Physical Chemistry Laboratory I
SCS
The Solubility of $CaSO_4 \cdot 2H_2O$ and Ionic Strength Effect
(Revised 1/24/18)

The concept of solubility is either simple or complex, depending on how far one pursues it. The IUPAC Gold Book {reference initially obtained from Wikipedia, a sometimes reliable source} gives the definition of solubility as "the analytical composition of a saturated solution". Pursuing the matter, one can find the IUPAC definition of a saturated solution as one "which has the same concentration of a solute as one that is in equilibrium with undissolved solute … ." Several Internet sites give the definition: "a solution in which the maximum amount of solute has been dissolved", although a few sites said "when no more solvent can be dissolved". One gave an "interesting" definition: "A saturated solution is one where there are about equal amounts or particles of solutes and solvents in the solution." {"A little learning is a dangerous thing …"}

Solubility becomes more complicated when ionic compounds are considered, because there are no "molecules" of the compounds in solution. There is often confusion between the solubility of a salt and the concentrations of ions in solution. Some recent texts for quantitative analysis include significant discussions of activity coefficients and introduce the concept of ion pairs.[1]

The solubility of $CaSO_4 \cdot 2H_2O$, S{$CaSO_4 \cdot 2H_2O$ }, and the variation of S{$CaSO_4 \cdot 2H_2O$}with concentration of added electrolytes illustrate the effects of activity coefficients and ion pairs. There have been many articles in the *Journal of Chemical Education* (J. Chem. Ed.) that discuss solubility and the use of solubility data to calculate K_{SP} and *vice versa*.[2,3,4,5,6] There is extensive chemical literature on the solubility of $CaSO_4 \cdot 2H_2O$ in different solutions.[7]

Gypsum, $CaSO_4 \cdot 2H_2O$, is a readily available mineral. Drywall or sheetrock is made with gypsum. Dehydrated to $CaSO_4$ and then mixed with water, gypsum was widely used for casts and splints. Gypsum is not very soluble in water or salt solutions and contributes to build up of scale in water pipes and also creates problems in desalination. Hence, there is an interest in predicting the solubility in different salt solutions. Standard sources on the composition of seawater give $[Ca^{2+}] \sim 10$ mM and $[SO_4^{2-}] \sim 28$ mM. These values give an ion product constant, $[Ca^{2+}][SO_4^{2-}] \sim 2.8*10^{-4}$. Literature values for K_{SP} are $\sim 4*10^{-5}$. There is a significant discrepancy here.

You have probably read about sinkholes, caused mostly by the dissolving limestone. However, there are some places where the sinkholes were caused by dissolving gypsum. An Internet search will give places where the sinkholes were attributed to the loss of gypsum – Spain and Portugal are mentioned.

There is much concern about the solubility of $CaCO_3$ in the ocean as a function of inert salt concentration, pH, temperature, and depth – much more than about $CaSO_4$. However, calcium sulfate will serve as a reasonable model to show the effects of ionic strength and ion pairs on solubility, without concern for pH and pressure of CO_2.

The standard treatment of solubility and solubility product constants in introductory chemistry courses is generally doubly simplified: first with the assumption that the activity coefficients are 1 and second with the assumption that the ionic salts are completely dissociated in solution. Both assumptions are reasonable for very slightly soluble 1/1 electrolytes (such as AgCl), but neither is correct for slightly soluble polyvalent salts.

Ion pairing is not as well known as it should be. Although we will be concerned only with the interactions of Ca^{2+} with SO_4^{2-} in this experiment, non-covalent bonding of Ca^{2+} is observed with other species.

The traditional model is that $CaSO_4$ is completely dissociated in aqueous solution.

$$CaSO_4 \cdot 2H_2O(s) \Leftrightarrow Ca^{2+}(aq) + SO_4^{2-}(aq). \quad (1)$$

From this equation, and this approximation to the species in solution, one may write the appropriate equilibrium expression, including activity coefficients:

$$\mathbf{K_{SP}^o} = a\{Ca^{2+}\} * a\{SO_4^{2-}\} = [Ca^{2+}]\,[SO_4^{2-}]\gamma_{\pm}^2 \quad (2a)$$

$$\mathbf{K_{SP}^o = K_{SP}\{Apparent\}}\gamma_{\pm}^2 = S^2\,\gamma_{\pm}^2 \quad (2b)$$

In these equations, $\mathbf{a\{X_i\}}$ = activity of X_i; the concentration of each species, $\mathbf{[X_i]}$, is given in mol{X_i}/L{sol'n}; $\boldsymbol{\gamma_{\pm}}$ refers to the geometric mean (average) activity coefficient for the two ions ($\gamma_{\pm}^2 = \gamma\{Ca^{2+}\} * \gamma\{SO_4^{2-}\}$). For present purposes, we assume that $\gamma\{Ca^{2+}\} = \gamma\{SO_4^{2-}\}$.

