

CHEMICAL EQUILIBRIUM

Reversible Reactions and Equilibrium

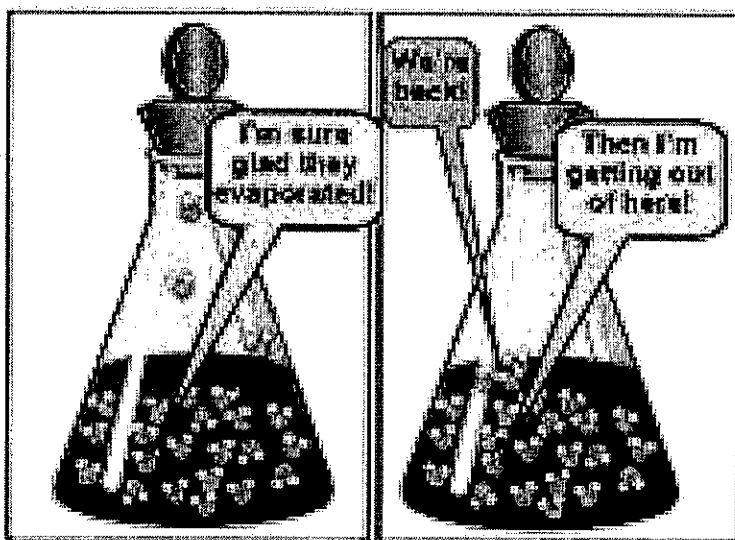
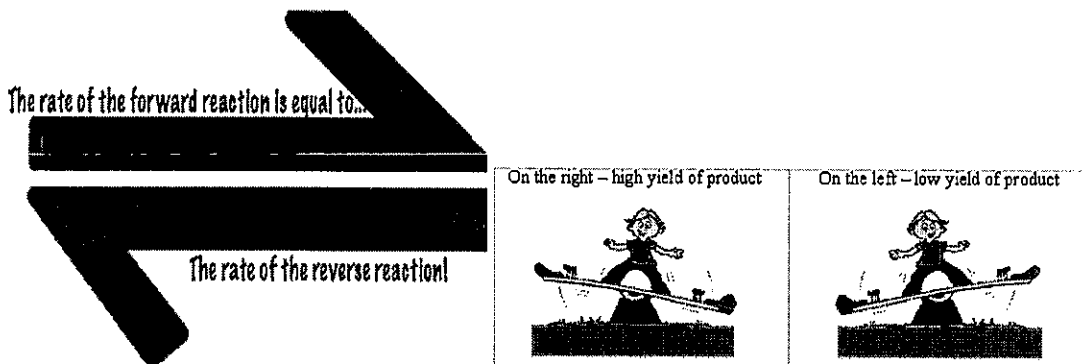
Rates of Reaction

Equilibrium Constant: K_{eq} , K_c

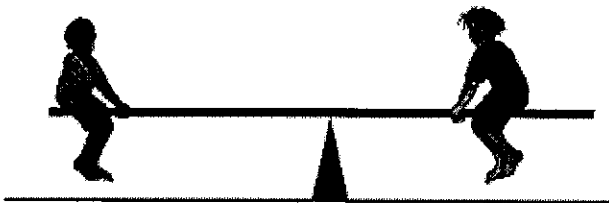
Solubility Product: K_{sp}

Factors that affect Equilibrium and LeChatliers Principle

Common Ion Effect



**METHYL IS
RED
BROMOTHYMOL IS
BLUE
I WANT TO
ESTABLISH A
CHEMICAL
EQUILIBRIUM
WITH YOU**

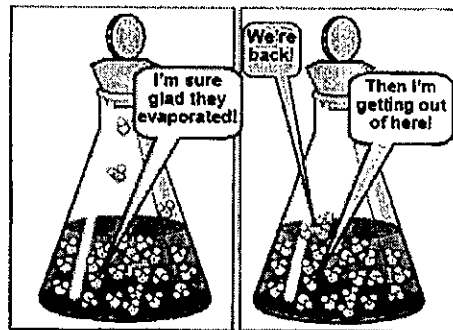


The Ins and Outs of Equilibrium

If you leave a closed, partly filled bottle of water in the sunlight, before long you will observe water droplets near the top of the bottle and in the neck. How did they get there? As the sun shines on the bottle, the water begins to evaporate. As the number of vapor molecules increases, so does the chance that they will interact with each other and recondense to form water. This is how the water droplets get to the top of the bottle.

Changing phase is a reversible process. In a closed container, as the amount of vapor increases and the amount of liquid decreases, the rate of condensation increases and the rate of vaporization decreases. Eventually the two rates become equal. When the rate of vaporization is equal to the rate of condensation, the amount of vapor and the amount of liquid stops changing. This is called **equilibrium**. Just because the rate of vaporization and condensation is equal at equilibrium, it doesn't mean that the amount of vapor and the amount of liquid is equal. For example, the amount of gas at equilibrium will be greater at a high temperature than at a low temperature.

There are other kinds of equilibrium besides phase equilibrium. Some chemical reactions are reversible and reach equilibrium too. When undissolved solid sits at the bottom of a saturated solution, there is solution equilibrium. It may look like the same undissolved solid at the bottom of the container the entire time, but dissolved material comes out of solution and new material dissolves continuously. Only the amount of undissolved material remains the same. This is often called **dynamic equilibrium** because there is constant activity although there is no real change.



The social dynamics of phase equilibrium

Answer the questions below based on the reading above and on your knowledge of chemistry.

1. What is a reversible reaction? _____

2. What is equilibrium? _____

3. The double replacement between silver nitrate solution and sodium chloride solution is written with a single arrow. $[\text{AgNO}_3(\text{aq}) + \text{NaCl}(\text{aq}) \rightarrow \text{NaNO}_3(\text{aq}) + \text{AgCl}(\text{s})]$ The double replacement between potassium iodide solution and lithium hydrogen carbonate is written with a double arrow. $[\text{KI}(\text{aq}) + \text{LiHCO}_3(\text{aq}) \rightleftharpoons \text{KHCO}_3(\text{aq}) + \text{LiI}(\text{aq})]$
 - a. What does the double arrow probably mean? _____
 - b. What accounts for the difference between the two reactions? _____

 - c. Will the reaction $\text{AgNO}_3(\text{aq}) + \text{NaCl}(\text{aq}) \rightarrow \text{NaNO}_3(\text{aq}) + \text{AgCl}(\text{s})$ ever reach equilibrium? Explain. _____

KINETICS AND EQUILIBRIUM

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4. An extremely soluble salt is added to water, and all of it dissolves. Is it at equilibrium? Explain. _____

5. A slightly soluble salt is added to water, and some of it dissolves. Is it at equilibrium? Explain. _____

6. Liquid water and water vapor reach equilibrium only in a closed container. Why? _____

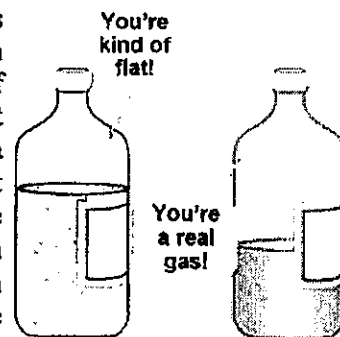
7. Explain equilibrium based on collision theory. _____

8. A glass of ice water is at equilibrium.
- What is its temperature? _____
 - What is happening to the amount of ice in the ice-water mixture? _____
 - What is happening to the amount of water in the ice-water mixture? _____
 - How does the amount of ice compare to the amount of water? _____
 - Describe what is happening in the ice-water mixture if the system is at equilibrium. _____

9. The reaction $\text{H}_2\text{O}(l) + \text{CO}_2(aq) \rightleftharpoons \text{H}_2\text{CO}_3(aq)$ is at equilibrium. What does this mean? _____

Are All Equilibria Created Equal?

