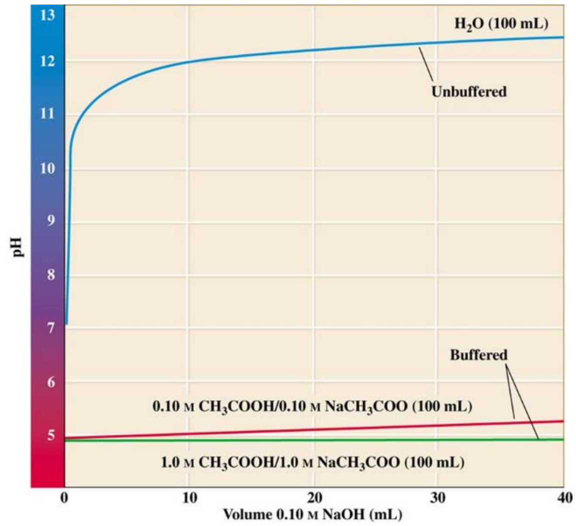
BUFFERS_______________________________________ H Ch 9-5, Z 8.1-8.4

a solution that is able to withstand changes in pH (so that the pH is almost constant) upon addition of small amounts of acid or base - based upon the common ion effect

pH of human body 7.4 (37^{o}C) – below 7 and above 7.8 death quickly follows. In the body the pH is maintained by carbonate, phosphate and protein buffers

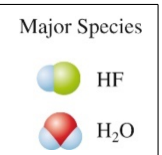


Common Ion Effect

shift of an ionic equilibrium upon addition of a solute which contains an ion that participates in the equilibrium

EX 1. What is the pH of 1.0 F HF? ($K_a = 6.6 \times 10^{-4}$) and the fraction (or percent) dissociated?

$$HF(aq) \quad + \quad H_2O(l) \quad \Longleftrightarrow \quad H_3O^+(aq) \quad + \quad F^-(aq)$$

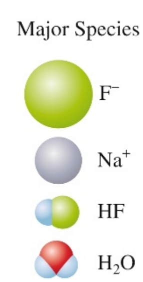


EX 2. Consider the addition of enough NaF to the solution in EX 1 to make the solution 1 F in both HF and NaF. Determine the pH and fraction dissociated. Since

$$NaF(s) \rightarrow Na^+(aq) + F^-(aq)$$

the concentration table changes:

$$HF(aq) \quad + \quad H_2O(l) \quad \Longleftrightarrow \quad H_3O^+(aq) \quad + \quad F^-(aq)$$



EX 3. What is the pH of a solution which is 1.0 F in both HF and 1.0 NaF ($K_a = 6.6 \times 10^{-4}$) and 0.1 M in HCl?

EX 4. What is the pH of a solution which is 1.0 F in both HF and 1.0 NaF ($K_a = 6.6 \times 10^{-4}$) and 0.1 M in NaOH?

Working with Buffer Solutions

*note ratio of base form to acid

based on a **weak acid** (HA) and its **conjugate base** (A-)

$$HA(aq) + H_2O(l) \iff H_3O^+(aq) + A^-(aq) \qquad K_a = \frac{[H_3O^+][A^-]}{[HA]} \quad \text{or } pH = pK_a + \log_{10}\frac{[A^-]}{[HA]}$$

$$\text{Henderson – Hasselbalch Equation:} \quad pH = pK_a + \log\frac{[A^-]}{[HA]}\,^{*}$$

do not forget about activities

$$pH = pK_a + \log\frac{[A^-]\gamma_{A^-}}{[HA]\gamma_{HA}}$$

based on a **weak base** (B:) and its **conjugate acid** (BH^+)

$$B:(aq) + H_2O(l) \iff OH^-(aq) + BH^+(aq)$$

$$BH^+(aq) + H_2O(l) \iff H_3O^+(aq) + B:(aq) \qquad K_a = \frac{[H_3O^+][B:]}{[BH^+]} \quad \text{or } pH = pK_a + \log_{10}\frac{[B:]}{[BH^+]}$$

$$\text{Henderson – Hasselbalch Equation:} \quad pH = pK_a + \log\frac{[B]}{[BH^+]}\,^{*}$$

pK_a applies to *this* acid

Henderson-Hasselbalch Equation

For most cases the Henderson-Hasselbalch equation can be simplified by not solving the equilibrium problem and making the substitutions (real Henderson-Hasselbalch equation)

$$\frac{[A^-]}{[HA]} \approx \frac{[A^-]_0}{[HA]_0} \qquad \text{or} \qquad \frac{[B:]}{[BH^+]} \approx \frac{[B:]_0}{[BH^+]_0}$$

If F_{HA} or F_{A-} is small (solution is too dilute) or if $[H^+]$ or $[OH^-]$ is large (too acidic or too basic) then this approximation cannot be used and the systematic approach must be used.

(BUT THEN THE SOLUTION IS NOT A USEFUL BUFFER!)

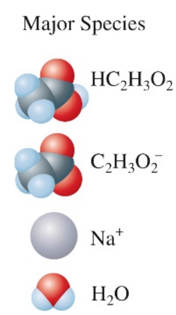
Preparation of a Buffer

1) Weak Acid and its Conjugate Base (or Weak Base and its Conjugate Acid)
2) Addition of Strong Base to Weak Acid (or Strong Acid to Weak Base)

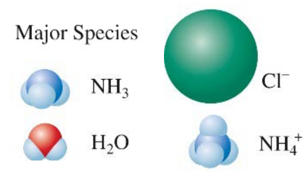
EX 5. $K_a(CH_3COOH) = 1.76 \times 10^{-5}$

a) Determine the pH of a solution which is simultaneously 0.500 M CH_3COOH and 0.300 M sodium acetate ($NaCH_3COO$).

b) Determine the pH when 100 mL of 0.200 M sodium acetate is added to 500 mL of 0.150 M acetic acid.



EX 6. Determine the pH when 100 mL of 0.500 M NH_3 is mixed with 200 mL of 0.300 M ammonium chloride (NH_4Cl) $K_b(NH_3) = 1.8 \times 10^{-5}$.



FIND THE RATIO then work in molarity or moles

EX 7. Prepare 500 mL of a solution buffered at pH = 4.50 with a buffer concentration of 0.40 M. This buffer is to be made from 1.00 M C_6H_5COOH ($K_a = 6.3 \times 10^{-5}$, $pK_a = 4.2006$) and 1.00 M NaC_6H_5COO. What volume of acid and its conjugate base would you need?

EX 8. An aqueous solution contains 0.331 F methylamine (CH_3NH_2, $K_b = 4.4 \times 10^{-4}$). How many mL of 0.293 M hydroiodic acid would have to be added to 225 mL of this solution in order to prepare a buffer with a pH of 11.100?

when working with buffers do **stoichiometry first** (first line of ICE table) then handle equilibrium