you-try-it-07answers.xlsx
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For use with:
Brian M. Tissue, *Basics of Analytical Chemistry and Chemical Equilibria,* (John Wiley: New York, 2013).
http://www.achem.org

Worksheets in this file

notes	This page with background information.
7.A free-metal	See example 7.2 in the text for set-up.
7.B metal-hydrolysis	Predicting pH of metal solutions.
7.C stepwise formation K_f	Converting beta to Kf and making alpha plots.
7.D precipitation-order	Removal of metals with a precipitating agent.
7.E intrinsic-solubility	Calculation of intrinsic solubility, *s* .
7.F ionic-strength	Effect of ionic strength on K_{sp}.
7.G common-ion	Common-ion effect calculation.

Background

Refer to Chapter 7 in the text for equations and explanations.
Each worksheet has instructions in the blue shaded box.
For step-by-step help see you-try-it-07guide.pdf.

You-Try-It 7.A **Free Metal Fraction**

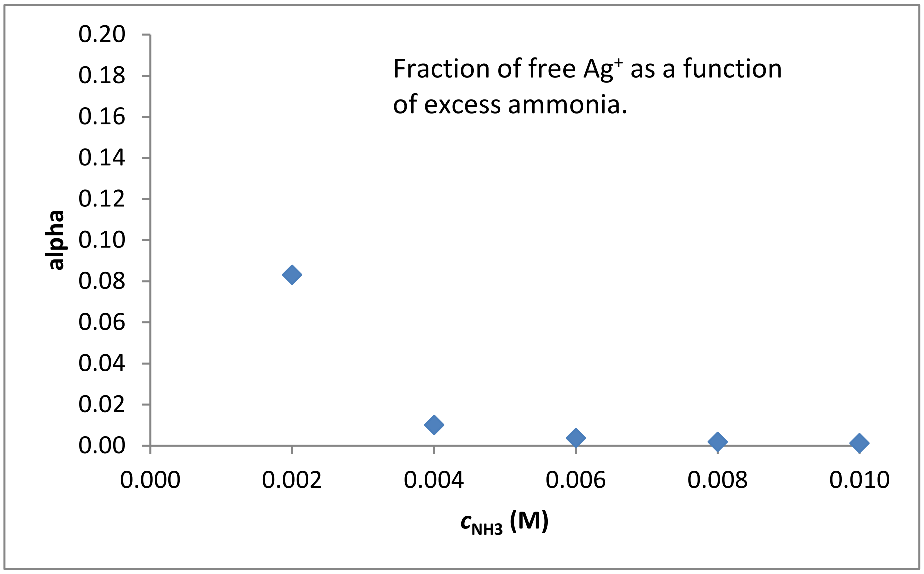
Table 7.A.1 lists different ammonia concentrations, where *c* _NH_3 represents formal concentration.

1. Predict the fraction of Ag^+ remaining as the free ion for each solution.
   You may do your calculations assuming that $\beta_2' = \beta_2$.
   The formal concentration of Ag^+ is $c_{Ag} = 5.0\times10^{-4}$ M.
   The equilibrium is:
   $$Ag^+ + 2\ NH_3 \rightleftharpoons Ag(NH_3)_2^+.$$
   Hint: spreadsheets are ideal to calculate using successive approximations.
2. Plot the alpha fraction versus *c* _NH_3.

