

## Relating qualitative analysis to equilibrium principles ©

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**Prerequisites:** This worksheet is intended as a pre-lab activity for a typical Qualitative Analysis experiment involving the separation of cations. Students must have been through Ionic Equilibria, which is typically covered in the second semester General Chemistry lecture course. Students must be familiar with basic Mathcad operations, including the use of the symbolic processor to solve for an unknown variable.

**Goal:** The goal of this document is to relate the typical laboratory scheme for separation of cations to equilibrium principles taught in the lecture course.

**Introduction:** In Qualitative Analysis ("Qual"), we try to determine whether something (such as an ion or molecule) is present in a sample of matter. The determination generally involves more than just doing one or several tests; it also involves the separation of other species in the sample that may interfere with the test (and lead to a false positive or false negative result). In this document, we will explore a common technique for separating cations in aqueous solutions: selective precipitation.

**Performance Objectives:** After completing the work described in this document you should be able to:

1. estimate the extent of removal of a cation from a solution based on the  $K_{sp}$  of the precipitated salt.
2. explain how adjustment of pH allows for the separation of cations which belong to Qual Group 2 from those that belong to Qual Group 3.

Note : Mathcad, by default, displays numbers less than  $10^{-15}$  as zero. This has been overridden in this document: zero threshold has been set to  $10^{-255}$ . Also, earlier versions of Mathcad may not support standard abbreviations for L, mol, and M, so we define them here, first.

mole := 1      mol := mole      L := liter      M :=  $\frac{\text{mole}}{\text{liter}}$

## Part 1. Separating Ag<sup>+</sup> from Cu<sup>2+</sup>

The typical first step in separating a mixture of cations is the addition of HCl. HCl provides chloride ions and will cause the precipitation of Ag<sup>+</sup>, Pb<sup>2+</sup> and Hg<sub>2</sub><sup>2+</sup> as AgCl, PbCl<sub>2</sub>, and Hg<sub>2</sub>Cl<sub>2</sub> (which are insoluble in water) while other cations remain in solution. Thus, Ag<sup>+</sup>, Pb<sup>2+</sup> and Hg<sub>2</sub><sup>2+</sup> are often referred to as "Qual Group 1, the insoluble chlorides".

We will now investigate how well Ag<sup>+</sup> can be separated from another ion, say, Cu<sup>2+</sup>.

**Note: select SI as your unit system.**

Let's assume 20 drops equals 1 mL

$$\text{drop} := \frac{1}{20} \cdot \text{mL}$$

Consider a mixture of 2 drops of 0.1M AgNO<sub>3</sub> and 2 drops 0.1M Cu(NO<sub>3</sub>)<sub>2</sub>. To this, we add 1 drop of 0.1M HCl. Define the molar concentrations of the solutions and number of drops below. The values for AgNO<sub>3</sub> is done for you as an example:

$$\text{MAgSoln} := 0.1 \cdot \text{M}$$

$$\text{VolAg} := 2 \cdot \text{drop}$$

$$\text{MCuSoln} := \blacksquare$$

$$\text{VolCu} := \blacksquare$$

$$\text{MHClSoln} := \blacksquare$$

$$\text{VolHCl} := \blacksquare$$

Complete the formula below for total volume of the reaction mixture (assuming volumes are additive) here and verify (express in drop)

$$\text{VTotal} := \text{VolAg} + \blacksquare + \blacksquare$$

$$\text{VTotal} = \blacksquare \text{ drop}$$

Now calculate the concentration of Ag<sup>+</sup>, Cu<sup>2+</sup>, and Cl<sup>-</sup> in the solution, *assuming no reaction has taken place*.

$$\text{AgConc} := \frac{\blacksquare}{\text{VTotal}}$$

$$\text{AgConc} = \blacksquare \text{ M}$$

$$\text{CuConc} := \blacksquare$$

$$\text{CuConc} = \blacksquare \text{ M}$$

$$\text{ClConc} := \blacksquare$$

$$\text{ClConc} = \blacksquare \text{ M}$$

We now investigate whether AgCl will precipitate by calculating the ion product of AgCl in this solution. Enter the formula here and verify.

$$IP_{AgCl} := AgConc \cdot ClConc$$

$$IP_{AgCl} = 1.6 \times 10^{-10} \text{ M}^2$$

**Compare with Ksp of AgCl, which is  $1.6 \times 10^{-10} \text{ M}^2$ . Will AgCl precipitate from this mixture?**

Let's calculate what the final Ag<sup>+</sup> concentration will be after precipitation of AgCl (i.e., at equilibrium). First, we define Ksp of AgCl.

$$K_{sp} := 1.6 \cdot 10^{-10} \cdot \text{M}^2$$

In the following equations (Eq. 1 and Eq. 2), we use Boolean equal signs to prevent Mathcad from trying to obtain a number for the left-hand-side.

Let Ageq = mol/L of Ag<sup>+</sup> left in solution at equilibrium.

The formula for mol/L of Cl<sup>-</sup> left in solution is

$$Cl_{eq} = ClConc - (AgConc - Ageq) \quad \text{Eq. 1}$$

**Explain Eq. 1 by answering the following**

- 1. What does the expression inside the parentheses represent?**
- 2. Why is the right hand side equal to the left hand side?**

Substitute the right-hand side of Eq.1 for Cl<sub>eq</sub> in Eq. 2 and label the resulting equation as Eq. 3

$$K_{sp} = Ageq \cdot Cl_{eq} \quad \text{Eq. 2}$$

$$K_{sp} = Ageq \cdot (ClConc - (AgConc - Ageq)) \quad \text{Eq. 3}$$

Eq. 3 is a quadratic equation in  $A_{\text{eq}}$  and solving for  $A_{\text{eq}}$  will yield two roots. Solve for  $A_{\text{eq}}$  from Eq. 3 using Mathcad's symbolic processor. Click on  $A_{\text{eq}}$  in Eq. 3, then click on "Solve for variable" in Mathcad's Symbolic menu. Paste the roots in the expression below.

roots :=

roots = M

roots<sub>0</sub> = M

roots<sub>1</sub> = M

One of these two roots cannot be the equilibrium concentration of  $\text{Ag}^+$ . Why?

