16.1 - 16.3 - Solubility Equilibria

Solubility

Equilibrium theory can be applied to the solubility of different chemicals, that is, how much (or little) will go into solution when it is surrounded by water molecules.

Solvent: substance that does the dissolving.

Solute: the substance dissolved.

Note: Solubility generally increases with temperature.

Solubility Product: K_{sp}

The solubility product is an expression of how much compound can dissolve under given conditions, and relies on equilibrium structure:

$$A_BC_{D(s)} \underset{}{\overset{H_2O}{\rightleftharpoons}} B\,A^{+}{}_{(aq)} + D\,C^{-}{}_{(aq)}$$

$$K_{sp} = [A]^B[C]^D$$

Realize that in a saturated solution, with maximum amount of solute dissolved, the dissolution rate equals the precipitation rate.

Realize further that the units of K_{sp} are usually omitted, as they would be a wide range of mol/L raised to various exponents (Ex: mol^4/L^4).

1. K_{sp} from Solubility Part I

Copper (I) bromide has a measured solubility of 2.0 E -4 mol/L. Calculate its K_{sp} value at 25ºC.

Determine the chemical formula: CuBr.

Next, determine the dissolution of CuBr:

$$CuBr_{(s)} \overset{H_2O}{\rightleftharpoons} Cu^{+}{}_{(aq)} + Br^{-}{}_{(aq)}$$

Finally, a K_{sp} expression:

$$K_{sp} = [Cu^+][Br^-] = [2.0E-4][2.0E-4]$$

$$= \boxed{4.0E-8}$$

Here, FYI, units would be mol^2/L^2.

2. K_{sp} from Solubility Part II

Bismuth sulfide (Bi_2S_3) has a measured solubility of 1.0 E -15 mol/L. Calculate its K_{sp} value at 25ºC.

Next, determine the dissolution of Bi_2S_3:

$$Bi_2S_{3(s)} \overset{H_2O}{\rightleftharpoons} 2Bi^{3+}{}_{(aq)} + 3S^{2-}{}_{(aq)}$$

This dissolution shows how many moles of each ion will be present at equilibrium, thus allowing us to calculate ionic concentration:

Bi: $2Bi^{3+} \bullet (1.0E-15M) = 2.0E-15M$

S: $3S^{2-} \bullet (1.0E-15M) = 3.0E-15M$

Finally, the K_{sp} expression:

$$K_{sp} = [Bi^{3+}]^2[S^{2-}]^3 = [2.0E-15]^2[3.0E-15]^3$$

$$= \boxed{1.1E-8}$$

Here, FYI, units would be mol^5/L^5.

3. Solubility from K_{sp}

The K_{sp} value of copper II iodate at 25ºC is 1.4 E -7. Calculate its solubility.

Chemical formula? $Cu(IO_3)_2$.

Dissolution?

$$Cu(IO_3)_{2(s)} \overset{H_2O}{\rightleftharpoons} Cu^{2+}{}_{(aq)} + 2IO_3^{-}{}_{(aq)}$$

Thus: $K_{sp} = 1.4E-7 = [Cu^{2+}][IO_3^-]^2$

and from the dissolution expression:

Cu = x mol/L, and IO_3 = 2 x mol/L:

We can calculate solubility:

$$K_{sp} = 1.4E-7 = [x][2x]^2 = 4x^3$$

$$x = \sqrt[3]{3.5E-8} = \boxed{3.3E-3M}$$

Relative Solubilties

Depending on a chemical's formula (and the ratio of cations to anions), comparisons of solubility can be made.
Two cases arise, though, whereby comparisons can be direct, or require further calculation.
Case 1. Compounds produce the same number of ions.
Case 2. Compounds produce different numbers of ions.

4. Solubilties Case 1.

Rank the following chemicals in order of decreasing solubility, based on K_{sp} values:

AgI: K_{sp} = 1.5 E -16
CuI: K_{sp} = 5.0 E -12
$CaSO_4$: K_{sp} = 6.1 E -5

Here, the ratio of cations/anions is 1:1 for all of the compounds, so a direct prediction is possible.

From largest to smallest K_{sp}:

$CaSO_4$, CuI, then AgI.

