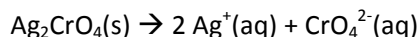


Measuring the Solubility Product Constant of Silver Chromate

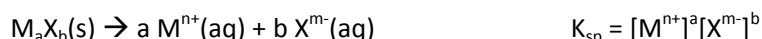
Goal

To accurately measure the solubility product constant of silver chromate.



Introduction

The solubility of a weak ionic electrolyte is measured by a specific type of equilibrium constant called the solubility product constant, K_{sp} . For a generic binary salt, M_aX_b , an equilibrium exists:



The process of writing a K_{sp} equation is identical to writing any other equilibrium constant.

In this experiment, you will prepare several samples of pure silver chromate solid and measure aqueous chromate concentration using UV-vis spectroscopy. According to Beer's Law, the absorption of light by a chemical species at a specific wavelength is directly proportional to its molar concentration:

$$A = \epsilon l [X] \quad \text{where} \quad \begin{array}{l} A = \text{absorption of light} \\ \epsilon = \text{molar absorptivity} \\ l = \text{path length} \\ [X] = \text{molar concentration of X} \end{array}$$

This relationship works best for dilute solutions ($< 10 \text{ mM}$) where the average distance between absorbing species is large. For UV-vis measurements taken on similar solutions, the relationship between absorption and concentration should be linear.

Solutions

You will use three solutions in this lab. Read the labels before you pour from the bottles.

- 0.25 M sodium nitrate—*This promotes the growth of large silver chromate crystals.*
- 4.00 mM silver nitrate—*Silver is a photosensitive ion.*
- 2.40 mM potassium chromate—*Chromium is a toxic heavy metal.*

Important Terms

In a precipitation reaction, the solid is the *precipitate* and the remaining solution is the *supernatant*. To *decant* means to pour carefully to separate the supernatant from the precipitate.

Cautions

Do not run the centrifuge if it is unbalanced or the rotor is loose. If you are unfamiliar with how to operate a centrifuge, ask for a demonstration.

Waste

All solutions must be discarded in the silver chromate waste container.

Measuring the Solubility Product Constant of Silver Chromate

Procedure

Part of your grade for this lab will be based on accuracy, so it is important to use proper volumetric glassware when necessary.

Preparation of Unknown Silver Chromate Samples

At the end of this step, you will have four individual samples of clean supernatant. The supernatants prior to the final step are dirty and need to be disposed of in the inorganic waste.

Prepare three samples of solid silver chromate by mixing ~6 mL of 4.00 mM silver nitrate and ~4 mL of 2.40 mM potassium chromate in separate large test tubes. Mixing these should produce a suspension of red solid. Cover a rubber stopper with parafilm so it will not contact the solution. This will prevent contamination by chemicals leached from the stopper. Stopper each test tube and shake them several times over a ten minute period. You do not need to shake your samples for the entire ten minutes.

After ten minutes, give each test tube a final shake and transfer the suspension to four smaller test tubes for centrifugation. Don't fill the small test tubes more than $\frac{3}{4}$ full.

This step will separate and wash the solid by centrifugation. Centrifuge the four small tubes for 2-3 minutes. Then, carefully decant most of the supernatant liquid, losing as little solid as possible. This supernatant can be discarded in inorganic waste. Add 2 mL of 0.25 M sodium nitrate to each test tube. Cap with a parafilm wrapped stopper and shake thoroughly for ~2 minutes. Repeat the centrifuge washing twice more, for a total of three washings.

This step will produce clean supernatant for you to measure. Add enough 0.25 M sodium nitrate to fill each test tube $\frac{3}{4}$ full. Shake several times over the next ten minutes and centrifuge again. This will establish the equilibrium between the solid and the solution. At the end of this step there **must** be a visible amount of solid in each test tube. Save the supernatant from each sample and keep them separate. If the supernatant appears cloudy, it will need to be centrifuged again.

