Short Primer: Buffers

A buffer is a solution that resists changes in pH upon:

- addition of small amounts of acid or base
- dilution

A buffer is produced by a solution containing comparable amounts of a weak acid and the corresponding conjugate base. For example, a 1:1 mixture of acetic acid (HOAc) and sodium acetate (OAC⁻) is a commonly used buffer:

$$HOAc \rightleftharpoons H^+ + OAc^- \qquad\qquad [HOAc] \cong [OAc^-] \qquad (1)$$

The pH of a buffer solution is calculated from the K_a expression for the acid dissociation:

$$K_a = \frac{[H^+][OAc^-]}{[HOAc]} \qquad \text{or solving for } [H^+] \text{ gives:} \quad [H^+] = K_a \frac{[HOAc]}{[OAc^-]} \qquad (2)$$

The pH is calculated from the previous expression by taking the – log of both sides:

$$-\log [H^+] = -\log K_a - \log\left(\frac{[HOAc]}{[OAc^-]}\right) \qquad (3)$$

Given the definitions of the pH = – log $[H^+]$ and pK_a = – log K_a the expression becomes:

$$pH = pK_a - \log\left(\frac{[HOAc]}{[OAc^-]}\right) \qquad (4)$$

The ratio of the acid to conjugate base concentrations is conventionally inverted to give:

$$pH = pK_a + \log\left(\frac{[OAc^-]}{[HOAc]}\right) \qquad (5)$$

which is nothing more than the K_a expression, Eq. 2, rearranged to solve for the pH directly. The response of a buffer to applied stresses is understood using Eq. 5. The addition of small amounts of strong base to the buffer converts acetic acid to acetate:
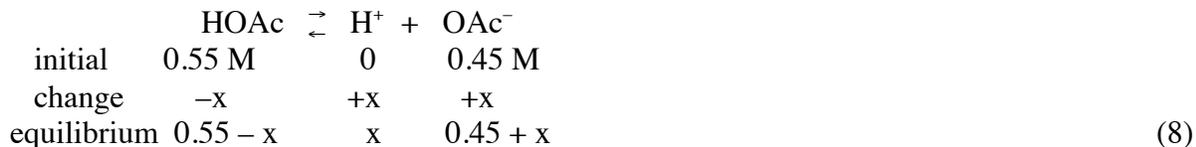
$$HOAc + OH^- \rightarrow OAc^- + H_2O \qquad (6)$$
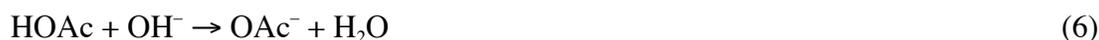
However, if the moles of added OH⁻ are small compared to the initial moles of acetic acid and acetate, the ratio [OAc⁻]/[HOAc] stays essentially constant and the pH remains relatively unchanged. The addition of small amounts of strong acid converts acetate to acetic acid:

$$OAc^- + H^+ \rightarrow HOAc \qquad (7)$$

However, if the moles of added H⁺ are small compared to the initial moles of acetic acid and acetate, the ratio [OAc⁻]/[HOAc] stays essentially constant and the pH remains relatively unchanged. Since a buffer contains large concentrations of both a weak acid and the conjugate base, significant amounts of the weak acid are available to react with any added base and significant amounts of the weak base are available to react with any added acid.

Consider a solution that contains 0.55 M acetic acid and 0.45 M acetate. The equilibrium position of the mixture is determined by evaluating the equilibrium concentrations:

$$\text{HOAc} \rightleftharpoons \text{H}^+ + \text{OAc}^-$$

initial	0.55 M	0	0.45 M
change	$-x$	$+x$	$+x$
equilibrium	0.55 $-$ x	x	0.45 + x	(8)
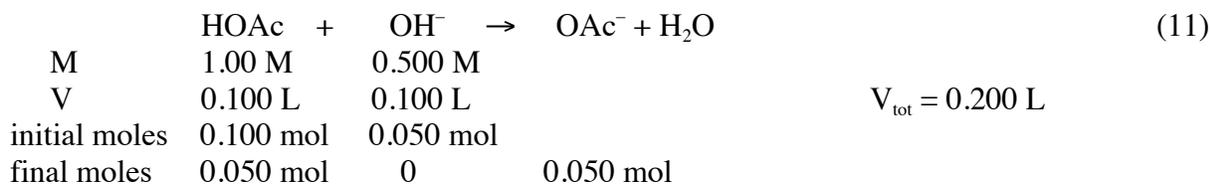
Substitution of the equilibrium concentrations into Eq. 5 gives:

$$pH = pK_a + \log\left(\frac{0.45 + x}{0.55 - x}\right) \tag{9}$$

For pure 0.5 M acetic acid the degree of dissociation is less than 1%. As a result, x in Eq. 9 is expected to be small. In a solution with comparable initial concentrations of HOAc and OAc⁻, LeChatelier's Principle predicts that x is even smaller than in pure acetic acid solutions. The value of x in Eq. 9 is negligible. The concentrations in the ratio are then well approximated by the initial analytical concentrations. In the general case, let the initial analytical concentration of the weak acid be c_a and the initial analytical concentration of the conjugate base be c_b. Then the pH of a buffer solution is well approximated by the Henderson Hasselbalch equation:

$$pH = pK_a + \log\left(\frac{c_b}{c_a}\right) \tag{10}$$

Dilution of the buffer solution affects c_a and c_b by the same factor, so the ratio is unchanged upon dilution.

   Preparation of a buffer solution is easily accomplished by mixing solutions of the pure weak acid and the pure conjugate base. For example, mixing 110 mL of 0.500 M acetic acid and 90.0 mL of 0.500 M sodium acetate produces a buffer with 0.275 M acetic acid and 0.225 M acetate, giving c_b/c_a = 0.82. If only one of the conjugate acid-base pair is available, then addition of strong acid or strong base creates a buffer. For example, the addition of 100.0 mL of 0.500 M NaOH to 100 mL of 1.00 M acetic acid produces acetate ion. Assuming the reaction with the strong base goes to completion:

$$\text{HOAc} + \text{OH}^- \rightarrow \text{OAc}^- + \text{H}_2\text{O} \tag{11}$$

	HOAc	OH⁻	OAc⁻ + H₂O	
M	1.00 M	0.500 M		
V	0.100 L	0.100 L		V_{tot} = 0.200 L
initial moles	0.100 mol	0.050 mol		
final moles	0.050 mol	0	0.050 mol	

The ratio of the conjugate base and acid is c_b/c_a = (0.050 mol/V_{tot})/(0.050 mol/V_{tot}) = 1.00. Notice that the total volume cancels, since both species are in the same solution. As a result, the problem can be worked directly in moles.