Two bottles of soda are sitting in the refrigerator. One is almost full. The other is almost empty. Slowly, the sodas are going flat. This is because the dissolved carbon dioxide is coming out of solution and going into the air space above. Of course, if you keep the bottle closed tightly, the soda doesn't go flat as fast. If the gas can't escape, it soon reaches equilibrium with the solution below. But are all equilibria the same? Does the almost empty bottle retain as much carbonation as the almost full bottle? The soda with the larger air space has more room for the carbon dioxide gas to spread out. As a result the gas particles are under lower pressure and have a lower concentration. This makes it easier for them to come out of solution. When the almost empty bottle reaches equilibrium, it will have more carbon dioxide in the space above the liquid and less carbon dioxide dissolved than the almost full bottle has. It will be flat.



When sodas discuss solution equilibrium

Equilibrium doesn't mean equal amounts of reactants and products. It means the reactants are turning into products at the same rate that the products are turning back to reactants. Many factors influence equilibrium. These include temperature, pressure, and concentration.

Answer the questions below based on the reading above, and on your knowledge of chemistry.

1. A reversible reaction is at equilibrium. The forward reaction is exothermic.
 - a. Is the reverse reaction exothermic or endothermic? _____
 - b. Which has the higher activation energy, the forward reaction or the reverse? _____
 - c. What affect does raising the temperature have on the speed of reaction for the forward reaction? Why? _____

 - d. What affect does raising the temperature have on the speed of reaction for the reverse reaction? Why? _____

 - e. Will the rate of the forward reaction and the reverse reaction be affected to the same extent by an increase in temperature? Explain. _____

Continue

-
-
2. A reversible reaction is at equilibrium. More reactant is added.
- Will the reaction remain at equilibrium after adding more reactant? Explain. _____

 - What happens to the probability of effective collisions on the reactant side when more reactant is added?

 - If a new equilibrium is reached how will the amount of reactant and product compare to the amounts in the old equilibrium. Explain. _____

 - In what direction does equilibrium shift when more reactants are added? _____

 - What would happen if more product was added? Explain. _____

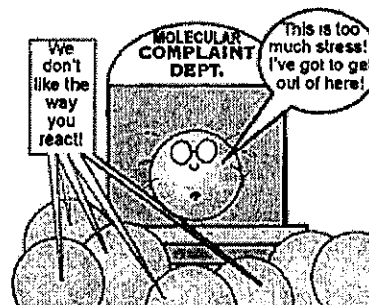
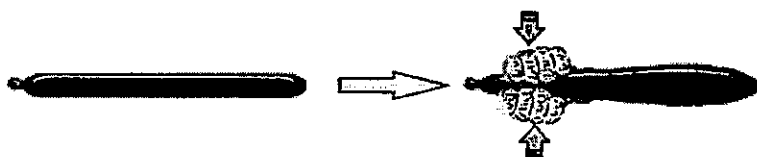
3. The following reversible reaction occurs in a closed chamber: $2A(g) + 3B(g) \rightleftharpoons 4C(g) + 6D(g)$
- How many moles of reactant are there to every mole of product? _____
 - If the pressure in the chamber is increased, what affect, if any, will it have on the concentration of either the reactant or the product? _____
 - Will the concentration of the reactants be affected to the same extent as the concentration of the products by an increase in pressure? Explain. _____

 - Will the reaction remain at equilibrium after increasing the pressure? Explain. _____

 - In what direction does equilibrium shift as a result of the increase in pressure? Explain. _____

Relieving Stress in Chemistry

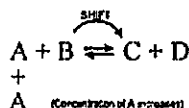
You squeeze a long balloon on one side. Air moves toward the other side causing the balloon to bulge. As a result, the pressure is reduced on the side where you are squeezing. The air moves in a way that relieves the pressure. See below.



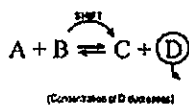
All systems respond in a way that relieves stress. Pressure is an example of a stress. Chemical reactions respond in a way that relieves stress too. This is known as *Le Chatelier's principle*. According to Le Chatelier's principle, when stress is applied to a system in equilibrium, the reaction will shift in a direction that relieves the stress and a new equilibrium will be established. Applied stresses include changes in concentration, pressure, or temperature. Following are descriptions of how reactions at equilibrium respond to these specific stresses:

CHANGE IN CONCENTRATION

- shift due to increase in concentration of a reactant

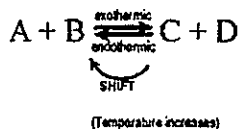


- shift due to decrease in concentration of a product

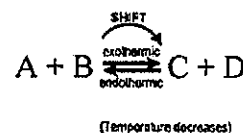


CHANGE IN TEMPERATURE

- shift due to increase in temperature

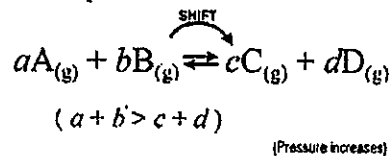


- shift due to decrease in temperature

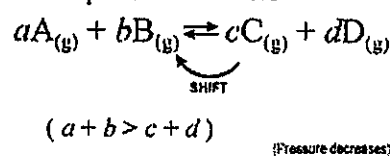


CHANGE IN PRESSURE

- shift due to pressure increases



- shift due to pressure decreases



Le Chatelier's principle applies only to reversible reactions at equilibrium, but it gives some insight into end reactions as well. When a precipitate, a gas, or water forms the reaction is not reversible. These are products that are not available for reaction. When they form, it is as if the concentration of one of the products in an equilibrium system is reduced to zero by removing it as soon as it is produced. Le Chatelier predicts that the reaction will shift in the direction of forming more product.

Continue

Answer the questions below based on your reading and on your knowledge of chemistry.