β_2 = 1.1E+07
c_{Ag} = 5.00E-04 M
α = 0.50 (first guess)

Table 7.A.1

case	c_ NH_3	$[Ag^+]$ 1st approx	alpha	$[Ag^+]$ 2nd approx	alpha	$[Ag^+]$ 3rd approx	alpha
1	2.00E-03	2.27E-05	4.55E-02	4.34E-05	8.68E-02	4.15E-05	0.083
2	4.00E-03	2.53E-06	5.05E-03	5.02E-06	1.00E-02	5.00E-06	0.010
3	6.00E-03	9.09E-07	1.82E-03	1.81E-06	3.63E-03	1.81E-06	0.004
4	8.00E-03	4.64E-07	9.28E-04	9.27E-07	1.85E-03	9.26E-07	0.002
5	1.00E-02	2.81E-07	5.61E-04	5.61E-07	1.12E-03	5.61E-07	0.001



You-Try-It 7.B **Metal Hydrolysis**

Table 7.B.1 lists several aqueous solutions of metal salts.

metal	pK_a
Mg^{2+}	11.4
Co^{2+}	9.7
Cu^{2+}	7.5
Co^{3+}	6.6
Al^{3+}	5.0

1. Use the adjacent pK_a values to predict p[H_3O^+] for each solution. You may assume that the solutions are degassed to remove CO_2.
2. Review the results and correct any discrepencies. Recalculate p[H_3O^+] using the corrected K_a' values.

Table 7.B.1

case	soluble salt	*c* (M)	K_a	[H_3O^+]	p[H_3O^+]
1	$Cu(NO_3)_2$	0.0010	3.16E-08	5.62E-06	5.25
2	$Al_2(SO_4)_3$	0.0010	1.00E-05	1.41E-04	3.85
3	$MgCl_2$	0.0010	3.98E-12	6.31E-08	7.20
4	$MgCl_2$	0.10	3.98E-12	6.31E-07	6.20

There are two calculations that we should revisit.

The first calculation to check is case 3, the 0.001 M $MgCl_2$.
If we expect metal hydrolysis to make a solution acidic, a basic pH of 7.2 does not make any sense.
In this case, the amount of H_3O^+ produced by the Mg^{2+} is lower than the autoionization of water.
We may neglect the metal hydrolysis and predict that the solution will have a pH of 7:

case	soluble salt	*c* (M)	K_a	[H_3O^+]	p[H_3O^+]
3	$MgCl_2$	0.0010	3.98E-12	<1e-7	7.0

In case 4, a higher concentration of Mg^{2+} does affect the solution pH.

The other calculation that we can revise is in case 2.
The calculated result of [H_3O^+] = 1.4E-4 M is not insignificant compared to the 1.0E-3 M metal concentration.
Recall that we calculated [H_3O^+] assuming that (*c* − [H3O+]) ≈ *c* .
We can recalculate using a successive approximation:

case	soluble salt	*c* (M)	K_a	[H_3O^+]	[H_3O^+]	p[H_3O^+]
2	$Al_2(SO_4)_3$	0.0010	1.00E-05	1.41E-04	1.31E-04	3.88

You-Try-It 7.C **Stepwise K_f**

Tables 7.C.1 and 2 list cumulative formation constants for two different metal-ligand combinations.

1. Use the β_n values to calculate stepwise formation constants, K_n.
   We will neglect activity effects in these calculations, i.e., $K_n' = K_n$.

2. Use the stepwise formation constants, K_n to plot alpha plots.
   Equations for alpha values are on page 264 of the text.

