you-try-it-07.xlsx
Step-by-Step Guide
ver. 8/8/2023

Abstract

This document provides step-by-step instructions for the workbook you-try-it-07.xlsx (saved from Microsoft® Excel® 365). Each worksheet contains data for practice exercises keyed to the You-Try-It boxes in Chapter 7 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.
8/8/2023	Updated for 2nd Edition.

For updates visit the text support website:

https://www.achem.org/

7.A free metal

This worksheet contains a table with different ammonia concentrations. The exercise is to determine the fraction of silver ion remaining as free Ag^+ as a function of NH_3 concentration.

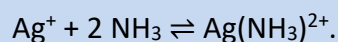| Concepts	Concept Synopsis
complexation equilibrium	Manipulating an equilibrium expression to be able to solve for an unknown quantity ([Ag^+] in this case).
alpha fraction	Determining how the amount or fraction of Ag^+ exists in equilibrium in the presence of an excess of NH_3 complexing agent.
successive approximation	An initial guess of the alpha fraction is used to find an approximate answer that is then refined by iterative calculations.

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.

Example 7.2 shows the full expression. The solution in that example was simplified due to two terms canceling to equal zero. The more general case requires a lot of algebra to generate a cubic expression. I will use successive approximations as an alternate approach. Given that we are interested in masking the silver ion, I will assume that the equilibrium silver ion concentration is much lower than the formal concentrations of ammonia or silver ion. When this condition is true, I can simplify the squared term in the denominator to be $(c_{NH3} - 2c_{Ag})^2$.

$$\beta_2' = \frac{(c_{Ag} - [Ag^+])}{[Ag^+](c_{NH3} - 2c_{Ag} + 2[Ag^+])^2}$$

$$\beta_2' = \frac{(c_{Ag} - [Ag^+])}{[Ag^+](c_{NH3} - 2c_{Ag})^2} = 1.1 \times 10^7$$

$$\beta_2' = \frac{(c_{Ag} - [Ag^+])}{[Ag^+](c_{NH3} - 2c_{Ag})^2}$$

Now to calculate ionic strength use the expression:

$$I_c = 0.5\sum c_i z_i^2$$

where c_i is the concentration of each ion and z_i is the charge of each ion.

The Excel formula that I typed in cell L15 for this calculation, using case 1 as an example, is:

=0.5*(C15*E15^2+F15*H15^2+I15*K15^2)

I illustrate the calculation here with case 2:

$$c_{\_NH3} = 1.0\times10^{-3} \text{ M}$$

where $c_{\_NH3}$ is the formal concentration of ammonia.

2. Plot the alpha fraction versus c_NH_3.

Highlight the concentrations in column C and the results in column I. Insert a scatter plot and adjust and label the axes. The result should look something like the following figure:

Fraction of free Ag^+ as a function of excess ammonia.
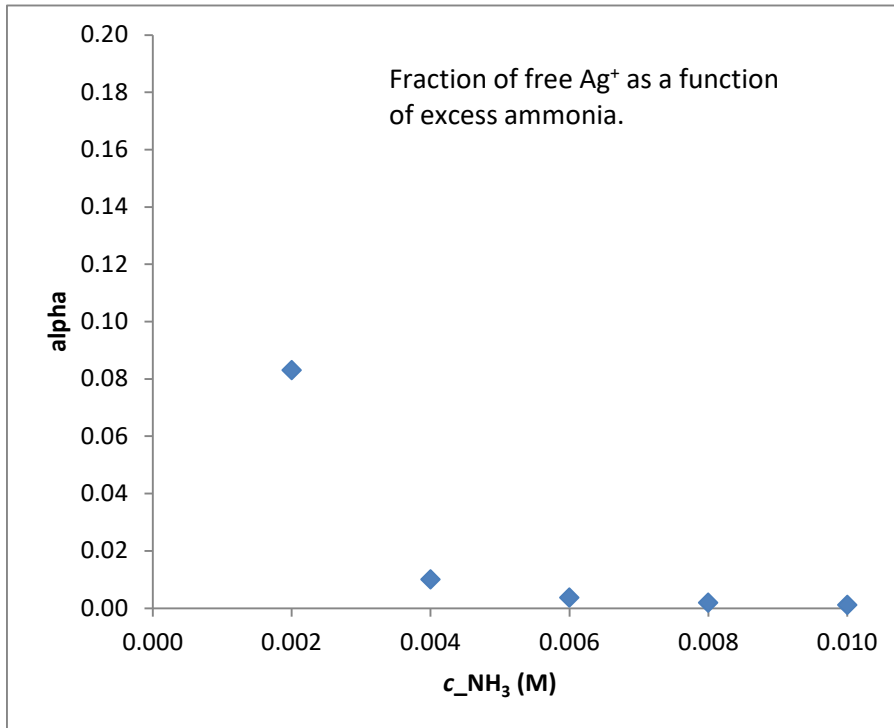
7.B metal-hydrolysis

