

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^+ from Cu^{2+}

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^+ , Pb^{2+} and Hg_2^{2+} as AgCl , PbCl_2 , and Hg_2Cl_2 (which are insoluble in water) while other cations remain in solution. Thus, Ag^+ , Pb^{2+} and Hg_2^{2+} are often referred to as "Qual Group 1, the insoluble chlorides".

We will now investigate how well Ag^+ can be separated from another ion, say, Cu^{2+} .

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_3 and 2 drops 0.1M $\text{Cu}(\text{NO}_3)_2$. 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_3 is done for you as an example:

$$\text{M}_{\text{AgSoln}} := 0.1 \cdot \text{M}$$

$$\text{Vol}_{\text{Ag}} := 2 \cdot \text{drop}$$

$$\text{M}_{\text{CuSoln}} := 0.1 \cdot \text{M}$$

$$\text{Vol}_{\text{Cu}} := 2 \cdot \text{drop}$$

$$\text{M}_{\text{HClSoln}} := 0.1 \cdot \text{M}$$

$$\text{Vol}_{\text{HCl}} := 1 \cdot \text{drop}$$

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

$$\text{V}_{\text{Total}} := \text{Vol}_{\text{Ag}} + \text{Vol}_{\text{Cu}} + \text{Vol}_{\text{HCl}}$$

$$\text{V}_{\text{Total}} = 5 \text{ drop}$$

Now calculate the concentration of Ag^+ , Cu^{2+} , and Cl^- in the solution, *assuming no reaction has taken place*.

$$\text{AgConc} := \frac{\text{M}_{\text{AgSoln}} \cdot \text{Vol}_{\text{Ag}}}{\text{V}_{\text{Total}}}$$

$$\text{AgConc} = 0.04 \text{ M}$$

$$\text{CuConc} := \frac{\text{M}_{\text{CuSoln}} \cdot \text{Vol}_{\text{Cu}}}{\text{V}_{\text{Total}}}$$

$$\text{CuConc} = 0.04 \text{ M}$$

$$\text{ClConc} := \frac{\text{M}_{\text{HClSoln}} \cdot \text{Vol}_{\text{HCl}}}{\text{V}_{\text{Total}}}$$

$$\text{ClConc} = 0.02 \text{ M}$$

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

$$\text{IPAgCl} := \text{AgConc} \cdot \text{ClConc}$$

$$\text{IPAgCl} = 8 \times 10^{-4} \text{ M}^2$$

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

Yes, since ion product exceeds Ksp.

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

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

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⁺ left in solution at equilibrium.

The formula for mol/L of Cl⁻ left in solution is

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

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?**

The expression inside the parentheses is the difference between initial and equilibrium concentrations of Ag⁺ ions. Therefore it is the amount of Ag⁺ that precipitated (in mol/L). The amount of Ag⁺ that precipitated is equal to the amount of Cl⁻ that precipitated since one mole of Ag⁺ requires one mole of Cl⁻ ions. Therefore the expression in parentheses is also equal to the amount of Cl⁻ that precipitated (in mol/L); when subtracted from the initial Cl⁻ concentration, we should get the equilibrium Cl⁻ concentration.

Substitute the right-hand side of Eq.1 for Cleq in Eq. 2 and label the resulting equation as Eq. 3

$$\text{Ksp} = \text{Ageq} \cdot \text{Cleq} \quad \text{Eq. 2}$$

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

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

$$\text{roots} := \left[\begin{array}{l} \frac{-1}{2} \cdot \text{ClConc} + \frac{1}{2} \cdot \text{AgConc} + \frac{1}{2} \cdot (\text{ClConc}^2 - 2 \cdot \text{ClConc} \cdot \text{AgConc} + \text{AgConc}^2 + 4 \cdot \text{Ksp})^{\left(\frac{1}{2}\right)} \\ \frac{-1}{2} \cdot \text{ClConc} + \frac{1}{2} \cdot \text{AgConc} - \frac{1}{2} \cdot (\text{ClConc}^2 - 2 \cdot \text{ClConc} \cdot \text{AgConc} + \text{AgConc}^2 + 4 \cdot \text{Ksp})^{\left(\frac{1}{2}\right)} \end{array} \right]$$

$$\text{roots} = \left(\begin{array}{l} 0.02 \\ -8 \times 10^{-9} \end{array} \right) \text{M} \quad \text{roots}_0 = 0.02 \text{M} \quad \text{roots}_1 = -8 \times 10^{-9} \text{M}$$

One of these two roots cannot be the equilibrium concentration of Ag⁺. Why?