Equilibrium constants, activities, and activity coefficients are dimensionless. For all of the equilibrium expressions, we are adopting the convention that the standard state is unit concentration.

$\mathbf{K_{SP}^o}$ is the "true" solubility product constant for $CaSO_4$, *i. e.*, the value at infinite dilution or "zero concentration" of ions; and $\mathbf{K_{SP}\{Apparent\}}$ is the product of the ionic concentrations, $[Ca^{2+}]*[SO_4^{2-}]$. $\mathbf{K_{SP}\{Apparent\}}$ is a function of ionic strength because activity coefficients are functions of ionic strength.

It was proposed many years ago that polyvalent salts did not ionize completely, even in relatively dilute solutions.[8] This concept was more or less ignored for many years but was reiterated several years ago.[9] Tables of formation constants for ion pairs are available in standard analytical texts[1] as well as standard reference works.[10]

Equation (2a) is always correct, whether or not ion pairs are considered. Equation (2b) is incorrect because $S\{CaSO_4 \cdot 2H_2O\} \neq [Ca^{2+}]$,

$$S\{CaSO_4 \cdot 2H_2O\} = [Ca^{2+}] + [CaSO_4] \quad \{3\}$$

In this equation $S\{CaSO_4 \cdot 2H_2O\}$ represents the total solubility, $[Ca^{2+}]$ represents the concentration of calcium ions in solution, and $[CaSO_4]$ represents the concentration of ion pairs in solution.

Ion pairs represent non-covalent, or electrostatic, interactions between pairs of ions, although there is a gradation to species like $FeOH^{2+}$, for which we are comfortable with covalent bonding in the complex ion.

Ion pairing is obviously more important for polyvalent ions than for monovalent ions as a consequence of Coulomb's Law. Ion pairs are in rapid equilibrium with the completely dissociated species.

$$Ca^{2+}(aq) + SO_4^{2-}(aq) \Leftrightarrow CaSO_4(aq) \quad (4)$$

Because the Ca/EDTA complex has a much larger formation constant than the ion pair constant, the titration of a solution of $CaSO_4$ with EDTA determines the total calcium in solution. Harris[1] gives $K_F\{Ca^{2+}/SO_4^{2-}\} = 170$ and $K_F\{Ca^{2+}/EDTA^{4-}\} = 4.9\ 10^{10}$. As you remember from QUANT, the effective formation constant for $Ca^{2+}/EDTA^{4-}$ is pH dependent; but at pH = 10, it is about $2*10^{10}$. The ISE (ion selective electrode) measures only $[Ca^{2+}]$.

Experimental Procedure:

You are to determine the solubility of $CaSO_4 \cdot 2H_2O$ in pure water and in one solution of an inert electrolyte, NaCl, using standard EDTA for the analysis. The solubility of $CaSO_4 \cdot 2H_2O$ is known, ~ 0.015 M, at 25.0 °C. You will also determine the concentration of free calcium ion, $[Ca^{2+}]$, using an ion selective electrode, ISE.

Obtaining a saturated solution of $CaSO_4 \cdot 2H_2O$ at a constant temperature is, or should be, a straightforward and simple procedure: add excess $CaSO_4 \cdot 2H_2O$ to water and equilibrate. However, attaining equilibrium is not instantaneous, there must be excess solid when equilibration is complete, and the excess solid must settle.

Some literature experiments involved long equilibration times – of the order of hours.[7]

A picture of the apparatus that you will use is given at the end of this experiment.

You will have to make three solutions: two solutions for Part A1 and one solution for Part 3B.

A. Distilled water solutions

1. Saturation

Prepare two solutions of saturated $CaSO_4 \cdot 2H_2O$ in 250 mL Erlenmeyer flasks for the equilibration experiments. There are two magnetic stirrers and two stations for equilibration in the constant temperature bath.

For the first solution, add a weighed amount of $CaSO_4 \cdot 2H_2O$ to the Erlenmeyer **(using top loading balance)** that is about twice the amount necessary for saturation (calculated assuming $S\{CaSO_4 \cdot 2H_2O\} = 0.02$ M), add ~ 200 mL of distilled water, stir in the constant temperature bath for 1 hour.

Repeat with a larger amount of $CaSO_4 \cdot 2H_2O$ and ~ 200 mL of distilled water.

Stir vigorously so that the solid is well dispersed – a cloudy system. Break up clumps of the $CaSO_4 \cdot 2H_2O$ with a mortar and pestle before adding to water to give a good dispersion. The rate of dissolution (and equilibration) depends on the size of the particles. Remember that there must be solid in the system at the end to ensure equilibrium.

Use a green lead "donut" to hold the flask in the circulating water bath.

Let the solution settle until clear in the constant temperature bath. There must be solid in the bottom of the flask after equilibration. If you need more solid, add, and stir.

