



**Green Chemistry Module
Level: High School Regents**

Solubility of a Sparingly Soluble Salt



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Solubility of a Sparingly Soluble Salt

In this laboratory experiment, students will be determining the K_{sp} of a sparingly soluble salt, Li_2CO_3 . The students will titrate a saturated solution of lithium carbonate with hydrochloric acid to determine its concentration and then calculate the K_{sp} .

This experiment is expected to take place during one 80-minute session. The instructor can provide background information during the 20-minute span that the students are waiting for the lithium carbonate to dissolve.

Two versions of the lab are provided, though the laboratory activity is exactly the same in each version, per the notes below regarding suitability for some Regents chemistry classes.

Basic Level Instruction: Note that this lab would be appropriate only for an advanced-level Regents chemistry class. The concept of solubility product constants is not included in the Regents Chemistry curriculum and as such, would be an extension topic in a Regents chemistry class. The math required for the calculations may be beyond the ability of some Regents Chemistry students. The extension activity involves practice writing K_{sp} expressions and calculating K_{sp} values given solution concentrations, and calculation of ion concentrations given K_{sp} values.

Advanced Level Instruction: For an advanced class (AP), the lab fulfills the recommendation of an acid-base titration lab and is an appropriate lab activity to explore the expression of solubility product constants. The extension activity invites the student to explore the Common Ion Effect and its practical applications. The laboratory write-up for the advanced level laboratory is a stand-alone report generated by the student.



Solubility of a Sparingly Soluble Salt: Teacher's Guide

Intended Audience: High School Regents Chemistry Students

This experiment is aimed at students in high school learning about chemical changes and reaction types. The experiment would also be suitable for an introductory college laboratory.

Recommended Student Background: Students should be familiar with using a buret and calculating molarities. It would also be helpful if students have knowledge of titration techniques. If acids and bases, including titration, have not yet been covered, additional instructional time may be required to teach titration.

Activity Timeline:

Prepare solution 20 min (background info while waiting)	Filter 5 min	3 titrations 25 min	Cleanup 5 min	Questions/ Calculations 25 min	Total 80 min
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During the 20 minute solution preparation time, background instruction can be provided in one or more of several topics, depending on students' background knowledge:

- Titration techniques
- Equilibrium concepts (solution equilibrium)
- Calculation of K_{sp}

Safety Issues: Wear approved safety goggles and suitable clothing when working with or near all chemicals in this experiment. As they leave the laboratory, students should wash hands well.

Lithium carbonate is considered an irritant, and it should be washed off the hands with a large amount of cold water (without soap).

Dilute hydrochloric acid is an irritant and it is slightly corrosive. Any spills can be cleaned up with water.

Keys to Success:

Students must carefully complete the titrations accurately in order to obtain precise results. If students have not previously completed instruction in titrations, it is advisable to spend time teaching proper procedure and allow students to practice before starting this lab activity.

During the calculations, it may be necessary to review the mole ratios of the ions in solution, pointing out that the lithium ion concentration is double that of the carbonate due to the formulation of the compound. Be certain students know how to account for the varying mole ratios in the K_{sp} calculation.

Advanced Preparation:

The instructor will need to prepare the 0.3M HCl solution ahead of time, being very precise with the concentration of the solution prepared. Students will need to be supplied with the precise acid concentration to complete calculations.

In order to allot time to complete three titrations in one 80 minute class period, it is recommended that the instructor assemble the titration apparatus prior to the start of class.

It may be easiest for the instructor to pre-weigh the 2g Li_2CO_3 starting samples prior to class for quick distribution to lab groups.



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Materials Check List:

Chemicals (per lab group)

- 2 g Li_2CO_3
- 100mL distilled water
- Methyl orange indicator
- Approximately 100mL of 0.3 M HCl
- pH indicator paper

Glassware (per lab group)

- Large waste beaker (600mL)
- Erlenmeyer flasks (for titrations, 3)
- Beaker (150 or 200mL) to prepare Li_2CO_3 solution
- Filter paper
- Funnel
- Beaker (150 or 200mL) to contain the saturated solution of Li_2CO_3
- Buret
- Buret clamp
- Ring stand
- Buret funnel
- Graduated cylinder (25mL)

Measurements:

- Volume of HCl delivered (buret)

Recycling and disposal:

The titration solutions are neutralized with the leftover lithium carbonate (this produces lithium bicarbonate, which is fairly neutral), and then the mixture can simply be washed down the drain with water.



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Green Chemistry: Making materials sustainably

Chemical manufacturing is as old as civilization and the discoveries of bronze and iron came to define the eras that ensued. In modern times, we take for granted a plentiful supply of metals, plastics, dyestuffs and medicines. We have come to depend on the chemical industry to provide us with all the materials we need for our "materialist" society.

But the supply of these materials is not infinite. As the human population grows, and demands an ever higher standard of living, the consumption of the Earth's materials is in danger of getting out of control. It is therefore essential that chemists become responsible stewards of the raw materials that remain. We need to develop methods for chemical processing that are both chemically and environmentally efficient, and which move us towards a sustainable society. We need new materials that can provide what we need without destroying the Earth.

Green chemistry is designed to help us meet these needs. It aims not just to treat waste, but to avoid producing waste in the first place. Products and processes should be "benign by design," but they must also be practicable.

