you-try-it-08.xlsx
Step-by-Step Guide
ver. 8/25/2023

Abstract

This document provides step-by-step instructions for the workbook you-try-it-08.xlsx (saved from Microsoft® Excel® 365). Each worksheet contains data for practice exercises keyed to the You-Try-It boxes in Chapter 8 of:

Brian M. Tissue, *Basics of Analytical Chemistry and Chemical Equilibria*, 2nd Ed. (John Wiley: New York, 2023).

General Advice

Work out or outline the first exercise of each worksheet on paper. Compare your result to the answer given in the worksheet. Next try writing formulas to do the calculations. If you do not get the same answer, error check your work by writing formulas step-wise to check intermediate steps. Try to write formulas to be general so that you can copy them to use for multiple cases.

Version History

6/21/2014	First draft.
7/26/2016	Revised formatting.
8/11/2023	Updated for 2nd edition.

For updates visit the text support website:

https://www.achem.org/

8.A Precipitation Order

This worksheet contains a table listing the K_{sp} values for a variety of metal sulfide insoluble salts. Given a fixed metal ion concentration, use the K_{sp} values to determine at what sulfide concentration a precipitate will form for each metal. Given these results, predict the precipitation order for a solution containing multiple metal ions.

Concepts	Concept Synopsis
precipitation	Salts range from very soluble, e.g., NaCl, to sparing soluble, to quite insoluble.
Using K_{sp}' values	The K_{sp}' value for a given insoluble salt provides the constant to predict if ion concentrations exceed the limit of solubility for a given material. When insoluble salts have different stoichiometries, it can be difficult to predict relative solubility easily from the K_{sp}' values.

1. Use a K_{sp} expression to determine the anion concentration at which calcium will precipitate. You may assume that the anion is not protonated and that there are no other competing equilibria.
   You may do the calculations assuming that $K_{sp}' = K_{sp}$.
   The concentration of the metal ion is in cell D15.

Table 8.A.1 lists examples of calcium insoluble salts with their K_{sp} values. When the stoichiometry of different salts varies, it is not always easy to determine their relative solubility. In these cases, the anion concentration that causes a metal to precipitate can be calculated from a K_{sp}' expression. A generic form for a precipitate equilibrium and the K_{sp}' expression is:

$$M_aX_b(s) \longleftrightarrow aM^{m+}(aq) + bX^{x-}(aq) \quad \text{and} \quad K_{sp}' = [M^{m+}]^a[X^{x-}]^b$$
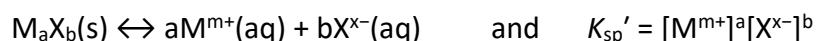
In Table 8.A.1 enter the stoichiometric factors for each insoluble salt in the cells under "exp_a" and "exp_b." You may ignore waters of hydration as they do not affect the stoichiometry. Using $CaCO_3$ as an example, the anion concentration at which precipitation will occur is given by:

$$K_{sp}' = [M^{m+}]^a[X^{x-}]^b = [Ca^{2+}]^1 [CO_3^{2-}]^1$$

where I include the "1" stoichiometric factors as exponents in the K_{sp}' expression for completeness. I will rearrange this expression to solve for the anion concentration and use the Table 8.A.1 labels to show how I will develop the worksheet formula:

$$[CO_3^{2-}]^{exp\_b} = K_{sp}'/ [Ca^{2+}]^{exp\_a}$$

$$[CO_3^{2-}] = (K_{sp}'/ [Ca^{2+}]^{exp\_a})^{(1/exp\_b)}$$

In cell H19 I enter the formula for this calculation:

= (E19/$D$15^F19)^(1/G19)

Copy cell H19 and paste it into cells H20 through H24. The results are shown in the following figure:

	B	C	D	E	F	G	H
14							
15		[metal] =	0.001	M			
16							
17		Table 8.A.1. Addition of anion to 0.001 M calcium chloride solution.					
18		insoluble salt	K_{sp}	K_{sp}'	exp_M	exp_X	[anion]
19		$CaCO_3$	2.8E-09	2.8E-09	1	1	2.8E-06
20		CaF_2	5.3E-09	5.3E-09	1	2	2.3E-03
21		$Ca(OH)_2$	5.5E-06	5.5E-06	1	2	7.4E-02
22		$CaC_2O_4.H_2O$	4.0E-09	4.0E-09	1	1	4.0E-06
23		$CaHPO_4$	1.0E-07	1.0E-07	1	1	1.0E-04
24		$CaSO_4$	9.1E-06	9.1E-06	1	1	9.1E-03

2. List the metal sulfides in the order in which they would precipitate as S^{2-} is added. You may assume that the metal ions are present in equal concentrations.

