
Properties of Systems in Equilibrium – Le Châtelier's Principle

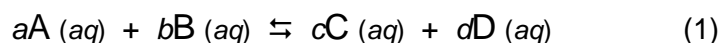
Objectives

- To perturb chemical reactions at equilibrium and observe how they respond.
- To explain these observations using Le Châtelier's Principle.
- To relate Le Châtelier's Principle to the concept of coupled reactions.

Background

All chemical reactions eventually reach a state in which the rate of the reaction in the forward direction is equal to the rate of the reaction in the reverse direction. When a reaction reaches this state, it is said to be at chemical equilibrium.

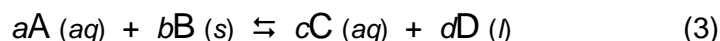
The concentrations of reactants and products at equilibrium are constant as a function of time. Thus, for a homogeneous aqueous system of the form



we can express the equilibrium-constant expression for this reaction as,

$$K_c = \frac{[C]^c [D]^d}{[A]^a [B]^b} \quad (2)$$

where the values of [A], [B], [C] and [D] correspond to the equilibrium concentrations (or equilibrium positions) of all the aqueous chemical components, and *a*, *b*, *c* and *d* are their respective stoichiometric coefficients. Note that for a heterogeneous system including pure solids or liquids of the form



the pure liquids and solids do not appear in the equilibrium-constant expression:

$$K_c = \frac{[C]^c}{[A]^a} \quad (4)$$

It has been observed that when a reaction at equilibrium is perturbed by applying a stress, the reaction will respond by shifting its equilibrium position so as to counteract the effect of the perturbation/stress. In other words, the concentrations of the reactants and products will shift so that the relationship described by Equation (2) is again satisfied. This idea was first proposed by Henri-Louis Le Châtelier and has since been referred to as, "Le Châtelier's Principle".

Note that when a reaction makes more products as a response to the perturbation, we call it a right-shift. When a reaction makes more reactants in response to the perturbation, we call it a left-shift. We often designate these respective shifts by drawing right and left arrows below the chemical equation.

For chemical reactions at equilibrium in aqueous solution, the most common types of perturbations include changing the concentration of one of the aqueous solutes, changing the concentrations of all aqueous solutes by changing the total solution volume, or changing the temperature. The general responses of an aqueous system to these particular perturbations are tabulated below.

Perturbation	Effect on Equilibrium Position	Effect on K_c
Increase in concentration of a single reactant, or, decrease in concentration of a single product.	Shift to the right	None
Decrease in concentration of a single reactant, or, increase in concentration of a single product.	Shift to the left	None
Decrease in all aqueous concentrations due to an increase in solution volume resulting from the addition of solvent	Shift towards side with more solute particles	None
Increase in all aqueous concentrations due to a decrease in solution volume resulting from the removal of solvent (evaporation)	Shift towards side with less solute particles	None
Increase temperature of an exothermic reaction	Shift to the left	Decrease
Decrease temperature of an exothermic reaction	Shift to the right	Increase
Increase temperature of an endothermic reaction	Shift to the right	Increase
Decrease temperature of an endothermic reaction	Shift to the left	Decrease
Addition of an inert substance, catalyst, pure liquid, or pure solid	None	None

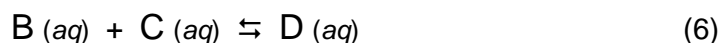
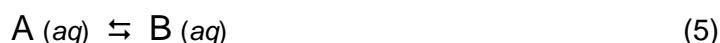
Notice that only a temperature change can affect the value of K_c ; in all other cases the value of K_c remains constant.

In this experiment you will perturb reactions that have attained equilibrium. You will then observe how each reaction responds to that perturbation in order to restore equilibrium. In your report you describe these changes in terms of Le Châtelier's Principle.

Part A – Acid-Base Equilibrium

Here you will use **coupled equilibria** to change the equilibrium position of an acid-base reaction.

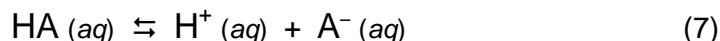
In order to understand how coupled equilibria work consider the reactions described by the chemical equations below:



Notice that the species B (aq) is common to both reactions. The presence of this common species couples these two reactions.

