EXPERIMENT 9

THE SOLUBILITY OF CALCIUM SULFATE

In this experiment you will determine the solubility of calcium sulfate in water and in a second solution that contains 0.050 $\underline{F}$ KNO_3, both at room temperature. We will call these the A solution and the B solution. I made these as follows:

<u>the A solution</u>: Excess $CaSO_4 \cdot 2H_2O$ was added to a jug of distilled water and mixed and shaken for a period of months. Solid $CaSO_4 \cdot 2H_2O$ remains in the mixture. We may be reasonably sure that the solution is <u>saturated</u> in calcium sulfate.

<u>the B solution</u>: Excess $CaSO_4 \cdot 2H_2O$ was added to a jug of 0.050 $\underline{F}$ KNO_3 (in water) and mixed and shaken as above. Again, solid $CaSO_4 \cdot 2H_2O$ remains. This solution is <u>saturated</u> in calcium sulfate. Note that the solution is <u>not</u> saturated in KNO_3 but simply contains 0.050 $\underline{F}$ KNO_3. (If some solid KNO_3 were added it would dissolve.)

The "solubility" of a substance is the concentration of a saturated solution of the substance. We have two saturated calcium sulfate solutions. Determination of the solubilities amounts to determination of the concentration of calcium sulfate in the saturated solutions. Because calcium sulfate supplies one mol of Ca^{2+} ions to a solution for each mole of calcium sulfate that dissolves, the solubilities of calcium sulfate are just the concentration of Ca^{2+} ions in the saturated solutions.

The method you will use to determine the Ca^{2+} concentration in the two saturated $CaSO_4$ solutions involves complexometric titration with EDTA (ethylenediaminetetraacetic acid). The reaction is symbolized by:

$$Ca^{2+} + Y^{4-} = CaY^{2-}$$
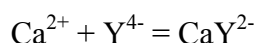
SOME NOTES: EDTA acts as a complexing agent for essentially all of the +2, +3, and +4 metal ions. It does not complex the alkali (Li^+, Na^+, etc.) metal ions. When complexed by EDTA, the metal ion is engulfed as if surrounded by some many clawed beast. This sort of complex is termed a chelate and EDTA titrations are sometimes termed <u>chelometric</u> titrations.

EDTA is a tetraprotic acid; it may lose up to four H^+ ions in aqueous solution. The term "EDTA" is not specific about the number of protons present in the substance. Instead this term simply refers to the substance without reference to the extent of protonation. To describe the extent of protonation we employ the symbol "Y" as follows. Y^{4-} is the 4- charged anion of EDTA, HY^{3-} is the monoprotonated (3- charged) anion of EDTA, etc. Most metal ion complexes

with EDTA involve Y^{4-} species. As examples, the Mg^{2+} and Ca^{2+} complexes with EDTA have the formulas MgY^{2-} and CaY^{2-}, respectively.

The titration method is a simple one involving titration of a known volume of Ca^{2+} solution with EDTA reagent of known concentration. In order for this method to work (that is, to give a sharp reproducible endpoint very close to the equivalence point) it is necessary that (1) the reaction between Ca^{2+} and EDTA is essentially complete and (2) that we have a suitable indicator for the titration. We fulfill the first requirement by appropriately adjusting the pH of the titration mixture. Because Y^{4-} is the salt of a weak tetraprotic acid H_4Y, the extent of its complexation with metal ions depends on the pH. By adjusting the pH to about 10 we assure that the reaction of EDTA with Ca^{2+} is essentially complete. (Under more acidic conditions H^+ ions would successfully compete with Ca^{2+} for Y^{4-}. At a pH of say 2-3 only a very small fraction of Ca^{2+} would be complexed by EDTA.) The second condition, that of a suitable indicator, is more difficult. Some indicators for Ca^{2+} are available and suitable for use at pH 10 but they tend to react rather slowly and are hard to use. To make matters worse, the color changes are hard to see. We will employ a trick called a displacement titration.

Consider a solution containing Ca^{2+} as the only species capable of complexing EDTA. Into the solution is added a certain amount of MgY^{2-} complex. The CaY^{2-} complex is stronger (has a larger formation constant) than the MgY^{2-} complex. As a consequence most of the Mg^{2+} is displaced from the complex. In other words, the reaction: $Ca^{2+} + MgY^{2-} = CaY^{2-} + Mg^{2+}$ is a favorable one.