The easiest way to order a table is to use the Sort function in the worksheet. I will first copy and paste the table below the heading for Table 8.A.2. Now highlight the cells in the table and use Data > Sort and choose Sort by: "column H" and "smallest to largest" (see next figure).

Table 8.A.2. Precipitation order for calcium on addition of different anions.

insoluble salt	K_{sp}	K_{sp}'	exp_M	exp_X	[anion]
$CaCO_3$	2.8E-09	2.8E-09	1	1	2.8E-06
$CaC_2O_4.H_2O$	4.0E-09	4.0E-09	1	1	4.0E-06
$CaHPO_4$	1.0E-07	1.0E-07	1	1	1.0E-04
CaF_2	5.3E-09	5.3E-09	1	2	2.3E-03
$CaSO_4$	9.1E-06	9.1E-06	1	1	9.1E-03
$Ca(OH)_2$	5.5E-06	5.5E-06	1	2	7.4E-02

We can see that of the listed anions, CO_3^{2-} will be the first to produce a calcium precipitate. The other thing to point out is that CaF_2 has a K_{sp} value similar to that of $CaCO_3$. Due to the different stoichiometry for these two insoluble salts, a higher concentration of the fluoride anion can be added to the solution before a precipitate forms.

The point of this exercise is The other case where this type of calculation is useful is when you have a solution containing multiple anions to which you plan to add a certain amount of a cation. The calculation can predict if a precipitate will form with any of the anions in the solution. This type of calculation is analogous for adding a certain anion to a solution containing a mixture of cations.
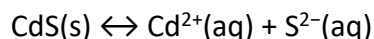
8.B intrinsic Solubility

Sulfide can be used to precipitate metal ions from industrial waste streams. The following calculation predicts the metal concentration that remains in solution. Actual metal concentrations might be higher due to formation of complexes or soluble particulates.

Concepts	Concept Synopsis
Solubility, s	The molar solubility, s, is the number of moles of solid that dissolves in 1 L of water when a solid precipitate is present. I refer to it as intrinsic solubility because it assumes that no other solution species are affecting the ion concentrations.
Concentration units	Solution concentrations are often expressed in different units to have convenient numerical values. You will want to get adept at interconverting common units to be able to make direct comparisons of values from different sources.

1. Use a K_{sp} expression to predict the intrinsic solubility, s, of each precipitate.
   You may do your calculations assuming $K_{sp}' = K_{sp}$.
   Optional: include the expressions for K_{sp} and s in the table.

This worksheet contains Table 8.B.1 listing a series of insoluble salts. I will include expressions for K_{sp} and s in my table, but it is much easier to write them on paper. It is important to write out the expressions, because it is easy to omit a factor or exponent when writing worksheet formulas. I will use the first two rows here as examples:

$CdS(s) \leftrightarrow Cd^{2+}(aq) + S^{2-}(aq)$
$K_{sp}' = [Cd^{2+}][S^{2-}]$
$s = [Cd^{2+}] = [S^{2-}]$
$K_{sp}' = s^2$
$s = (K_{sp}')^{1/2}$
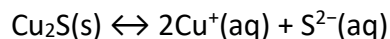
$Cu_2S(s) \leftrightarrow 2Cu^{+}(aq) + S^{2-}(aq)$
$K_{sp}' = [Cu^{+}]^2[S^{2-}]$
$s = 1/2[Cu^{+}] = [S^{2-}]$
$K_{sp}' = (2s)^2 s = 4s^3$
$s = (K_{sp}'/4)^{1/3}$

In cell H20 in Table 8.B.1 enter:

    =SQRT(E20)

Insoluble salts with the same stoichiometry will have the same expression for s. Copy H20 and enter it in column H for the other insoluble salts with 1:1 stoichiometry.

For Cu_2S, enter in cell H21:

    =(E21/4)^(1/3)

The results should look like the following figure. You can see that the solubility of these metal sulfides is quite low. The lanthanum case is sparingly soluble, and other precipitating agents are better for that metal.