In this lab manual, we will explore how we can this can be achieved in practice – how we can use chemistry to help solve our environmental problems. We will never be able to build a sustainable society if we don't understand the basic science of where our materials come from, and how they are produced. The goal of this manual is to provide that science, presented within the context of green chemistry.

The Twelve Principles of Green Chemistry

The basic principles of green chemistry were first laid out by two US chemists, Paul Anastas and John Warner, in their 1998 book, "Green Chemistry: Theory and Practice:"

1. **Prevent waste:** Design chemical syntheses to prevent waste, leaving no waste to treat or clean up.
2. **Design safer chemicals and products:** Design chemical products to be fully effective, yet have little or no toxicity.
3. **Design less hazardous chemical syntheses:** Design syntheses to use and generate substances with little or no toxicity to humans and the environment.
4. **Use renewable feedstocks:** Use raw materials and feedstocks that are renewable rather than depleting. Renewable feedstocks are often made from agricultural products or are the wastes of other processes; depleting feedstocks are made from fossil fuels (petroleum, natural gas, or coal) or are mined.
5. **Use catalysts, not stoichiometric reagents:** Minimize waste by using catalytic reactions. Catalysts are used in small amounts and can carry out a single reaction many times. They are preferable to stoichiometric reagents, which are used in excess and work only once.
6. **Avoid chemical derivatives:** Avoid using blocking or protecting groups or any temporary modifications if possible. Derivatives use additional reagents and generate waste.
7. **Maximize atom economy:** Design syntheses so that the final product contains the maximum proportion of the starting materials. There should be few, if any, wasted atoms.
8. **Use safer solvents and reaction conditions:** Avoid using solvents, separation agents, or other auxiliary chemicals. If these chemicals are necessary, use innocuous chemicals.
9. **Increase energy efficiency:** Run chemical reactions at ambient temperature and pressure whenever possible.
10. **Design chemicals and products to degrade after use:** Design chemical products to break down to innocuous substances after use so that they do not accumulate in the environment.
11. **Analyze in real time to prevent pollution:** Include in-process real-time monitoring and control during syntheses to minimize or eliminate the formation of byproducts.



12. Minimize the potential for accidents: Design chemicals and their forms (solid, liquid, or gas) to minimize the potential for chemical accidents including explosions, fires, and releases to the environment.

It must be recognized that these represent a target, and we will not be able to satisfy every principle immediately with every process and product. Nevertheless, if we design our chemistry with these principles in mind, we will make great strides towards achieving sustainability.

Why should you teach about the solubility of a sparingly soluble salt?

Understanding sparingly soluble salts is important in many industrial applications. Being able to design processes to maximize yields based on solubility principles is important in chemical engineering professions. Sodium chloride obtained from sea water is impure, but can be purified by application of a common ion effect. Chemists must be able to predict whether precipitation will occur upon mixing of two solutions, and understanding how to calculate solubility products will allow accurate predictions.

Correlation of the experiment with Green Chemistry

Green Chemistry Principles: 3. Design less hazardous chemical syntheses
 9. Increase energy efficiency

Curriculum alignment

Alignment to the NYS Regents Chemistry Curriculum:

IV.9 Physical properties of substances can be explained in terms of chemical bonds and intermolecular forces. These properties include...solubility... (5.2n)

V.8 A solution is a homogeneous mixture of a solute dissolved in a solvent. The solubility of a solute in a given amount of solvent is dependent on the temperature, the pressure, and the chemical natures of the solute and solvent. (3.10o)

IX.6 Titration is a laboratory process in which a volume of solution of known concentration is used to determine the concentration of another solution. (3.1zz)

This experiment correlates directly with the following sections of the New York State Core Curriculum:

Standard 4: The Physical Setting.

Key Idea 3: Matter is made up of particles whose properties determine the observable characteristics of matter and its reactivity.

Performance Indicator 3.1 Explain the properties of materials in terms of the arrangement and properties of the atoms that compose them.

Major Understandings 3.10o A solution is a homogeneous mixture of a solute dissolved in a solvent. The solubility of a solute in a given amount of solvent is dependent on the temperature, the pressure, and the chemical natures of the solute and solvent.

Major Understandings 3.1zz Titration is a laboratory process in which a volume of a solution of known concentration is used to determine the concentration of another solution.

Key Idea 5: Energy and matter interact through forces that result in changes in motion.

Performance Indicator 5: Explain chemical bonding in terms of the behavior of electrons.

Major Understandings 5.2n Physical properties of substances can be explained in terms of chemical bonds and intermolecular forces. These properties include conductivity, malleability, solubility, hardness, melting point, and boiling point.



Background and Fundamentals for Basic Level Instruction:

Many metal salts dissolve in water to some degree, to produce hydrated positive and negative ions. Up to a certain concentration, referred to casually as the *solubility*, the salt will completely dissolve; after this point, any further salt that is added will not apparently dissolve and the solution is said to be *saturated*.

In this experiment, we will measure the solubility of a slightly soluble salt, lithium carbonate. This compound is used to treat manic depression and bipolar disorder; although non-toxic, it should be handled with care. The solubility of this salt changes slightly with temperature, so the filtration of the saturated solution is performed at a fixed temperature of 20°C.

