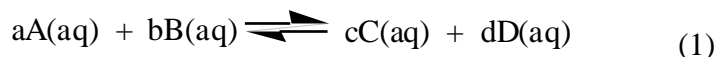# EXPERIMENT 6

## Determination of the Solubility Product Constant for Calcium Sulfate: The Effect of Ionic Strengths of Electrolyte Solutions

INTRODUCTION:
The equilibrium constant for a generalized chemical reaction,

$$aA(aq) \; + \; bB(aq) \rightleftharpoons \; cC(aq) \; + \; dD(aq) \qquad (1)$$

is defined as

$$K \; = \; \frac{a_C^c a_D^d}{a_A^a a_B^b} \qquad (2)$$

where the dimensionless quantity $a$ is the activity of a given chemical species involved in the equilibrium. The activity of a species in a mixture is related to the molar concentration of that species through

$$a = fM \qquad (3)$$

where f is the activity coefficient ($0 < f \leq 1$) and M is the molarity of that species. A fairly good approximation is to let $f = 1$ and thus let the values of the activities be the same as the values of the molar concentrations, which leads to the more familiar

$$K \; = \; \frac{[C]^c [D]^d}{[A]^a [B]^b} \qquad (4)$$

The equilibrium constant is a thermodynamic quantity which is related to the standard Gibbs free energy change by

$$\Delta G^o = -RT\ln K \qquad (5)$$

where T is the Kelvin temperature and $R = 8.314 \; J/mol \bullet K$.

For the dissociation of an insoluble salt the equilibrium constant is the solubility product, $K_{sp}$. Consider calcium sulfate, which is moderately insoluble. Its solubility equilibrium is

$$CaSO_4(s) \rightleftharpoons \; Ca^{2+}(aq) \; + \; SO_4^{2-}(aq) \qquad (6)$$
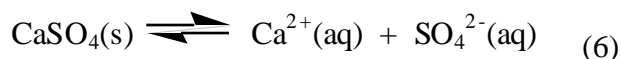
The solubility product $K_{sp}$ is given by

$$K_{sp} = a_{Ca^{2+}} a_{SO_4^{2-}} \qquad (7)$$

where

$$\Delta G^o = -RT\ln K_{sp} \qquad (8)$$

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If the concentrations of the ions are sufficiently low, then a fairly good approximation for the solubility product is

$$K_{sp} = [Ca^{2+}][SO_4^{2-}] \qquad (9)$$

In equation (9) the molar concentrations of each species are assumed to be approximately the same value as their respective activities. However, because any aqueous heterogeneous equilibrium involving salts results in a mixture of electrically charged particles (the cations and anions), there are Coulombic forces of interaction between the ions. Because Coulombic forces are short-range forces, they are less important at lower concentrations. Thus, the less soluble the salt is, the less important the Coulombic forces are. Thus, if the concentrations of ions in the saturated calcium sulfate solution are sufficiently small, then equation (9) is a fairly good approximation. However, if the concentrations of ions are sufficiently large, then small ion clusters can form (see the figure below) which effectively reduces the number of free ionic particles in solution.
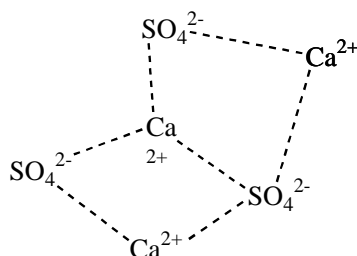


Representation of attractions between calcium and sulfate ions. Note that repulsive interactions also exist, but are not illustrated here.

This gives activities which are actually less than the molar concentrations of the ions. (This is analogous to the effect of intermolecular forces on pressure that is observed in real gases.) Therefore, it is often necessary to determine the activities of the ions in solution in order to experimentally determine $K_{sp}$. Thus, one needs a way to determine the activity coefficient, $f$.

