SCH 4UI **Unit 4 Chemical Systems and Equilibrium**

Chapter 7 Chemical Equilibrium

Sect 7.1 Chemical Systems in Balance

HMWK: Read pages 420-424

*Some reactions are reversible, ie not all reactions are as permanent as the reactions involved in burning a piece of wood.

-For example:

$$H_2O \leftrightarrow H^+ + OH^-$$

*When reactions proceed in the forward direction at the same rate as they proceed in the reverse direction, the reaction is said to have reached a state of ______________________.

*When at equilibrium, the ...

*At the macroscopic level, the concentration values do not change, but at the microscopic or molecular level, products are still forming in the forward direction and the reactants are still forming in the reverse direction. Remember molecules are always moving ...

*In order for dynamic equilibrium to occur the reaction must occur in a closed system, ie

Definition of Closed System: "A closed system is a system that does not allow input or escape of any component of the equilibrium system including energy"
-Therefore equilibrium can only be reached at constant temperature

Another example:

$$H_{2(g)} + I_{2(g)} \leftrightarrow 2\ HI_{(g)}$$

*Common Factors in Equilibrium Systems (4 Points) See page 424 in textbook

SCH 4UI **Sect 7.1 con't Equilibrium Constant and 7.3 Calculating Equilibrium Constants** (2 day note)

The Law of Chemical Equilibrium also known as Law of Mass Action states ...

-At equilibrium, for a chemical system, …

Background info:

$N_2O_4 \leftrightarrow 2\ NO_2$

Forward Rxtn: $N_2O_4 \rightarrow 2\ NO_2$ Reverse Rxtn: $2\ NO_2 \rightarrow N_2O_4$

-Each rxtn represents elementary steps therefore...

*At equilibrium, Forward rate = Reverse rate, therefore

*If the forward rate constant is divided by the reverse rate constant, the result is the equilibrium constant, K_{eq}

*The general equilibrium expression is ...

$aA + bB \leftrightarrow cC + dD$

Note: K_{eq} is dependent on temperature, therefore if T changes, so will K_{eq}

For the following equation answer the questions below;

$$H_2 + I_2 \leftrightarrow 2\ HI$$

Example 1

a) Write the K_{eq} expression

b) Calculate K_{eq} if the concentration of H_2 and I_2 is 0.22 M and the concentration of HI is 1.56 M at equilibrium.

Example 2 ... use the following equation ... $A + B \leftrightarrow C$

a) Determine K_{eq} if at equilibrium there are 0.95 moles of A and B and 0.03 moles of C in a solution of 600 ml.

What can be concluded about K_{eq} with respect to example 1 and 2?

NOTE: Expressions for Heterogeneous Equilibrium – The concentrations of solids and liquids are said to be constant therefore these reactants and products would not be included in equilibrium expression.

$NH_4Cl_{(s)} \leftrightarrow NH_{3(g)} + HCl_{(g)}$ K =

HWk: Read pages 424-431 PP#1-15 **AND** Read pages 442-445 PP#31-40

SCH 4UI Sect 7.3 Con't...

Remember...

-The reactants and products must be measured in mol/L or concentration values when using the equilibrium expression,

-When calculating K_{eq} the concentrations must be at equilibrium

Another type of question ... how to determine the concentrations of reactants and products at equilibrium using K_{eq}

Ex. 1 - If 0.100mol of $HI_{(g)}$ is placed in a 2L container, determine the concentration of $H_{2(g)}$, $I_{2(g)}$ and $HI_{(g)}$ at equilibrium when $K_{eq} = 1.84 \times 10^{-2}$

Ex. 2 **Using approximations**
-The concentration of iodine gas initially was 0.8 mol/L, determine the concentrations of $I_{2(g)}$ and $I_{(g)}$ at equilibrium. $K_{eq} = 3.8 \times 10^{-5}$

Ex 3 **Using the Quadratic Equation**

-At 1100 Kelvin, K_{eq} for the following reaction is 25. If the initial concentration of hydrogen gas is 2 mol/L and the initial concentration of iodine gas is 3 mol/L, determine the concentration of $H_{2(g)}$, $I_{2(g)}$ and $HI_{(g)}$ at equilibrium.

