

BUFFERS

Ch 9-5

SWITCHED TO HARRIS TEXT

Third midterm exam on Monday, November 22

9-5 Buffers

Due to upcoming exam buffer and polyprotic acid homework will be posted this weekend.

Buffer handout will be posted on web, complete with solutions.

Weak Acid Dissociation - $K_a = x^2 / (F - x)$

EX 7. What is the pH of 0.010 and 0.0010 M acetic acid, $K_a = 1.76 \times 10^{-5}$, and its fraction of dissociation

| | | | | | | | |
|---|------------------------------|---|-------------------------|----------------------|----------------------------|---|-------------------------------|
| | $\text{CH}_3\text{COOH}(aq)$ | + | $\text{H}_2\text{O}(l)$ | \rightleftharpoons | $\text{H}_3\text{O}^+(aq)$ | + | $\text{CH}_3\text{COO}^-(aq)$ |
| I | M | | | | ~ 0 | | 0 |
| C | $-x$ | | | | $+x$ | | $+x$ |
| E | $M - x$ | | | | x | | x |

$$K_a = \frac{x^2}{M - x} \quad \text{quadratic: } x^2 + K_a x - M K_a = 0$$

a) 0.010 M
 $[\text{H}^+] = 4.108 \times 10^{-4} \text{ M}$
 pH = **3.396**
 $\alpha = \mathbf{0.04}$

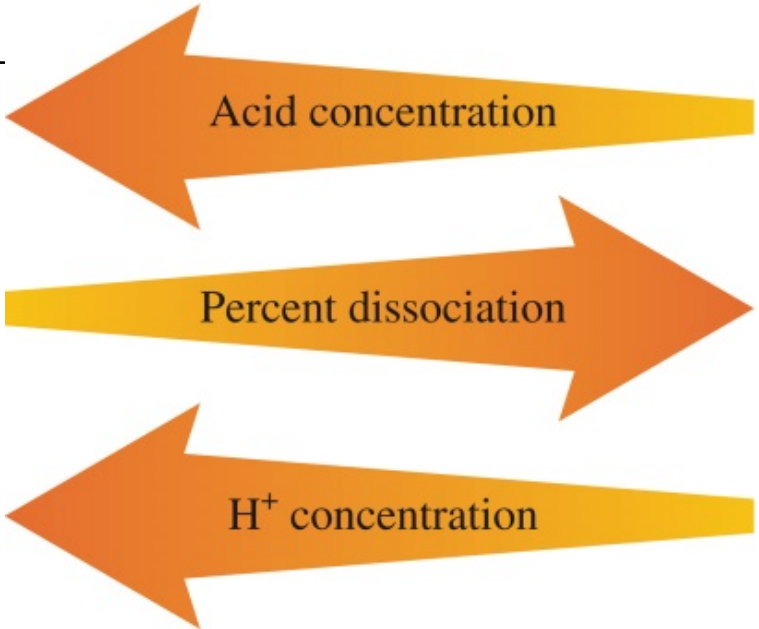
b) 0.0010
 $1.241 \times 10^{-4} \text{ M}$
3.906
0.1241

fraction dissociation (acids)
 $\alpha = [\text{A}^-]/[\text{HA}]_0$
fraction of association (bases)
 $\alpha = [\text{BH}^+]/[\text{B}]_0$

Weak Acid Dissociation - $K_a = x^2 / (F - x)$

| | |
|---|---|
| $\text{CH}_3\text{COOH}(aq) + \text{H}_2\text{O}(l) \rightleftharpoons \text{H}_3\text{O}^+(aq) + \text{CH}_3\text{COO}^-(aq)$ | |
| <p>a) 0.010 M</p> <p>$[\text{H}^+] = 4.108 \times 10^{-4} \text{ M}$</p> <p>pH = 3.396</p> <p>$\alpha = 0.04$</p> | <p>b) 0.0010 M</p> <p>$1.241 \times 10^{-4} \text{ M}$</p> <p>3.906</p> <p>0.1241</p> |

