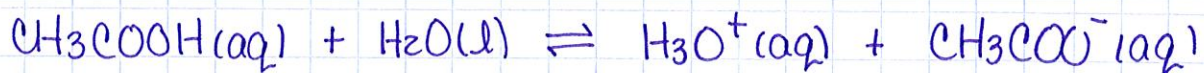


Ch 17: Additional Aspects of Aqueous Equilibria

1. The Common Ion Effect - consider solutions that contain a weak acid and a soluble salt of that acid. They 2 substances share a common ion.



According to LeChâtelier's Principle, what would happen to the equilibrium if more CH_3COO^- were added to the solution in the form of sodium acetate (NaCH_3COO)
shift to the left.

- A. The Common Ion Effect - whenever a weak electrolyte and a strong electrolyte contain a common ion, the weak electrolyte ionizes less than it would if it were alone in the solution.

ex (1) Calculate the fluoride ion concentration and pH of a solution that is 0.20M in HF and 0.10M in HCl.
 K_a for HF = 6.8×10^{-4} .

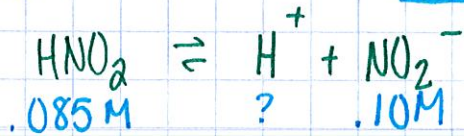


$$\frac{[.10][\text{F}^-]}{[.20]} = 6.8 \times 10^{-4}$$

$$[\text{F}^-] = 6.8 \times 10^{-4} \frac{[.20]}{[.10]} = 1.36 \times 10^{-3}$$

$$\text{pH} = -\log[\text{H}^+] = -\log[.1] = 1$$

Ex(2) calculate the pH of a solution containing .085M HNO_2 ($K_a = 4.5 \times 10^{-4}$) and .10M KNO_2 .



$$K_a = \frac{[\text{H}^+][\text{NO}_2^-]}{[\text{HNO}_2]} = 4.5 \times 10^{-4}$$

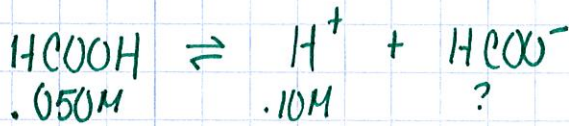
$$\text{pH} = -\log[3.83 \times 10^{-4}]$$

$$\text{pH} = 3.4$$

$$\frac{[\text{H}^+][.10]}{[.085]} = 4.5 \times 10^{-4}$$

$$[\text{H}^+] = 3.83 \times 10^{-4}$$

Ex(3) calculate the formate ion concentration and pH of a solution that is .050M in formic acid (HCOOH , $K_a = 1.8 \times 10^{-4}$) and .10M in HNO_3 .



$$K_a = \frac{[\text{H}^+][\text{HCOO}^-]}{[\text{HCOOH}]} = 1.8 \times 10^{-4}$$

$$\frac{[.10][\text{HCOO}^-]}{[.050]} = 1.8 \times 10^{-4}$$

$$[\text{HCOO}^-] = 9.0 \times 10^{-5}$$

$$\text{pH} = -\log[.10] = 1.0$$

* The common ion effect also works w/weak bases too.

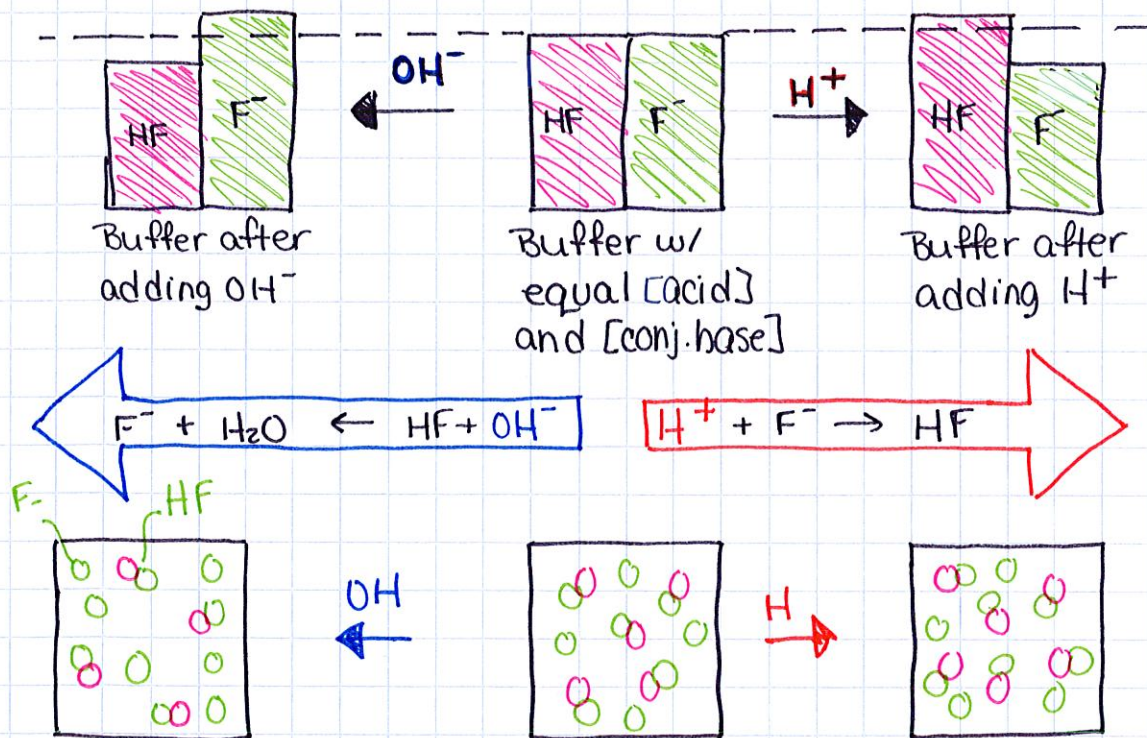
2. Buffers - solutions of a weak conjugate acid-base pair. Resistant to pH changes, even when a strong acid or base is added to the solution.

why? b/c it has both an acid to neutralize OH^- & a base to neutralize H^+ .

