Chapter 5. End-of-Chapter Solutions

1.
(a) bucket of deionized water:
    H_2O, H_3O^+, OH^-

(b) small amount of HNO_3 added:
    H_2O, H_3O^+, NO_3^-, OH^-
Note that NO_3^- is a strong electrolyte so we assume that HNO_3 dissociates completely. $[OH^-]$ 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:
    H_2O, CH_3COOH, H_3O^+, CH_3COO^-, OH^-
CH_3COOH dissociates to a small extent, so we call it a weak acid. $[CH_3COOH]$ is significant and much larger than $[H_3O^+]$ or $[CH_3COO^-]$. One way to define a weak acid is simply as an acid that does not dissociate completely in aqueous solution. Again, $[OH^-]$ will be very small relative to the other concentrations in solution, but OH^- is present.

2.
(a) $Ba(NO_3)_2$: neutral, barium nitrate is a strong electrolyte
(b) $Ca(ClO_4)_2$: 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 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 CH_3COONa (weak base, lower pH than strong base)
(c) 0.01 M CH_3COONa (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 $Ca(NO_3)_2$
$I_c = 0.5\{(+2)^2(0.250\text{ M}) + (-1)^2(0.500\text{ M})\} = 0.750\text{ M}$

(c) 0.250 M $AlCl_3$
$I_c = 0.5\{(+3)^2(0.250\text{ M}) + (-1)^2(0.750\text{ M})\} = 1.50\text{ M}$ (we neglect the reaction of Al^{3+} with water)

(d) 0.250 M $(NH_4)_2SO_4$
$I_c = 0.5\{(+1)^2(0.500\text{ M}) + (-2)^2(0.250\text{ M})\} = 0.750\text{ M}$

(e) 0.250 M CH_3COONa
$I_c = 0.5\{(+1)^2(0.250\text{ M}) + (-1)^2(0.250\text{ M})\} = 0.250\text{ M}$

For d) and e) there is some reaction of NH_4^+ and CH_3COO^- 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 M, use the Debye-Hűckel equation, inserting the d_i for each ion. Sample calculation for OH^-:

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

i. K^+: $\gamma_K = 0.899$
ii. I^-: $\gamma_I = 0.899$
iii. H_3O^+: $\gamma_{H3O} = 0.914$
iv. OH^-: $\gamma_{OH} = 0.900$

(b)
I_c = 0.750 M, use the Debye-Hűckel equation, inserting the d_i for each ion:
i. Ca^{2+}: $\gamma_{Ca} = 0.223$
ii. NO_3^-: $\gamma_{NO3} = 0.578$
iii. H_3O^+: $\gamma_{H3O} = 0.752$
iv. OH^-: $\gamma_{OH} = 0.602$

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.

$$K_w = (a_{H3O+})(a_{OH-}) = (\gamma_{H3O+})[H_3O^+](\gamma_{OH-})[OH^-] = (\gamma_{H3O+})(\gamma_{OH-})\, K_w'$$

$$K_w' = \frac{K_w}{(\gamma_{H3O+})(\gamma_{OH-})}$$

$$K_w' = \frac{1.01\times10^{-14}}{(0.914)(0.900)} = 1.23\times10^{-14}$$

b)

$$K_w' = \frac{1.01\times10^{-14}}{(0.752)(0.602)} = 2.23\times10^{-14}$$

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:

$$\%\text{-dissoc} = \frac{[H_3O^+]}{c_{HA}} \times 100\ \%$$

Sample calculation:

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

Enter K_a' and c_{HA}, then rearrange and solve with the quadratic equation. For $K_a' = 1\times10^{-2}$.

$$K_a' = 0.01 = \frac{[H_3O^+]^2}{= 0.01\ \text{M} - [H_3O^+]}$$

$[H_3O^+] = 0.0062$ 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.

$$CH_3COOH(aq) + H_2O(aq) \rightleftharpoons CH_3COO^-(aq) + H_3O^+(aq)$$

$$K_a' = \frac{[CH_3COO^-][H_3O^+]}{[CH_3COOH]}$$

$$1.75\times10^{-5} = \frac{[H_3O^+]^2}{c_{HA} - [H_3O^+]}$$

Enter 0.0100 M for the acetic acid formal concentration, rearrange, and solve with the quadratic equation.
$[H_3O^+] = 4.10\times10^{-4}$ M
$p[H_3O^+] = 3.39$.

