

The Solubility of AgBrO₃

Purpose: The $\Delta_r G^\circ$, $\Delta_r H^\circ$, and $\Delta_r S^\circ$ of a reaction will be calculated from the temperature dependence of the equilibrium constant. The reaction is the dissolution of AgBrO₃, and the equilibrium constant of this reaction is a K_{sp} . The Debye-Hückel theory of electrolytes will be used to calculate the ionic activities. The $\Delta_f G^\circ$ of BrO₃⁻ will also be calculated.

Theory

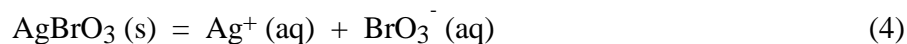
The three equations:

$$\Delta_r G^\circ = -RT \ln K_a \quad (1)$$

$$\ln \left(\frac{K_a T_2}{K_a T_1} \right) = -\frac{\Delta_r H^\circ}{R} \left(\frac{1}{T_2} - \frac{1}{T_1} \right) \quad (2)$$

$$\Delta_r G^\circ = \Delta_r H^\circ - T \Delta_r S^\circ \quad (3)$$

allow the complete thermodynamic characterization of a chemical reaction. $\Delta_r G^\circ$ can also be calculated from thermodynamic tables and compared to the result using equation 1. If more than two temperatures are studied, a more efficient way of calculating $\Delta_r H^\circ$ than using equation 2 is to plot $\ln K_a$ versus $1/T$, which gives a slope of $-\Delta_r H^\circ/R$. The reaction studied in this laboratory will be:



for which the equilibrium constant is:

$$K_a = a_{\text{Ag}^+} a_{\text{BrO}_3^-} \quad (5)$$

The activity coefficients for Ag⁺ and BrO₃⁻ cannot be determined separately, so the mean ionic activity coefficient must be used when relating concentrations to activities:

$$K_a = \gamma_{\pm}^2 c_{(\text{Ag}^+)} c_{(\text{BrO}_3^-)} \quad (6)$$

where γ_{\pm} is the mean ionic activity coefficient and the c's are concentrations.

The Debye-Hückel theory is an approximate theory for calculating activity coefficients for ionic species. The accuracy is limited to very dilute solutions, that is, the Debye-Hückel theory is a limiting law. The experimental error in this experiment will be large enough that the Debye-Hückel theory will be sufficient. The Debye-Hückel theory uses the fact that the activity coefficient of an ion is dependent on the concentration of all ions in solution. The measure of total ionic concentration is the ionic strength:

$$I = \frac{1}{2} \sum_{\text{all ions}} c_i z_i^2 \quad (7)$$

where c_i is the concentration of ion i and z_i is the charge on ion i . Since the dissolution of AgBrO_3 is the only source of ions in this experiment, the concentrations of Ag^+ and BrO_3^- are equal and are the only terms in the sum. The Debye-Hückel formula is then:

$$\log_{10} \gamma_{\pm} = -0.509 |z_+ z_-| \sqrt{I} \quad (8)$$

where z_+ is the charge on the positive ions and z_- is the charge on the negative ions. In this experiment, $z_+ = 1$ and $z_- = -1$. The vertical bars in equation 8 indicate that the absolute value is taken. Note that this equation is written in terms of base 10 logs.

Procedure

Equipment:

- 4- 15x150mm glass test tubes
- 4- #0 rubber stoppers
- 1- 10-mL graduated cylinder
- 1-ultrasonic bath
- 4- 5-mL plastic syringes with teflon needles
- 4-0.45- μm HPLC syringe filters (small volume)
- 1- 400-mL beaker
- 1- 500-mL plastic dewar
- 4- 15x120mm plastic culture tubes for samples in the ICP auto-sampler
- 4- 30x120mm plastic culture tubes for standards in the ICP auto-sampler
- 4- 50-mL volumetric flasks
- 1- each 2,3,4, and 5-mL volumetric pipets

Stock Solutions:

- 50 mL of 0.100 M AgNO_3
- 5 mL of concentrated NH_3

Throughout this experiment be careful to avoid contact of the solutions with surfaces that might have chloride on them. AgCl is less soluble than AgBrO_3 and will compete effectively for the available Ag^+ . Tap water and fingerprints contain significant amounts of chloride. Also remember that silver salts stain skin and clothing black.

