you-try-it-07.xlsx

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For use with:

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

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.

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 = (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	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.

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 and that the anion does not react with water.
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			
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 − [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				

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		
K_n		

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				
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						

[L]	log[L]	alpha0	alpha1	alpha2	alpha3	alpha4
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						