This worksheet provides K_a values for metal ions and a table listing different solutions. The calculation is the same as for a weak acid. First calculate p[H_3O^+] assuming the equilibrium concentration of the metal ion does not change from the formal concentration. After completing the calculation in part 1, review the results to see if they make sense. Revise the calculation as necessary in part 2.

Concepts	Concept Synopsis
Metal ion hydrolysis	Strong electrolyte ions, i.e., spectator ions, will not affect the pH of aqueous solutions directly. Any other soluble ions will react with water to change the pH.

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.

The adjacent figure shows the pK_a values given in the worksheet. The first step to set up a calculation is to calculate K_a in column E in Table 7.B.1. In cells E17 through E20, type:

=10^-$I$7

=10^-$I$9

=10^-$I$5

=10^-$I$5

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

The values will be:

	A	B	C	D	E	F	G
15		Table 7.B.1					
16		case	soluble salt	c (M)	K_a	[H_3O^+]	p[H_3O^+]
17		1	$Cu(NO_3)_2$	0.0010	3.16E-08		
18		2	$Al_2(SO_4)_3$	0.0010	1.00E-05		
19		3	$MgCl_2$	0.0010	3.98E-12		
20		4	$MgCl_2$	0.10	3.98E-12		

Next set up a weak acid problem to calculate $[H_3O^+]$. A metal ion can react with water to form the following equilibrium. Using a divalent metal ion as an example:

$$M^{2+}(aq) + 2\ H_2O \leftrightarrow M(OH)^+(aq) + H_3O^+(aq)$$

The equilibrium constant expression is:

$$K_a' = \frac{[M(OH)^+][H_3O^+]}{[M^{2+}]} = \frac{[H_3O^+]^2}{c_{metal} - [H_3O^+]}$$

Neglecting $[H_3O^+]$ compared to c_{metal} gives us the approximation: $[H_3O^+] \approx sqrt(c_{metal}\ K_a')$. This calculation is the same as we did in worksheet 5.3 for the weak acids. For case 1, I type in cells F17 and G17:

    =SQRT(D17*E17)   =-log(F17)

Copying these formulas down the next three rows gives the results in the next figure:

	A	B	C	D	E	F	G
15		Table 7.B.1					
16		case	soluble salt	c (M)	K_a	$[H_3O^+]$	$p[H_3O^+]$
17		1	$Cu(NO_3)_2$	0.0010	3.16E-08	5.62E-06	5.25
18		2	$Al_2(SO_4)_3$	0.0010	1.00E-05	1.41E-04	3.85
19		3	$MgCl_2$	0.0010	3.98E-12	6.31E-08	7.20
20		4	$MgCl_2$	0.10	3.98E-12	6.31E-07	6.20

2. Review the results to identify discrepancies.
    Recalculate $p[H_3O^+]$ as needed.

There are two calculations that are not quite right. The most obvious error is case 3 for the solution of 0.001 M $MgCl_2$. The result is 7.2, a slightly basic pH. Given that we expected the metal ion to make the solution acidic, this result is incorrect. In this solution, the Mg^{2+} concentration and K_a value are so low that the hydrolysis reaction produces less than 1×10^{-7} M of $[H_3O^+]$. In this case we can consider the Mg^{2+} a spectator ion and predict that the solution pH remains at 7. No further calculation is necessary.

The other calculation that we should revisit is 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 succes-

sive approximation. Copy row 18 and paste somewhere lower on the worksheet. Insert a new cell to recalculate [H_3O^+]. I've also copied the header, so I highlight cells G24:G26 and use Right-click, Insert…, and Shift cells right.

	A	B	C	D	E	F	G	H
23								
24		case	soluble salt	c (M)	K_a	[H_3O^+]		p[H_3O^+]
25								
26		2	$Al_2(SO_4)_3$	0.0010	1.00E-05	1.41E-04		3.85

In cell G26 I enter:

=SQRT(2*(D26-F26)*E26)

and I revise cell H26 to:

=-LOG(G26)

The recalculated result is:

	A	B	C	D	E	F	G	H
23								
24		case	soluble salt	c (M)	K_a	[H_3O^+]	[H_3O^+]	p[H_3O^+]
25								
26		2	$Al_2(SO_4)_3$	0.0010	1.00E-05	1.41E-04	1.31E-04	3.88

Recalculating does not show a large change in [H_3O^+], but checking that approximations are valid is an important process in any calculation.

