Titration-region & buffer calculations

CH102 Summer 1 2012
Boston University

An acid-base region is **a circumstance**

… **not** a sequence of operations

Region 1: **Only weak** acid (base)

Region 2: **Both weak** acid (base) and its **conjugate** base (acid)

Region 3: **Only conjugate** of weak acid (base)

Region 4: **Strong** base (acid), no matter what else

For each of these circumstances …

it **does not matter how they arise**

Region 1: Strong acid only

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

	HA	H_3O^+	A^-
Initial	c_a	10^{-7}	0
Revised initial, $K_a > 1$	0	$10^{-7} + c_a \approx c_a$	c_a
Change	$+x$	$-x$	$-x$
Equilibrium	x	$c_a - x \approx c_a$	$c_a - x \approx c_a$

$10^{-7} + c_a \approx c_a$ because $K_a > K_w$

$c_a - x \approx c_a$ because $K_a > 1$

$(HA) = x \approx c_a^2/K_a$

Region 1: Strong acid only example

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

K_a of HA is $1 \times 10^{+6}$

What is the pH and (HA) in 0.001 M HA?

$(H_3O^+) = c_a = 0.001 \rightarrow pH = 3.0$

$(HA) = x = c_a^2/K_a = (0.001)^2/(1 \times 10^{+6}) = 1 \times 10^{-12}$!!!

Region 1: Weak acid only

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

	HA	H_3O^+	A^-
Initial	c_a	10^{-7}	0
Change	$-x$	$+x$	$+x$
Equilibrium	$c_a - x \approx c_a$	$10^{-7} + x \approx x$	x

$10^{-7} + x \approx x$ because $K_a > K_w$

$c_a - x \approx c_a$ because $1 > K_a$

$(H_3O^+) = x \approx \surd(K_a\, c_a)$

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Region 1: Weak acid only example

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

K_a of HA is 1×10^{-7}

What is the pH of 0.001 M HA?

$(H_3O^+) = \surd(K_a\, c_a) = \surd(1 \times 10^{-10}) = 1 \times 10^{-5}$

pH = 5.0

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Region 2: Partially neutralized

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

	HA	H_3O^+	A^-
Initial	c_a	10^{-7}	c_b
Change	$-x$	$+x$	$+x$
Equilibrium	$c_a - x \approx c_a$	$10^{-7} + x \approx x$	$c_b + x \approx c_b$

$10^{-7} + x \approx x$ because $K_a > K_w$

$c_a - x \approx c_a$ and $c_b + x \approx c_b$ because $1 > K_a$

$(H_3O^+) = x \approx K_a\,(c_a/c_b) = K_a\,(mol_a/mol_b)$

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Region 2: Partially neutralized example

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

K_a of HA is 1×10^{-5}

1.0 L each of 0.012 M HA and 0.010 M NaOH are combined. What is the pH?

$mol_a = 0.002$ mol, $mol_b = 0.010$ mol

$(H_3O^+) = x = K_a\,(mol_a/mol_b) = 2 \times 10^{-6}$

pH = 6 – 0.3 = 5.7

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Region 3: Equivalence point

$H_2O(l) + A^-(aq) \rightarrow HA(aq) + OH^-(aq)$

	A^-	HA	OH^-
Initial	c_b	0	10^{-7}
Change	$-x$	$+x$	$+x$
Equilibrium	$c_b - x \approx c_b$	x	$10^{-7} + x \approx x$

