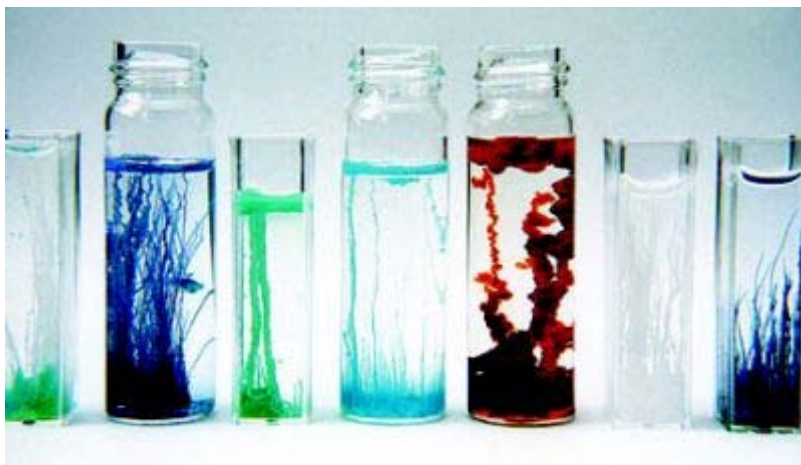


# Experiment 11

## *Precipitation and the Limits of Solubility*



## **The Task**

In this experiment you will investigate precipitation and solubility.

## **Skills**

At the end of the laboratory session you should be able to:

- calculate concentrations of diluted solutions,
- carry out spot tests,
- construct a table for recording experimental results.

## **Other Outcomes**

- You will observe precipitations and discover whether the ion sum or product determines the likelihood of precipitation.
- You will make crystal gardens.

## **The Assessment**

You will be assessed on your presentation of data in tabular format. Read Skill 2 and study the example (Table 1).

## Introduction

While gases and liquids are important components of our material world, it's the solids that give it shape. Rocks, wood, steel, skin, plastics, bone, *etc*; solids provide the rigidity from which comes structure. To understand how solids come into existence and how the manner of their appearance determines their subsequent properties is a question both important enough and intriguing enough to be worth exploring.

A solution consists of two parts - the solvent (the substance doing the dissolving) and the solute (the substance that dissolves). Very complex systems containing many solvents and solutes are common, but this experiment will deal with much simpler cases.

Consider a solution at constant temperature in which we increase the concentration of the solute until it starts to aggregate as a solid. This phenomenon is called precipitation. To study precipitation at room temperature we need a solute that meets two conditions: it must be soluble in the chosen solvent and its solid state must have a melting point that lies well above room temperature. With water as the solvent, a wide range of ionic compounds meet these two conditions.

Part A explores the process of precipitation and whether the sum or the product of ion concentrations determines whether or not a precipitate forms.

Part B explores the reversibility of precipitation - can we get a precipitate to dissolve.

Part C explores the special case of metal-silicate precipitation.

### *Concentration Scales*

The concentration of a solution can be specified in a number of ways. In the table below we provide definitions of the different types of concentration.

Name	Symbol	Definition
molarity	M	number of moles of solute per litre of final solution
molality	m	number of moles of solute per kg of solvent
mole fraction	X	number of moles of compound divided by total number of moles of solvent and solute present.
percentage weight of total volume	% (w/v)	number of grams of added material (either solid or liquid) per 100 mL of final solution
percentage volume of total volume	% (v/v)	number of mL of added material (usually liquid) per 100 mL of final solution
percentage weight of total weight	% (w/w)	number of grams of added material (either solid or liquid) per 100 g of the final solution

The concentration scales of % (w/v), % (v/v) and % (w/w) have the advantage that one doesn't need to know the formula weight of the added material to calculate the concentration. They're often used when the formula weight of the added material isn't known, or, even when the formula weight is known, simply for the sake of convenience.

## Safety

### *Chemical Hazard Identification*

**1.0 M calcium chloride** – low to moderate toxicity – irritant. Avoid eye or skin contact.

**0.10 M sodium carbonate** – low toxicity.

**1.0 M sodium sulfate** – non-hazardous.

**$1.2 \times 10^{-3}$  M silver nitrate** – irritant. Avoid eye or skin contact and inhalation.

**$2 \times 10^{-3}$  M sodium chloride** – non-hazardous

**1.0 M hydrochloric acid** – corrosive. Avoid eye or skin contact and inhalation.

**1.0 M sulfuric acid** – hazardous. Avoid eye or skin contact and inhalation.

**0.10 M sodium hydroxide** – slightly corrosive – irritant. Avoid eye and skin contact.

**1.0 M sodium hydroxide** – corrosive. Avoid eye or skin contact and inhalation.

**waterglass (sodium silicate solution)** – corrosive – irritant. Avoid eye or skin contact and inhalation.

**copper(II) chloride** – corrosive – toxic. Avoid eye or skin contact and inhalation.

**copper(II) sulfide** – moderate toxicity – irritant. Avoid eye or skin contact and inhalation. May evolve toxic/flammable hydrogen sulfide gas when in contact with moisture or acids, and inhalation of high levels may be fatal.