Assign the correct root to  $A_{\text{eq}}$  below. Should you lose the subscript while editing, you can get it back by typing [.

$A_{\text{eq}} := \text{roots}_$

$A_{\text{eq}} = \text{ M}$

Enter the formula to calculate the percent of  $\text{Ag}^+$  ions removed from solution due to precipitation of  $\text{AgCl}$ , and verify

$$\text{PercentAgRemoved} := \frac{\text{AgConc} - \text{AgConc}}{\text{AgConc}}$$

PercentAgRemoved = %

**Change amount of HCl used to 2 drops. Explain what happens to PercentAgRemoved. (Recall Le Chatelier's Principle. How can you shift the equilibrium  $\text{AgCl}(s) = \text{Ag}^+(\text{aq}) + \text{Cl}^-(\text{aq})$  to the left?)**

**Change amount of HCl used back to 1 drop and change HCl concentration to 6M, which is the typical concentration used in the laboratory Explain what happens to Percent\_Ag\_removed.**

## Part 2. Separating Cu<sup>2+</sup> from Fe<sup>2+</sup>

After the insoluble chlorides are precipitated, the next group (Qual Group 2) of ions is typically precipitated as sulfides. Cu<sup>2+</sup> is one of the ions belonging to this group. The third group, which includes Fe<sup>2+</sup>, is also precipitated as sulfides (some as hydroxides). How is it possible to have one group of insoluble sulfides precipitate before another group? By controlling the pH. Group 2 is also known as the "acid-insoluble sulfides". In the following, we try to explain the separation in terms of equilibrium principles.

In a typical experiment, S<sup>2-</sup> is produced in the reaction mixture by introducing H<sub>2</sub>S (by either bubbling H<sub>2</sub>S gas or adding thioacetamide which decomposes to produce H<sub>2</sub>S upon heating)



We can keep S<sup>2-</sup> really low by adding HCl. **Explain**

We can increase the S<sup>2-</sup> high by adding a base such as NH<sub>3</sub>. **Explain**

$$K_{\text{eq}} := 9.23 \cdot 10^{-22} \cdot \text{M}^2$$

Now we investigate how it is possible to precipitate CuS but not FeS.

Suppose we have a mixture of Cu<sup>2+</sup> and Fe<sup>2+</sup> ions in a solution

What if the pH of the solution were adjusted (by adding NH<sub>3</sub>) to 8. Define it here:

$$\text{pH} := \blacksquare$$

Let Hconc=[H<sup>+</sup>]. Complete the formula for Hconc below; note that we have to attach the unit (M).

$$\text{Hconc} := 10^{-\blacksquare} \cdot \text{M} \qquad \text{Hconc} = \blacksquare \text{ M}$$

A solution saturated with H<sub>2</sub>S will typically have an H<sub>2</sub>S concentration of 0.1 mol/L. Define it here:

$$\text{H}_2\text{Sconc} := \blacksquare \cdot \text{M}$$

Complete the formula for the equilibrium concentration of S<sup>2-</sup>. Let Seq=[S<sup>2-</sup>].

$$\text{Seq} := \frac{K_{\text{eq}} \cdot \blacksquare}{\blacksquare^2}$$

$$\text{Seq} = \blacksquare \text{ M}$$

Let's calculate how much  $\text{Cu}^{2+}$  and  $\text{Fe}^{2+}$  ions remain in solution at this point. First we define the  $K_{sp}$  values of  $\text{CuS}$  and  $\text{FeS}$  here.

$$K_{sp}\text{CuS} := 8.7 \cdot 10^{-36} \cdot \text{M}^2$$

$$K_{sp}\text{FeS} := 4.9 \cdot 10^{-18} \cdot \text{M}^2$$

Now enter the formulas for the maximum possible concentrations of  $\text{Cu}^{2+}$  and  $\text{Fe}^{2+}$  in solution.

$$\text{CuConc} := \frac{\quad}{\text{Seq}}$$

$$\text{FeConc} := \frac{\quad}{\text{Seq}}$$

$$\text{CuConc} = \quad \text{M}$$

$$\text{FeConc} = \quad \text{M}$$

Suppose the concentrations of  $\text{Cu}^{2+}$  and  $\text{Fe}^{2+}$  both originally 0.1 mol/L, would you say from the numbers above the  $\text{CuS}$  has precipitated? How about  $\text{FeS}$ ?

Adjust the pH downward so that  $\text{FeS}$  no longer precipitates but  $\text{CuS}$  still does. Then enter the formula for percent removal of  $\text{Cu}^{2+}$  from solution:

$$\text{PercentCuRemoved} := \frac{0.1 \cdot \text{M} - \quad}{0.1 \cdot \text{M}}$$

$$\text{PercentCuRemoved} = \quad \%$$

**At what threshold pH is it possible to remove >99.99% of  $\text{Cu}^{2+}$  without precipitating  $\text{FeS}$ ? Is this threshold a maximum or minimum pH value? What happens at pH 0?**

**Suggest an explanation for why, in a typical laboratory experiment, you are instructed to adjust the pH to about 0.5 when separating Group 2 from Group 3?**