Place about 30 mg of AgBrO_3 in each of 4 15x150mm glass test tubes. Weigh out only the first sample--estimate the others. Add 10 mL of reagent grade water using a graduated cylinder to each sample. Stopper the test tubes, swirl and hold the test tubes in an ultrasonic bath for about 30 sec. The samples should be uniform milky suspensions. Place the first tube in an ice water bath held in a labeled plastic dewar. Keep this sample in the refrigerator.. Place the remaining samples in the constant temperature baths in the laboratory. These baths should be set to about 8, 15 and 20°C. The samples should equilibrate for at least four hours. Measure the bath temperatures to 0.1°C.

While the samples are equilibrating, prepare standard solutions of AgNO_3 in the following manner. Prepare dilutions of the stock 0.100 M AgNO_3 solution with the

volumetric pipets and flasks listed above. Your solutions should contain $4.00 \times 10^{-3} \text{M}$, $6.00 \times 10^{-3} \text{M}$, $8.00 \times 10^{-3} \text{M}$, and $10.00 \times 10^{-3} \text{M}$ AgNO_3 . Use reagent grade water to prevent the formation of AgCl from residual Cl^- . Add the reagent grade water in the following way: add about 25 mL of water, then add six drops of concentrated NH_3 to prevent the formation of precipitates. Make sure any precipitates are dissolved and then dilute to the mark with reagent grade water.

The concentration of the Ag^+ ion will be determined in this experiment using Inductively Coupled Plasma Emission spectroscopy (ICP). A short description of ICP spectroscopy is attached as an appendix. Place the four standard AgNO_3 solutions in the four large auto-sampler plastic culture tubes in positions 2-5 of the standards auto-sampler tray. Place a vial of reagent grade water in position 1. Register the concentrations of your standards in the Standards form of the operating software for the ICP.

After at least four hours withdraw 5 mL of the clear supernatant above each sample with a plastic syringe fitted with a teflon needle. Take care to ensure that the samples don't warm appreciably while sampling and that the solid precipitate is not disturbed. Remove the needles and replace with $0.45\text{-}\mu\text{m}$ syringe filters. Directly filter the samples into the four 12x100mm plastic autosampler test tubes. Place the four samples, in random order, into the sample auto-sampler tray. Register the identity of your samples in the appropriately numbered entries in the Samples form of the operating software for the ICP. Using the attached instructions for the ICP or assistance from your instructor, determine the concentrations of Ag^+ in your samples.

Clean-up: Wash the residual AgBrO_3 into the labeled waste beaker. This material will be filtered and recycled. Rinse the syringe filters with a small amount of 6 M NH_3 , and then three rinses with reagent grade water. Wash all glassware with laboratory detergent and rinse all syringes and ICP sample tubes three times with small amounts of reagent grade water. Collect all AgNO_3 solutions in the labeled bottle. All AgNO_3 solutions are also periodically recycled.

Calculations

From the concentrations determined by ICP analysis, use equation 7 to calculate the ionic strength for each temperature. Then use equation 8 to calculate the mean ionic activity coefficient for each temperature. From the concentrations and the mean ionic activity coefficients calculate the K_a at each temperature using equation 6. Make an appropriate plot of the temperature dependent data to calculate $\Delta_r H^\circ$. This plot assumes that $\Delta_r H^\circ$ is constant over the temperature range. Use equation 1 to calculate the $\Delta_r G^\circ$ at each temperature. Use your least squares fit coefficients to calculate the value of $\ln K_a$ at 25°C . Use equation 1 to calculate $\Delta_r G^\circ$ and from that value $\Delta_r S^\circ$ at 25°C .