> NOTE: The equilibrium constant for this reaction is readily calculated from known formation constants for $Ca^{2+} + Y^{4-} = CaY^{2-}$ and $Mg^{2+} + Y^{4-} = MgY^{2-}$ which values are 4.9×10^{10} and 6.2×10^8, respectively. The equilibrium constant for the displacement reaction is the ratio of these values: 0.79×10^2.

The analyte solution now contains Mg^{2+} ions which will react with added EDTA reagent. The endpoint of the Mg^{2+}, EDTA reaction is readily detectable by any one of a number of so-called "metalochromic" indicators. We will use one called Erio T (also called Eriochrome black T). The uncomplexed dye has a blue color at pH 10 but Erio T forms a red complex with Mg^{2+} (and many other 2+ and 3+ ions).

The titration proceeds as follows. First, the Ca^{2+} solution is adjusted to pH 10 and treated with MgY^{2-} solution. The displacement reaction releases most of the Mg^{2+} into solution. Erio T is added and the red color of the Mg^{2+}, Erio T complex is visible.

Now the titration is begun as EDTA reagent is added. The effect is to complex the now

free Mg^{2+} ions. Eventually enough EDTA is added so that both Ca^{2+} and Mg^{2+} are present almost entirely as their complexes CaY^{2-} and MgY^{2-}. Mg^{2+} is no longer available for complexation with Erio T so the red color disappears and the blue color of free Erio T appears. Thus, the actual titration reaction is one between EDTA and Mg^{2+} with release of Erio T signaling the endpoint. However, the quantity of EDTA required to reach the endpoint depends only on the amount of Ca^{2+} initially present. In other words, we begin the titration with MgY^{2-} and Ca^{2+}. At the endpoint the solution contains MgY^{2-} and CaY^{2-}. The number of moles of EDTA required to cause this transformation is equal to the number of moles of Ca^{2+} present at the start.

We note at this point that any other substance present in the analyte solution that displaces Mg^{2+} from the MgY^{2-} complex will be titrated along with Ca^{2+}. As an example, suppose that a solution contains Zn^{2+} along with Ca^{2+}. The EDTA complex with Zn^{2+} is much stronger than the MgY^{2-} complex so that both Ca^{2+} and Zn^{2+} will displace Mg^{2+} from its complex. The quantity of EDTA reagent required to reach the endpoint will be the sum of the number of moles of Zn^{2+} and Ca^{2+} present. In our experiment this does not present a problem because Ca^{2+} is the only species available for reaction in the saturated calcium sulfate solutions.

BEFORE THE LABORATORY

Read through the lab directions carefully. Make up a DATA SHEET with a very brief description of just what things need to be measured and how. Record your data on the SHEET and turn it in with your lab report.

IN THE LABORATORY

1. Preparation of MgY^{2-} solution.

It is not necessary to know the exact concentration of this solution but it is essential that Mg^{2+} and EDTA be present in a one - to - one mole ratio.

In two small labeled beakers take about 40-50 mL each of approximate 0.05 $\underline{F}$ $MgSO_4$ and 0.05 $\underline{F}$ Na_2H_2Y from the laboratory stocks. (Beware. Two different concentrations of Na_2H_2Y solution are available.)

Measure about 30 mL of each solution into a small clean erlenmeyer flask. Add 1 drop of phenolphthalein to the flask and dropwise add 1 $\underline{F}$ NaOH to the first pink color. (The NaOH is required for the complexation reaction, $H_2Y^{2-} + Mg^{2+} + 2OH^- = MgY^{2-} + 2H_2O$.) About 2-3 mL of NaOH solution will be needed. Now add about 10 mL of pH 10 buffer and 2-3 drops of Erio T indicator solution. At this point the solution may be red, which signals the presence of uncomplexed Mg^{2+}. The solution may be blue, which signals an excess of EDTA. If a miracle happens, the solution will be purple, signaling an essentially exact one - to - one mole ratio of Mg^{2+} to EDTA. (Red + blue = purple.) In any case your objective is to make a solution that will turn blue upon addition of 1 - 2 drops of EDTA solution and will turn red upon addition of 1 - 2 drops of Mg^{2+} solution. Depending on the color of your solution add dropwise and carefully and with adequate mixing either Mg^{2+} or EDTA until the color just turns. (THINK FIRST.) Test the solution by adding 1-2 drops of the other reactant to see that the color changes back. At this point you have the required MgY^{2-} solution. Label and cover the flask.

