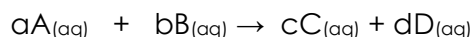


Chemical Equilibrium – Le Châtelier's Principle

Introduction

For a general chemical system at equilibrium



Quoting from **Wikipedia**, the Law of Mass Action states:

For a general chemical equilibrium



the equilibrium constant can be defined by

$$K = \frac{\{S\}^{\sigma} \{T\}^{\tau} \dots}{\{A\}^{\alpha} \{B\}^{\beta} \dots}$$

where {A} is the activity of the chemical species A, etc. (activity is a dimensionless quantity). It is conventional to put the activities of the products in the numerator and those of the reactants in the denominator. For equilibria in solution activity is the product of concentration and activity coefficient. It is common practice to determine equilibrium constants in a medium of high ionic strength. In those circumstances the quotient of activity coefficients is effectively constant and the equilibrium constant is taken to be a concentration quotient.

$$K_c = \frac{[S]^{\sigma} [T]^{\tau} \dots}{[A]^{\alpha} [B]^{\beta} \dots}$$

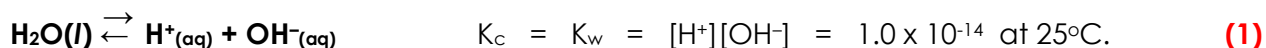
However, the value of K_c will depend on the ionic strength. **All equilibrium constants depend on temperature and pressure (or volume).**

In this laboratory we will study Le Châtelier's Principle

If a chemical system at equilibrium experiences a change in concentration, temperature, volume, or partial pressure, then the equilibrium shifts to counteract the imposed change and a new equilibrium is established.

For example, if a reactant is added or a product is removed from an equilibrium system at constant temperature, then the equilibrium is "shifted to the right", which means that the new equilibrium concentrations are obtained by a net increase of the forward reaction until the new equilibrium is established. The equilibrium constant remains unchanged. If, however, the temperature is changed, for example, the temperature is increased for an exothermic reaction, then the equilibrium constant is decreased and the equilibrium is "shifted to the left". The new equilibrium contains relatively more reactants.

In many equilibrium systems, several equilibria are present simultaneously. All equilibria in aqueous solution also involve



Note that if H^+ ions are added to a basic solution, they will react with the OH^- to form water, removing H^+ from solution. Similarly, the addition of hydroxide ion to an acidic solution removes hydronium ion from the solution.

Special equipment needed: disposable plastic pipets

Reagents: Obtain the following reagents in your smallest beakers:

20 mL	6 M	$\text{HCl}_{(\text{aq})}$
20 mL	6 M	$\text{NaOH}_{(\text{aq})}$
10 mL	0.3 M	$\text{HCl}_{(\text{aq})}$
10 mL	6 M	$\text{NH}_4\text{OH}_{(\text{aq})}$

General instructions:

1. **Estimate** the 1- and 2-mL volumes in your small test tubes, exact measurements are not required.
2. Solutions must be well mixed to react completely. Dissolving a solid takes time. Stir well and be patient.
3. Concentrated HCl (12 M) is used in Part C. It is in the fume hood and must **not** be removed from the fume hood.
4. Please complete each part of the experiment, including answers to the questions, before proceeding to the next part. Keep your answers short and to the point.

Part A. Acid – Base Indicators

Acid – base indicators are weak acids and bases which change color depending on the $[\text{H}^+]$ in solution. A typical indicator is methyl violet, HMv , which dissociates according to the equation:



The color of the solution depends very much on the H^+ concentration.

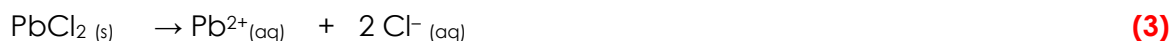
1. Place about 5 mL of deionized water into a regular test tube. Add a few drops of methyl violet indicator. Record the color of the solution in your laboratory notebook.
2. Select one of the 6 M reagents which you think will cause the equilibrium to shift and produce a color change. Add this reagent, drop by drop, until the color change is

complete. If the color does not change, try another reagent. Remember to record all your results in your laboratory notebook.

