

# Measuring the Solubility Product Constant of Silver Chromate

## Goal

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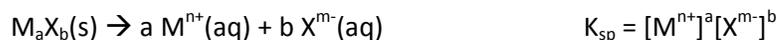
To accurately measure the solubility product constant of silver chromate.



## Introduction

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The solubility of a weak ionic electrolyte is measured by a specific type of equilibrium constant called the solubility product constant,  $K_{\text{sp}}$ . For a generic binary salt,  $\text{M}_a\text{X}_b$ , an equilibrium exists:



The process of writing a  $K_{\text{sp}}$  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 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

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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 in 0.25 M sodium nitrate —*Silver is a photosensitive ion.*
- 2.40 mM potassium chromate—*Chromium is a toxic heavy metal.*

## Important Terms

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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

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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. **DO NOT EVER REMOVE THE METAL TUBES THAT ARE IN THE CENTRIFUGE. Remove the caps from the centrifuge tubes before placing in the machine!!**

## Waste

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

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## Procedure

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

### *Preparation of Unknown Silver Chromate Samples*

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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 about 2 mL of 0.25 M sodium nitrate to each test tube. Cap with a parafilm wrapped stopper and shake thoroughly for about 2 minutes. Repeat the centrifuge washing once more, for a total of two washings. The sodium nitrate wash solution may be discarded.

In the previous section the supernatant was discarded. Now clean supernatant will be made for you to measure in the spectrophotometer. Add enough 0.25 M sodium nitrate to your washed silver chromate precipitate to fill each test tube  $\frac{1}{2}$  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*

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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 3.0 mL of 2.40 mM potassium chromate.

### *Absorbance Measurements*

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When all seven of your solutions (three standard solutions and four prepared unknown solutions) are ready, make the spectroscopic measurements. Calibrate the spectrophotometer just before making all your measurements. Set it to measure absorbance at 375 nm. Use 0.25 M sodium nitrate as the blank solution. Measure the absorbance of each calibrated solution and each unknown silver chromate solution. Record your results in your laboratory notebook as explained in the next section.

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**Calibration Curve** – Use a spreadsheet program like Excel.

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

TRIAL	ABSORPTION	$[\text{CrO}_4^{2-}]$
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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 ( $\epsilon$ ) 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<sub>sp</sub> Calculations

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

TRIAL	ABSORPTION	$[\text{Ag}^+]$	$[\text{CrO}_4^{2-}]$	K <sub>sp</sub>
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5. Calculate the average  $K_{\text{sp}}$  for your series of solutions. Do not remove an outlier yet.

## Statistical Analyses

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

## Discussion Questions

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1. Does reaction one favor products or reactants? Justify your answer.
2. How are the colors of the  $\text{CrO}_4^{2-}$  ion and of the light absorbed by the  $\text{CrO}_4^{2-}$  ion related to one another? Be specific.
3. Why are four samples prepared in exactly the same way for the unknown concentration of chromate?
4. Why do we measure absorbance at 375nm? What part of the electromagnetic spectrum is this wavelength?

Set up for laboratory

# Measuring the Solubility Product Constant of Silver Chromate

Please make fresh solutions of:

- 0.25 M  $\text{NaNO}_3$  (make 8.0 L)  
*Weigh 42.49 g  $\text{NaNO}_3$  and dilute to 2.0 L with water.*  
*Distribute in four separate bottles.*
- 4.00 mM  $\text{AgNO}_3$  in 0.25 M  $\text{NaNO}_3$  (make 2.0 L)  
*Weigh 1.36 g  $\text{AgNO}_3$  and dilute to 2.0 L with 0.25 M  $\text{NaNO}_3$ .*  
*Distribute in four separate bottles.*
- 2.40 mM  $\text{K}_2\text{CrO}_4$  in 0.25 M  $\text{NaNO}_3$  (make 2.0 L)  
*Weigh 0.932 g  $\text{K}_2\text{CrO}_4$  and dilute to 2.0 L with 0.25 M  $\text{NaNO}_3$ .*  
*Distribute in four separate bottles.*

## Equipment

- centrifuges—as many as possible – ideally eight of them.
- centrifuge tubes – 4 per set (64 for 16 sets)
- graduated pipets with bulbs – 1 per set (16 for 16 sets)
- 50mL volumetric flasks – 3 per set (48 for 16 sets)
- parafilm to wrap stoppers
- gloves for all students