You will titrate each of these solutions <u>three times</u> with standard EDTA.

Note: Please remember to save these solutions for ISE measurements.

2. Preparation of Standard EDTA:

In a **500 mL volumetric flask** prepare ~ 0.015 M EDTA from $Na_2H_2EDTA \cdot 2H_2O$. **Use an analytical balance to weigh the EDTA** to a tenth of a mg.

Report your concentration to **five decimals, 0.01XXX.** When preparing the solution, add five pellets of NaOH to the 500 mL volumetric flask before bringing the solution to the mark – to convert much of the H_2EDTA^{2-} to $EDTA^{4-}$.

You may store your solution of **EDTA** until the second week in a **<u>properly labeled</u>** 500 mL plastic container: your name, your partner's name, the concentration of the solution, the name of the compound, your lab section, and the date that the solution was prepared. There is a drawer for your solutions.

When you have finished all of your titrations, pour the remainder of the EDTA into the sink, rinse the container with distilled water, and allow it to dry. If you have saved any solutions, be sure to discard them.

3A. EDTA Titrations:

Reference Solution for EDTA Titration:

One way to recognize/remember the end point is to take ~ 75 mL of distilled water, bring to pH = 10 – 11 using 2 M sodium hydroxide, add a few drops of EDTA solution to complex any cations that might be present as impurities, add one tablet of the calcon indicator, and observe the blue color. Keep this solution as a reference for the blue color.

EDTA Titrations:

NOTE: Keep all solutions until you check that all values make sense (See below in highlighted red).

You need an accurately known aliquot of the saturated solution – without suspended solids – to determine the solubility by EDTA titration.

After the stirring has stopped and the system has settled, carefully decant (pour the liquid only) some of the liquid into a clean, dry, 50 or 100 mL beaker. Use a volumetric pipet to take a 25.00 mL aliquot (sample) of the solution. (Use the automatic pipetter.) Be careful with the pipet: glass is fragile and broken glass is dangerous, especially if a pipet breaks in your hands.

Rinse the pipet with solution and discard. Be careful that you do not take water into the pipetter: water ruins the seal.

Transfer the 25.00 mL aliquot to an Erlenmeyer flask, add ~ 50 mL of distilled water to keep the solution from splashing while being stirred during the titration, and add one tablet of the calcon indicator. This amount will give a "reasonable" intensity of color. Then adjust the pH of the solution to 10 - 11 with NH_3/NH_4Cl buffer. If necessary, increase the pH by adding a few drops of 2 M NaOH.

Use a pH meter. {See *Appendix* for general information about the pH meter. Operating instructions are provided. Check calibration.}

{Do not adjust the pH with the pH = 10 buffer that you use to calibrate the pH meter: it contains EDTA.}

Titrate the solution with standard EDTA to the appearance of a pure blue.

Analyze **triplicate samples of each solution**. The end point of the titration is the change to a pure blue in a solution that was initially a wine red {burgundy, purple, or however you wish to describe the color}. This end point is not as easy to see as the phenolphthalein end point from titrations of weak acids. However, accurate values can be {have been} achieved using this procedure. This analysis gives the total amount of calcium in solution in both forms: $Ca^{2+}(aq)$ and $CaSO_4(aq)$.

Calculate your results as $S\{CaSO_4 \cdot 2H_2O\}$ for each solution. Your values for the solubility should be similar between the two solutions. If you obtain significantly discordant values, check calculations, and/or repeat the titration.

You may pour the titrated solutions down the drain. **Do not discard the untitrated solution at this time.**

3B. NaCl solution:

In a 250 mL **volumetric flask**, prepare **one solution** of an inert electrolyte, NaCl, of accurately known concentration. The concentration should be ~ 0.1 M to ~ 0.2 M. The exact value is not critical but the concentration of NaCl in the solution should be known with an accuracy of ~ one part in 1000.

Use the analytical balance to weigh the NaCl to ± 0.1 mg.

You are to determine the total solubility of $CaSO_4 \cdot 2H_2O$ (s) in the salt solution by EDTA titration. In the previous part of the experiment you determined the conditions needed to establish equilibrium. The time for equilibration in the salt solution should be essentially the same as in distilled water.

Use an Erlenmeyer flask for equilibration, as before; don't add $CaSO_4 \cdot 2H_2O$ to the volumetric flask. Use least as much $CaSO_4 \cdot 2H_2O$ (s) as you used with distilled water. At these NaCl concentrations $S\{CaSO_4 \cdot 2H_2O\}$ is significantly larger in the solution than the value in pure water.

Titrate at least three 25.00 mL aliquots of the solution with EDTA as you did in the previous section. **Do not make ISE measurements for the salt solution.** The ionic strengths of the solutions are sufficiently different that the calibration curve is not valid for these experiments.