2. Standardization of 0.01 $\underline{F}$ Na_2H_2Y

Take about 100 mL of standard 0.01 $\underline{F}$ $MgSO_4$ solution (Record the actual concentration.) and pipet 20 mL portions into each of 3 erlenmeyer flasks. Add about 20 mL of water, 5 mL of MgY^{2-} solution, 3 mL of pH 10 buffer and 2-3 drops of Erio T to each flask. Rinse and fill a 25 mL buret with 0.01 $\underline{F}$ Na_2H_2Y solution (<u>NOT</u> 0.05 $\underline{F}$ Na_2H_2Y solution). Titrate to the blue color of Erio T. You should have three closely matched endpoint volumes, V_1*. If not, make a few more titrations.

> NOTE: Because you are using a Mg^{2+} solution to standardize the EDTA it might not seem necessary to add the MgY^{2-} solution. From the point of view of getting a good color change, the MgY^{2-} is not necessary. However, the conditions met in the standardization and the sample titrations should always be matched as closely as possible. Therefore, it is most wise to add all of the

same components here that will later be present in the sample titrations, including the MgY^{2-} solution.

3. Analysis of the Saturated CaSO₄ Solutions

At this point you have standardized the EDTA reagent and will use it to analyze the two saturated $CaSO_4$ mixtures, A and B. These analyses will be made by the same titration procedure as above. That is, mixtures of sample ($CaSO_4$ solution), water, buffer and MgY^{2-} solution are titrated with the EDTA reagent. Before doing so it is necessary to decide on how much of the saturated $CaSO_4$ solutions should be measured out.

The solubility of $CaSO_4$ (F.W. = 136.2 g/mol) in water is roughly 2 g/L near room temperature.

You will use a 25 mL buret for the titrations. In order to minimize the buret reading error, the sample size should be taken to give at least a 10 mL titration, but necessarily less than a 25 mL titration. In short you would like to use roughly 15 mL of EDTA reagent in a titration. Decide on an appropriate sample volume for the titrations. For the sake of simplicity use the same sample volume to analyze both the A and B solutions. Call this volume V_S.

a. Take an amount of saturated $CaSO_4$ in water, A, from the laboratory stock appropriate to 3 or 4 titrations. **Be very careful to not shake or disturb the stock solution in any way!** Pipet V_S mL of the solution into titration flasks and add water, buffer, etc. as before. You should have 3 closely spaced endpoint volumes, V_2^*.

b. Take an appropriate amount of the saturated $CaSO_4$ solution made up in 0.050 $\underline{F}$ KNO_3, B, and measure V_S mL into three titration flasks. Be **very careful to not shake or disturb the stock solution in any way!** Titrate as before. You should have 3 closely spaced endpoint volumes, V_3^*.

THE LABORATORY REPORT

1. Calculate the average V_1^*, its standard deviation, s_e, its standard error, s_m, and its 95 % CI for the standardization titrations.

2. Calculate the concentration of the EDTA titrant (0.01 $\underline{F}$ Na_2H_2Y). Determine the error in the [EDTA] by propagating the errors in the calculations based on the 95 % CI for V_1^* and the tolerances of the measuring devices (see Harris pgs 28-34 and see the opening preamble on the Guide to Statistics for how to propagate error).

3. Calculate the average V_2^*, its standard deviation, s_e, its standard error, s_m, and its 95 % CI for the titrations of the saturated $CaSO_4$ in water.

4. Calculate the solubility of $CaSO_4$ in water. Determine the error in the solubility of $CaSO_4$ in water by propagating the errors in the calculations based on the 95 % CI for V_2^* and the tolerances of the measuring devices (see Harris pgs 28-34 and see the opening preamble on the Guide to Statistics for how to propagate error).

5. Calculate the average V_3^*, its standard deviation, s_e, its standard error, s_m, and its 95 % CI for the titrations of the saturated $CaSO_4$ in 0.050 $\underline{F}$ KNO_3.

6. Calculate the solubility of $CaSO_4$ in 0.050 $\underline{F}$ KNO_3. Determine the error in the solubility of $CaSO_4$ in 0.050F KNO_3 by propagating the errors in the calculations based on the 95
%   CI for V_3^* and the tolerances of the measuring devices (see Harris pgs 28-34 and see the opening preamble on the Guide to Statistics for how to propagate error).

