

Solutions to pH and Buffers Problem Set

1. Here I will provide answers for the $pK_a = 6.5$ example only

(a) For this problem, as well as for problems (b) and (c), it is convenient to use the Henderson-Hasselbalch equation:

$$pH = pK_a + \log([A^-]/[HA]) = pK_a = 6.5$$

because when $[A^-] = [HA]$, $\log([A^-]/[HA]) = \log 1 = 0$.

(b) now $\log([A^-]/[HA]) = \log 10 = 1$, $\rightarrow pH = pK_a + 1 = 7.5$

(c) now $\log([A^-]/[HA]) = \log 0.1 = -1$, $\rightarrow pH = pK_a - 1 = 5.5$;

(d) here we can use the following equation: $\frac{[A^-]}{[HA]} = 10^{pH-pK_a}$

pH	pH - pKa	[A ⁻]/[HA]
4.5	-2	1/100
5.5	-1	1/10
6.5	0	1/1
7.5	1	10/1
8.5	2	100/1

2. It is convenient to use the same equation as in Problem 1(d).

(a) when $pH = pK_a$, $10^{pH-pK_a} = 10^0 = 1$, \rightarrow the molar concentrations of acid and conjugate base are equal

(b) when the pH is less than the pK_a , $pH-pK_a < 0$, hence $[A^-]/[HA] = 10^{pH-pK_a} < 1 \rightarrow$ HA is the predominant species

(c) when the pH is higher than the pK_a , $pH-pK_a > 0$, hence $[A^-]/[HA] = 10^{pH-pK_a} > 1 \rightarrow A^-$ is the predominant species

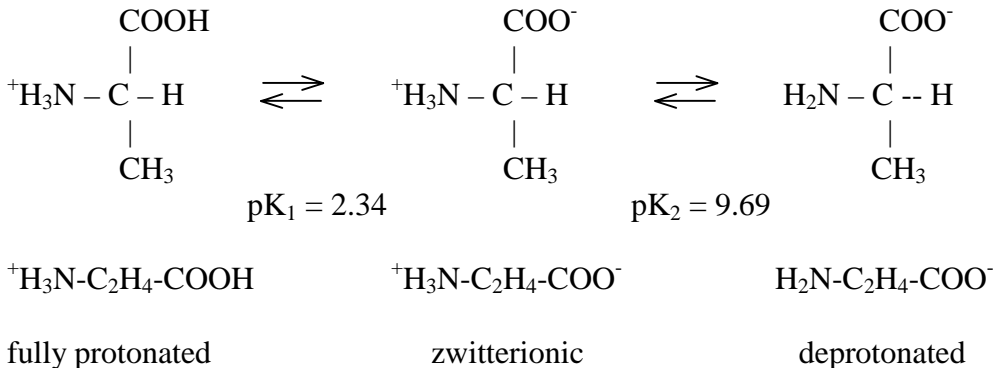
(d) When the pH is 1.0 pH unit above the pK_a , $pH-pK_a = 1$, $[A^-]/[HA] = 10$, \rightarrow the ratio of [HA] to $[A^-]$ is 1/10;

when the pH is 1.0 pH unit below the pK_a , $pH-pK_a = -1$, $[A^-]/[HA] = 10^{-1} = 1/10$, \rightarrow the ratio of [HA] to $[A^-]$ is 10/1;

(e) Likewise, when the pH is 2.0 pH units above the pK_a , $pH-pK_a = 2$, $[A^-]/[HA] = 10^2 = 100$, and the ratio of [HA] to $[A^-]$ is 1/100;

when the pH is 2.0 pH units below the pK_a , $pH-pK_a = -2$, $[A^-]/[HA] = 10^{-2} = 1/100$, and the ratio of [HA] to $[A^-]$ is 100/1;

3. (a)



(b) The relative concentrations of all three forms of alanine are controlled by the two equilibrium equations:

$$[\text{H}_2\text{N}-\text{C}_2\text{H}_4-\text{COO}^-]/[\text{H}_3\text{N}-\text{C}_2\text{H}_4-\text{COOH}] = 10^{\text{pH}-\text{pK}_1} \quad [\text{a}]$$

$$[\text{H}_2\text{N}-\text{C}_2\text{H}_4-\text{COO}^-]/[\text{H}_3\text{N}-\text{C}_2\text{H}_4-\text{COO}^-] = 10^{\text{pH}-\text{pK}_2} \quad [\text{b}]$$

You can use these equations to calculate the ratios of the various forms for the particular values of pH and pK_a's.