4. Ion Selective Electrode, ISE

You will use the data obtained in the ISE experiments below to predict the total solubility of $CaSO_4 \cdot 2H_2O$ in a salt solution and compare your predictions with the experiment. An ion selective electrode, ISE, can be used to determine concentrations of individual ions in aqueous solutions. The most common ISE is the pH electrode. All ion selective electrodes must be calibrated with solutions of known concentration – and at a constant ionic strength to account for activity coefficient effects. In this part of the experiment, you will use a Ca ISE to determine $[Ca^{2+}]$ $\{= [SO_4^{2-}]\}$ for the solutions for which you have determined the solubility {total Ca concentration} by EDTA titration.

The ISE must be calibrated shortly before the analysis.

The procedure for calibrating the ISE is given at the end of this experiment. Don't mix the standard solutions. **Carefully rinse the ISE between calibration solutions.** The ISA, ionic strength adjuster, has been added to these calibration solutions. **Do not add more.**

Plot your data as mV (vertical) vs. $\log[Ca^{2+}]$ (horizontal) to obtain the slope and intercept. Excel Trendline will be sufficient.

The Nernst equation shows that the voltage depends on the log of the concentration of ions. With the Ca ISE, there is a reference electrode with fixed $[Ca^{2+}]$. The voltage is measured against solutions of known concentration to determine the calibration curve. The calibration curve will be of the form[1]

$$E = a + b*\log[Ca^{2+}] \qquad (5)$$

With perfect Nernstian behavior, b should be 29.6 mv at 25 °C. The slope will probably not be exactly 29.6 mV; however, it should be close. Previous calibration curves had slopes between 26 and 31 mV. Use your equation for the calibration curve to determine $[Ca^{2+}]$ in the saturated solutions.

After calibrating the ISE with the standard solutions, take **a 50.00 mL aliquot of one saturated solution, add 1.00 mL of the ISA, stir briefly, stop stirring, and measure the voltage with the ISE.** The volume of the aliquot of your solutions and the volume of the ISA solution do matter. The ionic strength of the calibration solutions and your solutions must be similar to obtain reliable results.

As you did for the calibration plot, remove the electrode from the solution, re-immerse, stir, stop stirring, and measure the voltage with the ISE. These are duplicate measurements on the same solution and should agree within a few mV. If not, repeat. Report both values in the data table for this solution.

Repeat the procedure with a 50.00 mL aliquot of the second saturated solution. For the ISE analyses, a <u>little</u> solid $CaSO_4 \cdot 2H_2O$ will not affect the results.

With this method of analysis, you cannot pair one EDTA titration with one ISE result. You must use the average values. For each solution, you have <u>three values for $S\{CaSO_4 \cdot 2H_2O\}$</u> and <u>two values for $[Ca^{2+}]$ $\{=[SO_4^{2-}]\}$</u>. From the average values for each solution, calculate $[CaSO_4]$ = concentration of the ion pair for each solution.

$$S\{CaSO_4 \cdot 2H_2O\} = [Ca^{2+}] + [CaSO_4] \qquad \{3\}$$

Your values for $[Ca^{2+}]$ from ISE data should be significantly less than your values for $S\{CaSO_4 \cdot 2H_2O\}$ from the EDTA titrations. If not, check your calculations or repeat.

5. Data Analysis

If one assumes that there are no ion pairs in solution, then $S\{CaSO_4 \cdot 2H_2O\} = [Ca^{2+}] = [SO_4^{2-}]$ and Eq. (2b) applies. One can calculate K_{SP}^{o} and pK_{SP}^{o} from the experimental solubility and activity coefficients calculated with an appropriate equation.

However, the experimental data show that S{$CaSO_4$•$2H_2O$} ≠ [Ca^{2+}]; therefore, the traditional method of analysis with Eq. (2b) is incorrect. Equation (2a) must be used to determine K_{SP}^o.

There are many equations that describe the variation of activity coefficients, γ, with concentration. These equations express the variation in terms of ionic strength, I, Eq. (6).

$$I = \mu = \left(\frac{1}{2}\right)\sum_j m_j Z_j^2 \qquad (6)$$

The ionic strength includes **all ions** in the solution: $\mathbf{Z_j}$ is the charge of each ion of concentration, $\mathbf{m_j}$. The ionic strength should be expressed in molal units, but in dilute solutions, **m** ≅ **M** and no significant error is introduced by using molarity in equation (3) and subsequently.

The simplest and best known equation used to calculate activity coefficients is the Debye-Hückel Limiting Law, DHLL, which applies to very dilute solutions:

$$\log \gamma_X = -\ 0.509 Z_X^2 \sqrt{I} \qquad (7)$$

In this equation, $\boldsymbol{\gamma_X}$ is the activity coefficient of the ion of interest, X; $\mathbf{Z_X}$ is the charge of the ion of interest {+2 for Ca^{2+} and -2 for SO_4^{2-}}; **I** is the ionic strength, Eq. (6); and the constant 0.509 applies for aqueous solutions at 25.0 °C. The calculated activity coefficients for cations and anions of the same charge are the same. Base 10 logs.

