ACIDS AND BASES – 5 COMMON ION EFFECT AND BUFFERS

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COMMON ION EFFECT

The common–ion effect is the shift in an ionic equilibrium caused by the addition of a solute that takes part in the equilibrium.

For example:

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

Add 0.05 mol of CH₃COONa

 CH_3COONa in H_2O gives $Na^+ + CH_3COO^-$

<u>Net effect</u>: equilibrium shifts to left because more product is added. pH of the solution will change.

EXAMPLE: COMMON ION EFFECT

Calculate the pH of a 0.10 *M* HF solution to which sufficient sodium fluoride has been added to make the concentration 0.20 *M* NaF. K_a : HF is 6.8 × 10⁻⁴.

Solution:

Conc. of fluoride ion is 0.20 M (from NaF)

	HF	+	H_2O		${\rm H_{3}0^{+}}$	+ F⁻
Initial	0.10				0	0.20
Change	- X				+X	+X
Eq conc.	0.10-x				X	0.20 + x

$$\mathcal{K}_{a} = \frac{[H_{3}O^{+}][F^{-}]}{[HF]}$$

6.8×10⁻⁴ = $\frac{x(0.20 + x)}{(0.10 - x)}$
(assume x is minimal)

 $[H_{3}O^{+}] = x = 3.4 \times 10^{-4} M$ $pH = -\log[H_{3}O^{+}] = -\log(3.4 \times 10^{-4})$ pH = 3.47

BUFFERS

- Buffers are solutions containing weak acid and its conjugate base OR weak base and its conjugate acid.
- pH of buffers don't change on addition of small amounts of acid or base.
- In lab one makes buffers to do reactions in a controlled pH environment.
- pH of buffers can be calculated using the traditional ICE method or by Henderson-Hasselbalch equation, which can be derived from the K_a expression.
 - K_a expression: $K_a = \frac{[H^+][A^-]}{[HA]}$
 - Rearrange and take log $pH = pK_a + \log \frac{[A^-]}{[HA]}$

$$pH = pK_a + \log \frac{[conjugate base]}{[weak acid]}$$

MAKING BUFFERS

- Select the acid + conjugate base or base + conjugate acid pair.
- Depends on the pH range needed.
- Look through pK_a data for weak acids and bases and decide from there.
- Once decided; you know the pH you need the buffer to be in; so use the Hendersen-Hasselbalch equation to determine the ratio of the acid to conjugate base.

Example:

So if a buffer of 4.5 is needed use benzoic acid ($pK_a = 4.19$) then the ratio of conjugate base to acid should be 2.04 mol : 1 mol in a 1 L solution.

$$4.5 = 4.19 + \log \frac{[C_6H_5COO^-]}{[C_6H_5COOH]}$$
$$2.04 = \frac{[C_6H_5COO^-]}{[C_6H_5COOH]}$$

EXAMPLE: CALCULATION-BUFFER

What is the $[H_3O^+]$ for a buffer solution that is 0.250 M in acid and 0.600 M in the corresponding salt if the weak acid $K_a = 5.80 \times 10^{-7}$?

Solution:

 $HA(aq) + H_2O(l) \longrightarrow H_3O^+(aq) + A^-(aq)$ $pK_a = -\log(5.80 \times 10^{-7}) = -(-6.237) = 6.237$ [base] = 0.600 *M* and [acid] = 0.250 *M* $pH = pK_a + log \frac{[base]}{[acid]}$ $pH = 6.237 + log \frac{[0.600]}{[0.250]}$ $pH = 6.237 + \log 2.40$ pH = 6.237 + 0.380 = 6.617

$$[H_3O^+] = 10^{-6.617} = 2.42 \times 10^{-7} M_{\odot}$$

EXAMPLE: ACETIC ACID BUFFER

The following calculations how pH stays about the same on addition of acid or base to an acetic acid buffer. (Acetic acid buffer is made from adding acetic acid and its conjugate base in salt form – sodium acetate). In this example we will take 100 mL of a 0.100 M acetic acid+0.100 M acetate buffer.

1) Calculation of pH:

$$K_{a} = 1.8 \times 10^{-5}$$
 p $K_{a} = 4.74$
 $pH = pK_{a} + \log \frac{[A^{-}]}{[HA]}$
 $pH = 4.74 + \log \frac{[0.100 M]}{[0.100 M]}$

$$pH = 4.74$$

EXAMPLE: CONTD...2 ADDITION OF ACID/BASE

• Adding 0.001 mol HCl, a strong acid.

 H^+ + CH_3COO^- CH₃COOH 0.001 mol 0.01 mol 0.01 mol Before After HCl 0 mol 0.01-.001mol = 0.009 mol 0.01 + .001 mol = 0.011 molNow with new numbers: $pH = 4.74 + \log \frac{[0.009 M]}{[0.011 M]}$ pH = 4.65• Adding 0.001 mol NaOH, a strong base. OH- + CH₃COOH $CH_{3}COO^{-} + H_{2}O$ Before 0.001 mol 0.01 mol 0.01 mol After NaOH 0 mol 0.01-.001mol = 0.009 mol 0.01+.001mol = 0.011 mol Now with new numbers: $pH = 4.74 + \log \frac{[0.011M]}{[0.009M]}$ pH = 4.83

Original pH = 4.74; with little acid 4.65 and with little base 4.83. Not much change!

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KEY CONCEPTS

- Be able to identify what acid-base combinations are needed to make buffers.
- Do all calculations regarding buffers