Answers to Exercise 12.4 More Weak Acid Calculations

1.

(a) Step 1: Calculate nominal concentration of solution (initial concentration of acid)

 $\frac{1.25 \ g}{\frac{1.25 \ g}{1.000 \ L}} \times \frac{1 \ mol}{43.028 \ g}} = 0.0291 \ mol$

Step 2: Calculate K_a from pK_a

 $K_a = 10^{-pK_a} = 10^{-4.72} = 1.9 \times 10^{-5}$

Step 3: Write a balanced chemical equation and organize all known information

	$HA_{(aq)}$	\rightleftharpoons	$H^+_{(aq)}$	+	$A^{-}_{(aq)}$
I (M)	0.0291		10^{-7}		0
C (M)	-x		+ <i>x</i>		+ <i>x</i>
E (M)	$0.0291 - x \approx 0.02$	291	$10^{-7} + x \approx x$		x

Step 4: Write equilibrium constant expression and calculate x

$$K_{a} = \frac{(a_{H^{+}})(a_{A^{-}})}{a_{HA}}$$

$$1.9 \times 10^{-5} = \frac{(x)(x)}{0.0291}$$

$$(1.9 \times 10^{-5})(0.0291) = x^{2}$$

$$x = \sqrt{(1.9 \times 10^{-5})(0.0291)}$$

$$x = 7.4 \times 10^{-4}$$

Step 5: Check assumptions. If invalid, repeat calculation without the invalid assumption.

Assumption #1: $0.0291 - x \approx 0.0291$ 0.0291 - 0.00074 = 0.0283 close but not quite Assumption #2: $10^{-7} + x \approx x$ $10^{-7} + 0.00074 = 0.00074$ assumption okay Step 6: Try again without the first assumption (keep second one)

$$K_{a} = \frac{(a_{H^{+}})(a_{A^{-}})}{a_{HA}}$$

$$1.9 \times 10^{-5} = \frac{(x)(x)}{(0.0291 - x)}$$

$$(1.9 \times 10^{-5})(0.0291 - x) = x^{2}$$

$$5.5 \times 10^{-7} - (1.9 \times 10^{-5})x = x^{2}$$

$$x^{2} + (1.9 \times 10^{-5})x - (5.5 \times 10^{-7}) = 0$$
Use quadratic equation (or other tools) to solve, giving:

$$x = 7.3 \times 10^{-4}$$

$$(x = -7.5 \times 10^{-4} \text{ would give negative concentrations for H^{+} and A^{-} which is impossible})$$

Step 7: Calculate pH from a_{H^+}

 $a_{H^+} = x = 7.3 \times 10^{-4}$ $pH = -log(a_{H^+}) = -log(7.3 \times 10^{-4}) = 3.13$ Step 8: Check your work

It's an acid, so expect a pH below 7. If this had been a strong acid, the pH would have been -log(0.0291) = 1.537. Since it's a weak acid, it makes sense that the pH is higher. Note that if we had stuck with both initial assumptions, we'd have calculated pH = $-log(7.4 \times 10^{-4}) = 3.13$. So, maybe we could have left it as "close enough" after all...

(b) Step 1: Calculate nominal concentration of solution (initial concentration of acid)

 $1.25 g \times \frac{1 \ mol}{68.4594 \ g} = 0.0183 \ mol$ $\frac{0.0183 \ mol}{1.000 \ L} = 0.0183 \ M$ Step 2: Calculate K_a from pK_a

 $K_a = 10^{-pK_a} = 10^{-1.96} = 1.1 \times 10^{-2}$

Step 3: Write a balanced chemical equation and organize all known information

	$HA_{(aq)}$	\rightleftharpoons $H^+_{(aq)}$	+	$A^{-}_{(aq)}$
I (M)	0.0183	10^{-7}		0
C (M)	-x	+ <i>x</i>		+ <i>x</i>
E (M)	0.0183 - x	$10^{-7} + x \approx x$		x

