Polyprotic Acids and Bases____________Ch 10-1 – 10-5

SWITCHED TO HARRIS TEXT

Thursday afternoon I am helping with understanding buffers and solving buffer problems. Email me if you would like to discuss this.

Third midterm exam on Monday, November 23

9-5 Review of Buffers
10-1 Diprotic Acids and Bases (omit the intermediate form)
10-2 Diprotic Buffers
10-3 Polyprotic Acids and Bases (omit the intermediate form)
10-4 Principle Species
10-5 Fractional Composition (omit equations)

Friday quiz on buffers

REVIEW

Buffers – Common Ion Effect, HCl Addition

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

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

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

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

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

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

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

$$pH = pK_a + \log_{10}\frac{[base]}{[acid]} = -\log_{10}(6.66 \times 10^{-4}) + \log_{10}\frac{[0.9]}{[1.1]} = \mathbf{3.089}$$

Henderson-Hasselbalch

Buffers – Common Ion Effect, NaOH Addition

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

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

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

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

NaOH + HF → NaF + H_2O
=> OH^- + HF → F^- + H_2O
(net ionic)

	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

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

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=> $OH^- + HF \rightarrow F^- + H_2O$
(net ionic)

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C	$-x$		$+x$	$+x$
E	$0.9 - x$		x	$1.1 + x$

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

$$pH = pK_a + \log_{10}\frac{[base]}{[acid]} = -\log_{10}(6.66 \times 10^{-4}) + \log_{10}\frac{[1.1]}{[0.9]} = \mathbf{3.267}$$

Henderson-Hasselbalch

REVIEW

Working with Buffer Solutions

*note ratio of base form to acid form

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

$HA(aq) + H_2O(l) \Leftrightarrow H_3O^+(aq) + A^-(aq)$

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

Henderson-Hasselbalch

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

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

$B:(aq) + H_2O(l) \Leftrightarrow OH^-(aq) + BH^+(aq)$

$$K_a = \frac{[H_3O^+][B:]}{[BH^+]} \quad \text{or } pH = pK_a + \log \frac{[B:]}{[BH^+]}$$

Henderson-Hasselbalch

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

pK_a applies to *this* acid

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

$$pH = pK_a + \log_{10}\frac{[\text{base}]}{[\text{acid}]} = -\log_{10}(1.76 \times 10^{-5}) + \log_{10}\frac{[0.300]}{[0.500]} = \mathbf{4.533}$$

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

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

calculate new molarities when mixing

Buffers – Elementary

1. given molarities

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2. given volume/molarities of stock solutions

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calculate new molarities when mixing

Buffers – Elementary

2. given volume/molarities of stock solutions

EX 6. Determine the pH when **100 mL of 0.500 M NH_3** is mixed with **200 mL of 0.300 M ammonium chloride** (NH_4Cl), K_b (NH_3) = 1.8×10^{-5}

$$pH = pK_a + \log_{10}\frac{[\text{base}]}{[\text{acid}]} = -\log_{10}\frac{(1.01 \times 10^{-14})}{(1.8 \times 10^{-5})} + \log_{10}\frac{(0.100)(0.500)}{(0.200)(0.300)} = \mathbf{9.172}$$

weak acid + weak base => very little reaction

ratio of molarities = ratio of moles

Buffers – Preparation 1

3. given molarities of stock solutions, buffer concentration

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?

$$pH = pK_a + \log_{10}\frac{[B]}{[A]} \Rightarrow \textbf{ratio, R} = \frac{[B]}{[A]} = \frac{10^{pH}}{} = 10^{pH - pK_a} = 10^{4.50 - 4.2006} = \mathbf{1.992}$$

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

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

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

$$[B] = 1.992\,[A] = 1.992(0.1336) = 0.2661\text{ M}$$

$$= V_B\,(1.00) / 500 \Rightarrow \mathbf{133\text{ mL}}$$

check ratio: R = 0.133(1.00) / 0.0668(1.00) = 1.991

Buffers – Preparation 1

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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?

$$pH = pK_a + \log_{10}\frac{[B]}{[A]} \Rightarrow \text{ratio, } R = \frac{[B]}{[A]} = 10^{pH - pK_a} = 10^{4.50 - 4.2006} = 1.992$$

=> [B] = 1.992 [A]

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

= V_A (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

3. given volume/molarity of stock solution, molarity strong acid (or base)

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?

$$pH = pK_a + \log_{10}\frac{[B]}{[A]} \Rightarrow \textbf{ratio, R} = \frac{[B]}{[A]} = \frac{n_B}{n_A} = 10^{pH - pK_a} = 10^{11.10 - 10.6382} = \mathbf{2.896}$$

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

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

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

ratio of molarities = ratio of moles

constraint on molarities (buffer concentrat-ion) or constraint on total number of moles

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

Polyprotic Acids and Bases

polyprotic acid – capable of donating more than one proton
polyprotic base – capable of accepting more than one proton

EX 11. What is the concentration of all species present in a 1.00 M solution of sulfuric acid where $K_a = 1.2 \times 10^{-2}$?