5. Solubilties Case 2.

Rank the following chemicals in order of decreasing solubility, based on K_{sp} values:

CuS: K_{sp} = 8.5 E -45
Ag_2S: K_{sp} = 1.6 E -49
Bi_2S_3: K_{sp} = 1.1 E -73

Here, the ratio of cations/anions are all different:

CuS: 1 : 1
Ag_2S: 2 : 1
Bi_2S_3: 2: 3

Organizing by K_{sp} directly will result in an inaccurate listing.

Case 2 Answer (Slide 2).

To solve this, we have to use the full algebraic process to determine solubility for each:

CuS: $K_{sp} = 8.5E-45 = [x][x] = x^2$

$$x = \sqrt{1.4E-7} = \boxed{9.3E-23M}$$

Ag_2S: $K_{sp} = 1.6E-49 = [2x]^2[x] = 4x^3$

$$x = \sqrt[3]{4.0E-50} = \boxed{3.4E-17M}$$

Bi_2S_3: $K_{sp} = 1.1E-73 = [2x]^2[3x]^3 = 36x^5$

$$x = \sqrt[5]{3.06E-75} = \boxed{1.3E-15M}$$

Ranking them now shows the order (greatest to least:
Bi_2S_3, Ag_2S, then CuS.

Precipitation & Qualitative Analysis

So far we've looked at solids dissolving in solutions. Now we will look at the reverse process: precipitates forming under the right conditions.

To do this, we make use of the ion product, which is defined identically as K_{sp}, but looks at the product Q in terms of initial conditions in a solution:

$$Q = [A]_0^{\,B}[C]_0^{\,D}$$

Q is then compared to K_{sp} to determine if a precipitate forms:
A. If Q is greater than K_{sp}, precipitation occurs and will continue until concentrations of species are reduced to the extent that they equal K_{sp}.
B. If Q is less than K_{sp}, no precipitation occurs.

6. Will a Precipitate Form?

A solution is prepared by adding 750.0 mL of 4.00 E -3 M $Ce(NO_3)_3$ to 300.0 mL of 2.00 E -2 M KIO_3. Will $Ce(IO_3)_3$ precipitate? K_{sp} = 1.9 E -10

First, calculate $[Ce^{3+}]_0$ and $[IO_3]_0$:

$$[Ce]_0 = \frac{750.0\,mL \bullet 4.00E-3\,\frac{mmol}{mL}}{750.0mL + 300.0\,mL} = 2.86E-3M$$

$$[IO_3]_0 = \frac{300.0\,mL \bullet 2.00E-2\,\frac{mmol}{mL}}{750.0mL + 300.0\,mL} = 5.71E-3M$$

6. Precipitate Answer

Next: ion product:

$$Q = [Ce^{3+}]_0[IO_3]_0^3$$

$$= (2.86E-3)(5.71E-3)^3 = 5.32E-10$$

Since Q is greater than K_{sp}, $Ce(IO_3)_3$ will form a precipitate as the two solutions are mixed.

Other Topics to Explore

There is way more to solubility that we may cover in class at a later point, but you should consider delving into more details on the following topics:

1. Common Ion Effects.
The solubility of a compound diminishes if there is one of its ions already in solution.
Example: a 0.025 M NaF solution will cause less CaF_2 (K_{sp} = 4.0 E -11) to dissolve than if the CaF_2 were dissolved in pure water.

2. pH Effects on Solubility.
Depending on chemical behavior, high or low pH can cause more or less compound to dissolve.
Example: $Mg(OH)_2$ (K_{sp} = 8.9 E -12) dissolves more in low pH (acidic) solution, as the H^+ ions react with the OH^- ions, drawing more $Mg(OH)_2$ into solution by Le Chatelier's principle.

Other Topics to Explore

3. Selective Precipitation.
Mixtures of metal ions in aqueous solution can be separated sequentially by the slow addition of different chemicals.
Example: A mixture of Ba^{2+} and Ag^+ ions can be removed from a solution by first adding NaCl, which will first form solid AgCl (K_{sp} = 1.6 E -10).
Afterwards, Na_2SO_4 can be added, which will cause $BaSO_4$ (K_{sp} = 1.5 E -9) to precipitate.

Homework

Finish Solubility Scan problems

16.1 - 16.3 Problems in your Booklet
Due: Next Class