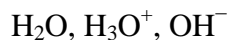


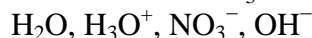
Chapter 5. End-of-Chapter Solutions

1.

(a) bucket of deionized water:

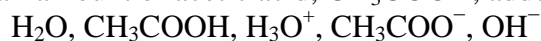


(b) small amount of HNO_3 added:



Note that NO_3^- is a strong electrolyte so we assume that HNO_3 dissociates completely. $[\text{OH}^-]$ will be very small relative to the concentrations of the other ions in solution, but OH^- is present.

(c) small amount of acetic acid, CH_3COOH , added:



CH_3COOH dissociates to a small extent, so we call it a weak acid. $[\text{CH}_3\text{COOH}]$ is significant and much larger than $[\text{H}_3\text{O}^+]$ or $[\text{CH}_3\text{COO}^-]$. One way to define a weak acid is simply as an acid that does not dissociate completely in aqueous solution. Again, $[\text{OH}^-]$ will be very small relative to the other concentrations in solution, but OH^- is present.

2.

(a) $\text{Ba}(\text{NO}_3)_2$: neutral, barium nitrate is a strong electrolyte

(b) $\text{Ca}(\text{ClO}_4)_2$: neutral, calcium perchlorate is a strong electrolyte

(c) KI : neutral, potassium iodide is a strong electrolyte

(d) NaF : basic, fluoride ion, F^- , is a weak base

(e) NH_4Br : acidic, ammonium ion, NH_4^+ , is a weak acid

(f) NH_4F : amphiprotic, compare K_a of NH_4^+ to K_b of F^- , the larger dominates, in this case the solution will be acidic

(g) ammonium acetate: amphiprotic, so compare K_a of NH_4^+ to K_b of CH_3COO^- , in this case $K_a \approx K_b$ and the solution will be close to neutral

3.

(a) below pH of 2.3 the charge is +1, pH between 2.3 and 9.9 the overall charge is 0 (zwitterionic form), for pH greater than 9.9 the charge is -1

(b) extracting into an organic solvent will not occur if the amino acid is charged, so adjust the pH to between 3-9.

4.

(a) 0.01 M HCl (hydrochloric acid is a strong acid and produces a lower pH than an equal amount of a weak acid)

(b) 0.01 M HClO_4 (perchloric acid is a strong acid and produces a lower pH than an equal amount of a weak acid)

(c) 1×10^{-4} M HClO_4 (pH = 4, 0.01 M HClO has pH 4.8)

5.

(a) 0.001 M KOH (a lower concentration of strong base will have lower pH, i.e., more acidic, than higher concentration of strong base)

(b) 0.01 M CH₃COONa (weak base, lower pH than strong base)

(c) 0.01 M CH₃COONa (pH ≈ 8.4, 1 × 10⁻⁴ M NaOH has pOH = 4 and pH = 10)

6.

(a) 0.010 M KI

$$I_c = 0.5\{(+1)^2(0.010 \text{ M}) + (-1)^2(0.010 \text{ M})\} = 0.010 \text{ M}$$

(b) 0.250 M Ca(NO₃)₂

$$I_c = 0.5\{(+2)^2(0.250 \text{ M}) + (-1)^2(0.500 \text{ M})\} = 0.750 \text{ M}$$

(c) 0.250 M AlCl₃

$$I_c = 0.5\{(+3)^2(0.250 \text{ M}) + (-1)^2(0.750 \text{ M})\} = 1.50 \text{ M (we neglect the reaction of Al}^{3+} \text{ with water)}$$

(d) 0.250 M (NH₄)₂SO₄

$$I_c = 0.5\{(+1)^2(0.500 \text{ M}) + (-2)^2(0.250 \text{ M})\} = 0.750 \text{ M}$$

(e) 0.250 M CH₃COONa

$$I_c = 0.5\{(+1)^2(0.250 \text{ M}) + (-1)^2(0.250 \text{ M})\} = 0.250 \text{ M}$$

For d) and e) there is some reaction of NH₄⁺ and CH₃COO⁻ with water, but if you write the equilibria you'll see that there is no change in the number of ions in solution.

7.