1. For each of the following, what effect would an increase in pressure have on equilibrium?
 - a. $\text{N}_2(\text{g}) + 3\text{H}_2(\text{g}) \rightleftharpoons 2\text{NH}_3(\text{g})$ _____
 - b. $4\text{H}_2(\text{g}) + \text{CS}_2(\text{g}) \rightleftharpoons \text{CH}_4(\text{g}) + 2\text{H}_2\text{S}(\text{g})$ _____
 - c. $\text{CO}(\text{g}) + \text{H}_2\text{O}(\text{g}) \rightleftharpoons \text{H}_2(\text{g}) + \text{CO}_2(\text{g})$ _____
 - d. $\text{H}_2(\text{g}) + \text{F}_2(\text{g}) \rightleftharpoons 2\text{HF}(\text{g})$ _____
 - e. $\text{PCl}_5(\text{g}) \rightleftharpoons \text{PCl}_3(\text{g}) + \text{Cl}_2(\text{g})$ _____
2. For each of the following, what effect would an increase in temperature have on equilibrium?
 - a. $\text{N}_2(\text{g}) + 3\text{H}_2(\text{g}) \rightleftharpoons 2\text{NH}_3(\text{g}) \quad \Delta H = -92 \text{ kJ}$ _____
 - b. $\text{C}(\text{s}) + \text{H}_2\text{O}(\text{g}) + \text{heat} \rightleftharpoons \text{CO}(\text{g}) + \text{H}_2(\text{g})$ _____
 - c. $\text{PCl}_5(\text{g}) + \text{Cl}_2(\text{g}) \rightleftharpoons \text{PCl}_3(\text{g}) + \text{heat}$ _____
 - d. $2\text{SO}_2(\text{g}) + \text{O}_2(\text{g}) \rightleftharpoons 2\text{SO}_3(\text{g}) + \text{heat}$ _____
 - e. $\text{H}_2\text{O}(\text{l}) \rightleftharpoons \text{H}^+(\text{aq}) + \text{OH}^-(\text{aq}) \quad \Delta H = 55.8 \text{ kJ}$ _____
3. For the reaction, $\text{H}_2(\text{g}) + \text{I}_2(\text{g}) \rightleftharpoons 2\text{HI}(\text{g})$ [$\Delta H = 52.7 \text{ kJ}$], what effect will each of the following have on equilibrium?
 - a. Addition of $\text{H}_2(\text{g})$ _____
 - b. Removal of $\text{I}_2(\text{g})$ _____
 - c. Increase in temperature _____
 - d. Increase in pressure _____
 - e. Addition of $\text{HI}(\text{g})$ _____
4. Explain LeChatelier's principal based on collision theory. _____

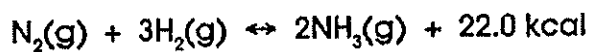
5. If heat speeds up all reactions, both forward and reverse, why does it effect equilibrium? _____

LE CHATELIER'S PRINCIPLE

Name _____

Le Chatelier's Principle states that when a system at equilibrium is subjected to a stress, the system will shift its equilibrium point in order to relieve the stress.

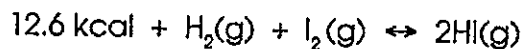
Complete the following chart by writing left, right or none for equilibrium shift, and decreases, increases or remains the same for the concentrations of reactants and products, and for the value of K.



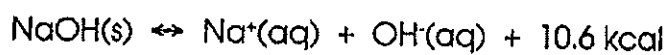
Stress	Equilibrium Shift	[N ₂]	[H ₂]	[NH ₃]	K
1. Add N ₂	right	_____	decreases	increases	remains the same
2. Add H ₂			_____		
3. Add NH ₃				_____	
4. Remove N ₂		_____			
5. Remove H ₂			_____		
6. Remove NH ₃				_____	
7. Increase Temperature					
8. Decrease Temperature					
9. Increase Pressure					
10. Decrease Pressure					

LE CHATELIER'S PRINCIPLE CONTINUED

Name _____



Stress	Equilibrium Shift	[H ₂]	[I ₂]	[HI]	K
1. Add H ₂	right	_____	decreases	increases	remains the same
2. Add I ₂			_____		
3. Add HI				_____	
4. Remove H ₂		_____			
5. Remove I ₂			_____		
6. Remove HI				_____	
7. Increase Temperature					
8. Decrease Temperature					
9. Increase Pressure					
10. Decrease Pressure					



(Remember that pure solids and liquids do not affect equilibrium values.)

Stress	Equilibrium Shift	Amount NaOH(s)	[Na ⁺]	[OH ⁻]	K
1. Add NaOH(s)		_____			
2. Add NaCl (Adds Na ⁺)			_____		
3. Add KOH (Adds OH ⁻)				_____	
4. Add H ⁺ (Removes OH ⁻)				_____	
5. Increase Temperature					
6. Decrease Temperature					
7. Increase Pressure					
8. Decrease Pressure					

Activity 6-6

Chemical Equilibrium II

Factors affecting equilibrium

- List the four factors from Activity 6-1 that affect rate of reaction. _____

- Which one of the above factors does *not* affect systems at equilibrium? Explain why. _____

- Explain why the amount of surface area of a reactant is a factor only in heterogeneous reactions (those that have components in more than one phase). _____

- Complete this statement of Le Chatelier's Principle: When a system at _____ is subjected to a _____, the equilibrium will _____ in the direction that tends to _____ the effect of the stress and move toward a new equilibrium.

Changes in equilibrium conditions

Changes in conditions of concentration, temperature, or pressure for systems at equilibrium are given in questions 5-8. In each example, all conditions other than the one specified remain constant. Choose one of the following to fill in the blanks in each table.

I—increases D—decreases R—remains the same

• Concentration Changes

5. For the system $A(g) + 2B(g) \rightleftharpoons C(g) + D(g)$

	As number of moles of B increases	As number of moles of B decreases
Rate of forward reaction		
Rate of reverse reaction		
moles A		
[A]		
moles C		
[C]		
moles D		
[D]		

- Temperature Changes

6. For the system $A(g) + B(g) + \text{heat} \rightleftharpoons C(g) + D(g)$

	As temperature increases	As temperature decreases
Rate of forward reaction		
Rate of reverse reaction		
[A]		
[B]		
[C]		
[D]		

7. For the system $A(g) + B(g) \rightleftharpoons C(g) + D(g) + \text{heat}$

	As temperature increases	As temperature decreases
Rate of forward reaction		
Rate of reverse reaction		
[A]		
[B]		
[C]		
[D]		

- Pressure Changes

8. For the system $A(g) + B(g) \rightleftharpoons 2C(g) + 3D(g)$

	As pressure increases	As pressure decreases
Rate of forward reaction		
Rate of reverse reaction		
Moles of A		
Moles of B		
Moles of C		
Moles of D		

NAME: _____ DATE: _____ SECTION _____ ACTIVITY _____

Life is like riding a bicycle.
To keep your balance you must keep moving.