HWk: Read pages 448-458, PP#51-80

 Sect 7.3 con't Predicting the Direction of a Reaction Rd pages 459-461 pp81-88

-Q_c is used to predict which direction the reaction will proceed in order to obtain equilibrium

-The Q_c expression is the same as the K_{eq} , the only difference is the values being subbed into the equation or expression

- **K_{eq}**

- **Q_c**

When …

$Q_c > K_{eq}$

$Q_c = K_{eq}$

$Q_c < K_{eq}$

SCH 4UI **Sect 7.2 Le Chatelier's Principle** Read pages 332-440, pp21-30

-Henri Louis Le Chatelier, a French chemist, created the following theory:

> **If a system at equilibrium is subjected to an external stress, the equilibrium will shift so as to minimize the stress.**

-This theory applies to three factors;

***Concentration** ***Pressure/Volume** ***Temperature**

-Catalysts have no effect on equilibrium except to perhaps aid in achieving equilibrium faster, because the catalyst speeds up both the forward and reverse reactions.

Concentration

-As the concentration of a reactant or product increases, there will be more collisions and therefore the chance of a reaction occurring will be greater. Therefore the equilibrium is forced to rebalance itself so that the rate of the forward reaction equals that of the reverse reaction.

$$A + B \leftrightarrow C + D$$

Situation	**Response**	**Result**
-as [A] increases	-A is used up by B Shifts to the Right	-more C and D form
-as [A] decreases	-C and D account for imbalance Therefore, Shifts to the Left	-more A and B form
-as [C] increases	-C and D react Shifts to the Left	-more A and B form
-as [C] decreases	-A and B react Shifts to the Right	-more C and D form

Changes in Volume and or Pressure
-the only phase or state this factor applies to is gas phase. Solids and liquids are not easily compressed
-A decrease in volume or an increase in pressure favours the side of the equation with the fewer number of moles
-The reverse is also true, an increase in volume or decrease in pressure favours the side of the reaction with the greatest number of moles

Explanation: An increase in pressure means an increase in concentration, therefore there is a greater chance of a collision and hence a reaction.

Example: $\mathbf{N_2O_{4(g)} \leftrightarrow 2\ NO_{2(g)}}$

An increase in pressure or a decrease in volume	Equation shifts to the Left
An decrease in pressure or an increase in volume	Equation shifts to the Right

Effect of Temperature
-The equilibrium will shift in the direction that absorbs heat
-Think of it as the system attempting to regain or replace the original temperature

-Therefore the effect of temperature is dependent on the type of reaction, whether the reaction is endothermic or exothermic.

-Endothermic, heat is a part of the reactant side $A + HEAT \leftrightarrow C + D$

-Exothermic, heat is a part of the product side $A + B \leftrightarrow C + HEAT$

Situation	**Response**
-endothermic, increase in T	-Shift to the Right, increase in products
-endothermic, decrease in T	-Shift to the Left, increase in reactants
-exothermic, increase in T	-Shift to Left, increase in reactants
-exothemic, decrease in T	-Shift to Right, increase in products

Inert Gases:
-In a rigid container, injecting more gas will cause a total increase in pressure, **BUT…**
-if the gas is a reactant or product, or reacts with the equilibrium reaction, treat the situation as an increase in concentration, … ie see above
-If the gas does not react with the equilibrium reaction, it is said that the gas has no effect on the system because it is not apart of the equilibrium system… therefore there is no net effect and no change in volume of container
EXCEPTION: if the container expands, when an inert gas is added, the effect is the same as increasing the volume of the container and therefore decreasing the pressure for the reacting gases.

SCH 4UI **Sect 7.2 Entropy, Gibbs Free Energy and Spontaneity**
Read sect 7.2, SR #1-5 (OLDtext)

Causes of Chemical Change:

Q - Why do reactions proceed as they do?

Q – Why do some processes not reverse themselves?

… The answer lies in the concept of ________________

-In chemistry, spontaneous reactions are ones that occur under natural conditions, for example…

*If an external input is required for a reaction to proceed the reaction is considered ______________

*Spontaneity depends on 2 factors, ______________ and ________________

***Entropy** – defined as the …

***Law of Disorder**: A spontaneous reaction in an isolated system always proceeds in the direction of increasing entropy
Ie. Spontaneous reactions change from order to disorder

Example:

Factors that affect change in entropy are …

1. Number of moles:

2. Phase Changes:

3. Temperature Changes:

Other Situations…

Formation of mixture or solution (ie dilutions)

Separation or Distillations

Gibbs Free Energy
-Any reaction where enthalpy is ____________ and entropy is ______________ will be spontaneous.