Step 4: Write equilibrium constant expression and calculate x

$$K_{a} = \frac{(a_{H^{+}})(a_{A^{-}})}{a_{HA}}$$
1.1 × 10⁻² = $\frac{(x)(x)}{(0.0183 - x)}$
(1.1 × 10⁻²)(0.0183 - x) = x²
2.0 × 10⁻⁴ - (1.1 × 10⁻²)x = x²
x² + (1.1 × 10⁻²)x - 2.0 × 10⁻⁴ = 0
Use quadratic equation (or other tools) to solve, giving:
x = 9.7 × 10⁻³
(x = -2.1 × 10⁻² would give negative concentrations for H⁺ and A⁻ which is impossible)
Step 5: Check assumption. If invalid, repeat calculation without it.
Assumption: 10⁻⁷ + x ≈ x 10⁻⁷ + 0.0097 = 0.0097 assumption okay

Step 6: Calculate pH from a_{H^+}

$$a_{H^+} = x = 9.7 \times 10^{-3}$$

 $pH = -log(a_{H^+}) = -log(9.7 \times 10^{-3}) = 2.01$

Step 8: Check your work

It's an acid, so expect a pH below 7. If this had been a strong acid, the pH would have been -log(0.0183) = 1.739. Since it's a weak acid, it makes sense that the pH is higher.

(c) Step 1: Calculate nominal concentration of solution (initial concentration of acid)

$$1.25 g \times \frac{1 \text{ mol}}{63.0128 \text{ g}} = 0.0198 \text{ mol}$$

$$\frac{0.0198 \text{ mol}}{1.000 \text{ L}} = 0.0198 \text{ M}$$

Step 2: Calculate K_a from pK_a
 $K_a = 10^{-pK_a} = 10^{-3.39} = 4.1 \times 10^{-4}$

Step 3: Write a balanced chemical equation and organize all known information

	$HA_{(aq)}$	⇒	$H^+_{(aq)}$	+	$A^{-}_{(aq)}$
I (M)	0.0198		10^{-7}		0
C (M)	-x		+x		+ <i>x</i>
E (M)	$0.0198 - x \approx 0.01$.98	$10^{-7} + x \approx x$		x

Step 4: Write equilibrium constant expression and calculate x

$$K_{a} = \frac{(a_{H^{+}})(a_{A^{-}})}{a_{HA}}$$

$$4.1 \times 10^{-4} = \frac{(x)(x)}{0.0198}$$

$$(4.1 \times 10^{-4})(0.0198) = x^{2}$$

$$x = \sqrt{(4.1 \times 10^{-4})(0.0198)}$$

$$x = 2.8 \times 10^{-3}$$

Step 5: Check assumptions. If invalid, repeat calculation without the invalid assumption.

Assumption #1: $0.0198 - x \approx 0.0198$ 0.0198 - 0.0028 = 0.0170 not close enough Assumption #2: $10^{-7} + x \approx x$ $10^{-7} + 0.0028 = 0.0028$ assumption okay

Step 6: Try again without the first assumption (keep second one)

$$K_{a} = \frac{(a_{H}^{+})(a_{A}^{-})}{a_{HA}}$$
4.1 × 10⁻⁴ = $\frac{(x)(x)}{(0.0198 - x)}$
(4.1 × 10⁻⁴)(0.0198 - x) = x²
5.5 × 10⁻⁷ - (8.1 × 10⁻⁶)x = x²
x² + (4.1 × 10⁻⁴)x - (8.1 × 10⁻⁶) = 0
Use quadratic equation (or other tools) to solve, giving:
x = 2.6 × 10⁻³
(x = -3.1 × 10⁻³ would give negative concentrations for H⁺ and A⁻ which is impossible)
Step 7: Calculate pH from $a_{H^{+}}$
 $a_{H^{+}} = x = 2.6 × 10^{-3}$
pH = $-log(a_{H^{+}}) = -log(2.6 × 10^{-3}) = 2.58$

Step 8: Check your work

It's an acid, so expect a pH below 7. If this had been a strong acid, the pH would have been -log(0.0198) = 1.703. Since it's a weak acid, it makes sense that the pH is higher.

2. General approach: Use the equilibrium constant expression, but this time, the activity of H^+ can be calculated directly from the pH provided.

