Solubility of $CaSO_4$
Experiment 2

Major Concepts and Learning Goals

- Application of the solubility product constant (Ksp)
- 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

$$CaSO_4(s) \leftrightarrow Ca^{2+} + SO_4^{2-}$$

$$Ksp(CaSO_4) = [Ca^{2+}][SO_4^{2-}] = 2.4\cdot10^{-5} \qquad \text{eq. 1}$$

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-}.
Based on the literature Ksp value for $CaSO_4$, of the $[Ca^{2+}]$ and $[SO_4^{2-}]$ concentrations of these first two saturated solutions are expected to be about $(2.4\cdot10^{-5})^{1/2} = 5.0\cdot10^{-3}$ M.

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,

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

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

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

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

$Ksp = x\ 0.10 = 2.4\cdot10^{-5}$ and $[Ca^{2+}] = 2.4\cdot10^{-4}$ 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 is lowering of the $[Ca^{2+}]$ is said to be 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 to the following equation.

$$\mu = ½ \sum(C_iZ_i^2)$$

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.

Saturated solution 1

$$\mu = ½ ([Ca^{2+}](2)^2 + [SO_4^{2-}](-2)^2))$$
$$\mu = ½ (5\cdot10^{-3}(2)^2 + 5.0\cdot10^{-3}(-2)^2)) = 0.02 \text{ M}$$

Saturated solution 2

$$\mu = ½ ([K^+](1)^2 + [NO_3^-](-1)^2 + [Ca^{2+}](2)^2 + [SO_4^{2-}](-2)^2))$$
$$\mu = ½ (0.1(1)^2 + 0.1(-1)^2 + 5\cdot10^{-3}(2)^2 + 5.0\cdot10^{-3}(2)^2)) = 0.12 \text{ M}$$

Saturated solution 3

$$\mu = ½ ([Na^+](1)^2 + [SO_4^{2-}](-2)^2) + [Ca^{2+}](2)^2)$$
$$\mu = ½ (0.2(1)^2 + 0.1(-2)^2 + 2.4\cdot10^{-4}(2)^2) = 0.20 \text{ M}$$

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 product of the $[Ca^{2+}]$ and the $[SO_4^{2-}]$ in the second saturated solution would be expected to be 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 and $[SO_4^{2-}]$ would be expected to be greater than 0.10 M.

Mathematically, the effect 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 activities. The more universal model expresses the equilibrium constants in terms of activities.

Equation 1 becomes

$$K_{sp(CaSO4)} = \mathcal{A}_{Ca2+}\mathcal{A}_{SO42-} = [Ca^{2+}]\gamma_{Ca2+}[SO_4^{2-}]\gamma_{SO42-} = 2.4\cdot 10^{-5} \qquad \text{eq. 2}$$

γ_{Ca2+} and γ_{SO42-} for solution 2 are much less than for 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.

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 uses 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 Ca2+ 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 the activity coefficient becomes a constant.

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

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

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 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 $CaSO_4$ was removed by prior filtration, the $[Ca^{2+}]$ in each of the samples is reduced by a known dilution factor, which will be taken into account during the calculations.

In the Lab

1. Using 0.500 M KNO_3 as the solvent, make serial dilutions of the 0.100 M $Ca(NO_3)_2$ solution using a 10 mL and a 100 mL volumetric flask. You should end up with solutions at the following concentrations; 0.0100 M, $1.00 \cdot 10^{-3}$ M, and $1.00 \cdot 10^{-4}$ M.
2. Similarly, dilute each of the saturated $CaSO_4$ solutions by a factor of ten with 0.500 M KNO_3.
3. Get help from one of your instructors to set up the apparatus. Measure the cell voltages of each of the five standards and the three samples saturated $CaSO_4$ solutions. Record all data on the Lab Pro Software and copy and paste the data into an Excel spread sheet.

Lab Report

Open the Excel file named "CASO4". In the "standard curve" worksheet enter the E_{cell} readings. Be sure that the cells where the data are inputted correspond to the correct concentration of the standard. The graph will show the calibration plot (mV vs log $\mathcal{A}_{Ca2+}$) for your Ca^{2+} ion selective electrode. The slope and intercept of the plot will automatically be calculated and used to determine the $[Ca^{2+}]$ of your three original (prior to dilution) $CaSO_4$ solutions. You should carefully examine your spreadsheets so you understand all the calculations that are performed.

Questions:

1. Compare and rationalize the relative magnitudes of the [Ca^{2+}] in the three saturated $CaSO_4$ solutions.

2. Does the common ion effect or the ion activity have the largest influence on the [Ca^{2+}] of the saturated $CaSO_4$ solution in 0.1 M Na_2SO_4 given that Ksp = $2.4 \cdot 10^{-5}$?