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H_2SO_4 strong acid => [acid] = [H+] = [conjugate base]

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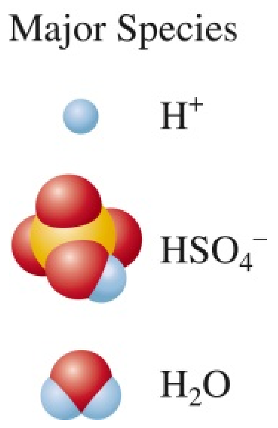
[OH-] = $K_w / [H^+]$ = **1.01×10^{-14}**



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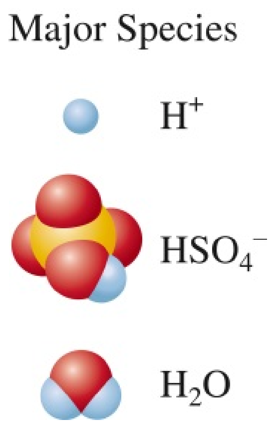
$$HSO_4^-(aq) + H_2O(l) \Longleftrightarrow H_3O^+(aq) + SO_4^{2-}(aq)$$



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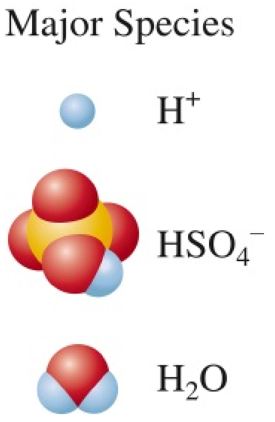
	$HSO_4^-(aq)$	+	$H_2O(l)$	<=>	$H_3O^+(aq)$	+	$SO_4^{2-}(aq)$
I	1.0				1.0		~0
C	$-x$				$+x$		$+x$
E	$1.0 - x$				$1.0 + x$		x



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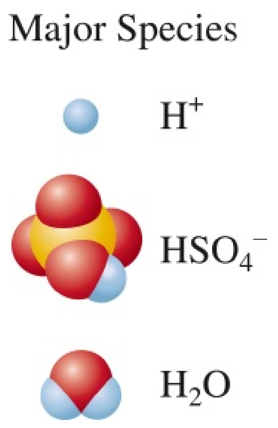

	$HSO_4^-(aq)$	+ $H_2O(l)$	<=>	$H_3O^+(aq)$	+ $SO_4^{2-}(aq)$
I	1.0			1.0	~0
C	- x			+ x	+ x
E	1.0 – x			1.0 + x	x

$$K_a = \frac{[H_3O^+][SO_4^{2-}]}{[HSO_4^-]} = \frac{(1.00 + x)\,x}{1.00 - x}$$ => x = **$[SO_4^{2-}]$ = 0.012 M**

100(0.012) = 1.2% OK by 5% rule, not OK by 1% rule, quadratic => x = $[SO_4^{2-}]$ = 0.0117 M, $[H^+]_{total}$ = 1.00 + 0.0117 = 1.01 M, [OH-] = 1.00×10^{-14} M

EX 2. What is the pH and concentration of all species present in a 5.00 M solution of phosphoric acid?

$K_{a1} = 7.11 \times 10^{-3}$ $H_3PO_4(aq) + H_2O(l) <=> H_3O^+(aq) + H_2PO_4^-(aq)$ $pK_{a1} = 2.1481$

$K_{a2} = 6.34 \times 10^{-8}$ $H_2PO_4^-(aq) + H_2O(l) <=> H_3O^+(aq) + HPO_4^{2-}(aq)$ $pK_{a2} = 7.1979$

$K_{a3} = 4.22 \times 10^{-13}$ $HPO_4^{2-}(aq) + H_2O(l) <=> H_3O^+(aq) + PO_4^{3-}(aq)$ $pK_{a3} = 12.3746$

Polyprotic Acids and Bases

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EQ $5.00 - x$ x x

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$$K_{a1} = \frac{[H_3O^+][H_2PO_4^-]}{[H_3PO_4]} = \frac{x^2}{5.00 - x}$$

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EQ $5.00 - x$ x x

$$K_{a1} = \frac{[H_3O^+][H_2PO_4^-]}{[H_3PO_4]} = \frac{x^2}{5.00 - x}$$

=> x = **$[H_3O^+] = [H_2PO_4^-] = 0.01939$ M**

Polyprotic Acids and Bases

EX 2. What is the pH and concentration of all species present in a 5.00 M solution of phosphoric acid?