Report

Include the experimental data in tabular format, the final values from your calculations, and the plot that you used to find $\Delta_r H^\circ$. Determine the uncertainty in $\ln K_a$, $\Delta_r G^\circ$, $\Delta_r H^\circ$,

and $\Delta_r S^\circ$ at 25°C using propagation rules from the uncertainty in the fit coefficients.

Answer the following questions in your report:

1. Use literature values for the $\Delta_f G^\circ$ of AgBrO_3 , Ag^+ , and BrO_3^- to calculate $\Delta_r G^\circ$, and compare with your experimental value¹. The literature values are for unit molality; will this fact make a difference in comparison with your K_a and $\Delta_r G^\circ$? Calculate the % difference in the K_a on a molarity and molality basis at 25°C assuming the density of the solution is the same as pure water.
2. Do you see any systematic curvature in your graph? What would cause the non-linearity? (Answer this question even if you don't see significant curvature.)
3. Calculate the $\Delta_r H^\circ$ if you had neglected the activity coefficients. What is the % difference?

Note:

1. There is some confusion in the literature about these values. If $\Delta_f G^\circ$ of $\text{AgBrO}_3(\text{aq})$ is listed as 54.39 kJ/mol then $\Delta_f G^\circ$ of BrO_3^- should be 1.67 kJ/mol (see 8th Ed. Lange's Handbook). Or if $\Delta_f G^\circ$ of AgBrO_3 is listed as 71.30 kJ/mol then $\Delta_f G^\circ$ of BrO_3^- should be 18.54 kJ/mol (see 66th and 71 Ed. of the CRC). Similarly, if $\Delta_f H^\circ$ of AgBrO_3 is listed as -27.20 kJ/mol then $\Delta_f H^\circ$ of BrO_3^- should be -83.68 kJ/mol (see 8th Ed. Lange's Handbook). Or if $\Delta_f H^\circ$ of AgBrO_3 is listed as -10.46 kJ/mol then $\Delta_f H^\circ$ of BrO_3^- should be -67.07 kJ/mol (see 66th and 71 Ed. CRC).

Appendix: Emission Spectroscopy

Emission spectroscopy has long been a sensitive and selective technique for analysis of metals. Flame emission spectroscopy of Na^+ and K^+ is regularly used in clinical and environmental laboratories. Geochemistry laboratories have long used high current arc sources, which are similar to search light and theatrical spotlight systems, for emission spectroscopy of mineral samples.

A simple example of emission spectroscopy is lighting a match. The yellow glow is emission from excited Na ions in the flame. In emission spectroscopy a sample is heated in a flame or electrical discharge to cause it to emit light. The emission frequencies are characteristic of the elements present in a sample and the intensity of the emission at each frequency is proportional to concentration, over a wide range of concentrations.

Conventional flame or arc sources suffer from a number of interferences and instabilities that limit the usefulness of emission determinations. The interferences, such as oxide formation, can largely be eliminated by choosing higher temperature sources. The instability problem is solved by choosing a plasma that is heated by radio frequency or microwave energy.

A plasma is an electrically conducting gas composed of free electrons and positive ions. Examples of plasmas include conventional flames, neon signs, fluorescent light fixtures, and the ionosphere of the earth. Plasmas are often considered a separate state of matter distinct from solids, liquids, and gases.

Plasmas require a constant input of energy for existence. The source of the energy can be chemical reactions, as in a flame, an electrical discharge, as in a neon sign, or radiant

energy, as in a radio frequency or microwave supported plasma. The gas chosen for the plasma is the most important determining factor for choosing the energy source.

