

Supporting Information

Is Your Henderson-Hasselbalch Calculation of Buffer pH Correct?

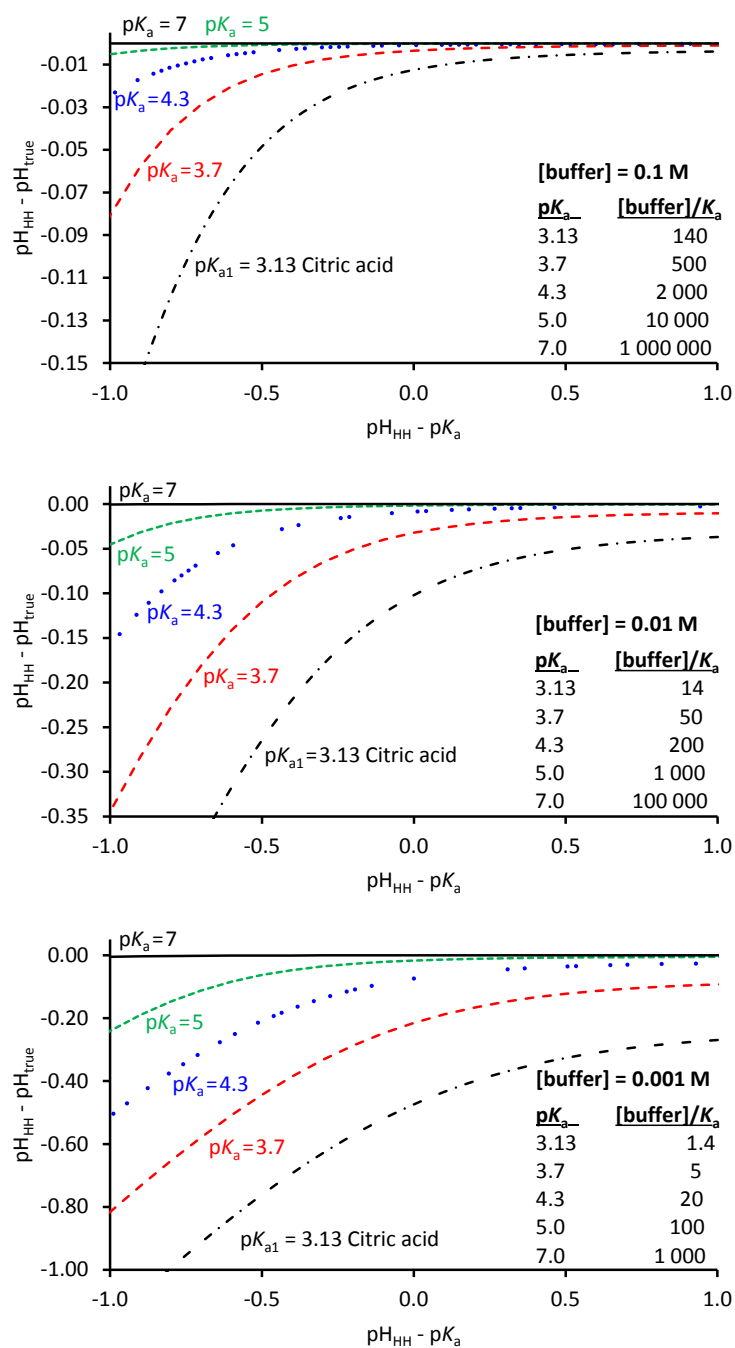
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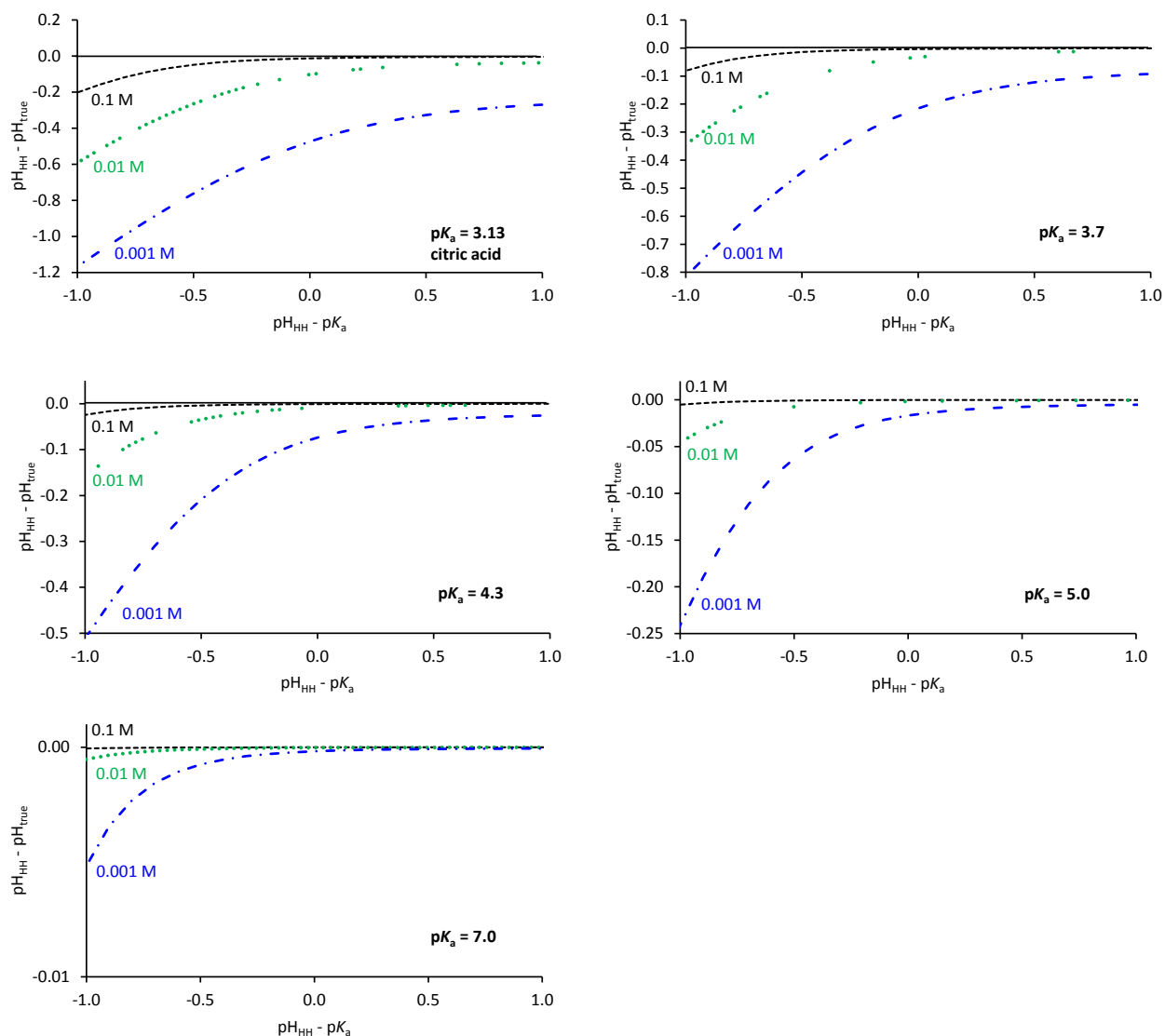
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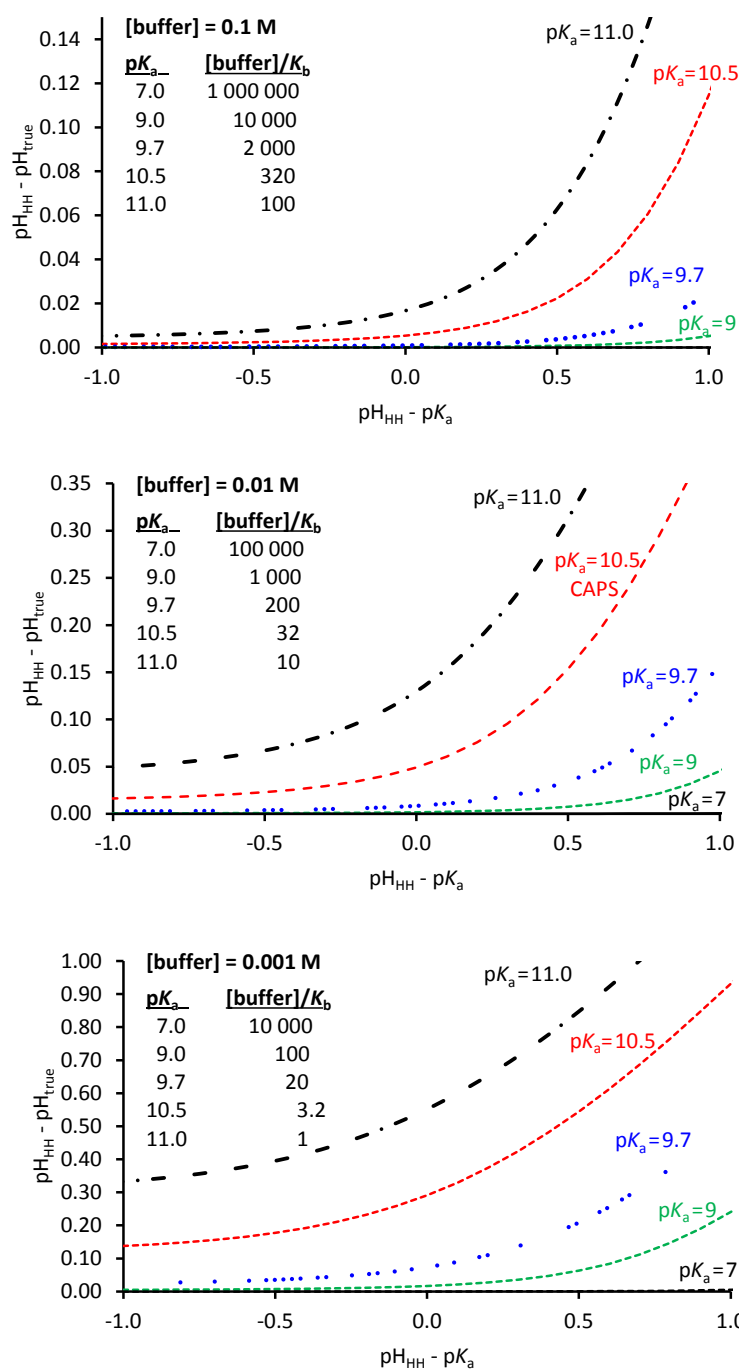
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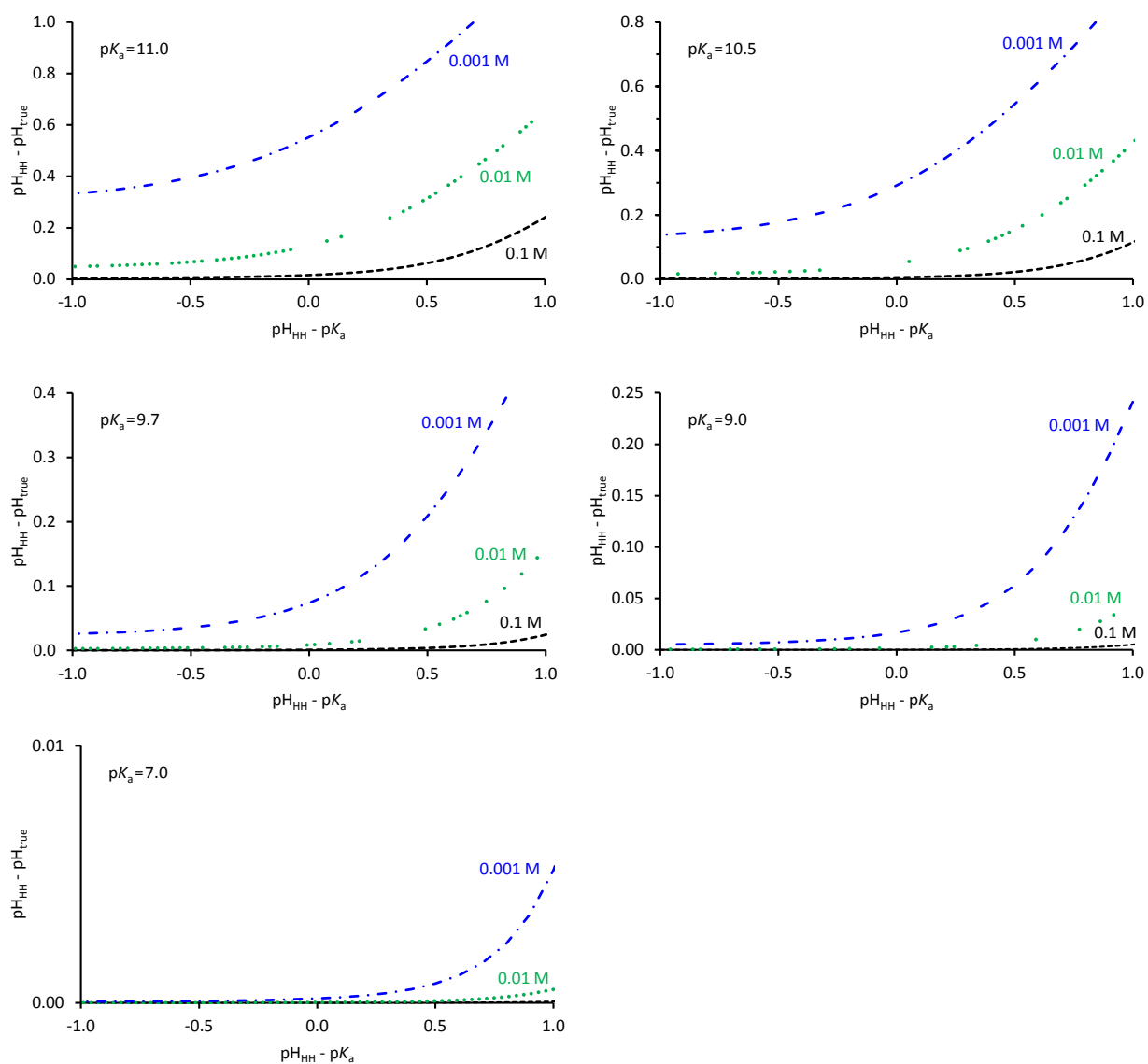
Supplementary Figure S1. Error in pH calculated for acidic ($pK_a \leq 7$) across the buffering range using the Henderson-Hasselbalch approximation (Equation 8) versus the correctly calculated pH (Equation 11) for 0.1, 0.01 and 0.001 M solutions. The 0.01 M buffer figure (Figure 1) is reproduced here for comparison.



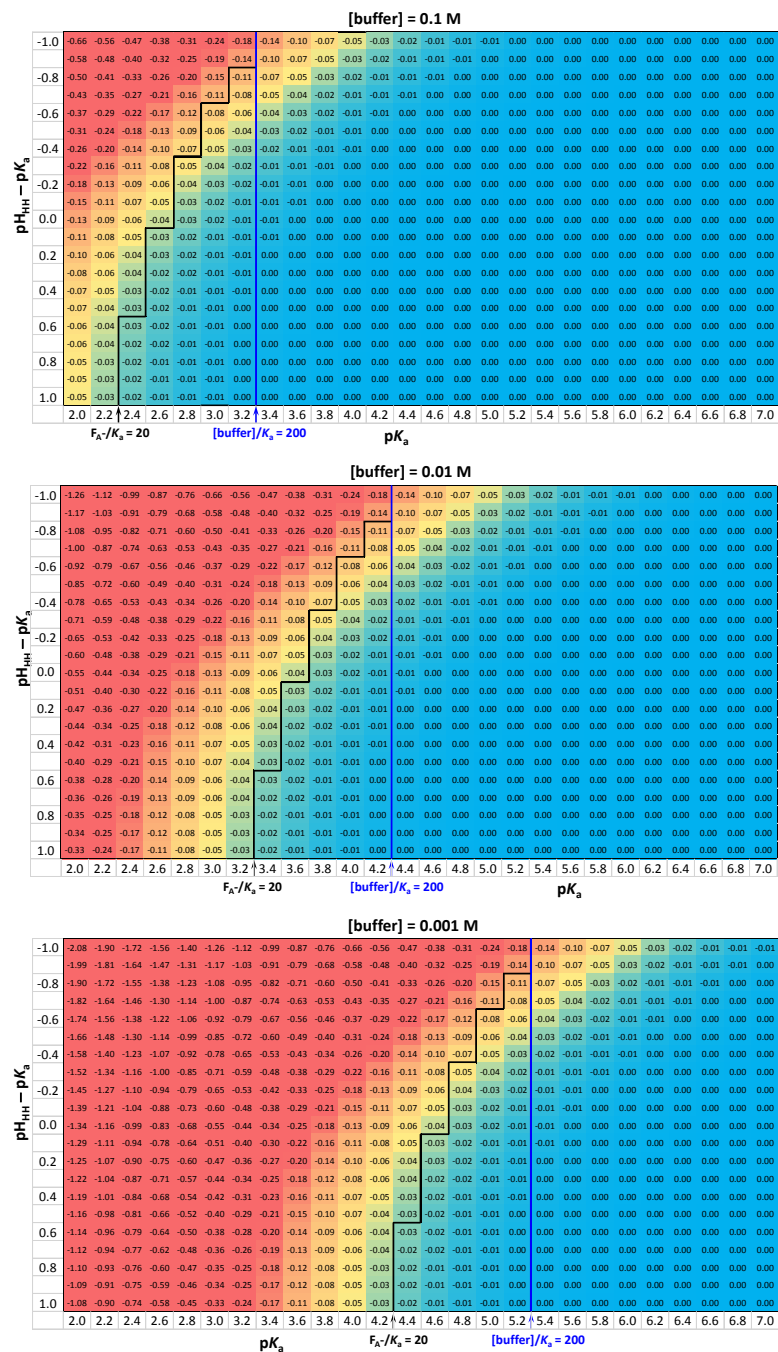
Supplementary Figure S2. Error in pH calculated for acidic ($\text{pK}_a \leq 7$) buffers across the buffering range using the Henderson-Hasselbalch approximation (Equation 8) versus the correctly calculated pH (Equation 11) for 0.1, 0.01 and 0.001 M solutions.



Supplementary Figure S3. Error in pH calculated for alkaline ($pK_a \leq 7$) buffers across the buffering range using the Henderson-Hasselbalch approximation (Equation 8) versus the correctly calculated pH (Equation 13) for 0.1, 0.01 and 0.001 M solutions. The 0.01 M buffer figure (Figure 2) is reproduced here for comparison.



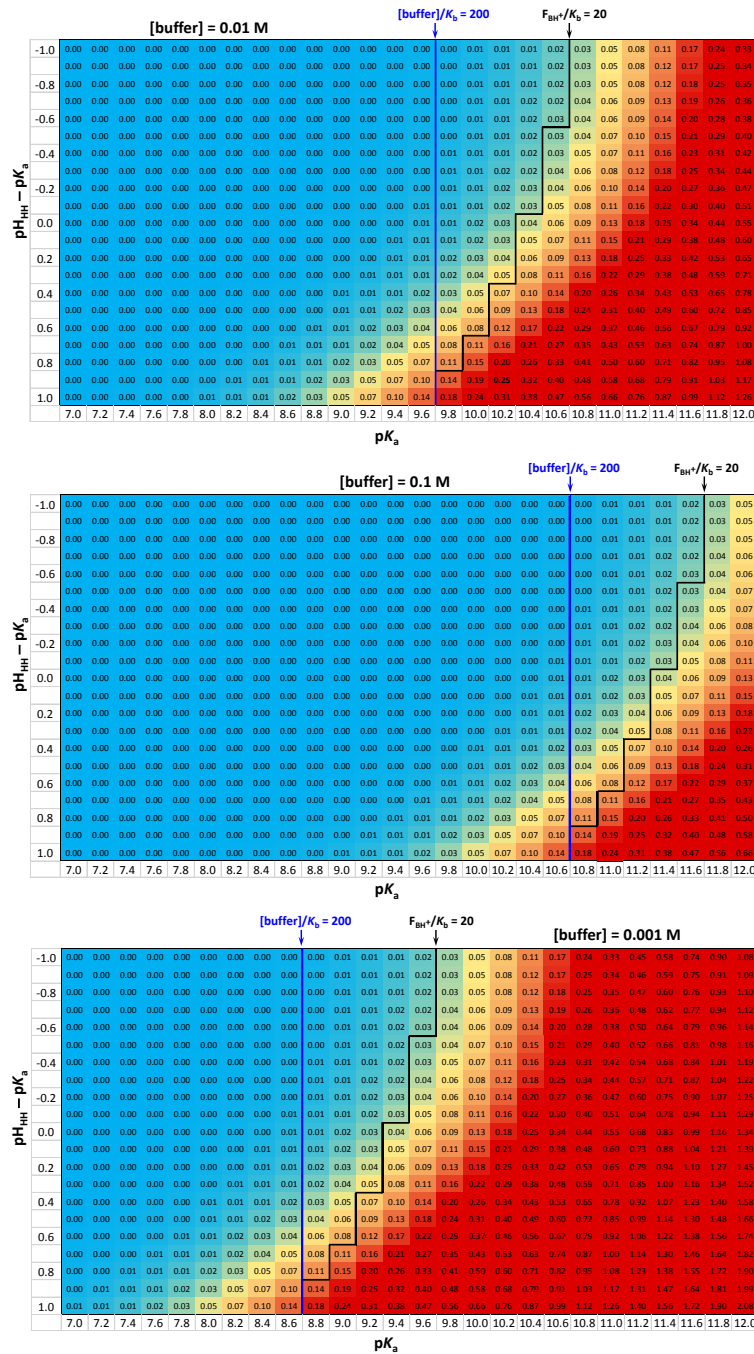
Supplementary Figure S4. Error in pH calculated for alkaline ($\text{pK}_a > \leq$) buffers across the buffering range using the Henderson-Hasselbalch approximation (Equation 8) versus the correctly calculated pH (Equation 13) for 0.1, 0.01 and 0.001 M solutions.



