Al-Rasheed University College

Department of Medical Laboratory Technique

Medical Chemistry

Lecture 4

Prepared by

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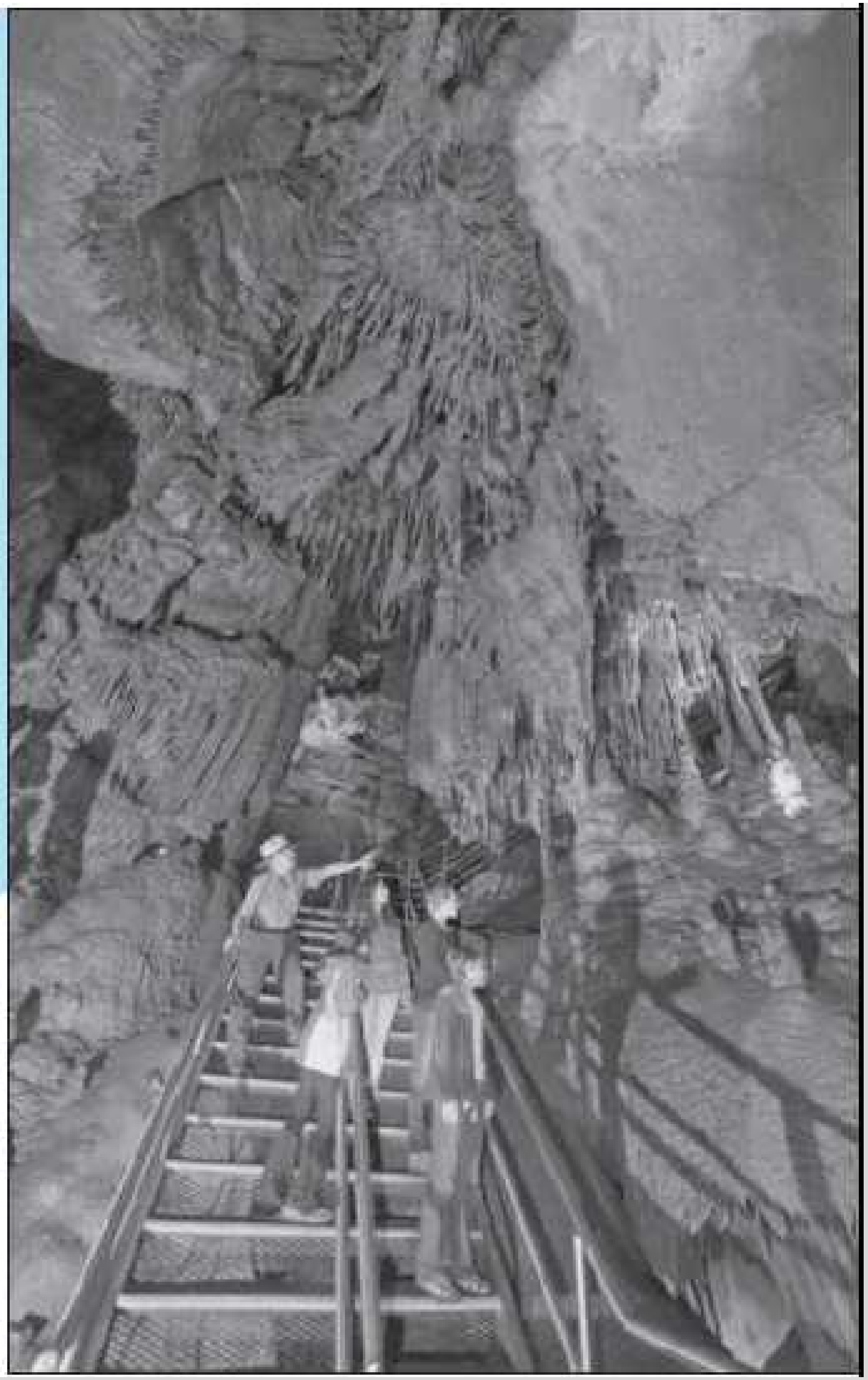


Weak Acids and Bases—What Is the pH?