Background:

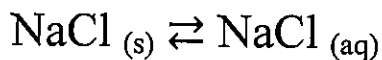
In a chemical process, chemical equilibrium is the state in which the chemical activities or concentrations of the reactants and products have no net change over time. Usually, this would be the state that results when the forward chemical process proceeds at the same rate as their reverse reaction. The reaction rates of the forward and reverse reactions are generally not zero but, being equal; there are no net changes in any of the reactant or product concentrations. This process is called dynamic equilibrium.

There are 3 types of equilibrium seen in chemistry: phase, solution and chemical.

For each of the following scenarios describe the equilibrium process.

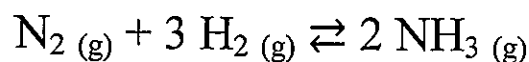
- 1) An ice cube is placed in a glass of water exactly at 0°C.
 - a) Write the equilibrium equation.
 - b) Based on your equation describe the forward reaction.
 - c) Based on your equation describe the reverse reaction.
 - d) In a sentence describe the rates of the forward and reverse reactions for the ice/water mixture is at equilibrium at °C.
 - e) Describe how the rates of the forward and reverse reactions will change if the temperature increases to 15°C.

2) An excess amount of NaCl (s) is dissolved in water to form a saturated solution.



- Based on the equation describe the forward reaction.
- Based on the equation describe the reverse reaction.
- In a sentence describe the rates of the forward and reverse reactions for the saturated solution.
- Discuss in terms of the forward and reverse reaction why heating this saturated solution will cause more solid NaCl to dissolve.

3) One mole of nitrogen gas and three moles of hydrogen gas are in equilibrium with two moles of ammonia gas.



- Based on the equation describe the forward reaction.
- Based on the equation describe the reverse reaction.
- In a sentence describe the rates of the forward and reverse reactions for the chemical equilibrium.
- In terms of the species involved in the reaction describe what would occur if the rate of the forward reaction were to increase.
- In terms of the species involved in the reaction describe what would occur if the rate of the reverse reaction were to increase.

Questions:

- 1) Which is a proper description of chemical equilibrium?
 - (1) The frequencies of reactant and of product collisions are identical.
 - (2) The concentrations of products and reactants are identical.
 - (3) The velocities of product and reactant molecules are identical.
 - (4) Reactant molecules are forming products as fast as product molecules are reacting to form reactants.
 - (5) The numbers of moles of reactants and products are equal.
- 2) Describe the effect of a catalyst on the forward and reverse reaction rates.
- 3) Which of the above 3 scenarios will be affected by changes in pressure? Explain.
- 4) Describe a real word situation which mimics a dynamic equilibrium.

Reflection:

Describe the rates of the forward and reverse reactions under equilibrium conditions.

Describe the concentration of the reactants and products under equilibrium conditions.

The title to this activity is a quote by Albert Einstein. Discuss how it applies to the concept of dynamic equilibrium.

Law of Chemical Equilibrium

The law of chemical equilibrium is shown in the box to the right. For the reaction $aA + bB \rightleftharpoons cC + dD$, A and B represent the reactants, C and D represent the products, and a , b , c , and d represent the respective coefficients. The equilibrium expression is equal to the multiple of the concentrations of the products raised to the power of their respective coefficients divided by the multiple of the reactants raised to the power of their respective coefficients.

If $aA + bB \rightleftharpoons cC + dD$

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

There are several things that can be done to interpret equilibrium using the law. First, since the numerator of the fraction is based on the concentration of the products, an equilibrium constant greater than one ($K_{eq} > 1$) refers to a reaction that favors the formation of product, while an equilibrium constant less than one ($K_{eq} < 1$) refers to a reaction that favors the formation of the reactants [example (a)]. Second, appropriate equilibrium expressions need to be written based on the balanced equation [example (b)]. And third, mathematical problems can be done substituting values for the concentration into the equilibrium expression, either to determine if equilibrium has been reached, or to determine the equilibrium concentration of one of the reactants or products. [examples (c) and (d)].

Sample Problems

The reaction $H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$ is at equilibrium at 1 atm and 298 K. The equilibrium constant for the reaction at 1 atm and 298 K is as follows: $K_{eq} = 3.5 \times 10^{-1}$

(a) Which is favored, the forward or the reverse reaction?

Answer: The reverse reaction is favored ($K_{eq} < 1$)

(b) What is the equilibrium expression?

Answer:

$$3.5 \times 10^{-1} = \frac{[HI]^2}{[H_2][I_2]}$$

(c) If the concentration of hydrogen iodide is $2.65 \times 10^{-2} M$, the concentration of hydrogen is $5.0 \times 10^{-3} M$, and the concentration of iodine is $4.0 \times 10^{-1} M$, is the reaction at equilibrium?

Answer:

$$K_{eq} = \frac{(2.65 \times 10^{-2})^2}{(5.0 \times 10^{-3})(4.0 \times 10^{-1})} = 3.5 \times 10^{-1}$$

(d) If the reaction is at equilibrium, what is the concentration of hydrogen iodide if the concentration of hydrogen is $3.0 \times 10^{-3} M$, and the concentration of iodine is $2.5 \times 10^{-2} M$?

Answer:

Yes!

$$3.5 \times 10^{-1} = \frac{[HI]^2}{(3.0 \times 10^{-3})(2.5 \times 10^{-2})}$$

$$[HI] = \sqrt{(3.5 \times 10^{-1})(3.0 \times 10^{-3})(2.5 \times 10^{-2})}$$

$$[HI] = \sqrt{2.625 \times 10^{-5}} = 5.1 \times 10^{-3} M$$

NEXT PAGE 

Refer to the table below to answer the questions that follow (assume all reactions are at 1 atm and 298 K):

