Common Ion Effect
Acid + Conjugate Base

For moderately concentrated solutions of a weak acid, HA, and significant added amounts of its conjugate base, A^-:

$$HA + H_2O \rightleftharpoons H_3O^+ + A^-$$

$$[HA] \approx C_{HA} \qquad\qquad [A^-] \approx C_{A^-}$$

$$K_a = \frac{[H_3O^+][A^-]}{[HA]} \approx \frac{[H_3O^+]C_{A^-}}{C_{HA}}$$

$$[H_3O^+] \approx K_a \times \left(\frac{C_{HA}}{C_{A^-}}\right)$$

Common Ion Effect
Base + Conjugate Acid

For moderately concentrated solutions of a weak base, B, and significant added amounts of its conjugate acid, BH^+:

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

$$[B] \approx C_B \qquad\qquad [BH^+] \approx C_{BH^+}$$

$$K_b = \frac{[OH^-][BH^+]}{[B]} \approx \frac{[OH^-]C_{BH^+}}{C_B}$$

$$[OH^-] \approx K_b \times \left(\frac{C_B}{C_{BH^+}}\right)$$

Henderson-Hasselbalch Equations

$$\mathrm{pH} = \mathrm{p}K_a + \log\left(\frac{C_{\mathrm{A}^-}}{C_{\mathrm{HA}}}\right)$$

$$\mathrm{pOH} = \mathrm{p}K_b + \log\left(\frac{C_{\mathrm{BH}^+}}{C_{\mathrm{B}}}\right)$$

Volume Is Irrelevant

☞ For a solution of an acid to which significant amounts of its conjugate base have been added so that *both* have moderate concentrations (>>10^{-5} M), the volume of the solution does not affect the pH.

If V is the volume of a solution made by adding significant amounts of both HA and A^-:

C_{HA} = mol HA/V $\qquad\qquad$ C_{A^-} = mol A^-/V

Substituting into K_a:

$$K_a \approx \frac{[H_3O^+]\left(\frac{\text{mol } A^-}{V}\right)}{\frac{\text{mol HA}}{V}} = \frac{[H_3O^+](\text{mol } A^-)}{\text{mol HA}}$$

$$[H_3O^+] \approx K_a \times \left(\frac{\text{mol HA}}{\text{mol } A^-}\right)$$

☞ This is also true for a solution of a base to which significant amounts of its conjugate acid have been added so that *both* have moderate concentrations (>>10^{-5} M).

Equimolar Solutions of a Conjugate Pair

If $C_{HA} = C_{A^-}$, then

$$K_a = \frac{[H_3O^+]C_{A^-}}{C_{HA}} = [H_3O^+]$$

And $$pH = pK_a$$

Likewise, if $C_B = C_{BH^+}$, then

$$K_b = \frac{[OH^-]C_{BH^+}}{C_B} = [OH^-]$$

And $$pOH = pK_b$$

Buffer Solutions

☞ A buffer solution is an equilibrium mixture of a weak acid and its conjugate base, or a weak base and its conjugate acid, with both members of the conjugate pair present in moderate concentrations.

☞ The essential properties of a buffer solution are:

1. pH does not change with moderate dilution.

2. pH does not change significantly with small additions of acid or base.

The Ideal Buffer

① Make

$$[HA] = [A^-] \text{ or } [B] = [BH^+].$$

Then,

$$pH = pK_a \text{ and } pOH = pK_b$$

✓ Response will be equally good to added H_3O^+ or OH^-.

② Make concentrations high.

✓ Then, the ratio $[A^-]/[HA]$ or $[BH^+]/[B]$ will not change *significantly* with small added amounts of H_3O^+ or OH^-.

Nearly Ideal Buffer

✓ To make a buffer with a desired pH:

① Try to choose a conjugate pair whose $pK_a \approx pH$.

② Adjust the ratio $[A^-]/[HA]$ or $[BH^+]/[B]$ to achieve the desired pH.

③ The practical limit on the choice of conjugate acid-base pair is

$$pH \approx pK_a \pm 1$$

✓ Otherwise, one member of the pair is present in too small an amount to make an effective buffer.