Table 7.C.1. Log formation constants for Fe^{3+}/SCN^- complexes

	n = 1	n = 2
log β_n	2.11	3.30
β_n	1.29E+02	2.00E+03
K_n	1.29E+02	1.55E+01

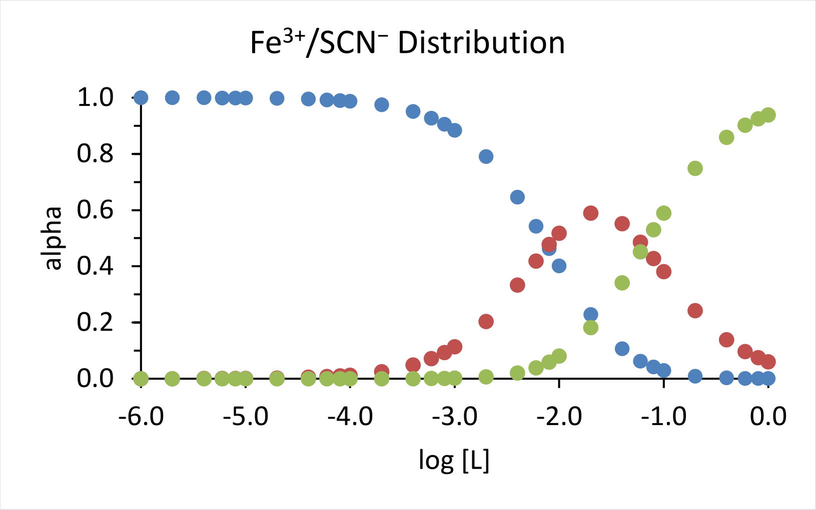
Table 7.C.2. Log formation constants for Cu^{2+}/NH_3 complexes

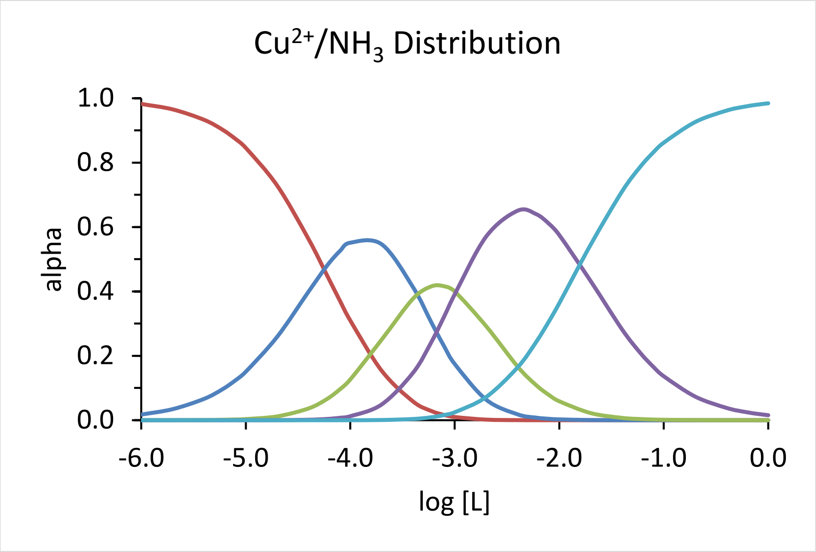
	n = 1	n = 2	n = 3	n = 4
log β_n	4.25	7.61	10.60	12.40
β_n	1.78E+04	4.07E+07	3.98E+10	2.51E+12
K_n	1.78E+04	2.29E+03	9.77E+02	6.31E+01

[L]	log[L]	alpha0	alpha1	alpha2
1.0E-06	-6.00	1.00E+00	1.29E-04	2.00E-09
2.0E-06	-5.70	1.00E+00	2.58E-04	7.98E-09
4.0E-06	-5.40	9.99E-01	5.15E-04	3.19E-08
6.0E-06	-5.22	9.99E-01	7.72E-04	7.18E-08
8.0E-06	-5.10	9.99E-01	1.03E-03	1.28E-07
1.0E-05	-5.00	9.99E-01	1.29E-03	1.99E-07
2.0E-05	-4.70	9.97E-01	2.57E-03	7.96E-07
4.0E-05	-4.40	9.95E-01	5.13E-03	3.18E-06
6.0E-05	-4.22	9.92E-01	7.67E-03	7.13E-06
8.0E-05	-4.10	9.90E-01	1.02E-02	1.26E-05
1.0E-04	-4.00	9.87E-01	1.27E-02	1.97E-05
2.0E-04	-3.70	9.75E-01	2.51E-02	7.78E-05
4.0E-04	-3.40	9.51E-01	4.90E-02	3.04E-04
6.0E-04	-3.22	9.28E-01	7.17E-02	6.66E-04
8.0E-04	-3.10	9.06E-01	9.33E-02	1.16E-03
1.0E-03	-3.00	8.84E-01	1.14E-01	1.76E-03
2.0E-03	-2.70	7.90E-01	2.04E-01	6.31E-03
4.0E-03	-2.40	6.46E-01	3.33E-01	2.06E-02
6.0E-03	-2.22	5.42E-01	4.19E-01	3.89E-02
8.0E-03	-2.10	4.63E-01	4.78E-01	5.92E-02
1.0E-02	-2.00	4.02E-01	5.18E-01	8.02E-02
2.0E-02	-1.70	2.29E-01	5.89E-01	1.82E-01
4.0E-02	-1.40	1.07E-01	5.51E-01	3.42E-01