Step 1: Calculate K_a from pK_a

 $K_a = 10^{-pK_a} = 10^{-3.39} = 4.1 \times 10^{-4}$

Step 2: Calculate a_{H^+} from *pH*

 $a_{H^+} = 10^{-pH} = 10^{-2.00} = 1.0 \times 10^{-2}$

Step 3: Write a balanced chemical equation and organize all known information

	$HA_{(aq)}$	\rightleftharpoons	$H^+_{(aq)}$	+	$A^{-}_{(aq)}$
I(M)	???		10^{-7}		0
C (M)	-x		+ <i>x</i>		+ <i>x</i>
E (M)	$???-x \approx ???$	-	$10^{-7} + x \approx x$		x

Since we don't know a_{HA} , start by assuming that both assumptions will be valid. $a_{H^+} = 1.0 \times 10^{-2}$ therefore $x = 1.0 \times 10^{-2}$

Step 4: Write equilibrium constant expression and calculate a_{HA}

$$K_{a} = \frac{(a_{H^{+}})(a_{A^{-}})}{a_{HA}}$$

$$4.1 \times 10^{-4} = \frac{(1.0 \times 10^{-2})(1.0 \times 10^{-2})}{a_{HA}}$$

$$a_{HA} = \frac{(1.0 \times 10^{-2})(1.0 \times 10^{-2})}{4.1 \times 10^{-4}} = 0.25$$

Step 5: Check assumptions. If invalid, repeat calculation without the invalid assumption.

Assumption #1: $0.25 - x \approx 0.25$	0.25 - 0.01 = 0.24	close enough*
Assumption #2: $10^{-7} + x \approx x$	$10^{-7} + 0.01 = 0.01$	assumption okay

*If you were to repeat the calculation without making the assumption, you'd get the same answer once rounded to the correct number of sig. fig. The solution to 1(a) demonstrated how this is possible.

Step 6: Calculate concentration of acid from activity

 $M_{HA} = a_{HA} \times 1M = 0.25 M$

Step 7: Check your work

Does your answer seem reasonable?

The solution has a higher concentration than in question 1(c) and therefore has a lower *pH*.

3. General approach: Use the equilibrium constant expression, but this time, the activity of H^+ can be calculated directly from the pH provided. Once you know the concentration of acid required, use stoichiometry to calculate the mass of acid required to make the solution.

Step 1: Calculate K_a from pK_a $K_a = 10^{-pK_a} = 10^{-4.72} = 1.9 \times 10^{-5}$ Step 2: Calculate a_{H^+} from pH

$$a_{H^+} = 10^{-pH} = 10^{-2.72} = 1.9 \times 10^{-3}$$

Step 3: Write a balanced chemical equation and organize all known information

	$HA_{(aq)}$	\rightleftharpoons	$H^+_{(aq)}$	+	$A^{-}_{(aq)}$
I(M)	???		10^{-7}		0
C (M)	-x		+x		+ <i>x</i>
E (M)	$???-x \approx ???$		$10^{-7} + x \approx x$		x

Since we don't know a_{HA} , start by assuming that both assumptions will be valid. $a_{H^+} = 1.9 \times 10^{-3}$ therefore $x = 1.9 \times 10^{-3}$

Step 4: Write equilibrium constant expression and calculate a_{HA}

$$K_{a} = \frac{(a_{H^{+}})(a_{A^{-}})}{a_{HA}}$$

1.9 × 10⁻⁵ = $\frac{(1.9 \times 10^{-3})(1.9 \times 10^{-3})}{a_{HA}}$
 $a_{HA} = \frac{(1.9 \times 10^{-3})(1.9 \times 10^{-3})}{1.9 \times 10^{-5}} = 0.19$

Step 5: Check assumptions. If invalid, repeat calculation without the invalid assumption.

Assumption #1: $0.19 - x \approx 0.19$	0.19 - 0.0019 = 0.19	assumption okay
Assumption #2: $10^{-7} + x \approx x$	$10^{-7} + 0.0019 = 0.0019$	assumption okay

Step 6: Calculate concentration of acid from activity

$$M_{HA} = a_{HA} \times 1M = 0.19 M$$

Step 7: Calculate moles of acid required to make solution

$$n_{HA} = 250. \, mL \, \times 0.19 \, \frac{mol}{L} \times \frac{1 \, L}{1000 \, mL} = 0.048 \, mol$$

Step 8: Calculate mass of acid required to make solution

$$m_{HA} = 0.048 \ mol \times \frac{43.028 \ g}{1 \ mol} = 2.0 \ g$$

Step 9: Check your work

Does your answer seem reasonable?

The solution has a higher concentration than in question 1(a) and therefore has a lower *pH*.