7. The object of this question is to calculate the "thermodynamic solubility product" for $CaSO_4$. We need to talk.

     The thermodynamic solubility product for $CaSO_4$ is symbolized K_{SP} (sometimes $K_{SP}^{\,o}$) and defined by $K_{SP} = (\mathbf{a}_{Ca})(\mathbf{a}_{SO4})$. The **a**'s symbolize **activities** and are related to concentrations by $\mathbf{a}_{Ca} = \gamma_{Ca}[Ca^{2+}]$ and $\mathbf{a}_{SO4} = \gamma_{SO4}[SO_4^{2-}]$. The γ's are called the "activity coefficients" of the ions. In general the value of γ for any ion is not equal to 1.00 so that activities are not the same as concentrations. However, in <u>very</u>, <u>very</u> dilute solutions the values of ionic activity coefficients <u>all</u> approach 1.00. Activity coefficient values deviate from 1.00 at higher ionic

concentrations because the presence of other ions in the solution provides electrical attraction and repulsion interactions with any given ion. The effect of these interactions is to "shield" a given ion and so, in general, cause its apparent concentration, the activity, to differ from the actual concentration.

The **Debye-Huckel** theory allows calculation of activity coefficient values with good accuracy at ionic strengths below about 0.2 $\underline{M}$. (And what, pray tell, is an ionic strength?)

The ionic strength of a solution is a numerical measure of the number and strength of electrical interactions that occur between ions in a given solution. Its value is symbolized by μ or I and is defined by $\mu = 1/2 \Sigma C_i z_i^2$. C_i is the concentration of a given ion in a solution and z_i is the charge of that ion. The sum involves <u>all</u> of the ions in the solution.

> AN EXAMPLE: A certain solution contains 0.0100 $\underline{F}$ $CaSO_4$ in pure water. The only ions present in appreciable concentrations here are Ca^{2+} and SO_4^{2-} with concentrations of 0.0100 $\underline{M}$ each. The ionic strength is $1/2[(0.0100)(+2)^2 + (0.0100)(-2)^2] = 0.0400$ $\underline{M}$.

> ANOTHER EXAMPLE: A certain solution contains 0.0100 $\underline{F}$ $CaSO_4$ and 0.050 $\underline{F}$ KNO_3 in water. The ions present are: 0.0100 $\underline{M}$ Ca^{2+}, 0.0100 $\underline{M}$ SO_4^{2-}, 0.050 $\underline{M}$ K^+, and 0.050 $\underline{M}$ NO_3^-. The ionic strength is $1/2[(0.0100)(+2)^2 + (0.0100)(-2)^2 + (0.050)(+1)^2 + (0.050)(-1)^2] = 0.090$ $\underline{M}$.

The activity coefficient for any given ion in the solution may now be calculated directly from the equation:

$$- \log \gamma_i = 0.511 z_i^2 \mu^{1/2}/(1 + 3.3 \times 10^{-3} \alpha \mu^{1/2})$$

γ_i is the activity coefficient of a certain ion; z_i is the charge of that ion and α is called the "ion-size" parameter and is essentially the size of the ion in units of nm. The numerical coefficients pertain to the solvent water and while they are slightly temperature-dependent the values given (0.511 and 3.3) are appropriate to the temperature range from about $20°C$ to about $30°C$. Values of α for Ca^{2+} and SO_4^{2-} are 0.6 nm and 0.35 nm, respectively.

Once the activity coefficient of an ion is found its **activity** is readily calculated from $a_i = \gamma_i[conc]$.

> AN EXAMPLE: What is the activity of Ca^{2+} ions in a solution of 0.0100 $\underline{F}$ $CaSO_4$ in water?
>
> We have already found $\mu = 0.0400$ $\underline{M}$. Substituting for μ (= 0.0400), z_i (= +2) and α (= 0.6) into the Debye-Huckel equation gives $-\log\gamma_{Ca} = 0.511(+2)^2(0.0400)^{1/2}/(1 + 3.3(0.6)(0.0400)^{1/2}$; $-\log\gamma_{Ca} = 0.293$; $\gamma_{Ca} = 0.510$
>
> Now, the activity of calcium ions, $a_{Ca} = \gamma_{Ca}[Ca^{2+}]$

$$\mathbf{a}_{Ca} = (0.510)(0.0100) = 0.00510.$$

The result in this example indicates that although the actual concentration of Ca^{2+} ions in the solution is 0.0100 $\underline{M}$, it behaves - interacts with other things in the solution - as if it had a much lower concentration, 0.00510 $\underline{M}$.