More concentrated More dilute



fraction dissociation (acids)

$$\alpha = [\text{A}^-] / [\text{HA}]_0$$

fraction of association (bases)

$$\alpha = [\text{BH}^+] / [\text{B:}]_0$$

dilution effect on

1. equilibrium
2. $[\text{H}^+]$
3. pH
4. ionization

$$[\text{H}_3\text{O}^+] = n_{\text{H}_3\text{O}^+} / \text{L of solution}$$

Weak Base Dissociation - $K_b = x^2 / (F - x)$

EX 6. What is the pH of 0.25 M solution of ammonia, $K_b = 1.8 \times 10^{-5}$

| | | | | | | | |
|---|--------------------------|-----|--------------------------------|----------------------|--------------------------|-----|----------------------------|
| | $\text{NH}_3(\text{aq})$ | $+$ | $\text{H}_2\text{O}(\text{l})$ | \rightleftharpoons | $\text{OH}^-(\text{aq})$ | $+$ | $\text{NH}_4^+(\text{aq})$ |
| I | M | | | | ~ 0 | | 0 |
| C | $-x$ | | | | $+x$ | | $+x$ |
| E | $M - x$ | | | | x | | x |

$$K_b = \frac{x^2}{M - x} \quad \text{quadratic: } x^2 + K_b x - M K_b = 0$$

$$[\text{OH}^-] = 0.00211 \quad \Rightarrow \quad [\text{H}^+] = K_w / [\text{OH}^-] = 4.7811 \times 10^{-12} \text{ M}$$

pH = 11.32

Acid/Base Properties of Salt Solutions

| cation* | anion** | example | pH of solution |
|---|---|--|---|
| from strong base | from strong acid (conjugate base of) | MgI ₂ , KClO ₄ | neutral |
| from strong base | from weak acid (conjugate base of) | KF, AgCN | basic |
| from weak base (conjugate acid of) | from strong acid (conjugate base of) | NH ₄ Br | acidic |
| from weak base (conjugate acid of) | from weak acid (conjugate base of) | NH ₄ NO ₂ | acidic if $K_a > K_b$ basic if $K_b > K_a$ neutral if $K_a = K_b$ |
| highly charged metal ion (hydrated in water) | from strong acid (conjugate base of) | Al(NO ₃) ₃ , Cr(H ₂ O) ₆ ³⁺ | acidic |

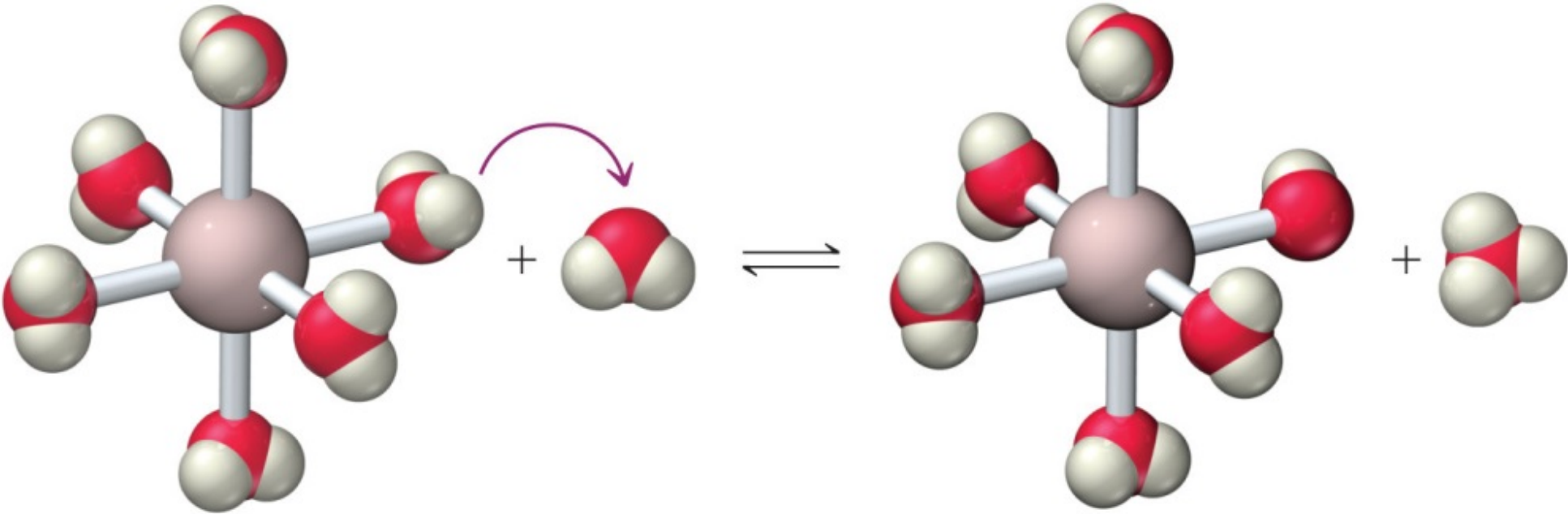
*cation from strong base (Group I and II hydroxides, excluding Be) and silver:

Li⁺, Na⁺, K⁺, Rb⁺, Cs⁺ Mg²⁺, Ca²⁺, Sr²⁺, Ba²⁺ Ag⁺

**anion from strong acid: conjugate base of six of the seven common strong acids

Cl⁻, Br⁻, I⁻ ClO₄⁻, ClO₃⁻, NO₃⁻ (not HSO₄⁻) **WHY? HSO₄⁻ is the conjugate base of a strong acid => ineffective base but it does have an acidic proton => solutions are acidic**

Acidity of Aqueous Solutions of Metal Ions

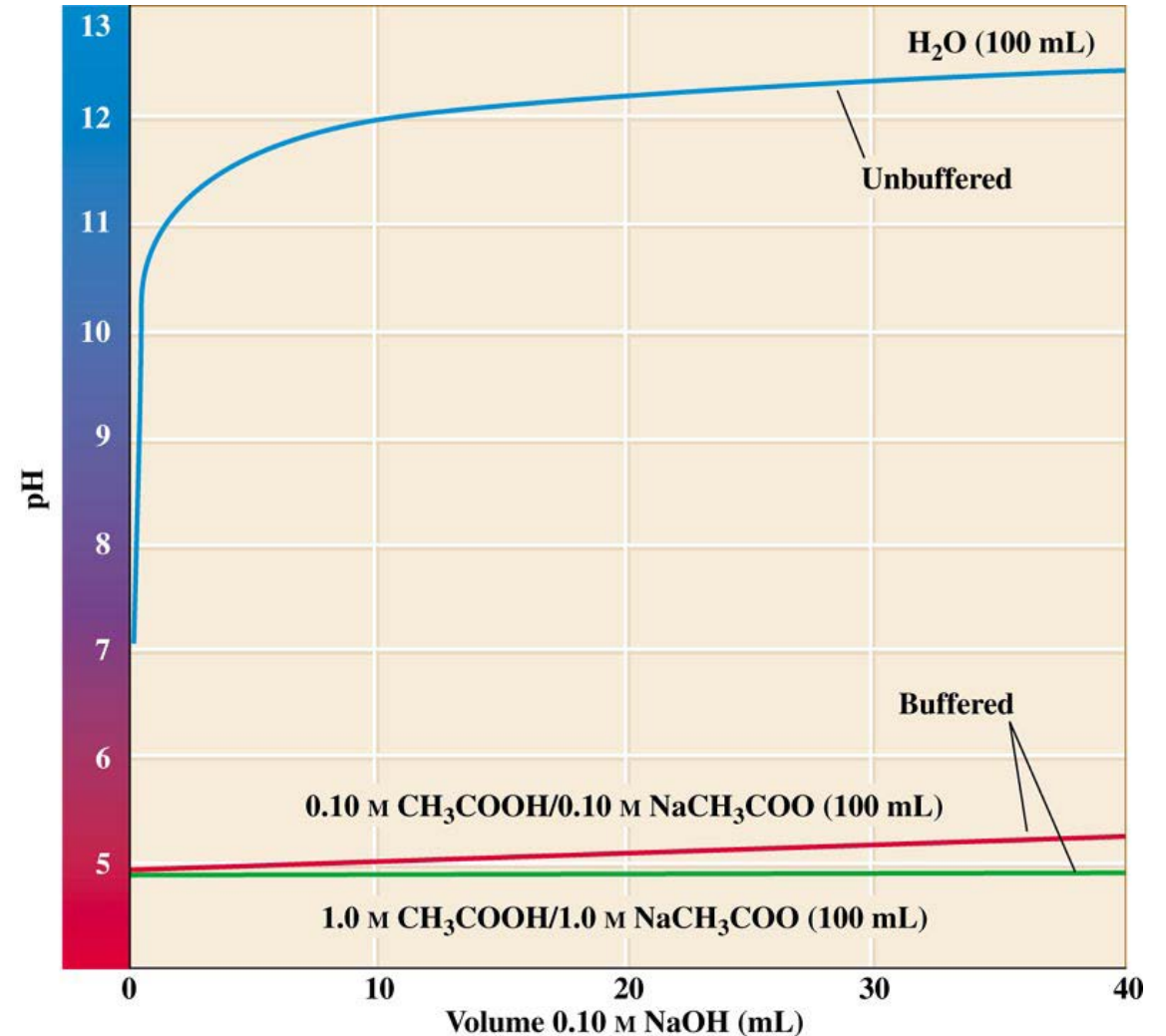


Buffers

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**

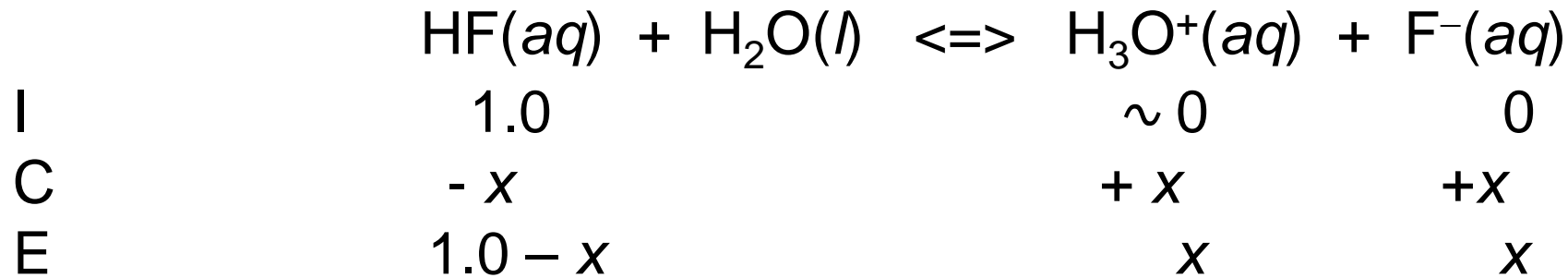
pH of human body 7.4 (37°C) – below 7 and above 7.8 death quickly follows. In the body the pH is maintained by carbonate, phosphate, and protein buffers

addition of NaOH so that solution is 0.05 M NaOH