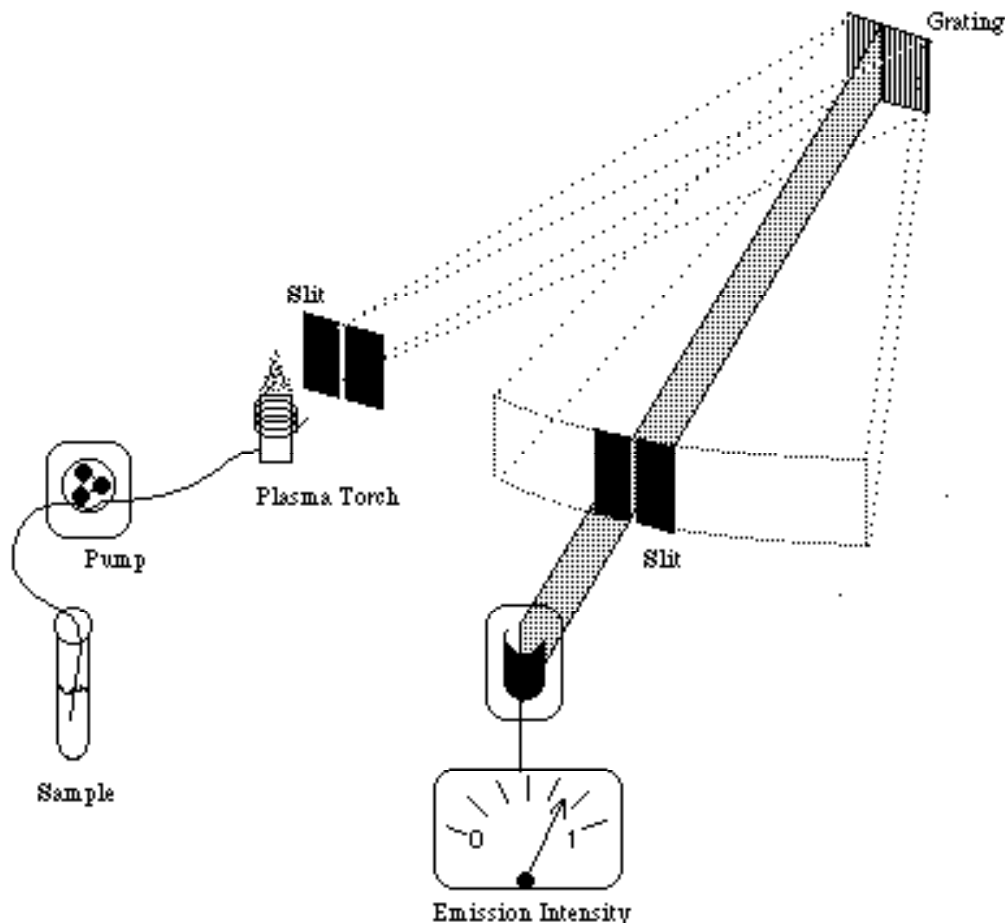


Figure 1. ICP optical layout

The most generally used gas for analytical plasmas is argon. Argon plasmas are very hot, stable, and provide a minimum of background emission. Argon plasmas are started with an electrical discharge, but in emission spectroscopy the energy for heating the plasma is provided by a 1 kWatt radiofrequency (R.F.) source, generally at a frequency of 12 MHz. This frequency lies between the AM and FM bands on your radio dial. The R.F. energy is coupled into the plasma by wrapping a coil of wire (essentially a transmitter antenna) around the plasma. A coil of wire acts as an inductor, hence the name for this emission source, inductively coupled plasma, or ICP.

ICP sources are easy to use, very hot (around 10,000°K), stable, and provide relatively low background emission. The sample is introduced into the flowing argon stream as an aerosol from a nebulizer. The light emitted from the plasma is analyzed by a very high resolution monochromator and a sensitive photomultiplier detector. A diagram of the instrument is shown in Figure 1.