CONSTANTS FOR VARIOUS EQUILIBRIA AT 1 atm AND 298 K			
$\text{H}_2\text{O}(\ell) = \text{H}^+(\text{aq}) + \text{OH}^-(\text{aq})$		$K_w = 1.0 \times 10^{-14}$	
$\text{H}_2\text{O}(\ell) + \text{H}_2\text{O}(\ell) = \text{H}_3\text{O}^+(\text{aq}) + \text{OH}^-(\text{aq})$		$K_w = 1.0 \times 10^{-14}$	
$\text{CH}_3\text{COO}^-(\text{aq}) + \text{H}_2\text{O}(\ell) = \text{CH}_3\text{COOH}(\text{aq}) + \text{OH}^-(\text{aq})$		$K_b = 5.6 \times 10^{-10}$	
$\text{NaF}(\text{aq}) + \text{H}_2\text{O}(\ell) = \text{Na}^+(\text{aq}) + \text{OH}^-(\text{aq}) + \text{HF}(\text{aq})$		$K_b = 1.5 \times 10^{-11}$	
$\text{NH}_3(\text{aq}) + \text{H}_2\text{O}(\ell) = \text{NH}_4^+(\text{aq}) + \text{OH}^-(\text{aq})$		$K_b = 1.8 \times 10^{-5}$	
$\text{CO}_3^{2-}(\text{aq}) + \text{H}_2\text{O}(\ell) = \text{HCO}_3^-(\text{aq}) + \text{OH}^-(\text{aq})$		$K_b = 1.8 \times 10^{-4}$	
$\text{Ag}(\text{NH}_3)_2^+(\text{aq}) = \text{Ag}^+(\text{aq}) + 2\text{NH}_3(\text{aq})$		$K_{eq} = 8.9 \times 10^{-8}$	
$\text{N}_2(\text{g}) + 3\text{H}_2(\text{g}) = 2\text{NH}_3(\text{g})$		$K_{eq} = 6.7 \times 10^5$	
$\text{H}_2(\text{g}) + \text{I}_2(\text{g}) = 2\text{HI}(\text{g})$		$K_{eq} = 3.5 \times 10^{-1}$	
Compound	K_{sp}	Compound	K_{sp}
AgBr	5.0×10^{-13}	Li_2CO_3	2.5×10^{-2}
AgCl	1.8×10^{-10}	PbCl_2	1.6×10^{-5}
Ag_2CrO_4	1.1×10^{-12}	PbCO_3	7.4×10^{-4}
AgI	8.3×10^{-17}	PbCrO_4	2.8×10^{-13}
BaSO_4	1.1×10^{-10}	PbI_2	7.1×10^{-9}
CaSO_4	9.1×10^{-6}	ZnCO_3	1.4×10^{-11}

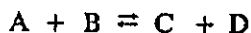
- A solution of ammonia is prepared [$\text{NH}_3(\text{aq}) + \text{H}_2\text{O}(\ell) = \text{NH}_4^+(\text{aq}) + \text{OH}^-(\text{aq})$]
 - Which is favored, the forward or reverse reaction? _____
 - What is the equilibrium expression?
 - If the reaction is at equilibrium and $[\text{NH}_4^+] = [\text{OH}^-] = 7.35 \times 10^{-3} \text{ M}$, what is the concentration of $\text{NH}_3(\text{aq})$?
- Ammonia is prepared from its elements [$\text{N}_2(\text{g}) + 3\text{H}_2(\text{g}) = 2\text{NH}_3(\text{g})$]
 - Which is favored, the forward or reverse reaction? _____
 - What is the equilibrium expression?
 - If the reaction is at equilibrium, $[\text{N}_2] = 0.500 \text{ M}$, and $[\text{H}_2] = 0.300 \text{ M}$, what is the concentration of $\text{NH}_3(\text{g})$?

Activity 6-5

Chemical Equilibrium I

The nature of equilibrium

1. A reaction in which the products can recombine, under suitable conditions, to produce the reactants is called a _____ reaction.
2. When the rate of the forward reaction in a reversible reaction such as



equals the rate of the reverse reaction, a state of chemical _____ exists.

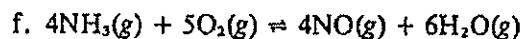
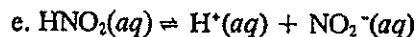
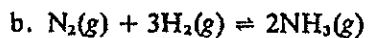
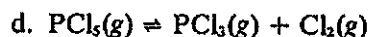
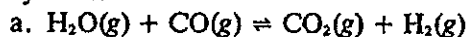
The mass-action expression

3. The mass-action expression for any reversible chemical reaction $aA + bB \rightleftharpoons cC + dD$ has the form

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

where the symbols [] are used to represent _____ in moles per liter.

Write the mass-action expressions for each of the following reversible, homogeneous reaction systems.



The equilibrium constant

For systems at equilibrium, the numerical value of the mass-action expression equals the equilibrium constant:

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

4. Numerical values for the equilibrium constant are always _____ (positive/negative). They show the extent to which a reaction proceeds to form products.

When the value of the equilibrium constant is _____ (*large/small*), the equilibrium favors the formation of products. When the value of the constant is _____ (*large/small*), the equilibrium favors the formation of reactants.

Achieving equilibrium

5. The reversible reaction $2A(g) + 3B(g) \rightleftharpoons C(g) + 2D(g)$ takes place in a 10-liter container. The amounts of the reactants in the original mixture and the amounts of B at equilibrium are given in the following table. Calculate the missing amounts and write them in the table.

	A(g)	B(g)	C(g)	D(g)
Moles in original mixture	4.0	5.0	_____	_____
Change due to chemical reaction				
Moles at equilibrium		2.6		
Concentration in moles/L at equilibrium		0.26		

6. Write the mass-action expression for the reaction in question 5.
7. Using values from the table above, calculate the numerical value for the equilibrium constant for the reaction in question 5.
8. The reversible reaction $A(g) \rightleftharpoons B(g) + 2C(g)$ takes place in a 5.0-liter flask. Complete the following table for this reaction.

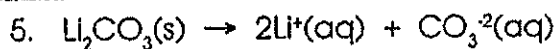
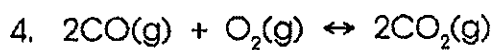
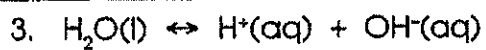
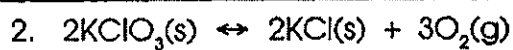
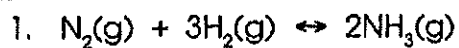
	A(g)	B(g)	C(g)
Moles in original mixture	0.75	_____	_____
Change due to chemical reaction			
Moles at equilibrium			0.30
Concentration in moles/L at equilibrium			

9. Write the mass-action expression for the reaction in question 8.
10. Calculate the numerical value for the equilibrium constant for the reaction in question 8.

EQUILIBRIUM CONSTANT (K)

Name _____

Write the expression for the equilibrium constant K for the reactions below.



CALCULATIONS USING THE EQUILIBRIUM CONSTANT

Name _____

Using the equilibrium constant expressions you determined on page 79, calculate the value of K when:

1. $[\text{NH}_3] = 0.0100 \text{ M}$, $[\text{N}_2] = 0.0200 \text{ M}$, $[\text{H}_2] = 0.0200 \text{ M}$

2. $[\text{O}_2] = 0.0500 \text{ M}$

3. $[\text{H}^+] = 1 \times 10^{-8} \text{ M}$, $[\text{OH}^-] = 1 \times 10^{-6} \text{ M}$

4. $[\text{CO}] = 2.0 \text{ M}$, $[\text{O}_2] = 1.5 \text{ M}$, $[\text{CO}_2] = 3.0 \text{ M}$

5. $[\text{Li}^+] = 0.2 \text{ M}$, $[\text{CO}_3^{2-}] = 0.1 \text{ M}$

NAME: _____ DATE: _____ PERIOD _____ LAB _____

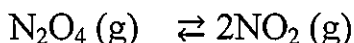
Why are you CONSTANTLY doing this?