ANOTHER EXAMPLE: What is the activity of Ca^{2+} ions in a solution containing 0.0100 $\underline{F}$ $CaSO_4$ in 0.050 $\underline{F}$ KNO_3?

We already have found the ionic strength of this solution above; $\mu = 0.090$ $\underline{M}$. Substituting into the Debye-Huckel equation as before gives

$-\log\gamma_{Ca} = 0.385$; $\gamma_{Ca} = 0.412$. The activity of Ca^{2+}, $\mathbf{a}_{Ca}$, is $(0.412)(0.0100)$ $= 0.00412$.

Consider the two examples. The solutions contain the same analytical concentrations of Ca^{2+} ions, 0.0100 $\underline{M}$. However, the activity of Ca^{2+} ions in the second, higher ionic strength mixture, is lower than in the first. The presence of other ions in the solution influences the behavior of the Ca^{2+} ions.

Activity coefficients calculated from the Debye-Huckel equation are generally accurate to about ± 1% up to $\mu = 0.1$ $\underline{M}$ for +1 and -1 ions. They are somewhat less accurate for divalent ions like Ca^{2+} and SO_4^{2-}, typically ± 5% at $\mu = 0.1$ $\underline{M}$. Furthermore, the γ values get worse and worse as the ionic strengths increase. At present there is no way to calculate reliable activity coefficient values in concentrated ionic solutions.

FINALLY, the question: Calculate the activity coefficients of Ca^{2+} and SO_4^{2-} in the A solution ($CaSO_4$ in water) and use these to calculate the thermodynamic solubility product of $CaSO_4$. Your text gives a value for K_{SP}; look it up. Did they get close?

8.   Calculate the activity coefficents of Ca^{2+} and SO_4^{2-} for the B solution ($CaSO_4$ in 0.050 $\underline{F}$ KNO_3) and calculate a value for K_{sp}.

We wish to compare this value with the one in 4, and recognize that both values depend on calculated activity coefficients. We expect these (γ_{Ca} and γ_{SO4}) to be accurate to about ± 5% and will be satisfied if the two K_{sp} values match to within about ± 10%. Is this the case?

9.   (EXTRA CREDIT - 3 points) A certain solution is prepared by adding together 10.0 mL of 0.0200 $\underline{F}$ Ca^{2+}, 5.00 mL of 0.0200 $\underline{F}$ MgY^{2-}, pH 10 buffer and water to make 50.0 mL.

(This solution is suspiciously like ones you have titrated.) Ca^{2+} displaces some Mg^{2+} from the EDTA complex. What percentage of Mg^{2+} remains as MgY^{2-}?

> HINT: Essentially all of the 0.100 mmol of EDTA present exists in either MgY^{2-} or CaY^{2-} complexes. The total concentration of EDTA is 0.100 mmol/50.0 mL = 2.00×10^{-3} $\underline{F}$. Consequently [MgY^{2-}] + [CaY^{2-}] = 2.00×10^{-3}. Use this and mass balance equations for Ca^{2+} and Mg^{2+} along with the equilibrium constant
> $$Ca^{2+} + MgY^{2-} = CaY^{2-} + Mg^{2+} \quad K = 0.79 \times 10^2$$
> to solve for [MgY^{2-}].

10. (EXTRA CREDIT - 2 points) The pH is defined as -log $\mathbf{a}_H$ where $\mathbf{a}_H$ is the activity of H^+ ions.

   a. What is the pH value of an aqueous solution containing 1.00×10^{-2} $\underline{F}$ HCl?

   b. What is the pH value of an aqueous solution containing 1.00×10^{-2} $\underline{F}$ HCl <u>and</u> 0.10 $\underline{F}$ KCl?

Note to instructor:

Preparation of the MgEDTA solution is problematic. It is important that there is no excess EDTA of Mg^{2+}. However, achieving this in a precise manner by adjusting to a purple color is not possible. The experiment could be improved in one of two ways.

   1. Buy a MgEDTA reagent instead of preparing your own.
   2. Instead of erichrome black T and the titration of Mg2+ at pH =10, you could perform the titration of Ca2+ directly at pH 12 using hydroxynaphthal blue (I think).

Also be sure to warn the students not to shake or disturb the stock solutions.