An alternative way to describe solubility is in terms of the *solubility product constant* or K_{sp} . In this description, the solid form is described as being in equilibrium (balance) with the dissolved (hydrated) form. If there is more salt present than can dissolve in the given amount of water, we can say that the amount of solid dissolving is equal to the amount of dissolved salt that is precipitating.

The dissolved form is present as positive and negative ions, and the solubility product constant is based upon the concentration of these ions. For a simple 1:1 salt such as lithium fluoride (LiF), the K_{sp} value is equal to the concentration of Li^+ times the concentration of F^- , written as:

$$K_{sp} = [Li^+][F^-]$$

The square brackets mean "molar concentration of." With lithium carbonate, the situation is more complicated, because we have two lithiums for one carbonate. Therefore we use this equation:

$$K_{sp} = [Li^+]^2[CO_3^{2-}]$$

In this experiment, you will measure the solubility of lithium carbonate. This is done by performing an acid-base titration on a saturated solution to measure the concentration of lithium carbonate present, = $[Li_2CO_3]$. From this, you can calculate the K_{sp} . The equation for the titration is:



Guidance Notes:

Students should already be familiar with titration procedures before beginning this lab. If instruction has not been provided in proper titration technique (including how to read volume from a buret), then additional time should be allotted for procedural instructions.

While the lab calls for running the titrations at a fixed temperature (20°C), students should be able to obtain reliable results at ambient temperature, eliminating the need for temperature control mechanisms.

Answers

Pre-lab Questions:

The solubility of lithium fluoride, LiF, is 1.6g/L, or 0.062 M.

- A. What is the molar concentration of the lithium ion? (Hint – this is pretty easy!)

Molar concentration of Li^+ is 0.062 M

- B. What is the molar concentration of the fluoride ion? (Also easy!)

Molar concentration of F^- is 0.062 M

- C. What is the K_{sp} for lithium fluoride?

The K_{sp} of LiF is 0.003844 M



Questions:

1. If the concentration of $[Li^+]$ were doubled (say, by adding a highly soluble Li salt such as LiI), what would be the new concentration of $[CO_3^{2-}]$ in the saturated solution?

$$K_{sp} = [Li^+]^2 [CO_3^{2-}] \rightarrow [CO_3^{2-}] = \frac{K_{sp}}{[Li^+]^2}$$

Students should use the above formula to calculate the carbonate ion concentration, using their lithium ion concentration and K_{sp} as the starting point for the calculation.

2. If the concentration of $[CO_3^{2-}]$ were doubled (say, by adding a highly soluble carbonate salt such as Ca_2CO_3), what would be the new concentration of $[Li^+]$ in the saturated solution? Why is the effect less than in question 1?

$$[Li^+]^2 = \frac{K_{sp}}{[CO_3^{2-}]} \rightarrow [Li^+] = \sqrt{\frac{K_{sp}}{[CO_3^{2-}]}}$$

The effect is less than in question one because of the molar ratio which requires you to take the square root to get the final lithium ion concentration.

3. Strontium sulfate has the formula $SrSO_4$. Write an expression for its K_{sp} in terms of $[Sr^{2+}]$ and $[SO_4^{2-}]$

$$K_{sp} = [Sr^{2+}][SO_4^{2-}]$$

4. The K_{sp} of strontium sulfate is 3.4×10^{-7} . Calculate the concentration (molarity) of strontium ions present in solution, $[Sr^{2+}]$.

$$K_{sp} = X^2 \text{ where } X = [Sr^{2+}] = [SO_4^{2-}]$$

$$K_{sp} = 3.4 \times 10^{-7} = X^2 \rightarrow X = \sqrt{3.4 \times 10^{-7}} = [Sr^{2+}] = 5.83 \times 10^{-4}$$

Extension Activities:

1. For each of the following substances, write the correct K_{sp} expression.

- $BaSO_4$

$$K_{sp} = [Ba^{2+}][SO_4^{2-}]$$

- PbI_2

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

- $MgCO_3$

$$K_{sp} = [Mg^{2+}][CO_3^{2-}]$$

- Ag_2CrO_4

$$K_{sp} = [Ag^+]^2 [CrO_4^{2-}]$$



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2. Calculate the K_{sp} in the following examples.

- The concentration of a saturated solution of $BaSO_4$ is $3.90 \times 10^{-5}M$. Calculate K_{sp} for barium sulfate at $25^\circ C$.

$$\begin{aligned}K_{sp} &= [Ba^{2+}][SO_4^{2-}] \\ &= (3.90 \times 10^{-5})(3.90 \times 10^{-5}) \\ K_{sp} &= 1.52 \times 10^{-9}\end{aligned}$$

- The concentration of lead ions in a saturated solution of PbI_2 at $25^\circ C$ is $1.3 \times 10^{-3} M$. What is its K_{sp} ?