Background:

By using the equilibrium expression K_{eq} you can determine in which direction a reaction will like to go. By filling in the K_{eq} for a number of reactions you will be able to determine in which direction does a large K_{eq} favor and a small K_{eq} . The only variable that can change the K_{eq} is temperature.

Problems:

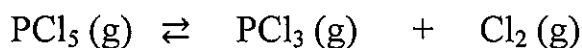
1) Write the K_{eq} expression for the following reaction.



A) Substitute the following concentrations $[\text{N}_2\text{O}_4] = 0.0014\text{M}$ and $[\text{NO}_2] = 0.0172\text{M}$. Calculate the equilibrium constant.

B) By looking at the K_{eq} and the concentrations which side is favored by the equilibrium?

2) Write the K_{eq} expression for the following reaction.



A) Substitute the following concentrations: $[\text{PCl}_5] = 1.271\text{M}$, $[\text{PCl}_3] = 0.229\text{M}$, and $[\text{Cl}_2] = 0.229\text{M}$. Calculate the constant.

B) By looking at the K_{eq} and the concentrations which side is favored by the equilibrium?

16A

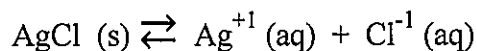
3) Write the K_{eq} expression for the following reaction.



A) Substitute the following concentrations: $[\text{HI}] = 0.389 \text{ M}$, $[\text{H}_2] = 0.0505 \text{ M}$, and $[\text{I}_2] = 0.0505 \text{ M}$. Calculate the constant.

B) By looking at the K_{eq} and the concentrations which side is favored by the equilibrium?

4) Write the K_{sp} expression for the following reaction.



A) Substitute the following concentrations: $[\text{Ag}^+] = 0.0000134$ and $[\text{Cl}^-] = 0.0000134$. Calculate the constant.

B) By looking at the K_{eq} and the concentrations which side is favored by the equilibrium?

C) Using Table F in your CRT, what is silver chloride's solubility? How does this K_{sp} value relate to a substance's solubility?

D) Using Table F in your CRT, would you expect sodium bromide to have a large K_{sp} or a small K_{sp} ? Why?

E) Using Table E in your CRT, which substance would have the larger K_{sp} : Calcium Hydroxide or Lead Hydroxide? Why?

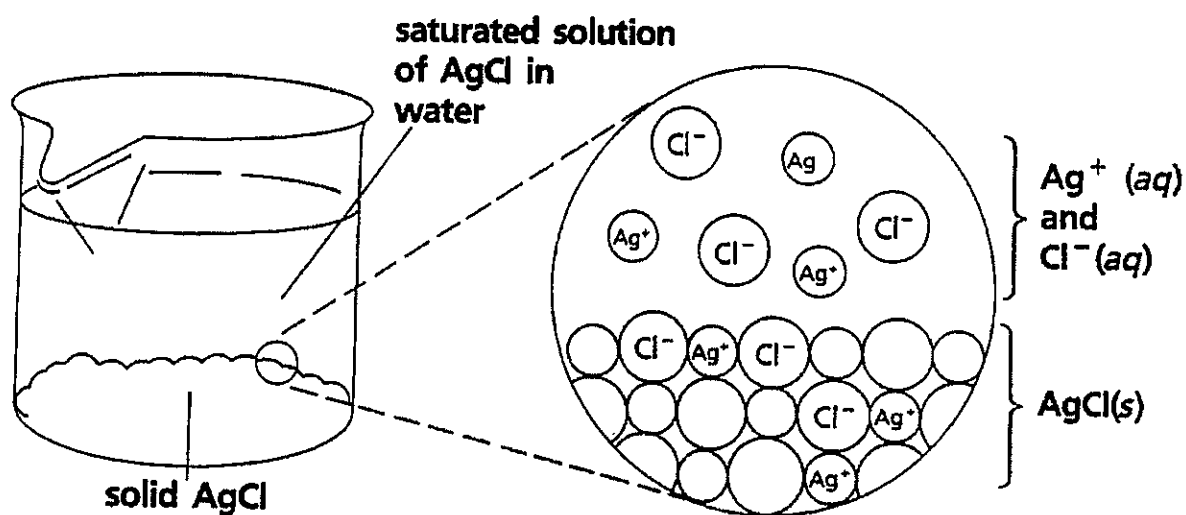
5) Write reaction and the K_{sp} expression for the dissociation of CuCrO_4 (s):

Given that the K_{sp} for this reaction is 3.6×10^{-6} calculate the concentrations of the Cu^{+2} ions and the CrO_4^{-2} ions.

6) Write reaction and the K_{sp} expression for the dissociation of PbCl_2 (s):

Using a K_{sp} 1.57×10^{-5} value, calculate the concentrations of the Pb^{+2} ions and the Cl^{-1} ions.

Solubility Equilibrium in a Saturated Solution of AgCl



$$\text{Rate}_{\text{FWD}} = \text{Rate}_{\text{REV}}$$

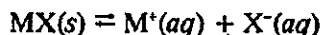
The rate at which solid AgCl dissolves is equal to the rate at which dissolved ions of Ag⁺ and Cl⁻ precipitate out of solution to become part of the solid phase.

Activity 6-7

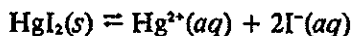
Solubility Equilibrium I

Dissociation equations

A type of chemical equilibrium exists between excess solid in contact with a saturated solution of that solid in water. If $MX(s)$ represents a slightly soluble compound, then the general dissociation equation



represents the equilibrium that exists between the excess solid phase of the compound and its dissolved ions, M^+ and X^- , in a saturated aqueous solution. A number of slightly soluble compounds are listed in reference table C in the Appendix. For any of these compounds, we can write a dissociation equation. For example, the dissociation equation for mercury (II) iodide is:

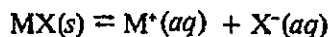


Write dissociation equations for each of the following.

1. barium chromate _____
2. aluminum phosphate _____
3. mercury (I) carbonate _____
4. copper (I) sulfide _____
5. silver chloride _____

Solubility product constant

From the equation



we can derive the mass-action expression

$$\frac{[M^+] \times [X^-]}{[MX(s)]}$$

Then, the equilibrium constant for the system would be

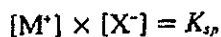
$$\frac{[M^+] \times [X^-]}{[MX(s)]} = K_{sp}$$

6. However, since the solid phase cannot become more dilute or concentrated, its concentration is _____ (*constant/variable*).
7. Thus, the solubility equilibrium is described by rearranging the terms of the above expression:



In this arrangement, the variable terms are collected on the _____ (*right/left*) of the equals sign, with the constant terms on the _____ (*right/left*).

8. The collected constants on the right are given the symbol K_{sp} , representing solubility equilibrium:

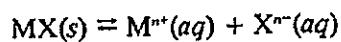


The product of the concentrations of the ions, K_{sp} , is a constant, called the _____ constant.