6.0E-02	-1.22	6.28E-02	4.86E-01	4.51E-01
8.0E-02	-1.10	4.15E-02	4.28E-01	5.30E-01
1.0E-01	-1.00	2.96E-02	3.81E-01	5.90E-01
2.0E-01	-0.70	9.38E-03	2.42E-01	7.49E-01
4.0E-01	-0.40	2.69E-03	1.39E-01	8.59E-01
6.0E-01	-0.22	1.26E-03	9.70E-02	9.02E-01
8.0E-01	-0.10	7.24E-04	7.46E-02	9.25E-01
1.0E+00	0.00	4.71E-04	6.06E-02	9.39E-01

[L]	**log[L]**	**alpha0**	**alpha1**	**alpha2**	**alpha3**	**alpha4**
1.0E-06	-6.00	9.82E-01	1.75E-02	4.00E-05	3.91E-08	2.47E-12
2.0E-06	-5.70	9.66E-01	3.43E-02	1.57E-04	3.07E-07	3.88E-11
4.0E-06	-5.40	9.33E-01	6.64E-02	6.08E-04	2.38E-06	6.00E-10
6.0E-06	-5.22	9.02E-01	9.63E-02	1.32E-03	7.76E-06	2.94E-09
8.0E-06	-5.10	8.73E-01	1.24E-01	2.28E-03	1.78E-05	8.99E-09
1.0E-05	-5.00	8.46E-01	1.50E-01	3.45E-03	3.37E-05	2.13E-08
2.0E-05	-4.70	7.29E-01	2.59E-01	1.19E-02	2.32E-04	2.93E-07
4.0E-05	-4.40	5.62E-01	4.00E-01	3.66E-02	1.43E-03	3.61E-06
6.0E-05	-4.22	4.50E-01	4.80E-01	6.60E-02	3.87E-03	1.46E-05
8.0E-05	-4.10	3.70E-01	5.26E-01	9.64E-02	7.54E-03	3.81E-05
1.0E-04	-4.00	3.10E-01	5.51E-01	1.26E-01	1.23E-02	7.79E-05
2.0E-04	-3.70	1.54E-01	5.46E-01	2.50E-01	4.89E-02	6.17E-04
4.0E-04	-3.40	5.80E-02	4.13E-01	3.78E-01	1.48E-01	3.73E-03
6.0E-04	-3.22	2.84E-02	3.03E-01	4.16E-01	2.44E-01	9.23E-03
8.0E-04	-3.10	1.59E-02	2.27E-01	4.16E-01	3.25E-01	1.64E-02
1.0E-03	-3.00	9.82E-03	1.75E-01	4.00E-01	3.91E-01	2.47E-02
2.0E-03	-2.70	1.79E-03	6.37E-02	2.92E-01	5.71E-01	7.20E-02
4.0E-03	-2.40	2.55E-04	1.82E-02	1.66E-01	6.51E-01	1.64E-01
6.0E-03	-2.22	7.45E-05	7.95E-03	1.09E-01	6.40E-01	2.42E-01
8.0E-03	-2.10	2.99E-05	4.26E-03	7.80E-02	6.10E-01	3.08E-01
1.0E-02	-2.00	1.45E-05	2.57E-03	5.89E-02	5.75E-01	3.63E-01
2.0E-02	-1.70	1.36E-06	4.83E-04	2.21E-02	4.32E-01	5.45E-01
4.0E-02	-1.40	1.11E-07	7.86E-05	7.21E-03	2.82E-01	7.11E-01
6.0E-02	-1.22	2.42E-08	2.58E-05	3.55E-03	2.08E-01	7.88E-01
8.0E-02	-1.10	8.10E-09	1.15E-05	2.11E-03	1.65E-01	8.33E-01
1.0E-01	-1.00	3.43E-09	6.10E-06	1.40E-03	1.37E-01	8.62E-01
2.0E-01	-0.70	2.30E-10	8.20E-07	3.76E-04	7.34E-02	9.26E-01
4.0E-01	-0.40	1.50E-11	1.06E-07	9.75E-05	3.81E-02	9.62E-01
6.0E-01	-0.22	2.99E-12	3.19E-08	4.39E-05	2.57E-02	9.74E-01
8.0E-01	-0.10	9.53E-13	1.36E-08	2.48E-05	1.94E-02	9.81E-01
1.0E+00	0.00	3.92E-13	6.97E-09	1.60E-05	1.56E-02	9.84E-01