Buffers – Common Ion Effect

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



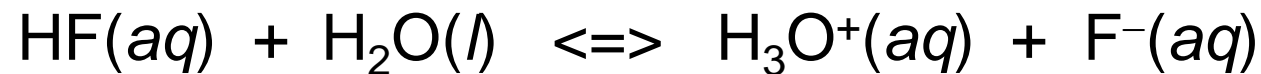
$$K_a = \frac{x^2}{1.0 - x} \quad \text{quadratic: } x^2 + (6.6 \times 10^{-4})x - (1.0)(6.6 \times 10^{-4}) = 0$$

$$x = 0.0253 \Rightarrow \text{pH} = 1.595 \Rightarrow \mathbf{1.60}$$

$$\alpha = \mathbf{0.025} \text{ or } 2.5\% \text{ dissociated}$$

Buffers – Common Ion Effect

EX 2. What is the pH of a solution which is 1.0 F HF and 1.0 F NaF ($K_a = 6.6 \times 10^{-4}$) and the fraction (or percent) dissociated?



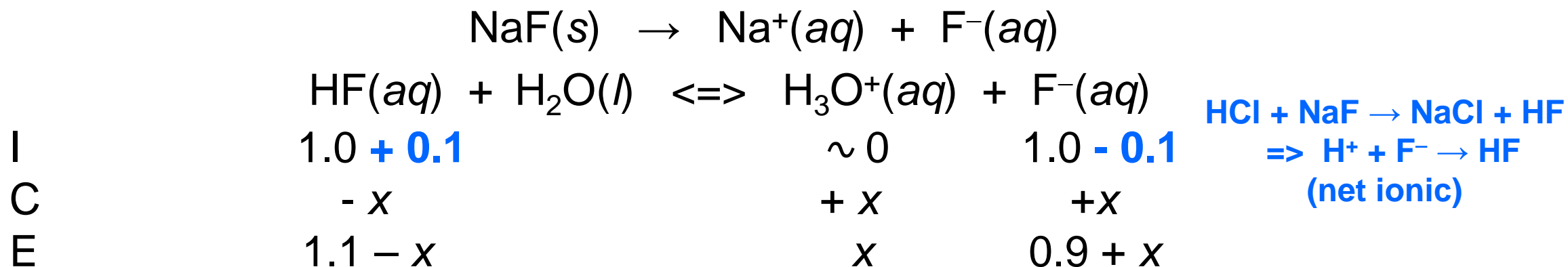
| | | | |
|---|---------|----------|---------|
| I | 1.0 | ~ 0 | 1.0 |
| C | - x | + x | +x |
| E | 1.0 - x | x | 1.0 + x |