First, determine concentration of the ions. Take care to determine the concentration of I^- ions:

$$\begin{aligned}[PbI_2] &= 1.30 \times 10^{-3}M \\ [Pb^{2+}] &= 1.30 \times 10^{-3}M \\ [I^-] &= 2 \times 1.30 \times 10^{-3} = 2.60 \times 10^{-3}\end{aligned}$$

Substitute values into the K_{sp} expression and solve for the unknown:

$$\begin{aligned}K_{sp} &= [Pb^{2+}][I^-]^2 \\ &= (1.30 \times 10^{-3})(2.60 \times 10^{-3})^2 \\ &= (1.30 \times 10^{-3})(6.76 \times 10^{-6}) \\ K_{sp} &= 8.79 \times 10^{-9}M\end{aligned}$$

3. Calculate the concentration of each of the ions in solution for the following examples.

- K_{sp} for $MgCO_3$ at $25^\circ C$ is 2.0×10^{-8} . What are the ion concentrations in a saturated solution at this temperature?

$$\begin{aligned}K_{sp} &= [Mg^{2+}][CO_3^{2-}] \\ 2.0 \times 10^{-8} &= (x)(x) = x^2 \\ x^2 &= 2.0 \times 10^{-8} \\ x &= \sqrt{2.0 \times 10^{-8}} \\ &= 1.4 \times 10^{-4}M \\ x = [Mg^{2+}] &= 1.4 \times 10^{-4}M \\ x = [CO_3^{2-}] &= 1.4 \times 10^{-4}M\end{aligned}$$



Background and Fundamentals for Advanced Level Instruction:

The background and fundamentals of the lab are the same as in the basic level: the lab illustrates the concepts of sparingly soluble materials and generates quantitative data for calculation of K_{sp} for a given substance. Students will complete the experiment and prepare an independent lab write-up, including percent error calculation based on their experimental results, a discussion of possible sources of error, and investigation into real-world applications of the K_{sp} concepts.

Guidance Notes:

It is assumed that students are already familiar with titration procedures. If instruction has not been provided in proper titration technique (including how to read volume from a buret), then additional time should be allotted for procedural instructions.

While the lab calls for running the titrations at a fixed temperature (20°C), students should be able to obtain reliable results at ambient temperature, eliminating the need for temperature control mechanisms.

Answers:

Pre-Lab:

- Write the balanced dissociation equation.
 $\text{LiF} \rightarrow \text{Li}^{+1} + \text{F}^{-1}$
- Determine the concentration of the lithium ion and the fluoride ion.
 $[\text{Li}^{+1}] = [\text{F}^{-1}] = 6.2 \times 10^{-2}$
- Write the K_{sp} expression for the reaction.
 $K_{sp} = [\text{Li}^{+1}] [\text{F}^{-1}]$
- Calculate K_{sp} for lithium fluoride.
The K_{sp} of LiF is 0.003844 M

Questions:

- If the concentration of $[\text{Li}^{+}]$ were doubled (say, by adding a highly soluble Li salt such as LiI), what would be the new concentration of $[\text{CO}_3^{2-}]$ in the saturated solution?

$$K_{sp} = [\text{Li}^{+}]^2 [\text{CO}_3^{-2}] \rightarrow [\text{CO}_3^{-2}] = \frac{K_{sp}}{[\text{Li}^{+}]^2}$$

Students should use the above formula to calculate the carbonate ion concentration, using their lithium ion concentration and calculated K_{sp} as the starting point for the calculation.

- If the concentration of $[\text{CO}_3^{2-}]$ were doubled (say, by adding a highly soluble carbonate salt such as Cs_2CO_3), what would be the new concentration of $[\text{Li}^{+}]$ in the saturated solution? Why is the effect less than in question 1?

$$[\text{Li}^{+}]^2 = \frac{K_{sp}}{[\text{CO}_3^{-2}]} \rightarrow [\text{Li}^{+}] = \sqrt{\frac{K_{sp}}{[\text{CO}_3^{-2}]}}$$



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The effect is less than in question one because of the molar ratio which requires you to take the square root to get the final lithium ion concentration.

3. Strontium sulfate has the formula SrSO_4 . Write an expression for its K_{sp} .

$$K_{\text{sp}} = [\text{Sr}^{+2}][\text{SO}_4^{-2}]$$

4. The K_{sp} of strontium sulfate is 3.4×10^{-7} . Calculate the concentration of strontium ions present in solution, $[\text{Sr}^{2+}]$.

$$K_{\text{sp}} = X^2 \quad \text{where} \quad X = [\text{Sr}^{+2}] = [\text{SO}_4^{-2}]$$

$$K_{\text{sp}} = 3.4 \times 10^{-7} = X^2 \rightarrow X = \sqrt{3.4 \times 10^{-7}} = [\text{Sr}^{+2}] = 5.83 \times 10^{-4}$$

5. Calculate K_{sp} for a saturated nickel(II) sulfide, NiS , solution with a molar concentration of 3.27×10^{-11}

$$K_{\text{sp}} = [\text{Ni}^{+2}][\text{S}^{-2}] = (3.27 \times 10^{-11})^2 = 1.07 \times 10^{-21}$$

6. Calculate the concentration of ions in a saturated solution of CaCO_3 in water at 25°C . K_{sp} for CaCO_3 is 4.8×10^{-9} .

$$K_{\text{sp}} = [\text{Ca}^{+2}][\text{CO}_3^{-2}] = x^2 = 4.8 \times 10^{-9}$$

$$x = \sqrt{4.8} \times 10^{-9} = 6.9 \times 10^{-5} = [\text{Ca}^{+2}] = [\text{CO}_3^{-2}]$$

Extension Activities:

Use any resources available to investigate the "Common Ion Effect". Write one to two paragraphs explaining the Common Ion Effect. Include at least two examples that illustrate the concept and how it can be used to precipitate certain ions from solution while keeping another ion in solution.