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EQ $5.00 - x$ x x

$$K_{a1} = \frac{[H_3O^+][H_2PO_4^-]}{[H_3PO_4]} = \frac{x^2}{5.00 - x}$$

=> x = **$[H_3O^+] = [H_2PO_4^-] = 0.1939$ M**

$[H_3PO_4]$ = 5.00 - 0.19 = **4.81, $[OH^-] = 5.2 \times 10^{-13}$ M**

pH = 0.71

100(0.1939)/5.00 = 3.9%,
OK by 5%, not by **1% rule**
quadratic => x = 0.1901
$[H_3O^+] = [H_2PO_4^-] = 0.190$,
$[OH^-] = 5.3 \times 10^{-13}$ M

Polyprotic Acids and Bases

EX 2. What is the pH and concentration of all species present in a 5.00 M solution of phosphoric acid?

100(0.1939)/5.00 = 3.9%, OK by 5%, not by **1% rule**
quadratic => x = 0.1901
$[H_3O^+] = [H_2PO_4^-] = 0.190$, $[OH^-] = 5.3 \times 10^{-13}$ M

$K_{a1} = 7.11 \times 10^{-3}$ $\quad H_3PO_4(aq) + H_2O(l) \Leftrightarrow H_3O^+(aq) + H_2PO_4^-(aq)$

EQ $\quad 5.00 - x \quad\quad x \quad\quad x$

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$[H_3PO_4]$ = 5.00 - 0.19 = **4.81, $[OH^-] = 5.2 \times 10^{-13}$ M** $\quad$ **pH = 0.71**

$K_{a2} = 6.34 \times 10^{-8}$ $\quad H_2PO_4^-(aq) + H_2O(l) \Leftrightarrow H_3O^+(aq) + HPO_4^{2-}(aq)$

$$K_{a2} = \frac{[H_3O^+][HPO_4^{2-}]}{[H_2PO_4^-]}$$

Polyprotic Acids and Bases – Intermediate Form

Consider a diprotic acid

$$H_2A(aq) + H_2O(l) \iff H_3O^+(aq) + HA^-(aq)$$ **base**

acid $$HA^-(aq) + H_2O(l) \iff H_3O^+(aq) + A^{2-}(aq)$$

Polyprotic Acids and Bases – Intermediate Form

Consider a diprotic acid

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acid $$HA^-(aq) + H_2O(l) \iff H_3O^+(aq) + A^{2-}(aq)$$

If H_2A is a weak acid its conjugate base, HA^- is amphoteric. It can act as an acid (second equation) or as a base (reverse of first reaction). What is the pH of a solution of HA^- such as NaHA?

Exact Treatment (H pp. 216 - 218) for NaHA

species: H_2A, HA^-, A^{2-}, H^+, OH^-, Na^+ => need 6 equations

Polyprotic Acids and Bases – Intermediate Form

Consider a diprotic acid

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species: H_2A, HA^-, A^{2-}, H^+, OH^-, Na^+ => need 6 equations

charge balance: $[H^+] + [Na^+] = [HA^-] + 2[A^{2-}] + [OH^-]$

material balance: $M_{NaHA} = [Na^+] = [H_2A] + [HA^-] + [A^{2-}]$

Polyprotic Acids and Bases – Intermediate Form

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material balance: $M_{NaHA} = [Na^+] = [H_2A] + [HA^-] + [A^{2-}]$

equilibria: $K_{a1} = \frac{[H^+][HA^-]}{[H_2A]}$ $K_{a2} = \frac{[H^+][A^{2-}]}{[HA^-]}$ $K_w = [H^+][OH^-]$

Polyprotic Acids and Bases – Intermediate Form

Consider a diprotic acid

$$H_2A(aq) + H_2O(l) \Longleftrightarrow H_3O^+(aq) + \boxed{HA^-(aq)}$$ **base**

acid $$\boxed{HA^-(aq)} + H_2O(l) \Longleftrightarrow H_3O^+(aq) + A^{2-}(aq)$$

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charge balance: $[H^+] + [Na^+] = [HA^-] + 2[A^{2-}] + [OH^-]$

material balance: $M_{NaHA} = [Na^+] = [H_2A] + [HA^-] + [A^{2-}]$

equilibria: $K_{a1} = \dfrac{[H^+][HA^-]}{[H_2A]}$ $\quad K_{a2} = \dfrac{[H^+][A^{2-}]}{[HA^-]}$ $\quad K_w = [H^+][OH^-]$

One can show that

$$\boxed{[H^+]^2 = \frac{K_{a1}K_{a2}[HA^-] + K_{a1}K_w}{K_{a1} + [HA^-]}}$$ **exact relation**