$$K_a = \frac{x(1.0 + x)}{1.0 - x} \sim x \Rightarrow \text{pH} = 3.18$$

$\alpha = 6.6 \times 10^{-4}$ or 0.066% dissociated

Buffers – Common Ion Effect, HCl Addition

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

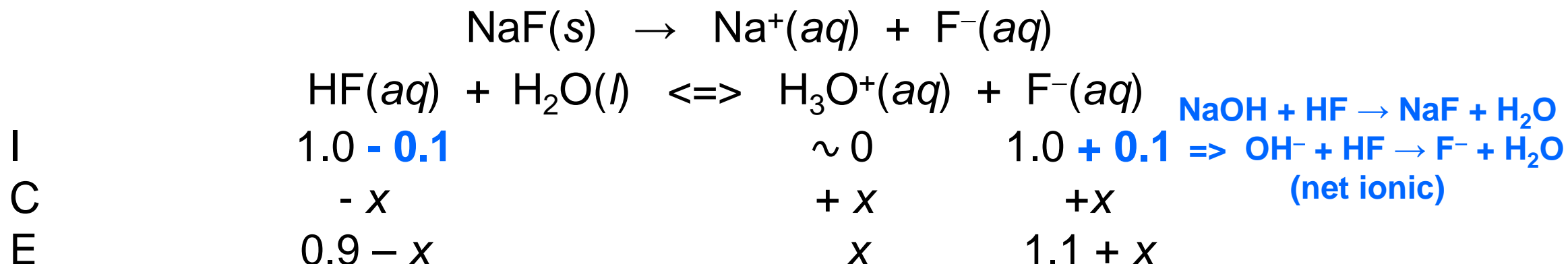


$$K_a = \frac{x(0.9 + x)}{1.1 - x} \sim 0.9x / 1.1 \Rightarrow \text{pH} = 3.09$$

solution behave like a buffer, originally before HCl addition pH was 3.18

Buffers – Common Ion Effect, NaOH Addition

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



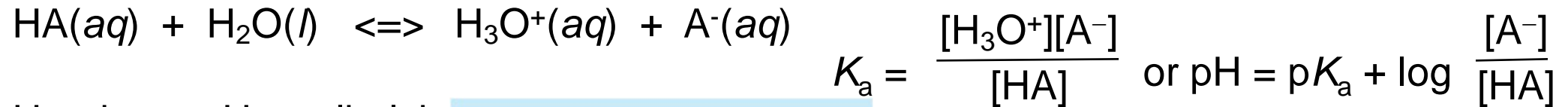
$$K_a = \frac{x(1.1 + x)}{0.9 - x} \sim 1.1x / 0.9 \Rightarrow \text{pH} = 3.27$$

solution behave like a buffer, originally before NaOH addition pH was 3.18

Working with Buffer Solutions

*note ratio of base form to acid form

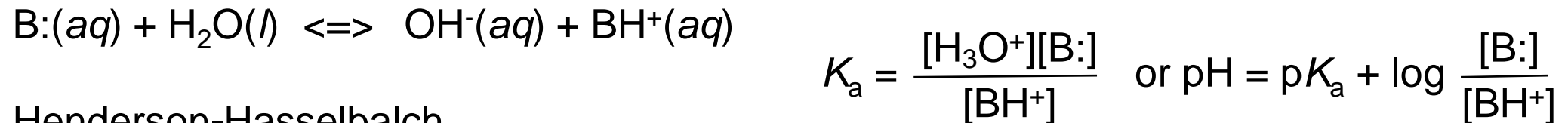
based on a **weak acid** (HA) and its **conjugate base** (A⁻)



Henderson-Hasselbalch

$$\text{pH} = \text{p}K_a + \log \frac{[\text{A}^-]_o}{[\text{HA}]_o}$$

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



Henderson-Hasselbalch

$$\text{pH} = \text{p}K_a + \log \frac{[\text{B}]_o}{[\text{BH}^+]_o}$$

* \swarrow $\text{p}K_a$ applies to *this acid*