The Debye-Hückel Limiting Law gives activity coefficients that are too small at higher concentrations and other empirically based equations are generally used. The equation that is often used for activity coefficients that fits data better over a wider range of concentrations than the DHLL is the Davies equation,

$$\log \gamma_X = -\ 0.509 Z_X^2 \left(\frac{\sqrt{I}}{1+\sqrt{I}} - 0.3I \right) \qquad (8)$$

The symbols in Eq. (8) have the same meaning as above.

In **Table 1**, report your three values for the solubility of $CaSO_4$•$2H_2O$ in distilled water: V{EDTA}, S{$CaSO_4$•$2H_2O$ }, and the average value for each solution. The volume of the aliquot and concentration of your EDTA solution are constant and should be given as footnotes to the table. Include all of your data in the table and identify any values that you do not include in your analysis.

Also include both values that you obtained for [Ca^{2+}] for each solution from the ISE data and the average value.

Calculate [$CaSO_4$], the ion pair concentration, for each solution from the average values of S{$CaSO_4$•$2H_2O$ } and [Ca^{2+}] and include these values in the table.

Include values for K_{SP}{Apparent} = [Ca^{2+}][$SO_4^{=}$] and pK_{SP}{Apparent}. Also include values for K_{SP}^o and pK_{SP}^o, calculated from these data with activity coefficients calculated using the DHLL equation, Eq. (7), and the Davies equation, Eq. (8).

The values of the derived quantity, pK_{SP}^o, depend on the model used in the calculations – a frequent occurrence in the analysis of data. The ion pair is neutral and does not affect the ionic strength.

The ion pair is in equilibrium with the ions according to the dissociation reaction,
The dissociation equilibrium constant expression for this chemical reaction is given by the following equation, with the assumption that the activity coefficient of the neutral ion pair is unity,

$$K_D^o = \frac{\left[Ca^{2+}, aq\right]\left[SO_4^{2-}, aq\right]\gamma^2}{\left[CaSO_4, aq\right]} \qquad (9)$$

Calculate values for K_D, pK_D and and K_D^o and pK_D^o from your data for the two solutions with activity coefficients calculated using the DHLL and Davies equations.

Use the values that you obtained for K_{SP}^{o} and [$CaSO_4$] from the ISE experiments to predict S{$CaSO_4 \bullet 2H_2O$} in the NaCl solution that you prepared and compare the results of your calculations with your experimental data. Use both models to determine the activity coefficients of Ca^{2+} and SO_4^{2-}. The activity coefficient of the neutral ion pair is taken to be one.

From Eq. (3), $S = [Ca^{2+}] + [CaSO_4]$. Since $CaSO_4$ is neutral, a reasonable approximation is that [$CaSO_4$] is independent of ionic strength.

You will make this prediction by an iterative procedure because the concentrations of calcium ions and sulfate ions are not negligible compared with the concentration of NaCl in the ionic strength calculations.

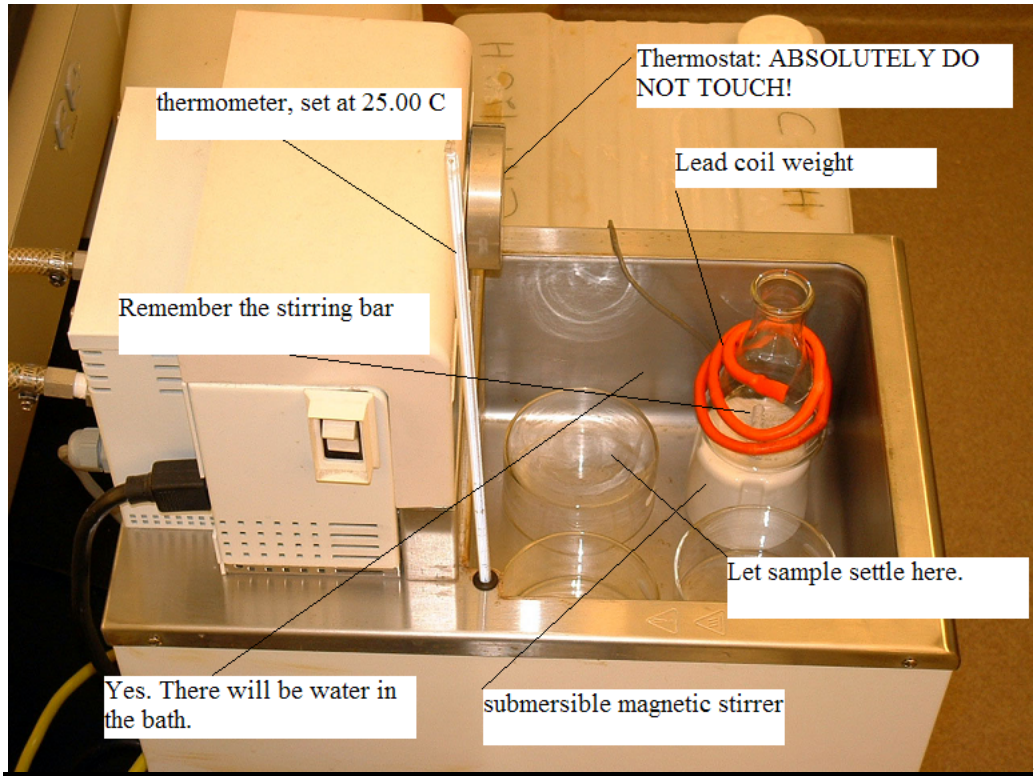
Assume initially that the ionic strength is determined only by the concentration of NaCl to calculate ionic strength, activity coefficients, and $[Ca^{2+}]$, using Eq. (2a) and the two values for K_{SP}^{o} from the different equations.

