you-try-it-06.xlsx
Step-by-Step Guide
ver. 7/26/2016

Abstract

This document provides step-by-step instructions for the Excel workbook you-try-it-06.xlsx (saved from Excel 2010). The worksheets contain data for practice exercises keyed to Chapter 6 of:

> *Basics of Analytical Chemistry and Chemical Equilibria* by Brian M. Tissue
> (John Wiley: New York, 2013).

Worksheets in the workbook **page in this guide**

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

10/9/09	First posting.
7/26/2016	Revised formatting.

For updates visit the text support website:

> **http://www.achem.org**

6.A Henderson-Hasselbalch

This worksheet contains a table with solutions containing a weak acid and its conjugate base. The exercise is to predict $p[H_3O^+]$ using the Henderson-Hasselbalch equation and compare to an exact calculation.

Concepts	Concept Synopsis
pH buffer	A solution containing a weak acid and its conjugate base will resist changes in pH.
Henderson-Hasselbalch equation	The Henderson-Hasselbalch equation provides a simple calculation to predict $p[H_3O^+]$. It makes the approximation that the equilibrium concentrations of the weak acid and conjugate base are equal to their formal concentrations: $[HA] = c_{HA}$ and $[A^-] = c_{A-}$.

1. Use the Henderson-Hasselbalch equation to predict the $p[H_3O^+]$ for each buffer solution.
    You may do your calculations assuming that $K_a' = K_a$.

The Henderson-Hasselbalch equation is usually written as:

$$p[H_3O^+] = pK_a' + \log \frac{c_{A-}}{c_{HA}}$$

It is simply a rearrangement of a K_a' expression:

$$K_a' = \frac{[H_3O^+]c_{A-}}{c_{HA}}$$

where the approximations $[HA] = c_{HA}$ and $[A^-] = c_{A-}$ have been included. Either of the above expressions may be used in a calculation.

The worksheet lists several weak acid/base buffers with c_{HA} and c_{A-}. In these cases, $c_{HA} = c_{A-}$ to simplify the comparison of the Henderson-Hasselbalch and exact calculations. The exact calculation of $p[H_3O^+]$ is in column H. The formulas are taken from pH-calculation.xlsx, and do not need to change these formulas.

I will use the K_a' expression, so in cell F21 I type:
        =VLOOKUP(C21,$C$14:$D$16,2,FALSE)

You may simply type the value of K_a' or pK_a' if you wish. I copy this formula down the column for the other cases. In cell G21 I type:

    =-LOG(F21*D21/E21)

I copy this formula down the column and I am done. Note that the Henderson-Hasselbalch calculation gives the same result even when the total concentration of the weak acid/base pair changes by orders of magnitude. Most buffer solutions are made at relatively concentration to have sufficient buffer capacity for a given application. The Henderson-Hasselbalch equation works well for most common buffers. It is not useful to predict $p[H_3O^+]$ for any arbitrary weak acid/base pair. As an extreme example, predict the $p[H_3O^+]$ for an acetic acid/acetate buffer of $c_{HA} = c_{A-} = 0.1 \times 10^{-8}$ M. These concentrations are so low that the buffer system has little effect, and the solution pH will remain near 7.0.

2. Calculate the difference in $p[H_3O^+]$ between the Henderson-Hasselbalch and exact results.
   What factors affect the accuracy of the Henderson-Hasselbalch equation?

For case 1, I type: =H21-G21

I copy this formula down the column and I am done. All of the results are shown in the next figure.

