HENDERSON-HASSELBALCH EQUATION

pH of solutions of weak acids cont'd

Example pH of solutions of weak acids

- The K_a for a weak acid, is 1.6×10^{-6}. The molarity of acid is 10^{-3} M. What are the:

A) pH.

B) Calculate pK_a and pK_b.

A) $pH = \frac{1}{2} (pK_a + p\,[HA])$

$pK_a = -\log K_a$

$pK_a = -\log K_a = -\log 1.6 \times 10^{-6}$

$pK_a = 5.796$

$P\,[HA] = -\log\,[HA] = -\log 10^{-3}$

$P\,[HA] = 3$

$pH = \frac{1}{2}\,(\,pK_a + p\,[HA])$

$pH = \frac{1}{2}\,(5.79 + 3$

$pH = 4.398$

B)

$pK_a = -\log K_a$

$pK_a = -\log K_a = -\log 1.6 \times 10^{-6}$

$pK_a = 5.796$

$pK_a + pK_b = 14$

$pK_b = 14 - pK_a = 14 – 5.796$

$pK_b = 8.204$

Henderson-Hasselbach equation

- A buffer is a solution that can resist changes in pH when small amounts of acid or base is added.
- It is a mixture of a weak acid and its salt of a strong base (an acidic buffer) **OR** it is a mixture of a weak base and it’s salt of a strong acid (a basic buffer).

Handerson-Hasselbalch equation cont’ed

For acidic: $HA \rightleftharpoons H^+ + A^-$

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

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

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

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

$$pH = pK_a + \text{Log} \frac{[A^-]}{[HA]}$$

Handerson-Hasselbalch equation cont'ed

For basic: $MOH \rightleftharpoons M^+ + OH^-$

$$K_b = \frac{[M^+]\,[OH^-]}{[MOH]}$$

$$[OH^-] = K_b \frac{[MOH]}{[M^+]}$$

$$\mathrm{Log}[OH^-] = \mathrm{Log}\,K_b + \mathrm{Log}\frac{[MOH]}{[M^+]}$$

$$-\,\mathrm{Log}[OH^-] = -\,\mathrm{Log}\,K_b - \mathrm{Log}\frac{[MOH]}{[M^+]}$$

$$pOH = pK_b + \mathrm{Log}\frac{[M^+]}{[MOH]}$$

Handerson-Hasselbalch equation cont'ed

- When the condensation of conjugate acid = conjugate base, pH = pK_a ***OR*** pOH = pK_b

Buffers

- **Buffer Capacity:**
- It is the ability of buffer to resist changes in pH.
- It is the number of moles of H^+ ions that can be added to one liter of the buffer that can decrease the pH by one unit **OR** the number of moles of OH^- ions that can be added to one liter of the buffer that can increase the pH by one unit .
- Unit buffer capacity = mole.

Buffers cont'ed

How does a buffer resist changes in pH?

- *For Example:* in the acetate buffer which is made of acetic acid CH_3COOH and sodium acetate.
  - When H^+ are added it will react with the salt:

$$CH_3COO^- + H^+ \Longleftrightarrow CH_3COOH$$

Thus the buffer converted the free H^+ into acetic acid which does not affect the pH because it is a weak acid, so the pH is not effected.

Buffers cont'ed

- When OH^- are added it will react with the acetic acid:

$$CH_3COOH + OH^- \Leftrightarrow CH_3COO^- + H_2O$$

Thus the buffer converted the free OH^- in the into water and salt which does not affect the pH.

Preparation of buffers

- Example 1: What is the concentration of acetic acid and acetate in 0.2 M acetate buffer, and which has a pH = 5 and pK_a = 4.77

Acetate buffer

Acetic acid + Acetate

HA + A^-

$[HA] + [A^-] = 0.2$ M

$[HA] = ?$

$[A^-] = ?$

$$HA \Longleftrightarrow H^+ + A^-$$

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

$pK_a = -\log K_a$

$4.77 = -\log K_a$

$\log K_a = \text{anti log} - 4.77$

$K_a = 1.7 \times 10^{-5}$

$pH = -\log [H^+]$

$5 = -\log [H^+]$

$[H^+] = \text{anti log} - 5$

$[H^+] = 1 \times 10^{-5}$

Let us assume $[A^-] = y$

Since $[HA] + [A^-] = 0.2$ M

$$[HA] = 0.2 – y$$

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

$$1.7 \times 10^{-5} = [(1 \times 10^{-5})(y)] / (0.2 – y)$$

$$1.7 \times 10^{-5}\,(0.2 – y) = 1 \times 10^{-5}\,y$$

$$(3.4 \times 10^{-6}) – (1.7 \times 10^{-5}\,y) = 1 \times 10^{-5}\,y$$

$$3.4 \times 10^{-6} = 1 \times 10^{-5}\,y + 1.7 \times 10^{-5}\,y$$

$$3.4 \times 10^{-6} = 2.7 \times 10^{-5}\,y$$

$$y = (3.4 \times 10^{-6} / 2.7 \times 10^{-5})$$

$$y = 0.126\text{ M} = [A^-]$$

$$[HA] = 0.2 – 0.126 = 0.074\text{ M}$$

Example 2

- Describe the preparation of 3 L of 0.2 M acetate buffer. Starting from solid sodium acetate trihydrate (A^-), Mwt = 136 and a 1 M solution of acetic acid (HA) the pK_a = 4.77; The concentration of $[A^-]$ = 0.126 M, [HA] = 0.074 M in 0.2 M solution in 1 L.

The no. of moles in buffer = 3 × 0.2 = 0.6 moles

The no. of moles of A^- + the no. of moles of HA = 0.6 moles

SINCE the concentration of $[A^-]$ = 0.126 M in 1 L; the ***Total*** no. of moles in buffer = 0.126 × 3 = 0.378 moles

SINCE the concentration of [HA] = 0.073 M in 1 L; the ***Total*** no. of moles in buffer = 0.073 × 3 = 0.222 moles **OR** The no. of moles of HA = 0.6 - no. of moles of A^- = 0.222 moles

SINCE A^- is solid the wt needed = M × Mwt = 0.378 × 136 = 51.4 g

The **volume** if HA needed = no. of moles / M = 0.222 / 1 = 0.222 L = 222 ml

51.4 g of solid sodium acetate trihydrate is added to 222 ml of acetic acid and the volume is brought up to 3 L.