BUFFERS

Ch 9-5

SWITCHED TO HARRIS TEXT

Group A will perform the ONLINE Buffer lab this week.

Group B will perform the ONLINE Molar Mass lab this week and the ONLINE Buffer lab. Both lab presentations will be given during the same lab meeting.

Third midterm exam on Monday, November 23

Due to upcoming exam buffer and polyprotic acid homework has been posted

Buffer handout posted on web, complete with solutions.

QUIZ 9 AVERAGE = 8.4 (highest I have ever had!)

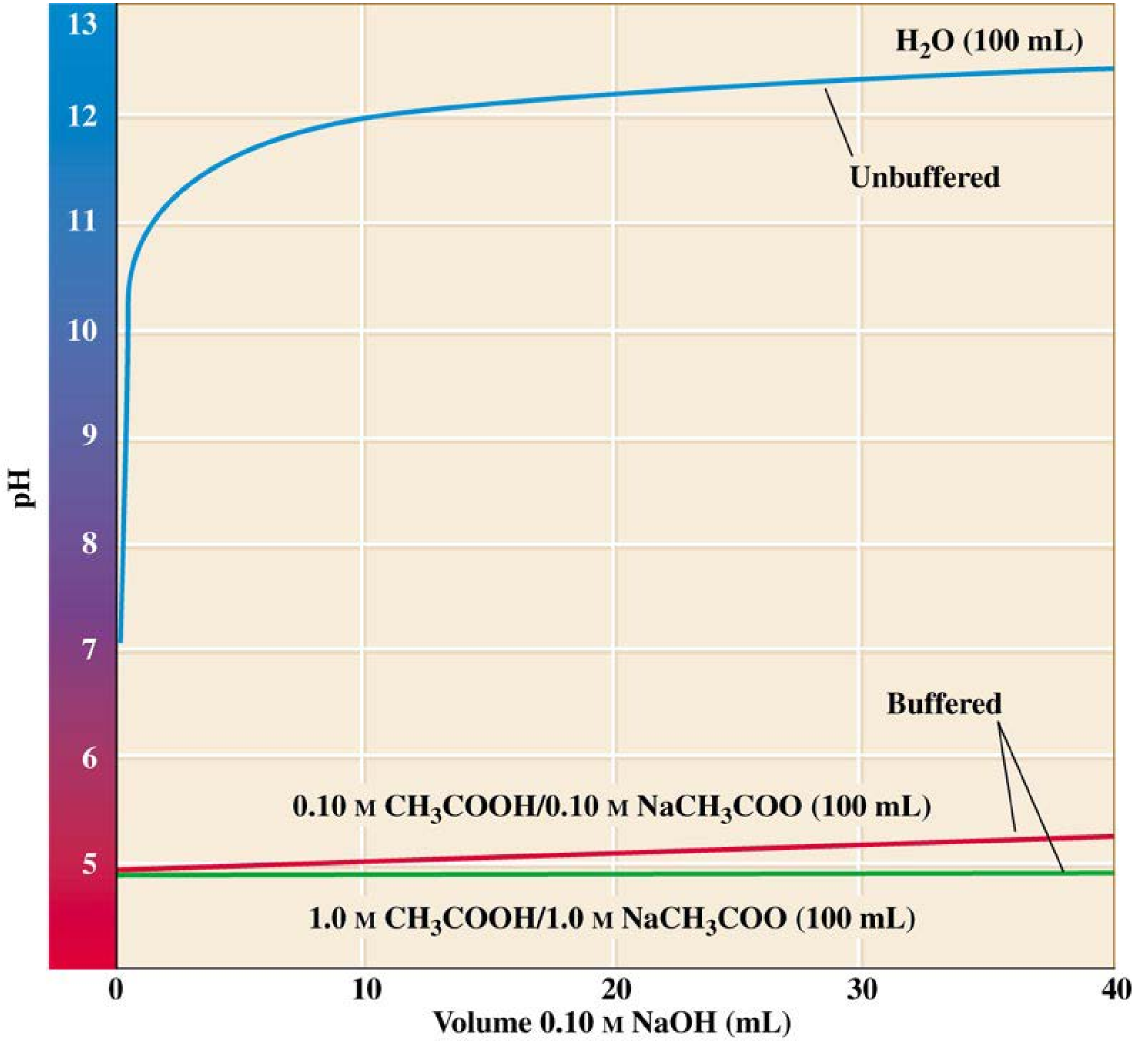
9-5 Buffers

Buffers

a solution that is able to withstand changes in pH (so that the pH is almost constant) upon addition of small amounts of acid or base - based upon the **common ion effect**