Fe^{3+}/SCN^- Distribution
alpha
1.0
0.8
0.6
0.4
0.2
0.0
-6.0
-5.0
-4.0
-3.0
-2.0
-1.0
0.0
log [L]


Cu^{2+}/NH_3 Distribution
alpha
1.0
0.8
0.6
0.4
0.2
0.0
-6.0
-5.0
-4.0
-3.0
-2.0
-1.0
0.0
log [L]

You-Try-It 7.D **Precipitation Order**

Table 7.D.1 lists K_{sp} values for several metal sulfide precipitates.

1. Use a K_{sp} expression to determine the sulfide concentration at which each cation precipitates.
   You may assume that the sulfide is not protonated and that there are no other competing equilibria.
   You may also do your calculations assuming that $K_{sp}' = K_{sp}$.
   The concentration of the metal ions is in cell D15.

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

[metal] = 0.001 M

Table 7.D.1. Addition of Na_2S to 0.001 M metal nitrate solution.

insoluble salt	K_{sp}	K_{sp}'	exp_M	exp_X	$[S^{=}]$
CdS	8.00E-27	8.00E-27	1	1	8.0E-24
Cu_2S	2.50E-48	2.50E-48	2	1	2.5E-42
CuS	6.30E-36	6.30E-36	1	1	6.3E-33
FeS	6.30E-18	6.30E-18	1	1	6.3E-15
La_2S_3	2.00E-13	2.00E-13	2	3	5.8E-03
PbS	8.00E-28	8.00E-28	1	1	8.0E-25

Table 7.D.2. Precipitation order on addition of Na_2S to mixed metal nitrate solution.

insoluble salt	K_{sp}	$[S^{=}]$
Cu_2S	2.50E-48	2.50E-42
CuS	6.30E-36	6.30E-33
PbS	8.00E-28	8.00E-25
CdS	8.00E-27	8.00E-24
FeS	6.30E-18	6.30E-15
La_2S_3	2.00E-13	5.85E-03

You-Try-It 7.E **Intrinsic Solubility**

Table 7.E.1 lists a series of insoluble salts.

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 will be higher due to formation of complexes and soluble particulates.

1. Use a K_{sp} expression to predict the intrinsic solubility, *s*, of each precipitate.
   You may do your calculations assuming that $K_{sp}' = K_{sp}$.
   Include the expressions for K_{sp} and *s* in the table.
2. Use the calculated values of *s* to determine the metal concentration in solution.
   Copy values to Table 7.E.2 to organize the calculation.
3. Copy the previous results to Table 7.E.3. Use Paste Values for *s* so you can reorder.
   Convert the M concentration to ppm, ppb, or ppt to show convenient values.
   Reorder the list from low to high concentration.

