

# CALCULATION OF PH

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

$$[\text{H}_3\text{O}^+] \cong C_a \quad (7-89)$$

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

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

# SOLUTIONS CONTAINING ONLY A WEAK ACID

$$[\text{H}_3\text{O}^+] = \sqrt{K_a C_a}$$

## 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  $2.3 \times 10^{-5}$ .

- a. The ephedrine sulfate,  $(\text{BH}^+)_2\text{SO}_4$ , dissociates completely into two  $\text{BH}^+$  cations and one  $\text{SO}_4^{2-}$  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. 
$$[\text{H}_3\text{O}^+] = \sqrt{(4.35 \times 10^{-10}) \times (4.67 \times 10^{-2})}$$

$$= 4.51 \times 10^{-6} \text{ M}$$

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

## *SOLUTIONS CONTAINING ONLY A WEAK BASE*

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

### Example 7-14

#### Calculate pH

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

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

All assumptions are valid. Thus,

$$\begin{aligned} \text{pOH} &= -\log(9.26 \times 10^{-5}) = 4.03 \\ \text{pH} &= 14.00 - 4.03 = 9.97 \end{aligned}$$

## *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

$$[\text{H}_3\text{O}^+] = \frac{K_a C_a}{C_b} \quad (7-109)$$

**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

$$\begin{aligned} [\text{H}_3\text{O}^+] &= \frac{(1.75 \times 10^{-5}) \times (0.3)}{5.0 \times 10^{-2}} \\ &= 1.05 \times 10^{-4} \text{ M} \end{aligned}$$

All assumptions are valid. Thus,

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

**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  $2.3 \times 10^{-5}$ ; thus, the acidity constant for its conjugate acid is  $4.35 \times 10^{-10}$ .

$$\begin{aligned} [\text{H}_3\text{O}^+] &= \frac{(4.35 \times 10^{-10}) \times (1.0 \times 10^{-2})}{1.0 \times 10^{-1}} \\ &= 4.35 \times 10^{-11} \text{ M} \end{aligned}$$

All assumptions are valid. Thus,

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

# *SOLUTIONS CONTAINING TWO WEAK ACIDS*

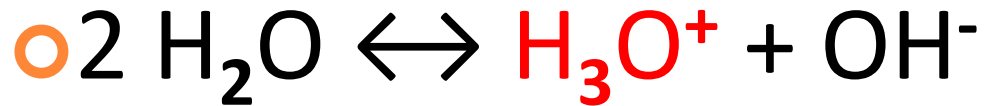
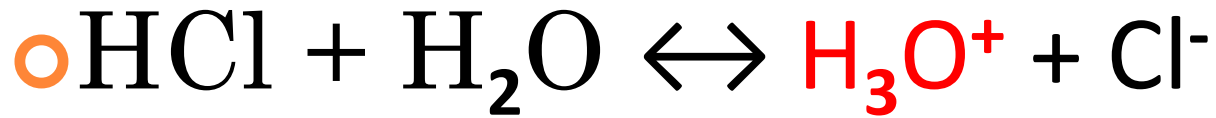
$$[\text{H}_3\text{O}^+] = \sqrt{K_1 C_{a1} + K_2 C_{a2}} \quad (7-127)$$

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

$$\begin{aligned}[\text{H}_3\text{O}^+] &= \sqrt{(1.75 \times 10^{-5})(1.0 \times 10^{-2}) + (1.77 \times 10^{-4})(1.0 \times 10^{-3})} \\ &= 5.93 \times 10^{-4} \text{ M} \\ \text{pH} &= -\log(5.93 \times 10^{-4}) = 3.23\end{aligned}$$

# CALCULATION OF PH

**From proton balance electrolyte  
and  
charge balance**



○ so  $[\text{OH}^-] = K_w / [\text{H}_3\text{O}^+]$

○ The charge balance equation is:

$$[\text{H}_3\text{O}^+] = [\text{OH}^-] + [\text{Cl}^-]$$

$$[\text{H}_3\text{O}^+] = [\text{Cl}^-] + (K_w / [\text{H}_3\text{O}^+])$$

thus  $[\text{Cl}^-] = [\text{HCl}] = C_a$

# 1- SOLUTION OF STRONG ACID

- A- concentrated acidic solution

- $[\text{H}_3\text{O}^+] = C_{\text{acid}}$

- **B- for diluted acidic solution:** using the charge balance eq.