7.C Stepwise Formation Constants, K_f

This worksheet contains tables of cumulative formation constants for two different metal-ligand complexes. The two exercises are to convert these values to stepwise formation constants and use the K_f constants to generate alpha plots.

Concepts	Concept Synopsis
Converting cumulative and stepwise formation constants	Formation constants are generally tabulated as cumulative formation constants. For certain calculations we must convert to stepwise formation constants.
Alpha plots	Alpha plots are calculated from K_f values to visualize graphically the predominant species as a function of ligand concentration.

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

Tables 7.C.1 and 7.C.2 contain $\log\beta_n$ for two different metal-ligand systems. The tables have empty cells for convert the $\log\beta_n$ to β_n and the β_n to K_n:

	A	B	C	D	E	F	G
13							
14			Table 7.C.1. Log formation constants for Fe^{3+}/SCN^- complexes				
15				n = 1	n = 2		
16			log β_n	2.11	3.30		
17			β_n				
18			K_n				
19							
20							
21			Table 7.C.2. Log formation constants for Cu^{2+}/NH_3 complexes				
22				n = 1	n = 2	n = 3	n = 4
23			log β_n	4.25	7.61	10.60	12.40
24			β_n				
25			K_n				

In cells D17 and E17 type:
=10^D16 and =10^D17

For n = 1, β_1 to K_1. Since cell D18 equals D17, simply type in D18:

=D17

For n = 2, $\beta_2 = K_1 K_2$ so $K_2 = \beta_2/K_1$. In cell E18 type:

=E17/D18

The formulas are similar for Table 7.C.2. For the n = 4 case, the formulas in cells G24 and G25 are:

=

=10^G23

=G24/D25/E25/F25

The results for both tables are displayed in the following figure:

	A	B	C	D	E	F	G
13							
14			Table 7.C.1. Log formation constants for Fe^{3+}/SCN^- complexes				
15				n = 1	n = 2		
16			log β_n	2.11	3.30		
17			β_n	1.29E+02	2.00E+03		
18			K_n	1.29E+02	1.55E+01		
19							
20							
21			Table 7.C.2. Log formation constants for Cu^{2+}/NH_3 complexes				
22				n = 1	n = 2	n = 3	n = 4
23			log β_n	4.25	7.61	10.60	12.40
24			β_n	1.78E+04	4.07E+07	3.98E+10	2.51E+12
25			K_n	1.78E+04	2.29E+03	9.77E+02	6.31E+01
26							

2. Use the stepwise formation constants, K_n to plot alpha plots.

Equations for alpha values are on page 264 (1st Ed.) or 273 (2nd Ed.) of the text.

The first step is to calculate a table of alpha values versus ligand concentration. The equations from the textbook for the tetradentate case are:

$$\alpha_M = \frac{1}{1 + K_1[L] + K_1K_2[L]^2 + K_1K_2K_3[L]^3 + K_1K_2K_3K_4[L]^4}$$

$$\alpha_{ML} = \frac{K_1[L]}{1 + K_1[L]^2 + K_1K_2[L]^2 + K_1K_2K_3[L]^3 + K_1K_2K_3K_4[L]^4}$$

$$\alpha_{ML_2} = \frac{K_1K_2[L]^2}{1 + K_1[L] + K_1K_2[L]^2 + K_1K_2K_3[L]^3 + K_1K_2K_3K_4[L]^4} \qquad (7.1)$$

$$\alpha_{ML_3} = \frac{K_1K_2K_3[L]^3}{1 + K_1[L] + K_1K_2[L]^2 + K_1K_2K_3[L]^3 + K_1K_2K_3K_4[L]^4}$$

$$\alpha_{ML_4} = \frac{K_1K_2K_3K_4[L]^4}{1 + K_1[L] + K_1K_2[L]^2 + K_1K_2K_3[L]^3 + K_1K_2K_3K_4[L]^4}$$

Metal-ligand complexes with a different number of ligands will have fewer or more equations, but they will follow the same pattern as shown here. In labeling alpha in the worksheet tables, I use a number for the number of ligands, i.e., α_M is alpha0, α_{ML} is alpha1, and so on.

