Ye Olde Titration of Calcium Ion and Measurement of a Solubility Product Constant

I. Introduction

If one had to make a list of "the most important elements", one would probably commence with carbon, hydrogen, nitrogen, and oxygen. These are the principal elements of organic chemistry--biochem, too.

It is easy to argue, however, that calcium should also grace the short list. It is a ubiquitous element in nature with a famously diverse set of roles. For example...

(1) Calcium is used in the manufacture of steel as an oxygen scavenger. Without calcium, there would be no modern-day cars and buildings.

(2) Calcium in its carbonate form is the principal ingredient of marble and limestone. Without calcium, there would be no timeless sculpture and architecture to admire.

(3) Calcium in its carbonate form is also the principal ingredient of pearls, seashells, and bones. Life without any of these entities would be a very different and poorer life.

(4) Calcium in its sulfate form is the main component of drywall. This material is produced largely in the combustion of coal by power plants. It is found in virtually every residential and commercial building.

Suffice to say that calcium is important. It is also not surprising to find that the chemist has investigated the element intensely for well over a century. In particular, the chemist has developed very accurate methods for assaying materials for their calcium content. Not incidentally, calcium is a member of a quirky family of elements: the alkalai earth metals. Space does allow any extensive discussion here. However, one gets an idea of the family quirkiness by looking at their solid phase density values:

Beryllium	1.86 grams/cm^3
Magnesium	1.75 grams/cm^3
Calcium	1.55 grams/cm^3
Strontium	2.60 grams/cm^3
Barium	3.61 grams/cm^3
Radium	4.45 grams/cm^3

Note how the density decreases with increasing atomic number and then starts increasing again. Any explanations? Why does calcium demonstrate the rock bottom density on the list?

Calcium is interesting and important. This Chem 112 experiment will provide experience assaying **aqueous samples** for their calcium content. Along the way, the lab exercises will also aim at values of a solubility product constant. In achieving both of these aims, experience will also be provided with a ubiquitous organic compound: **ethylenediaminetetraacetic acid**. The trade name for this famous compound is a well-known acronym, namely **EDTA**. It is found, perhaps to a fault, in many food products of modern day.

II. The Reaction Involving Calcium and EDTA

As discussed in Chem 101 and 102, calcium is soluble in aqueous solution as a divalent cation: $Ca^{2+}(aq)$. In solid form, it thus combines with **monovalent counterions** as would be expected: $CaF_2(s)$, $CaI_2(s)$, $Ca(NO_3)_2(s)$, and so forth.

Consider a calcium salt with a monovalent counterion which is **sparingly soluble in water.** A good example here would be something like the organic salt **calcium benzoate**: $Ca(OBz)_2(s)$. If a chemist adds a sizable quantity of calcium benzoate to a beaker of distilled water, the following equilibrium is established sooner or later:

$$Ca(OBz)_2(s) \;=\; Ca^{2+}(aq) \;+\; 2\,OBz^{-}(aq)$$

The temperature dependent equilibrium constant K for the above reaction would *first* be considered via:

$$\frac{[Ca^{2+}(aq)]\,[OBz^{-}(aq)]^2}{[Ca(OBz)_2(s)]}$$

However, the density of any solid material, calcium benzoate included, is only *weakly dependent* on temperature. Thus the only concentrations whose values can vary significantly involve the ions dissolved in the aqueous phase. Thus the chemist **follows a convention** by featuring in K-expressions only the concentration terms which can vary significantly. In adhering to the convention, the above K-expression is re-phrased as

$$[Ca^{2+}(aq)]\,[OBz^{-}(aq)]^2$$

Since the above involves the products of concentrations dependent on the salt solubility, the expression is often referred to as K_{sp}; the "sp" is an abbreviation for "solubility product". There are several ways for a chemist to measure a solubility product constant (K_{sp}) of a salt of interest.

In this experiment, we will perform an EDTA titration of divalent calcium ions in order to measure their concentration. EDTA combines with $Ca^{2+}(aq)$ in a mole ratio of 1:1.

After measuring the calcium ion concentration, the chemist can *infer* the monovalent counterion concentration to be twice that of the calcium concentration.

Thus if the chemist refers to the concentration of calcium ions x, then the monovalent counterion concentration must be 2x. And the value of K_{sp} must be

$$\mathbf{x \bullet 2x \bullet 2x}$$

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But now there is another puzzle piece to consider. In order to make headway with a calcium ion titration, the chemist must know with certainty the concentration of the EDTA solution. To achieve this certainty, the chemist must use a prepared EDTA solution to titrate a solution whose calcium ion concentration is known.

Important: we will carry out two essential tasks in this experiment. We will first prepare a calcium ion solution of known concentration. We will titrate this known solution with EDTA solution in order to ascertain the concentration of EDTA. Only after that task has been completed can we titrate a solution whose calcium ion concentration is unknown.