We can perturb the equilibrium position of Reaction (6) by the addition of some C (aq). The addition of C (aq) will cause the equilibrium position of Reaction (6) to shift right in accordance with Le Châtelier's Principle. This right shift in the equilibrium position of Reaction (6) will also result a corresponding decrease in the concentration of B (aq). Because B (aq) is also present in Reaction (5), the decrease in the concentration of B (aq) will in turn result in a right shift in the equilibrium position of Reaction (5). Thus, the addition of C (aq) to Reaction (6) actually results in a right shift in the equilibrium position of Reaction (5) because the equilibria are coupled.

In Part A we will observe the effect of various solutes on an acid-base indicator (a weak acid) at equilibrium. The equilibrium system can be written in the general form

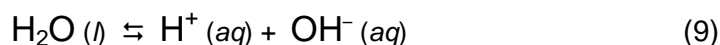


The equilibrium-constant expression for this reaction is

$$K_a = \frac{[\text{H}^+][\text{A}^-]}{[\text{HA}]} \quad (8)$$

where we denote the equilibrium constant, K , with a subscript a for acid. In this experiment, HA and A^- , are the acidic and basic forms of the indicator bromothymol blue. Since the two forms are different colors, you will be able to determine which form is predominant in the equilibrium mixture. In other words you will be able to determine whether the equilibrium position lies to the left (more reactants and less products) or whether the equilibrium lies to the right (more products and less reactants).

Your goal will be to find a reagent that will shift the position of this equilibrium to the opposite side, and then another reagent that will shift it back towards its original position. Instead of directly adding HA or A^- to the system, you will effect these shifts by adding H^+ or OH^- . Note that in order to determine the effect of OH^- we must consider a second chemical reaction that shares a common species with the Reaction (7). The second reaction is the autoionization of water, which can be described by the equation



The equilibrium constant for this reaction is denoted by K_w , where the subscript w stands for water, and the associated equilibrium constant expression is

$$K_w = [\text{H}^+][\text{OH}^-] \quad (10)$$

Because Reactions (7) and (9) share a common chemical species (H^+), you can use the concept of coupled equilibria to shift the equilibrium position of Reaction (7) by increasing or decreasing the concentration of OH^- (aq).

Part B – Solubility Equilibrium

Here you will test the effects of changing temperature and volume on the solubility of a slightly soluble salt at equilibrium. Some examples of slightly soluble salts are AgCl, Cu(OH)_2 , PbCl_2 , and Fe_2S_3 , which you should recall are, "insoluble in water," according to the solubility rules you learned in Chemistry 11. In fact, a very small amount of each of these substances does

dissolve in aqueous solution, but the amount is so small that we often classify each of these compounds as, “insoluble”.

This type of equilibrium is often called a **solubility equilibrium** because it is written in the direction of the dissolution of the solid, as shown in the following example:



The equilibrium-constant expression for Reaction (11) is

$$K_{sp} = [A^+]^x[B^-]^y \quad (12)$$

where we denote the equilibrium constant, K , with a subscript sp for **solubility product**.

Now let's consider the process of precipitation. In a typical precipitation reaction two aqueous salt solutions are mixed together resulting in the production of an insoluble salt. Notice that this process corresponds to a left shift of Reaction (11), and so Equation (12) can also be used to examine the conditions required for the precipitation of a solid to occur. We can denote the product $[A^+]^x[B^-]^y$ under arbitrary conditions (not necessarily at equilibrium) as,

$$Q_{sp} = [A^+]^x[B^-]^y \quad (13)$$

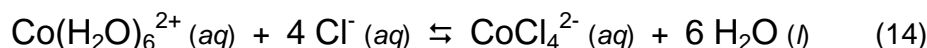
where Q_{sp} is called the solubility product **reaction quotient**. Note that, upon mixing two solutions, one containing A^+ and the other containing B^- , if $Q_{sp} < K_{sp}$ the system is not at equilibrium, but since no solid A_xB_y is present the reaction cannot shift to the right and therefore no reaction will be observed. In contrast, if $Q_{sp} > K_{sp}$ the solution contains an excess of aqueous species, and Reaction (11) will shift left, forming the solid precipitate A_xB_y until the system reaches a state of equilibrium where $Q_{sp} = K_{sp}$. Thus, we can use the values of Q_{sp} and K_{sp} to predict the conditions under which a precipitation reaction will occur.