(a)

$I_c = 0.010 \text{ M}$, use the Debye-Hückel equation, inserting the d_i for each ion. Sample calculation for OH⁻:

$$\log \gamma_{\text{OH}^-} = \frac{-0.509(-1)^2(0.010)^{0.5}}{1 + (3.29(0.35)(0.010)^{0.5}}$$

i. K⁺: $\gamma_{\text{K}} = 0.899$

ii. I⁻: $\gamma_{\text{I}} = 0.899$

iii. H₃O⁺: $\gamma_{\text{H}_3\text{O}^+} = 0.914$

iv. OH⁻: $\gamma_{\text{OH}^-} = 0.900$

(b)

$I_c = 0.750 \text{ M}$, use the Debye-Hückel equation, inserting the d_i for each ion:

i. Ca²⁺: $\gamma_{\text{Ca}} = 0.223$

ii. NO₃⁻: $\gamma_{\text{NO}_3^-} = 0.578$

iii. H₃O⁺: $\gamma_{\text{H}_3\text{O}^+} = 0.752$

iv. OH⁻: $\gamma_{\text{OH}^-} = 0.602$

8.

(a) Using the activity coefficients from the previous question, set up the expression for K_w and substitute activity coefficients and concentrations for the activities.

$$K_w = (a_{\text{H}_3\text{O}^+})(a_{\text{OH}^-}) = (\gamma_{\text{H}_3\text{O}^+})[\text{H}_3\text{O}^+](\gamma_{\text{OH}^-})[\text{OH}^-] = (\gamma_{\text{H}_3\text{O}^+})(\gamma_{\text{OH}^-}) K_w'$$

$$K_w' = \frac{K_w}{(\gamma_{\text{H}_3\text{O}^+})(\gamma_{\text{OH}^-})}$$

$$K_w' = \frac{1.01 \times 10^{-14}}{(0.914)(0.900)} = 1.23 \times 10^{-14}$$

b)

$$K_w' = \frac{1.01 \times 10^{-14}}{(0.752)(0.602)} = 2.23 \times 10^{-14}$$

9.

0.2 M CH_3COOH . acid dissociation is approximately 1%, $I_c = 0.002$ M

0.2 M CH_3COONa . $I_c = 0.2$ M (a small amount of acetate reacts with water to form CH_3COOH and OH^- , since the OH^- has the same charge as CH_3COO^- , there is no effect on ionic strength)

0.2 M CH_3COOH in 0.2 M NaCl . I_c slightly higher than 0.2 M due to acid dissociation in addition to the 0.2 M NaCl

0.2 M CH_3COONa in 0.2 M NaCl . $I_c = 0.4$ M

1.0 M CH_3COOH . acid dissociation is 0.5%, I_c 0.005M

(a) Ranking the solutions from lowest to highest ionic strength.

0.2 M CH_3COOH ,

1.0 M CH_3COOH ,

0.2 M CH_3COONa ,

0.2 M CH_3COOH in 0.2 M NaCl ,

0.2 M CH_3COONa in 0.2 M NaCl

(b) Activity coefficients decrease with increasing I_c , so the solution with the highest I_c , 0.2 M CH_3COONa in 0.2 M NaCl , will produce activity coefficients farthest from the ideal case of 1.0.

10.

Percent-dissociation is equal to:

$$\% \text{-dissoc} = \frac{[\text{H}_3\text{O}^+]}{c_{\text{HA}}} \times 100 \%$$

Sample calculation:

$$K_a' = \frac{[\text{H}_3\text{O}^+]^2}{c_{\text{HA}} - [\text{H}_3\text{O}^+]}$$

Enter K_a' and c_{HA} , then rearrange and solve with the quadratic equation. For $K_a' = 1 \times 10^{-2}$.

$$K_a' = 0.01 = \frac{[\text{H}_3\text{O}^+]^2}{= 0.01 \text{ M} - [\text{H}_3\text{O}^+]}$$

$$[\text{H}_3\text{O}^+] = 0.0062 \text{ M}$$

$$\% \text{-dissoc} = \frac{0.0062 \text{ M}}{0.01 \text{ M}} \times 100 \% = 62 \%$$

(a rather strong “weak acid”)

Other results:

(a) 3.1 %

(b) 27 %

(c) 62 %

11.

The ionic strength is approximately 0.75 M (slightly higher due to acid dissociation). Activity coefficients are 0.75 for H_3O^+ and 0.62 for A^- . Correct K_a to obtain K_a' , then do the calculation in the same way as above.