-Any reaction where enthalpy is ____________ and entropy is ______________ will be non spontaneous.

Gibb came up with the **Gibb's Free Energy Equation**:

-If < 0, the reaction is spontaneous in the forward direction

-If > 0, the reaction is not spontaneous in the forward direction, but is spontaneous in the reverse direction

-If $= 0$, reaction is at equilibrium, therefore no net change can occur at that temperature

Table 7.1, page 332

	Enthalpy	Entropy	Apply to Equation	Explanation
1	Negative	Positive		
2	Positive	Negative		
3	Negative	Negative		
4	Positive	Positive		

 8.2 and 8.3 Acid and Base Dissociation Constants... Ka, Rd p509-516, PP51-67
Kb, Rd p519-526, PP70-90

Review - $[H_3O^+]$ of a strong base is 1.2×10^{-6}, calculate the pH and pOH

What is the definition of a Strong Acid and a Weak Acid... Same idea applies to Strong Base and Weak Base

Acid Dissociation Constant.... ONLY applies to weak acids, WHY?

$$HA + H_2O \leftrightarrow A^- + H_3O^+$$

Question: Determine the pH of a 2.8 M acetic acid solution with a Ka value = 1.8×10^{-5}

Percent Dissociation – refers to the amount of product produced compared to the initial concentration of the reactant

*Calculate the percent dissociation for the previous question.

Base Dissociation Constant, Kb

$B + H_2O \leftrightarrow HB^+ + OH^-$

Is there a connection between Ka and Kb? YES.....

$CH_3COOH + H_2O \leftrightarrow$ _________ + __________

$CH_3COO^- + H_2O \leftrightarrow$ _______ + _________

Write Ka =

Write Kb =

Question – Methanoic acid has a Ka value of 1.8×10^{-4}, determine the following;
a) what is the conjugate base for methanoic acid?
b) write the chemical reaction with the conjugate base and water
c) determine Kb for the reaction
d) determine the pOH for the reaction if the initial concentration of the conjugate base is 1.2 M

 Sect 8.2 **Polyprotic acids**... See page 517

Polyprotic acids, have more than one hydrogen atom that dissociates

Example: Sulfuric Acid, H_2SO_4

If the initial concentration of sulfuric acid is 3.2 mol/L, determine the concentration of the sulfate ion and the pH of the acidic solution.

Important Notes to Self:

Section 8.4 Buffer Solutions … see pages 530-531

*Buffers or Buffer solutions are composed of either a

-Buffer solutions resist changes in pH when a moderate amount of an acid/base is added

Example 1 **Weak acid** and it's conjugate base resist against pH in the following way

Example 2 **Weak base** and it's conjugate acid resist against pH in the following way

Note: Often the textbook refers to the fact that a buffer is made with a weak acid and it's salt. Remember that the salt will dissociate producing the conjugate base and a cation. Hence a conjugate acid/base or salt of an acid/base means the same thing.

How does Le Chatelier's principle apply to the above reactions?

-Buffer capacity is a measure of the quantity of acid or base that can be added before a noticeable change in pH occurs

-Buffer capacity is dependent on the concentration of the acid/conj base or base/conj acid pair

-The more concentrated a buffer solution the higher the buffer capacity and hence a smaller change in pH

Buffer Question:

A buffer solution was made with 100ml of 0.2M acetic acid and 100ml of 0.2M sodium acetate. If the Ka for acetic acid is 1.8×10^{-5} determine the pH of this system.

Hint 1: must determine the concentration of acetic acid and it's salt in the solution wrt total volume of solution
Hint 2: what is the concentration of acetic acid and salt initially

-An acid and a base react together to produce a “neutralized” solution

-**Sometimes the salt itself will react with water causing the pH of the aqueous solution to alter the pH to be above 7 or below 7**

Remember:
-if a salt reacts with water to produce H_3O^+ , the solution will be acidic and have a pH less than 7

-if a salt reacts with water to produce OH^- , the solution will be basic and have a pH greater than 7

A salt is composed of...

A **strong acid** completely dissociates therefore...

A **strong base** completely dissociates therefore...

A **weak acid**, does not completely dissociate, therefore the conjugate base is relatively strong and will react with water

A **weak base** also does not completely dissociate, therefore the conjugate acid is relatively strong and will react with water

The **salt of a weak base and a weak acid**...

