations were measured:

$[NH_3] = 0.20$ mol/L

$[N_2] = 0.50$ mol/L

$[H_2] = 0.20$ mol/L

(a) Write the expression for K_c and calculate its value.

(b) What is the value of K_p for the reaction?

(c) Describe how the concentration of H_2 will be affected by each of the following changes to the system at equilibrium:

(i) The temperature is increased.

(ii) The volume of the reaction chamber is increased.

(iii) N_2 gas is added to the reaction chamber.

(iv) Helium gas is added to the reaction chamber.

4. $$CaCO_3(s) \rightleftharpoons Ca^{2+}(aq) + CO_3^{2-}(aq) \qquad K_{sp} = 2.8 \times 10^{-9}$$

$$CaSO_4(s) \rightleftharpoons Ca^{2+}(aq) + SO_4^{2-}(aq) \qquad K_{sp} = 9.1 \times 10^{-6}$$

The values for the solubility products for the two reactions above are given at 25°C.

(a) What is the concentration of CO_3^{2-} ions in a saturated 1.00 liter solution of $CaCO_3$ at 25°C?

(b) Excess $CaSO_4(s)$ is placed in the solution in (a). Assume that the volume of the solution does not change.

(i) What is the concentration of the SO_4^{2-} ion?

(ii) What is the concentration of the CO_3^{2-} ion?

(c) A 0.20 mole sample of $CaCl_2$ is placed in the solution in (b). Assume that the volume of the solution does not change.

(i) What is the concentration of the Ca^{2+} ion?

(ii) What is the concentration of the SO_4^{2-} ion?

(iii) What is the concentration of the CO_3^{2-} ion?

CHAPTER 10 ANSWERS AND EXPLANATIONS

MULTIPLE-CHOICE QUESTIONS

1. **B** K_p is used for gaseous reactions, and the units used are partial pressures.

2. **D** K_w is the dissociation constant for water.

   At 25°C, $K_w = [H^+][OH^-] = 1 \times 10^{-14}$.

3. **C** K_a is known as the acid dissociation constant.

4. **E** K_{sp} is the solubility product. It always has a solid as the reactant. Since the reactant is always in the denominator and solids are ignored in the equilibrium expression, K_{sp} never has a denominator.

5. **A** From Le Chatelier's law, the equilibrium will shift to counteract any stress that is placed on it. Increasing temperature favors the endothermic direction of a reaction because the endothermic reaction absorbs the added heat. So the salt becomes more soluble, increasing the number of dissociated particles, thus increasing the value of K_{sp}.

6. **E** According to Le Chatelier's law, the equilibrium will shift to counteract any stress that is placed on it. If the temperature is decreased, the equilibrium will shift toward the side that produces energy or heat. That's the product side where I_2 is produced.

   Choices (A) and (B) are wrong because there are equal numbers of moles of gas (3 moles) on each side, so changing the volume will not affect the equilibrium. Choice (C) is wrong because the addition of a substance that does not affect the reaction will not affect the equilibrium conditions.

7. **C** From the balanced equation:

   If 1 mole of CH_3OH was created, then 1 mole of CO was consumed and 1 mole of CO remains; and if 1 mole of CH_3OH was created, then 2 moles of H_2 were consumed and 1 mole of H_2 remains. So at equilibrium, there are

   (1 mol CH_3OH) + (1 mol CO) + (1 mol H_2) = 3 moles of gas

8. **D** According to Le Chatelier's law, equilibrium will shift to relieve any stress placed on a system. If N_2 is removed, the equilibrium will shift to the right to produce more N_2, with the result that more H_2O will also be produced.

   If the volume is decreased (A), the equilibrium will shift toward the left, where there are fewer moles of gas. If the temperature is increased (B), the equilibrium will shift to the left. That's the endothermic reaction, which absorbs the added energy of the temperature increase. If NH_3 (C) or O_2 (E) is removed, the equilibrium will shift to the left to replace the substance removed.

9. **D** According to Le Chatelier's law, equilibrium will shift to relieve any stress placed on a system. If the temperature is increased, the equilibrium will shift to favor the endothermic reaction because it absorbs the added energy. In this case, the equilibrium will be shifted to the right, increasing the concentration of both K^+ and NO_3^- ions.

   Changing the volume of the solution, (A) and (B), will change the *number* of K^+ ions in solution, but not the *concentration* of K^+ ions. Since solids are not considered in the equilibrium expression, adding more solid KNO_3 to the solution (C) will not change the equilibrium. Decreasing the temperature (E) will favor the exothermic reaction, driving the equilibrium toward the left and decreasing the concentration of K^+ ions.

10. **A** The three dissociation reactions can be added to get the desired reaction as shown below.

$$(H_3C_6H_5O_7 \rightleftharpoons H^+ + H_2C_6H_5O_7^-)$$
$$+(H_2C_6H_5O_7^- \rightleftharpoons H^+ + HC_6H_5O_7^{2-})$$
$$+(HC_6H_5O_7^{2-} \rightleftharpoons H^+ + C_6H_5O_7^{3-})$$
$$H_3C_6H_5O_7 \rightleftharpoons 3\,H^+ + C_6H_5O_7^{3-}$$

When two or more reactions can be added to get a resulting reaction, their equilibrium constants can be multiplied to get the equilibrium constant of the resulting reaction.