III. Experimental and Calculations

A. Getting Started

Please put on both safety glasses and latex gloves. Every team should then organize the following equipment:

small graduated cylinders
large graduated cylinders
beaker with volume ≥ 250 milliliters
beakers with volume ≥ 50 milliliters
watch glasses

5 milliliter volumetric pipette
pipette pump
25 milliliter volumetric pipette
rubber stopper
250 milliliter volumetric flask
buret and working stopcock

The first set of items should be found in one's lab drawer. The second set of items will be available from the center area of the lab.

As per usual, each team member should apportion five to seven pages of the lab notebook to record all data for the experiment.

Now use two clean small beakers to collect:

50 milliliters of EDTA solution
25 milliliters of pH 10 buffer solution

Please do not take more than the above chemicals, especially the buffer solution.

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Now weigh out approximately 0.40 grams of solid calcium carbonate ($CaCO_3(s)$). Close enough is good enough here, but the precise amount must be recorded. And please do not exceed 0.40 grams; 0.30 grams is even OK for this experiment. This sample of calcium carbonate will be used to ascertain the EDTA concentration.

Pour the entirety of the calcium carbonate sample into the beaker with volume ≥ 250 milliliters. It is important to push every grain of solid material into the beaker and onto the bottom.

Add approximately 25 milliliters of distilled water to the beaker. The calcium carbonate will not dissolve, but that is OK.

Now take the beaker to one of the hoods. Locate a bottle of 6 molar HCl. This is a concentrated strong acid solution. Use gloves, the hood, and every caution when handling. If one is wearing contact lenses, please pass this task to one's team member.

Now begin to add the HCl **slowly, carefully, and dropwise** to the $CaCO_3(s)$ / water sample. The following reaction will begin to take place:

$$CaCO_3(s) + 2\,H^+(aq) \;=\; Ca^{2+}(aq) + 2\,H_2O(liq) + H_2CO_3(aq)$$

But wait, there is more! The $H_2CO_3(aq)$ is carbonic acid. This acid will demonstrate more aqueous phase chemistry as follows:

$$H_2CO_3(aq) \;=\; H_2O(liq) + CO_2(g)$$

Thus by adding the HCl to the calcium carbonate, the chemist will convert all of the calcium into dissolved ions; the solution will moreover give off carbon dioxide gas as it is formed.

!!!!!Extremely important: Please use a minimum amount of HCl to dissolve the calcium carbonate. To blow off this admonition screw up the results and turn the lab into a complete waste of time!!!!!!!

After the calcium carbonate has dissolved, the solution should be crystal clear. Use a hot plate to heat the solution to a gentle boil. Please apply the heat for several minutes in order to jettison the carbon dioxide from solution. However, do not let the liquid boil off entirely; add more distilled water if necessary.

After the heating step, please add about 50 milliliters of distilled water. Stir thoroughly and then transfer the solution to the 250 milliliter volumetric flask. Then fill the flask to the volumetric mark with additional distilled water. Plug in a stopper and set the sample aside to cool completely to room temperature.

Now use the $CaCO_3(s)$ weighing data in order to calculate the calcium ion concentration in the volumetric flask.

B. The First Calcium/EDTA Titration

(1) Please clean and drain thoroughly a buret. Then rinse and drain the buret with a few milliliters of the EDTA solution. It is important that the EDTA solution coat all of the insides of the buret, and then be allowed to drain thoroughly.

(2) Now use a volumetric pipette to transfer 25.00 milliliters of the calcium solution from the volumetric flask to an Erlenmeyer flask with volume $\geq$ 250 milliliters.

!!!!!Very Important: The pipette has a thin glass stem that snaps off very readily. When this accident happens--and it unfortunately does--the sharp edge of the broken stem causes terrible cuts to one's hands that require multiple stitches at a hospital emergency room. Please use every and all caution in handling these fragile glass devices. Do not use unnecessary force when connecting the pipette to the pump. Please seek assistance if there are any doubts or questions!!!!!

(3) To the Erlenmeyer flask, add 5.00 milliliters of pH 10 buffer. Add several drops of **Eriochrome Black T** indicator. Finally, please add fifteen drops of 0.03 molar magnesium chloride solution.

Important: Each team will know they are on the right track if the solution appears faint red in color. The faint red color indicates that calcium ions are present in solution in their free, dissolved form.

(4) Now add fresh EDTA solution to the buret with the stopcock in the closed position. We are now ready to rumble.

Please titrate the faint red sample slowly and carefully with EDTA solution. The EDTA is a chelating agent: the molecules will diffuse through the solution and wrap around (i.e. EDTA hug) any calcium ions they encounter. One EDTA molecule wraps around one calcium ion.