Template tables are set up in the worksheet with ligand concentrations ranging from 1.0E-6 to 1.0 M, e.g.:

A	B	C	D	E	F
27					
28	[L]	log[L]	alpha0	alpha1	alpha2
29	1.0E-06				
30	2.0E-06				
31	4.0E-06				
32	6.0E-06				
33	8.0E-06				
34	1.0E-05				
35	2.0E-05				
36	4.0E-05				
37	6.0E-05				

For plots over many orders of magnitude, the x axis is easier to visualize on a log scale. In cell C29, type:

=log(B29)

Using the K_1 and K_2 values in cells D18 and E18, respectively, the formula for alpha0 is:

    =1/(1+$D$18*$B29+$D$18*$E$18*$B29^2)

Formulas for alpha1 and alpha2 in cells E29 and F29 are similar, with only the numerator changing:

    =$D$18*$B29/(1+$D$18*$B29+$D$18*$E$18*$B29^2)

    =$D$18*$E$18*$B29^2/(1+$D$18*$B29+$D$18*$E$18*$B29^2)

Highlight cells C29 to F29 and double click the small square at lower right of the highlighted area to copy the formulas in the rest of the table. The process is the same for the Cu–NH3 case. Partial results are shown in the next two figures.

	A	B	C	D	E	F
27						
28		[L]	log[L]	alpha0	alpha1	alpha2
29		1.0E-06	-6.00	1.00E+00	1.29E-04	2.00E-09
30		2.0E-06	-5.70	1.00E+00	2.58E-04	7.98E-09
31		4.0E-06	-5.40	9.99E-01	5.15E-04	3.19E-08
32		6.0E-06	-5.22	9.99E-01	7.72E-04	7.18E-08
33		8.0E-06	-5.10	9.99E-01	1.03E-03	1.28E-07
34		1.0E-05	-5.00	9.99E-01	1.29E-03	1.99E-07
35		2.0E-05	-4.70	9.97E-01	2.57E-03	7.96E-07
36		4.0E-05	-4.40	9.95E-01	5.13E-03	3.18E-06
37		6.0E-05	-4.22	9.92E-01	7.67E-03	7.13E-06
38		8.0E-05	-4.10	9.90E-01	1.02E-02	1.26E-05
39		1.0E-04	-4.00	9.87E-01	1.27E-02	1.97E-05
40		2.0E-04	-3.70	9.75E-01	2.51E-02	7.78E-05

	A	B	C	D	E	F	G	H
61								
62		[L]	log[L]	alpha0	alpha1	alpha2	alpha3	alpha4
63		1.0E-06	-6.00	9.82E-01	1.75E-02	4.00E-05	3.91E-08	2.47E-12
64		2.0E-06	-5.70	9.66E-01	3.43E-02	1.57E-04	3.07E-07	3.88E-11
65		4.0E-06	-5.40	9.33E-01	6.64E-02	6.08E-04	2.38E-06	6.00E-10
66		6.0E-06	-5.22	9.02E-01	9.63E-02	1.32E-03	7.76E-06	2.94E-09
67		8.0E-06	-5.10	8.73E-01	1.24E-01	2.28E-03	1.78E-05	8.99E-09
68		1.0E-05	-5.00	8.46E-01	1.50E-01	3.45E-03	3.37E-05	2.13E-08
69		2.0E-05	-4.70	7.29E-01	2.59E-01	1.19E-02	2.32E-04	2.93E-07
70		4.0E-05	-4.40	5.62E-01	4.00E-01	3.66E-02	1.43E-03	3.61E-06
71		6.0E-05	-4.22	4.50E-01	4.80E-01	6.60E-02	3.87E-03	1.46E-05
72		8.0E-05	-4.10	3.70E-01	5.26E-01	9.64E-02	7.54E-03	3.81E-05
73		1.0E-04	-4.00	3.10E-01	5.51E-01	1.26E-01	1.23E-02	7.79E-05
74		2.0E-04	-3.70	1.54E-01	5.46E-01	2.50E-01	4.89E-02	6.17E-04

We can now use these values to plot each alpha versus log[L]. For the Fe/SCN data, highlight cells C29 to F59 and use Insert > Scatter Plot. Do the same for the Cu/NH3 data.

After adjusting the fonts and axes for a cleaner look, I get the following two figures:

Fe^{3+}/SCN$^-$ Distribution Plots

alpha vs. log [L]

Cu^{2+}/NH$_3$ Distribution Plots

alpha vs. log [L]