The Debye-Huckel limiting law provides a method for calculating the activity coefficient of an ion in solution. This relationship takes into account the ionic charges and ionic radii of all ions in the solution. We will use a simplified version which only considers the ionic charges. The activity coefficient is thus given by

$$\log_{10} f = -0.510 Z^2 \sqrt{\mu} \qquad (10)$$

where $f$ = the activity coefficient of an ion; Z = the charge of that ion; $\mu$ = the ionic strength, a measure of the concentration of all ions in solution.

The ionic strength $\mu$ is calculated by

$$\mu = 0.5(M_1 Z_1^2 + M_2 Z_2^2 + M_3 Z_3^2 + ...) \qquad (11)$$

where $M_1$ is the molarity of the first ion with charge $Z_1$, etc. An example of calculating the the ionic strength and activity coefficient is presented below.

*Example:* For a 0.0010 M $MgCl_2$ solution, calculate the molarity of all of the ions, the ionic strength, the activity coefficient for each ion, and the activity of each ion.
<u>Molarities:</u> Since 1 mol $Mg^{2+}$ = 1 mol $MgCl_2$, and 2 mol $Cl^-$ = 1 mol $MgCl_2$,
$[Mg^{2+}]$ = .0010 M, and $[Cl^-]$ = .0020 M.
Now, to calculate the ionic strength, m, remember that for magnesium ion Z = +2 and for chloride ion Z = -1. From equation (11), the ionic strength of all of the ions in solution is

$$\mu = 0.5([Mg^{2+}](+2)^2 + [Cl^-](-1)^2)$$
$$= 0.5((.0010)(4) + (.0020)(1))$$
$$= \underline{0.0030}$$

Next, calculate the activity coefficient using equation (10):

$$\log_{10} f(Mg^{2+}) = -0.510(+2)^2\sqrt{0.003} = -0.112$$
Thus $f(Mg^{2+}) = 10^{-0.112} = 0.773$
A similar calculation for chloride ion gives $f(Cl^-) = 0.94$.

Finally, the activities are calculated according to equation (3):

$$a(Mg^{2+}) = (0.773)(0.0010) = 0.00077$$

and

$$a(Cl^-) = (0.94)(0.0020) = 0.0019$$

In this experiment, you will determine the $K_{sp}$ for calcium sulfate, $CaSO_4$. To determine the concentration of calcium ion present in the saturated calcium sulfate solution you will titrate with diprotic EDTA, $H_2(EDTA)^{2-}$ (see your text for the structure of the completely deprotonated ethylenediaminetetraacetate ion). EDTA is a very effective chelating agent (from the Greek chelos = claw) which is often used as a therapeutic agent for removing toxic metal ions, such as $Pb^{2+}$ and $Hg^{2+}$, from the body. It is also a common ingredient in shampoos used for chelating calcium ion found in hard water. The reaction with calcium is

$$Ca^{2+}(aq) + H_2(EDTA)^{2-} \rightarrow CaEDTA^{2-} + 2 H^+(aq) \tag{12}$$

Given the stoichiometries of equations (6) and (12) it is straightforward to determine the moles of $Ca^{2+}$ and $SO_4^{2-}$ in your 25.00 mL aliquot of the saturated calcium sulfate solution. From this and the fact that you know that the volume of each sample of solution analyzed is 25.00 mL you can determine $[Ca^{2+}]$ and $[SO_4^{2-}]$. Then you can use the Debye_Huckel limiting law to determine the activity coefficients and activities of the calcium ion and sulfate ion, and thus the solubility product for calcium sulfate.

**OBJECTIVES:**
  **(1) Calculate the $K_{sp}$ for calcium sulfate experimentally and compare it to the literature value.**
  **(2) Determine if $K_{sp}$ or $Q_{sp}$ is being measured by comparing a saturated solution prepared days ago to a freshly made sample.**
  **(3) Determine which of the possible calcium sulfate solids were used to prepare the saturated solutions.**

**Literature $K_{sp}$ Values for calcium sulfate**

| Calcium sulfate anhydrous | $CaSO_4$ | $4.93 \times 10^{-5}$ |
|---|---|---|
| Calcium sulfate dihydrate | $CaSO_4 \bullet 2H_2O$ | $3.14 \times 10^{-5}$ |
| Calcium sulfate hemihydrate | $CaSO_4 \bullet 0.5H_2O$ | $3.10 \times 10^{-7}$ |