	B	C	D	E	F	G	H
17							
18		Table 8.B.1. Intrinsic solubility of metal sulfides.					
19		insoluble salt	K_{sp}	K_{sp}'	expression	s	s (M)
20		CdS	8.0E-27	8.0E-27	$K_{sp} = s^2$	$s = sqrt(K_{sp})$	8.9E-14
21		Cu_2S	2.5E-48	2.5E-48	$K_{sp} = (2s)^2 s$	$s = (K_{sp}/4)^{1/3}$	8.5E-17
22		CuS	6.3E-36	6.3E-36	$K_{sp} = s^2$	$s = sqrt(K_{sp})$	2.5E-18
23		FeS	6.3E-18	6.3E-18	$K_{sp} = s^2$	$s = sqrt(K_{sp})$	2.5E-09
24		La_2S_3	2.0E-13	2.0E-13	$K_{sp} = (2s)^2(3s)^3$	$s = (K_{sp}/108)^{1/5}$	1.1E-03
25		PbS	8.0E-28	8.0E-28	$K_{sp} = s^2$	$s = sqrt(K_{sp})$	2.8E-14
26							

2. Use the calculated values of s to determine the metal concentration in solution. Copy values to Table 8.B.2 to organize the calculation.

The K_{sp}' and s values are copied from Table 8.B.1. by typing in cells D30 and E30:

    =E20
    =H20

Highlight cells D30 and E30 and double click the small black box at lower right of highlighted area to copy down the table. Enter the metal stoichiometric factor for each insoluble salt in Column F. The metal concentration is then the solubility, s, multiplied by the stoichiometric factor. In cell G30 type:

    =E30*F30

Copy this cell down to cell G35. The results are:

	B	C	D	E	F	G
27						
28		**Table 8.B.2. Metal concentration in presence of precipitate.**				
29		**insoluble salt**	K_{sp}'	s (M)	[m] = x*s	[m] (M)
30		CdS	8.0E-27	8.9E-14	1	8.9E-14
31		Cu_2S	2.5E-48	8.5E-17	2	1.7E-16
32		CuS	6.3E-36	2.5E-18	1	2.5E-18
33		FeS	6.3E-18	2.5E-09	1	2.5E-09
34		La_2S_3	2.0E-13	1.1E-03	2	2.3E-03
35		PbS	8.0E-28	2.8E-14	1	2.8E-14
36						

We can see why sulfide is used as a precipitating agent. Except for lanthanum, the concentration of metal remaining in solution is extremely low.

8.C Ionic Strength Effects

This worksheet contains two tables: Table A with two different solutions of acids and Table B with two different solutions of bases. The first step is to identify strong versus weak acids and bases. Knowing the nature of each acid or base, you can then determine their relative acidity or basicity.

| Concepts	Concept Synopsis
Converting K_{sp} to K_{sp}'	The ion concentration due to the intrinsic solubility of insoluble salts is usually low enough that we may neglect ionic strength. If spectator ions are present, ionic strength can have a large effect on K_{sp}' values.

Table 8.C.1 lists average activity coefficients for solutions at different ionic strengths.
  The ion concentration due to intrinsic solubility is usually low enough that we may neglect ionic strength.
  We will calculate K_{sp}' to see how ionic strength, due to spectator ions, can affect solubility.

1. Write the K_{sp} and K_{sp}' expressions for these compounds.

The thermodynamic and formal equilibrium expressions have the same form. They are as follows for the generic precipitation equilibrium:

$$M_aX_b(s) \leftrightarrow aM^{m+}(aq) + bX^{x-}(aq)$$
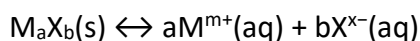
$$K_{sp}' = [M^{m+}]^a[X^{x-}]^b \quad \text{and} \quad K_{sp} = a_M{}^a a_X{}^b$$

where a is activity of the M and X ions.

Substituting for concentration gives:

$$K_{sp}' = [M^{m+}]^a[X^{x-}]^b = (\gamma_M a_M)^a(\gamma_X a_X)^b = \gamma_M{}^a \gamma_X{}^b K_{sp}$$
$$K_{sp}' = K_{sp} / \gamma_M{}^a \gamma_X{}^b$$

The expressions are easier to write out on paper, but I include them in Table 8.C.2:

B	C	D	E	F	G
23					
24	**Table 8.C.2. K_{sp}' expressions for select precipitates.**				
25	insoluble salt	K_{sp}	K_{sp}		K_{sp}'
26	CdS	8.0E-27	$K_{sp} = a_{Cd}a_S$ $= \gamma_2[Cd^{2+}]\,\gamma_2[S^{2-}]$		$K_{sp}' = K_{sp}/\gamma_2\gamma_2$
27	Cu_2S	2.5E-48	$K_{sp} = a_{Cu}{}^2a_S$ $= (\gamma_1[Cu^+])^2\,\gamma_2[S^{2-}]$		$K_{sp}' = K_{sp}/\gamma_1{}^2\gamma_2$
28	CuS	6.3E-36	$K_{sp} = a_{Cu}a_S$ $= \gamma_2[Cu^{2+}]\,\gamma_2[S^{2-}]$		$K_{sp}' = K_{sp}/\gamma_2\gamma_2$
29	FeS	6.3E-18	$K_{sp} = a_{Fe}a_S$ $= \gamma_2[Fe^{2+}]\,\gamma_2[S^{2-}]$		$K_{sp}' = K_{sp}/\gamma_2\gamma_2$
30	La_2S_3	1.0E-85	$K_{sp} = a_{La}{}^2a_S{}^3$ $= (\gamma_3[La^{3+}])^2(\gamma_2[S^{2-}])^3$		$K_{sp}' = K_{sp}/\gamma_3{}^2\gamma_2{}^3$
31	PbS	8.0E-28	$K_{sp} = a_{Pb}a_S$ $= \gamma_2[Pb^{2+}]\,\gamma_2[S^{2-}]$		$K_{sp}' = K_{sp}/\gamma_2\gamma_2$

2. Use the average activity coefficients to correct K_{sp} and calculate s for one or more precipitate.

Table 8.C.3 copies activity coefficients as a function of ionic strength for CdS. Both ions have a charge of ±2, so use the γ values from column E in Table 8.C.1. K_{sp} is copied in cell F36, and K_{sp}' values are calculated from this value in the lower rows. For example, cell F37 for $I_c = 0.001$ is:

    =$F$36/E37/D37

The solubility, s, for CdS is $(K_{sp}')^{1/2}$. In cell G36 type:

    =SQRT(F36)

Highlight cells F36:G36 and copy to the other rows in Table 8.C.3. The results are:

B	C	D	E	F	G
33					
34	**Table 8.C.3. Solubility of CdS versus I_c.**				
35	I_c	γ_m	γ_x	K_{sp}'	s (M)
36	≈0	1	1	8.0E-27	8.9E-14
37	0.001	0.87	0.87	1.1E-26	1.0E-13
38	0.005	0.75	0.75	1.4E-26	1.2E-13
39	0.010	0.67	0.67	1.8E-26	1.3E-13
40	0.050	0.47	0.47	3.6E-26	1.9E-13
41	0.100	0.40	0.40	5.0E-26	2.2E-13

In this case, solubility at $I_c = 0.1$ M increases by more than a factor of 2.

Table 8.C.4 illustrates the calculation for La_2S_3. The process is the same as before but using γ values for +3 and −2 ions. In cells F47 and G47 type:

     =$F$46/D47^3/E47^2
     =(F47/108)^(1/5)

Copy these cells to the other rows in Table 8.C.4. The results are:

	B	C	D	E	F	G
43						
44		**Table 8.C.4. Solubility of La$_2$S$_3$ versus I_c.**				
45		I_c	γ_m	γ_x	K_{sp}'	s (M)
46		≈0	1	1	1.0E-85	3.9E-18
47		0.001	0.73	0.87	3.4E-85	5.0E-18
48		0.005	0.52	0.75	1.3E-84	6.5E-18
49		0.010	0.42	0.67	3.0E-84	7.7E-18
50		0.050	0.20	0.47	5.7E-83	1.4E-17
51		0.100	0.14	0.40	2.3E-82	1.8E-17

In this case with an ion of higher charge, the increase in solubility is a factor of 5 at I_c = 0.1 M.

8.D Common Ion Effect

This worksheet contains a table of K_{sp} values of selected insoluble salts. Precipitation of these compounds are used in industrial process to purify brines for Li or Na production.

Concepts	Concept Synopsis
precipitation	Precipitation of insoluble salts is a cost-effective way to remove undesirable cations from solution. Generally low-cost precipitating agents will be used on an industrial scale.
Common-ion effect	The presence of an excess of one of the ions in a precipitation equilibrium will suppress the concentration of the other ion. Using an excess of a precipitating agent therefore makes removal of one species even more efficient.

Table 8.D.1 lists K_{sp} values of selected precipitates.

Precipitation of these compounds is an industrial process to purify brines for Li or Na productions.

1. First, use a K_{sp} expression to determine the anion concentration in pure water. You may do the calculation assuming that $K_{sp}' = K_{sp}$.

Table 8.D.1 lists K_{sp} values for several insoluble salts. We will neglect ionic strength because the common-ion effect usually has a much larger effect. First calculate the intrinsic solubility, s, for each case. These formulas are the same as developed in worksheet 8.B. I will list them here with the relationship between the anion concentration and s.