Common ion effect describes an effect when two or more substances ionize to produce the same ion in solution. When this happens, the solubility of a sparingly soluble substance can be reduced. This can be used for purification of water by precipitating out undesirable ions. The process is also incorporated into soap making. It can also suppress ionization of weak acids and bases.



Solubility of a Sparingly Soluble Salt

Laboratory Experiment # _____

Name _____

Date _____

Partner _____

Introduction:

Many metal salts dissolve in water to some degree, to produce hydrated positive and negative ions. Up to a certain concentration, referred to casually as the *solubility*, the salt will completely dissolve; after this point, any further salt that is added will not apparently dissolve and the solution is said to be *saturated*.

In this experiment, we will measure the solubility of a slightly soluble salt, lithium carbonate. This compound is used to treat manic depression and bipolar disorder; although non-toxic, it should be handled with care. The solubility of this salt changes slightly with temperature, so the filtration of the saturated solution is performed at a fixed temperature.

An alternative way to describe solubility is in terms of the *solubility product constant* or K_{sp} . In this description, the solid form is described as being in equilibrium (balance) with the dissolved (hydrated) form. If there is more salt present than can dissolve in the given amount of water, we can say that the amount of solid dissolving is equal to the amount of dissolved salt that is precipitating.

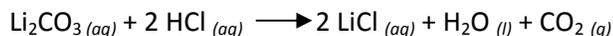
The dissolved form is present as positive and negative ions, and the solubility product constant is based upon the concentration of these ions. For a simple 1:1 salt such as lithium fluoride (LiF), the K_{sp} value is equal to the concentration of Li^+ times the concentration of F^- , written as:

$$K_{sp} = [Li^+][F^-]$$

The square brackets mean "molar concentration of whatever is within the brackets." With lithium carbonate, the situation is more complicated, because we have two lithium ions for one carbonate. Therefore we use this equation:

$$K_{sp} = [Li^+]^2[CO_3^{2-}]$$

In this experiment, you will measure the solubility of lithium carbonate. This is done by performing an acid-base titration on a saturated solution to measure the concentration of lithium carbonate present, = $[Li_2CO_3]$. From this, you can calculate the K_{sp} . The equation for the titration is:



What is Green Chemistry?

The goal of green chemistry is to design chemicals and processes that reduce or eliminate negative environmental impacts. This includes products and processes that use or generate less hazardous substances, reduced waste products, less or non-toxic components, and using substances more efficiently. Green chemistry is a highly effective approach to pollution prevention because it applies innovative scientific solutions to real-world environmental situations.

Green chemistry provides a number of benefits, including:

- reduced waste, eliminating costly end-of-the-pipe treatments
- safer products
- reduced use of energy and resources
- improved competitiveness of chemical manufacturers and their customers.



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There are twelve principles that green chemistry relies on that were first laid out by two US chemists, Paul Anastas and John Warner, in their 1998 book, "Green Chemistry: Theory and Practice":

1. **Prevent waste:** Design chemical syntheses to prevent waste, leaving no waste to treat or clean up.
2. **Design safer chemicals and products:** Design chemical products to be fully effective, yet have little or no toxicity.
3. **Design less hazardous chemical syntheses:** Design syntheses to use and generate substances with little or no toxicity to humans and the environment.
4. **Use renewable feedstocks:** Use raw materials and feedstocks that are renewable rather than depleting. Renewable feedstocks are often made from agricultural products or are the wastes of other processes; depleting feedstocks are made from fossil fuels (petroleum, natural gas, or coal) or are mined.
5. **Use catalysts, not stoichiometric reagents:** Minimize waste by using catalytic reactions. Catalysts are used in small amounts and can carry out a single reaction many times. They are preferable to stoichiometric reagents, which are used in excess and work only once.
6. **Avoid chemical derivatives:** Avoid using blocking or protecting groups or any temporary modifications if possible. Derivatives use additional reagents and generate waste.
7. **Maximize atom economy:** Design syntheses so that the final product contains the maximum proportion of the starting materials. There should be few, if any, wasted atoms.
8. **Use safer solvents and reaction conditions:** Avoid using solvents, separation agents, or other auxiliary chemicals. If these chemicals are necessary, use innocuous chemicals.
9. **Increase energy efficiency:** Run chemical reactions at ambient temperature and pressure whenever possible.
10. **Design chemicals and products to degrade after use:** Design chemical products to break down to innocuous substances after use so that they do not accumulate in the environment.
11. **Analyze in real time to prevent pollution:** Include in-process real-time monitoring and control during syntheses to minimize or eliminate the formation of byproducts.
12. **Minimize the potential for accidents:** Design chemicals and their forms (solid, liquid, or gas) to minimize the potential for chemical accidents including explosions, fires, and releases to the environment.

Why is this experiment green?

This experiment is designed with the following green principles in mind: 3) Design less hazardous chemical syntheses and 9) Increases energy efficiency. The experiment generates end products which are not hazardous and may be safely washed down the drain, eliminating a hazardous chemical waste stream. The energy efficiency is addressed by completing the experiment at ambient (room) temperatures, eliminating the need for additional processes for maintaining a higher or lower temperature.



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Safety

Wear approved safety goggles and suitable clothing when working with or near all chemicals in this experiment. As they leave the laboratory, students should wash hands well.

Lithium carbonate is considered an irritant, and it should be washed off the hands with a large amount of cold water (without soap).