Then include the concentrations that you obtain for calcium and sulfate ions with the concentration of NaCl to calculate a new ionic strength, new activity coefficients, and a new solubility. One iteration will be sufficient.

Present these comparisons in **Table 2**. Which, if either, of the models gives good agreement with your experimental data?

Learning goals for this experiment: K_{SP}; K_{SP}^{o}; inert ion effect; ion pairs; ISE; analyzing, and modeling experimental data; Excel for data analysis; working with others; writing technical reports.

An Excel table for the data from this experiment is provided on Canvas. Download it as an Excel file. Complete as requested NO CHANGES and NO OMISSIONS and submit to the Lab Instructor grading the report. Do not include any other data or analysis. This data table is not part of your laboratory report.



pH METER INSTRUCTIONS

PLEASE TREAT THIS EXPENSIVE EQUIPMENT WITH CARE

The measuring electrode is fragile: do not stir with it; do not allow a stirring bar to hit it; do not jam it into bottom of any container.
Unscrew the plastic storage container to remove it from the electrode, leaving the cap on the electrode. Do not pull the container or container cap off of the electrode.
Always rinse the electrode with distilled water when moving it to a different solution or buffer. Rinse, but do not wipe or blot it.
The white ring at the top of electrode must remain in its closed position.
The electrode must **NEVER** dry out: it must always be either in the solution being measured, or in the filled storage container!
At the end of your experiment session, as part of your clean up, empty the storage container, rinse it out with distilled water, refill it (to about ¾–full) with the KCl storage solution provided, and then return the electrode into the container, standing upright.
To properly standardize the meter, refer to instructions in the ***Operation Manual*** at the station for the experiment.

Instructions for ISE

PLEASE TREAT THIS EXPENSIVE EQUIPMENT WITH CARE

The Calcium electrode needs to be conditioned by standing in 0.1 M Ca solution for at least an hour. Consequently, we will leave the Ca ISE in a solution of 0.1 M Ca when it is not in use between lab periods. When you finish the experiment return the ISE to the proper solution.

The meter needs to "warm up" before taking readings. Turn it on ~ 15 minutes before beginning the calibration.

1. Rinse the electrode in distilled water: squirt bottle and separate beaker. Blot dry.

2. Transfer ~ 50 mL of 0.0050 M{Ca^{2+}} to the marked 100 mL beaker. The exact volume is not critical because the ISE buffer has already been added to this solution.

Insert the electrodes to the water level mark.

3. Stir the solution for two minutes. Gently tapping or more vigorous stirring for several seconds may remove bubbles if there are any. Be careful in the position of the electrodes and stirring bar so that the stirring bar does not hit the electrodes – as with the pH electrode.

4. Read the voltage from the meter after ~ 10 minutes or when it has reached a stable value.

5. Record this value in your notebook as the voltage for this calibration solution.

6. Remove the electrode from the solution, put it back into the solution, stir, and record the reading again. Your results should agree within a few tenths of a mV. If not, repeat. Plot BOTH values in your calibration curve.

7. Although it is generally not good procedure, pour this electrode solution back into the correct container. **DO NOT MIX STANDARD SOLUTIONS.**

8. Then repeat steps 1 – 6 with the 0.0100 M Ca^{2+} solution for the second point in your calibration curve.

9. Repeat steps 1 – 6 with the 0.0250 M Ca^{2+} solution for the third point in your calibration curve.

10. Plot voltage, in mV, against log(M{Ca^{2+}}) for your calibration curve. According to the Nernst equation the voltage must be a linear function of the log of the concentration. Use base 10 logarithms.