However, the answers to these problems can be obtained from a simple qualitative analysis, as follows:

(1) pH = 1.0 is smaller than both pK₁ and pK₂, so ⁺H₃N-C₂H₄-COOH is the predominant form. Indeed, because pH < pK₁, the concentration of the fully protonated form, ⁺H₃N-C₂H₄-COOH, is greater than that of its conjugate base, ⁺H₃N-C₂H₄-COO⁻. The concentration of H₂N-C₂H₄-COO⁻ (a conjugate base for the zwitterionic form) is even smaller (practically negligible!) than that of ⁺H₃N-C₂H₄-COO⁻ because the pH is lower than the pK_a (pK₂) for the equilibrium between these two forms.

(2) Since 6.2 > pK₁, the concentration of the zwitterionic form is greater than that of the fully protonated form (its conjugate acid). Since 6.2 < pK₂, the concentration of the zwitterionic form is also greater than that for its conjugate base, H₂N-C₂H₄-COO⁻.

(3) Since pK₁ < 8.02 < pK₂, the answer is same as in Problem 3(2): the zwitterionic form is predominant.

(4) pH 11.9 is higher than both pK_a's. This means that the concentration of the deprotonated form (H₂N-C₂H₄-COO⁻) is significantly greater than the concentration of the zwitterionic form (11.9 exceeds pK₂ by more than 2.0 pH units). The concentration of the fully protonated form is practically negligible

(compare $pK_1 = 2.34$ with $pH = 11.9!$). Therefore, the deprotonated form is predominant at this pH.

(c) Let the total concentration of Ala be c and let x denote the fraction of Ala in the zwitterionic form at $pH = pI$. Recall that $pI = (pK_1 + pK_2)/2$. From equation [a] (see above) the concentration of the fully protonated form is then

$$[{}^+H_3N-C_2H_4-COOH] = x/10^{pH-pK_1} = x/10^{3.675} = x/4732.$$

The concentration of the deprotonated form can be determined from equation [b] as

$$[H_2N-C_2H_4-COO^-] = x \cdot 10^{pH-pK_2} = x \cdot 10^{-3.675} = x/4732.$$

From the 'matter conservation' principle, the total concentration of Ala is the sum of the concentrations of all three forms (we neglect the uncharged form):

$$[{}^+H_3N-C_2H_4-COOH] + [{}^+H_3N-C_2H_4-COO^-] + [H_2N-C_2H_4-COO^-] = c$$

or using the above relationships:

$$x/4732 + x + x/4732 = c \quad \text{which leads to } x(1 + 2/4732) = c$$

The fraction of Ala in the zwitterionic form is then $x/c = 0.9996$, or 99.96%.

4. $pH = 2.0$ corresponds to $[H^+] = 10^{-2}$ M. When 1M HCl contains 1M H^+ and 1M Cl^- . This means that in order to make 10^{-2} M H^+ , the original 1M HCl has to be diluted 100 fold. Since we are adding HCl to 250 mL of water, a 100-fold dilution will be achieved if we take $250\text{mL}/100 = 2.5$ mL of 1M HCl.

The OH^- concentration in pure water is $[OH^-] = 10^{-7}$ M; at $pH=2$ (i.e. $[H^+] = 10^{-2}$ M) it can be calculated from the ion product of water: $[OH^-] = 10^{-14}M^2/[H^+] = 10^{-12}$ M.

Now assume we added 2.5 mL 1M NaOH instead of HCl. This amounts to 0.01 M concentration of NaOH, which then provides 0.01 M OH^- . The H^+ concentration can be calculated from the ion product of water: $[H^+] = 10^{-14}M^2/10^{-2}M = 10^{-12}$ M, hence the $pH = 12.0$.

5.

(a) $[OAc^-] = [HOAc] = 0.1M$; from the Henderson-Hasselbalch equation: $pH = pK_a = 4.76$ (because $\log([OAc^-]/[HOAc]) = \log 1 = 0$). $[H^+] = 10^{-pH}$ M = $1.74 \cdot 10^{-5}$ M

(b) 0.01 M HCl will dissociate completely into 0.01M H^+ and 0.01M Cl^- ; 0.01M H^+ will essentially completely react with the base OAc^- to form an acid, HOAc. As a result, the concentration of OAc^- will decrease by 0.01M to 0.09M; the concentration of the acid will increase to 0.11 M.