- Weak acids (or bases) are only partially ionized.
- The ionization constant can be used to calculate the amount ionized and, from this, the pH.
- The acidity constant for acetic acid at 25◦C is 1.75×10^{-5}:

$$\mathrm{HOAc} \rightleftharpoons \mathrm{H}^{+} + \mathrm{OAc}^{-} \qquad \frac{[\mathrm{H}^{+}][\mathrm{OAc}^{-}]}{[\mathrm{HOAc}]} = 1.75 \times 10^{-5}$$

- When acetic acid ionizes, it dissociates to equal portions of H^{+} and OAc^{-} by such an amount.
- If the original concentration of acetic acid is C and the concentration of ionized acetic acid species (H^{+} and OAc^{-}) is $\boldsymbol{x}$, then the final concentration for each species at equilibrium is given by

$$\begin{array}{cccc} \mathrm{HOAc} & \rightleftharpoons \mathrm{H}^{+} & + & \mathrm{OAc}^{-} \\ (C - x) & x & & x \end{array}$$

Example 7.7

Calculate the pH and pOH of a $1.00 \times 10^{-3}\ M$ solution of acetic acid.

Solution

$$\mathrm{HOAc} \rightleftharpoons \mathrm{H^+} + \mathrm{OAc^-}$$

	[HOAc]	$[H^+]$	$[OAc^-]$
Initial	1.00×10^{-3}	0	0
Change (x = mmol/mL HOAc ionized)	$-x$	$+x$	$+x$
Equilibrium	$1.00 \times 10^{-3} - x$	x	x

$$\frac{[\mathrm{H^+}][\mathrm{OAc^-}]}{[\mathrm{HOAc}]} = 1.75 \times 10^{-5} \qquad \frac{(x)(x)}{1.00 \times 10^{-3} - x} = 1.75 \times 10^{-5}$$

$$\frac{x^2}{1.00 \times 10^{-3}} = 1.75 \times 10^{-5} \qquad x = 1.32 \times 10^{-4}\ M \equiv [\mathrm{H^+}]$$

$$\mathrm{pH} = -\log(1.32 \times 10^{-4}) = 4 - \log 1.32 = 4 - 0.12 = 3.88$$

$$\mathrm{pOH} = 14.00 - 3.88 = 10.12$$

Example 7.8

The basicity constant K_b for ammonia is 1.75×10^{-5} at 25°C. (It is only coincidental that this is equal to K_a for acetic acid.) Calculate the pH and pOH for a 1.00×10^{-3} M solution of ammonia.

Solution

$$\begin{array}{ccccccc} NH_3 & + & H_2O & \rightleftharpoons & NH_4^+ & + & OH^- \\ (1.00 \times 10^{-3} - x) & & & & x & & x \end{array}$$

$$\frac{[NH_4^+][OH^-]}{[NH_3]} = 1.75 \times 10^{-5}$$

The same rule applies for the approximation applied for a weak acid. Thus,

$$\frac{(x)(x)}{1.00 \times 10^{-3}} = 1.75 \times 10^{-5}$$

$$x = 1.32 \times 10^{-4}\ M = [OH^-]$$

$$pOH = -\log 1.32 \times 10^{-4} = 3.88$$

$$pH = 14.00 - 3.88 = 10.12$$

Salts of Weak Acids and Bases

- The salt of a weak acid, for example. CH_3COONa, is a strong electrolyte, like (almost) all salts, and completely ionizes.

$$CH_3COONa \rightarrow CH_3COO^- + Na^+$$

- In addition, the anion of the salt of a weak acid is a **conjugate base,** which will accept protons. It partially hydrolyzes in water to form hydroxide ion and the corresponding undissociated acid. For example,

$$CH_3COO^- + H_2O = CH_3COOH + OH^-$$

- This ionization is also known as **hydrolysis** of the salt ion.
- The weaker the acid, the stronger its conjugate base, that is, the more strongly will combine with a proton, as from the water.

We can write an equilibrium constant:

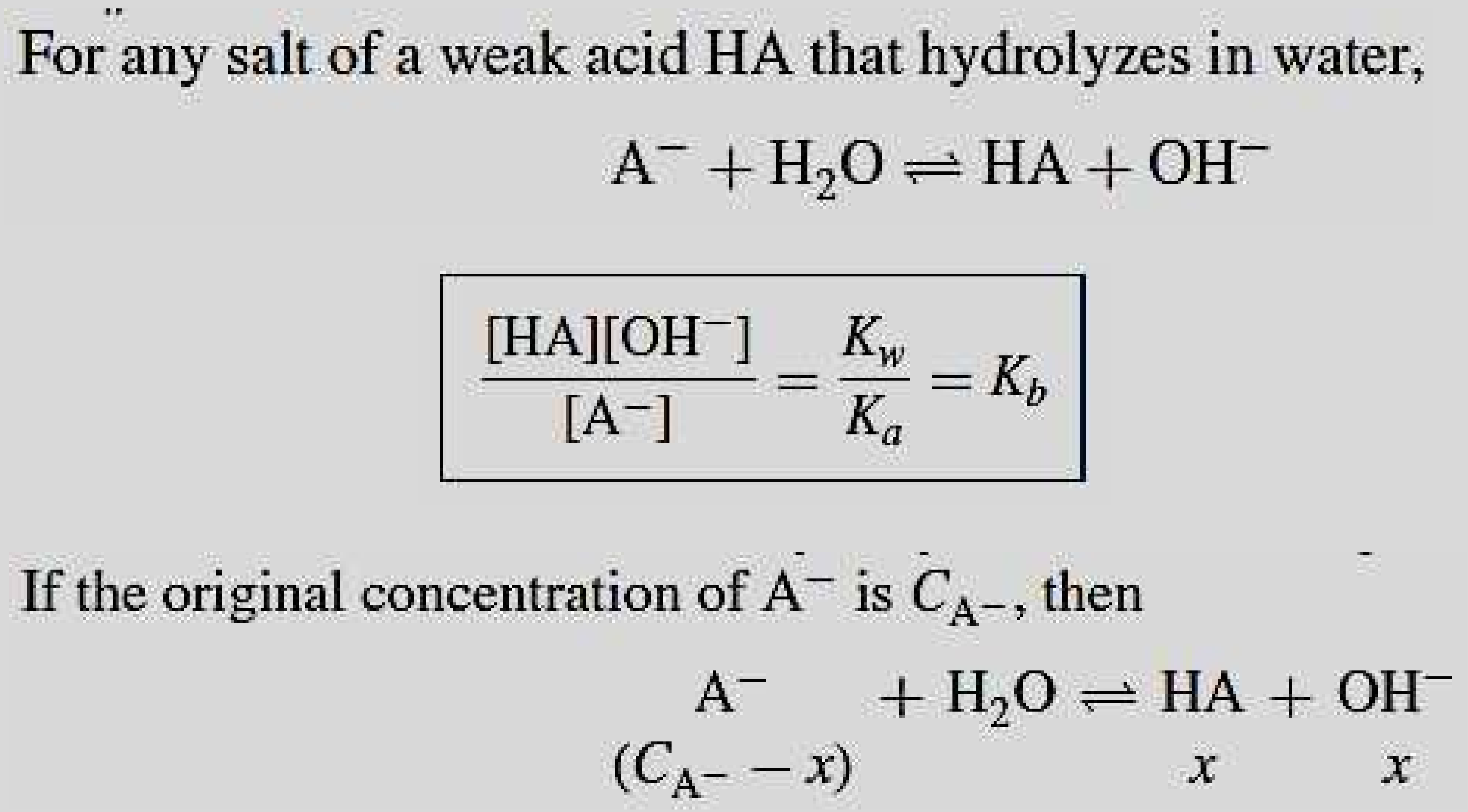
$$K_b = \frac{[\mathrm{HOAc}][\mathrm{OH^-}]}{[\mathrm{OAc^-}]}$$

The value of K_b can be calculated from K_a of acetic acid and K_w

$$K_b = \frac{K_w}{K_a} = \frac{1.0 \times 10^{-14}}{1.75 \times 10^{-5}} = 5.7 \times 10^{-10}$$

The product of K_a *of any weak acid and* K_b *of its conjugate base is always equal to* K_w*:*

$$\boxed{K_a K_b = K_w}$$



For any salt of a weak acid HA that hydrolyzes in water,

$$A^- + H_2O \rightleftharpoons HA + OH^-$$

$$\boxed{\frac{[HA][OH^-]}{[A^-]} = \frac{K_w}{K_a} = K_b}$$

If the original concentration of A^- is C_{A^-}, then

$$\begin{array}{cccc} A^- & + H_2O \rightleftharpoons & HA & + OH^- \\ (C_{A^-} - x) & & x & x \end{array}$$

- The quantity x can be neglected compared to C_{A^-} if $C_{A^-} > 100K_b$, which will generally be the case for such weakly ionized bases.

We can solve for the OH^- concentration using Equation above

$$\frac{[OH^-][OH^-]}{C_{A^-}} = \frac{K_w}{K_a} = K_b$$

$$\boxed{[OH^-] = \sqrt{\frac{K_w}{K_a} \cdot C_{A^-}} = \sqrt{K_b \cdot C_{A^-}}}$$

Example 7.9

Calculate the pH of a 0.10 M solution of sodium acetate.