In many instruments, such as UV/Visible spectrophotometers, fluorescence spectrophotometers, and some ICP's the different emission wavelengths are selected by rotating the grating in the monochromator. In the Leeman Lab's ICP, for increased

accuracy and stability, the grating is held fixed while the exit slits and the detector move. Even so, the accuracy of the monochromator must periodically be checked. This is done by placing a mercury lamp in front of the monochromator and scanning one of the mercury emission lines. Any wavelength error is then applied as a correction to all subsequent measurements.

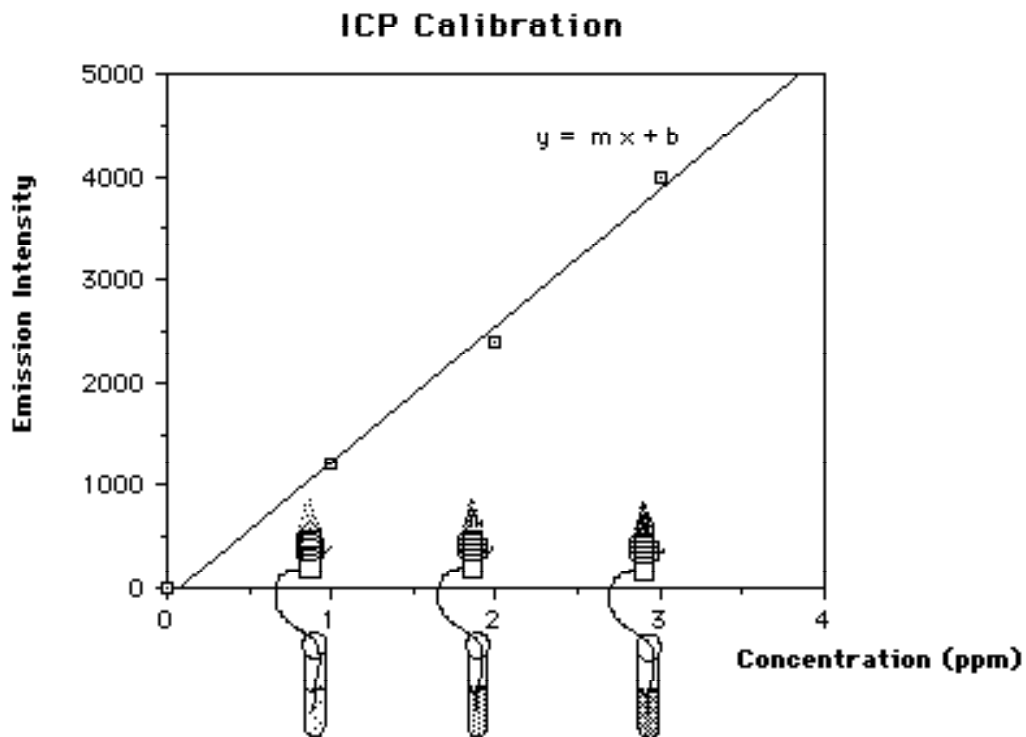


Figure 2. ICP calibration curve for three standard solutions.

The analytical wavelength to use is determined by introducing a known sample of the desired element and scanning the monochromator to determine the emission spectrum (In our instrument the exit slit is scanned to determine spectra). The wavelength of maximum emission is then used in subsequent measurements. The computer system on the instrument records the monochromator settings for this emission wavelength in a "Peak Table", to which it can return whenever determinations of this particular element are desired.

ICP emission spectrometers are calibrated by introducing a series of solutions of known concentration and fitting the emission intensities to a linear or polynomial calibration function. This is exactly the same process as is used for a visible absorption spectrophotometer (such as Spectronic 20's) except that emission intensity is used rather than absorbance. We will be able to use a linear calibration function in this laboratory. The solution of unknown concentration is then introduced into the plasma, the resulting emission intensity is then used to calculate the concentration using the calibration. This procedure is shown schematically in Figure 2.