-8x10⁻⁹ M cannot be the equilibrium concentration of Ag⁺, a negative concentration is not realistic

Assign the correct root to Ageq below. Should you lose the subscript while editing, you can get it back by typing [.

$$\text{Ageq} := \text{roots}_0 \quad \text{Ageq} = 0.02 \text{M}$$

Enter the formula to calculate the percent of Ag⁺ ions removed from solution due to precipitation of AgCl, and verify

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

$$\text{PercentAgRemoved} = 50\%$$

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?)

Percent removal increases from 50% to 99.962%. Increasing the drops of HCl increases the Cl⁻ concentration, causing the equilibrium to shift to the left (formation of more AgCl).

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.

Percent removal is essentially 100%. Same reason as above.

Part 2. Separating Cu^{2+} from Fe^{2+}

After the insoluble chlorides are precipitated, the next group (Qual Group 2) of ions is typically precipitated as sulfides. Cu^{2+} is one of the ions belonging to this group. The third group, which includes Fe^{2+} , 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^{2-} is produced in the reaction mixture by introducing H_2S (by either bubbling H_2S gas or adding thioacetamide which decomposes to produce H_2S upon heating)



We can keep S^{2-} really low by adding HCl. **Explain**

HCl yields $\text{H}^+(\text{aq})$ which shifts the equilibrium to the left, lowering the S^{2-} concentration.

We can increase the S^{2-} high by adding a base such as NH_3 . **Explain**

NH_3 converts H^+ to NH_4^+ , which shifts the equilibrium to the right, increasing S^{2-} concentration.

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

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

Suppose we have a mixture of Cu^{2+} and Fe^{2+} ions in a solution

What if the pH of the solution were adjusted (by adding NH_3) to 8. Define it here:

$$\text{pH} := 8$$

Let $\text{Hconc} = [\text{H}^+]$. Complete the formula for Hconc below; note that we have to attach the unit (M).

$$\text{Hconc} := 10^{-\text{pH}} \cdot \text{M} \qquad \text{Hconc} = 1 \times 10^{-8} \text{ M}$$

A solution saturated with H_2S will typically have an H_2S concentration of 0.1 mol/L. Define it here:

$$\text{H2Sconc} := 0.1 \cdot \text{M}$$

Complete the formula for the equilibrium concentration of S^{2-} . Let $\text{Seq} = [\text{S}^{2-}]$.

$$\text{Seq} := \frac{K_{\text{eq}} \cdot \text{H2Sconc}}{\text{Hconc}^2}$$

$$\text{Seq} = 9.23 \times 10^{-7} \text{ M}$$

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

$$\text{CuConc} := \frac{K_{sp}\text{CuS}}{\text{Seq}}$$

$$\text{FeConc} := \frac{K_{sp}\text{FeS}}{\text{Seq}}$$

$$\text{CuConc} = 9.426 \times 10^{-30} \text{ M}$$

$$\text{FeConc} = 5.309 \times 10^{-12} \text{ M}$$

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

Yes, for both.

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

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

$$\text{PercentCuRemoved} = 100\%$$

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

At around pH 2.8-2.9, FeS no longer precipitates but CuS still does precipitate essentially to 100%. This pH threshold is a maximum; even at pH 0, CuS still precipitates to 100%.

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?

We are generally not just separating Cu^{2+} from Fe^{2+} . This is probably the optimum pH for separating the Group 2 ions from the Group 3 ions.