Dilute hydrochloric acid is an irritant and it is slightly corrosive. Any spills can be cleaned up with water.

Materials and Equipment

Chemicals (per lab group)

- 2 g Li_2CO_3
- 100mL distilled water
- Methyl orange indicator
- Approximately 100mL of 0.3 M HCl
- pH indicator paper

Glassware (per lab group)

- Large waste beaker (600mL)
- Erlenmeyer flasks (for titrations, 3)
- Beaker (150 or 200mL) to prepare Li_2CO_3 solution
- Filter paper
- Funnel
- Beaker (150 or 200mL) to contain the saturated solution of Li_2CO_3
- Buret
- Buret funnel
- Buret clamp
- Ring stand
- Graduated cylinder (25mL)

Experiment

Pre-lab:

The solubility of lithium fluoride, LiF, is 1.6g/L, or 0.062 M.

- What is the molar concentration of the lithium ion? (Hint – this is pretty easy!)
- What is the molar concentration of the fluoride ion? (Also easy!)
- What is the K_{sp} for lithium fluoride? (Show your work.)



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Procedure:

1. Weigh approximately 2 g lithium carbonate, and add this to 100 mL room temperature distilled water. **Record the mass of Li_2CO_3 used in the data table on the next page.**
2. Set the cloudy mixture to stir for 15-20 minutes on a magnetic stirplate, or swirl by hand. You will have some solid material that will not dissolve.
3. Filter the mixture at room temperature using simple gravity filtration, collecting the filtrate in a 150 or 200 ml beaker. The liquid portion (the "filtrate") is the saturated solution you will test.
4. Measure 25 mL of this saturated Li_2CO_3 solution and dispense this into a 250 mL Erlenmeyer flask. Add two drops of methyl orange indicator.
5. Titrate the solution against 0.3 M hydrochloric acid (around 30 mL will be needed). Note the exact concentration of HCl (provided by your teacher). At the endpoint, the indicator should turn from yellow to orange-red. **Record the volume of HCl used for each titration in the data table on the next page.**
6. Carry out the titration two more times, recording the data from each titration in the data table.
7. After titration, the orange-red solutions can be mixed with the leftover lithium carbonate and washed directly down the drain with water. Check the pH of the solution with pH paper before washing down the drain. It should be a pH of 6 – 8. If necessary, add more acid and swirl to neutralize the solution until an appropriate pH is reached.

Recycling and disposal: As described in the procedure, the titration solutions are neutralized with the leftover lithium carbonate (this produces lithium bicarbonate, which is fairly neutral), and then the mixture can simply be washed down the drain with water.

Data:

Mass of lithium carbonate used (g)			
Exact HCl concentration (mol/L)			
Titration Number	Vol _{final} (mL)	Vol _{initial} (mL)	Vol _{delivered} = $V_f - V_i$
1			
2			
3			



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Calculations:

Fill out the table below, by carrying out the calculations shown underneath.

Titration #		Vol of HCl (mL)	Moles of HCl (A)	Moles of Li ₂ CO ₃ in 25mL (B)	[Li ₂ CO ₃] (C)	[Li ⁺] (D)	K _{SP} (E)
	1						
	2						
	3						

- A. Calculate the number of moles of HCl in each titration, from the volume used in each titration:

$$mol_{HCl} = V_{HCl} \times \frac{1L}{1000mL} \times M_{HCl}$$

$$mol = mL \times \frac{1L}{1000mL} \times \frac{mol}{L}$$

- B. Calculate the **number of moles lithium carbonate present in 25 mL**, using the number of moles HCl used in each titration. Since one mole of Li₂CO₃ reacts with two moles of HCl, the number of moles of Li₂CO₃ is simply half the number of moles of HCl.



$$mol_{Li_2CO_3} = mol_{HCl} \times \frac{1 mol_{Li_2CO_3}}{2 mol_{HCl}}$$

- C. Calculate the molarity of lithium carbonate or, which is the number of moles of lithium carbonate present in 1000 mL, from the amount present in 25 mL (B):

$$[Li_2CO_3] = \frac{1000mL}{25mL} \times (\text{your answer from calculation B})$$

- D. Calculate [Li⁺]

$$[Li^+] = 2[CO_3^{2-}] = 2[Li_2CO_3]$$

- E. Calculate K_{SP} of Li₂CO₃. This should be a very small number.

$$K_{sp} = [Li^+]^2[CO_3^{2-}]$$



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Conclusions:

1. Calculate the average value for the K_{sp} of lithium carbonate at 20°C.
2. Use a reference book or on-line sources to find the actual K_{sp} of lithium carbonate.
3. Calculate the % error of your calculated K_{sp} of lithium carbonate.
4. Discuss possible sources of error that would account for a discrepancy of greater than 10%.

Questions:

1. If the concentration of $[Li^+]$ were doubled (say, by adding a highly soluble Li salt such as LiI), what would be the new concentration of $[CO_3^{2-}]$ in the saturated solution?
2. If the concentration of $[CO_3^{2-}]$ were doubled (say, by adding a highly soluble carbonate salt such as Cs_2CO_3), what would be the new concentration of $[Li^+]$ in the saturated solution? Why is the effect less than in question 1?
3. Strontium sulfate has the formula $SrSO_4$. Write an expression for its K_{sp} in terms of $[Sr^{2+}]$ and $[SO_4^{2-}]$
4. The K_{sp} of strontium sulfate is 3.4×10^{-7} . Calculate the concentration (molarity) of strontium ions present in solution, $[Sr^{2+}]$.