-which ion will influence the pH value?

-must compare the Ka and Kb associated with the cation and the anion of the salt

-if Ka Kb

-if Ka Kb

-if Ka Kb

Ex. Which type of solution will NH_4ClO produce?

Ex. a) Write the neutralization reaction for the formation of the salt potassium nitrite.

b) Determine the pH of the solution if the salt potassium nitrite has an initial concentration of 0.15M

Note:
**The pH at equivalence point in a titration is the same as the pH of the aqueous solution of the salt*
**The pH of the salt influences which indicator to use...* *see page 532 in text*

Practice...

Complete the chart below

Acid	**Base**	**Salt**	**Rxtn with salt and water**	**Approx pH**
HNO_3	KOH			
HOCN	NaOH			
HCl	NH_3			
H_2S	$Mg(OH)_2$			
HBr	N_2H_4			
HIO_3	N_2H_4			

Summary

-Salt of a strong acid

-Salt of a strong base

-Salt of a weak acid

-Salt of a weak base

-Salt of a weak acid and weak base

Practice...

1. Predict whether an aqueous solution of each salt is neutral, acidic or basic. Write the appropriate reactions to support your answers.

a) NaCN	b) LiF	c) $Mg(NO_3)_2$	d) NH_4I
e) NH_4BrO_4	f) NaOBr	g) NH_4Br	h) $NaBrO_4$

2. Ka for benzoic acid, C_6H_5COOH is 6.3×10^{-5}. Ka for phenol, C_6H_5OH is 1.3×10^{-10}. Which is the stronger base, $C_6H_5COO^-$ or $C_6H_5O^-$? Explain your answer.

3. Sodium hydrogen sulfite, $NaHSO_3$ is a preservative that is used to prevent the discolouration of dried fruit. In aqueous solution, the hydrogen sulfite ion can act as either an acid or a base. Predict whether $NaHSO_3$ dissolves to produce an acidic or basic solution.

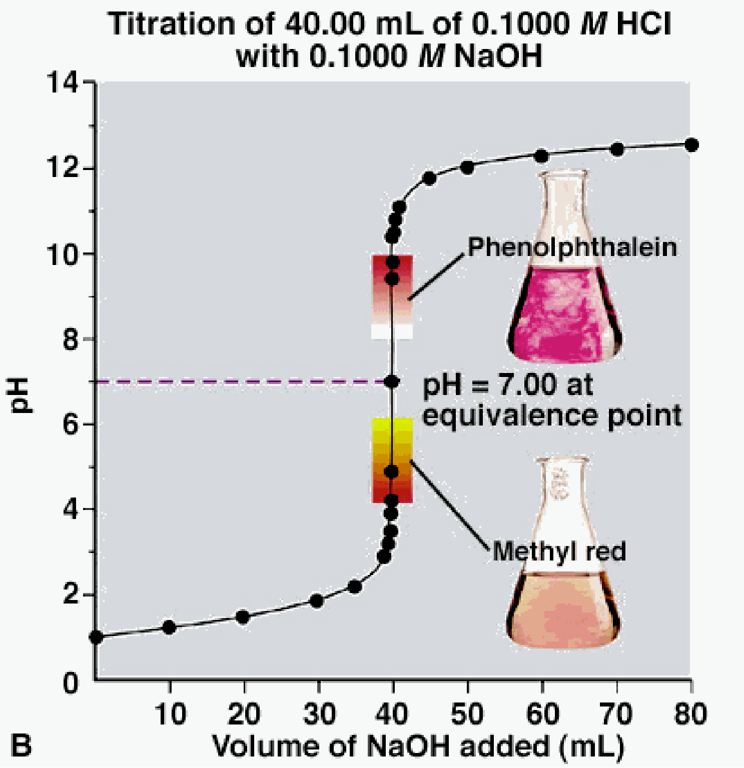
SCH 4UI **Titration Curves and the Effect of the Salts produced**