3. Select a 6 M reagent which will cause the equilibrium to shift back and return the solution to its original color (that is, the color of methyl violet in water). Add it carefully drop by drop, until you have restored the original color. Again, if your first choice was wrong, try another reagent.
4. Answer all questions for Part A before going on to Part B.

Part B. Solubility Equilibrium; Finding a Value for K_{sp}

Many ionic substances have very limited solubility. For example lead (II) chloride dissolves to a small extent according to the equation:



The equilibrium constant is called the solubility product, K_{sp} , and has the form

$$K_c = [\text{Pb}^{2+}][\text{Cl}^{-}]^2 = K_{sp} \quad (4)$$

For reaction (3) to be at equilibrium, some solid lead (II) chloride must be present in the system. If there is no solid present, then the system is not at equilibrium and equation (4) does not apply to a non-equilibrium situation.

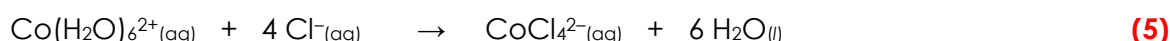
Question: Why isn't $\text{PbCl}_2(s)$ included in the equilibrium constant expression?

1. Set up a hot water bath, using a 400-mL beaker half full of water. Start heating the water.
2. Place 5.0 mL of 0.30 M $\text{Pb}(\text{NO}_3)_2$ into a regular test tube. Add 0.5 mL of 0.30 M HCl, stir, wait about 15 seconds, record your observations.
3. To the lead (II) nitrate solution, continue adding the 0.30 M HCl in 0.5 mL increments. Stir after each addition. Continue adding until a just noticeable amount of white solid lead (II) chloride is present after stirring. Record the total volume of hydrochloric acid added.
4. Put the test tube containing the precipitated lead (II) chloride in the hot water bath. Stir.
5. Record your observations. Cool the test tube under the cold water tap. Stir. Record your observations.
6. Place about 5 mL of deionized water in your 10-mL graduated cylinder. From the cylinder, add 1-mL increments of deionized water to the mixture in the test tube, stirring well after each addition. Record the volume of deionized water added when the precipitate dissolves.
7. Answer all questions and carry out all calculations for Part B before going on to Part C.

Part C. Complex Ion Equilibria

Most metallic ions in solution exist not as simple ions, but as complex ions, that is, in combination with other ions or molecules called ligands. For example, the Co^{2+} ion in aqueous solution exists as the pink $\text{Co}(\text{H}_2\text{O})_6^{2+}$ complex ion, and Cu^{2+} as the blue $\text{Cu}(\text{H}_2\text{O})_4^{2+}$ complex ion. For both of these ions the ligands are water molecules. Complex ions are reasonably stable but their stability varies depending on the ligand. When a stronger bonding ligand is added to a complex ion solution, then the more stable complex ion will form. Common ligands that forms stable complexes are OH^- , NH_3 , and Cl^- .

An interesting Co(II) complex is the CoCl_4^{2-} ion, which is blue. This ion is stable in concentrated Cl^- solutions. The equilibrium reaction is:



1. Place a few small crystals (~0.1 g) of solid $\text{CoCl}_2 \cdot 6 \text{H}_2\text{O}$ in a regular test tube. Under the hood, carefully add 2 mL of 12 M HCl. Record the color of the solution.
2. Carefully add 2-mL portions of deionized water, stirring after each addition, until no further color change occurs. Record the new color.
3. Place the test tube in the hot water bath and note any change in color. Cool the test tube under the cold water tap and record your observations.
4. Complete all questions for Part C before going on to Part D.

Part D. Dissolving Insoluble Salts

Substances which are called "insoluble", can be dissolved by addition of reagents which cause the equilibrium to shift to the right, that is, towards the products, which are the ions in solution. Consider the dissolution of $\text{Zn}(\text{OH})_2$:



$$K_c = K_{sp} = [\text{Zn}^{2+}][\text{OH}^-]^2 = 5 \times 10^{-17} \text{ at } 25^\circ\text{C} \quad (7)$$

The very small value of K_{sp} means that $\text{Zn}(\text{OH})_2$ is almost completely insoluble in water, but the addition of a reagent which will remove OH^- from solution, will require $[\text{Zn}^{2+}]$ to increase according to equation (7). An acid will remove OH^- from the solution, that is, the addition of H^+ will remove OH^- by forming water molecules. In this way the concentration of OH^- can be forced to be so small that the Zn^{2+} concentration in equation (7) becomes reasonably large.

