Buffers

- Example: Ammonia is combined with its salt, NH₄Cl, in sol'n:
- If acid is added to this solution, ammonia reacts with the H⁺ :

 $\mathrm{NH}_{3\,(\mathrm{aq})} + \mathrm{H}^{+}_{(\mathrm{aq})} \rightarrow \mathrm{NH}_{4}^{+}_{(\mathrm{aq})}$

• If a base is added to this solution, the NH₄⁺ from the dissolved salt will react with the OH⁻ :

 $NH_4^+_{(aq)} + OH^-_{(aq)} \rightarrow NH_3_{(aq)} + H_2O_{(1)}$

BUFFER SOLUTION

- When an acid is added, the conjugate base converts the excess H_3O^+ ion into its acid (conjugate base removes excess H_3O^+) $H_3O^+(aq) + A^-(aq) \rightarrow HA(aq) + H_2O(1)$

- When a base is added, the acid converts the excess OH^- ion into its conjugate base and water (acid removes excess OH^- ion) $HA(aq) + OH^-(aq) \rightarrow A^-(aq) + H_2O(1)$

- These reactions go to completion (large equilibrium constants)

pH calculations of buffer solutions

Buffer consisting of a weak acid and its salt with a strong base

 $HA + H_2O \iff A^- + H_3O^+ K_a$ Henderson – Hasselbalch equation

pH = pKa + log[A-]/[HA]

HA – weak acid A⁻ – conjugated base

Buffer consisting of a weak base and its salt with a strong acid

 $B + H_2O \iff BH^+ + OH^-$

pOH = pK_b + log[BH⁺]/[B] B - weak base BH⁺ - conjugated acid

The Henderson-Hasselbalch Equation $HA(aq) + H_2O(l) \Rightarrow A^{-}(aq) + H_3O^{+}(aq)$ $\mathcal{K}_a = \frac{[H_3O^+][A^-]}{[HA]} \qquad [H_3O^+] = \mathcal{K}_a \times \frac{[HA]}{[A^-]}$

$$-\log[H_{3}O^{+}] = -\log K_{a} - \log \left(\frac{[HA]}{[A^{-}]}\right)$$

$$pH = pK_a + log \begin{bmatrix} [base] \\ [acid] \end{bmatrix}$$

HENDERSON-HASSELBALCH EQUATION

In general

$$pH = pK_a + log\left(\frac{C_b}{C_a}\right)$$
 or $pH = pK_a + log\left(\frac{n_b}{n_a}\right)$

- C_a and C_b are the analytical concentrations of the acid and the conjugate base, respectively

- n_a and n_b are the number of moles of the acid and the conjugate base, respectively

 $C_a = n_a/V$ and $C_b = n_b/V$ (concentration ratio equals mole ratio)

PREPARING BUFFERS

- Measure the amount of weak acid (HA) to be used [or weak base (B)]

- Calculate the amount of strong base (OH⁻) to be added [or strong acid (H⁺)]

- This makes a mixture of HA and A⁻ which is a buffer [or B and BH⁺]

Or

- Add the correct proportions of the acid and its conjugate base, then check the pH

Question 1

A buffer solution is made by adding 0.3 mol of acetic acid and 0.3 mol of sodium acetate to enough water to make 1L of solution. Determine the pH of the buffer solution. The K_a for acetic acid is 1.8×10^{-5}

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pH = pK_a + log [A^-] / [HA] A^- = sodium acetate HA = acetic acid
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pH = -log (1.8 \times 10^{-5}) + log (0.3) / (0.3)
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pH = 4.74Question2

Calculate the pH of the buffer solution after 0.02 moles of sodium hydroxide is added?

1 litre of buffer contains 0.3 moles of sodium acetate and 0.3 moles of acetic acid. Sodium hydroxide is a strong base. The acetic acid will react with the base added to try to maintain the pH. What the acid loses in concentration, the salt (sodium acetate) will gain.

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

	CH ₃ COOH	OH-	CH ₃ COO ⁻
Initial conc	0.3	0	0.3
Change	0.3 – 0.02	0.02	0.3 + 0.02
Equil. Conc.	0.28	0.02	0.32

 $pH = pK_a + \log [A^-] / [HA]$ $pH = - \log (1.8 \times 10^{-5}) + \log (0.32) / (0.28)$ pH = 4.74 + 0.058pH = 4.8

Calculating the pH of an acidic buffer solution

Calculate the pH of a buffer whose [HA] is 0.1 mol dm⁻³ and [A⁻] of 0.1 mol dm⁻³. The K_a of the weak acid HA is 2 x 10⁻⁴ mol dm⁻³

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 $K_a = [H^+(aq)] [A^-(aq)]$ [HA(aq)]