HMWK Rd pages532-544, PP #91-120

Strong Acid-Base Titration Curve

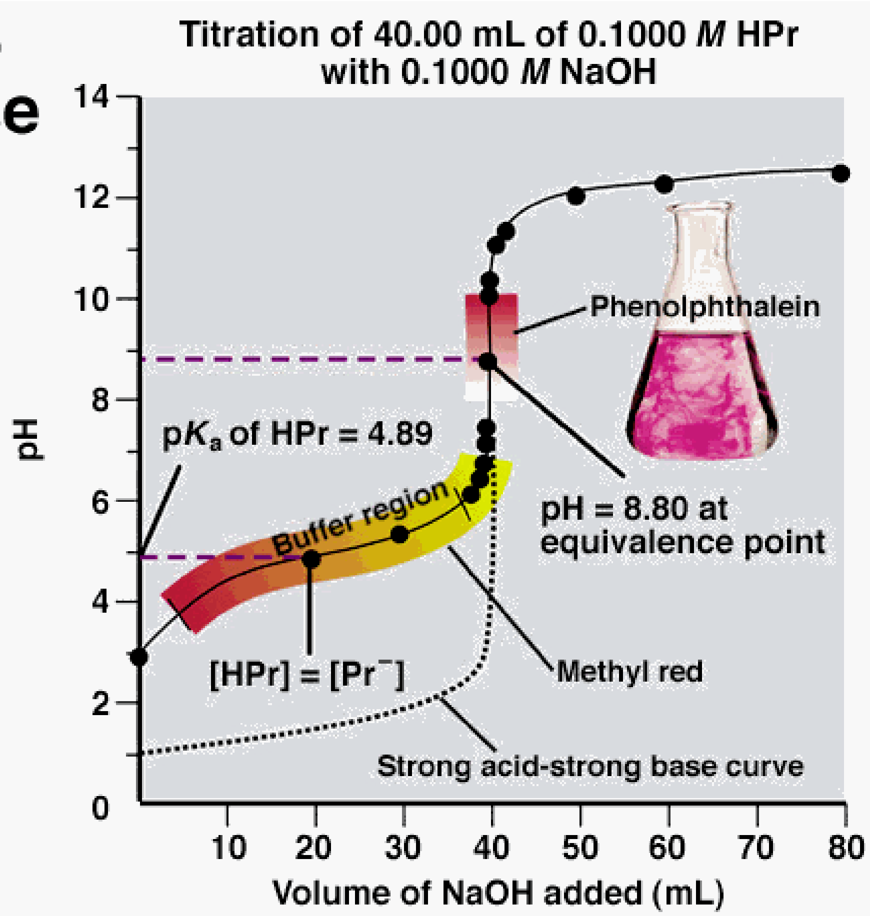
Volume of NaOH added (mL)	pH
00.00	1.00
10.00	1.22
20.00	1.48
30.00	1.85
35.00	2.18
39.00	2.89
39.50	3.20
39.75	3.50
39.90	3.90
39.95	4.20
39.99	4.90
40.00	7.00
40.01	9.40
40.05	9.80
40.10	10.40
40.25	10.50
40.50	10.79
41.00	11.09
45.00	11.76
50.00	12.05
60.00	12.30
70.00	12.43
80.00	12.52