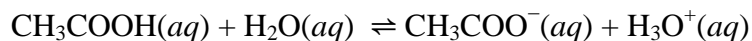
(a) 4.6 %

(b) 37 %

(c) 75 %

You can see there can be a significant difference even for monoprotic acids at high ionic strength.

12.



$$K_a' = \frac{[\text{CH}_3\text{COO}^-][\text{H}_3\text{O}^+]}{[\text{CH}_3\text{COOH}]}$$

$$1.75 \times 10^{-5} = \frac{[\text{H}_3\text{O}^+]^2}{c_{\text{HA}} - [\text{H}_3\text{O}^+]}$$

Enter 0.0100 M for the acetic acid formal concentration, rearrange, and solve with the quadratic equation.

$$[\text{H}_3\text{O}^+] = 4.10 \times 10^{-4} \text{ M}$$

$$\text{p}[\text{H}_3\text{O}^+] = 3.39.$$

13.

$$I_c = 0.5\{(+1)^2(4.1 \times 10^{-4} \text{ M}) + (-1)^2(4.1 \times 10^{-4} \text{ M})\}$$
$$= 4.1 \times 10^{-4} \text{ M}$$

Activity coefficients are 0.978 for H_3O^+ and 0.977 for CH_3COO^- , so $K_a' = 1.83 \times 10^{-5}$.

Using this value in the calculation results in an insignificant change in the result.

$$[\text{H}_3\text{O}^+] = 4.19 \times 10^{-4} \text{ M}$$

$$\text{p}[\text{H}_3\text{O}^+] = 3.38.$$

14.

Activity coefficients are 0.765 for H_3O^+ and 0.667 for CH_3COO^- , so $K_a' = 3.43 \times 10^{-5}$.

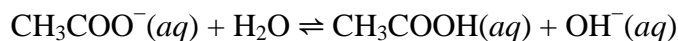
Using this value in the calculation results in a change of 0.15 pH units.

$$[\text{H}_3\text{O}^+] = 5.69 \times 10^{-4} \text{ M}$$

$$\text{p}[\text{H}_3\text{O}^+] = 3.25.$$

15.

The equilibrium is:



$$K_b' = \frac{K_w'}{K_a'} = \frac{[\text{CH}_3\text{COOH}][\text{OH}^-]}{[\text{CH}_3\text{COO}^-]}$$

$$K_b' = \frac{1.01 \times 10^{-14}}{1.75 \times 10^{-5}} = 5.77 \times 10^{-10}$$

$$5.77 \times 10^{-10} = \frac{[\text{OH}^-]^2}{0.0100 \text{ M} - [\text{OH}^-]}$$

Solve for $[\text{OH}^-]$ using the quadratic equation, then convert to $[\text{H}_3\text{O}^+]$.

$$[\text{OH}^-] = 2.40 \times 10^{-6} \text{ M}$$

$$\text{p}[\text{OH}^-] = 5.62$$

$$\text{p}[\text{H}_3\text{O}^+] = 14.00 - 5.62 = 8.38.$$

16.

Activity coefficients are 0.90 for both CH_3COO^- and OH^- . Given the form of the K_b' expression

$$K_b' = \frac{K_w'}{K_a'} = \frac{[\text{CH}_3\text{COOH}][\text{OH}^-]}{[\text{CH}_3\text{COO}^-]}$$

The effect of the activity coefficients cancel and $K_b' = K_b$. The result is the same as in question 15.

17.

Using the spreadsheet allows you to do multiple calculations quickly. Find the result by tabulating $\text{p}[\text{H}_3\text{O}^+]$ for each weak acid for $c_{\text{HA}} = 0.1 \text{ M}$, 0.01 M , 0.001 M , etc. Here I set up the calculation using acetic acid and dichloroacetic acid at $c_{\text{HA}} = 0.01 \text{ M}$. If c_{HA} is high and K_a' is not large, we expect the approximate solution to give the same result as using the quadratic equation.