**copper(II) sulfate** – moderate toxicity – irritant. Avoid eye or skin contact and inhalation.

**iron(III) sulfate** – moderate toxicity – irritant. Avoid eye or skin contact and inhalation.

**iron(III) chloride** – corrosive. Avoid eye or skin contact and inhalation.

**iron(III) nitrate** – moderate toxicity – irritant. Avoid eye or skin contact and inhalation.

**iron(II) chloride** – corrosive. Avoid eye or skin contact and inhalation.

**iron(II) sulfate** – moderate toxicity – irritant. Avoid eye or skin contact and inhalation. Toxic by ingestion, although fatal poisonings in adults are rare.

**iron(II) sulfide** – low to moderate toxicity. Avoid eye or skin contact and inhalation.

**0.10 M calcium nitrate** – hazardous. Irritating to eyes and skin.

**0.10 M copper(II) nitrate** – hazardous. Irritating to eyes and skin.

**0.10 M strontium nitrate** – hazardous. Irritating to eyes and skin.

**0.10 M zinc nitrate** – hazardous. Irritating to eyes and skin.

## ***Risk Assessment and Control***

Low risk

Silver salts stain the skin (and anything else they contact).

Avoid contact with all chemicals.

## ***Waste Disposal***

All silver residues from Part A are to be placed in the silver residue container in the fumehood. All the solutions from Part B and can be rinsed down the sink with plenty of water. All the solutions from Parts C and D must be disposed of in the Heavy Metal Waste container in the fumehood.

## **Experimental**

***This experiment is to be carried out in pairs.***

### **Part A Changing concentrations and determining solubilities**

Let's start by looking at the solubility of AgCl and how the concentrations of the ions ( $\text{Ag}^+$  and  $\text{Cl}^-$ ) influence the solubility. The aim of this part of the experiment is to determine the factors that control whether or not a precipitate forms, *i.e.* is it the sum of the ion concentrations (in this case  $[\text{Ag}^+] + [\text{Cl}^-]$ ) or the product of the ion concentrations (in this case  $[\text{Ag}^+] \times [\text{Cl}^-]$ ). Label 2 large test tubes as AgNO<sub>3</sub> and NaCl.

- (A1) Collect 5 mL of the  $1.2 \times 10^{-3}$  M AgNO<sub>3</sub> solution provided in a clean, dry 10 mL measuring cylinder then transfer to the AgNO<sub>3</sub> test tube. Rinse the measuring cylinder and collect 5 mL of the  $2 \times 10^{-3}$  M NaCl solution provided then transfer to the NaCl test tube.
- (A2) Add 10 mL of deionised water to each of 6 large test tubes and label them 1 to 6.
- (A3) Add the following volumes of the AgNO<sub>3</sub> and NaCl solutions to each test tube (Note: Assume that 1 mL = 20 drops, *i.e.* 0.05 mL = 1 drop):
- Test tube 1 – 0.05 mL AgNO<sub>3</sub>, 0.05 mL NaCl
  - Test tube 2 – 0.20 mL AgNO<sub>3</sub>, 0.10 mL NaCl
  - Test tube 3 – 0.50 mL AgNO<sub>3</sub>, 0.50 mL NaCl
  - Test tube 4 – 1.00 mL AgNO<sub>3</sub>, 1.00 mL NaCl
  - Test tube 5 – 2.00 mL AgNO<sub>3</sub>, 0.00 mL NaCl
  - Test tube 6 – 0.00 mL AgNO<sub>3</sub>, 2.00 mL NaCl
- (A4) **Record in your logbook** which solutions gave a precipitate. To check for a precipitate, look down the length of the test tube onto a black tile and compare this with a test tube containing 10 mL of deionised water.

- (A5) **Construct a table in your logbook** containing the  $\text{Ag}^+$  and  $\text{Cl}^-$  concentrations in each test tube, the sum of the ion concentrations ( $[\text{Ag}^+] + [\text{Cl}^-]$ ), the product of the ion concentrations ( $[\text{Ag}^+] \times [\text{Cl}^-]$ ) and whether or not a precipitate formed.

***For your logbook:***

*Based on your observations, is it the ion sum or the ion product that determines whether or not a precipitate forms?*

*Based on your observations, can you provide a mathematical limiting condition for precipitation of  $\text{AgCl}$  to occur?*

## **Part B The reversibility of precipitations**

In this part of the experiment you will look at how reversible various precipitation processes are. There are various 'degrees' of reversibility that might interest us.