Solution

Write the equilibria

$$\text{NaOAc} \rightarrow \text{Na}^+ + \text{OAc}^- \text{(ionization)}$$

$$\text{OAc}^- + \text{H}_2\text{O} \rightleftharpoons \text{HOAc} + \text{OH}^- \text{(hydrolysis)}$$

Write the equilibrium constant

$$\frac{[\text{HOAc}][\text{OH}^-]}{[\text{OAc}^-]} = K_b = \frac{K_w}{K_a} = \frac{1.0 \times 10^{-14}}{1.75 \times 10^{-5}} = 5.7 \times 10^{-10}$$

Let x represent the concentration of HOAc and OH^- at equilibrium. Then, at equilibrium,

$$[\text{HOAc}] = [\text{OH}^-] = x$$

$$[\text{OAc}^-] = C_{\text{OAc}^-} - x = 0.10 - x$$

Since $C_{\mathrm{OAc^-}} \gg K_b$, neglect x compared to $C_{\mathrm{OAc^-}}$. Then,

$$\frac{(x)(x)}{0.10} = 5.7 \times 10^{-10}$$

$$x = \sqrt{5.7 \times 10^{-10} \times 0.10} = 7.6 \times 10^{-6}\,M$$

$$[\mathrm{OH^-}] = 7.6 \times 10^{-6}\,M$$

$$[\mathrm{H^+}] = \frac{1.0 \times 10^{-14}}{7.6 \times 10^{-6}} = 1.3 \times 10^{-9}\,M$$

$$\mathrm{pH} = -\log 1.3 \times 10^{-9} = 9 - 0.11 = 8.89$$

Similar equations can be derived for the cations of salts of weak bases (the salts are completely dissociated). These are **Brønsted acids** and ionize (hydrolyze) in water:

$$BH^+ + H_2O \rightleftharpoons B + H_3O^+$$

$$K_a = \frac{[B][H_3O^+]}{[BH^+]}$$

$$\boxed{\frac{[B][H_3O^+]}{[BH^+]} = \frac{K_w}{K_b} = K_a}$$

and for $NH_4{}^+$,

$$K_a = \frac{K_w}{K_b} = \frac{1.0 \times 10^{-14}}{1.75 \times 10^{-5}} = 5.7 \times 10^{-10}$$

The salt of a weak base ionizes to form equal amounts of B and H_3O^+ (H^+ if we disregard hydronium ion formation as was done previously). We can therefore solve for the hydrogen ion concentration (by assuming $C_{BH^+} > 100K_a$):

$$\frac{[H^+][H^+]}{C_{BH^+}} = \frac{K_w}{K_b} = K_a$$

$$\boxed{[H^+] = \sqrt{\frac{K_w}{K_b} \cdot C_{BH^+}} = \sqrt{K_a \cdot C_{BH^+}}}$$

Again, this equation only holds if $C_{BH^+} > 100K_a$. Otherwise, the quadratic formula must be solved.

Example 7.10

Calculate the pH of a 0.25 *M* solution of ammonium chloride.

Solution

Write the equilibria

$$NH_4Cl \rightarrow NH_4^+ + Cl^- \quad \text{(ionization)}$$

$$NH_4^+ + H_2O \rightleftharpoons NH_4OH + H^+ \quad \text{(hydrolysis)}$$

$$(NH_4^+ + H_2O \rightleftharpoons NH_3 + H_3O^+)$$

Write the equilibrium constant

$$\frac{[NH_4OH][H^+]}{[NH_4^+]} = K_a = \frac{K_w}{K_b} = \frac{1.0 \times 10^{-14}}{1.75 \times 10^{-5}} = 5.7 \times 10^{-10}$$

Let x represent the concentration of $[NH_4OH]$ and $[H^+]$ at equilibrium. Then, at equilibrium,

$$[NH_4OH] = [H^+] = x$$

$$[NH_4{}^+] = C_{NH_4{}^+} - x = 0.25 - x$$

Since $C_{NH_4{}^+} \gg K_a$, neglect x compared to $C_{NH_4{}^+}$. Then,

$$\frac{(x)(x)}{0.25} = 5.7 \times 10^{-10}$$

$$x = \sqrt{5.7 \times 10^{-10} \times 0.25} = 1.2 \times 10^{-5}\ M$$

Compare this last step with Equation 7.39. Also, compare the entire setup and solution with those in Example 7.7. The NH_4OH formed is undissociated and does not contribute to the pH:

$$[H^+] = 1.2 \times 10^{-5}\ M$$

$$\text{pH} = -\log(1.2 \times 10^{-5}) = 5 - 0.08 = 4.92$$