Important: the solution color will turn magically from red to blue when all of the calcium ions have been wrapped by EDTA molecules. This color change marks the endpoint of the titration.

(5) Now calculate the number of moles of calcium ion in the 25.00 milliliters withdrawn from

the volumetric flask. Then convert the volume of added EDTA solution to liters. Compute the EDTA concentration by dividing the calcium concentration by the liters of added EDTA.

C. The Second Calcium/EDTA titration.

Please repeat steps (2) - (5) of the foregoing section. It is important to obtain **two values** for the EDTA concentration. Then compute the average of the two concentration values. This **average value** will be critical for the measurement of K_{sp}.

D. The Third Calcium/EDTA titration.

(1) Please use a volumetric pipette to transfer 5.00 milliliters of the unknown calcium solution to a clean 250 milliliter Erlenmeyer flask.

(2) Add several drops of Eriochrome Black T indicator. Then add fifteen drops of 0.03 molar magnesium chloride solution.

(3) Please titrate the sample with EDTA solution whose concentration is now known. Titrate the unknown calcium sample to the blue endpoint.

(4) Now calculate the number of moles of EDTA which were added during the titration. This is equal to the number of moles of calcium ion in the 5.00 milliliter sample.

(5) Compute the calcium ion concentration in the unknown sample. This is **value "x"** referred to in **Section I.**

(6) Compute the monovalent counterion concentration discussed in **Section I.** This is quantity 2x.

(7) Compute the value of K_{sp} of the calcium salt.

D. The Fourth and Final Calcium/EDTA titration.

Please repeat all the steps of **Section IIIC**. Please compute an average value of K_{sp}.

IV. Preliminary Report

Please complete the preliminary report sheet found on the last page of this handout. Each lab partner should complete his/her own sheet based on the team data. Please turn in the preliminary report to the lab assistant before leaving.

V. Final Report

Please write a final report based on data recorded for this experiment. Each partner of a team must write and submit his/her own lab report. Each report must be typewritten and should adhere to the following outline.

A. Introduction: Please describe the purpose of the experiment in your own words. Please explain the concept of the Solubility Product Constant. Why does the chemist express it via only numerator terms?

B. Experimental: Please summarize the experimental method. Please note any deviations from the procedure described in the handout.

C. Results: Please clearly present the results of **four Calcium/EDTA titration experiments.** For the first two titrations, please construct a table which organizes the following quantities:

volume of $Ca^{2+}(aq)$ solution
concentration of $Ca^{2+}(aq)$
moles of $Ca^{2+}(aq)$
liters of EDTA added
moles of EDTA added
concentration of EDTA solution

Please report the average and standard deviation for the EDTA concentration.

For the last two titrations, please construct a table which relates:

volume of unknown $Ca^{2+}(aq)$ solution
liters of EDTA added
moles of EDTA added
moles of $Ca^{2+}(aq)$ in unknown solution
concentration of $Ca^{2+}(aq)$
concentration of counterion
value of K_{sp}

Please report the average and standard deviation of K_{sp}.

D. Discussion: Please discuss the significance of experimental results in your own words. What happened in the experiment that was expected? What--if anything--happened that was not anticipated?

Please explain why the concentration of only one type of ion needed to be measured in order to obtain a value for K_{sp}.

Please explain the importance of knowing the Calcium ion-EDTA stoichiometry.

The solubility product constant is temperature dependent. Is it likely or unlikely that K_{sp} for this experiment increases with temperature? Please discuss.

Ye Olde Pre-Lab Assignment

1. A chemist prepares a calcium ion solution by dissolving 0.4848 grams of calcium carbonate using hydrochloric acid and ca. 50 milliliters of water. Water is added such that the solution volume is increased to 250 milliliters.

(a) What is calcium ion concentration in the 250 milliliter sample?

(b) How many milliliters of 0.0325 molar EDTA are needed to titrate 25.00 milliliters of the calcium ion sample to the endpoint?

(c) EDTA and dissolved calcium ions combine in what ratio?

2. A chemist finds that 21.30 milliliters of 0.0325 molar EDTA are required to titrate 5.00 milliliters of an unknown calcium sample to the endpoint. This sample was prepared by dissolving a maximum amount of calcium salt in which the counterion is monovalent.

(a) What is the calcium ion concentration in the sample?

(b) What is the counterion concentration in the sample?

(c) What is **Ksp** for the calcium salt?

Preliminary Report

Name:

Lab Partner's Name:

Lab Assistant's Name

1. Concentration of EDTA measured in the first titration:

2. Concentration of EDTA measured in the second titration:

3. Concentration of Calcium Ion and K_{sp} measured in the third titration:

4. Concentration of Calcium Ion and K_{sp} measured in the fourth titration: