Solubility of $CaSO_4$
Experiment 8

Major Concepts and Learning Goals

- Application of the solubility product constant (K_{sp})
- Saturated solutions
- Le Chatlier's Principle/Common ion effect
- Activities and activity coefficients
- Ion selective electrodes
- Calibration curves

Laboratory Task

- Produce a calibration curve using standard solutions of $CaNO_3$
- Measure the $[Ca^{2+}]$ of three different solutions
    1) a saturated solution of $CaSO_4$ in H_2O
    2) a saturated solution of $CaSO_4$ in 0.10 M KNO_3
    3) a saturated solution of $CaSO_4$ in 0.10 M Na_2SO_4
- Observe the effect of ionic strength on the $[Ca^{2+}]$ by comparing the results of solution 1 and 2.
- Observe the effect of the Na_2SO_4 on the $[Ca^{2+}]$ (common ion effect).

Introduction

The solubility of $CaSO_4$ at 25 ºC is described by the following reaction and equilibrium

$$CaSO_{4(s)} \leftrightarrow Ca^{2+} + SO_4^{2-}$$

$$K_{sp(CaSO4)} = [Ca^{2+}][SO_4^{2-}] = 2.4\cdot10^{-5} \qquad \text{eq. 1}$$

In words, this equilibrium expression implies that the product of the calcium ion concentration and the sulfate ion concentration can be no larger than $2.4\cdot10^{-5}$ in any aqueous solution.

Saturated solutions

Any aqueous solution in which the product of the calcium ion concentration and the sulfate ion concentration is about $2.4\cdot10^{-5}$ is said to be a saturated $CaSO_4$ solution.
If a little more Ca^{2+} or SO_4^{2-} is added to a saturated $CaSO_4$ solution the equilibrium will shift to the left to form solid $CaSO_4$ and the value of the product of the calcium ion

concentration and the sulfate ion concentration would be restored to about $2.4\cdot10^{-5}$. This statement is the basis of Le Chatlier's Principle.

> *When an equilibrium position of a reaction is disturbed, a new equilibrium position will be established by shifting the reaction in a direction that alleviates the stress caused by the disturbance*

Saturated solutions can be prepared by a variety of methods. In this experiment the first saturated solution has been prepared by adding solid $CaSO_4$ to purified water (the water comes from a purification system that includes a carbon filter, an ion-exchange resin and a UV lamp). The solution was mixed for several days and allowed to settle and reach equilibrium for several weeks. Then the solution was filtered to remove any suspended $CaSO_4$ particles that did not dissolve or settle to the bottom. Because the only source of the calcium ions and sulfate ions come from the dissolution of $CaSO_4$, $[Ca^{2+}] = [SO_4^{2-}]$. In fact, the same statement can also be made for the second saturated solution, since KNO_3 is not a source of Ca^{2+} or SO_4^{2-}.
When we ignore the impact of ionic strength, the $[Ca^{2+}]$ and $[SO_4^{2-}]$ concentrations of these first two saturated solutions are expected to be about $5.0\cdot10^{-3}$ M, based on the literature K_{sp} value for $CaSO_4$ $\{(2.4\cdot10^{-5})^{1/2}\}$.

Le Chatlier's Principle and the Common Ion Effect

One general case in which Le Chatlier's principle can be applied is when the solution contains a soluble salt of an ion that is in common with the insoluble salt in question. This is the case in the third saturated solution; $CaSO_4$ in dissolved 0.10 M Na_2SO_4. In this solution there are two sources of the sulfate ion; the Na_2SO_4 and the $CaSO_4$. The SO_4^{2-} coming from the Na_2SO_4 is 0.10 M, because Na_2SO_4 is a completely soluble salt. The sulfate ion coming from the $CaSO_4$ is equal to the calcium ion concentration.

Thus,

$$K_{sp} = [Ca^{2+}]\,([SO_4^{2-}]_{CaSO4+} + [SO_4^{2-}]_{Na2SO4}) = 2.4\cdot10^{-5}$$

Letting $[Ca^{2+}] = x$, we arrive at

$$K_{sp} = x\,(x + 0.10) = 2.4\cdot10^{-5}$$

If we assume $x <<< 0.10$ M, then

$$K_{sp} = x\ 0.10 = 2.4\cdot10^{-5} \text{ and } [Ca^{2+}] = 2.4\cdot10^{-4}\text{ M},$$

This is considerably lower than the first saturated solution. It is also worth pointing out that our solution to the problem verifies that our stated assumption was valid.

This lowering of the $[Ca^{2+}]$ is due to the common ion effect.

Activities and Activity Coefficients

In reality, equilibria are affected by the concentration of ions, any ions, in solution. The ionic strength (μ) is used as a measure of the total ion concentration of a solution. It is calculated by incorporating each of the "i" ionic species in solution into the following equation, where C is the concentration in mol/L and Z is the charge on the ion.

$$\mu = \frac{1}{2} \sum (C_i Z_i^2)$$

So, why does the ionic strength matter? Well let's look at the $CaSO_4$ equilibrium as an example. The ionic strengths of the saturated solution 2 and 3 are considerably greater than that of saturated solution 1.

> Initial estimates of the ionic strength of these three saturated solutions (these are initial estimates because the concentrations of $[Ca^{2+}]$ and $[SO_4^{2-}]$ were determined ignoring the impact of ionic strength)
>
> Saturated solution 1
>
> $$\mu = \frac{1}{2} ([Ca^{2+}](2)^2 + [SO_4^{2-}](-2)^2))$$
> $$\mu = \frac{1}{2} (5\cdot10^{-3}(2)^2 + 5.0\cdot10^{-3}(-2)^2)) = 0.02 \text{ M}$$
>
> Saturated solution 2
>
> $$\mu = \frac{1}{2} ([K^+](1)^2 + [NO_3^-](-1)^2 + [Ca^{2+}](2)^2 + [SO_4^{2-}](-2)^2))$$
> $$\mu = \frac{1}{2} (0.1(1)^2 + 0.1(-1)^2 + 5\cdot10^{-3}(2)^2 + 5.0\cdot10^{-3}(2)^2)) = 0.12 \text{ M}$$
>
> Saturated solution 3
>
> $$\mu = \frac{1}{2} ([Na^+](1)^2 + [SO_4^{2-}](-2)^2) + [Ca^{2+}](2)^2)$$
> $$\mu = \frac{1}{2} (0.2(1)^2 + 0.1(-2)^2 + 2.4\cdot10^{-4}(2)^2) = 0.20 \text{ M}$$

Electrostatic interactions between the negative ions and the Ca^{2+} ions in solution cause the formation of an ion cloud around the Ca^{2+} ions. The larger the ionic strength of the solution the greater the radius of this ion cloud. A similar ion cloud forms around the SO_4^{2-} ions from the positive ions in solution. The size of the ion clouds about Ca^{2+} and SO_4^{2-} defines the energetics associated with these ions finding each other in solution and forming $CaSO_{4(s)}$. Thus, the $[Ca^{2+}]$ and the $[SO_4^{2-}]$ in the second saturated solution would be expected to be significantly greater than $5.0\cdot10^{-3}$ M, and in the third saturated solution the $[Ca^{2+}]$ would be expected to be greater than $2.4\cdot10^{-4}$ M.

Mathematically, the impact of ionic strength is accounted for by introducing the concept of ion activity, $\mathcal{A}$. The activity of an ion can be thought of as its effective concentration and is given by product of its concentration and activity coefficient, γ. The activity coefficient depends upon the size of the ion, its charge, and the ionic strength of the solution. For example:

$$\mathcal{A}_{Ca2+} = [Ca^{2+}]\, \gamma_{Ca+}$$

The activity coefficient can be calculated using the Debye-Huckle equation.

The most important concept to appreciate in terms of activities is that the definition of the equilibrium expression that we first learned and used (eq. 1) is only a model. It works very well at low ionic strengths, where the activity coefficients are close to unity, but breaks down at higher ionic strengths. The more universal model expresses the equilibrium constants in terms of activities.

Equation 1 becomes

$$K_{sp(CaSO4)} = \mathcal{A}_{Ca2+}\mathcal{A}_{SO42-} = [Ca^{2+}]\gamma_{Ca2+}[SO_4^{2-}]\gamma_{SO42-} = 2.4\cdot10^{-5} \qquad \text{eq. 2}$$

γ_{Ca2+} and γ_{SO42-} for solution 2 are less than for solution 1 because the ionic strength of solution 2 is greater than the ionic strength of solution 1, and as a result $[Ca^{2+}]$ and $[SO_4^{2-}]$ must be larger in solution 2 for both solutions to satisfy the K_{sp} expression. However, it is important to appreciate that the ionic strength of solution 1 is large enough to have an impact on the solubility. So, even for this solution, it is expected that the solubility will be significantly larger than the 5.0 mM predicted above.

Ion- Selective Electrodes

Ion-selective electrodes are electrochemical cells that have been carefully crafted into a probe that is useful for measuring the activity of a specific ion in solution. An ion-selective electrode most often consists of two reference electrodes, which give a constant potential. The two reference electrodes are electrically linked via a voltmeter and a salt bridge through the solution being measured. The salt bridge consists of a membrane between the solution being measured and the inner reference electrode solution. This membrane is made of a unique material that preferentially allows the ion of interest to partially penetrate the membrane. This partial penetration leads to the development of a junction potential, the magnitude of which depends entirely on the activity of the ion in the solution being measured. The Ca^{2+} selective electrode used in this application contains a membrane that preferentially chelates Ca^{2+}. The potential measured by the voltmeter depends upon the potential at each of the reference electrodes and the junction potential. The potential of the reference electrodes is constant and junction potential is only influenced by the activity of the Ca^{2+} in the solution being measure.

$$E_{cell} = \text{constant} + 59.16/2 \log \mathcal{A}_{Ca2+} = \text{constant} + 59.16/2 \log [Ca^{2+}]\gamma_{Ca2+}$$

Typically, one would measure the voltage of several standard Ca^{2+} solutions in the range of $0.1\text{-}10^{-6}$ M Ca^{2+} at a constant ionic strength. To measure the concentration of $[Ca^{2+}]$, the usual procedure is to measure the potentials of the standard solutions with a Ca^{2+} selective electrode and use the data to produce a calibration plot. To make the analysis of the data straightforward and simple all of the standards and samples are prepared using an electrolyte of high ionic strength. As a result, all of the solutions have the same ionic strength and, as a result, the activity coefficient becomes a constant.

Applying the rule of logs $\log AB = \log A + \log B$

$$E_{cell} = \text{constant} + 59.16/2 \log [Ca^{2+}]\gamma_{Ca2+}$$

Becomes

$$E_{cell} = \text{constant} + 59.16/2 \log [Ca^{2+}] + 59.16/2 \log \gamma_{Ca2+}$$

$$E_{cell} = \text{constant}_1 + 59.16/2 \log [Ca^{2+}] + \text{constant}_2$$

Combining constants

$$E_{cell} = \text{constant} + 59.16/2 \log [Ca^{2+}]$$

Then, a calibration plot is produced by plotting the cell potential as a function of the log $[Ca^{2+}]$.

Then, your samples are prepared by diluting it quantitatively with the same electrolyte. This ensures that the ionic strength of your sample solutions match that of your standards.

Experimental Note:
In this experiment once you dilute the saturated solutions, they will no longer be saturated. Since all of the left over $CaSO_4$ will be removed by filtration, the $[Ca^{2+}]$ in each of the samples is reduced by a known dilution factor, which will be taken into account during your calculations.

In the Lab
Work in pairs. Several of these steps can be performed simultaneously, which will allow us to complete this lab within the allotted time. I have assigned the tasks to student A and B.

1. Use a syringe filter to filter approximately 4 or 5 mL of the each of the three saturated solutions in to three clean, dry and labeled 20 mL screw top bottles. (Student A)

2. Obtain about 600 mL of 0.5 M KNO_3 in a clean beaker. Rinse your 25 mL pipet at least four times with the DI water and once with 0.5 M KNO_3. Add 25 mL of 0.5 M KNO_3 to each of twelve clean, dry Erlenmeyer flasks. Label them std 1-6 and test 1-6. (Student B)

3. Obtain about 40 mL of the 0.100 M $Ca(NO_3)_2$ master standard in a clean, dry beaker and label it. Pipet 25 mL of the 0.100 M $Ca(NO_3)_2$ standard into a clean, dry 100 mL volumetric flask and dilute to the mark with 0.50 M KNO_3. Place the cap on and mix thoroughly by inverting the flask back and forth about 20 times. Pour the contents into a clean and dry beaker. Label this solution 0.0250 M $Ca(NO_3)_2$. Immediately, rinse your 25 mL pipet at least four times with the de-ionized water. (Student A)

   Preparation of the six standards

4. Use the micropipeter to pipet, 1.000 mL of the 0.100 M $Ca((NO_3)_2$ master standard into the flask labeled standard 1 and 0.500 mL of the 0.100 M $Ca((NO_3)_2$ master standard into the flask labeled standard 2. Swirl each flask to mix thoroughly. (STUDENT B)

5. Switch tips. Use the micropipeter to pipet 1.000 mL of the 0.0250 M $Ca((NO_3)_2$ standard into the flask labeled standard 3 and 0.500 mL of the 0.0250 M $Ca((NO_3)_2$ standard into the flask labeled standard 4. Swirl each flask to mix thoroughly. (STUDENT B)

6. Switch tips. Use the micropipeter to pipet 2.000 mL of the standard 1 into the flask labeled standard 5 (use the 1 mL micropipeter twice) and 1.000 mL of standard 1 into the flask labeled standard 6. Swirl each flask to mix thoroughly. (STUDENT A)

Preparation of the six test samples

7. Switch tips. Use the micropipeter to pipet 2.000 mL of the *filtered solution* of saturated $CaSO_4$ in DI water into the flask labeled “TEST 1” (use the 1 mL micropipeter twice) and 1.000 mL of the filtered solution of saturated $CaSO_4$ in DI water into the flask labeled “TEST 2”. (STUDENT A)

8. Switch tips. Use the micropipeter to pipet 2.000 mL of the *filtered solution* of saturated $CaSO_4$ in 0.10 M KNO_3 into the flask labeled “TEST 3” (use the 1 mL micropipeter twice) and 1.000 mL of the filtered solution of saturated $CaSO_4$ in 0.10 M KNO_3 into the flask labeled “TEST 4”. (STUDENT B)

9. Switch tips. Use the micropipeter to pipet 2.000 mL of the *filtered solution* of saturated $CaSO_4$ in 0.10 M Na_2SO_4 into the flask labeled “TEST 5” (use the 1 mL micropipeter twice) and 1.000 mL of the filtered solution of saturated $CaSO_4$ in 0.10 M Na_2SO_4 into the flask labeled “TEST 6”. (STUDENT B)

Summary Tables of Solution Preparation

Standards (Calculate the [Ca$^{2+]}$ for these standards and show work to instructor prior to leaving lab)

solution	0.25 M KNO_3	0.100 M Ca^{2+}	0.0250 M Ca^{2+}	std 1	[Ca^{2+}]
0.0250 M	75.00	25.00	0.000	0.000	
std 1	25.00	1.000	0.000	0.000	
std 2	25.00	0.500	0.000	0.000	
std 3	25.00	0.000	1.000	0.000	
std 4	25.00	0.000	0.500	0.000	
std 5	25.00	0.000	0.000	2.000	
std 6	25.00	0.000	0.000	1.000	

Test solutions of diluted saturated solutions

solution	0.25 M KNO_3	$(CaSO_4)_{\text{sat. in H2O}}$	$(CaSO_4)_{\text{sat. in KNO3}}$	$(CaSO_4)_{\text{sat. in Na2SO4}}$
test 1	25.00	2.000	0.000	0.000
test 2	25.00	1.000	0.000	0.000
test 3	25.00	0.000	2.000	0.000
test 4	25.00	0.000	1.000	0.000
test 5	25.00	0.000	0.000	2.000
test 6	25.00	0.000	0.000	1.000

10. Get help from one of your instructors to set up the apparatus. Measure the cell voltages of each of the six standards and the six test solutions. To make the measurement you will have to transfer 15-20 mL of each solution into the 20 mL screw cap bottle. This is necessary to ensure that the salt bridge of the Ca-ion selective electrode is submersed when making the measurements. When switching between samples, thoroughly rinse the 20 mL screw cap bottle with several portion of DI water and then with a couple of milliliters of the test solution. Record all data on the Lab Pro Software and copy and paste the data into an Excel spread sheet. Give each solution at least 3 minutes to equilibrate with the ion-selective membrane prior to taking a reading.

Lab Report

Data

Use the template to do the following calculations:

1. Calculate the [Ca^{2+}] of your six standards. (5 pts)
2. Plot the log[Ca^{2+}] vs. the voltage readings from the Ca-ion selective electrode. (10 pts)
3. Use the Analysis Tools function to obtain the regression parameters and statistics. (5 pts)
4. Using the regression parameters to determine the [Ca^{2+}] of the six diluted test samples that were measured. Determine the uncertainty in these measurements using the regression statistical analysis outline in the "Introduction to Statistics". This particular analysis is complicated by the logarithm. The Linear Regression statistical analysis (the ugly S_y/m equation) provides the uncertainty in the log[Ca^{2+}]. You need to apply the rule for propagating uncertainty for logarithmic functions ($s_{Ca2+} = S_{log[Ca2+]}[Ca^{2+}]$) (10 pts)
5. Use the dilution factors to determine the [Ca^{2+}] in the three saturated solutions. You will have two independent measurements for each. Propagate all uncertainties. Report the average of the two results. (10 pts)
6. Based on the [Ca^{2+}] you found for the saturated solution in DI water, estimate the product of the activity coefficients of Ca^{2+} and SO_4^{2-} in this solution ($\gamma_{Ca2+}\gamma_{SO42-}$). (5 pts)
7. Using the [Ca^{2+}] you found for the saturated solution in DI water, calculate the ionic strength of the solution and use the extended Debye-Huckle equation Harris in the Activities chapter) to calculate the γ_{Ca2+} and γ_{SO42-}. (5 pts)

$$\log \gamma = -0.51z^2\mu^{1/2}/[1+(\alpha\mu^{1/2}/305)]$$

Points to address in the context of your discussion:

1. Were the two independent measurements for each saturated solution in agreement? Calculate the differences between two independent measurements for each of the three saturated solutions. (5 pts)
2. Are the solubilities of $CaSO_4$ in these three different solutions significantly different? *Compare* and *rationalize* the relative magnitudes of the [Ca^{2+}] in the three saturated $CaSO_4$ solutions. (5 pts)
3. Does the ionic strength of the solution of saturated $CaSO_4$ in de-ionized water have a significant impact on its solubility? In other words how does the solubility of $CaSO_4$ in de-ionized water compare to the prediction in the write-up above from K_{sp}? How well does the product of the activity coefficients calculated in #6 above match the activity coefficients estimated from the extended Debye-Huckle Equation in #7? (5 pts)
4. The solubility of $CaSO_4$ is actually more complicated than what has been considered in this experiment because there are some complex ion issues (see section 8-5 in your Harris textbook). Discuss how this complicates the interpretation of the results in this experiment. (5 pts)
5. Is the common ion effect evident in the data for the [Ca^{2+}] of the saturated $CaSO_4$ solution in 0.1 M Na_2SO_4? Explain your answer. (5 pts)