So $K_{eq} = K_1K_2K_3 = xyz$

11. **C** From the definition of equilibrium, the rates of the forward and reverse reactions must be equal. The volume of a system has no effect on the equilibrium constant.

12. **D** $K_p = \frac{[NO]^2[Br_2]}{[NOBr]^2} = \frac{(4)^2(2)}{(4)^2} = 2$

13. **B** We can think of the reaction given in the question as the sum of two other reactions.

$$HCrO_4^- \leftrightarrow H^+ + CrO_4^{2-} \quad K_{eq} = K_a$$
$$Ca^{2+} + CrO_4^{2-} \leftrightarrow CaCrO_4 \quad K_{eq} = \frac{1}{K_{sp}}$$

Notice that we are using the reverse reaction for the solvation of $CaCrO_4$, so the reactants and products are reversed and we must take the reciprocal of the solubility product.

When reactions can be added to get another reaction, their equilibrium constants can be multiplied to get the equilibrium constant of the resulting reaction.

So $K_{eq} = (K_a)(\frac{1}{K_{sp}}) = \frac{K_a}{K_{sp}}$

14. **A** The equilibrium expression for the reaction is as follows:

$$\frac{P_{IBr}^{\ 2}}{P_{Br_2}P_{I_2}} = 300$$

When all of the values are plugged into the expression, (A) is the only choice that works.

$$\frac{(3)^2}{(0.1)(0.3)} = \frac{9}{0.03} = 300$$

15. **E** Use a table to see how the partial pressures change. Based on the balanced equation, we know that if 2 atm of $CO(g)$ were formed, then 2 atm of $H_2O(g)$ must also have formed. We also know that the reactants must have lost 2 atm each.

	$H_2(g)$	$CO_2(g)$	$H_2O(g)$	$CO(g)$
Before	6 atm	4 atm	0	0
Change	–2	–2	+2	+2
At Equilibrium	4 atm	2 atm	2 atm	2 atm

Now plug the numbers into the equilibrium expression.

$$K_{eq} = \frac{P_{H_2O}P_{CO}}{P_{H_2}P_{CO_2}} = \frac{(2)(2)}{(4)(2)} = \frac{1}{2}$$

PROBLEMS

1. (a) $K_{sp} = [Ba^{2+}][F^-]^2$

(b) Use the K_{sp} expression.

$K_{sp} = [Ba^{2+}][F^-]^2$

Two F^-s are produced for every Ba^{2+}, so $[F^-]$ will be twice as large as $[Ba^{2+}]$.

Let $x = [F^-]$

$$1.0 \times 10^{-6} = \left(\frac{x}{2}\right)(x)^2 = \frac{x^3}{2}$$

$x = [F^-] = 0.01\ M$

(c) First we need to find the concentrations of the Ba^{2+} and F^- ions.

Moles = (molarity)(volume)

Moles of Ba^{2+} = (0.0060 M)(0.400 L) = 0.0024 mol

Moles of F^- = (0.0060 M)(0.500 L) = 0.0030 mol

Remember to add the two volumes: (0.400 L) + (0.500 L) = 0.900 L

$$\text{Molarity} = \frac{\text{moles}}{\text{liters}}$$

$$\left[Ba^{2+}\right] = \frac{(0.0024\ \text{mol})}{(0.900\ \text{L})} = 0.0027M$$

$$\left[F^-\right] = \frac{(0.0030\ \text{mol})}{(0.900\ \text{L})} = 0.0033M$$

Now test the solubility expression using the initial values to find the reaction quotient.

$Q = [Ba^{2+}][F^-]^2$

$Q = (0.0027)(0.0033)^2 = 2.9 \times 10^{-8}$

Q is less than K_{sp}, so no precipitate forms.

(d) Use the standard free energy expression.

$$\Delta G^\circ = -2.303RT \log K$$

$$\Delta G^\circ = (-2.303)(8.31\text{J/mol} - \text{K})(298\ \text{K})(\log 1.0 \times 10^{-6}) = 34{,}000\ \text{J/mol}$$

The positive value of ΔG° means that the reaction is not spontaneous under standard conditions.

