Chapter 16: Buffer Calculations – Answer Key

Example 1 - Buffer Method 1
What is the pH of a buffer made by adding 4.68g of sodium benzoate ($NaC_7H_5O_2$) to 250.0mL of 0.15M benzoic acid solution? $K_a = 6.5 \times 10^{-5}$

Need concentration of the conjugate base benzoate ion ($C_7H_5O_2^-$):

$$\left(4.68\text{g NaC}_7\text{H}_5\text{O}_2\right)\left(\frac{1\text{mol NaC}_7\text{H}_5\text{O}_2}{144.1\text{g NaC}_7\text{H}_5\text{O}_2}\right)\left(\frac{1\text{mol C}_7\text{H}_5\text{O}_2^-}{1\text{mol NaC}_7\text{H}_5\text{O}_2}\right) = 0.325\text{mol C}_7\text{H}_5\text{O}_2^-$$

$$\left[\text{C}_7\text{H}_5\text{O}_2^-\right] = \frac{0.0325\text{mol C}_7\text{H}_5\text{O}_2^-}{0.25\text{L}} = 0.13\text{M C}_7\text{H}_5\text{O}_2^-$$

	$HC_7H_5O_2$	+	H_2O	⇔	H_3O^+	+	$C_7H_5O_2^-$
I	0.15M				0		0.13M
C	–x				+x		+x
E	0.15 – x				x		0.13 + x

$$K_a = \frac{[H_3O^+][C_7H_5O_2^-]}{[HC_7H_5O_2]} \qquad 6.5\text{x}10^{-5} = \frac{(x(0.13 + x))}{(0.15 - x)} \qquad x = 7.5 \text{ x } 10^{-5}\text{M} \qquad \text{pH} = 4.13$$

CHECK: Henderson - Hasselbalch Equation
If assume x is small compared to initial concentrations of acid and conjugate base, one can use the initial values of the acid and conjugate base for equilibrium concentrations.

$$K_a = \frac{[H^+][A^-]}{[HA]}$$

$$[H^+] = \frac{K_a[HA]}{[A^-]}$$

$$-\log[H^+] = -\log K_a - \log\left(\frac{[HA]}{[A^-]}\right)$$

$$\text{pH} = \text{p}K_a + \log\left(\frac{[A^-]}{[HA]}\right)$$

$$\text{pH} = \text{p}K_a + \log\left(\frac{[\text{base}]}{[\text{acid}]}\right)$$

$$\text{pH} = -\log(6.5\text{x}10^{-5}) + \log\left(\frac{0.13}{0.15}\right) = 4.19 + (-0.062) = 4.13$$

Example 2 - Buffer Method 2
What is the pH of a buffer made by adding 125mL of 0.14M $HC_7H_5O_2$ solution with 165mL of 0.16M $NaC_7H_5O_2$ solution? $K_a = 6.5 \times 10^{-5}$

Need concentrations of the conjugate acid and base in the mixture.

$$(0.125\text{L})\left(\frac{0.14\text{mol } HC_7H_5O_2}{\text{L solution}}\right) = 0.0175\text{mol } HC_7H_5O_2$$

$$[HC_7H_5O_2] = \left(\frac{0.0175\text{mol } HC_7H_5O_2}{0.290\text{L solution}}\right) = 0.060\text{M } HC_7H_5O_2$$

$$(0.165\text{L})\left(\frac{0.16\text{mol } NaC_7H_5O_2}{\text{L solution}}\right) = 0.0264\text{mol } NaC_7H_5O_2$$

$$[C_7H_5O_2^-] = \left(\frac{0.0264\text{mol } C_7H_5O_2^-}{0.290\text{L solution}}\right) = 0.091\text{M } C_7H_5O_2^-$$

	$HC_7H_5O_2$	+	H_2O	⇔	H_3O^+	+	$C_7H_5O_2^-$
I	0.060M				0		0.091M
C	–x				+x		+x
E	0.060 – x				x		0.091 + x

$$K_a = \frac{[H_3O^+][C_7H_5O_2^-]}{[HC_7H_5O_2]} \qquad 6.5\text{x}10^{-5} = \frac{(x(0.091 + x))}{(0.060 - x)} \qquad x = 4.3 \times 10^{-5}\text{M} \qquad pH = 4.37$$

$$\text{CHECK:} \quad pH = -\log(6.5\text{x}10^{-5}) + \log\left(\frac{0.091}{0.060}\right) = 4.19 + (+0.18) = 4.37$$

Example 3 – Buffer Range
At what pH does buffer work best? Best buffer system when $pH = pK_a$
What is the range of a buffer? Buffer works within ±1 of pK_a value so buffer $pH = pK_a \pm 1$

What is the buffer range of benzoic acid/benzoate buffer?
$pK_a = -\log(6.5\text{x}10^{-5}) = 4.19$ Buffer range = 4.19 ± 1 so 3.19 to 5.19

What is the pH for best buffer capacity and what is the buffering range for each of the following?

