

Chapter 6. End-of-Chapter Solutions

1.

Note that the question asked for monoprotic acids only.

(a) pH = 5.0: acetic acid, $pK_a = 4.76$.

(b) pH = 7.0: there is not a good monoprotic organic acid in Table 5.8 to buffer at this pH. Alternate choices are the inorganic hypochlorous acid, $pK_a = 7.54$, or the diprotic carbonic acid, $pK_{a1} = 6.35$.

(c) pH = 9.0: phenol, $pK_a = 9.99$. Phenol is not used as a pH buffer in practice due to toxicity, ammonium ion, $pK_a = 9.25$, is an alternate inorganic choice.

2.

(a) pH = 5.0: citric acid, $pK_{a2} = 4.76$.

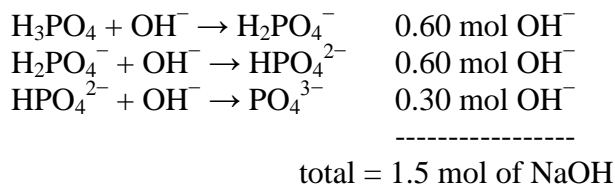
(b) pH = 7.0: carbonic acid, $pK_{a1} = 6.35$.

(c) pH = 9.0: carbonic acid, $pK_{a2} = 10.33$. (A bit far from 9.0, but the best choice in Table 5.8.)

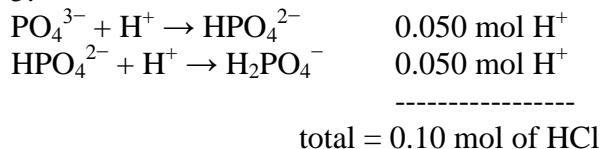
3.

$\sum \alpha_i = 1.0$. Since alpha is a fraction, the total of all alpha's must be one. This condition is always true and it does not depend on ionic strength. Individual fractions might change slightly as I_c changes, but the total must still be 1.0.

4.



5.



6.

Contents of initial solution: (0.15 M Na⁺, 0.05 M PO₄³⁻):

$$I_c = 0.5\{(+1)^2(0.15 \text{ M}) + (-3)^2(0.05 \text{ M})\} = 0.30 \text{ M}$$

Contents of solution after adding HCl: (0.15 M Na⁺, 0.10 M Cl⁻, 0.05 M H₂PO₄⁻):

$$I_c = 0.5\{(+1)^2(0.15 \text{ M}) + (-1)^2(0.10 \text{ M}) + (-1)^2(0.05 \text{ M})\} = 0.15 \text{ M}$$

7.

(a) Adding 0.070 moles of NaOH to a solution containing 0.040 moles of a monoprotic weak acid: excess OH⁻, so basic but not a buffer solution.

(b) Adding 0.040 moles of NaOH to a solution containing 0.070 moles of a monoprotic weak acid: significant amounts of a weak acid and conjugate base, so a buffer solution, pH depends on pK_a of HA.

(c) Adding 0.040 moles of NaOH to a solution containing 0.070 moles of a potassium hydrogen phthalate: Buffer solution at pH = 5.4.

(d) Adding 0.040 moles of HCl to a solution containing 0.070 moles of a potassium hydrogen phthalate: Buffer solution at pH = 2.9.

8.

Using $p[\text{H}_3\text{O}^+] = 0.5(pK_{a1} + pK_{a2})$:

a) $p[\text{H}_3\text{O}^+] = 0.5(7.20 + 12.35) = 9.78$

b) $p[\text{H}_3\text{O}^+] = 0.5(6.35 + 10.33) = 8.34$

c) $1.0 \times 10^{-8} \text{ M}$ is less than the intrinsic $[\text{H}_3\text{O}^+]$ of pure water, so $p[\text{H}_3\text{O}^+]$ is expected to be 7.0 or just slightly higher.

9.

From the phosphate alpha plots (Figure 6.6) at pH = 3, we see that we need H₃PO₄ = 0.1 and H₂PO₄⁻ = 0.9. Since we are starting with 0.500 moles of phosphate, we will need 0.0500 moles of H₃PO₄ and 0.450 moles of H₂PO₄⁻ to achieve this ratio. Protonating all of the PO₄³⁻ to obtain HPO₄²⁻ requires 0.500 mol of HCl. Protonating all of the HPO₄²⁻ to obtain H₂PO₄⁻ requires another 0.500 mol of HCl. Finally we add 0.050 mol of HCl to convert 0.050 mol of H₂PO₄⁻ to 0.050 mol of H₃PO₄. The total amount of strong acid added is 0.500 mol + 0.500 mol + 0.050 mol = 1.05 mol HCl.