In Part B we will study the solubility equilibrium of $PbCl_2 (s)$. We will observe the effect on this solubility equilibrium of changes in solution volume (quantity of solvent) and temperature. We will express these changes in terms of the respective values of Q_{sp} and K_{sp} .

Part C – Complex Ion Equilibrium

Certain metal ions, most often transition metals, exist in solution as **complex ions** in combination with other ions or molecules, called **ligands**. Common ligands include H_2O , NH_3 , Cl^- and OH^- . Many of these complex ions exhibit vibrant colors in solution. For example, the $Co(H_2O)_6^{2+} (aq)$ complex ion is pink and the $CoCl_4^{2-} (aq)$ complex ion is blue.

In Part C you will study the following complex ion formation reaction:



The equilibrium-constant expression for Reaction (14) is

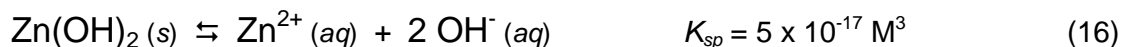
$$K_f = \frac{[CoCl_4^{2-}]}{[Co(H_2O)_6^{2+}][Cl^-]^4} \quad (15)$$

where we denote the equilibrium constant, K , with a subscript f for complex ion *formation*.

Your goal in Part C is to observe how Reaction (14) shifts from its equilibrium position as the result of various perturbations.

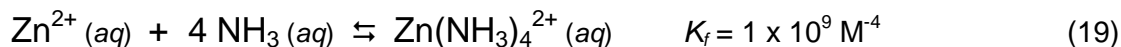
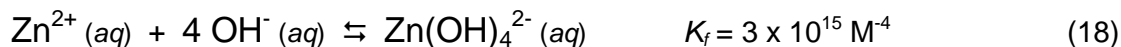
Part D – Dissolving Insoluble Solids

In Part D you will use coupled equilibria to affect the solubility equilibrium of Zn(OH)_2 (s). The solubility equilibrium can be described by the equation



Notice that $K_{\text{sp}} \ll 1$ for this reaction, demonstrating that Zn(OH)_2 (s) is only very slightly soluble in aqueous solution.

Now consider the reactions described by the following chemical equations, each of which shares a common species with the Reaction (16):



Because Reactions (17), (18), and (19) each share a common species with Reaction (16) they can be coupled together. In Part D of this experiment you will observe the effect of coupling each of these equilibria on the solubility of Zn(OH)_2 (s).

Procedure

Equipment

From lab/locker: Six large test tubes, test tube rack, stirring rod, scoopula, small 10-mL graduated cylinder, large 100-mL graduated cylinder, 400-mL beaker, wire gauze, stand with ring clamp, and Bunsen burner.

From stockroom: Bucket of ice

Chemicals

Bromothymol blue, a 6 M strong acid, a 6 M strong base, 0.3 M $\text{Pb}(\text{NO}_3)_2$ (aq), 0.3 M HCl (aq), $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ (s), 12 M HCl (aq), 0.1 M $\text{Zn}(\text{NO}_3)_2$ (aq), 0.1 M $\text{Mg}(\text{NO}_3)_2$ (aq), 6 M NaOH (aq), 6 M HCl (aq), 6 M NH_3 (aq) (often labeled as NH_4OH), and deionized water

Safety and Waste Disposal

- ① 12-M HCl is extremely caustic and great care must be taken to avoid contact with eyes or skin. The bottle should be kept in a plastic tray and not removed from the fume hood. Should any of this solution enter your eyes rinse immediately in the emergency eyewash. Should any of this solution come in contact with your skin rinse with copious amounts of water and apply saturated sodium bicarbonate to the affected area from the stock bottle located on the sink.
- ② The solutions you will use in Part B contain lead. Be certain that all of these lead-containing solutions are disposed of in the proper waste container and rinse your hands following this procedure.
- ③ Many of the chemicals used in this lab are hazardous to the environment. All waste must be disposed of in the hazardous-waste container in the fume hood. Rinse all glassware directly into the waste container twice using a small squirt bottle to be certain all hazardous waste ends up in the waste container.

General Procedural Notes

The amounts of reagents used in this experiment are approximate only. If you are unsure how to estimate a milliliter, then measure out about one milliliter of water using your graduated cylinder, transfer this amount to a large test tube, and then use this approximate volume as a reference throughout the experiment.

All glassware needs to be rinsed at least once with deionized water. It is not necessary to dry glassware since all reagent volumes are approximate and all solutions are aqueous.