Table 7.E.1. Intrinsic solubility of metal sulfides.

insoluble salt	K_{sp}	K_{sp}'	expression	*s*	*s* (M)
CdS	8.0E-27	8.0E-27	$K_{sp} = s^2$	$s = \text{sqrt}(K_{sp})$	8.9E-14
Cu_2S	2.5E-48	2.5E-48	$K_{sp} = (2s)^2 s$	$s = (K_{sp}/4)^{1/3}$	8.5E-17
CuS	6.3E-36	6.3E-36	$K_{sp} = s^2$	$s = \text{sqrt}(K_{sp})$	2.5E-18
FeS	6.3E-18	6.3E-18	$K_{sp} = s^2$	$s = \text{sqrt}(K_{sp})$	2.5E-09
La_2S_3	1.0E-85	1.0E-85	$K_{sp} = (2s)^2(3s)^3$	$s = (K_{sp}/108)^{1/5}$	3.9E-18
PbS	8.0E-28	8.0E-28	$K_{sp} = s^2$	$s = \text{sqrt}(K_{sp})$	2.8E-14

Table 7.E.2. Metal concentration in presence of precipitate.

insoluble salt	K_{sp}	*s* (M)	[m] = x*s	[m] (M)
CdS	8.0E-27	8.9E-14	1	8.9E-14
Cu_2S	2.5E-48	8.5E-17	2	1.7E-16
CuS	6.3E-36	2.5E-18	1	2.5E-18
FeS	6.3E-18	2.5E-09	1	2.5E-09
La_2S_3	2.0E-13	3.9E-18	2	7.8E-18
PbS	8.0E-28	2.8E-14	1	2.8E-14

Table 7.E.3. Metal concentration conversion.

insoluble salt	K_{sp}	[m] (M)	m f.w. (g/mol)	[m]	
CuS	6.3E-36	2.5E-18	63.55	1.6E-07	ppt
La_2S_3	2.0E-13	7.8E-18	138.9	1.1E-06	ppt
Cu_2S	2.5E-48	1.7E-16	63.55	1.1E-05	ppt
PbS	8.0E-28	2.8E-14	207.2	0.0059	ppt
CdS	8.0E-27	8.9E-14	112.4	0.010	ppt
FeS	6.3E-18	2.5E-09	55.85	0.14	ppb

You-Try-It 7.F **Ionic Strength Effects on K_{sp}'**

Table 7.F.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.

Table 7.F.2 lists several inorganic precipitates with their K_{sp} values.

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

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

Table 7.F.1. Average activity coefficents for given charge.

I_c	±1	±2	±3
0.001	0.96	0.87	0.73
0.005	0.93	0.75	0.52
0.010	0.90	0.67	0.42
0.050	0.82	0.47	0.20
0.100	0.77	0.40	0.14

(values from Kielland, J. *J. Am. Chem. Soc.* **1937**, *59* , 1675.)

Table 7.F.2. K_{sp}' expressions for select precipitates.