Preparation of Standard Chromate Solutions

Prepare three separate calibration solutions using volumetric glassware. These will be used to plot a calibration curve for measuring the concentration of chromate anion using Beer's Law.

Measure 1.0 mL of 2.40 mM potassium chromate with a delivery pipet and transfer to a 50 mL volumetric flask. Dilute to the mark with 0.25 M sodium nitrate. Mix thoroughly and transfer the solution to a clean and dry 100 mL beaker. Repeat twice, once using 2.0 mL of 2.40 mM potassium chromate and again using 5.0 mL of 2.40 mM potassium chromate.

Absorbance Measurements

When all seven of your solutions are ready, make the spectroscopic measurements. Use a spectrophotometer set to 375 nm. Use 0.25 M sodium nitrate as the blank solution. Measure the absorbance of each calibration solution and each unknown silver chromate solution. Record your results in your laboratory notebook as explained in the next section.

Measuring the Solubility Product Constant of Silver Chromate

Calibration Curve – Use a spreadsheet program like Excel.

1. Tabulate the absorption and $[\text{CrO}_4^{2-}]$ for each calibration solution.

TRIAL	ABSORPTION	$[\text{CrO}_4^{2-}]$
-------	------------	-----------------------

2. Construct a calibration curve by plotting absorption versus $[\text{CrO}_4^{2-}]$. This is the Beer's Law plot of absorption versus concentration. Use regression analysis to calculate the best-fit line. Write a brief caption.
3. In a linear Beer's Law plot, the terms in the equation $y = mx + b$ have the following values:
 - $y = A$, absorption
 - $x = [X]$, the molar concentration of the absorbing species
 - $m = \epsilon l$, the product of the molar absorptivity (ϵ) and the path length (l)
 - b = The intercept is ideally zero if the spectrometer has been properly zeroed. Often times it is not zero due to both systematic and random error. It cannot be ignored in your calculations.

Calculate the percent error of the molar absorptivity of your calibration curve. For the chromate ion, $\epsilon = 4,820 \text{ M}^{-1}\text{cm}^{-1}$ at 375 nm.

K_{sp} Calculations

4. Using your calibration curve and the absorption data from the four equilibrium solutions, calculate $[\text{CrO}_4^{2-}]$, $[\text{Ag}^+]$, and K_{sp} for each trial. Tabulate the data and pay attention to significant figures.

TRIAL	ABSORPTION	$[\text{Ag}^+]$	$[\text{CrO}_4^{2-}]$	K_{sp}
-------	------------	-----------------	-----------------------	-----------------

5. Calculate the average K_{sp} for your series of solutions. Do not remove an outlier yet.

Statistical Analyses

6. Test for an outlier among your four K_{sp} values. Remove if it is properly justified. Recalculate the K_{sp} , or state: "No outlier can be removed."

Discussion Questions

1. Does this reaction favor products or reactants? Justify your answer.
2. How are the colors of the CrO_4^{2-} ion and of the light absorbed by the CrO_4^{2-} ion related to one another? Be specific.

Measuring the Solubility Product Constant of Silver Chromate

Set up for laboratory

Please make fresh solutions of:

- 0.25 M NaNO_3 (make 8.0 L)
Weigh 42.49 g NaNO_3 and dilute to 2.0 L with water.
Distribute in four separate bottles.
- 4.00 mM AgNO_3 in 0.25 M NaNO_3 (make 2.0 L)
Weigh 1.36 g AgNO_3 and dilute to 2.0 L with 0.25 M NaNO_3 .
Distribute in four separate bottles.
- 2.40 mM K_2CrO_4 in 0.25 M NaNO_3 (make 2.0 L) \
Weigh 0.932 g K_2CrO_4 and dilute to 2.0 L with 0.25 M NaNO_3 .
Distribute in four separate bottles.
- centrifuges—as many as possible
- volumetric pipets and glassware
- parafilm to wrap stoppers