Supplementary Figure S5. Heat map of error in pH calculated for acidic ($pK_a \leq 7$) buffers across the

buffering range if the Henderson-Hasselbalch approximation (Equation 8) is used. Color scale: $|\text{error}| > 0.20$

is red; > 0.05 is yellow; and < 0.05 is blue. The 0.01 M heat map is the same as Figure 3.



Supplementary Figure S6. Heat map of error in pH calculated for alkaline ($pK_a \geq 7$) buffers across the

buffering range if the Henderson-Hasselbalch approximation (Equation 8) is used. Color scale: $|\text{error}| > 0.20$

is red; > 0.05 is yellow; and < 0.05 is blue.

Table S1. Validation of Equations 11 and 13^a

Buffer	F _{HA} or F _{BH⁺} (M)	F _{A⁻} or F _B (M)	pK _a	pH (Eq. 11 or 13) ^b	pH by GoalSeek ^c	“pH” by CurTiPot ^a	pH by CurTiPot ^a (with activity)
Phosphate (pK _{a1})	0.050 0	0.050 0	2.148 (pK _{a1})	2.247	2.247	2.247	2.193
Chloroacetate	0.030 0	0.010 0	2.865	2.541	2.541	2.541	2.504
Citrate (pK _{a1})	0.017 5	0.002 5	3.128 (pK _{a1})	2.632	2.632	2.627	2.610
Acetate	0.004 0	0.001 0	4.757	4.189 (11) 4.155 (13)	4.189	4.189	4.125
Phosphate (pK _{a2})	0.000 1	0.000 9	7.199	8.147 (13) 8.153 (11)	8.147	8.146	7.916
Ammonia	0.000 3	0.002 7	9.244	10.044 (13) 10.198 (11)	10.044	10.043	10.080
CAPS	0.002 0	0.008 0	10.50	10.908	10.908	10.907	10.828

- pK_a and right most columns from CurTiPot_xlsm (). Value reported is “pH” (cell B25) which is uncorrected for the activity coefficient. Cell B23 provides the pH including activity effects.
- Normal font indicates Equation 11 was used; italic font indicates Equation 13 was used.
- D. C. Harris and C. A. Lucy, *Quantitative Chemical Analysis*, 10th edition, 2020, W. H. Freeman and Company. Page 212 shows use of Excel’s GoalSeek function.

Python Script for pH Calculation

(Provided by Dr. Shuai Sun, Department of Chemistry, Kansas University, Nov. 23, 2023.)

Copy the script in pH_calculation.py using any regular text editor and paste the script to an online Python compiler, such as <https://www.programiz.com/python-programming/online-compiler/> or <https://www.online-python.com/> (tested Nov. 25, 2022).

Once you run the script, it will ask you to input the pK_a and formal concentrations, and then provide the pH based on Equation 11 for acidic buffers or Equation 13 for alkaline buffers, the pH calculated by the Henderson-Hasselbalch approximation, and the magnitude of $[H^+]$ or versus HA and A^- or $[OH^-]$ versus $[BH^+]$ and $[B]$.

Script

```
# Online Python compiler (interpreter) to run Python online.
# Write Python 3 code in this online editor and run it.
import math
pKa = float(input("What is the value of pKa? "))
Ka = 10**(-pKa)
Kw = 10**(-14)
if pKa < 7:
    HA = float(input("What is the formal concentration of HA? "))
    A = float(input("What is the formal concentration of A-? "))
    T = HA + A
    pH = -math.log10((-A-Ka+math.sqrt((A+Ka)**2+4*(HA*Ka)))/2)
    pHHH = pKa + math.log10(A/HA)
    HHH = 10**(-pHHH)
    print ("True pH =", round(pH, 2))
    print ("Henderson-Hasselbalch approximation pH =", round(pHHH, 2))
    print ("[H+]_HH/F_HA =", round(HHH*100/HA, 1), "%")
    print ("[H+]_HH/F_A- =", round(HHH*100/A, 1), "%")
else:
    BH = float(input("What is the formal concentration of BH+? "))
    B = float(input("What is the formal concentration of B? "))
    T = BH + B
    pH = -math.log10((BH*Ka+Kw+math.sqrt((BH*Ka+Kw)**2+4*(B*Ka*Kw)))/(2*B))
    pHHH = pKa + math.log10(B/BH)
    HHH = 10**(pHHH-14.0)
    print ("True pH =", round(pH, 2))
    print ("Henderson-Hasselbalch approximation pH =", round(pHHH, 2))
    print ("[H+]_HH/F_HA =", round(HHH*100/BH, 1), "%")
    print ("[H+]_HH/F_A- =", round(HHH*100/B, 1), "%")
```

Example input and output for 0.0175/0.0025 M citrate buffer:

What is the value of pKa?3.128

What is the formal concentration of HA?0.0175

What is the formal concentration of A-?0.0025

True pH = 2.63

Henderson-Hasselbalch approximation pH = 2.28

[H+]_{HH/F_HA} = 29.8 %

[H+]_{HH/F_A-} = 208.5 %