

## 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

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

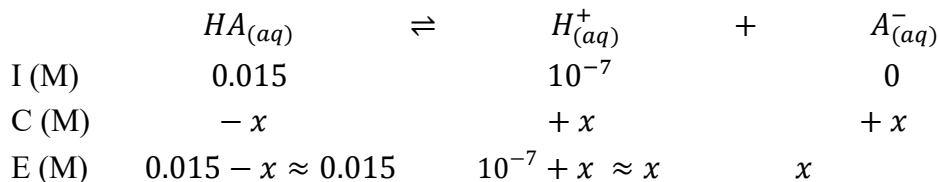
$$a_{HA} = 8 \times 10^{-8}$$

$K_a \cdot a_{HA} = (6.5 \times 10^{-5})(8 \times 10^{-8}) = 5.2 \times 10^{-12}$  (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**



*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  $pK_a$**

$$pK_a = -\log K_a$$

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

$$K_a = 10^{-6.62}$$

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

**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.**

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

$$\text{Assumption \#2: } 0.015 - x \approx 0.015 \quad 0.015 - 0.000060 = 0.015 \quad \text{assumption okay}$$

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

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

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

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

$$pH = 4.22$$

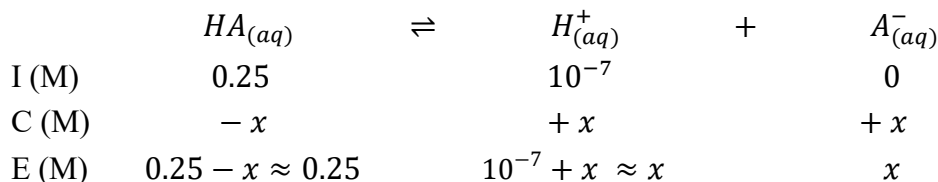
**Step 7: Check your work**

*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**



*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  $pK_a$**

$$pK_a = -\log K_a$$

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

$$K_a = 10^{-9.95}$$

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

**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.**

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

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

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

$$a_{H^+} = x = 5.3 \times 10^{-6}$$

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

$$pH = -\log(5.3 \times 10^{-6})$$

$$pH = 5.28$$

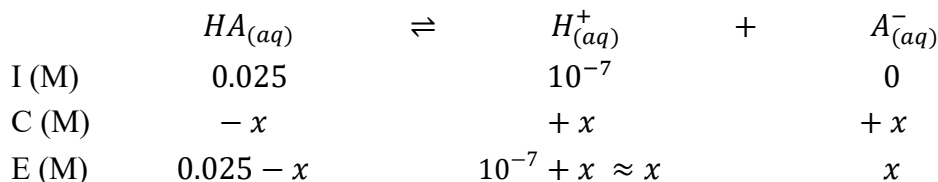
**Step 7: Check your work**

*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**



*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  $pK_a$**

$$pK_a = -\log K_a$$

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

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

$$K_a = 0.24$$

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.**

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

**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 stoichiometry (not an equilibrium ICE table) since the reaction goes to completion.

	$HA_{(aq)}$	$\rightleftharpoons$	$H^+_{(aq)}$	+	$A^-_{(aq)}$
$M_{\text{initial}}$	$8 \times 10^{-8}$		$1.0 \times 10^{-7}$		0
$M_{\text{change}}$	$- 8 \times 10^{-8}$		$+ 8 \times 10^{-8}$		$+ 8 \times 10^{-8}$
$M_{\text{final}}$	$\approx 0$		$1.8 \times 10^{-7}$		$8 \times 10^{-8}$

**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)	$n/a$		$1.8 \times 10^{-7}$		$1.0 \times 10^{-7}$
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**

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

**Step 4: Calculate x**

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

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

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

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

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

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.