- (B1) Add 5 drops of 1.0 M  $\text{CaCl}_2$  to equal volume of 0.10 M  $\text{Na}_2\text{CO}_3$  and mix well.
- (B2) Repeat step (B1) using 1.0 M  $\text{Na}_2\text{SO}_4$  instead of  $\text{Na}_2\text{CO}_3$ .
- (B3) Repeat step (B1) using 0.10 M  $\text{NaOH}$  instead of  $\text{Na}_2\text{CO}_3$ .
- (B4) Add 1 M  $\text{HCl}$  dropwise to each test tube and **record your results in your logbook**. Were any gases evolved? How can you tell? Did any of the precipitates dissolve? If yes, what happens when you add an equal volume of 1 M  $\text{NaOH}$ ? Did the precipitates reappear? Record all your observations in your logbook.

***For your logbook:***

*What are the formulae of the three insoluble calcium salts being investigated?*

*Why did some dissolve in acid and some didn't? Give equations for the reactions that are taking place. Did the addition of 1 M  $\text{NaOH}$  reverse the action of the  $\text{HCl}$  in all cases?*

## **Part C Patterns of precipitation**

Precipitation is an aggregation process. This means that ions have to move from the surrounding solution to join in the precipitation. How the ions move can change the spatial pattern of the precipitation.

In this part of the experiment you will explore the difference in precipitation occurring when the precipitating ions are well mixed and very poorly mixed.

- (C1) For this experiment use the magnifying glass to examine any solid material formed. For each of the following reactions, **record in your logbook** the *appearance* and *colour* of the solid formed using one of the following four descriptors: a) no solid was formed, b) a finely dispersed powder, c) a coarse dispersion of aggregates, or d) a complete membrane or framework (*i.e.* resembling a creased tissue).
- (C2) Collect 10 micro test tube from your drawer and put them in a test tube rack. Place the rack on your bench and be careful not to move it or bump it for the remainder of this exercise.
- (C3) Fill the first test tube gently with 5 drops 10 % w/v waterglass (sodium silicate solution). Add **ONE** drop only of 0.1 M  $\text{SrCl}_2$ . Wait for 2 - 3 minutes and record your observations **in your logbook**, using the descriptors given in step (C1).
- (C4) Fill another test tube with 5 drops 10 % w/v waterglass. Add **ONE** drop only of 0.1 M  $\text{Fe}_2(\text{SO}_4)_3$ . Wait for 2 - 3 minutes and record your observations **in your logbook**, using the descriptors given in step (C1).
- (C5) Repeat step (C4) with each of the following:
- 0.1 M  $\text{Zn}(\text{NO}_3)_2$
  - 0.1 M  $\text{Cu}(\text{NO}_3)_2$
  - 0.1 M  $\text{Ca}(\text{NO}_3)_2$
- (C6) Fill another test tube with 1.0 M  $\text{CaCl}_2$  and add **ONE** drop only of 0.1 M  $\text{Na}_2\text{CO}_3$ . Wait for 2 - 3 minutes and record your observations **in your logbook**, using the descriptors given in step (C1).
- (C7) Repeat step (C6) using, instead of  $\text{Na}_2\text{CO}_3$ :
- 0.1 M  $\text{NaOH}$
  - 1 M  $\text{H}_2\text{SO}_4$
- (C8) Using a glass rod, gently poke the solid that has formed. Gently stir the test tube with the glass rod. Record your observations **in your logbook**.
- (C9) Wash the test tube before returning them to your drawer.

***For your logbook:***

*When a precipitate forms it can either form as an ordered crystal or as something more amorphous. Based on your observations, identify one compound that you believe most likely to have precipitated as a crystal (we would need to make more measurements – e.g. melting points, x-ray diffraction, etc. – to verify this) and one compound that you suspect of precipitating into some more disordered solid.*

## **Part D At play in the chemical garden**

In this part of the experiment you will combine the peculiarity of metal-silicate precipitation, specifically its membrane-like quality, with diffusion-dominated precipitation to produce what are known as ‘chemical gardens’. A diagram of this process is given in Figure 1. You will then set about exploring some properties of these gardens.

