

Selectivity and Solubility Analysis Using Ion Selective Potentiometry: A Soil Chemistry Experiment

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ABSTRACT

The principles and applications of electrochemistry can be used in soil chemistry courses to illustrate concepts involving the master variable pH as well as ion activities. An experiment is described that utilizes a calcium-ion selective electrode to determine Ca^{2+} activity in aqueous solutions. Because there is a potential for interferences in determining Ca^{2+} activity, we have included a study of cations (Mg^{2+} , Cu^{2+} , and Pb^{2+}) that affect the mV response of the Ca^{2+} electrochemical cell. Determination of solubility products of two Ca-containing minerals—calcite (CaCO_3) and fluorite (CaF_2)—are described based on the determination of Ca^{2+} activities as well as stoichiometric and activity coefficient assumptions. The soil chemistry experiments presented in this paper will educate students in the use of ion-selective electrodes, enhance their understanding of an analytical tool, provide examples of potential problems that can occur with the use of electrochemistry, and provide them with a practical application, i.e., the determination of solubility products, which will enhance their appreciation of mineral/solution theory that is a major area of discussion in soil chemistry courses. We have included several prob-

lems that will assist the students in gaining a better understanding of electrochemical determinations and applications.

ION-SELECTIVE ELECTRODES, such as the glass electrode, are used to measure dissolved ion activities in soil solutions and natural waters. In addition to pH measurements, several ion-selective electrodes have been developed for analysis of cations (e.g., Ca^{2+} , Cu^{2+} , K^+ , NH_4^+) and anions (e.g., F^- , Cl^- , NO_3^- , I^-) (Fricke and Kuntz, 1977; Orion, 1986). Electrochemistry applications have been used for several applications in soil solution and natural waters chemistry, including: oxidation-reduction potentials, proton and metal complexation, soil nutrient concentrations, geochemistry of soils and sediments, and surface and groundwater characterization (Pankow, 1991; Sposito, 1994; Stevenson, 1994; Wolt, 1994; Sparks, 1995). Bioavailability of some trace elements can be determined directly with ion-selective electrodes (Pierzynski et al., 1994).

The Ca^{2+} ion-selective electrode has a membrane surface that acts as a liquid ion-exchanger with ions inside and outside of the electrode (Fischer, 1974; Orion, 1982). An electrical potential (mV) develops due to ion activity differences on the membrane surface. The Ca^{2+} ion-selective electrode system that is used to measure Ca^{2+} activities is called an

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Abbreviations: mV, millivolt; ISE, ion selective electrode.

electrochemical cell, which can be illustrated as follows (Lloyd et al., 1976; Willard et al., 1981):

Internal reference electrode	Ca ²⁺ _(aq) internal reference solution	Membrane containing Ca ²⁺ ion- exchanger	Sample solution containing Ca ²⁺	External reference electrode
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A relationship exists between the measured potential of the electrochemical cell and the activity of the thermodynamically effective free Ca²⁺ ion in standard and sample solutions. The relationship between the mV potential and Ca²⁺ activity obeys the Nernst equation:

$$E = E^\circ + \frac{2.3 RT}{ZF} \log (\text{Ca}^{2+}) \quad [1]$$

where E is the cell potential expressed in millivolts (mV), E° is the standard cell potential that is dependent upon both the internal and external reference electrodes, R is the molar gas constant (8.314 J mol⁻¹ K⁻¹), T is the absolute temperature, Z represents the valence of the ion analyzed (e.g., 2 for Ca²⁺), F is Faraday's constant (96 487 coulombs mol⁻¹), and (Ca²⁺) is the activity of free Ca²⁺ in standard or sample solutions. Generally, the conditions used to measure an ion of interest in most environmental samples, under laboratory conditions, are close enough to standard conditions that Eq. [1] simplifies to:

$$E = E^\circ + \frac{59.2}{Z} \log (\text{Ca}^{2+}) \quad [2]$$

where $2.3 RT/F$ becomes 59.2 mV at 298 K (25°C).

The purpose of this paper is to describe a soil chemistry experiment that uses ion selective potentiometry to: (i) develop standard curves, (ii) determine selectivity coefficients, and (iii) compute ion activity products and saturation indices for solutions containing Ca minerals. A Ca²⁺ ion-selective electrode will be used to describe how to determine the activity of dissolved Ca²⁺ ions by the direct measurement technique. In addition, the electrode response due to the interference of other ions in solution will be examined; interference results in electrode potentials that are not true measurements of the ion of interest. Correct ion activity measurements are important in assessing the factors controlling chemical processes in soil and aquatic ecosystems (Lindsay, 1979a,b,c; Wang and Huang, 1990). The specific objectives of the soil chemistry experiment will be to: (i) evaluate the electrochemical response of standard solutions containing Ca²⁺, with and without Mg²⁺, Cu²⁺, and Pb²⁺ ions, using a Ca²⁺ ion-selective electrode; and (ii) determine the ion activity products of representative soil Ca-containing minerals from dissolved Ca²⁺ activity values measured with the Ca²⁺ ion-selective electrode.

MATERIALS AND METHODS

For any soil chemistry laboratory, reliable experimental results can only be obtained when using uncontaminated pipettes, beakers, and volumetric flasks. There are no hazardous chemicals described in this experiment, but, as always, proper precautions, such as wearing safety glasses, should always be followed while in the laboratory.

Equipment. Corning Ion Analyzer 250¹ or equivalent. A pH/mV meter that has a readout of 0.1 mV can also be used. Orion Model 93-20 Calcium Ion Selective Electrode or equivalent. Orion Model 90-01 Single Junction Reference Electrode or equivalent. Magnetic stirrer and stirring bars.

Glassware. Twelve 100-mL beakers. Nine 10-mL pipettes. Nine 100-mL volumetric flasks.

Reagents. 0.1 M CaCl₂, 0.01 M MgCl₂, 0.01 M CuCl₂, 0.01 M PbCl₂.

Minerals. Calcite (CaCO₃) and fluorite (CaF₂).

Relationship between Activity and Concentration

In infinitely dilute solutions, solute activity is equal to concentration. However, when working with solutions that contain a significant ionic composition, e.g., total soluble salts greater than approximately 10⁻⁴ M, the relationship between ionic activity, (γ), and ionic concentration, [X], must be considered. The formula for determining the activity of ion X is:

$$(X) = \gamma_x [X] \quad [3]$$

where γ_x is the activity coefficient of ion X . Activity coefficients can be determined by one of several approaches. A commonly used approach utilizes the Davis equation (Pankow, 1991):

$$\log \gamma_x = -AZ_x^2 \left(\frac{IS^{1/2}}{1 + IS^{1/2}} - 0.2 \right) IS \quad [4]$$

where $A = 0.51$ for water at 298 K (25°C), Z_x is the charge valence of ion X , and IS is the ionic strength. Ionic strength can be calculated if the solution ionic concentrations are known:

$$IS = \frac{1}{2} \sum [X] Z_x^2 \quad [5]$$

where [X] is the concentration of X in M (mol L⁻¹) and Σ is the summation of the product of each of the solution ion concentrations multiplied by its charge valence squared.

Ion Measurement Techniques

When using the direct-measurement technique with an ion-selective electrode, potentiometric measurements are required for several standard solutions and the sample solution. For the determination of Ca²⁺ activity in a sample solution, one must first measure the mV response (potential) of standard solutions containing known Ca²⁺ concentrations. Standard solution Ca²⁺ activities can then be calculated using the Davies equation described previously. A standard curve of mV response vs. Ca²⁺ activity is then developed. The mV readings from sample solutions are compared to the standard curve to obtain Ca²⁺ activity. This is typically done by determining the linear relationship between mV response

¹ The mention of trade or manufacture names and products is for informational purposes only and does not imply an endorsement, recommendation, or exclusion by the University of Wyoming or the Tennessee Valley Authority.

and Ca^{2+} activity for standard solutions and then using the slope and intercept values for calculating sample Ca^{2+} activities.

Electrode Calibration and Standard Curve Preparation

The ISE system must first be calibrated using standard solutions of known Ca^{2+} concentration and activity.

1. Prepare six (100 mL) calibration solutions containing 10^{-1} , 10^{-2} , 10^{-3} , 10^{-4} , 10^{-5} , and 10^{-6} M CaCl_2 by serial dilution, starting with the 10^{-1} (0.1 M) Ca stock solution.
2. Place the Ca-ISE and reference electrode in a beaker of distilled water and allow the mV reading to stabilize.
3. Pour approximately 50 mL of a standard solution, starting with the 10^{-6} M CaCl_2 solution, into a 100-mL beaker, add stirring bar, and lower the electrodes into the standard solution.
4. Turn on stirrer immediately after placing electrodes in solution and record the time required for the reading to stabilize (i.e., less than 1 mV change per min^{-1}) and the final mV potential. Turn the stirrer off and again record the time required for the reading to stabilize and the final mV potential.
5. Repeat Steps 3 and 4, measuring the next concentrated standard solution, until all the solutions have been analyzed. Starting with the most dilute solution and continuing with the more concentrated solutions reduces the stabilization time and minimizes contamination.

Note: Always carefully rinse electrodes with deionized water and blot dry before placing electrodes into standard or sample solutions.

Selectivity Coefficients

1. Prepare 100-mL solutions containing 10^{-3} M CaCl_2 alone and with 10^{-3} M MgCl_2 , 10^{-3} M CuCl_2 , or 10^{-3} M PbCl_2 .
2. Determine the mV potential of each solution, starting with the 10^{-3} M CaCl_2 solution, noting the time for the readings to stabilize and the mV reading. After each measurement, soak the electrodes in the 10^{-3} M CaCl_2 solution until the original mV reading is obtained.

Solubility Products

1. Determine the mV potential of the solutions containing the calcium minerals—calcite (CaCO_3) and fluorite (CaF_2). *Instructor Note:* minerals should remain in closed containers filled completely with deionized-distilled water for at least 1 mo. Opening the calcite-containing vessel and leaving headspace for gas diffusion can result in inaccurate ion activity product (IAP) values based on the methods used in this experiment.

RESULTS AND DISCUSSION

The electrode measures Ca^{2+} activity directly in the unknown solutions. Therefore, the ionic strength need not be controlled or known in the unknown solution. However, if the determination of Ca^{2+} concentration is required, one must know the ionic strength so Ca^{2+} concentration can be determined from Ca^{2+} activity. If the ionic strength is less than 10^{-4} M, the Ca^{2+} concentration is nearly equal to Ca^{2+}

activity because the activity coefficient is very close to 1. If the ionic strengths of unknown solutions are greater than 10^{-4} M and variable, the ionic strength can be adjusted to a high level in both unknown samples and standards with a highly concentrated, nonreactive salt solution. With the same ionic strength in both standards and unknowns, the activity coefficient is constant and becomes part of the intercept for the standard curve. For example, if the Ca^{2+} activity is equivalent to the product of Ca^{2+} concentration and Ca^{2+} activity coefficient, γ_x , then:

$$(\text{Ca}^{2+}) = \gamma_x [\text{Ca}^{2+}] \quad [6]$$

and Eq. [2] can be written as:

$$E = E^\circ + 29.6 \log \gamma_{\text{Ca}} + 29.6 \log [\text{Ca}^{2+}] \quad [7]$$

Because γ_{Ca} is constant, the intercept of the Ca concentration standard curve is $E^\circ + 29.6 \log \gamma_{\text{Ca}}$. When unknown solutions have the same γ_{Ca} as standard solutions, Ca^{2+} concentrations can be determined from a standard curve of E vs. $\log [\text{Ca}^{2+}]$ with slope 29.6 and intercept $E^\circ + 29.6 \log \gamma_{\text{Ca}}$. It should be noted that 29.6 is a theoretical value that assumes the Ca^{2+} ion selective electrode system accurately follows the Nernst equation. Also, Eq. [7] only defines the linear portion of the standard curve that occurs generally at Ca^{2+} concentrations of 10^{-5} M and greater. Below this concentration, the standard curve becomes curvilinear and the electrode response is referred to as non-Nernstian.

Errors that arise in ion-selective potentiometry methods include response time variations, temperature and pH effects, electrode drift, and interferences by other sample ions (Orion, 1986). Although the response time for the Ca^{2+} ion-selective electrode is rapid (generally less than 1 min), at low Ca^{2+} concentrations the response time can vary up to several minutes. To control temperature and pH effects that can result in misleading mV readings, both standards and sample solutions should be at room temperature ($\pm 1^\circ\text{C}$) and should be in the pH range of 4 to 10. Drift occurs when electrodes age, when temperature and pH fluctuates, or when an electrode is used for long periods of time. Recalibration or checking standard solution potentials (mV) every hour will help prevent possible problems with reproducibility.

Selectivity Coefficients

Interferences result from inorganic and organic solution ions or components (other than the ion of interest) that influence electrode potential readings, thus causing positive and negative measurement errors (Willard et al., 1981; Dempsey and O'Melia, 1983; Sikora and Stevenson, 1987). The most common cause of interference is due to high levels of sample ions other than the ion of interest; however, some ions can result in significant measurement errors when present at low concentrations. A selectivity coefficient is an index of the relative interference of an ion measured in the presence of another ion. An example of an ion interfering with the measurement of Ca^{2+} would be the H^+ ion at low pH (i.e., below pH 4).

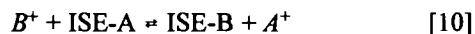
The principal advantage of ion-selective electrodes is their selective nature to respond only to an ion of interest;

however, other ions can affect electrode response. Usually the potential interfering ions are at very low concentrations in natural waters or soil solutions. There are cases when high ion concentrations may result in an interference, e.g., salt-affected soil solutions or contaminated waters. The existence of an interference effect on an electrode is difficult to detect unless the sample composition is known or a non-Nernstian response occurs in a standard curve derived with solutions containing the suspected interfering ion in addition to the analyte (ion) of interest.

An interfering ion will bias the electrode potential measurement for an ion of interest; the actual electrode potential is thus a measure of competing exchange equilibria between the two ions with the electrode membrane (Lloyd et al., 1976; Martin and Freiser, 1980). The equilibrium resulting between an ion of interest, A^+ , or an interfering ion, B^+ , with the Ca^{2+} ion-selective electrode surface (ISE^-) can be illustrated as follows:



The above example for the treatment of an interference is not universal and only applies to membrane-based ion-exchange electrodes. However, for these specific types of ISEs, a combination of the two competing reactions listed in Eq. [8] and [9] describes the equilibrium between the ions and the ISE surface:



The relative stability of complexes ISE-A and ISE-B in Eq. [10] determines the equilibrium position of the reaction, i.e., which complex is favored. Therefore, if the stability of ISE-A is significantly greater than that of ISE-B, then the formation of ISE-A would be predicted to dominate, and thus the equilibrium described in Eq. [10] would favor the left side of the reaction. This would indicate the ISE has a high

degree of selectivity for A^+ relative to B^+ , and therefore B^+ will not be an interfering ion at low concentrations. If, however, the concentration of B^+ increases relative to A^+ , the equilibrium may shift due to mass action effects.

When a significant interaction occurs between an interfering ion and ISE^- , the measured cell potential will change based on the activity of the interfering ion, e.g., (B^+), as described by the selectivity coefficient, k_{AB} , determined for A^+ and B^+ competitive equilibria. The relationship among (A^+), (B^+), and k_{AB} is:

$$E = E^\circ + 59.2 \log((A^+) + k_{AB}(B^+)) \quad [11]$$

assuming that both ions have a common charge valence, Z . This is a modification of the Nernst relationship described in Eq. [1].

The general indication of the interference in the determination of A^+ caused by B^+ is related to k_{AB} . For example, a large k_{AB} suggests there is greater interference caused by B than if k_{AB} is small. A simple method of determining selectivity coefficients is to compare cell potentials of solutions containing known activities of A^+ against another solution of an equivalent amount of A^+ , which also contains B^+ . The difference in total cell potentials of these two solutions can be described as:

$$E_{AB} - E_A = \Delta E = 59.2 \log \left(\frac{(A^+) + k_{AB}(B^+)}{(A^+)} \right) \quad [12]$$

which is a combination of Eq. [2] and [11]. This method is referred to as the *separate solution method* and is a simple technique for determining k_{AB} values. However, the method only involves the determination of mV response in two samples, thus limiting accurate k_{AB} determinations. To improve accuracy, a number of samples can be created with varying activities of A^+ with a constant activity of B^+ . For a positively charged analyte, the asymptote at the lower limit of detection will be at a mV response greater than a standard curve of A^+ alone. The Ca^{2+} activity at the intersection of the lower limit asymptote and the linear portion of the curve (see Fig. 1) is used to calculate the k_{AB} as (Guilbalt, 1979):

$$k_{AB} = (A)/(B)^{z_A/z_B} \quad [13]$$

where (A) is the activity of the analyte at the intersection, (B) is the activity of the interferent, and z_A and z_B are the charge of analyte and interferent, respectively. This method of determining the selectivity coefficient is referred to as the *fixed interference method*.

Solubility Products

The dissolution of a simple mineral, AB , can be illustrated as:



which under equilibrium conditions defines the dissolution constant

$$K_d = \frac{(A)(B)}{(AB_2)_{(\text{solid})}} \quad [15]$$

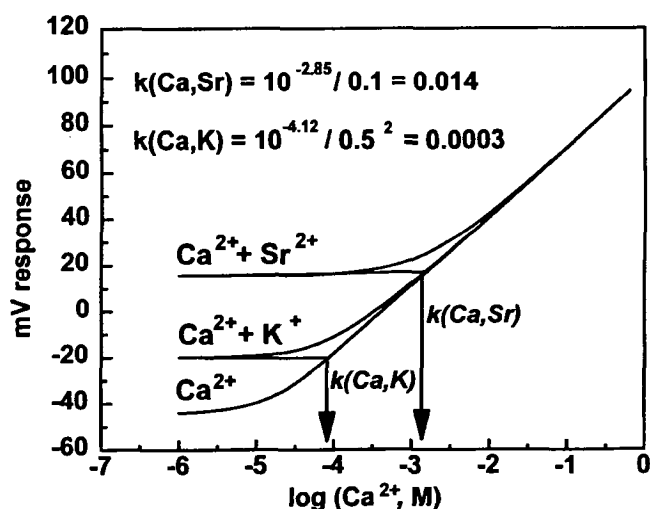


Fig. 1. Response of Ca ion-selective electrode to Ca activity (Ca^{2+}) at various concentrations with 0.5 M K^+ (Ca^{2+} and K^+), and with 0.1 M Sr (Ca^{2+} and Sr^{2+}). Selectivity coefficients were calculated according to the fixed interference method (see Eq. [13] in text).

The dissolution reaction and dissolution constant for a more complex mineral, such as AB_2 , is as follows:



$$K_d = \frac{(A)(B)^2}{(AB_2)_{(solid)}} \quad [17]$$

The product terms in Eq. [15] and [17] correspond to the activity of ions A and B ; the solid-phase mineral terms represent the activity of AB and AB_2 . A common assumption is that solid-phase minerals have constant activities when they are pure and without structural imperfections. In this case, the solid-phase activity term is defined as equal to 1.0. Using these assumptions, new constants called solubility products, K_{sp} , can be calculated as follows:

$$AB_{(solid)} \quad K_{sp} = K_d(AB)_{(solid)} = (A)(B) \quad [18]$$

$$AB_{2(solid)} \quad K_{sp} = K_d(AB_2)_{(solid)} = (A)(B)^2 \quad [19]$$

Analytical methods for determining solubility products of solid-phase minerals can involve the measurement of total ion concentrations in solution so that ionic strength calculations and activity coefficients can be determined. Activities or concentrations may be determined depending on the element of interest and analytical method employed (Lutwick et al., 1988). Solubility products, based on thermodynamic data, have been reported for hundreds of solid-phase minerals (Lindsay, 1979a,b,c).

With ion-selective potentiometry, ion activity is determined directly. Therefore, K_{sp} values for simple systems, such as a single mineral system with an AB type mineral as described in Eq. [18], can be easily calculated if the ion activity of A or B can be analyzed. For example, upon dissolution of $AB_{(solid)}$, an approximately equivalent relationship exists between the activity of A and B ions. With the activity of A determined by ion-selective potentiometry, the K_{sp} can be calculated from the following relationships:

$$K_{sp} = (A)(B) \quad [20]$$

$$[A] = [B] \quad [21]$$

$$K_{sp} = (A)^2 (\gamma_B/\gamma_A) \quad [22]$$

If the assumption is made that $\gamma_B = \gamma_A$, then Eq. [22] becomes

$$K_{sp} = (A)^2 \quad [23]$$

For AB_2 type minerals, the relationship between A and B ion activities will depend on molar concentrations and activity coefficients. If A has an ionic charge of 2, then the ionic charge of B would be 1, and activity coefficients for the two ions would differ. With the activity of A determined by ion-selective potentiometry, K_{sp} values for AB_2 -type minerals can be calculated from the following relationships:

$$K_{sp} = (A)(B)^2 \quad [24]$$

$$[A] = \frac{1}{2} [B] \quad [25]$$

$$K_{sp} = 4 (A)^3 (\gamma_B/\gamma_A)^2 \quad [26]$$

Equations [20] and [24] define the ion activity in solution if the system contains one solid-phase mineral dissolved in pure H_2O . The activity of A can be calculated if the K_{sp} of the solid-phase mineral is known or K_{sp} can be calculated if activity of A is known. In more heterogeneous systems found in nature, many solid phases can control ion activities in solution. Therefore, assumptions that $[A] = [B]$ for AB and $[A] = 1/2[B]$ for AB_2 may not be sufficiently valid. The solid phases controlling ion activities in the aqueous phase in natural systems can be surmised by comparing IAPs to the solubility products reported for known minerals. The IAP for the AB and AB_2 minerals would correspond to:

$$IAP_{AB} = (A)(B) \quad [27]$$

$$IAP_{AB_2} = (A)(B)^2 \quad [28]$$

To evaluate the equilibrium conditions of soil solutions and natural waters, the saturation index (SI) for different solid-phase minerals must be calculated. The SI value is determined as follows:

$$SI = \frac{IAP}{K_{sp}} \quad [29]$$

If SI values are less than 1, the system is undersaturated, greater than 1, oversaturated, and equal to 1, saturated with respect to the solid-phase mineral evaluated. A system with an SI of 1 suggests a particular solid-phase mineral is controlling the solution activities of the mineral constituents. Undersaturated conditions ($SI < 1$) for a particular solid-phase mineral may be an indication that the solution phase ionic activities are not controlled by the designated mineral, the system is not in equilibrium, or the mineral may not form under the given environmental conditions (McBride, 1994). Oversaturated concentrations ($SI > 1$) indicate the solution phase ionic activities are favorable for the mineral to form, but may not due to kinetic constraints on precipitation.

STUDENT ASSIGNMENT

1. Prepare tables that include the Ca^{2+} concentration, Ca^{2+} activity coefficient (using the Davies equation), Ca^{2+} activity, cell potential (mV readings), and stability time for each of the standard solutions, selectivity coefficient samples, and the mineral-containing solutions.
2. For standard curve data, graph the cell potential against the $\log [Ca^{2+}]$ and $\log (Ca^{2+})$ on the same graph; use $\log [Ca^{2+}]$ and $\log (Ca^{2+})$ as independent variables, i.e., x axis.
3. Determine the least squares fit for the linear regions for both the Ca^{2+} concentration and activity values. Also compare the slopes between the stirred and unstirred readings.

4. Calculate the selectivity coefficients $k_{\text{Ca},x}$ for $x = \text{Mg}^{2+}$, Cu^{2+} , and Pb^{2+} from Eq. [12].
5. Determine the K_{sp} values for CaCO_3 and CaF_2 using Eq. [23] and [26] and the linear regression equation developed in Step 3 for determining Ca^{2+} activities.

SUGGESTED QUESTIONS

(* indicates the more difficult problems)

1. How did stabilization time vary with Ca^{2+} concentration or activity and what effect would constant time intervals between readings have on your final results?
- 2.* Suppose an electrode that detects an ion with a univalent charge yields a mV response with a precision of ± 1 mV. What is the precision of the concentration determined in an unknown sample? What is the precision of the concentration of a divalent ion determined in an unknown sample? Answer—The precision actually depends on the value chosen on the logarithmic scale. A mV response corresponding to a concentration of $\log X = -3.1$ is going to be greater than that corresponding to a concentration of $\log X = -3.8$. The student should choose a $\log X$ at the two extremes and determine the concentration corresponding to $+1$ mV and -1 mV to determine the variance in precision.
3. What are some errors that can result in calibrating the Ca^{2+} ion-selective electrode? Also discuss some of the errors that may occur when plotting $\log (\text{Ca}^{2+})$ vs. the cell potential, and how these might impact the analysis of Ca^{2+} activity.
4. What can be done to minimize the errors associated with ion-selective potentiometry?
5. Compare the slopes you obtained for $\log [\text{Ca}^{2+}]$ and $\log (\text{Ca}^{2+})$ vs. the cell potentials and discuss how the slopes compare with the expected Nernst response and why they differ.
6. What determines the detection limit of the Ca^{2+} ion-selective electrode?
7. Derive Eq. [12].
8. Discuss the relevance of the calculated k_{AB} values for the different cations with respect to the interference with Ca^{2+} measurements.
9. Based on the k_{AB} values calculated in this experiment, which cation would cause the greatest interference with Ca^{2+} using ion-selective potentiometry?
- 10.* Explain with a set of mathematical equations how the fixed interference method can be used to determine the selectivity coefficient as shown in Eq. [13], i.e., derive Eq. [13].
- 11.* Derive Eq. [26].
12. Compare your K_{sp} values with cited K_{sp} values. Assuming your K_{sp} value equals IAP, calculate the SI for each mineral. Discuss how the SI values differ from what you would expect at equilibrium.
- 13.* The CaCO_3 used in the experiment was dissolved in water in a closed system. Why would Eq. [23] not be valid for determining the K_{sp} of CaCO_3 dissolved in an open system? In an open system, would Eq. [23] calculate a value for K_{sp} that would be greater than or less than the actual K_{sp} for CaCO_3 ?

- 14.* If an organic acid, such as citric acid, was present in the solution phase of the systems containing CaF_2 and CaCO_3 , why would Eq. [23] and [26] not be valid for determining the K_{sp} for these minerals? Would the calculated K_{sp} be greater than or less than the actual K_{sp} for these minerals.
15. Suggest how this experiment might be improved.

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