Molar solubility

The solubility product constant, K_{sp} , gives a measure of the solubility of the solute in moles per liter at 25°C. For substances that dissolve and dissociate in a similar manner, comparison of the values of K_{sp} for each substance permits comparison of molar solubility.

Table K in the Appendix lists 8 compounds with their K_{sp} values. In this table, find the 6 compounds that dissociate according to the general equation

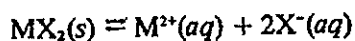


For each of the 6 compounds, write the dissociation equation, the ion-product expression, and the value of K_{sp} .

Equation	Ion-product expression	Value of $K_{sp}(25^\circ\text{C})$
9.		
10.		
11.		
12.		
13.		
14.		

15. List these 6 compounds in order of increasing molar solubility. _____

In table K there are two compounds that dissociate according to the general equation



For each of those 2 compounds, write the dissociation equation, the ion-product expression, and the value of K_{sp} .

Equation	Ion-product expression	Value of $K_{sp}(25^\circ\text{C})$
16.		
17.		

SOLUBILITY PRODUCT CONSTANT (K_{sp})

Name _____

1. What is the solubility, in moles/liter, of AgBr if the $K_{sp} = 5.0 \times 10^{-13}$?

2. If the solubility of $Li_2CO_3 = 0.15$ moles/liter, what is its K_{sp} at this temperature?

3. What is the solubility, in moles/liter, of PbI_2 if the $K_{sp} = 8.5 \times 10^{-9}$?

4. If the solubility of $Ag_2CrO_4 = 7.2 \times 10^{-5}$ moles/liter, what is its K_{sp} ?

5. How many moles of AgCl will dissolve in 500. mL of water if the $K_{sp} = 1.7 \times 10^{-10}$?

Activity 6-8

Solubility Equilibrium II

Calculating K_{sp} from solubility data

When the solubility in grams per liter (or moles per liter) of a substance is known, we can calculate the value for the solubility product, K_{sp} .

Sample Problem 1 Given that the solubility of PbI_2 is 0.558 gram per liter, find the value of the K_{sp} .

Solution To convert 0.558 gram to moles, we use a conversion factor formed from the equality 1 mole $PbI_2 = 461$ grams PbI_2 :

$$\frac{0.558 \text{ g } PbI_2}{1 \text{ L}} \times \frac{1 \text{ mole } PbI_2}{461 \text{ g } PbI_2} = 1.21 \times 10^{-3} \text{ mole } PbI_2/\text{liter}$$

From the dissociation equation $PbI_2(s) \rightleftharpoons Pb^{2+}(aq) + 2I^{-}(aq)$, we know that if 1 mole of PbI_2 dissolves, then it will yield 1 mole of Pb^{2+} and 2 moles of I^{-} . Thus, to convert 1.21×10^{-3} mole PbI_2 /liter to moles Pb^{2+} /liter, we use the conversion factor $\frac{1 \text{ mole } Pb^{2+}}{1 \text{ mole } PbI_2}$:

$$\frac{1.21 \times 10^{-3} \text{ mole } PbI_2}{1 \text{ L}} \times \frac{1 \text{ mole } Pb^{2+}}{1 \text{ mole } PbI_2} = 1.21 \times 10^{-3} \text{ mole } Pb^{2+}/\text{liter}$$

To convert 1.21×10^{-3} mole PbI_2 /liter to moles I^{-} /liter, we use the conversion factor $\frac{2 \text{ moles } I^{-}}{1 \text{ mole } PbI_2}$:

$$\frac{1.21 \times 10^{-3} \text{ mole } PbI_2}{1 \text{ L}} \times \frac{2 \text{ moles } I^{-}}{1 \text{ mole } PbI_2} = 2.42 \times 10^{-3} \text{ mole } I^{-}/\text{liter}$$

Thus, $[Pb^{2+}] = 1.21 \times 10^{-3}$ and $[I^{-}] = 2.42 \times 10^{-3}$

The solubility product expression for PbI_2 is

$$[Pb^{2+}] \times [I^{-}]^2 = K_{sp}$$

Substituting the above values in the expression, we have

$$\begin{aligned} [Pb^{2+}] \times [I^{-}]^2 &= (1.21 \times 10^{-3})(2.42 \times 10^{-3})^2 \\ &= 7.10 \times 10^{-9} \end{aligned}$$

Practice problems

Solve the following problems, in which you are given the solubility of a compound and asked to find its solubility product. In the space below each problem, write the dissociation equation for the substance and show a labeled setup. Do any necessary arithmetic on scrap paper. Write your answers in the spaces at the right.

1. The solubility of SrCrO_4 in water is 1.2 gram per liter of solution.

Calculate K_{sp} .

1. _____

2. The solubility of CaSO_4 in water is 0.41 gram per liter of solution. Calculate K_{sp} .

2. _____

3. The solubility of $\text{Cu}(\text{OH})_2$ in water is 3.4×10^{-7} mole per liter of solution. Calculate K_{sp} .

3. _____

4. The solubility of MgF_2 in water is 0.17 gram per liter of solution. Calculate K_{sp} .

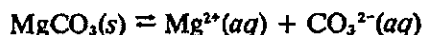
4. _____

Calculating solubility from K_{sp} values

When the solubility product constant is known, we can determine the value for solubility in moles per liter or grams per liter.

Sample Problem 2 Given that K_{sp} for $MgCO_3$ is 2.0×10^{-8} , find the solubility of $MgCO_3$ in moles per liter. How many grams per liter is this?

Solution From the dissociation equation



we derive the solubility product expression:

$$\begin{aligned} [Mg^{2+}] \times [CO_3^{2-}] &= K_{sp} \\ [Mg^{2+}] \times [CO_3^{2-}] &= 2.0 \times 10^{-8} \end{aligned}$$

Let x = moles of $MgCO_3$ that dissolve in 1.0 liter of solution.

Then $x = [Mg^{2+}]$ and $x = [CO_3^{2-}]$

Substituting x in the solubility product expression, we solve for x :

$$\begin{aligned} (x)(x) &= 2.0 \times 10^{-8} \\ x^2 &= 2.0 \times 10^{-8} \\ x &= \sqrt{2.0 \times 10^{-8}} = \frac{1.4 \times 10^{-4} \text{ mole } MgCO_3}{1 \text{ liter}} \end{aligned}$$

We use the conversion factor

$$\frac{84.3 \text{ grams}}{1 \text{ mole } MgCO_3}$$

to find the solubility of $MgCO_3$ in grams/L:

$$\frac{1.4 \times 10^{-4} \text{ moles}}{1 \text{ L}} \times \frac{84.3 \text{ g}}{1 \text{ mole } MgCO_3} = \frac{1.2 \times 10^{-2} \text{ gram}}{1 \text{ L } MgCO_3}$$

Practice problems

Solve the following problems in which you are given the solubility product of a compound and asked to find its solubility in moles per liter or grams per liter. In the space below each problem, show a labeled setup. Do any necessary arithmetic on scrap paper. Write your answers in the spaces at the right.