Supporting Information
Original experimental procedure

A. Water
1. Saturation

Use 250 mL Erlenmeyer flasks for the equilibration experiments. Approximately 200 mL of solution should be sufficient for multiple analyses. There are two magnetic stirrers and two stations for equilibration in the constant temperature bath.

Add a weighed amount of $CaSO_4 \cdot 2H_2O$ to the Erlenmeyer **(top loading balance)** that is about twice the amount necessary for saturation (calculated assuming S{$CaSO_4 \cdot 2H_2O$ } = 0.02 M), add ~ 200 mL of distilled water {graduated cylinder OK}, stir in the constant temperature bath for ~ 45 minutes.

Repeat with a larger amount of $CaSO_4 \cdot 2H_2O$ and ~ 200 mL of distilled water. You will have two flasks of saturated solution.

Record all values of weights, volumes, and times. You may not need them, but you can't "create" them if you need them.

Stir vigorously so that the solid is well dispersed – a cloudy system. Break up clumps of the $CaSO_4 \cdot 2H_2O$ with a mortar and pestle before adding to water to give a good dispersion. The rate of dissolution (and equilibration) depends on the size of the particles. Remember that there must be solid in the system at the end to ensure equilibrium.

Use a lead "donut" to hold the flask in the circulating water bath.

Let the solution settle until clear in the constant temperature bath. There must be solid in the bottom of the flask after equilibration. If you need more solid, add, and stir.

You will titrate each of these solutions <u>three times</u> with standard EDTA.

2. Preparation of Standard EDTA:

In a **<u>500 mL volumetric flask</u>** prepare ~ 0.015 F EDTA from $Na_2H_2EDTA \cdot 2H_2O$. {This is not a typographical error: EDTA titrations are generally done with dilute solutions.} Do not waste time trying to prepare a solution that is exactly 0.01500 F: any concentration from ~ 0.01 to 0.02 will give satisfactory volumes of EDTA for the titrations. **Use an analytical balance to weigh the EDTA** to a tenth of a mg.

Report your concentration to **five decimals (or about ~1/1000), 0.01XXX.** When preparing the solution, add five pellets of NaOH to the 500 mL volumetric flask before bringing the solution to the mark – to convert much of the H_2EDTA^{2-} to $EDTA^{4-}$.

You may store your solution of **EDTA** until the second week in a **<u>properly labeled</u>** 500 mL plastic container: your name, your partner's name, the concentration of the solution, the name of the compound, your lab section, and the date that the solution was prepared. There is a drawer for your solutions.

When you have finished all of your titrations, pour the remainder of the EDTA into the sink, rinse the container with distilled water, and allow it to dry. If you have saved any solutions, be sure to discard them.

3A. EDTA Titrations:

Reference Solution for EDTA Titration:

One way to recognize/remember the end point is to take ~ 75 mL of distilled water, bring to pH = 10 – 11 using 2 M sodium hydroxide, add a few drops of EDTA solution to complex any cations that might be present as impurities, add one tablet of indicator, and observe the blue color. Keep this solution as a reference for the blue color.

EDTA Titrations:

You need an accurately known aliquot of the saturated solution – without suspended solids – to determine the solubility by EDTA titration.

After the stirring has stopped and the system has settled, carefully decant (pour the liquid only) some of the liquid into a clean, dry, 50 or 100 mL beaker. Use a volumetric pipet to take a 25.00 mL aliquot (sample) of the solution. (Use the automatic pipetter.) Be careful with the pipet: glass is fragile and broken glass is dangerous, especially if a pipet breaks in your hands.

Rinse the pipet with solution and discard. Be careful that you do not take water into the pipetter: water ruins the seal.

Transfer the 25.00 mL aliquot to an Erlenmeyer flask, add ~ 50 mL of distilled water {graduated cylinder OK} to keep the solution from splashing while being stirred during the titration, and add one tablet of the indicator. This amount will give a "reasonable" intensity of color. Then adjust the pH of the solution to 10 - 11 with NH_3/NH_4Cl buffer. If necessary, increase the pH by adding a few drops of 2 M NaOH.

Use a pH meter. {See *Appendix* for general information about the pH meter. Operating instructions are provided. Check calibration.}

{Do not adjust the pH with the pH = 10 buffer that you use to calibrate the pH meter: it contains EDTA.}

Titrate the solution with standard EDTA to the appearance of a pure blue as you did in QUANT.

Analyze **triplicate samples of each solution**. EDTA titrations are discussed in Harris, Christian, or other quantitative analysis texts. One mole of EDTA reacts with one mole of Ca^{2+}. The end point of the titration is the change to a pure blue in a solution that was initially a wine red {burgundy, purple, or however you wish to describe the color}. This end point is not as easy to see as the phenolphthalein end point from titrations of weak acids. However, accurate values can be {have been} achieved using this procedure. This analysis gives the total amount of calcium in solution in both forms: $Ca^{2+}(aq)$ and $CaSO_4(aq)$.

