Answers to Exercise 12.3
Calculating pH of Weak Acid Solutions

1.

(a) i. and ii. both valid

$K_a = 10^{-pK_a} = 10^{-6.62} = 2.4 \times 10^{-7}$

$a_{HA} = 0.015$

$K_a \cdot a_{HA} = (2.4 \times 10^{-7})(0.015) = 3.6 \times 10^{-9}$ (significantly larger than 10^{-14} so the initial concentration of H^+ will be dwarfed by that produced by dissociation of HA)

$K_a \ll a_{HA}$ so only a tiny fraction of the acid will dissociate.

(b) i. and ii. both valid

$K_a = 10^{-pK_a} = 10^{-9.95} = 1.1 \times 10^{-10}$

$a_{HA} = 0.25$

$K_a \cdot a_{HA} = (1.1 \times 10^{-10})(0.25) = 2.8 \times 10^{-11}$ (significantly larger than 10^{-14} so the initial concentration of H^+ will be dwarfed by that produced by dissociation of HA)

$K_a \ll a_{HA}$ so only a tiny fraction of the acid will dissociate.

(c) ii. valid

$K_a = 10^{-pK_a} = 10^{-0.62} = 0.24$

$a_{HA} = 0.025$

$K_a \cdot a_{HA} = (0.24)(0.025) = 0.0060$ (significantly larger than 10^{-14} so the initial concentration of H^+ will be dwarfed by that produced by dissociation of HA).

It is not true, however, that $K_a \ll a_{HA}$. As such, expect a significant fraction of acid to dissociate.

(d) neither assumption valid

$K_a = 10^{-pK_a} = 10^{-4.19} = 6.5 \times 10^{-5}$

$a_{HA} = 8 \times 10^{-8}$

$K_a \cdot a_{HA} = (6.5 \times 10^{-5})(8 \times 10^{-8}) = 5.2 \times 10^{-12}$ (not significantly larger than 10^{-14}, so expect the initial concentration of H^+ to be relevant and to also need to address the effect of the $H_2O_{(l)} \rightleftharpoons H^+_{(aq)} + OH^-_{(aq)}$ equilibrium).

Note that since the pK_a of the acid is significantly lower than 7, you can predict that the acid almost entirely dissociates. The Distribution Curves notes/practice questions will show you why.

2.

(a) **Step 1: Write a balanced chemical equation and organize all known information**

	$HA_{(aq)}$	$\rightleftharpoons$	$H^+_{(aq)}$	$+$	$A^-_{(aq)}$
I (M)	0.015		10^{-7}		0
C (M)	$-x$		$+x$		$+x$
E (M)	$0.015 - x \approx 0.015$		$10^{-7} + x \approx x$		x

Both assumptions described in question 1 have been made since both were deemed to be reasonable. Always check assumptions at the end of the calculation!

Step 2: Write equilibrium constant expression

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

Step 3: Calculate K_a from pK_a

$pK_a = -logK_a$

$K_a = 10^{-pK_a}$

$K_a = 10^{-6.62}$

$K_a = 2.4 \times 10^{-7}$

Step 4: Calculate x

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

$2.4 \times 10^{-7} = \frac{(x)(x)}{0.015}$

$(2.4 \times 10^{-7})(0.015) = x^2$

$x = \sqrt{(2.4 \times 10^{-7})(0.015)}$

$x = 6.0 \times 10^{-5}$

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

Assumption #1: $10^{-7} + x \approx x$	$10^{-7} + 0.000060 = 0.000060$	assumption okay
Assumption #2: $0.015 - x \approx 0.015$	$0.015 - 0.000060 = 0.015$	assumption okay

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

$a_{H^+} = x = 6.0 \times 10^{-5}$

$pH = -log(a_{H^+})$

$pH = -log(6.0 \times 10^{-5})$

$pH = 4.22$

Step 7: Check your work

Does your answer seem reasonable?

The pK_a tells us that this is a weak acid, so expect a pH below 7.

If this had been a strong acid, the pH would have been $-log(0.015) = 1.82$. *Since it is a weak acid, it makes sense that the pH is higher than that.*

(b) **Step 1: Write a balanced chemical equation and organize all known information**

	$HA_{(aq)}$	$\rightleftharpoons$	$H^+_{(aq)}$	$+$	$A^-_{(aq)}$
I (M)	0.25		10^{-7}		0
C (M)	$-x$		$+x$		$+x$
E (M)	$0.25 - x \approx 0.25$		$10^{-7} + x \approx x$		x

Both assumptions described in question 1 have been made since both were deemed to be reasonable. Always check assumptions at the end of the calculation!

Step 2: Write equilibrium constant expression

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

Step 3: Calculate K_a from pK_a

$$pK_a = -logK_a$$
$$K_a = 10^{-pK_a}$$
$$K_a = 10^{-9.95}$$
$$K_a = 1.1 \times 10^{-10}$$

Step 4: Calculate x

$$K_a = \frac{(a_{H^+})(a_{A^-})}{a_{HA}}$$
$$1.1 \times 10^{-10} = \frac{(x)(x)}{0.25}$$
$$(1.1 \times 10^{-10})(0.25) = x^2$$
$$x = \sqrt{(1.1 \times 10^{-10})(0.25)}$$
$$x = 5.3 \times 10^{-6}$$

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

Assumption #1: $10^{-7} + x \approx x$ $\quad 10^{-7} + 0.000005 = 0.0000053$ assumption okay

Assumption #2: $0.25 - x \approx 0.25$ $\quad 0.25 - 0.0000053 = 0.25$ assumption okay

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

$$a_{H^+} = x = 5.3 \times 10^{-6}$$
$$pH = -log(a_{H^+})$$
$$pH = -log(5.3 \times 10^{-6})$$
$$pH = 5.28$$

Step 7: Check your work

Does your answer seem reasonable?

