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 = pKa + logR. The ΔpH value has to be ±1 unit, that is:

$$|\log R^{fin} - \log R| < 1$$
$$|\log(R^{fin}/R)| < 1$$
$$0.1 < R^{fin}/R < 10$$
$$0.1R < R^{fin} < 10R$$

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

$$AH + B \rightarrow A^- + BH^+$$

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

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

Using these 2 equations we get:

$$(C_{A-} + C)/(C_{HA} – C) < 10R$$

Substituting R into the last equation we get:

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

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

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

From (2):

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

Substituting this into (1) gives:

$$(RC_{HA} + C)/(C_{HA} – C) < 10R\cancel{C_{HA}}/\cancel{C_{HA}}$$
$$(RC_{HA} + C)/(C_{HA} – C) < 10R$$
$$RC_{HA} + C < 10RC_{HA} – 10RC$$
$$10RC + C < 10RC_{HA} – RC_{HA}$$
$$10RC_{HA} – RC_{HA} > 10RC + C$$
$$C_{HA}(10R – R) > C(10R + 1)$$
$$C_{HA} > C(10R + 1)/(10R – R)$$
$$C_{HA} > C(R + 0.1)/(R – 0.1R)$$
$$\mathbf{C_{HA} > C(R + 0.1)/0.9R}$$

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

$$C_{A-} > RC(R + 0.1)/0.9R$$
$$\mathbf{C_{A-} > C(R + 0.1)/0.9}$$

} For adding a strong base

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

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

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

$$A^- + HJ \rightarrow AH + J^-$$

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:

$(C_{A-} - C)/(C_{HA} + C) > 0.1C_{A-}/C_{HA}$ **(1)**

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

$C_{A-}/C_{HA} = R$ **(2)**

From (2):

$C_{A-} = RC_{HA}$ **(2')**

Substituting this into (1) gives:

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

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

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

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

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

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

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

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

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

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

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

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:

$pH = pKa + \log R$
$\log R = pH - pKa$
$R = C_{A^-}/C_{HA} = 10^{pH - pKa} = 10^{4.50 - 4.74} = 10^{-0.24} = 0.575$

a) **For adding HCl, a strong acid:**

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

b) **For adding NaOH, a strong base:**

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

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.