acetic acid

approximate solution:

$$1.75 \times 10^{-5} = \frac{[\text{H}_3\text{O}^+]^2}{0.001 \text{ M}}$$

$$[\text{H}_3\text{O}^+] = 4.18 \times 10^{-4} \text{ M}$$

$$\text{p}[\text{H}_3\text{O}^+] = 3.38$$

quadratic equation:

$$1.75 \times 10^{-5} = \frac{[\text{H}_3\text{O}^+]^2}{0.001 \text{ M} - [\text{H}_3\text{O}^+]}$$

$$[\text{H}_3\text{O}^+] = 4.10 \times 10^{-4} \text{ M}$$

$$\text{p}[\text{H}_3\text{O}^+] = 3.39$$

dichloroacetic acid

$$5.5 \times 10^{-2} = \frac{[\text{H}_3\text{O}^+]^2}{0.001 \text{ M}}$$

$$[\text{H}_3\text{O}^+] = 2.35 \times 10^{-2} \text{ M}$$

$$\text{p}[\text{H}_3\text{O}^+] = 1.63$$

$$5.5 \times 10^{-2} = \frac{[\text{H}_3\text{O}^+]^2}{0.001 \text{ M} - [\text{H}_3\text{O}^+]}$$

$$[\text{H}_3\text{O}^+] = 0.864 \times 10^{-2} \text{ M}$$

$$\text{p}[\text{H}_3\text{O}^+] = 2.06$$

For acetic acid the approximate calculation is very close to the quadratic result. For the strong dichloroacetic acid, the approximation introduces a significant error.

(a) $\approx 1 \times 10^{-4}$ M

(b) ≈ 0.1 M, so the quick approximation mostly fails for weak acids with relatively large K_a values except at fairly high formal concentrations.

18.

0.001 M acetic acid has a pH of 3.91 using $K_a = 1.75 \times 10^{-5}$. Setting pH = 3.81 and working backwards requires a K_a' of 2.85×10^{-5} . Using the usual means of correcting K_a :

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

$$1.75 \times 10^{-5} = \gamma^2 (2.85 \times 10^{-5})$$

results in $\gamma^2 = 0.625$ and $\gamma = 0.79$. Inserting values for $[Na^+]$ and $[Cl^-]$ in ionic-strength-activity-coefficients.xls leads to an ionic strength of 0.11 M.

19.

This problem is a K_a' calculation worked backwards.

$$p[H_3O^+] = 3.85$$

$$[H_3O^+] = 10^{-3.85} = 1.41 \times 10^{-4} \text{ M}$$

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

$$K_a = \frac{(1.41 \times 10^{-4})^2}{0.01 - 1.41 \times 10^{-4}}$$

$$K_a = 2.02 \times 10^{-6}$$

Repeating for the measured pH:

$$p[H_3O^+] = 3.79$$

$$[H_3O^+] = 10^{-3.79} = 1.62 \times 10^{-4} \text{ M}$$

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

$$K_a' = \frac{(1.62 \times 10^{-4})^2}{0.01 - 1.62 \times 10^{-4}}$$

$$K_a' = 2.67 \times 10^{-6}$$

Usually we look up K_a from a reference table, calculate I_c to find activity coefficients, and use the activity coefficients to determine K_a' , which provides a more realistic prediction of a weak acid equilibrium. Here we know K_a and K_a' and we can calculate the ionic strength of the solution.

$$[\text{H}_3\text{O}^+] = 10^{-3.85} = 1.62 \times 10^{-4} \text{ M}$$

$$K_a = \frac{\gamma[\text{A}^-]\gamma[\text{H}_3\text{O}^+]}{[\text{HA}]} = \gamma^2 K_a'$$

$$\gamma = (K_a / K_a')^{0.5}$$

$$\gamma = (2.02 \times 10^{-6} / 2.67 \times 10^{-6})^{0.5}$$

$$\gamma = 0.870$$

Now use the Debye-Huckel expression to find I_c

$$\log(0.870) = \frac{-0.509(1)^2(I_c)^{0.5}}{1 + (3.29(0.4))(I_c)^{0.5}}$$

$$-0.0605 = \frac{-0.509(I_c)^{0.5}}{1 + 1.32(I_c)^{0.5}}$$

$$0.0605 = \frac{0.509(I_c)^{0.5}}{1 + 1.32(I_c)^{0.5}}$$

$$0.0605 + 0.0796(I_c)^{0.5} = 0.509(I_c)^{0.5}$$

$$0.0605 = 0.429(I_c)^{0.5}$$

$$(I_c)^{0.5} = 0.141$$

$$(I_c) = 0.020 \text{ M}$$