Lab 8: Ksp of $Ca(OH)_2$

Introduction

Up until now, the solubility of a salt has been defined in absolute terms: soluble or insoluble. However, with your newly acquired understanding of chemical equilibrium, you can now expand your definitions to allow for the calculation of the *degree* of solubility displayed by each salt. All salts can be made slightly soluble if the conditions (concentrations, temperature, pressure) are right. The calculation of this solubility introduces a special equilibrium constant, called the solubility product constant or Ksp. This experiment is designed to give you experience writing expressions for and calculating this constant.

Relevance

The importance of Ksp can be demonstrated with the current application of fluoride in toothpaste. The major component of teeth is a calcium hydroxyapatite. The Ksp of pure calcium hydroxyapatite is 2.3×10^{-59}. However, the hydroxyapatite found in teeth is referred to as biological apatite and has a higher Ksp value, between 10^{-10} and 10^{-30}. As a result, there is an appreciable concentration of apatite ions present in the mouth. Bacterial action dissolves this biological apatite, causing tooth decay. When fluoride ions are introduced, the apatite precipitates as calcium flouroapatite, hardening the teeth. Pure calcium fluoroapatite has a Ksp of $3.0\text{x}10^{-60}$. While the exact Ksp of “biological flouroapatite” has not been determined satisfactorily, it is at least 400% less soluble than biological apatite. This hardening of the tooth enamel, and the fact that fluoride ions are lethal to bacteria causing decay and plaque, has cemented fluoride used as part of oral health.

Background

Solubility is an equilibrium process. A solution is saturated with a given solute when the solvent has dissolved the maximum amount of that solute at a given temperature and pressure. At saturation, the solute in solution is in equilibrium with the pure undissolved solute (at that given temperature and pressure). The amount of solute that dissolves in 100 g of solvent at a given temperature (and pressure) is defined as the **solubility of the solute**. The number of moles of solute required to form a saturated solution in one liter of solution at a given temperature is its **molar solubility** (usually reported at 25°C).

The factors that affect the solubility of a substance are the:

1. Solute-solute interactive forces
2. Solvent-solvent interactive forces
3. Solute-solvent interactive forces
4. Temperature of the system
5. Pressure of the system

Because the pressure has very little effect upon the solubility of most solids in liquids, the solubility of a solid in a given solvent is constant at a specified temperature. For the purpose of this experiment, only liquids and solids will be discussed. Before discussing the solubility product constant, Ksp, some discussion of solubility must be undertaken.

It is first necessary to define what is meant by soluble and insoluble. Generally, when a compound is soluble, it will dissolve to some extent in a particular solvent. What complicates this general understanding is the fact that an **insoluble** compound will also dissolve in a particular solvent, although to a much smaller extent. In short, the terms soluble and insoluble describe the relative quantity of a particular material that dissolves in a given amount of solvent. To further complicate the definition, there are the sparingly soluble or slightly soluble compounds that do not dissolve sufficiently to qualify for being soluble and yet dissolve too well to be considered insoluble. Arbitrarily, for inorganic compounds this means:

- A compound is considered **soluble** if it dissolves in water to give a solution with a concentration of at least 0.1M at room temperature
- A compound is considered **insoluble** if it dissolves in water to give a solution with a concentration of less than 0.0001 M at room temperature.
- Compounds with solubility between 0.0001 M and 0.1 M are considered to be **slightly soluble** or **sparingly soluble**.

Solubility Product, Ksp

Ksp is a special type of equilibrium constant that describes the equilibrium established between the solid solute and its dissociated ions. The equilibrium expression is written in exactly the same manner as other equilibrium expressions *with the solid being considered the "starting material" and the dissociated ions the "products" in this reaction*. As with other equilibrium constants you are familiar with, the concentration of each of the ions present in the Ksp expression must be raised to the power of its coefficient in the balanced equation. The molar concentration of the solid is a constant so the solid can be eliminated from this equation.

Examples:

$$Mg(OH)_{2(s)} \leftrightharpoons Mg^{2+}_{(aq)} + 2OH^{-}_{(aq)}$$

$$Ksp = [Mg^{2+}][OH^{-}]^{2}$$

$$Ca(OH)_{2(s)} \leftrightharpoons Ca^{2+}_{(aq)} + 2OH^{-}_{(aq)}$$

$$Ksp = [Ca^{2+}][OH^{-}]^{2}$$

$$Al_2(SO_4)_{3(s)} \leftrightharpoons 2Al^{3+}_{(aq)} + 3SO_4{}^{2-}_{(aq)}$$

$$Ksp = [Ag^{3+}]^{2}[SO4^{2-}]^{3}$$

In each case, the solution must be saturated and the solid must be in contact with the solution. The substance must also dissociate into ions in solution. In order to calculate the Ksp as shown it is critical that you clearly identify the number and type of ions formed when a specific substance dissolves. **Unless you can accurately predict the number and type of ions a substance will dissociate into when in solution, you will NOT be successful in understanding or using Ksp.**

Calculations Involving Ksp

It is essential that you clearly understand how a compound dissociates into ions. You must know how the relative number of each type of ion in the solution is related. This way you only need to determine the concentration of one of the ions in solution and by knowing this concentration, you can calculate the concentration of the other ion. With either value, you can then calculate both the molar solubility and the Ksp of the salt.