**PROCEDURE:**

*1. Preparation of the saturated calcium sulfate solution:*
Prepare a saturated calcium sulfate solution by adding approximately 1 g of calcium sulfate to about 250 mL deionized water in a 400 mL beaker. ***This experiment will be performed only at room temperature.***

*2. Titration of freshly made solutions with standardized EDTA:*
Stir the solution. Withdraw 25.00 mL of the solution with a 25.00 mL volumetric pipette. Obtain filter paper from your instructor and <u>filter</u> the aliquot of solution into clean 125-mL Erlenmeyer flask. No solid calcium sulfate should be in your flask at this point. (Think about why.) To your flask add 10 mL of the ammonia buffer (pH = 10) and 3 to 4 drops of eriochrome black 1 indicator. Fill your burette with the 0.015 M EDTA solution, which is standardized to three significant figures. Do not forget to write this molarity of the EDTA solution in your notebook! Titrate with constant swirling until the endpoint, when the red color turns <u>completely</u> to blue. There should be no hint of red. Be sure to periodically rinse the sides of your flask with your wash bottle during the course of your titration. Repeat the experiment until you have two reproducible titration trials.

*3. Titration of previously prepared solutions with standardized EDTA:*
In the hood, measure out about 60 mL of saturated calcium sulfate solution into a beaker and return to your workstation. Withdraw 25.00 mL of the solution with a 25.00 mL volumetric pipette. Obtain filter paper from your instructor and <u>filter</u> the aliquot of solution into clean 125-mL Erlenmeyer flask. No solid calcium sulfate should be in your flask at this point. (Think about why.) To your flask add 10 mL of the ammonia buffer (pH = 10) and 3 to 4 drops of eriochrome black 1 indicator. Fill your burette with the 0.015 M EDTA solution, which is standardized to three significant figures. Do not forget to write this molarity of the EDTA solution in your notebook! As before, titrate with constant swirling until the endpoint, when the red color turns <u>completely</u> to blue. Repeat this experiment until you have two reproducible titration trials.

DATA ANALYSIS:

1. *Experimental $K_{sp}$ from molarities at room temperature*:   For your data at <u>your room temperature</u> (which should be close to 25 °C) use the experimentally determined molarities of $Ca^{2+}$ and $SO_4^{2-}$ to calculate $K_{sp}$.

2. *Experimental $K_{sp}$ from activities at room temperature*:  Convert your molarities to activities as described in this handout and recalculate $K_{sp}$ using the activities.

3. *Literature value of $\Delta G^o$ and $K_{sp}$ at room temperature:*  Use the appropriate enthalpies and entropies in Appendix B of your text to calculate $\Delta G^o$ at room temperature.  Use this $\Delta G^o$ to calculate $K_{sp}$ at this temperature.  This will be your calculated "*literature*" value for $\Delta G^o$ and $K_{sp}$ for the dissociation of calcium sulfate in water at room temperature.  Next look up the "true" literature value for the $K_{sp}$ of calcium sulfate in the latest CRC Handbook of Physics and Chemistry, internet, or use the table provided.

4. *Comparison of methods:*  Compare your experimental $K_{sp}$ values that you determined using molarities and activities to the literature values.  Determine if it is better to calculate $K_{sp}$ with activities or uncorrected molarities.  The method that gives you values closest to the literature values should be the best method.  Which calcium sulfate solid was used? Were you measuring $K_{sp}$ or $Q_{sp}$ with the freshly made solutions?  In your report discuss any differences and their sources and comment on the validity of the Debye-Huckel limiting law.  Calculate the percent error between your experimental $K_{sp}$ and the literature value of the $K_{sp}$ at your temperature.  Use your "better" Ksp value to calculate $\Delta G^o$ for the dissociation of calcium sulfate, compare to the literature value and report the percent error.