pH of human body 7.4 (37°C) – below 7 and above 7.8 death quickly follows. In the body the pH is maintained by carbonate, phosphate and protein buffers

addition of NaOH so that solution is 0.05 M NaOH



Buffers – Common Ion Effect

EX 2. What is the pH of a solution which is 1.0 F HF and 1.0 F NaF ($K_a = 6.6 \times 10^{-4}$) and the fraction (or percent) dissociated?

$$NaF(s) \rightarrow Na^+(aq) + F^-(aq)$$

$$HF(aq) + H_2O(l) \Leftrightarrow H_3O^+(aq) + F^-(aq)$$

	HF	H_3O^+	F^-
I	1.0	∼ 0	1.0
C	$-x$	$+x$	$+x$
E	$1.0 - x$	x	$1.0 + x$

$$K_a = \frac{x(1.0 + x)}{1.0 - x} \sim x \quad \Rightarrow$$

pH = 3.18

α = 6.6 × 10^{-4} or 0.066% dissociated

REVIEW FROM FRIDAY

Buffers – Common Ion Effect, HCl Addition

EX 3. What is the pH of a solution which is 1.0 F in both HF and 1.0 NaF (K_a = 6.6 × 10^{-4}) and 0.1 M in HCl

$$NaF(s) \rightarrow Na^+(aq) + F^-(aq)$$

	$HF(aq)$ + $H_2O(l)$	<=>	$H_3O^+(aq)$	+ $F^-(aq)$
I	1.0 **+ 0.1**		∼ 0	1.0 **- 0.1**
C	- x		+ x	+ x
E	1.1 – x		x	0.9 + x

HCl + NaF → NaCl + HF
=> $H^+ + F^- \rightarrow HF$
(net ionic)

$$K_a = \frac{x(0.9 + x)}{1.1 - x} \sim 0.9x / 1.1 \quad \Rightarrow \quad \textbf{pH = 3.09}$$

solution behave like a buffer, originally before HCl addition pH was 3.18

REVIEW FROM FRIDAY

Buffers – Common Ion Effect, NaOH Addition

EX 4. What is the pH of a solution which is 1.0 F in both HF and 1.0 NaF (K_a = 6.6×10^{-4}) and 0.1 M in NaOH

$$NaF(s) \rightarrow Na^+(aq) + F^-(aq)$$

$$HF(aq) + H_2O(l) \iff H_3O^+(aq) + F^-(aq)$$

	$HF(aq)$	$H_3O^+(aq)$	$F^-(aq)$
I	1.0 **- 0.1**	∼ 0	1.0 **+ 0.1**
C	$-x$	$+x$	$+x$
E	$0.9 - x$	x	$1.1 + x$

$NaOH + HF \rightarrow NaF + H_2O$

=> $OH^- + HF \rightarrow F^- + H_2O$

(net ionic)

$$K_a = \frac{x(1.1 + x)}{0.9 - x} \sim 1.1x / 0.9 \quad \Rightarrow \quad \mathbf{pH = 3.27}$$

solution behave like a buffer, originally before NaOH addition pH was 3.18

REVIEW FROM FRIDAY

Working with Buffer Solutions

*note ratio of base form to acid form

based on a **weak acid** (HA) and its **conjugate base** (A^-)

$HA(aq) + H_2O(l)$ <=> $H_3O^+(aq) + A^-(aq)$

$$K_a = \frac{[H_3O^+][A^-]}{[HA]} \text{ or } pH = pK_a + \log \frac{[A^-]}{[HA]}$$