2. (a) Use the equilibrium expression.

$$K_1 = \frac{[H^+][HCO_3^-]}{[H_2CO_3]}$$

$$[H^+] = [HCO_3^-] = x$$

$$[H_2CO_3] = (0.050\ M - x)$$

Assume that x is small enough so that we can use $[H_2CO_3] = (0.050\ M)$

$$4.3 \times 10^{-7} = \frac{x^2}{(0.050)}$$

$$x = [H^+] = 1.5 \times 10^{-4}$$

$$\text{pH} = -\log[H^+] = -\log(1.5 \times 10^{-4}) = 3.8$$

(b) Use the equilibrium expression.

$$K_2 = \frac{[H^+][CO_3^{2-}]}{[HCO_3^-]}$$

From (a) we know: $[H^+] = [HCO_3^-] = 1.5 \times 10^{-4}$

$$5.6 \times 10^{-11} = \frac{(1.5 \times 10^{-4})[CO_3^{2-}]}{(1.5 \times 10^{-4})} = [CO_3^{2-}]$$

$$[CO_3^{2-}] = 5.6 \times 10^{-11}\ M$$

(c) (i) Adding HCl will increase $[H^+]$, lowering the pH.

(ii) From Le Chatelier's law, you can see that adding $NaHCO_3$ will cause the first equilibrium to shift to the left to try to use up the excess HCO_3^-. This will cause a decrease in $[H^+]$, raising the pH.

You may notice that adding $NaHCO_3$ will also cause the second equilibrium to shift toward the right, which should increase $[H^+]$, but because K_2 is much smaller than K_1, this shift is insignificant.

(iii) Adding NaOH will neutralize hydrogen ions, decreasing $[H^+]$ and raising the pH.

(iv) Adding NaCl will have no effect on the pH.

(d) The reaction in (d) is just the sum of the two reactions given. When two reactions can be added to give a third reaction, the equilibrium constants for those reactions can be multiplied to give K_{eq} for the third reaction.

$$K_{eq} = (K_1)(K_2) = (4.3 \times 10^{-7})(5.6 \times 10^{-11}) = 2.4 \times 10^{-17}$$

3. (a) $K_c = \dfrac{[NH_3]^2}{[N_2][H_2]^3}$

$$K_c = \frac{(0.20)^2}{(0.50)(0.20)^3} = 10$$

(b) Use the formula that relates the two constants.

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

Δn is the change in the number of moles of gas from reactants to products. So $\Delta n = -2$.

$$K_p = (10)[(0.082)(570)]^{-2} = (10)(46.7)^{-2} = 4.7 \times 10^{-3}$$

(c) (i) An increase in temperature favors the endothermic direction. In this case, that's the reverse reaction, so the concentration of H_2 will increase.

(ii) An increase in volume favors the direction that produces more moles of gas. In this case, that's the reverse direction, so the concentration of H_2 will increase.

(iii) According to Le Chatelier's law, increasing the concentration of the reactants forces the reaction to proceed in the direction that will use up the added reactants. In this case, adding the reactant N_2 will shift the reaction to the right and decrease the concentration of H_2.

(iv) The addition of He, a gas that takes no part in the reaction, will have no effect on the concentration of H_2.

4. (a) Use the solubility product.

$$K_{sp} = [Ca^{2+}][CO_3^{2-}]$$

$$[Ca^{2+}] = [CO_3^{2-}] = x$$

$$2.8 \times 10^{-9} = x^2$$

$$x = [CO_3^{2-}] = 5.3 \times 10^{-5} M$$

(b) Use the solubility product.

(i) $K_{sp} = [Ca^{2+}][SO_4^{2-}]$

$$[Ca^{2+}] = [SO_4^{2-}] = x$$

$$K_{sp} = 9.1 \times 10^{-6} = x^2$$

$$x = [SO_4^{2-}] = 3.0 \times 10^{-3} M$$

(ii) $K_{sp} = [Ca^{2+}][CO_3^{2-}]$

Now use the value of $[Ca^{2+}]$ that you found in (b)(i).

$$[Ca^{2+}] = x = 3.0 \times 10^{-3} M$$

$$K_{sp} = 2.8 \times 10^{-9} = (3.0 \times 10^{-3})[CO_3^{2-}]$$

$$[CO_3^{2-}] = 9.3 \times 10^{-7} M$$

(c) (i) The $CaCl_2$ dissociates completely, so the solution can be assumed to contain 0.2 moles of Ca^{2+} ions. We can ignore the ions from $CaCO_3$ and $CaSO_4$ because there are so few of them.

$$\text{Molarity} = \frac{\text{moles}}{\text{volume}}$$

$$\left[Ca^{2+}\right] = \frac{(0.20\text{mol})}{(1\text{ L})} = 0.20M$$

(ii) Use K_{sp} again with the new value of $[Ca^{2+}]$.

$$K_{sp} = \left[Ca^{2+}\right]\left[SO_4^{2-}\right]$$

$$9.1 \times 10^{-6} = (0.20)\left[SO_4^{2-}\right]$$

$$\left[SO_4^{2-}\right] = 4.6 \times 10^{-5}M$$

(iii) Use K_{sp} again with the new value of $[Ca^{2+}]$.

$$K_{sp} = \left[Ca^{2+}\right]\left[CO_3^{2-}\right]$$

$$2.8 \times 10^{-9} = (0.20)\left[CO_3^{2-}\right]$$

$$\left[CO_3^{2-}\right] = 1.4 \times 10^{-8}M$$