$$[\text{H}_3\text{O}^+] = [\text{OH}^-] + [\text{Cl}^-] = \frac{K_w}{[\text{H}_3\text{O}^+]} + C_a \quad (7-84)$$

$$[\text{H}_3\text{O}^+]^2 - C_a[\text{H}_3\text{O}^+] - K_w = 0 \quad (7-85)$$

- $aX^2 + bX + c = 0 \quad (7-86)$

- which has the solution

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

- Thus, equation (7-85) becomes

$$[\text{H}_3\text{O}^+] = \frac{C_a + \sqrt{C_a^2 + 4K_w}}{2} \quad (7-88)$$

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

$$[\text{H}_3\text{O}^+] = \frac{C_a + \sqrt{C_a^2 + 4K_w}}{2} \quad (7-88)$$

- $= [10^{-8} + \sqrt{(10^{-16} + 4 * 10^{-14})}] / 2$
- $= [10^{-8} + \sqrt{(4.01 * 10^{-14})}] / 2$
- $= [0.1 * 10^{-7} + 2.0025 * 10^{-7}] / 2$
- $[\text{H}_3\text{O}^+] = 1.051 * 10^{-7}$
- $\text{pH} = 6.978$

## Solutions Containing Only a Weak Acid

If the solution contains only a weak acid,  $C_b$  is zero, and  $[\text{H}_3\text{O}^+]$  is generally much greater than  $[\text{OH}^-]$ .

Thus, equation (7-99) simplifies to

$$[\text{H}_3\text{O}^+]^2 + K_a[\text{H}_3\text{O}^+] - K_a C_a = 0 \quad (7-100)$$

which is a quadratic equation with the solution

$$[\text{H}_3\text{O}^+] = \frac{-K_a + \sqrt{K_a^2 + 4K_a C_a}}{2} \quad (7-101)$$

In many instances,  $C_a$  is much greater than  $[\text{H}_3\text{O}^+]$ , and equation (7-100) simplifies to

$$[\text{H}_3\text{O}^+] = \sqrt{K_a C_a} \quad (7-102)$$

### 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

$$\begin{aligned} [\text{H}_3\text{O}^+] &= \sqrt{(1.06 \times 10^{-3}) \times (1.0 \times 10^{-2})} \\ &= 3.26 \times 10^{-3} \text{ M} \end{aligned}$$

The approximation that  $C_a \gg \text{H}_3\text{O}^+$  is not valid.

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

$$\begin{aligned} [\text{H}_3\text{O}^+] &= \frac{-(1.06 \times 10^{-3})}{2} \\ &\quad + \frac{\sqrt{(1.06 \times 10^{-3})^2 + 4(1.06 \times 10^{-3})(1.0 \times 10^{-2})}}{2} \\ &= 2.77 \times 10^{-3} \text{ M} \\ \text{pH} &= -\log(2.77 \times 10^{-3}) = 2.56 \end{aligned}$$

- Dilutes strong base:

$$[\text{OH}^-] = [C_b + v(C_b^2 + 4K_w)]/2$$

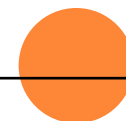
- For weak base:

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

*Common  
pH  
calculation*



No.	Type of acid ,base	Description
1	Strong Acid ( HCl , H <sub>2</sub> SO <sub>4</sub> ,HNO <sub>3</sub> .....)	$\text{pH} = -\log[\text{acid}]$
2	Strong Base ( NaOH , KOH , NaHCO <sub>3</sub> , .....)	$\text{pH} = \text{pK}_w + \log[\text{Base}]$
3	Weak acid ( CH <sub>3</sub> COOH , H <sub>2</sub> PO <sub>4</sub> <sup>-</sup> , H <sub>2</sub> C <sub>2</sub> O <sub>4</sub> , ...)	$\text{pH} = \frac{1}{2} \text{pK}_a - \frac{1}{2} \log[\text{acid}]$
4	Weak base ( NH <sub>4</sub> OH , R <sub>3</sub> NHOH , .... )	$[\text{OH}^-] = \sqrt{K_b C_b}$ (7-120)
5	Acidic buffer ( HAC + NaAC )	$\text{pH} = \text{pK}_a + \log \frac{[\text{Salt}]}{[\text{Acid}]}$ (8-8)
6	Basic buffer ( NH <sub>4</sub> OH + NH <sub>4</sub> Cl )	$\text{pH} = \text{pK}_w - \text{pK}_b + \log \frac{[\text{Base}]}{[\text{Salt}]}$ (8-10)
7	Acidic salt ( NH <sub>4</sub> Cl )	$\text{pH} = \frac{1}{2} \text{pK}_w - \frac{1}{2} \text{pK}_b - \frac{1}{2} \log[\text{salt}]$
8	Basic salt ( NaAC . NaCN , .... )	$\text{pH} = \frac{1}{2} \text{pK}_w + \frac{1}{2} \text{pK}_a + \frac{1}{2} \log[\text{salt}]$
9	Very weak acid	$[\text{H}_3\text{O}^+] = \frac{-K_a + \sqrt{K_a^2 + 4K_a C_a}}{2}$ (7-101)
10	Very weak base	$[\text{OH}^-] = \frac{-K_b + \sqrt{K_b^2 + 4K_b C_b}}{2}$ (7-107)
11	Very dilute strong acid	$[\text{H}_3\text{O}^+] = \frac{C_a + \sqrt{C_a^2 + 4K_w}}{2}$ (7-88)
12	Very dilute strong base	$[\text{OH}^-] = \frac{C_b + \sqrt{C_b^2 + 4K_w}}{2}$ (7-90)



# CHAPTER 8

# BUFFER

# AND

# ISOTONIC SOLUTION

# THE BUFFER EQUATIONS

- 1-For acidic buffer solution:
- $\text{pH} = \text{pK}_a + \log \left( \frac{[\text{salt}]}{[\text{acid}]} \right)$
  
- 2- for basic buffer solution:
- $\text{pOH} = \text{pK}_b + \log \left( \frac{[\text{salt}]}{[\text{base}]} \right)$
- $\text{pH} = \text{pK}_w - \text{pK}_b - \log \left( \frac{[\text{salt}]}{[\text{base}]} \right)$

# 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
  - $\beta = \Delta[B]/\Delta[\text{pH}]$
- A more exact equation of  $\beta$  is:
  - $\beta = 2.303 C \{ K_a[\text{H}_3\text{O}^+]/(K_a + [\text{H}_3\text{O}^+])^2 \}$
- C: C salt+ C acid

## MAXIMUM BUFFER CAPACITY $\beta_{\text{MAX}}$

- Maximum buffer capacity occurs where  $\text{pH} = \text{pKa}$

$$\beta_{\text{max}} = 2.203 C \left\{ \frac{[\text{H}_3\text{O}^+]^2}{(2[\text{H}_3\text{O}^+])^2} \right\} = \mathbf{2.303C/4}$$

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

$$\beta_{\max} = 2.303C \frac{[\text{H}_3\text{O}^+]^2}{(2[\text{H}_3\text{O}^+])^2} = \frac{2.303}{4}C$$

$$\beta_{\max} = 0.576C \quad (8-29)$$

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

$$\begin{aligned} \beta_{\max} &= 0.576 \times 0.020 \\ &= 0.01152 \text{ or } 0.012 \end{aligned}$$



#### Key Concept

#### Buffer Capacity

The buffer capacity depends on (a) the value of the ratio  $[\text{Salt}]/[\text{Acid}]$ , 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.

# BUFFERS IN PHARMACY AND BIOLOGICAL SYSTEM

- The plasma contains buffer systems:
- Carbonic acid/  $\text{Na}_2\text{HPO}_4$
- Acid/ $\text{Na}_2\text{HPO}_4$
- Base/ plasma proteins
- Acid/ $\text{K}_2\text{HPO}_4$
- Hemoglobin/Oxyhemoglobin
- All these constituents are buffers
- The pH of blood is about 7.4 with  $\beta \approx 0.025$