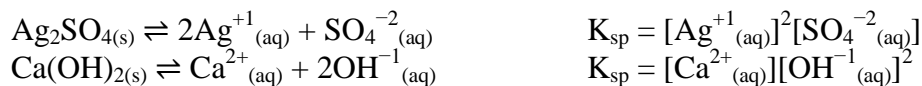**Experiment 22: Molar Solubility (Part A) and Common Ion Effect (Part B)**

Background Information

A saturated solution of a salt with limited solubility has a reversible reaction and an equilibrium constant expression. The equilibrium constant (K_{sp}) is called the **solubility product**.

$$Ag_2SO_{4(s)} \rightleftharpoons 2Ag^{+1}{}_{(aq)} + SO_4{}^{-2}{}_{(aq)} \qquad K_{sp} = [Ag^{+1}{}_{(aq)}]^2[SO_4{}^{-2}{}_{(aq)}]$$
$$Ca(OH)_{2(s)} \rightleftharpoons Ca^{2+}{}_{(aq)} + 2OH^{-1}{}_{(aq)} \qquad K_{sp} = [Ca^{2+}{}_{(aq)}][OH^{-1}{}_{(aq)}]^2$$

The aqueous concentration of an aqueous *compound* (not its individual ions) is called the **molar solubility**. If there is only one of an ion in the compound's formula unit, the ion's concentration is the same as the molar solubility. Otherwise, the ion's concentration is a multiple of the molar solubility.

$$molsol = [Ag_2SO_{4(aq)}] = [SO_4{}^{-2}{}_{(aq)}] = (\tfrac{1}{2}) [Ag^{+1}{}_{(aq)}]$$
$$molsol = [Ca(OH)_{2(aq)}] = [Ca^{+2}{}_{(aq)}] = (\tfrac{1}{2})[OH^{-1}{}_{(aq)}]$$

$[OH^{-1}{}_{(aq)}]$ is easy to determine with a titration against $[H_3O^{+1}{}_{(aq)}]$, and is twice the $[Ca(OH)_{2(aq)}]$ molar solubility, as seen in the equation above. Substituting the same molar solubility value for $[Ca^{+2}{}_{(aq)}]$ creates a simple equation for the solubility product.

$$K_{sp} = [Ca^{+2}{}_{(aq)}][OH^{-1}{}_{(aq)}]^2 = (\tfrac{1}{2}) [OH^{-1}{}_{(aq)}][OH^{-1}{}_{(aq)}]^2 = (\tfrac{1}{2})[OH^{-1}{}_{(aq)}]^3$$

If $[Ca^{2+}{}_{(aq)}]$ is increased by adding $CaCl_2$, then LeChatelier's principle tells us that the equilibrium will shift to the left. This equilibrium shift is called the **common ion effect**. Now $[Ca^{2+}{}_{(aq)}]$ is no longer the same as the molsol, $[Ca(OH)_{2(aq)}]$, or $(\tfrac{1}{2})[OH^{-1}{}_{(aq)}]$. Also, $[Ca^{+2}{}_{(aq)}]$ can be large enough that the shift is negligible in comparison to the amount from the added $CaCl_2$. Therefore, we would not calculate K_{sp} without knowing $[Ca^{+2}{}_{(aq)}]$, the concentration of the added common ion. However, molar solubility can still be determined with a titration because it can still be calculated as $molsol = (\tfrac{1}{2})[OH^{-1}]$. As a result, we can experimentally determine the effect of the common ion on the molar solubility, as predicted by LeChatelier's principle.

Review the Common Ion Effect section in the Ch 16 class notes also.

Procedure Notes

1. Skip steps 1 and 2 of part A, and step 1 of part B.
   Use a beaker to obtain 100 ml of the $Ca(OH)_2$ sample solution from the supply bench.
   Pipet a 25-ml sample from the beaker to the flask for each of the three trials.
2. Read Laboratory Technique 16 (Measuring Volume) in the front portion of your lab manual.
   This will provide you with important instructions on how to record a volume,
   pipette a liquid, and perform a titration.
3. Skip the standard deviations on your report sheet.

Pre-Lab Hints

1. a) Molar solubility (molsol) is the saturated concentration of PbI_2. Refer to the molsol equations above, and use stoichiometry to find the ratio of PbI_2 to I^{-1}.
   b) Refer to the Ksp equations above, and use stoichiometry to find $[Pb^{+2}_{(aq)}]$.
   Put the concentrations of Pb^{+2} and I^{-1} into the K_{sp} expression for PbI_2.
   Your calculated K_{sp} for this problem will be slightly larger than values for
   K_{sp} reported in your textbook (Table 17.1) and elsewhere.
   c) Review the description of the common ion effect in the Introduction section.
2. Consider how any DI water remaining in the pipette would affect the solution.
3. Methyl orange is initially yellow (in base), and then turns red beyond the endpoint (in acid). The endpoint is between these two colors. What would that color be?
4. Read step 2 of laboratory technique 16A in the front of your lab manual.
   This step describes which digits are significant. Your explanation needs to include this.
5. Review molar solubility and common ion effect in the lab manual's Introduction section.
6. Line 5   Volume of HCl equals final reading minus initial reading.
   Line 6   (moles H_3O^{+1} added) = (H_3O^{+1} concentration in mol/L)(H_3O^{+1} volume in L)
   Line 7   (moles OH^{-1} in sample solution) = (moles H_3O^{+1} added)
   Line 8 $[OH^{-1}]$ = (moles OH^{-1}) ÷ (sample volume from line 1 in L)
   Lines 9/10 Molar solubility = $[Ca^{+2}]$ = (½)$[OH^{-1}]$ if no common ion is present.
   Line 11 K_{sp} of $[Ca(OH)_{2(aq)}]$ = $[Ca^{+2}][OH^{-1}]^2$ = (½) $[OH^{-1}][OH^{-1}]^2$ = (½)$[OH^{-1}]^3$
   Skip 6b completely.

Lab Questions

1. Generally, some solid $Ca(OH)_2$ is present in the sample. Given that acid removes OH^{-1} from the right side of the dissociation reaction, what will happen to the solid and its equilibrium when the acid is added? Explain how this will affect the moles of acid needed to reach the stoichiometric point.

2. During the titration, you added (neutral) DI water from the squirt bottle to wash the acid from the walls of the beaker. Explain whether or not this added water will affect the moles of acid needed to reach the stoichiometric point. How is the calculated Ksp affected?

3. It is not uncommon to add excess acid near the stoichiometric point, so that a larger stoichiometric volume of acid solution is observed in the experiment. Refer to the color pictures of pH indicators at the end of chapter 16 in your textbook. Explain what happens to the color of the solution as the stoichiometric point is passed. Also, explain what will happen to the experimental molar solubility and Ksp if the larger volume is recorded.

4. Suppose the solution in part A was made with tap water instead of DI water.
   Tap water typically contains what common ion that could affect your results?
   Explain how the tap water could shift the solubility equilibrium and
   change your experimental molar solubility.

5. Explain how you used the experimental $[OH^{-1}_{(aq)}]$ in part A to find $[Ca^{+2}_{(aq)}]$.
   Also, explain whether $[Ca^{+2}_{(aq)}]$ in part B would be larger or smaller than in part A.