insoluble salt	K_{sp}	K_{sp}		K_{sp}'
CdS	8.0E-27	$K_{sp} = a_{Cd}a_S$	$= \gamma_2[Cd^{2+}]\ \gamma_2[S^{2-}]$	$K_{sp}' = K_{sp}/\gamma_2\gamma_2$
Cu_2S	2.5E-48	$K_{sp} = a_{Cu}^2 a_S$	$= (\gamma_1[Cu^+])^2\ \gamma_2[S^{2-}]$	$K_{sp}' = K_{sp}/\gamma_1^2\gamma_2$
CuS	6.3E-36	$K_{sp} = a_{Cu}a_S$	$= \gamma_2[Cu^{2+}]\ \gamma_2[S^{2-}]$	$K_{sp}' = K_{sp}/\gamma_2\gamma_2$
FeS	6.3E-18	$K_{sp} = a_{Fe}a_S$	$= \gamma_2[Fe^{2+}]\ \gamma_2[S^{2-}]$	$K_{sp}' = K_{sp}/\gamma_2\gamma_2$
La_2S_3	1.0E-85	$K_{sp} = a_{La}^2 a_S^3$	$= (\gamma_3[La^{3+}])^2(\gamma_2[S^{2-}])^3$	$K_{sp}' = K_{sp}/\gamma_3^2\gamma_2^3$
PbS	8.0E-28	$K_{sp} = a_{Pb}a_S$	$= \gamma_2[Pb^{2+}]\ \gamma_2[S^{2-}]$	$K_{sp}' = K_{sp}/\gamma_2\gamma_2$

Table 7.F.3. Solubility of CdS versus I_c.

I_c	γ_m	γ_x	K_{sp}'	*s* (M)
≈0	1	1	8.0E-27	8.9E-14
0.001	0.87	0.87	1.1E-26	1.0E-13
0.005	0.75	0.75	1.4E-26	1.2E-13
0.010	0.67	0.67	1.8E-26	1.3E-13
0.050	0.47	0.47	3.6E-26	1.9E-13
0.100	0.40	0.40	5.0E-26	2.2E-13

Table 7.F.4. Solubility of La_2S_3 versus I_c.

I_c	γ_m	γ_x	K_{sp}'	*s* (M)
≈0	1	1	1.0E-85	3.9E-18
0.001	0.73	0.87	3.4E-85	5.0E-18
0.005	0.52	0.75	1.3E-84	6.5E-18
0.010	0.42	0.67	3.0E-84	7.7E-18
0.050	0.20	0.47	5.7E-83	1.4E-17
0.100	0.14	0.40	2.3E-82	1.8E-17

You-Try-It 7.G **Common-ion Effect**

Table 7.G.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 $K_{sp}' = K_{sp}$.

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

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

Table 7.G.1. K_{sp}' values of metal hydroxides and carbonates.

	K_{sp}	K_{sp}'	*s*	[anion] (M)
$CaCO_3$	3.4E-09	3.4E-09	5.83E-05	5.83E-05
$Ca(OH)_2$	5.5E-06	5.5E-06	1.11E-02	2.22E-02
$Mg(OH)_2$	5.6E-12	5.6E-12	1.12E-04	2.24E-04
$Fe(OH)_3$	2.8E-39	2.8E-39	5.65E-11	1.70E-10

Table 7.G.2 Calculation of metal concentration versus pH.

		$Mg(OH)_2$	$Ca(OH)_2$	$Fe(OH)_3$
pH	$[OH^-]$ (M)	$[Mg^{2+}]$ (M)	$[Ca^{2+}]$ (M)	$[Fe^{3+}]$ (M)
7	1.000E-07			2.8E-18
8	1.000E-06			2.8E-21
9	1.000E-05			2.8E-24
10	1.000E-04	5.6E-04		2.8E-27
11	1.000E-03	5.6E-06		2.8E-30
12	1.000E-02	5.6E-08	5.5E-02	2.8E-33
13	1.000E-01	5.6E-10	5.5E-04	2.8E-36
14	1.000E+00	5.6E-12	5.5E-06	2.8E-39

Table 7.G.3. Calculation of $[Ca^{2+}]$ versus $[CO_3^{2-}]$.

$NaCO_3$ (g/100 mL)	$[CO_3^{2-}]$ (M)	$[Ca^{2+}]$ (M)
0.0003	2.83E-05	
0.003	2.83E-04	2.1E-01
0.03	2.83E-03	2.1E-02
0.3	2.83E-02	2.1E-03
3	2.83E-01	2.1E-04
30	2.83E+00	2.1E-05

$NaCO_3$ f.w.: 106 g/mol