However, the weak acid-base combo in the buffer cannot neutralize each other.

A. Buffers are often made by mixing a weak acid or base with a salt of that acid or base.

B. Buffer Action



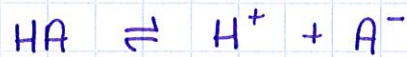
when a small portion of OH^- is added to a buffer, the OH^- reacts with the HF, decreasing $[\text{HF}]$ & increasing $[\text{F}^-]$

when a small portion of H^+ is added to a buffer, the H^+ reacts with the F^- , decreasing $[\text{F}^-]$ and increasing $[\text{HF}]$.

Since the pH is dependent on the ratio of F^- to HF, the resulting pH change is small.

c. Calculating the pH of a Buffer

- consider the equilibrium expression for a generic acid, HA



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

can be rearranged to get:

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

take the $-\log$ of both sides to get:

$$-\log K_a = -\log [H^+] + -\log \frac{[A^-]}{[HA]}$$

pKa *pH* *base* *acid*

which is:

$$pK_a = pH - \log \frac{[base]}{[acid]}$$

OR

$$pH = pK_a + \log \frac{[base]}{[acid]}$$

Henderson - Hasselbalch Equation

In doing equilibrium calculations, we have seen that we can normally neglect the amounts of acid and base of the buffer that ionize. \therefore we can usually use the starting concentrations of the acid and base components of the buffer directly.

Ex (4) What is the pH of a buffer that is 0.12M in lactic acid, $\text{CH}_3\text{CH}(\text{OH})\text{COOH}$, and 0.10M in sodium lactate? K_a for lactic acid is 1.4×10^{-4} .

$$\text{pH} = \text{p}K_a + \log \frac{[\text{base}]}{[\text{acid}]}$$

$$\text{pH} = -\log[1.4 \times 10^{-4}] + \log \frac{[.10]}{[.12]}$$

$$\text{pH} = 3.85 + -.079$$

$$\text{pH} = 3.77$$

Ex (5) Calculate the pH of a buffer composed of 0.12M benzoic acid and 0.20M sodium benzoate. K_a is 6.3×10^{-5} .

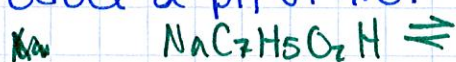
$$\text{pH} = -\log(6.3 \times 10^{-5}) + \log \frac{[.20\text{M}]}{[.12\text{M}]}$$

$$\text{pH} = 4.2 + .222$$

$$\text{pH} = 4.42$$

Ex (6) Calculate the concentration of sodium benzoate, $\text{NaC}_7\text{H}_5\text{O}_2$, that must be present in a 0.20M solution of benzoic acid to produce a pH of 4.0.

$$K_a = 6.3 \times 10^{-5}$$



$$\text{pH} = 4.0 = -\log[6.3 \times 10^{-5}] + \log \left[\frac{\text{base}}{.20\text{M}} \right]$$

$$\frac{4.0}{-4.20} = \frac{4.80}{-4.20} + \log \left[\frac{\text{base}}{.20\text{M}} \right]$$

$$-.2 = \log \left[\frac{\text{base}}{.20\text{M}} \right]$$

$$10^{-.2} = \frac{\text{base}}{.20\text{M}}$$

$$[0.20\text{M}] \cdot .63 = \left[\frac{\text{base}}{.20\text{M}} \right] \cdot .20\text{M}$$

$$\text{base} = 0.126\text{M}$$

D. Buffer capacity and pH range

- Buffer capacity - amount of acid or base the buffer can neutralize before the pH begins to change to an appreciable degree.
 - depends on the amount of acid and base the buffer is made from.
 - pH of a buffer depends on K_a for the acid and relative $[base]$ and $[acid]$ $pH = pK_a + \log \frac{[base]}{[acid]}$

For example,

$[H^+]$ for a 1L solution that is 1M CH_3COOH & 1M in CH_3COONa

= $[H^+]$ for a 1L solution that is .1M in CH_3COOH and .1M in CH_3COONa

↑ But this solution has a greater buffering capacity. why?

higher $[CH_3COOH]$ & $[CH_3COONa]$

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- The pH range of a buffer is one that has an acid with a pK_a close to the desired pH of the solution

$$pH = pK_a \pm 1$$

Ex (7) An employer is interviewing 4 applicants for a laboratory technician and asks each how to prepare a buffer solution with a $pH \approx 9.0$.

Archie A says he would mix acetic acid and sodium acetate solutions

Bonny B says she would mix NH_4Cl and HCl solutions.

Carla C says she would mix NH_4Cl and NH_3 solutions.

Dexter D says he would mix NH_3 and $NaOH$ solutions.

K_a acetic acid = 1.8×10^{-5} K_a for NH_4^+ = 5.6×10^{-10}

who gets the job and why?