

Q1: Find minimum concentrations of buffer components, C_{HA} , and C_{A^-} , that are required to keep pH change within ± 1 unit when a strong base or acid of concentration C (calculated for total volume) is added to the buffer. Assume that buffer ratio is known: $C_{A^-}/C_{HA} = R$.

Qualitative Clarification:

- From the H-H equation, $pH = pK_a + \log R$. The ΔpH value has to be ± 1 unit, that is:

$$|\log R^{\text{fin}} - \log R| < 1$$

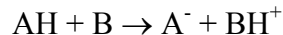
$$|\log(R^{\text{fin}}/R)| < 1$$

$$0.1 < R^{\text{fin}}/R < 10$$

$$0.1R < R^{\text{fin}} < 10R$$

- This is a double inequality; a half of it, $R^{\text{fin}} < 10R$ is for adding a strong base and another half, $R^{\text{fin}} > 0.1R$ for adding a strong acid.

1. Lets first consider the case of adding a strong base, B. The reaction of neutralization takes place under stoichiometric conditions (no equilibrium):



We can write a table similar to the ICE table:

Concentration	AH	B	A^-	BH^+
Initial	C_{HA}	C	C_{A^-}	0
Change	$-C$	$-C$	C	C
Final	$C_{HA} - C$	0	$C_{A^-} + C$	C

$$R^{\text{fin}} = (C_{A^-} + C)/(C_{HA} - C)$$

$$R^{\text{fin}} < 10R$$

Using these 2 equations we get:

$$(C_{A^-} + C)/(C_{HA} - C) < 10R$$

Substituting R into the last equation we get:

$$(C_{A^-} + C)/(C_{HA} - C) < 10C_{A^-}/C_{HA} \quad (1)$$

There are two unknowns in this equation, C_{A^-} and C_{HA} , therefore an additional equation is required to find the unknowns:

$$C_{A^-}/C_{HA} = R \quad (2)$$

From (2):

$$C_{A^-} = RC_{HA} \quad (2')$$

Substituting this into (1) gives:

$$(RC_{HA} + C)/(C_{HA} - C) < 10RC_{HA}/C_{HA}$$

$$(RC_{HA} + C)/(C_{HA} - C) < 10R$$

$$RC_{HA} + C < 10RC_{HA} - 10RC$$

$$10RC + C < 10RC_{HA} - RC_{HA}$$

$$10RC_{HA} - RC_{HA} > 10RC + C$$

$$C_{HA}(10R - R) > C(10R + 1)$$

$$C_{HA} > C(10R + 1)/(10R - R)$$

$$C_{HA} > C(R + 0.1)/(R - 0.1R)$$

$$C_{HA} > C(R + 0.1)/0.9R$$

Substituting the last expression into (2') we get:

$$C_{A^-} > RC(R + 0.1)/0.9R$$

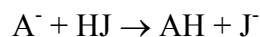
$$C_{A^-} > C(R + 0.1)/0.9$$

For adding a strong base

The formula for a total concentration of a buffer for adding a strong base is:

$$C_{HA} + C_{A^-} > C \frac{(R + 0.1)(1 + R)}{0.9R} \quad \text{for adding strong base}$$

2. Let's now consider the case of adding a strong acid, HJ. The reaction of neutralization takes place under stoichiometric conditions (no equilibrium):



We can write a table similar to the ICE table:

Concentration	A^-	HJ	AH	J^-
Initial	C_{A^-}	C	C_{AH}	0
Change	$-C$	$-C$	C	C
Final	$C_{A^-} - C$	0	$C_{AH} + C$	C

$$R^{fin} = (C_{A^-} - C)/(C_{HA} + C)$$

$$R^{fin} > 0.1R$$

Using these 2 equations we get:

$$(C_{A^-} - C)/(C_{HA} + C) > 0.1R$$

Substituting R into the last equation we get:

$$(C_{A^-} - C)/(C_{HA} + C) > 0.1C_{A^-}/C_{HA} \quad (1)$$

There are two unknowns in this equation, C_{A^-} and C_{HA} , therefore an additional equation is required to find the unknowns:

$$C_{A^-}/C_{HA} = R \quad (2)$$

From (2):

$$C_{A^-} = RC_{HA} \quad (2')$$

Substituting this into (1) gives:

$$(RC_{HA} - C)/(C_{HA} + C) > 0.1RC_{HA}/C_{HA}$$

$$(RC_{HA} - C)/(C_{HA} + C) > 0.1R$$

$$RC_{HA} - C > 0.1R(C_{HA} + C)$$

$$RC_{HA} - C > 0.1RC_{HA} + 0.1RC$$

$$RC_{HA} - 0.1RC_{HA} > C + 0.1RC$$

$$C_{HA} \times 0.9R > C(1 + 0.1R)$$

$$C_{HA} > C(1 + 0.1R)/0.9R$$

$$C_{HA} > C(1 + 0.1R)/0.9R$$

Substituting the last expression into (2') we get:

$$C_{A^-} > RC(1 + 0.1R)/0.9R$$

$$C_{A^-} > C(1 + 0.1R)/0.9$$

For adding strong acid

The formula for a total concentration of a buffer for adding an acid is:

$$C_{HA} + C_{A^-} > C \frac{(1 + 0.1R)(1 + R)}{0.9R} \quad \text{for adding strong acid}$$

Q2: Find minimum total concentrations of the components of acetic buffer, $C_{HA} + C_{A^-}$, at pH 4.5 that are required to keep pH change within ± 1.00 unit when:

a) 0.010 M (calculated for total volume) HCl is added

b) 0.010 M (calculated for total volume) HCl is added

The initial buffer ratio can be found from the H-H equation:

$$pH = pK_a + \log R$$

$$\log R = pH - pK_a$$

$$R = C_{A^-}/C_{HA} = 10^{pH - pK_a} = 10^{4.50 - 4.74} = 10^{-0.24} = 0.575$$

a) For adding HCl, a strong acid:

$$C_{HA} + C_{A^-} > C \frac{(1 + 0.1R)(1 + R)}{0.9R} = 0.01 \times \frac{(1 + 0.1 \times 0.575)(1 + 0.575)}{0.9 \times 0.575} = 0.0322 \text{ M}$$

b) For adding NaOH, a strong base:

$$C_{HA} + C_{A^-} > C \frac{(R + 0.1)(1 + R)}{0.9R} = 0.01 \times \frac{(0.575 + 0.1)(1 + 0.575)}{0.9 \times 0.575} = 0.0205 \text{ M}$$

It is what we expect for the buffer whose $pH < pK_a$. Such a buffer better withstand the addition of a base than an acid, and therefore to withstand HCl we need a higher concentration of the buffer.