The Experiment

Calcium hydroxide, $Ca(OH)_2$ is a slightly soluble strong base. This means that while not all of the compound will dissolve, the portion that does dissolves will fully dissociate into its component ions. Therefore, a simple acid-base titration of a saturated solution of calcium hydroxide can be used to determine the amount of hydroxide ions present. From this it will be possible to calculate both the molar solubility and Ksp of $Ca(OH)_2$ at the current laboratory temperature.

Example

We will be using calcium hydroxide in this experiment; but let us consider an example using magnesium hydroxide. Magnesium hydroxide is also a base but unlike $Ca(OH)_2$, $Mg(OH)_2$ is *insoluble* in water at room temperature. Like most compounds, the solubility of $Mg(OH)_2$ increases in hot water. While it would be impossible to run this same experiment in our laboratory, it can serve as a good example to demonstrate the approach and calculations that you will do for this experiment.

A student placed 10g of $Mg(OH)_2$ into a flask and added 500 mL of water. The suspension was heated and stirred at 95°C for 24 hours. Hot water was added periodically to replace any water lost to evaporation. At the end of 24 hours, the suspension was filtered through a heated funnel. *If it took 13.75 mL of 0.0100 M HCl to titrate 100.00 mL portion of this hot saturated solution, calculate the molar solubility and Ksp of* $Mg(OH)_2$ *at 95°C.*

First consider how $Mg(OH)_2$ dissociates when it dissolves in water:

$$Mg(OH)_{2(s)} \leftrightharpoons Mg^{2+}{}_{(aq)} + 2OH^{-}{}_{(aq)}$$

Magnesium hydroxide dissociates into one Mg^{2+} ion and two OH^- ions. The concentration of Mg^{2+} is equal to the molar solubility of the compound. The concentration of the OH^- ion is twice the concentration of the Mg^{2+} ion. Therefore, if the concentration of OH^- can be determined, both the molar solubility and Ksp can be determined.

Now to determine the concentration of the hydroxide ion, it is best to examine the balanced equation first:

$$HCl + OH^- \rightarrow H_2O + Cl^-$$

Every mole of OH^- present will react with one mole of HCl during neutralization. As result, we can calculate concentration of OH^- in the original solutions, based on the volume of HCl needed to reach the endpoint.

$$13.75\,mL\,HCl\ \times \frac{0.0100\,moles\,HCl}{1000\,mL} \times \frac{1\,mole\,OH-}{1\,mole\,HCl} \times \frac{1000\,mmol}{1\,mole} = 0.138\,mmol\,OH-$$

$$[OH^-] = \frac{0.138\,mmol\,OH-}{100\,mL\,solution} = 1.38 \times 10^{-3} M$$

To determine the concentration of Mg^{2+}, remember that 2 x $[Mg^{2+}] = [OH^-]$ so:

$$[Mg^{2+-}] = \frac{[OH^-]}{2} = \frac{1.38 \times 10^{-3} M}{2} = 6.90 \times 10^{-4} M$$

$$[Mg^{2+-}] = \ molar\ solubility = 6.90 \times 10^{-4} M$$

Ksp can be calculated because we know both the Mg^{2+} and OH^- concentrations

$$Ksp = [Mg^{2+}][OH^-]^2$$

$$Ksp = [6.90 \times 10^{-4}][1.38 \times 10^{-3}]^2$$

$$Ksp = 1.31 \times 10^{-9}$$

Procedure

1) Using a 100mL graduated cylinder, transfer 20.0 mL of $Ca(OH)_2$ solution into each of three erlenmeyer flasks.
2) Add 5 drops of phenolphthalein to each flask and swirl. The solution should be hot pink.
3) Obtain 50-100mL of HCl titration solution in one of the 250 mL beakers, record the HCl concentration written on the container.
4) Fill your buret until the volume is between 0.00-4.00mL with the HCl solution.
5) Record the starting volume.
6) Start your titration, you will notice the pink color becoming lighter.
7) The endpoint will be when the pink color disappears completely. **Be careful the endpoint will come suddenly, slow down as it approaches!**
8) Record the final buret reading.
9) Repeat with the other two samples .
    a. Refill buret as needed between trials.
    b. Be sure to record the initial and final buret readings for each trial time!

Report Sheet

Please ensure that you document all of the values in **black** on your lab notebook page! These are numbers that you will enter into LabFlow's Data Report Sheet, and will be used to calculate the values in **red.**

Conc. Of HCl used (M)	

	Trial 1	Trial 2	Trial 3
Volume Sat'd $Ca(OH)_2$ Solution (mL)			
Initial Buret Reading (mL)			
Final Buret Reading (mL)			
Volume HCl Used (mL)			
Millimoles OH^-			
Concentration $[OH^-]$ (M)			
Average Concentration $[OH^-]$ (M)			
Average Concentration $[Ca^{2+}]$ (M)			
Ksp of $Ca(OH)_2$			
Molar Solubility of $Ca(OH)_2$ (mol/L)			
Solubility of $Ca(OH)_2$ in (g/L)			