Insoluble Salt	K_{sp} expression	Solubility, s	[anion] M
$CaCO_3$	$K_{sp}' = [Ca^{2+}][CO_3^{2-}]$	$s = (K_{sp}')^{1/2}$	$[CO_3^{2-}] = s$
$Ca(OH)_2$	$K_{sp}' = [Ca^{2+}][OH^-]^2$	$s = (K_{sp}'/4)^{1/3}$	$[OH^-] = 2s$
$Mg(OH)_2$	$K_{sp}' = [Mg^{2+}][OH^-]^2$	$s = (K_{sp}'/4)^{1/3}$	$[OH^-] = 2s$
$Fe(OH)_3$	$K_{sp}' = [Fe^{3+}][OH^-]^3$	$s = (K_{sp}'/27)^{1/4}$	$[OH^-] = 3s$

Entering formulas in column F and G for these expressions give the following results:

	B	C	D	E	F	G
16						
17		**Table 8.D.1. K_{sp}' values of metal hydroxides and carbonates.**				
18			K_{sp}	K_{sp}'	s	[anion] (M)
19		$CaCO_3$	3.4E-09	3.4E-09	5.83E-05	5.83E-05
20		$Ca(OH)_2$	5.5E-06	5.5E-06	1.11E-02	2.22E-02
21		$Mg(OH)_2$	5.6E-12	5.6E-12	1.12E-04	2.24E-04
22		$Fe(OH)_3$	2.8E-39	2.8E-39	1.01E-10	3.03E-10

2. Calculate the concentration of metal ion remaining in solution as a function of pH. Plot $[Mg^{2+}]$ and $[Ca^{2+}]$ versus pH.

Table 8.D.2 is set up to find metal concentrations as a function of pH. First convert pH to $[OH^-]$. Recall that pOH = 14 − pH and $[OH^-] = 10^{-pOH}$. The formula in cell D29 is:

=10^(-14+C29)

Copy D29 and paste into D30 through D36.

Neglecting the intrinsic solubility, the cation concentration is found from the K_{sp}' expression at each $[OH^-]$. This simple calculation can give unrealistic results. After typing in formulas, I delete values that are larger than the intrinsic solubility found in Table 8.D.1. For $Mg(OH)_2$, the expression is:

$K_{sp}' = [Mg^{2+}][OH^-]^2$
$[Mg^{2+}] = K_{sp}'/[OH^-]^2$

I enter in cell E29:

=$E$21/$D29^2

Formulas are similar for $[Mg^{2+}]$ and $[Fe^{3+}]$:

=$E$20/D29^2
=$E$22/D29^3

Finish by copying E29:G29 through the rest of the table. Inspecting values, delete any calculated value that is larger than the intrinsic solubility for each metal. The results are:

	B	C	D	E	F	G
24						
25		Table 8.D.2 Calculation of metal concentration versus pH.				
26				$Mg(OH)_2$	$Ca(OH)_2$	$Fe(OH)_3$
27			$[OH^-]$	$[Mg^{2+}]$	$[Ca^{2+}]$	$[Fe^{3+}]$
28		pH	(M)	(M)	(M)	(M)
29		7	1.000E-07			2.8E-18
30		8	1.000E-06			2.8E-21
31		9	1.000E-05			2.8E-24
32		10	1.000E-04	5.6E-04		2.8E-27
33		11	1.000E-03	5.6E-06		2.8E-30
34		12	1.000E-02	5.6E-08	5.5E-02	2.8E-33
35		13	1.000E-01	5.6E-10	5.5E-04	2.8E-36
36		14	1.000E+00	5.6E-12	5.5E-06	2.8E-39

You can see in principle that the common-ion effect can change solubility by orders of magnitude. In practice, the actual solubility will depend on species that are present to form complexes with the metal and keep it in solution.

3. Determine the carbonate concentration needed to leave less than 1 mM of Ca^{2+} in solution.

Concentrations of the soluble salt sodium carbonate are listed in Table 8.D.3 up to the solubility limit for this salt. First convert the g/100 mL units to molarity. In cell D42 type:

=10*C42/$D$49

where cell D49 has the formula weight for Na_2CO_3.

The concentration of Ca^{2+} in the presence of CO_3^{2-} is:

=$E$19/D43

Highlighting cells and use "Insert > Charts > Scatter" to plot the data. After adjusting formatting and adding labels and a legend, my plots look like the following figure:

Soluble metal ion versus pH