Part A: Acid-Base Equilibrium

Here you will find a reagent that will shift the acid-base equilibrium given by Reaction (7) in one direction and then a second reagent that will cause the equilibrium position to shift back in the opposite direction.

Reagents needed for this part are: deionized water, bromothymol blue solution, a 6 M strong acid and a 6 M strong base.

1. Add approximately 5 mL of deionized water to a large test tube. Add 3 drops of the bromothymol blue indicator solution. Report the color of your solution on your data sheet.
2. Your solution from Step 1 currently contains one form of bromothymol blue (see background). Now predict which of the two 6 M reagents you obtained, the strong acid or the strong base, will cause a color change in your solution by making the bromothymol blue indicator shift to its other form. Add the 6 M reagent of your choice drop-by-drop and if your solution changes color, write the color of the solution and formula of the reagent on your data sheet. If the addition of your reagent does not result in a color change, try other reagents until you are successful.
3. Since equilibrium systems are reversible, it is possible to shift a reaction left or right repeatedly by changing the conditions. Now find another 6 M reagent that will cause your solution from Step 2 to revert back to its original color. Add the 6 M reagent of your choice drop-by-drop and if your solution changes color, write the formula of the reagent on the data sheet. If the addition of your second reagent does not result in a color change, try other reagents until you are successful.

Part B: Solubility Equilibrium

You will test the effects of changing the solution volume and temperature on the solubility equilibrium of lead (II) chloride.

Reagents needed are: 0.3 M $\text{Pb}(\text{NO}_3)_2$ (aq), 0.3 M HCl (aq), and deionized water.

1. Set up a hot-water bath by filling a 400-mL beaker about half-full with tap water and heating the water using a Bunsen burner while you work on the following steps. The hot-water bath will be used in Step 6 (and also in Part C).
2. Measure 5.0 mL of the 0.3 M $\text{Pb}(\text{NO}_3)_2$ solution into a large test tube using a 10-mL graduated cylinder.
3. Thoroughly rinse the graduated cylinder with deionized water, then measure 5.0 mL of the 0.3 M HCl solution using the 10-mL graduated cylinder.
4. Add about 1 mL of the 0.3 M HCl solution to the $\text{Pb}(\text{NO}_3)_2$ solution in the large test tube. Stir the mixture gently using your stirring-rod and record your observations on your data sheet.

- Continue to add the 0.3 M HCl solution to the $\text{Pb}(\text{NO}_3)_2$ solution in the large test tube in roughly 1 mL increments until you just begin to see white PbCl_2 solid appear in your test tube. To confirm that the solid is present, let the test tube sit on the bench for about 3 minutes, allowing all solid to settle to the bottom where it is easier to see. On your data sheet record the total volume of 0.3 M HCl needed to produce the solid.
- Put the test tube containing the solid into your hot-water bath from Step 1. Stir the contents of the test tube gently for a few seconds using the glass stirring-rod and record your observations on your data sheet. Continue heating and stirring until a change is observed.
- Make a cold-water bath by filling a 400-mL beaker half full with tap water and ice. Cool the test tube down by placing it into this cold-water bath. Observe what happens and record your observations. Save this cold-water bath for use in Part C.
- Dispose of the remainder of the 0.3 M HCl solution in your 10-mL graduated cylinder by pouring it into the appropriate waste container and then rinse the cylinder using deionized water. Next measure 5.0 mL of deionized water using this graduated cylinder.
- Add about 1 mL of deionized water to the large test tube containing the PbCl_2 solid. Stir the mixture and observe what happens. Continue to add the deionized water in 1 mL increments until the white PbCl_2 solid *just dissolves* (or disappears). On your data sheet record the volume of water needed to dissolve the solid.
- Pour the contents of the large test tube into your large graduated cylinder and measure the total volume of the solution. Record this volume on your data sheet.
- Dispose of all solutions used in Part B in the proper waste container. Rinse all glassware twice using a wash bottle of deionized water to ensure that all of the lead solution has been removed and transferred to the waste container. Save the hot- and cold-water baths for Part C.

Part C: Complex Ion Equilibrium

Here you will test the effects of changing the volume and temperature on the complex ion equilibrium between $\text{Co}(\text{H}_2\text{O})_6^{2+}(\text{aq})$ and $\text{CoCl}_4^{2-}(\text{aq})$ as in Reaction (14).

Reagents needed for this part are: $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}(\text{s})$, 12 M HCl (aq) (*do not remove from fume hood*), and deionized water.

- Reheat your hot-water bath from part B to a near boil. The hot-water bath will be used in Step 4.
- Put a few small crystals (an amount that fits at the tip of the scoopula) of $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}(\text{s})$ in a large test tube. Working in the fume hood, carefully add 2 mL of 12 M HCl (aq) (*this acid is extremely caustic; see cautions in the safety section of this experiment*). Stir to dissolve the crystals. Record the color of this solution.
- Using a 10-mL graduated cylinder, add deionized water to the solution in your test tube in approximately 2 mL increments, stirring after each addition, until no further color change occurs. Record the new color.

4. Place the test tube into the hot-water bath from Step 1 and record any color change.
5. Cool the solution down in the cold-water bath and record any color change.

Part D: Dissolving Insoluble Solids

Here you will further examine how one reaction can affect the behavior of another reaction when the reactions share one or more common chemical species.

Reagents needed for are: 0.1 M $\text{Zn}(\text{NO}_3)_2$ (aq), 0.1 M $\text{Mg}(\text{NO}_3)_2$ (aq), 6 M NaOH (aq), 6 M HCl (aq), and 6 M NH_3 (aq) (often labeled as NH_4OH).

1. Label three large test tubes A, B, and C. Add about 2 mL of 0.1 M $\text{Zn}(\text{NO}_3)_2$ solution to each test tube. Add one drop of 6 M NaOH solution to each test tube. Stir each solution and record your observations.
2. Into test tube A, add at least 20 drops of 6 M HCl (aq) drop-by-drop while stirring. Record all observations.
3. Into test tube B, add at least 20 drops of 6 M NaOH (aq) drop-by-drop while stirring. Record all observations.
4. Into test tube C, add at least 20 drops of 6 M NH_3 (aq) drop-by-drop while stirring. Record all observations.
5. Label three additional large test tubes D, E, and F. Add about 2 mL of 0.1 M $\text{Mg}(\text{NO}_3)_2$ solution to each test tube. Add one drop of 6 M NaOH solution to each test tube. Stir each solution and record your observations.
6. Into test tube D, add at least 20 drops of 6 M HCl (aq) drop-by-drop while stirring. Record all observations.
7. Into test tube E, add at least 20 drops of 6 M NaOH (aq) drop-by-drop while stirring. Record all observations.
8. Into test tube F, add at least 20 drops of 6 M NH_3 (aq) drop-by-drop while stirring. Record all observations.

Name: _____

Date: _____

Lab Partner: _____

Lab Section: _____

Lab Report: Properties of Systems in Equilibrium - Le Châtelier's Principle

Part A – Equilibrium and an Acid-Base IndicatorEquilibrium system: $\text{HA} (aq) \rightleftharpoons \text{H}^+ (aq) + \text{A}^- (aq)$ **Observations**

Record your results upon completing each of the following steps:

Step 1	Color of bromothymol blue in distilled water	
Step 2	Name of reagent "A" causing color change when added	
Step 3	Name of reagent "B" causing a return to original color	

Analysis

- Complete the following:

The acidic form of the bromothymol blue indicator, $\text{HA} (aq)$, is _____ in color.The basic form of the bromothymol blue indicator, $\text{A}^- (aq)$, is _____ in color.

- Explain why reagent A (in Step 2) caused the color change observed.

- Explain why reagent B (in Step 3) caused the color change observed.

Part B – Solubility Equilibrium and K_{sp}

Equilibrium system: $\text{PbCl}_2 (s) \rightleftharpoons \text{Pb}^{2+} (aq) + 2 \text{Cl}^- (aq)$

Observations

Step 4	Observations upon addition of just 1.0 mL of HCl to the $\text{Pb}(\text{NO}_3)_2$ solution	
Step 5	Total volume of HCl required for noticeable precipitation	mL
Step 6	Observations upon placing the test tube with precipitate in hot water	
Step 7	Observations upon placing the test tube with precipitate in cold water	
Step 9	Volume of water added to just dissolve PbCl_2 precipitate	mL
Step 10	Total solution volume upon completion	mL

Analysis

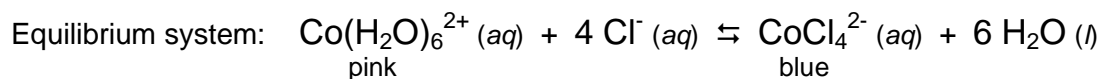
- Why didn't any solid PbCl_2 form immediately upon addition of 1 mL of HCl (aq) in Step 4? What condition must be met by $[\text{Pb}^{2+}]$ and $[\text{Cl}^-]$ if solid PbCl_2 is to form?