A	B	C	D	E	F	G	H	I
13		weak acid	K_a	pK_a				
14		acetic acid	1.75E-05	4.756				
15		chloroacetic acid	1.36E-03	2.867				
16		dichloroacetic acid	4.47E-02	1.35				
17								
18	Table 6.A.1							
19						H-H Eqn	Exact	Difference
20	case		c_{HA}	c_{A-}	K_a'	$p[H_3O^+]$	$p[H_3O^+]$	$p[H_3O^+]$
21	1	acetic acid	1.000E-01	1.000E-01	1.754E-05	4.76	4.756	0.000
22	2	acetic acid	1.000E-02	1.000E-02	1.754E-05	4.76	4.758	0.002
23	3	acetic acid	1.000E-03	1.000E-03	1.754E-05	4.76	4.771	0.015
24	4	acetic acid	1.000E-04	1.000E-04	1.754E-05	4.76	4.873	0.117
25	5	chloroacetic acid	1.000E-01	1.000E-01	1.358E-03	2.87	2.878	0.011
26	6	chloroacetic acid	1.000E-02	1.000E-02	1.358E-03	2.87	2.962	0.095
27	7	chloroacetic acid	1.000E-03	1.000E-03	1.358E-03	2.87	3.320	0.453
28	8	chloroacetic acid	1.000E-04	1.000E-04	1.358E-03	2.87	4.056	1.189
29	9	dichloroacetic acid	1.000E-01	1.000E-01	4.467E-02	1.35	1.583	0.233
30	10	dichloroacetic acid	1.000E-02	1.000E-02	4.467E-02	1.35	2.142	0.792
31	11	dichloroacetic acid	1.000E-03	1.000E-03	4.467E-02	1.35	3.019	1.669
32	12	dichloroacetic acid	1.000E-04	1.000E-04	4.467E-02	1.35	4.002	2.652

We see that the differences between the Henderson-Hasselbalch and the exact calculation are not great for any concentration of the acetic acid/acetate system. Only at $c_{HA} = c_{A-} = 0.1$ mM do the calculations differ by 0.1 pH units. For the stronger weak acids, the difference is larger. This difference results because the approximations that $[H_3O^+]$ can be neglected compared to c_{HA} and c_{A-} is no longer valid.

6.B polyprotic-acid

This worksheet contains a table listing solutions containing polyprotic acids in various forms.

Concepts	Concept Synopsis
polyprotic acids	A species that can have more than one acidic proton.
p[H$_3$O$^+$] calculations for polyprotic acids	There are four cases that we encounter with polyprotic acids. Solutions of: • the fully protonated acid • the fully deprotonated base • a buffer solution (mixture of weak acid and conjugate base) • an amphiprotic species The calculation of p[H$_3$O$^+$] is different for each case.

1. Predict the p[H$_3$O$^+$] for each solution.
   You may do your calculations assuming that $K_a' = K_a$.
   You may use the Henderson-Hasselbalch equation for buffer solutions.

The first step to do these calculations is to identify the nature of the species. Below Table 6.B.1 I start a new table and identify the nature of each case. I set up the table for the different types of calculations as shown in the next figure. I enter concentrations in columns D and E as needed. In column F I enter or copy the K_a', K_b', or pK_a' for acid, base, or buffer calculations, respectively. In column G I enter the second pK_a' needed for the amphiprotic cases.

	B	C	D	E	F	G	H	I	J
22	Table 6.B.1								
23	case								
24	1	0.01 M phthalic acid							
25	2	0.01 M sodium hydrogen phthalate							
26	3	0.01 M disodium phthalate							
27	4	0.03 M phosphoric acid, 0.01 M sodium dihydrogen phosphate							
28	5	0.01 M disodium hydrogen phosphate							
29	6	0.01 M sodium dihydrogen phosphate, 0.005 M disodium hydrogen phosphate							

	B	C	D	E	F	G	H	I	J
32					K_a', K_b', or				
33	case	calc. type	c_{HA}	c_{A-}	pK_a'	pK_{a2}'	$[H_3O^+]$	$[OH^-]$	$p[H_3O^+]$
34	1	weak acid	0.01		0.001122				
35	2	amphiprotic			2.950	5.408			
36	3	weak base		0.01	2.584E-09				
37	4	buffer	0.03	0.01	2.148				
38	5	amphiprotic			7.198	12.32			
39	6	buffer	0.01	0.005	12.32				

For example for case 1, a solution of phthalic acid, I need the acid concentration and the K_a'. In cell D34 I type 0.01 and in F34 I type:

=H14

Similarly for case 2, I copy in cells F35 and G35:

=I14   and   =I15

Continuing with case 1, in cell H34 I type a formula for the quadratic equation (see worksheet '5.5 equilibrium-calculation' or you-try-it05guide.pdf for an example):

=(-F34+SQRT(F34^2+4*D34*F34))/2

The last step is to take the –log. In cell J34 I type:

=-log (H34)

Case 3 is a similar calculation, except solving for $[OH^-]$ using K_b'. The last step in cell J36 is:

=14+LOG(I36)

Cases 2 and 5 are amphiprotic species. This calculation is $0.5(pK_{a1}' + pK_{a2}')$, i.e., the average of the pK_a' values that bracket the amphiprotic species. For case 2 the formula that I enter in cell J35 is:

=0.5*(F35+G35)

Note that there is no dependence on concentration. As with the Henderson-Hasselbalch equation, we must use some judgement to evaluate if a result makes sense. A very low concentration of an amphiprotic species will not produce the predicted $p[H_3O^+]$ if $[H_3O^+]$ is on the order of 10^{-7} M.

Case 4 and 6 are buffer solutions so I will use the Henderson-Hasselbalch equation. For case 4 I type in cell J37:

        =F37+LOG(E37/D37)

The final results are shown in the next figure.

				$K_a', K_b',$ or				
case	calc. type	c_{HA}	c_{A^-}	pK_a'	pK_{a2}'	$[H_3O^+]$	$[OH^-]$	$p[H_3O^+]$
1	weak acid	0.01		0.001122		2.84E-03		2.55
2	amphiprotic			2.950	5.408			4.18
3	weak base		0.01	2.584E-09			5.08E-06	8.71
4	buffer	0.03	0.01	2.148				1.67
5	amphiprotic			7.198	12.32			9.76
6	buffer	0.01	0.005	12.32				12.02

6.C polyprotic-buffer

Table 6.C.1 on this worksheet contains a list of desired buffer solutions and the available starting material. Use the Henderson-Hasselbalch equation to determine the ratio of the base and acid necessary for a given pH. From this ratio you can determine the amount of the acid and base, and then give a procedure to obtain that ratio from the starting material.

Concepts	Concept Synopsis
Preparing buffer solutions	To obtain a conjugate weak acid/base pair: • mix a weak acid and its conjugate base • add strong base to a weak acid • add strong acid to a weak base

1. Give a procedure to prepare 1.0 L of the listed buffer from the starting material. You may use the Henderson-Hasselbalch equation assuming that $K_a' = K_a$.

Repeating the Henderson-Hasselbalch equation from worksheet 6.A:

$$p[H_3O^+] = pK_a' + \log \frac{c_{A-}}{c_{HA}}$$

We select a suitable acid/base system so that the pK_a' is within one pH unit of the desired $p[H_3O^+]$. Inserting the desired $p[H_3O^+]$ and the pK_a' of the buffer in the Henderson-Hasselbalch equation, we can calculate the necessary ratio of the base to acid.

$$\frac{c_{A-}}{c_{HA}} = 10\text{^}(p[H_3O^+] - pK_a')$$

This ratio still has two unknowns, but we also know the total concentration of the acid and base:

$$c_{HA} + c_{A-} = c_{total}$$

We can use these two equations to solve for both c_{HA} and c_{A-}. Illustrating with case 1, we want a buffer at pH = 3.0. The suitable phosphate forms are H_3PO_4 and $H_2PO_4^-$, which has $pK_a' = 2.15$.

$$\frac{c_{A-}}{c_{HA}} = 10^{(3.0-2.15)} = 7.08$$

Since we also know:

$$c_{HA} + c_{A-} = 0.10 \text{ M}$$

We can combine these two equations to solve:

$$c_{HA} + 7.08 c_{HA} = 0.10 \text{ M}$$
$$c_{HA} = 0.0124 \text{ M}$$

Subtracting this result from the total gives:

$$c_{A-} = 0.10 \text{ M} - 0.0124 \text{ M} = 0.876 \text{ M}$$

Given that we were starting with 0.10 mol of $H_2PO_4^-$ (0.5 L of 0.2 M NaH_2PO_4), the procedure to prepare the pH=3.0 buffer is to add 0.0124 mol of strong acid. For 0.5 M HCl:

$V = 0.0124 \text{ mol}/0.5 \text{ M} = 0.0248 \text{ L or } 24.8 \text{ mL}$

For Excel I begin a new table and copy the desired $p[H_3O^+]$ and pK_a' for each case. For case 1 these are in cells C29 and D29, respectively. I type in cell E29 the rearranged Henderson-Hasselbalch equation to find the base to acid ratio:

=10^(C29-D29)

For the total phosphate concentration being in cell F21, the concentration of the acid in cell F29 is given by:

=F21/(1+E29)

Subtracting the acid concentration from the total gives the base concentration in cell G29:

=F21-F29

Highlight cells E29:G29 and copying down for the other cases results in the next figure.

	A	B	C	D	E	F	G	H
12					formula	f.w. (g/mol)	K_a	pK_a
13		phosphoric acid			H_3PO_4	98.00	7.11E-03	2.148
14		sodium dihydrogen phosphate			NaH_2PO_4	119.98	6.34E-08	7.198
15		disodium hydrogen phosphate			Na_2HPO_4	141.96	4.79E-13	12.32
16		trisodium phosphate			Na_3PO_4	163.94		
17								
18		Table 6.C.1						
19						total	desired	
20		case	starting material			$c_{phosphate}$	$p[H_3O^+]$	
21		1	0.5 L of 0.2 M sodium dihydrogen phosphate			0.10	3.0	
22		2	0.5 L of 0.2 M sodium dihydrogen phosphate			0.10	6.5	
23		3	trisodium phosphate			0.20	11.5	
24		4	trisodium phosphate			0.20	7.4	
25								
26								
27			desired					
28		case	$p[H_3O^+]$	pK_a	c_{base}/c_{acid}	c_{acid}	c_{base}	
29		1	3.0	2.15	7.11	0.012	0.088	
30		2	6.5	7.20	0.20	0.083	0.017	
31		3	11.5	12.32	0.15	0.174	0.026	
32		4	7.4	7.20	1.59	0.077	0.123	

At this point, the preparation of each buffer depends on the specific starting materials, and it is as easy to work out the procedure on paper as to write formulas. Since we have 1.0 L of solution, the concentrations are equal to the moles of each species that we need.

case	desired p[H_3O^+]	final mol H_3PO_4	final mol $H_2PO_4^-$	final mol HPO_4^{2-}	final mol PO_4^{3-}	
1	3.0	0.012	0.088			
2	6.5		0.083	0.017		
3	11.5			0.174	0.026	
4	7.4		0.077	0.123		

case	starting	reagent to add	mol reagent	
1	0.10 mol $H_2PO_4^-$	HCl	0.012	24 mL 0.5 M HCl
2	0.10 mol $H_2PO_4^-$	NaOH	0.017	34 mL 0.5 M NaOH
3	0.20 mol PO_4^{3-}	HCl	0.174	348 mL 0.5 M HCl
4	0.20 mol PO_4^{3-}	HCl	0.20 + 0.077	554 mL 0.5 M HCl

For cases 3 and 4 the weight of Na_3PO_4 for 0.20 mol is: (0.20 mol)(163.94 g/mol) = 32.79 g.

The final procedures are:

case 1: Add 24 mL of 0.5 M HCl to 0.5 L of 0.2 M NaH_2PO_4 and dilute to 1.0 L.
case 2: Add 34 mL of 0.5 M NaOH to 0.5 L of 0.2 M NaH_2PO_4 and dilute to 1.0 L.
case 3: dissolve 32.79 g Na_3PO_4 in 348 mL of 0.5 M HCl and dilute to 1.0 L.
case 4: dissolve 32.79 g Na_3PO_4 in 554 mL of 0.5 M HCl and dilute to 1.0 L.

6.D carbonic-acid

This worksheet contains a table of solutions to calculate ionic strength. For two cases the activity coefficients are calculated for the reactants and products of the equilibrium reaction.

Concepts	Concept Synopsis
alpha fraction	All forms of a polyprotic acid will exist in solution, although some forms will be of neglible concentration at a given pH. The alpha fraction is the concentration of one form divided by the total concentration of the polyprotic species.

1. For each solution calculate the fraction of total carbonate that exists as CO_3^{2-}. Use this fraction to calculate the equilibrium concentration, $[CO_3^{2-}]$. Do the calculations using K_a and K_a' values.

The alpha fraction for the fully deprotonated form of a diprotic acid is:

$$\alpha_{CO3} = \frac{K_{a1}'K_{a2}'}{[H_3O^+]^2 + [H_3O^+]K_{a1}'K_{a2}' + K_{a1}'K_{a2}'}$$

To set up the calculation so that I will not need to revise my formula, I copy the information given in the worksheet to a new table as shown in the next figure.

◢ A	B	C	D	E	F	G	H	I
23								
24			total					
25	case		$c_{carbonate}$ (M)	$[H_3O^+]$	K_{a1}'	K_{a2}'	alpha	$[CO_3^{2-}]$
26	1	pre-1800	2.2E-03	6.3E-09	4.45E-07	4.69E-11		
27	2	2000	2.2E-03	7.9E-09	4.45E-07	4.69E-11		
28	3	2100	2.2E-03	1.6E-08	4.45E-07	4.69E-11		
29	1	pre-1800	2.2E-03	6.3E-09	1.45E-06	1.10E-09		
30	2	2000	2.2E-03	7.9E-09	1.45E-06	1.10E-09		
31	3	2100	2.2E-03	1.6E-08	1.45E-06	1.10E-09		

Using case 1 as an example, the Excel formula that I typed in cell H26 for the alpha fraction calculation is:

        =(F26*G26)/(E26^2+E26*F26+F26*G26)

Convert the listed p to $[H_3O^+]$ using $[H_3O^+] = 10^{-p[H3O+]}$.

Given that the definition of the alpha fraction is the equilibrium concentration, $[CO_3^{2-}]$, divided by the total concentration of all forms of carbonate:

$$\alpha_{CO3} = \frac{[CO_3^{2-}]}{c_{carbonate}}$$

$$[CO_3^{2-}] = (\alpha_{CO3})(c_{carbonate})$$

For case 1 I type in cell I26:

=H26*D26

These formulas will be correct for all cases, so I copy them down columns H and I. The final results are:

	B	C	D total	E	F	G	H	I
	case		$c_{carbonate}$ (M)	$[H_3O^+]$	K_{a1}'	K_{a2}'	alpha	$[CO_3^{2-}]$
26	1	pre-1800	2.2E-03	6.3E-09	4.45E-07	4.69E-11	7.3E-03	1.60E-05
27	2	2000	2.2E-03	7.9E-09	4.45E-07	4.69E-11	5.8E-03	1.27E-05
28	3	2100	2.2E-03	1.6E-08	4.45E-07	4.69E-11	2.8E-03	6.27E-06
29	1	pre-1800	2.2E-03	6.3E-09	1.45E-06	1.10E-09	1.5E-01	3.25E-04
30	2	2000	2.2E-03	7.9E-09	1.45E-06	1.10E-09	1.2E-01	2.66E-04
31	3	2100	2.2E-03	1.6E-08	1.45E-06	1.10E-09	6.4E-02	1.41E-04

Note that the results are quite sensitive to the K_a values. The difference in $[CO_3^{2-}]$ using the measured K_a' values (rows 29-31) versus the thermodynamic K_a values (rows 26-28) is a factor of approximately 20. Using the measured K_a' values much more closely replicate measured values of $[CO_3^{2-}]$, e.g., 152±24 µmol kg^{-1} (K. K. Yates and R. B. Halley, "CO_3^{2-} concentration and pCO$_2$ thresholds for calcification and dissolution on the Molokai reef flat, Hawaii," *Biogeosciences*, **2006**, *3*, 357–369).