13.
$I_c = 0.5\{(+1)^2(4.1\times10^{-4}\text{ M}) + (-1)^2(4.1\times10^{-4}\text{ M})\}$
$= 4.1\times10^{-4}$ M
Activity coefficients are 0.978 for H_3O^+ and 0.977 for CH_3COO^-, so $K_a' = 1.83\times10^{-5}$.
Using this value in the calculation results in an insignificant change in the result.
$[H_3O^+] = 4.19\times10^{-4}$ M
$p[H_3O^+] = 3.38$.

14.
Activity coefficients are 0.765 for H_3O^+ and 0.667 for CH3COO$^-$, so $K_a' = 3.43\times10^{-5}$.
Using this value in the calculation results in a change of 0.15 pH units.
$[H_3O^+] = 5.69\times10^{-4}$ M
$p[H_3O^+] = 3.25$.

15.
The equilibrium is:

$$CH_3COO^-(aq) + H_2O \rightleftharpoons CH_3COOH(aq) + OH^-(aq)$$

$$K_b' = \frac{K_w'}{K_a'} = \frac{[CH_3COOH][OH^-]}{[CH_3COO^-]}$$

$$K_b' = \frac{1.01\times10^{-14}}{1.75\times10^{-5}} = 5.77\times10^{-10}$$

$$5.77\times10^{-10} = \frac{[OH^-]^2}{0.0100\text{ M} - [OH^-]}$$

Solve for $[OH^-]$ using the quadratic equation, then convert to [H3O$^+$].
$[OH^-] = 2.40\times10^{-6}$ M
$p[OH^-] = 5.62$
$p[H_3O^+] = 14.00 - 5.62 = 8.38$.

16.
Activity coefficients are 0.90 for both CH_3COO^- and OH^-. Given the form of the K_b' expression

$$K_b' = \frac{K_w'}{K_a'} = \frac{[CH_3COOH][OH^-]}{[CH_3COO^-]}$$

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 $p[H_3O^+]$ for each weak acid for c_{HA} = 0.1 M, 0.01 M, 0.001 M, etc. Here I set up the calculation using acetic acid and dichloroacetic acid at c_{HA} = 0.01 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.

<u>acetic acid</u>

approximate solution:

$$1.75\times10^{-5} = \frac{[H_3O^+]^2}{0.001\ M}$$

$[H_3O^+] = 4.18\times10^{-4}$ M
$p[H_3O^+] = 3.38$

quadratic equation:

$$1.75\times10^{-5} = \frac{[H_3O^+]^2}{0.001\ M - [H_3O^+]}$$

$[H_3O^+] = 4.10\times10^{-4}$ M
$p[H_3O^+] = 3.39$

<u>dichloroacetic acid</u>

$$5.5\times10^{-2} = \frac{[H_3O^+]^2}{0.001\ M}$$

$[H_3O^+] = 2.35\times10^{-2}$ M
$p[H_3O^+] = 1.63$

$$5.5\times10^{-2} = \frac{[H_3O^+]^2}{0.001\ M - [H_3O^+]}$$

$[H_3O^+] = 0.864\times10^{-2}$ M
$p[H_3O^+] = 2.06$

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) ≈ 1×10^{-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 $K_a = 1.75\times10^{-5}$. Setting pH = 3.81 and working backwards requires a K_a' of 2.85×10^{-5}. Using the usual means of correcting K_a:

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

$$1.75\times10^{-5} = \gamma^2(2.85\times10^{-5})$$

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

19.
This problem is a K_a' calculation worked backwards.
$p[H_3O^+] = 3.85$
$[H_3O^+] = 10^{-3.85} = 1.41\times10^{-4}$ M

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

$$K_a = \frac{(1.41\times10^{-4})^2}{0.01 - 1.41\times10^{-4}}$$

$$K_a = 2.02\times10^{-6}$$

Repeating for the measured pH:

$p[H_3O^+] = 3.79$
$[H_3O^+] = 10^{-3.79} = 1.62\times10^{-4}$ M

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

$$K_a' = \frac{(1.62\times10^{-4})^2}{0.01 - 1.62\times10^{-4}}$$

$$K_a' = 2.67\times10^{-6}$$

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.

$[H_3O^+] = 10^{-3.85} = 1.62\times10^{-4}$ M

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

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

$$\gamma = (2.02\times10^{-6}/2.67\times10^{-6})^{0.5}$$

$$\gamma = 0.870$$

Now use the Debye-Huckel expression to find I_c

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

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

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

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

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

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

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