- Consider your observation in hot water in Step 6:
 - In which direction did the equilibrium shift? _____
 - Did the value of K_{sp} get smaller or larger? _____
 - Is the dissolution of $\text{PbCl}_2 (s)$ exothermic or endothermic? _____

Explain below.

- Explain why the solid PbCl_2 dissolved when water was added to it in Step 9. What was the effect of this water on $[\text{Pb}^{2+}]$, $[\text{Cl}^-]$, and Q_{sp} ? In which direction would such a change drive the equilibrium system?
- The point at which the PbCl_2 precipitate just dissolves in Step 9 can be used to determine the value of K_{sp} for this equilibrium system, where $K_{sp} = [\text{Pb}^{2+}][\text{Cl}^-]^2$. Calculate $[\text{Pb}^{2+}]$ and $[\text{Cl}^-]$ in the final solution (consider the "dilution effect"). Then use these equilibrium concentrations to determine the value of K_{sp} for this system. Show all work below.

Part C – Complex Ion Equilibria



Observations

Step 2	Color of solution in 12 M HCl	
Step 3	Color of solution upon addition of water	
Step 4	Color of solution in hot water	
Step 5	Color of solution in cold water	

Analysis

- What form of the complex ion, $\text{Co}(\text{H}_2\text{O})_6^{2+} (aq)$ or $\text{CoCl}_4^{2-} (aq)$, is predominate in:
 - the 12 M HCl (aq) _____
 - the diluted solution _____
 - the heated solution _____
- Explain why you obtained the observed color in 12 M HCl (aq) (Step 2).
- Explain the observed color change that occurred when water was added to the solution in Step 3. Consider how water affects the ion concentrations and Q in this system.
- Consider your observations in the hot water bath in Step 4.
 - In which direction did the equilibrium shift? _____
 - Did the value of K get smaller or larger? _____
 - Is the reaction (as written) exothermic or endothermic? _____Explain.

Part D – Dissolving Insoluble Solids

Equilibrium system: $\text{Zn(OH)}_2 (s) \rightleftharpoons \text{Zn}^{2+} (aq) + 2 \text{OH}^- (aq)$ $K_{sp} \ll 1$

Observations

Step 1	Adding 1 drop of NaOH (aq) to Zn(NO ₃) ₂ (aq)	
Step 2	Tube A: Effect when HCl (aq) is added	
Step 3	Tube B: Effect when NaOH (aq) is added	
Step 4	Tube C: Effect when NH ₃ (aq) is added	

Analysis

- Explain your observation upon addition of HCl (aq) to the precipitate in Tube A. You must consider the various equilibria that are occurring in solution and the effect of HCl on [OH⁻].

- Explain your observations upon addition of NaOH (aq) to the precipitate in Tube B. Consider the various equilibria that are occurring in solution and remember that Zn²⁺ forms stable complex ions with OH⁻ at sufficiently high concentrations.

- Explain your observations upon addition of NH₃ (aq) to the precipitate in Tube C. Consider the various equilibria that are occurring in solution and remember that Zn²⁺ forms stable complex ions with NH₃.

Equilibrium system: $\text{Mg(OH)}_2(\text{s}) \rightleftharpoons \text{Mg}^{2+}(\text{aq}) + 2 \text{OH}^{-}(\text{aq}) \quad K_{\text{sp}} \ll 1$

Observations

Step 1	Adding 1 drop of NaOH (aq) to $\text{Mg(NO}_3)_2$ (aq)	
Step 2	Tube A: Effect when HCl (aq) is added	
Step 3	Tube B: Effect when NaOH (aq) is added	
Step 4	Tube C: Effect when NH_3 (aq) is added	

Analysis

- Explain your observation upon addition of HCl (aq) to the precipitate in Tube A.

1.

- Based on your observations in Steps 3 and 4 do you think that Mg^{2+} forms stable complex ions? Explain your reasoning.