Buffer components	pH best buffering capacity	Buffer range
$HC_2H_3O_2$ / $C_2H_3O_2^-$	$pK_a = 4.74$	3.74 – 5.74
$HClO$ / ClO^-	$pK_a = 7.52$	6.52 – 8.52
HCO_3^- / CO_3^{2-}	$pK_a = 10.25$	9.25 – 11.25
$HCHO_2$ / CHO_2^-	$pK_a = 3.74$	2.74 – 4.74
NH_4^+ / NH_3	$pK_a = 9.25$	8.25 – 10.25

Example 4 –Addition of base to buffer
What is the new pH if 5.0 mL of 0.50M NaOH is added to 50.0mL of benzoic acid-benzoate buffer from problem 1?

$[HC_7H_5O_2] = 0.15M \quad [C_7H_5O_2^-] = 0.13M$

First determine how much buffer reacts since NaOH is a strong <u>base</u>, NaOH will react 100% <u>with the acid component of the buffer</u>. MUST WORK STOICHIOMETRY IN MOLES.

	$HC_7H_5O_2$	+ NaOH	–> H_2O	+ $NaC_7H_5O_2$
	(0.0500L x 0.15M)	(0.0050L x 0.50M)		(0.0500L x 0.13M)
Initial mol	0.0075 mol	0.0025 mol		0.0065 mol
Reaction	– 0.0025 mol	– 0.0025 mol		+ 0.0025 mol
Final mol	0.0050 mol	0 mol		0.0090 mol

Note: <u>Must divide by the total volume before entering new values into ICE chart</u>.
Total volume = 50.0 mL + 5.0 mL = 55.0 mL or 0.0550L

$$[HC_7H_5O_2]=\frac{0.0050mol}{0.0550L}=0.091M \qquad [C_7H_5O_2^-]=\frac{0.0090mol}{0.0550L}=0.16M$$

	$HC_7H_5O_2$	+	H_2O	⇔	H_3O^+	+	$C_7H_5O_2^-$
I	0.091M				0		0.16M
C	–x				+x		+x
E	0.091 – x				x		0.16 + x

$$K_a=\frac{[H_3O^+][C_7H_5O_2^-]}{[HC_7H_5O_2]} \qquad 6.5x10^{-5}=\frac{(x(0.16+x))}{(0.091-x)} \qquad x = 3.7 \times 10^{-5}M \qquad pH = 4.43$$

<u>Note small change 4.13 -> 4.43</u>

CHECK: $pH =-\log(6.5x10^{-5}) + \log\left(\frac{0.16}{0.091}\right)= 4.19 + (+0.25)= 4.44$

Example 5 –Addition of acid to buffer
What is the new pH if 10.0 mL of 0.15M HCl was added to 50.0mL of benzoic acid-benzoate buffer from problem 1?

$[HC_7H_5O_2] = 0.15M \quad [C_7H_5O_2^-] = 0.13M$

First determine how much buffer reacts since HCl is a strong <u>acid,</u> HCl will react 100% with the <u>base component of the buffer</u>. MUST WORK STOICHIOMETRY IN MOLES.

	$NaC_7H_5O_2$	+ HCl	–> $HC_7H_5O_2$	+ NaCl
	(0.0500L x 0.13M)	(0.010L x 0.15M)	(0.0500L x 0.15M)	
Initial mol	0.0065 mol	0.0015 mol	0.0075 mol	
Reaction	– 0.0015 mol	– 0.0015 mol	+ 0.0015 mol	
Final mol	0.0050 mol	0 mol	0.0090 mol	

Note: Must divide by the total volume before entering new values into ICE chart.
Total volume = 50.0 mL + 10.0 mL = 60.0 mL or 0.0600L

$$[HC_7H_5O_2]=\frac{0.0090\text{mol}}{0.0600\text{L}}=0.15\text{M} \qquad [C_7H_5O_2^-]=\frac{0.0050\text{mol}}{0.0600\text{L}}=0.083\text{M}$$

	$HC_7H_5O_2$	+	H_2O	⇔	H_3O^+	+	$C_7H_5O_2^-$
I	0.15M				0		0.083M
C	–x				+x		+x
E	0.15 – x				x		0.083 + x

$$K_a=\frac{[H_3O^+][C_7H_5O_2^-]}{[HC_7H_5O_2]} \qquad 6.5\text{x}10^{-5}=\frac{(x(0.083+x))}{(0.15\text{-}x)} \qquad x = 1.2 \text{ x } 10^{-4}\text{M} \qquad \text{pH} = 3.93$$

Note small change 4.13 -> 3.93

CHECK: $\text{pH} = -\log(6.5\text{x}10^{-5}) + \log\left(\frac{0.083}{0.15}\right) = 4.19 + (-0.26) = 3.93$

Example 6 – Depleting buffer
How much of the 0.15M HCl would have to be added to 50.0 mL of the benzoic acid/benzoate buffer to deplete it completely?