Also, the concentration of zinc ion can be reduced by adding a reagent which forms a stable complex ion with Zn^{2+} . For example:



Thus, solutions which contain high concentrations of OH^- or NH_3 , will have a very low concentration of Zn^{2+} , causing any solid $\text{Zn}(\text{OH})_2$ present to dissolve so that the equation (7) is satisfied.

1. Place about 2 mL of 0.1 M $\text{Zn}(\text{NO}_3)_2$ in each of three small test tubes. Add one drop of 6 M NaOH to each test tube and stir. Record your observations.
2. To the first test tube add 6 M HCl drop by drop while stirring. To the second test tube add 6 M NaOH drop by drop while stirring. To the third test tube add 6 M NH_3 .
3. Record what happens in each case.
4. Repeat steps 1 and 2, but using a solution of 0.1 M $\text{Mg}(\text{NO}_3)_2$ instead of the zinc solution. Record your observations.
5. Answer the questions for Part D.

The following data sheet will help you organize your observations. There are also questions to guide you through this laboratory. DO NOT WRITE ON THIS SHEET! Copy this information into your laboratory notebook.

Part A. Acid-Base Indicators

What is the color of methyl violet in water ?

What reagent causes a color change?

What reagent causes a shift back to the original color?

In terms of equilibrium of reaction (2), explain why the reagents for Steps 2 and 3 worked.

Part B. Solubility Equilibrium; Finding a Value for K_{sp}

Calculate the number of moles of lead (II) ion.

What volume of 0.30 M HCl was used ? How many moles of chloride ion is this?

Record your observations in hot water and in cold water.

What volume of water was added to dissolve PbCl_2 ? What is the total volume of the solution?

Why didn't lead (II) chloride precipitate immediately on addition of HCl. (What conditions must be met by $[\text{Pb}^{2+}]$ and $[\text{Cl}^-]$ if PbCl_2 is to form?)

Explain your observations in Step 4 in terms of the increase or decrease of K_{sp} due to heating and the sign of ΔH for reaction (3).

In terms of the equilibrium of reaction (3), explain why PbCl_2 dissolved when water was added in Step 5. In which direction did the added water drive the reaction?

Calculate $[\text{Pb}^{2+}]$ and $[\text{Cl}^-]$ in the final solution of Step 5 from the number of moles of ions and the final volume of the solution. Calculate K_{sp} for PbCl_2 using equation (4).

Part C. Complex Ion Equilibria

Color of solid $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ _____

Color of solution in 12 M HCl _____

Color of diluted solution _____

Color of hot solution _____

Color of cooled solution _____

Formula of Co(II) complex in solution in:

12 M HCl _____

diluted solution _____

hot solution _____

cooled solution _____

In terms of reaction (5) explain the color change which occurs when water was added in step two. In terms of reaction (5) explain the color change which occurs when the diluted solution was heated (How did heating affect the value of K_c ? What is the sign of ΔH of reaction (5)?)

Part D. Dissolving Insoluble Solids

Record your observations on addition of a drop of 6 M NaOH to $\text{Zn}(\text{NO}_3)_2$ solution:

What is the effect on solubility of $\text{Zn}(\text{OH})_2$ of:

- a. added HCl b. added NaOH c. added NH_3

Record your observations on addition of a drop of 6M NaOH to $\text{Mg}(\text{OH})_2$ solution:

What is the effect on solubility of $\text{Mg}(\text{OH})_2$ of:

- a. added HCl b. added NaOH c. added NH_3

Explain your observations. Consider how reaction (6) is affected by addition of OH^- ions. Consider how reaction (1) is affected by addition of H^+ ions. What does that do to reaction (6)? Consider how reaction (8) is affected by addition of OH^- ions. What does that do to reaction (6)? Consider how reaction (9) is affected by addition of the NH_3 . What does that do to reaction (6)? In Step 3, you found that $\text{Mg}(\text{OH})_2$ in some ways is similar to $\text{Zn}(\text{OH})_2$, but different in others. **State** and **explain** your observations in your laboratory notebook.