

**you-try-it-07.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  $K_f$  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**

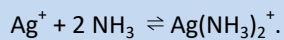
Table 7.A.1 lists different ammonia concentrations, where  $c_{\text{NH}_3}$  represents formal concentration.

1. Predict the fraction of  $\text{Ag}^+$  remaining as the free ion for each solution.

You may do your calculations assuming that  $\beta_2' = \beta_2$ .

The formal concentration of  $\text{Ag}^+$  is  $c_{\text{Ag}} = 5.0 \times 10^{-4}$  M.

The equilibrium is:



Hint: spreadsheets are ideal to calculate using successive approximations.

2. Plot the alpha fraction versus  $c_{\text{NH}_3}$ .

$$\beta_2 = 1.1\text{E}+07$$

$$c_{\text{Ag}} = 5.00\text{E}-04 \text{ M}$$

$$\alpha = \text{[ ] (first guess)}$$

**Table 7.A.1**

case	$c_{\text{NH}_3}$	$[\text{Ag}^+]$		$[\text{Ag}^+]$		$[\text{Ag}^+]$	
		1st approx	alpha	2nd approx	alpha	3rd approx	alpha
1	2.00E-03						
2	4.00E-03						
3	6.00E-03						
4	8.00E-03						
5	1.00E-02						

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

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

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 discrepancies.  
Recalculate  $p[H_3O^+]$  using the corrected  $K_a'$  values.

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

**Table 7.B.1**

case	soluble salt	$c$ (M)	$K_a$	$[H_3O^+]$	$p[H_3O^+]$
1	$Cu(NO_3)_2$	0.0010			
2	$Al_2(SO_4)_3$	0.0010			
3	$MgCl_2$	0.0010			
4	$MgCl_2$	0.10			

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			

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  $(c - [H_3O^+]) \approx c$ .

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				

**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  $\beta_n$  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  $\text{Fe}^{3+}/\text{SCN}^-$  complexes**

	n = 1	n = 2
$\log \beta_n$	2.11	3.30
$\beta_n$		
$K_n$		

**Table 7.C.2. Log formation constants for  $\text{Cu}^{2+}/\text{NH}_3$  complexes**

	n = 1	n = 2	n = 3	n = 4
$\log \beta_n$	4.25	7.61	10.60	12.40
$\beta_n$				
$K_n$				

[L]	log[L]	alpha0	alpha1	alpha2
1.0E-06				
2.0E-06				
4.0E-06				
6.0E-06				
8.0E-06				
1.0E-05				
2.0E-05				
4.0E-05				
6.0E-05				
8.0E-05				
1.0E-04				
2.0E-04				
4.0E-04				
6.0E-04				
8.0E-04				
1.0E-03				
2.0E-03				
4.0E-03				
6.0E-03				
8.0E-03				
1.0E-02				
2.0E-02				
4.0E-02				

6.0E-02  
8.0E-02  
1.0E-01  
2.0E-01  
4.0E-01  
6.0E-01  
8.0E-01  
1.0E+00

<b>[L]</b>	<b>log[L]</b>	<b>alpha0</b>	<b>alpha1</b>	<b>alpha2</b>	<b>alpha3</b>	<b>alpha4</b>
1.0E-06						
2.0E-06						
4.0E-06						
6.0E-06						
8.0E-06						
1.0E-05						
2.0E-05						
4.0E-05						
6.0E-05						
8.0E-05						
1.0E-04						
2.0E-04						
4.0E-04						
6.0E-04						
8.0E-04						
1.0E-03						
2.0E-03						
4.0E-03						
6.0E-03						
8.0E-03						
1.0E-02						
2.0E-02						
4.0E-02						
6.0E-02						
8.0E-02						
1.0E-01						
2.0E-01						
4.0E-01						
6.0E-01						
8.0E-01						
1.0E+00						

**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  $S^{2-}$  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	$[S^{2-}]$
CdS	8.00E-27	8.00E-27			
$Cu_2S$	2.50E-48	2.50E-48			
CuS	6.30E-36	6.30E-36			
FeS	6.30E-18	6.30E-18			
$La_2S_3$	2.00E-13	2.00E-13			
PbS	8.00E-28	8.00E-28			

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

insoluble salt	$K_{sp}$	$[S^{2-}]$

**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			
Cu <sub>2</sub> S	2.5E-48	2.5E-48			
CuS	6.3E-36	6.3E-36			
FeS	6.3E-18	6.3E-18			
La <sub>2</sub> S <sub>3</sub>	1.0E-85	1.0E-85			
PbS	8.0E-28	8.0E-28			

**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			
Cu <sub>2</sub> S	2.5E-48			
CuS	6.3E-36			
FeS	6.3E-18			
La <sub>2</sub> S <sub>3</sub>	2.0E-13			
PbS	8.0E-28			

**Table 7.E.3. Metal concentration conversion.**

insoluble salt	$K_{sp}$	$[m]$ (M)	m f.w. (g/mol)	$[m]$
CuS	6.3E-36		63.55	
La <sub>2</sub> S <sub>3</sub>	2.0E-13		138.9	
Cu <sub>2</sub> S	2.5E-48		63.55	
PbS	8.0E-28		207.2	
CdS	8.0E-27		112.4	
FeS	6.3E-18		55.85	

**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 coefficients for given charge.**

$I_c$	$\pm 1$	$\pm 2$	$\pm 3$
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	$K_{sp} = a_{Cd}a_S$	
Cu <sub>2</sub> S	2.5E-48	$K_{sp} = a_{Cu}^2a_S$	
CuS	6.3E-36	$K_{sp} = a_{Cu}a_S$	
FeS	6.3E-18	$K_{sp} = a_{Fe}a_S$	
La <sub>2</sub> S <sub>3</sub>	1.0E-85	$K_{sp} = a_{La}^2a_S^3$	
PbS	8.0E-28	$K_{sp} = a_{Pb}a_S$	

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

$I_c$	$\gamma_m$	$\gamma_x$	$K_{sp}'$	$s$ (M)
$\approx 0$	1	1	8.0E-27	8.9E-14
0.001	0.87	0.87		
0.005	0.75	0.75		
0.010	0.67	0.67		
0.050	0.47	0.47		
0.100	0.40	0.40		

**Table 7.F.4. Solubility of La<sub>2</sub>S<sub>3</sub> versus  $I_c$ .**

$I_c$	$\gamma_m$	$\gamma_x$	$K_{sp}'$	$s$ (M)
$\approx 0$	1	1	1.0E-85	3.9E-18
0.001	0.73	0.87		
0.005	0.52	0.75		
0.010	0.42	0.67		
0.050	0.20	0.47		
0.100	0.14	0.40		



**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		
$Ca(OH)_2$	5.5E-06	5.5E-06		
$Mg(OH)_2$	5.6E-12	5.6E-12		
$Fe(OH)_3$	2.8E-39	2.8E-39		

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

pH	$[OH^-]$ (M)	$Mg(OH)_2$	$Ca(OH)_2$	$Fe(OH)_3$
		$[Mg^{2+}]$ (M)	$[Ca^{2+}]$ (M)	$[Fe^{3+}]$ (M)
7				
8				
9				
10				
11				
12				
13				
14				

**Table 7.G.3. Calculation of  $Ca^{2+}$  versus carbonate concentration.**

$NaCO_3$ (g/100 mL)	$[CO_3^{2-}]$ (M)	$[Ca^{2+}]$ (M)
0.0003		
0.003		
0.03		
0.3		
3		
30		

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