Extension Activities:

1. For each of the following substances, write the correct K_{sp} expression.
 - $BaSO_4$
 - PbI_2
 - $MgCO_3$
 - Ag_2CrO_4
2. Calculate the K_{sp} in the following examples.
 - The concentration of a saturated solution of $BaSO_4$ is $3.90 \times 10^{-5} M$. Calculate K_{sp} for barium sulfate at $25^\circ C$.
 - The concentration of lead ions in a saturated solution of PbI_2 at $25^\circ C$ is $1.3 \times 10^{-3} M$. What is its K_{sp} ?
3. Calculate the concentration of each of the ions in solution for the following examples.
 - K_{sp} for $MgCO_3$ at $25^\circ C$ is 2.0×10^{-8} . What are the ion concentrations in a saturated solution at this temperature?



Solubility of a Sparingly Soluble Salt

Laboratory Experiment # _____

Name _____

Date _____

Partner _____

Many metal salts dissolve in water to some degree, to produce hydrated positive and negative ions. Up to a certain concentration, referred to casually as the *solubility*, the salt will completely dissolve; after this point, any further salt that is added will not apparently dissolve and the solution is said to be *saturated*.

In this experiment, we will measure the solubility of a slightly soluble salt, lithium carbonate. This compound is used to treat manic depression and bipolar disorder; although non-toxic, it should be handled with care. The solubility of this salt changes slightly with temperature, so the filtration of the saturated solution is performed at a fixed temperature.

An alternative way to describe solubility is in terms of the *solubility product constant* or K_{sp} . In this description, the solid form is described as being in equilibrium (balance) with the dissolved (hydrated) form. If there is more salt present than can dissolve in the given amount of water, we can say that the amount of solid dissolving is equal to the amount of dissolved salt that is precipitating.

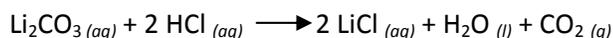
The dissolved form is present as positive and negative ions, and the solubility product constant is based upon the concentration of these ions. For a simple 1:1 salt such as lithium fluoride (LiF), the K_{sp} value is equal to the concentration of Li^+ times the concentration of F^- , written as:

$$K_{sp} = [Li^+][F^-]$$

The square brackets mean "molar concentration of whatever is within the brackets." With lithium carbonate, the situation is more complicated, because we have two lithium ions for one carbonate. Therefore we use this equation:

$$K_{sp} = [Li^+]^2[CO_3^{2-}]$$

In this experiment, you will measure the solubility of lithium carbonate. This is done by performing an acid-base titration on a saturated solution to measure the concentration of lithium carbonate present, $[Li_2CO_3]$. From this, you can calculate the K_{sp} . The equation for the titration is:



What is Green Chemistry?

The goal of green chemistry is to design chemicals and processes that reduce or eliminate negative environmental impacts. This includes products and processes that use or generate less hazardous substances, reduced waste products, less or non-toxic components, and using substances more efficiently. Green chemistry is a highly effective approach to pollution prevention because it applies innovative scientific solutions to real-world environmental situations.

Green chemistry provides a number of benefits, including:

- reduced waste, eliminating costly end-of-the-pipe treatments
- safer products
- reduced use of energy and resources
- improved competitiveness of chemical manufacturers and their customers.



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There are twelve principles that green chemistry relies on that were first laid out by two US chemists, Paul Anastas and John Warner, in their 1998 book, "Green Chemistry: Theory and Practice":

1. **Prevent waste:** Design chemical syntheses to prevent waste, leaving no waste to treat or clean up.
2. **Design safer chemicals and products:** Design chemical products to be fully effective, yet have little or no toxicity.
3. **Design less hazardous chemical syntheses:** Design syntheses to use and generate substances with little or no toxicity to humans and the environment.
4. **Use renewable feedstocks:** Use raw materials and feedstocks that are renewable rather than depleting. Renewable feedstocks are often made from agricultural products or are the wastes of other processes; depleting feedstocks are made from fossil fuels (petroleum, natural gas, or coal) or are mined.
5. **Use catalysts, not stoichiometric reagents:** Minimize waste by using catalytic reactions. Catalysts are used in small amounts and can carry out a single reaction many times. They are preferable to stoichiometric reagents, which are used in excess and work only once.
6. **Avoid chemical derivatives:** Avoid using blocking or protecting groups or any temporary modifications if possible. Derivatives use additional reagents and generate waste.
7. **Maximize atom economy:** Design syntheses so that the final product contains the maximum proportion of the starting materials. There should be few, if any, wasted atoms.
8. **Use safer solvents and reaction conditions:** Avoid using solvents, separation agents, or other auxiliary chemicals. If these chemicals are necessary, use innocuous chemicals.
9. **Increase energy efficiency:** Run chemical reactions at ambient temperature and pressure whenever possible.
10. **Design chemicals and products to degrade after use:** Design chemical products to break down to innocuous substances after use so that they do not accumulate in the environment.
11. **Analyze in real time to prevent pollution:** Include in-process real-time monitoring and control during syntheses to minimize or eliminate the formation of byproducts.
12. **Minimize the potential for accidents:** Design chemicals and their forms (solid, liquid, or gas) to minimize the potential for chemical accidents including explosions, fires, and releases to the environment.