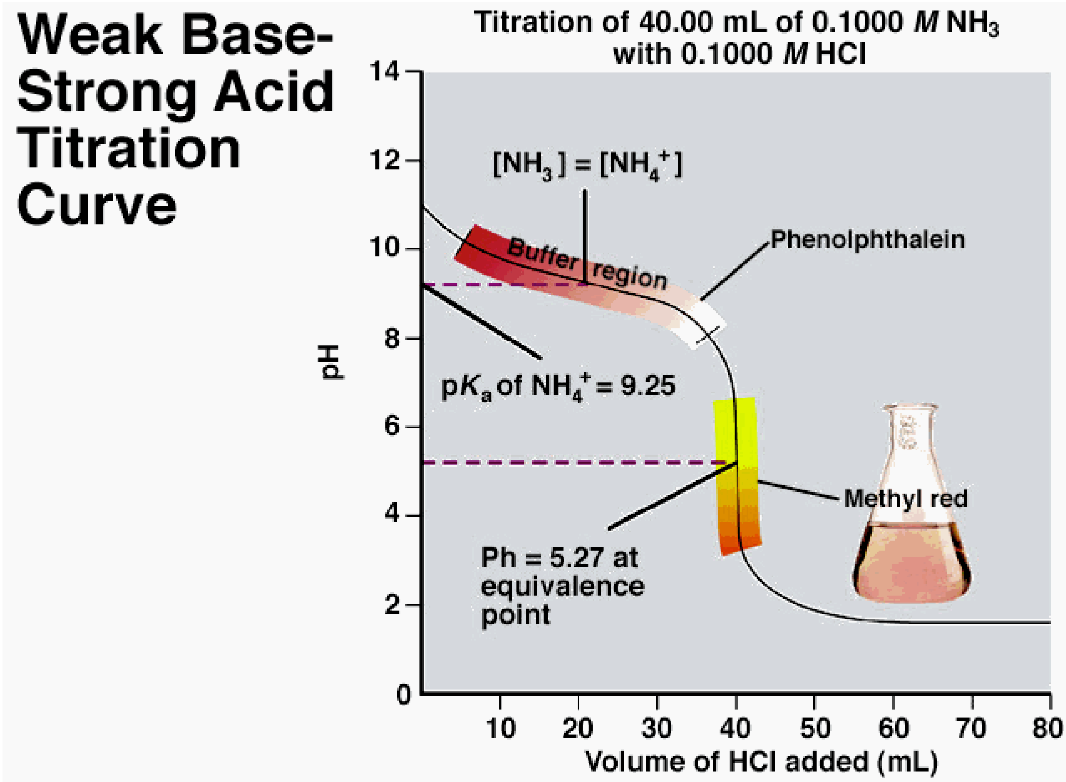
A



B

Weak Acid-Strong Base Titration Curve





Key Definitions:

Equivalence Point – Is the point in a titration in which the moles of the acid equal the moles of the base, ie stoichiometrically

End Point – Is the point in a titration in which the indicator changes colour

Calculation Questions...

1. Answer the questions below using the following data, 0.15M and 30 ml of HCl is titrated with 0.10M of sodium hydroxide,

   a) What is the pH initially of the acid?
   b) What is the pH when only 12ml of NaOH has been added?
   c) What is the pH at the equivalence point?
   d) What is the pH when 40ml of NaOH has been added?

2. If 30.0 ml of 0.12M of acetic acid is titrated with 0.1M of sodium hydroxide, determine the following;

   a) The pH when 15ml of NaOH has been added
   b) The pH at the equivalence point

SCH 4UI **Sect 8.4 Calculations with Ksp, Solubility Product Read pages 544-549 pp121-128**

The BASICS

-Solid NaCl is added to a solution, what happens?

-Determine the concentration of Na^+ and Cl^- if a 0.6 mol/L is the concentration of the NaCl solution

-Determine the concentration for each ion for the following solution, $Fe(NO_3)_3$ if the concentration of iron (III) nitrate is 0.3 mol/L

NOTE: the solubility of most solids is an endothermic process therefore,
As TEMP Increases, ___________________________________

-Except for carbonates, this is an example of an exothermic reaction, therefore
As TEMP Increases, ___________________________________

Solubility Product Constant
*applies to saturated solutions of ionic compounds

Reaction:

Equilibrium Expression:

Ksp, solubility product constant

-can be used to determine at what concentration's ions will form a precipitate
-can be used to determine if a precipitate will form
-Ksp is a known value for ionic compounds that are insoluble or slightly soluble in water

Note: Ksp is temperature dependent

Ex. Calculate the concentration of lithium and carbonate ions in a saturated solution of Li_2CO_3, given the Ksp = 1.7×10^{-3}

Common Ion Effect…

Question – How is solubility affected when mixing 2 solutions with the same ion?

Ex. $\mathbf{PbCrO_{4(s)} \leftrightarrow Pb^{2+} + CrO_4^{-2}}$

*If one beaker contains **Lead chromate** and another contains **sodium chromate**, which direction will the above reaction shift? Left or Right? Why?

*What will happen to the concentration of the lead ions?

Application

-Predict what will happen to the molar solubility of the solid? Will more dissolve if a common ion is present in a secondary solution or less? Explain

Let's prove our point using a practice problem… practice problem #21

Question: What is the molar solubility of AgCl in a) in water and in b) 0.15 M NaCl?
Ksp= 1.77×10^{-10}

SCH 4UI Predicting the Formation of a Precipitate

-To predict the formation of a precipitate Qsp is used
-Qsp is called …

If… Solid ↔ dissolves into ions

Qsp Ksp

Qsp Ksp

Qsp Ksp

Question:

Determine if silver chloride will form a precipitate if 0.05 mlof 6.0 M of silver nitrate is added to 1.0L of 0.1M of sodium chloride

****__IMPORTANT__*** must determine concentration of ions with respect to volume of solution!