Calculation of pH

- Solutions of Strong Acids and Bases
- Strong acids and bases are considered to ionize 100% when placed in water.

$$[H_3O^+] \cong C_a \qquad (7\text{–}89)$$

- A similar treatment for a solution of a strong base such as NaOH gives

$$[OH^-] \cong C_b \qquad (7\text{–}91)$$

Solutions Containing Only a Weak Acid

$$[H_3O^+] = \sqrt{K_a C_a}$$

Example 7-13

Calculate pH

Calculate the pH of a 1-g/100 mL solution of ephedrine sulfate. The molecular weight of the salt is 428.5, and K_b for ephedrine base is 2.3×10^{-5}.

a. The ephedrine sulfate, $(BH^+)_2SO_4$, dissociates completely into two BH^+ cations and one SO_4^{2-} anion. Thus, the concentration of the weak acid (ephedrine cation) is twice the concentration, C_s, of the salt added.

$$C_a = 2C_s = \frac{2 \times 10 \text{ g/liter}}{428.5 \text{ g/mole}} = 4.67 \times 10^{-2}\ \text{M}$$

b. $$K_a = \frac{1.00 \times 10^{-14}}{2.3 \times 10^{-5}} = 4.35 \times 10^{-10}$$

c. $$[H_3O^+] = \sqrt{(4.35 \times 10^{-10}) \times (4.67 \times 10^{-2})} = 4.51 \times 10^{-6}\ \text{M}$$

$$\text{pH} = -\log(4.51 \times 10^{-6}) = 5.35$$

Solutions Containing Only a Weak Base

$$[OH^-] = \sqrt{K_b C_b}$$

Example 7-14

Calculate pH

What is the pH of a 0.0033 M solution of cocaine base, which has a basicity constant of 2.6 × 10^{-6}? We have

$$[OH^-] = \sqrt{(2.6 \times 10^{-6}) \times (3.3 \times 10^{-3})}$$
$$= 9.26 \times 10^{-5}\ M$$

All assumptions are valid. Thus,

$$pOH = -\log(9.26 \times 10^{-5}) = 4.03$$
$$pH = 14.00 - 4.03 = 9.97$$

Solutions Containing a Single Conjugate Acid–Base Pair

- In a solution composed of a weak acid and a salt of that acid (e.g., acetic acid and sodium acetate) or a weak base and a salt of that base (e.g., ephedrine and ephedrine hydrochloride.
- Hint: sodium acetate is basic salt

$$[H_3O^+] = \frac{K_a C_a}{C_b} \qquad (7\text{–}109)$$

Example 7-16

Calculate pH

What is the pH of a solution containing acetic acid 0.3 M and sodium acetate 0.05 M? We write

$$[H_3O^+] = \frac{(1.75 \times 10^{-5}) \times (0.3)}{5.0 \times 10^{-2}}$$
$$= 1.05 \times 10^{-4}\ M$$

All assumptions are valid. Thus,

$$pH = -\log(1.05 \times 10^{-4}) = 3.98$$

Example 7-17

Calculate pH

What is the pH of a solution containing ephedrine 0.1 M and ephedrine hydrochloride 0.01 M? Ephedrine has a basicity constant of 2.3 × 10^{-5}; thus, the acidity constant for its conjugate acid is 4.35 × 10^{-10}.

$$[H_3O^+] = \frac{(4.35 \times 10^{-10}) \times (1.0 \times 10^{-2})}{1.0 \times 10^{-1}}$$
$$= 4.35 \times 10^{-11}\ M$$

All assumptions are valid. Thus,

$$pH = -\log(4.35 \times 10^{-11}) = 10.36$$

SOLUTIONS CONTAINING TWO WEAK ACIDS

$$[H_3O^+] = \sqrt{K_1C_{a1} + K_2C_{a2}} \qquad (7\text{–}127)$$

What is the pH of a solution containing acetic acid, 0.01 mole/liter, and formic acid, 0.001 mole/liter? We have

$$[H_3O^+] = \sqrt{(1.75\times10^{-5})(1.0\times10^{-2})+(1.77\times10^{-4})(1.0\times10^{-3})}$$

$$= 5.93 \times 10^{-4}\ M$$

$$pH = -\log(5.93\times10^{-4}) = 3.23$$

Calculation of pH

From proton balance electrolyte
and
charge balance

- $HCl + H_2O \leftrightarrow H_3O^+ + Cl^-$
- $2\ H_2O \leftrightarrow H_3O^+ + OH^-$
- so $[OH^-] = Kw/\ [H_3O^+]$
- The charge balance equation is:

$[H_3O^+] = [OH^-] + [Cl^-]$

$\mathbf{[H_3O^+] = [Cl^-] + (Kw/[H_3O^+])}$

thus $[Cl-] = [HCl] = C_a$

1- SOLUTION OF STRONG ACID

- <u>A- concentrated acidic solution</u>
- $[H_3O^+] = C_{acid}$
- B- for diluted acidic solution: using the charge balance eq.

$$[H_3O^+] = [OH^-] + [Cl^-] = \frac{K_w}{[H_3O^+]} + C_a \quad (7\text{–}84)$$

$$[H_3O^+]^2 - C_a[H_3O^+] - K_w = 0 \qquad (7\text{–}85)$$

- We have:

$$aX^2 + bX + c = 0 \qquad (7\text{–}86)$$

- which has the solution

$$X = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a} \qquad (7\text{–}87)$$

- Thus, equation **(7-85) becomes**

$$[H_3O^+] = \frac{C_a + \sqrt{C_a^2 + 4K_w}}{2} \qquad (7\text{–}88)$$

- Calculate pH of 10^{-8} M HCl

$$[H_3O^+] = \frac{C_a + \sqrt{C_a^2 + 4K_w}}{2} \qquad (7\text{–}88)$$

- $= [10^{-8} + \sqrt{(10^{-16} + 4 * 10^{-14})}]/2$
- $= [10^{-8} + \sqrt{(4.01 * 10^{-14})}]/2$
- $= [0.1 * 10^{-7} + 2.0025 * 10^{-7}]/2$
- $[H_3O^+] = 1.051 * 10^{-7}$
- pH = 6.978

Solutions Containing Only a Weak Acid

If the solution contains only a weak acid, C_b is zero, and $[H_3O^+]$ is generally much greater than $[OH^-]$. Thus, equation (**7–99**) simplifies to

$$[H_3O^+]^2 + K_a[H_3O^+] - K_aC_a = 0 \qquad \textbf{(7–100)}$$

which is a quadratic equation with the solution

$$[H_3O^+] = \frac{-K_a + \sqrt{K_a^2 + 4K_aC_a}}{2} \qquad \textbf{(7–101)}$$

In many instances, C_a is much greater than $[H_3O^+]$, and equation (7-100) simplifies to

$$[H_3O^+] = \sqrt{K_aC_a} \qquad \textbf{(7–102)}$$

Example 7-12

Calculate pH

Calculate the pH of a 0.01 M solution of salicylic acid, which has a $K_a = 1.06 \times 10^{-3}$ at 25°C.

a. Using equation (7-102), we find

$$[H_3O^+] = \sqrt{(1.06 \times 10^{-3}) \times (1.0 \times 10^{-2})}$$
$$= 3.26 \times 10^{-3}\ \text{M}$$

The approximation that $C_a \gg H_3O^+$ is not valid.

b. Using equation (7-101), we find

$$[H_3O^+] = -\frac{(1.06 \times 10^{-3})}{2} + \frac{\sqrt{(1.06 \times 10^{-3})^2 + 4(1.06 \times 10^{-3})(1.0 \times 10^{-2})}}{2}$$
$$= 2.77 \times 10^{-3}\ \text{M}$$
$$\text{pH} = -\log(2.77 \times 10^{-3}) = 2.56$$

- Dilutes strong base:

$[OH^-] = [C_b+\sqrt{(C_b^2+4Kw)}]/2$

- For weak base:

$$[OH^-] = \frac{-K_b + \sqrt{K_b^2 + 4K_bC_b}}{2} \qquad (7\text{–}107)$$

Common pH calculation

No.	Type of acid ,base	Description
1	Strong Acid (HCl , H_2SO_4 ,HNO_3 …….)	pH = -log[$acid$]
2	Strong Base (NaOH , KOH , $NaHCO_3$, ……)	pH = pK_w +log[$Base$]
3	Weak acid (CH_3COOH , $H_2PO_4^-$, $H2C_2O_4$, …)	pH = ½ pK_a - ½ log[$acid$]
4	Weak base (NH_4OH , R_3NHOH , ….)	$[OH^-] = \sqrt{K_{b1} C_b}$ (7–120)
5	Acidic buffer (HAC + NaAC)	$pH = pK_a + \log \frac{[Salt]}{[Acid]}$ (8–8)
6	Basic buffer (NH_4OH + NH_4Cl)	$pH = pK_w - pK_b + \log \frac{[Base]}{[Salt]}$ (8–10)
7	Acidic salt (NH_4Cl)	pH =½ pK_w - ½ pK_b - ½ log[$salt$]
8	Basic salt (NaAC . NaCN , ….)	pH =½ pK_w + ½ pK_a + ½ log[$salt$]
9	Very weak acid	$[H_3O^+] = \frac{-K_a + \sqrt{K_a^2 + 4K_aC_a}}{2}$ (7–101)
10	Very weak base	$[OH^-] = \frac{-K_b + \sqrt{K_b^2 + 4K_bC_b}}{2}$ (7–107)
11	Very dilute strong acid	$[H_3O^+] = \frac{C_a + \sqrt{C_a^2 + 4K_w}}{2}$ (7–88)
12	Very dilute strong base	$[OH^-] = \frac{C_b + \sqrt{C_b^2 + 4K_w}}{2}$ (7–90)

CHAPTER 8
BUFFER
AND
ISOTONIC SOLUTION

THE BUFFER EQUATIONS

- 1-For acidic buffer solution:
- pH= pKa + log ([salt]/[acid])

- 2- for basic buffer solution:
- pOH= pKb+ log ([salt]/[base])
- pH = pKw – pKb – log ([salt]/base])

Buffer capacity

- Also (buffer efficiency, buffer index, buffer value)
- The buffer capacity defined as the magnitude of resistance of buffer to pH changes or defined as the ratio of increment of strong base or acid to the small change in pH
  - $\beta = \Delta[B]/\Delta[pH]$
- A more exact equation of β is:
  - $\beta = 2.303\ C\ \{ Ka[H_3O^+]/(Ka+[H_3O^+])^2\}$
- C: C salt+ C acid

MAXIMUM BUFFER CAPACITY B $_{MAX}$

- Maximum buffer capacity occurs where pH =pKa

$\beta max = 2.203\ C\ \{[H_3O^+]^2/(2[H_3O^+])^2\} = \mathbf{2.303C/4}$

- $\boldsymbol{\beta_{max} = 0.576\ C}$, C: C salt+ C acid

$$\beta_{max} = 2.303C\frac{[H_3O^+]^2}{(2[H_3O^+])^2} = \frac{2.303}{4}C$$

$$\beta_{max} = 0.576C \qquad (8\text{–}29)$$

where *C* is the total buffer concentration.

Example 8-8

Maximum Buffer Capacity

What is the maximum buffer capacity of an acetate buffer with a total concentration of 0.020 mole/liter? We have

$$\beta_{max} = 0.576 \times 0.020$$
$$= 0.01152 \text{ or } 0.012$$

Key Concept

Buffer Capacity

The buffer capacity depends on (*a*) the value of the ratio [Salt]/[Acid], increasing as the ratio approaches unity, and (*b*) the magnitude of the individual concentrations of the buffer components, the buffer becoming more efficient as the salt and acid concentrations are increased.

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BUFFERS IN PHARMACY AND BIOLOGICAL SYSTEM

- The plasma contains buffer systems:
- Carbonic acid/ Na_2HPO_4
- Acid/Na_2HPO_4
- Base/ plasma proteins
- Acid/K_2HPO_4
- Hemoglobin/Oxyhemoglobin
- All these constituents are buffers
- The pH of blood is about 7.4 with $\beta \approx 0.025$