Why is this experiment green?

This experiment is designed with the following green principles in mind: 3) Design less hazardous chemical syntheses and 9) Increases energy efficiency. The experiment generates end products which are not hazardous and may be safely washed down the drain, eliminating a hazardous chemical waste stream. The energy efficiency is addressed by completing the experiment at ambient (room) temperatures, eliminating the need for additional processes for maintaining a higher or lower temperature.

Safety

Wear approved safety goggles and suitable clothing when working with or near all chemicals in this experiment. As they leave the laboratory, students should wash hands well.

Lithium carbonate is considered an irritant, and it should be washed off the hands with a large amount of cold water (without soap).

Dilute hydrochloric acid is an irritant and it is slightly corrosive. Any spills can be cleaned up with water.



Materials and Equipment

Chemicals (per lab group)

- 2 g Li_2CO_3
- 100mL distilled water
- Methyl orange indicator
- Approximately 100mL of 0.3 M HCl
- pH indicator paper

Glassware (per lab group)

- Large waste beaker (600mL)
- Erlenmeyer flasks (for titrations, 3)
- Beaker (150 or 200mL) to prepare Li_2CO_3 solution
- Filter paper
- Funnel
- Beaker (150 or 200mL) to contain the saturated solution of Li_2CO_3
- Buret
- Buret funnel
- Buret clamp
- Ring stand
- Graduated cylinder (25mL)

Experiment

Pre-lab:

The solubility of lithium fluoride, LiF, is 1.6g/L, or $6.2 \times 10^{-2}\text{M}$.

- Write the balanced dissociation equation.
- Determine the concentration of the lithium ion and the fluoride ion.
- Write the K_{sp} expression for the reaction.
- Calculate K_{sp} for lithium fluoride.

Procedure:

- Weigh approximately 2 g lithium carbonate, and add this to 100 mL room temperature distilled water.
- Stir the mixture for 15-20 minutes on a magnetic stirplate, or swirl by hand. You will have some solid material that will not dissolve.
- Filter the mixture at room temperature using simple gravity filtration, collecting the filtrate in a 150 or 200 ml beaker. The liquid portion (the "filtrate") is the saturated solution you will test.
- Measure 25 mL of this saturated Li_2CO_3 solution and dispense this into a 250 mL Erlenmeyer flask. Add two drops of methyl orange indicator.
- Titrate the solution against 0.3 M hydrochloric acid (around 30 mL will be needed). Note the exact concentration of HCl (provided by your teacher). At the endpoint, the indicator should turn from yellow to orange-red.
- Repeat the titration two more times.



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7. After titration, the titrated solutions can be mixed with the leftover lithium carbonate and washed directly down the drain with water. Check the pH of the solution with pH paper before washing down the drain. It should be a pH of 6 – 8. If necessary, add more acid and swirl to neutralize the solution until an appropriate pH is reached.

Recycling and disposal: As described in the procedure, the titration solutions are neutralized with the leftover lithium carbonate (this produces lithium bicarbonate, which is fairly neutral), and then the mixture can simply be washed down the drain with water.

Calculations:

- A. Calculate the number of moles of HCl in each titration, from the volume used in each titration:
- B. Calculate the number of moles lithium carbonate present in 25 mL, using the number of moles HCl used in each titration.
- C. Calculate the molarity of lithium carbonate.
- D. Calculate $[\text{Li}^+]$
- E. Calculate K_{SP} of Li_2CO_3 .

Conclusions:

1. Calculate the average value for the K_{SP} of lithium carbonate at 20°C.
2. Use a reference book or on-line source to determine the actual K_{SP} of lithium carbonate.
3. Calculate the % error of your experimental K_{SP} of lithium carbonate.
4. Discuss possible sources of error that would account for a discrepancy of greater than 10%.

Questions:

1. If the concentration of $[\text{Li}^+]$ were doubled (say, by adding a highly soluble Li salt such as LiI), what would be the new concentration of $[\text{CO}_3^{2-}]$ in the saturated solution?
2. If the concentration of $[\text{CO}_3^{2-}]$ were doubled (say, by adding a highly soluble carbonate salt such as Cs_2CO_3), what would be the new concentration of $[\text{Li}^+]$ in the saturated solution? Why is the effect less than in question 1?
3. Strontium sulfate has the formula SrSO_4 . Write an expression for its K_{SP} .
4. The K_{SP} of strontium sulfate is 3.4×10^{-7} . Calculate the concentration of strontium ions present in solution, $[\text{Sr}^{2+}]$.
5. Calculate K_{SP} for a saturated nickel(II) sulfide, NiS , solution with a molar concentration of 3.27×10^{-11} .
6. Calculate the concentration of ions in a saturated solution of CaCO_3 in water at 25 ° C. K_{SP} for CaCO_3 is 4.8×10^{-9} .

Extension Activities: Use any resources available to investigate the “Common Ion Effect”. Write one to two paragraphs explaining the Common Ion Effect. Include at least two examples that illustrate the concept and how it can be used to precipitate certain ions from solution while keeping another ion in solution.

Report: The lab report should consist of an introduction, answers to pre-lab questions, brief description of procedures, data table including all relevant data, calculations, and a conclusion. Be sure to include answers to the Questions and the Extension activities.