The Henderson-Hasselbalch equation then gives: $pH = pK_a + \log(0.09/0.11) = 4.67$, a very small change in pH!

$$[H^+] = 10^{-pH}$$
 M = $2.12 \cdot 10^{-5}$ M.

(c) Initial conditions: $[OAc^-]/[HOAc] = 0.02/0.18=1/9$; the Henderson-Hasselbalch equation gives: $pH = pK_a + \log(1/9) = 3.81$, and $[H^+] = 1.56 \cdot 10^{-4}$ M; $pH = 3.81$.

After 0.01 M HCl has been added: $[OAc^-]$ will decrease to 0.01M, $[HOAc]$ will increase to 0.19 M, so that $pH = pK_a + \log(1/19) = 3.48$; and $[H^+] = 3.3 \cdot 10^{-4}$ M. Still small change in the pH.

(d) Initial conditions: $[OAc^-]/[HOAc] = 0.18/0.02=9/1$; $pH = pK_a + \log(9/1) = 5.71$; $[H^+] = 1.93 \cdot 10^{-6}M$.

After 0.01 M HCl has been added: $[OAc^-]$ will decrease to 0.17M, $[HOAc]$ will increase to 0.03 M, so that $pH = pK_a + \log(0.17/0.03) = 5.51$; and $[H^+] = 3.3 \cdot 10^{-4}M$. → A small change in the pH: there was enough base to resist the addition of this amount of HCl..

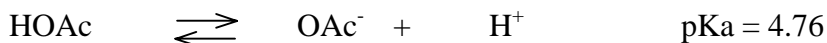
(e) The initial concentrations of protons and the pH are same. The added 0.15M HCl is completely ionized, which results in 0.15M H^+ .

(b) 0.1M H^+ will react with the base, the remaining 0.05M H^+ will determine the pH: $[H^+] = 0.05M$; $pH = 1.30$. The solution became very acidic!

(c) Similarly, only 0.02 M H^+ could be neutralized by the available amount of OAc^- , the remaining 0.13 M H^+ will lower the pH to $pH = 0.89$, resulting in a very acidic solution.

(d) Now there is enough base to completely neutralize 0.15M H^+ , thus making additional 0.15M of HOAc. The remaining concentration of OAc^- is 0.03 M: $[OAc^-]/[HOAc] = 0.03/0.17 = 3/17$; hence $pH = 4.76 + \log(3/17) = 4.01$; $[H^+] = 9.85 \cdot 10^{-5} M$: this solution.

6. (1) Let us first calculate the pH for 1M acetate buffer.



The concentration of H^+ ions before the acid was added was $[H^+] = 10^{-7} M$. The total acetate concentration added to the solution is 1.0 M. Let x be the total number of moles HOAc per liter that dissociated into H^+ and OAc^- ; the final concentration of HOAc is then $[HOAc] = 1M - x$.

Since the dissociation of each molecule of HOAc releases one acetate ion and one hydrogen ion, the final concentration of OAc^- will be $[OAc^-] = x$; and the increase in the concentration of H^+ will also be x , so that the final concentration of protons is now $[H^+] = 10^{-7}M + x$.

Now we can plug all this into the equilibrium equation (Equation [1]):

$$K_a = \frac{[H^+][OAc^-]}{[HOAc]} = \frac{(10^{-7} + x)x}{1 - x}$$

Here, for simplicity, I dropped the 'molar' units assuming that x is also expressed in M, as well as K_a . After some algebra we get: $x^2 + x(10^{-7} + K_a) - K_a = 0$;

Solving this equation for x gives:

$$x = \frac{-(10^{-7} + K_a) + \sqrt{(10^{-7} + K_a)^2 + 4K_a}}{2}$$

We can now plug in particular values for K_a for acetic acid and get: $x = 0.0042 M$.

