Chemical equilibrium calculations

CH102 General Chemistry, Spring 2009

Strong acid (CPS lesson)

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

	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 $K_a > 1$

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

Strong acid 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?

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

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

Weak acid (CPS lesson)

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

	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 $1 > K_a$

$(H_3O^+) = x = \sqrt{K_a c_a}$

Weak acid 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?

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

pH = 5.0

Conjugate base (CPS lesson)

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

	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 $K_b = K_w/K_b > K_w$

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

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

Conjugate base example

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

K_a of HA is 1×10^{-7}.

What is the pH of 0.001 M NaA?

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

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

pOH = 5.0 → pH = 9.0

Weak acid + conjugate base

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

	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 $1 > K_a$

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

Weak acid + conjugate base

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

K_a of HA is 1×10^{-5}

Equal volumes of 0.002 M HA and 0.01 M NaA are combined. What is the pH?

$c_a = 0.001$ M, $c_b = 0.005$ M

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

pH = 6 – 0.3 = 5.7

Conjugate base

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

	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 $1 > K_b$

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

Conjugate base example

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

K_a of HA is 1×10^{-7}.

What is the pH of 0.001 M NaA?

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

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

pOH = 5.0 → pH = 9.0

Weak acid + conjugate base = buffer

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

	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 $1 > K_a$

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

Weak acid + conjugate base = buffer

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

K_a of HA is 1×10^{-5}

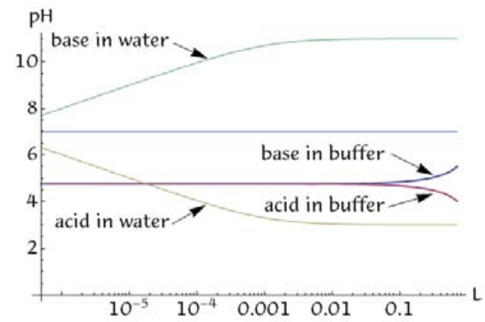
Equal volumes of 0.002 M HA and 0.01 M NaA are combined. What is the pH?

$c_a = 0.001$ M, $c_b = 0.005$ M

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

pH = 6 – 0.3 = 5.7

Buffers resist change in pH (demo)



Buffers resist change in pH

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

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

c_a lowered, c_b raised, c_a/c_b lowered

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

$HCl(aq)$ + $\downarrow$**A^-**$(aq) \rightarrow$ $\uparrow$**HA**$(aq) + Cl^-(aq)$

c_b lowered, c_a raised, c_a/c_b rasied

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

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

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

A^- →1.00 mol + 0.100 mol = **1.01 mol**

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

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

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

$HCl(aq)$ + $\downarrow$**A^-**$(aq) \rightarrow$ $\uparrow$**HA**$(aq) + Cl^-(aq)$

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

A^- →1.00 mol - 0.100 mol = **0.99 mol**

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

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

Add strong acid/base to water

1 L of water, $K_a = 1 \times 10^{-14}$, **pH = 14.00**

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!)

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

c_a/c_b → 1.01/0.99, **pH → 4.99**

Solubility equilibria

$MX_2(s) \rightarrow M^{2+}(aq) + 2\,X^-(aq)$

	MX_2	M^{2+}	X^-
Initial	excess	0	0
Change	− x	+ x	+ 2 x
Equilibrium	**excess**	x	**2x**

$K_{sp} = (M^{2+})(X^-)^2 = (x)(2x)^2 = 4\,x^3$

Common ion effect

$MX_2(s) \rightarrow M^{2+}(aq) + 2\,X^-(aq)$

	MX_2	M^{2+}	X^-
Initial	excess	0	c_{ion}
Change	− x	+ x	+ 2 x
Equilibrium	**excess**	x	c_{ion} **+ 2x ≈** c_{ion}

$K_{sp} = (M^{2+})(X^-)^2 = (x)(c_{ion})^2$

Large c_{ion} makes *x* smaller

Will precipitation occur?

$MX_2(s) \rightarrow M^{2+}(aq) + 2\,X^-(aq)$

	MX_2	M^{2+}	X^-
Initial	0	c_M	c_X

Is $(M^{2+})(X^-)^2 = (c_M)(c_{ion})^2 > K_{sp}$?

If no, no precipitation.

If yes, precipitate will form.

Calculate precipitation

$MX_2(s) \rightarrow M^{2+}(aq) + 2\,X^-(aq)$

	MX_2	M^{2+}	X^-
Initial	0	c_M	$c_X > 2\,c_M$
Revised	excess	0	$c_X - 2\,c_M$
Change	− x	+ x	+ 2 x
Equilibrium	**excess**	x	$\mathbf{c_X - 2\,c_M + 2\,x \approx c_X - 2\,c_M}$

$K_{sp} = (M^{2+})(X^-)^2 = (x)(c_X - 2\,c_M)^2$