10.

(a) halfway point (for the first acidic proton): the solution contains equal amounts of $C_6H_4(COOH)_2$ and $C_8H_5O_4^-$, so $p[H_3O^+] = pK_{a1} = 2.95$.

(b) the first equivalence point: the solution contains predominantly $C_8H_5O_4^-$, so $p[H_3O^+] = 0.5(pK_{a1} + pK_{a2}) = 4.18$

(c) the second equivalence point: the solution contains $C_8H_4O_4^{2-}$, so solve as a weak base problem correcting for dilution during titration:

$$K_b = \frac{K_w}{3.91 \times 10^{-6}} = \frac{[C_8H_5O_4^-][OH^-]}{[C_8H_4O_4^{2-}]}$$

$$2.58 \times 10^{-9} = \frac{[OH^-]^2}{0.0333 \text{ M} - [OH^-]}$$

$$[OH^-] = 9.28 \times 10^{-6} \text{ M}$$

$$p[OH^-] = 5.03$$

$$p[H_3O^+] = 14.0 - 5.02 = 8.97$$

11.

Determining the error in the previous answer requires predicting $p[H_3O^+]$ after correcting pK_a for ionic strength. The solution at the halfway point contains 0.05 M Na^+ and 0.05 M $C_8H_5O_4^-$, and the ionic strength is 0.05 M. Activity coefficients are 0.834 and 0.854 for $C_8H_5O_4^-$ and H_3O^+ , respectively. Correcting K_a :

$$K_a' = \frac{[H_3O^+]^2}{c_{HA} - [H_3O^+]}$$

$$p[H_3O^+] = 2.95 + \log \frac{1.12 \times 10^{-3}}{(0.834)(0.854)} = 1.57 \times 10^{-3}$$

Now using this K_a' , $[H_3O^+] = 1.57 \times 10^{-3} \text{ M}$ and $p[H_3O^+] = 2.80$. The difference in results is 0.15 pH units.

12.

The predominant form of phosphate can be viewed from the alpha plots directly. Find the desired pH on the x-axis and then determine which curve has the largest alpha value at that pH.

- a) pH = 4: $H_2PO_4^-$
- b) pH = 6: $H_2PO_4^-$
- c) pH = 8: HPO_4^{2-}
- d) pH = 10: HPO_4^{2-}

13.

Since the pH of a saturated solution is approximately halfway between pK_{a1} and pK_{a2} , the form of NTA in the solution must be H_2NTA^- .

14.

After the neutralization reaction, the solution contains $[C_6H_4(COOH)_2] = 0.010\text{ M}$ and $[C_8H_5O_4^-] = 0.015\text{ M}$. Using the Henderson-Hasselbalch expression gives:

$$p[H_3O^+] = 2.95 + \log \frac{0.015\text{ M}}{0.010\text{ M}} = 3.13\text{ M}$$

15.

Interpolating in the raw data values in alpha-plot-3protic.xls gives $\alpha_{HPO_4^{2-}} = 4.5 \times 10^{-6}$. The value can also be found using Equation 6.17.

16.

The concentration of any given species is the fraction of that species times the total concentration:

$$[HPO_4^{2-}] = (4.5 \times 10^{-6})(0.0500\text{ M}) = 2.2 \times 10^{-7}\text{ M } HPO_4^{2-}$$

17.

The values can be obtained by Henderson-Hasselbalch calculations or from alpha plot data. Some pH values are as follows:

$HCO_3^- : CO_3^{2-}$	$p[H_3O^+]$
0.05	9.0
0.10	9.3
0.15	9.5
0.50	10.3
0.85	11.1
0.90	11.3
0.95	11.6

18.

Using alpha-plot-3protic or a direct calculation shows that α_{CO_3} is 1.5×10^{-5} . The $[CO_3^{2-}]$ concentration is $1.5 \times 10^{-6}\text{ M}$, which is much smaller than $[HCO_3^-]$.

19.

Note that the recipe specifies adjusting the pH to 7.4, which is done by adding a small amount of strong acid or strong base to this buffer solution. Due to the high ionic strength and day-to-day temperature fluctuations, it is easier to measure and adjust the pH than to try to calculate the pH. Using formula weights and combining common ions, the solution contains:

1.616 mol +1 ions

1.413 mol -1 ions

0.101 mol -2 ions

in a solution volume of 1 L.

$$I_c = 0.5\{(+1)^2(1.616 \text{ M}) + (-1)^2(1.413 \text{ M}) + (-2)^2(0.101 \text{ M})\} = 1.72 \text{ M}$$