So, the equilibrium concentrations are:

$$[HOAc] = 1.0 M - x = 1.0 M - 0.0042 M = 0.9958 M$$

$$[OAc^-] = x = 0.0042 M$$

$$[\text{H}^+] = 10^{-7} \text{ M} + x = 0.0042 \text{ M} \text{ hence } \text{pH} = 2.38.$$

Similar calculations give

For 1M dihydrogen phosphate ($K_a = 1.38 \cdot 10^{-7} \text{ M}$): $x = 3.71 \cdot 10^{-4}$, and $\text{pH} = 3.43$.

For 1M ammonium ion ($K_a = 5.62 \cdot 10^{-10} \text{ M}$): $x = 2.37 \cdot 10^{-5}$; and $\text{pH} = 4.63$

(2) Now let's titrate our buffer.

The starting concentrations are: $[\text{HOAc}] = 0.9958 \text{ M}$; $[\text{OAc}^-] = 0.0042 \text{ M}$; $[\text{H}^+] = 0.0042 \text{ M}$.

(a) First we add 0.05 M OH^- . 0.0042 M OH^- will be neutralized by the available amount of H^+ . The remaining $0.05 \text{ M} - 0.0042 \text{ M} = 0.0458 \text{ M}$ OH^- will react with HOAc, thus reducing $[\text{HOAc}]$ and increasing the amount of the conjugate base, OAc^- , so that the equilibrium concentrations will become:

$$[\text{HOAc}] = 0.9958 \text{ M} - 0.0458 \text{ M} = 0.95 \text{ M};$$

$$[\text{OAc}^-] = 0.0042 \text{ M} + 0.0458 \text{ M} = 0.05 \text{ M};$$

hence $\text{pH} = 4.76 + \log(0.05/0.95) = 3.48$. → the pH increased by more than 1.0.

(b) Now we add 0.1M OH^- . This amount of OH^- will essentially completely react with HOAc. The equilibrium concentrations will then be:

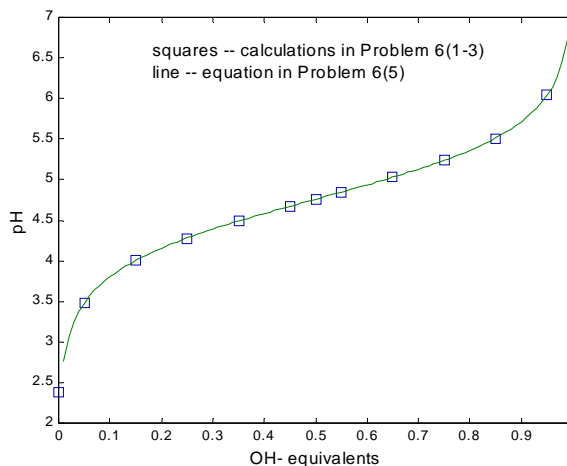
$$[\text{HOAc}] = 0.95 \text{ M} - 0.1 \text{ M} = 0.85 \text{ M};$$

$$[\text{OAc}^-] = 0.05 \text{ M} + 0.1 \text{ M} = 0.15 \text{ M};$$

hence $\text{pH} = 4.76 + \log(0.15/0.85) = 4.01$. Despite the two-fold increase in the amount of added OH^- , the increase in the pH is less than one-half of the previous one.

and so on (see the table).

Total OH-equivalents added	pH
0	2.38
0.05	3.48
0.15	4.01
0.25	4.28
0.35	4.49
0.45	4.67
0.50	4.76
0.55	4.85
0.65	5.03
0.75	5.24
0.85	5.51
0.95	6.04



7. Method 1.

(1) The molar amount of the acid (H_2PO_4^-) in 50 mL initial solution is $0.1 \text{ M} \cdot 0.05 \text{ L} = 5 \cdot 10^{-3}$ moles.

From the equation $[\text{H PO}_4^{2-}] / [\text{H}_2\text{PO}_4^-] = 10^{\text{pH}-\text{pK}_a}$, we can determine the molar ratio of base/acid. Given the molar amount of the acid (H_2PO_4^-) present in 50 mL of the initial solution ($5 \cdot 10^{-3}$ moles), the molar amount of the conjugate base to be added is $5 \cdot 10^{-3} \cdot 10^{\text{pH}-\text{pK}_a}$ moles. Dividing this by the molar concentration ($0.1\text{M} = 0.1 \text{ mole/L}$) of the stock solution, we then find the amount of solution B that we have to add:
 $5 \cdot 10^{-2} \cdot 10^{\text{pH}-\text{pK}_a} \text{ L} = 50 \cdot 10^{\text{pH}-\text{pK}_a} \text{ mL}$.