$10^{-7} + x \approx x$ because **$K_b = K_w/K_a >> K_w$**

$c_b - x \approx c_b$ because **$1 >> K_b$**

$(OH^-) = x \approx \sqrt{(K_b\, c_b)}$

Region 3: Equivalence point example

$H_2O(l) + A^-(aq) \rightarrow HA(aq) + OH^-(aq)$

K_a of HA is 1×10^{-7}

1.0 L each of 0.002 M HA and 0.002 M NaOH are combined. What is the pH?

$c_b = 0.002 \text{ mol}/(2 \text{ L}) = 0.001$ M

$K_b = K_w/K_a = 1 \times 10^{-7}$

$(OH^-) = \sqrt{(K_b\, c_b)} = \sqrt{(1 \times 10^{-10})} = 1 \times 10^{-5}$

pOH = 5.0 → pH = 9.0

Region 4: Beyond equivalence example

$H_2O(l) + A^-(aq) \rightarrow HA(aq) + OH^-(aq)$

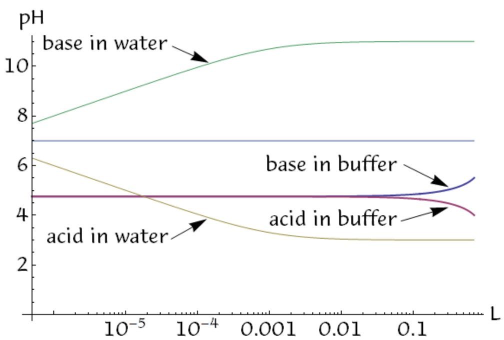
K_a of HA is 1×10^{-7}

1.0 L each of 0.002 M HA and 0.003 M NaOH are combined. What is the pH?

$(OH^-) = 0.001 \text{ mol}/(2 \text{ L}) = 0.0005$ M

pOH = 4 – 0.7 = 3.3 → pH = 10.7

Buffers resist change in pH

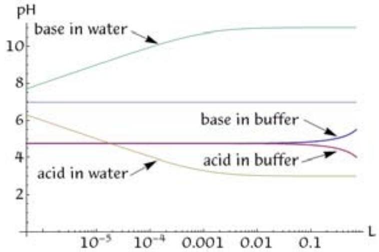


Buffers resist change in pH

Let's see what causes these changes in pH to be

so **drastic in pure water**,

but so **muted in a buffer**.



13

Titration-region & buffer calculations

Buffers resist change in pH

Added strong base (say, OH^-) is gobbled up …

↓**HA**(*aq*) + OH^-(*aq*) → H_2O(*l*) + ↑**A^-**(*aq*)

c_a lowered, **c_b raised**, **c_a/c_b lowered**

Added strong acid (say, HCl) is gobbled up …

HCl(*aq*) + ↓**A^-**(*aq*) → ↑**HA**(*aq*) + Cl^-(*aq*)

c_b lowered, **c_a raised**, **c_a/c_b raised**

14

Titration-region & buffer calculations

Add **strong base** to buffer

1 L buffer, $c_a = c_b = 1.00$ M, $K_a = 1 \times 10^{-5}$, **pH = … 5.00**

Add 100. mL of 0.100 M NaOH

↓**HA**(*aq*) + OH^-(*aq*) → H_2O(*l*) + ↑**A^-**(*aq*)

HA → 1.00 mol – 0.010 mol = **0.99 mol**

A^- → 1.00 mol + 0.010 mol = **1.01 mol**

c_a = 0.99 mol/1.10 L, c_b = 1.01 mol/1.10 L

c_a/c_b = 1.00 → **0.99/1.01**, **pH → 5.01 (tiny change!)**

15

Titration-region & buffer calculations

Add **strong acid** to buffer

1 L buffer, $c_a = c_b = 1.00$ M, $K_a = 1 \times 10^{-5}$, **pH = 5.00**

Add 100. mL of 0.100 M HCl

HCl(*aq*) + ↓**A^-**(*aq*) → ↑**HA**(*aq*) + Cl^-(*aq*)

HA → 1.00 mol + 0.010 mol = **1.01 mol**

A^- → 1.00 mol – 0.010 mol = **0.99 mol**

c_a = 1.01 mol/1.10 L, c_b = 0.99 mol/1.10 L

c_a/c_b = 1.00 → **1.01/0.99**, **pH → 4.99 (tiny change!)**

16

Add strong acid/base **to water**

1 L of water, $K_a = 1 \times 10^{-14}$, **pH = 7.00**

Add 100. mL of 0.100 M HCl

(H_3O^+) = 0.010 mol/1.10 L = 0.0091

pH = 2.04 (huge change!)

Add 100. mL of 0.100 M NaOH

(OH^-) = 0.010 mol/1.10 L = 0.0091

pOH = 2.04, **pH = 11.96 (huge change!)**

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Buffers resist change in pH