Henderson-Hasselbalch

$$pH = pK_a + \log \frac{[A^-]_o}{[HA]_o}$$ *

based on a **weak base** (B:) and its **conjugate acid** (BH^+)

$B:(aq) + H_2O(l)$ <=> $OH^-(aq) + BH^+(aq)$

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$$pH = pK_a + \log \frac{[B]_o}{[BH^+]_o}$$ *

pK_a applies to *this* acid

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Working with Buffer Solutions

Henderson-Hasselbalch Equation

For most cases the Henderson-Hasselbalch equation can be simplified by not solving the equilibrium problem and making the substitutions (real Henderson-Hasselbalch equation)

If F_{HA} or F_{A^-} is small (solution is too dilute) or if $[H^+]$ or $[OH^-]$ is large (too acidic or too basic) then this approximation cannot be used and the systematic approach must be employed.

(BUT THEN THE SOLUTION IS NOT A USEFUL BUFFER!)

Buffers – Elementary

EX 5. K_a (CH_3COOH) = 1.76×10^{-5})

a) Determine the pH of a solution which is simultaneously 0.500 M CH_3COOH and 0.300 M sodium acetate

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b) Determine the pH when 100 mL 0.200 M sodium acetate is added to 500 mL of 0.150 M acetic acid.   **weak acid + weak base => very little reaction**

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weak acid + weak base => very little reaction

$$pH = pK_a + \log_{10}\frac{[\text{base}]}{[\text{acid}]} = -\log_{10}(1.76 \times 10^{-5}) + \log_{10}\frac{100(0.200)/\mathbf{600}}{500(0.150)/\mathbf{600}} = \mathbf{4.879}$$

calculate new molarities when mixing

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ratio of molarities = ratio of moles

Buffers – Preparation 1

EX 7. Prepare 500 mL of a solution buffered at pH = 4.50 with a **buffer concentration of 0.40 M**. This buffer is to be made from 1.00 M C_6H_5COOH (K_a = 6.3×10^{-5}, pK_a = 4.2006) and 1.00 M NaC_6H_5COO. What volume of acid and its conjugate base would you need?

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$$\Rightarrow [B] = 1.992\,[A]$$

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$$\mathbf{[B] + [A] = 0.40} = 1.992\,[A] + [A] \Rightarrow [A] = 0.1336\ M$$

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$$= V\,(1.00)\,/\,500 \Rightarrow \mathbf{66.8\ mL}$$

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$\Rightarrow [B] = 1.992\,[A]$

[B] + [A] = 0.40 = 1.992 [A] + [A] => [A] = 0.1336 M

= V (1.00) / 500 => **66.8 mL**

[B] = 1.992 [A] = 1.992(0.1336) = 0.2661 M

= V_B (1.00) / 500 => **133 mL**

check ratio:

R = 0.133(1.00) / 0.0668(1.00) = 1.991

Buffers – Preparation 2

EX 8. Prepare a solution buffered at pH = 11.10. This buffer is to be made from 225 mL of 0.331 M CH_3NH_2 (K_a = 2.3 × 10^{-11}, pK_a = 10.6382) to which 0.293 M HI is added. What volume of HI would you need?

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$$CH_3NH_2 + HI \rightarrow CH_3NH_3^+ + I^-$$

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$$\Rightarrow n_B = 2.896\, n_A$$

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=> $n_B = 2.896\, n_A$

$CH_3NH_2 + HI \rightarrow CH_3NH_3^+ + I^-$

$\boldsymbol{n_B + n_A = 0.225(0.331)}$

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$$\Rightarrow n_B = 2.896\, n_A$$

$$CH_3NH_2 + HI \rightarrow CH_3NH_3^+ + I^-$$

$$\boldsymbol{n_B + n_A = 0.225(0.331)} = 0.074475 = 2.896\, n_A + n_A \Rightarrow n_A = 0.01911 \text{ mol}$$

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$$\boldsymbol{n_B + n_A = 0.225(0.331)} = 0.074475 = 2.896\, n_A + n_A \Rightarrow n_A = 0.01911 \text{ mol}$$

$$0.01911 = V\,(0.293) \Rightarrow \mathbf{65.2\ mL}$$