Plugging in particular values for pH, we obtain:

PH	Added volume of solution B
6.0	6.9 mL
7.0	69 mL
7.3	137.7mL

Note that the change in the volume (e.g. when 69 mL of solution B are added to 50 mL of solution A) as well as the subsequent addition of water, to bring the final volume to 200 mL, will not change the molar ratio of the acid to base, and therefore will not affect the pH.

(2) The pH will be equal to $\text{pK}_a = 6.86$.

(3) When we add 5 mL of B to 50 mL of A, the molar ratio of H PO_4^{2-} to H_2PO_4^- is $[\text{H PO}_4^{2-}] / [\text{H}_2\text{PO}_4^-] = 5/50 = 1/10$ (Since the numerical values of molar concentrations in both stock solutions are equal, the number of moles of each compound added to the mixture will be proportional to the added volume of the corresponding stock solution).

Then $\text{pH} = \text{pK}_a + \log(1/10) = 5.86$.

Likewise, if we add 100 mL of B to 50 mL of A, we get

$[\text{H PO}_4^{2-}] / [\text{H}_2\text{PO}_4^-] = 100/50 = 2$, and $\text{pH} = \text{pK}_a + \log(2) = 7.16$.

Method 2.

100 mL of 0.1M TRISbase contain $0.1\text{M} \cdot 0.1\text{L} = 0.01$ moles of TRISbase. Assume we added x moles of HCl, that completely ionized in water to give x moles of H^+ . These protons reacted with x moles of TRISbase to make x moles of $\text{TRIS}\cdot\text{H}^+$. The remaining amount of moles of TRISbase is then $0.01 - x$. The ratio of molar amounts of TRISbase and $\text{TRIS}\cdot\text{H}^+$ must satisfy the following equation:

$$(0.01 - x)/x = 10^{\text{pH} - \text{pK}_a}$$

Solving it for x , we obtain: $x = 0.01 / (1 + 10^{\text{pH} - \text{pK}_a})$.

For $\text{pH} = 9.0$, $x = 0.01 / (1 + 10^{0.92}) = 0.00107$ moles.

This corresponds to $0.00107 \text{ moles} / 0.1\text{M} = 0.0107 \text{ L} = 10.7 \text{ mL}$ of 0.1M HCl.

Similarly, for $\text{pH} = 8.0$, $x = 0.01 / (1 + 10^{-0.08}) = 0.00546$ moles, $\rightarrow 54.6 \text{ mL}$ of 0.1M HCl.

For $\text{pH} = 7.2$, $x = 0.01 / (1 + 10^{-0.8}) = 0.00884$ moles, $\rightarrow 88.4 \text{ mL}$ of 0.1M HCl.

The results are summarized in the table below.

PH	Added volume of 0.1M HCl
9.0	10.7 mL
8.0	54.6 mL
7.2	88.4mL

8. According to Problem 7 Method 1 example (2), we mixed 50 mL 0.1 M H_2PO_4^- and 50 mL 0.1 M HPO_4^{2-} and then adjusted the total volume to 200 mL by adding water. The molar concentrations of both acid and base are now 0.025M (four-fold dilution). 1 mL 1M HCl added to this solution will be diluted ~200 fold. It will completely ionize into 0.005 M H^+ and 0.005 M Cl^- ions. These additional protons will essentially completely react with HPO_4^{2-} to produce H_2PO_4^- . The final concentrations then will be $[\text{H}_2\text{PO}_4^-] = 0.025\text{M} + 0.005\text{M} = 0.03\text{ M}$ and $[\text{HPO}_4^{2-}] = 0.025\text{M} - 0.005\text{M} = 0.02\text{ M}$. Using the Henderson-Hasselbalch equation, we obtain: $\text{pH} = \text{pK}_a + \log(0.02/0.03) = 6.68$.

If we add 10 mL HCl, the added concentration of H^+ will be 0.05 M. There is not enough base to neutralize this amount of hydrogen ions: 0.025M HPO_4^{2-} will essentially completely react with H^+ , the remaining 0.025 M H^+ will then determine the pH: $\text{pH} = -\log(0.025) = 1.6$.