5. $K_{sp} = 4.8 \times 10^{-22}$ for the dissolving of $CoS(s)$ in water. Calculate the solubility of $CoS(s)$ in moles per liter of solution.

5. _____

6. $K_{sp} = 8.6 \times 10^{-5}$ for the dissolving of $\text{MgC}_2\text{O}_4(s)$ in water. Calculate the solubility of $\text{MgC}_2\text{O}_4(s)$ in grams per liter of solution.

6. _____

7. $K_{sp} = 1.3 \times 10^{-22}$ for the dissolving of $\text{ZnS}(s)$ in water. Calculate the solubility of $\text{ZnS}(s)$ in moles per liter of solution.

7. _____

8. $K_{sp} = 8.3 \times 10^{-17}$ for the dissolving of $\text{AgI}(s)$ in water. Calculate the solubility of $\text{AgI}(s)$ in grams per liter of solution.

8. _____

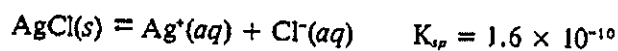
Activity 6-9 Predicting Precipitation

Precipitation from aqueous solution

1. The solubility product constant, K_{sp} , gives the value for the product of the ion concentrations in a _____ (*saturated/unsaturated*) solution. Solubility equilibrium can be achieved by the dissolving and dissociating of slightly soluble compounds. However, solubility equilibrium can also be achieved using the opposite reaction, the precipitation of the nearly insoluble substance. For example, sulfate ions from a solution of sodium _____ and barium ions from a solution of _____ chloride can be mixed together. A precipitate of $\text{BaSO}_4(s)$ will form if the ion product for a _____ (*saturated/unsaturated*) solution of the ions $\text{Ba}^{2+}(aq)$ and $\text{SO}_4^{2-}(aq)$ has been exceeded; that is, if $[\text{Ba}^{2+}] \times [\text{SO}_4^{2-}]$ for the mixture is greater than its K_{sp} value, which is _____ (see table K in the Appendix).

Sample Problem When 10.0 mL of 0.0500 M AgNO_3 is added to 125 mL of 0.0100 M KCl , does a precipitate form?

Solution The table of solubilities of different combinations of ions shows that the Ag^+ ions from the AgNO_3 solution will combine with the Cl^- ions from the KCl solution to form the insoluble substance AgCl . Write the dissociation equation for $\text{AgCl}(s)$ and find the value of the K_{sp} in table K. Note that equilibrium is approached by means of the reverse reaction.



Find the number of moles of Ag^+ and of Cl^- present:

$$\text{Moles Ag}^+: \quad 0.010 \text{ L} \times \frac{0.0500 \text{ mole Ag}^+}{1 \text{ L}} = 5.00 \times 10^{-4} \text{ mole Ag}^+$$

$$\text{Moles Cl}^-: \quad 0.125 \text{ L} \times \frac{0.0100 \text{ mole Cl}^-}{1 \text{ L}} = 1.25 \times 10^{-3} \text{ mole Cl}^-$$

Since 10.0 mL of AgNO_3 solution are added to 125 mL of KCl solution, the final volume is 0.135 L. Therefore,

$$[\text{Ag}^+] = \frac{5.00 \times 10^{-4} \text{ mole}}{0.135 \text{ L}} = 3.7 \times 10^{-3}$$

$$[\text{Cl}^-] = \frac{1.25 \times 10^{-3} \text{ mole}}{0.135 \text{ L}} = 9.3 \times 10^{-3}$$

Find the ion product $[\text{Ag}^+] \times [\text{Cl}^-]$ for this mixture:

$$[\text{Ag}^+][\text{Cl}^-] = (3.7 \times 10^{-3}) \times (9.3 \times 10^{-3}) = 3.4 \times 10^{-5}$$

Comparing the ion product, 3.4×10^{-5} , with the K_{sp} , 1.6×10^{-10} , we see that the value of the ion product is greater than the value of the K_{sp} . Therefore, we conclude that precipitation occurs.

Practice problems

For problems 2-6, show labeled setups where appropriate, and write your answers in the spaces between questions.

2. Given that 0.500 g NaBr(s) is added to 1.00 L of 0.0100 M AgNO₃(aq).
 - a. Write the dissociation equation for AgBr(s).
 - b. What is the K_{sp} value for this equilibrium?
 - c. Calculate the number of moles of Br⁻ being added.
 - d. What is [Br⁻] in this mixture?
 - e. What is the [Ag⁺] in this mixture?
 - f. Does precipitation of AgBr(s) occur? Use appropriate calculations to justify your answer.

3. Given that 0.750 g Pb(NO₃)₂(s) is added to 3.00 L of 0.10 M NaCl(aq) solution.
 - a. Write the dissociation equation for PbCl₂(s).
 - b. What is the K_{sp} value for this equilibrium?
 - c. Calculate the number of moles of Pb²⁺ being added.
 - d. Before equilibrium is achieved, what is [Pb²⁺] in this mixture?
 - e. What is [Cl⁻] in this mixture?

Name _____ Class _____ Date _____

- f. Does precipitation of $\text{PbCl}_2(s)$ occur? Use appropriate calculations to justify your answer.
4. A solution is to be prepared by dissolving $\text{Pb}(\text{NO}_3)_2(s)$ in 100 mL of 0.075 M HCl with no precipitation of $\text{PbCl}_2(s)$ occurring.
- Write the dissociation equation for $\text{PbCl}_2(s)$.
 - What is the K_{sp} value for this equilibrium?
 - What is $[\text{Cl}^-]$ in this mixture?
 - What is the maximum $[\text{Pb}^{2+}]$ permitted in this mixture?
 - What is the maximum mass of $\text{Pb}(\text{NO}_3)_2$ that could be dissolved in this solution with no precipitation of PbCl_2 ?
5. A mixture of 0.020 L of 0.0070 M $\text{ZnCl}_2(aq)$ and 0.100 L of 0.010 M $\text{H}_2\text{S}(aq)$ is prepared.
- Write the dissociation equation for $\text{ZnS}(s)$.
 - What is the K_{sp} value for this equilibrium?
 - After mixing, what are the values for $[\text{S}^{2-}]$ and $[\text{Zn}^{2+}]$?
 - Does precipitation of $\text{ZnS}(s)$ occur? Use appropriate calculations to justify your answer.

6. A solution is to be prepared by dissolving $K_2CrO_4(s)$ in 2.50 L of 0.040 M $Pb(NO_3)_2(aq)$ with no precipitation of $PbCrO_4(s)$ occurring.
- Write the chemical equation for the solubility equilibrium.
 - What is the K_{sp} value for this equilibrium?
 - What is the $[Pb^{2+}]$ in this solution?
 - What is the maximum $[CrO_4^{2-}]$ permitted in this solution?
 - What mass of K_2CrO_4 could be dissolved in this 2.50-L solution?