The pK_a tells us that this is a weak acid, so expect a pH below 7.

If this had been a strong acid, the pH would have been $-log(0.25) = 0.60$. Since it is a weak acid, it makes sense that the pH is higher than that.

(c) **Step 1: Write a balanced chemical equation and organize all known information**

	$HA_{(aq)}$	$\rightleftharpoons$	$H^+_{(aq)}$	$+$	$A^-_{(aq)}$
I (M)	0.025		10^{-7}		0
C (M)	$-x$		$+x$		$+x$
E (M)	$0.025-x$		$10^{-7}+x\approx x$		x

The first assumption described in question 1 has been made since it was deemed to be reasonable. Always check assumptions at the end of the calculation!

Step 2: Write equilibrium constant expression

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

Step 3: Calculate K_a from pK_a

$pK_a=-logK_a$

$K_a=10^{-pK_a}$

$K_a=10^{-0.62}$

$K_a=0.24$ 1 sig. fig.; however, all digits will be used in later steps

Step 4: Calculate x

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

$$0.24=\frac{(x)(x)}{0.025-x}$$

$0.24(0.025-x)=x^2$

$0.0060-0.24x=x^2$

$x^2+0.24x-0.0060=0$

Use quadratic equation (or other tools) to solve, giving:

$x=0.023$

($x=-0.26$ would give negative concentrations for H^+ and A^- – which is impossible)

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

Assumption #1: $10^{-7}+x\approx x$ $10^{-7}+0.023=0.023$ assumption okay

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

$a_{H^+}=x=0.023$

$pH=-log(a_{H^+})$

$pH=-log(0.023)$

$pH=1.64$

Step 7: Check your work

Does your answer seem reasonable?

The pK_a tells us that this is (just barely) a weak acid, so expect a pH below 7.

If this had been a strong acid, the pH would have been $-log(0.025)=1.60$. Given that this is almost a strong acid (pK_a extremely close to 0), it's not entirely surprising that the two values are so close.

(d) **Step 1: Calculate the amount of H^+ generated when benzoic acid dissociates fully**

This is <u>*stoichiometry*</u> *(not an equilibrium ICE table) since the reaction goes to completion.*

	$HA_{(aq)}$	$\rightleftharpoons$	$H^+_{(aq)}$	$+$	$A^-_{(aq)}$
Minitial	8×10^{-8}		1.0×10^{-7}		0
Mchange	$-\ 8 \times 10^{-8}$		$+\ 8 \times 10^{-8}$		$+\ 8 \times 10^{-8}$
Mfinal	≈ 0		1.8×10^{-7}		8×10^{-8}

Step 2: Set up ICE table for the $H_2O/H^+/OH^-$ equilibrium after acid fully dissociates

	$H_2O_{(l)}$	$\rightleftharpoons$	$H^+_{(aq)}$	$+$	$OH^-_{(aq)}$
I (M)	n/a		1.8×10^{-7}		1.0×10^{-7}
C (M)	$+x$		$-x$		$-x$
E (M)	n/a		$1.8 \times 10^{-7} - x$		$1.0 \times 10^{-7} - x$

You could also write –x in the water column and +x in the other two columns. If you do that, you'll get a negative value for x. As long as you factor in that negative sign properly, the calculation will work perfectly well.

It is very important that you use the correct initial concentrations of H^+ and OH^- and that you do NOT approximate either as 0.

Step 3: Write equilibrium constant expression

$K_w = \frac{(a_{H^+})(a_{OH^-})}{a_{H_2O}} = (a_{H^+})(a_{OH^-})$ *since* $a_{H_2O} = 1$

Step 4: Calculate x

$K_w = (a_{H^+})(a_{OH^-})$

$1.00 \times 10^{-14} = (1.8 \times 10^{-7} - x)(1.0 \times 10^{-7} - x)$

$1.00 \times 10^{-14} = (1.8 \times 10^{-14}) - (2.8 \times 10^{-7})x + x^2$

$0 = (8 \times 10^{-15}) - (2.8 \times 10^{-7})x + x^2$

<u>*or*</u> $x^2 - (2.8 \times 10^{-7})x + (8 \times 10^{-15}) = 0$

Use quadratic equation (or other tools) to solve, giving:

$x = 3.2 \times 10^{-8}$

($x = 2.5 \times 10^{-7}$ gives negative concentrations for H^+ and OH^- – which is impossible)

Step 5: Calculate pH from a_{H^+}

$a_{H^+} = (1.8 \times 10^{-7}) - x = (1.8 \times 10^{-7}) - (3.2 \times 10^{-8}) = 1.5 \times 10^{-7}$

$pH = -log(a_{H^+})$

$pH = -log(1.5 \times 10^{-7})$

$pH = 6.83$

Step 6: Check your work

Does your answer seem reasonable?

The pK_a tells us that this is a weak acid, so expect a pH below 7. It's a very dilute solution, so expect the pH to be fairly close to 7. 6.83 is therefore a reasonable answer.