$[HC_7H_5O_2]$ = 0.15M $[C_7H_5O_2^-]$ = 0.13M

Since an acid added to a buffer will act with the conjugate base, determine how much acid will be required to react with 50.0 mL of 0.13M $C_7H_5O_2^-$.

	$NaC_7H_5O_2$	+	HCl	–>	$HC_7H_5O_2$	+	NaCl
	(0.0500L x 0.13M)		(? L x 0.15M)		(0.0500L x 0.15M)		
Initial mol	0.0065 mol		0.0065 mol		0.0075 mol		
Reaction	– 0.0065 mol		– 0.0065 mol		+ 0.0065 mol		
Final mol	0 mol		0 mol		0.0140 mol		

$$(0.0065\text{mol HCl})\left(\frac{1\text{L}}{0.15\text{mol HCl}}\right)=0.043\text{L}=43\text{mL}$$

Buffer would be depleted when 43mL of 0.15M HCl has been added.
At this point only acid $HC_7H_5O_2$ remains. Note: can NOT use Henderson-Hasselbalch equation since NO longer a buffer.

$$[HC_7H_5O_2]=\frac{0.0140\text{ mol}}{0.093\text{L}}=0.15\text{M} \qquad \text{Volume} = 50.\text{ mL} + 43\text{ mL} = 93\text{ mL}$$

What would be the pH of the resulting solution?

	$HC_7H_5O_2$	+	H_2O	⇔	H_3O^+	+	$C_7H_5O_2^-$
I	0.15M				0		0
C	–x				+x		+x
E	0.15 – x				x		x

$K_a = \frac{[H_3O^+][C_7H_5O_2^-]}{[HC_7H_5O_2]}$ $\quad 6.5x10^{-5} = \frac{x^2}{(0.15\text{-}x)}$ $\quad x = 3.1 \text{ x } 10^{-3}M$ $\quad pH = 2.51$

Note: Much larger pH change 4.13 -> 2.51 since no longer a buffer.

Example 7 – Determining acid/base ratio needed for buffer pH

When need to know either
(A) how much of one of the buffer components to add to produce a certain pH or
(B) what ratio of conjugate base to acid is needed to produce a certain pH,
use Henderson-Hasselbalch equation.

How many grams of sodium benzoate ($NaC_7H_5O_2$) must be added to 100. mL of 0.13M benzoic acid ($HC_7H_5O_2$) to produce a buffer with a pH of 4.30?

$K_a = 6.5 \text{ x } 10^{-5}$ $\quad pK_a = \text{-log } K_a = \text{-log}(6.5 \text{ x } 10^{-5}) = 4.19$

$$pH = pK_a + \log\left(\frac{[base]}{[acid]}\right)$$

$$4.30 = 4.19 + \log\left(\frac{[base]}{0.13M}\right)$$

$$\log\left(\frac{[base]}{0.13M}\right) = 4.30\text{-}4.19 = 0.11$$

$\frac{[base]}{0.13M} = 10^{0.11} = 1.3$ $\quad$ So ratio of [base] must be 1.3 x [acid].

$[base] = [NaC_7H_5O_2] = 1.3 \text{ x } 0.13M = 0.17M$

$$(0.100\text{ L})\left(\frac{0.17\text{mol } NaC_7H_5O_2}{L}\right)\left(\frac{144.1\text{g } NaC_7H_5O_2}{1\text{mol } NaC_7H_5O_2}\right) = 2.4\text{g } NaC_7H_5O_2$$

Since need to prepare 100. mL of buffer at pH 4.30, measure out 2.4 g $NaC_7H_5O_2$ and add 0.13M acid $HC_7H_5O_2$ to total volume of 100. mL.

Blood Buffer System

H_2CO_3 conjugate acid (formed when blood gas $CO_2 + H_2O <=> H_2CO_3$)
$Na^+ HCO_3^-$ conjugate base

If add base:
$H_2CO_3 + NaOH -> H_2O + Na^+ HCO_3^-$
If add acid:
$Na^+ HCO_3^- + HCl -> H_2CO_3 + Na^+Cl^-$

Cell Buffer System

$H_2PO_4^-$ conjugate acid
HPO_4^{2-} conjugate base

If add base:
$H_2PO_4^- + NaOH -> H_2O + Na^+ HPO_4^{2}$
If add acid:
$HPO_4^{2-} + HCl -> H_2PO_4^- + Cl^-$