Calculate your results as S{$CaSO_4 \cdot 2H_2O$}for each solution. Your values for the solubility should be similar between the two solutions. If you obtain significantly discordant values, check calculations, and/or repeat the titration.

You may pour the titrated solutions down the drain. **Do not discard the untitrated solution at this time.**

3B. NaCl solution:

You will use the data obtained in the ISE experiments below to predict the total solubility of $CaSO_4 \cdot 2H_2O$ in a salt solution and compare your predictions with the experiment.

In a 250 mL **volumetric flask**, prepare **one solution** of an inert electrolyte, NaCl, of accurately known concentration. The concentration should be ~ 0.1 M to ~ 0.2 M. The exact value is not critical but the concentration of NaCl in the solution should be known with an accuracy of ~ one part in 1000.

Use the analytical balance to weigh the NaCl to ± 0.1 mg.

You are to determine the total solubility of $CaSO_4 \cdot 2H_2O$ (s) in the salt solution by EDTA titration. In the previous part of the experiment you determined the conditions needed to establish equilibrium. The time for equilibration in the salt solution should be essentially the same as in pure water.

Use an Erlenmeyer flask for equilibration, as before; don't add $CaSO_4 \cdot 2H_2O$ to the volumetric flask. Use least as much $CaSO_4 \cdot 2H_2O$ (s) as you used with pure water. At these NaCl concentrations S{$CaSO_4 \cdot 2H_2O$} is significantly larger in the solution than the value in pure water.

Titrate at least three 25.00 mL aliquots of the solution with EDTA as you did in the previous section. **Do not make ISE measurements for the salt solutions.** The ionic strengths of the solutions are sufficiently different that the calibration curve is not valid for these experiments.

4. Ion Selective Electrode, ISE

An ion selective electrode, ISE, can be used to determine concentrations of individual ions in aqueous solutions. The most common ISE is the pH electrode. All ion selective electrodes must be calibrated with solutions of known concentration – and at a constant ionic strength to account for activity coefficient effects. In this part of the experiment, you will use a Ca ISE to determine $[Ca^{2+}]$ {= $[SO_4^{2-}]$} for the solutions for which you have determined the solubility {total Ca concentration} by EDTA titration.

The ISE must be calibrated shortly before the analysis.

The procedure for calibrating the ISE is given at the end of this experiment. Don't mix the standard solutions. **Carefully rinse the ISE between calibration solutions.** The ISA, ionic strength adjuster, has been added to these calibration solutions. **Do not add more.**

Plot your data as mV (vertical) vs. log$[Ca^{2+}]$ (horizontal) to obtain the slope and intercept. Excel Trendline will be sufficient.

The Nernst equation shows that the voltage depends on the log of the concentration of ions. With the Ca ISE, there is a reference electrode with fixed $[Ca^{2+}]$. The voltage is measured against solutions of known concentration to determine the calibration curve. The calibration curve will be of the form[1]

$$E = a + b*\log[Ca^{2+}] \qquad (5)$$

With perfect Nernstian behavior, b should be 29.6 mv at 25 °C. The slope will probably not be exactly 29.6 mV; however, it should be close. Previous calibration curves had slopes between 26 and 31 mV. Use your equation for the calibration curve to determine $[Ca^{2+}]$ in the saturated solutions.

After calibrating the ISE with the standard solutions, take **a 50.00 mL aliquot of one saturated solution, add 1.00 mL of the ISA, stir briefly, stop stirring, and measure the voltage with the ISE.** The volume of the aliquot of your solutions and the volume of the ISA solution do matter. The ionic strength of the calibration solutions and your solutions must be similar to obtain reliable results.

As you did for the calibration plot, remove the electrode from the solution, re-immerse, stir, stop stirring, and measure the voltage with the ISE. These are duplicate measurements on the same solution and should agree within a few mV. If not, repeat. Report both values in the data table for this solution.

Repeat the procedure with a 50.00 mL aliquot of the second saturated solution. For the ISE analyses, a little solid $CaSO_4 \cdot 2H_2O$ will not affect the results.

With this method of analysis, you cannot pair one EDTA titration with one ISE result. You must use the average values. For each solution, you have three values for S{$CaSO_4 \cdot 2H_2O$} and two values for $[Ca^{2+}]$ {=$[SO_4^{2-}]$}. From the average values for each solution, calculate $[CaSO_4]$ = concentration of the ion pair for each solution.

$$S\{CaSO_4 \cdot 2H_2O\} = [Ca^{2+}] + [CaSO_4] \quad \{3\}$$

Your values for $[Ca^{2+}]$ from ISE data should be significantly less than your values for $S\{CaSO_4 \cdot 2H_2O\}$ from the EDTA titrations. If not, check your calculations or repeat.

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