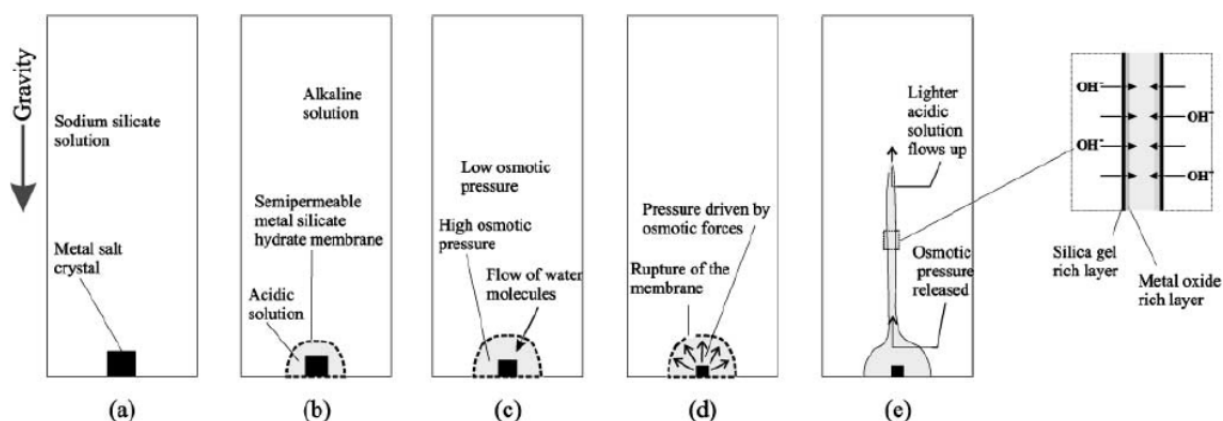


Figure 1: Chemical-garden growth: (a) setup at start of the reaction, (b) membrane formation between acidic and basic solutions, (c) osmotic pressure is higher within the membrane than outside, so it expands, (d) the membrane ruptures under osmotic forces, and (e) a tube forms. [Reference 1]

(D1) Choose one of the following metal ions series, *i.e.* either copper(II), iron(III) or iron(II) compounds.

copper(II)	iron(III)	iron(II)
$\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$	$\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$	$\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$
$\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$	$\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$	$\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$
$\text{CuS}$	$\text{Fe}_2(\text{SO}_4)_3$	$\text{FeS}$

(D2) In the plastic vial provided, place three distinct ‘spots’ of the different metal salts in your series. The size of your spots needs to be between 5 and 10 mg. Have a look at the samples of metal salts in the semi-micro test-tubes at the front of your laboratory for comparison. In your logbook draw a diagram of where you have positioned the metal salts.

(D3) Place the vial where it won’t be disturbed and then very CAREFULLY, add ~15 mL 10 % w/v waterglass to the vial, until it is about 2/3 full. You don’t want the metal salts moving and mixing.

(D4) Leave for a while and observe periodically. **Record your observations in your logbook**; including: which salt grew the fastest, is it tubular, thick/thin, no visible reaction (nvr), *etc.*

(D5) Dispose of the waterglass solution containing the metal salts into the “Heavy Metal” waste. Wash the vial and put it into the “bucket” with the disposable test-tubes.



***In your logbook:***

*Have a look at the crystal gardens for the other metal ion series that you did not do.*

*Did any of the metal ions not give tubular crystals?*

(D6) Your demonstrator will assign you one of the following tasks:

Task 1: What do you observe when a growing crystal structure meets an obstacle? (Try pieces of filter paper.)

Task 2: What happens when you break a crystal structure during growth? (Clamp your sample tube in a retort stand so that it can't fall over and use plastic tweezers to break the growth.)

Task 3: Describe what happens when you grow the garden in a shallow garden? (Use a Petri dish.)

Task 4: Wet a small piece (so that it fits into the bottom of a sample vial) of filter paper in 10 % w/v waterglass. Using plastic tweezers drain off the excess liquid and place it in the bottom of the sample vial. Place approximately 5 mg of metal ion crystals on the filter paper and allow it to stay there for 10 minutes. What do you observe? Then very carefully add some more 10 % w/v waterglass to the sample vial so that the solution is about 1 cm deep. Describe what happens? If the 'chimneys' reach the top of the waterglass solution, very carefully add another 1 cm of 10 % w/v waterglass. Record your observations.

Task 5: Make up a crystal garden as you did in steps (D1) - (D3), place a lid on the vial and clamp the sample tube to a retort stand. As the crystal structure grows, change the angle of the sample vial. Feel free to change the angle of the sample vial as many times as you like. Record your observations.

## **Group Discussion**

Discuss as a group your results from Part A. Does this agree with literature values? (You can look up values in the SI Chemical Data book).

In Part A, you suggested a mathematical expression allowing you to determine the likelihood of precipitation of AgCl (a 1:1 salt). What form do you think the expression would take for a 1:2 salt, *e.g.* ZnCl<sub>2</sub>?

In part B, which salts dissolve in acid and which don't. Why?

## ***References***

1. Julyan H. E. Cartwright, Jaun Manuel García-Riuz, María Luisa Novella and Fermín Otalora, *Journal of Colloid and Interface Science*, 256, 351-359 (2002).