Al-Rasheed University College
Department of Medical Laboratory Technique

Medical Chemistry

Lecture 5

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Buffers—Keeping the pH Constant (or Nearly So)

➢ A **buffer** is defined as a solution that resists change in pH when a small amount of an acid or base is added or when the solution is diluted.

➢ A buffer solution consists of a mixture of:

   ➢ A weak acid and its salt (conjugate base); CH_3COOH/CH_3COONa

$$pH = pK_a + \log \frac{[A^-]}{[HA]}$$

$$pK_a = -\log K_a$$

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

   ➢ A weak base and its salt (conjugate acid); NH_4OH/NH_4Cl

$$pH = pK_a + \log \frac{[B]}{[BH^+]} = (pK_w - pK_b) + \log \frac{[B]}{[BH^+]}$$

$$K_a K_b = K_w$$
$$K_a = K_w / K_b$$
$$pK_a = -\log K_a$$

$$pK_b = -\log K_b$$
$$pK_a + pK_b = pK_w$$
$$pK_a = pK_w - pK_b$$

$$pOH = pK_b + \log \frac{[BH^+]}{[B]}$$

$$pK_b = -\log K_b$$

$$pH + pOH = 14$$
$$pH = 14 - pOH$$

Example 7.11

Calculate the pH of a buffer prepared by adding 10 mL of 0.10 M acetic acid to 20 mL of 0.10 M sodium acetate.

Solution

We need to calculate the concentration of the acid and salt in the solution. The final volume is 30 mL:

$$M_1 \times mL_1 = M_2 \times mL_2$$

For HOAc,

$$0.10 \text{ mmol/mL} \times 10 \text{ mL} = M_{HOAc} \times 30 \text{ mL}$$

$$M_{HOAc} = 0.033 \text{ mmol/mL}$$

For OAc$^-$,

$$0.10 \text{ mmol/mL} \times 20 \text{ mL} = M_{OAc^-} \times 30 \text{ mL}$$

$$M_{OAc^-} = 0.067 \text{ mmol/mL}$$

$$pH = -\log K_a + \log \frac{[\text{proton acceptor}]}{[\text{proton donor}]}$$

$$pH = -\log(1.75 \times 10^{-5}) + \log \frac{0.067 \text{ mmol/mL}}{0.033 \text{ mmol/mL}}$$

$$= 4.76 + \log 2.0$$

$$= 5.06$$

We could have shortened the calculation by recognizing that in the log term the volumes cancel. So we can take the ratio of millimoles only:

$$mmol_{HOAc} = 0.10 \text{ mmol/mL} \times 10 \text{ mL} = 1.0 \text{ mmol}$$

$$mmol_{OAc^-} = 0.10 \text{ mmol/mL} \times 20 \text{ mL} = 2.0 \text{ mmol}$$

$$H = 4.76 + \log \frac{2.0 \text{ mmol}}{1.0 \text{ mmol}} = 5.06$$

We can use millimoles of acid and salt in place of molarity. Because the terms appear in a ratio, as long as the units are the same, they will cancel out. But it has to relate to moles or molarity, not mass.
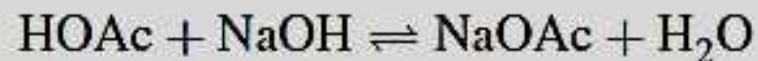
Example 7.12

Calculate the pH of a solution prepared by adding 25 mL of 0.10 M sodium hydroxide to 30 mL of 0.20 M acetic acid (this would actually be a step in a typical titration).

Solution

$$\text{mmol HOAc} = 0.20\ M \times 30\ \text{mL} = 6.0\ \text{mmol}$$

$$\text{mmol NaOH} = 0.10\ M \times 25\ \text{mL} = 2.5\ \text{mmol}$$

These react as follows:

$$\text{HOAc} + \text{NaOH} \rightleftharpoons \text{NaOAc} + \text{H}_2\text{O}$$

	6.0	2.5	2.5
After reaction,	3.5	0	2.5

$$\text{mmol NaOAc} = 2.5\ \text{mmol}$$

$$\text{mmol HOAc} = 6.0 - 2.5 = 3.5\ \text{mmol}$$

$$\text{pH} = 4.76 + \log \frac{2.5}{3.5} = 4.61$$

Example 7.13:

Calculating the pH of a buffer when strong acid or base is added

➢ As an example, suppose you have 100 mL of a buffer containing 0.100 *M* acetic acid and 0.0500 *M* sodium acetate. Calculate the pH of the buffer when 3 mL of 1.0 *M* HCl is added to it.

  ▪ As a first step, calculate the pH of the buffer before adding the strong acid using the Henderson–Hasselbalch equation:

$$\text{pH} = \text{p}K_a + \log \frac{[\text{A}^-]}{[\text{HA}]} \qquad \text{pH} = 4.76 + \log \frac{0.0500}{0.100} = 4.46$$

➢ The best way to solve this problem is to calculate the moles of acetic acid, moles of sodium acetate, and added moles of HCl:

$$100 \text{ mL} \times \frac{0.100 \text{ moles}}{1000 \text{ mL}} = 0.0100 \text{ moles acetic acid}$$

$$100 \text{ mL} \times \frac{0.0500 \text{ moles}}{1000 \text{ mL}} = 0.00500 \text{ moles sodium acetate}$$

$$3.00 \text{ mL} \times \frac{1.00 \text{ moles}}{1000 \text{ mL}} = 0.00300 \text{ moles hydrochloric acid}$$

➤ We need to know the chemical reaction occurring when strong acid is added to the buffer:

$$A^- + H^+ \rightarrow HA$$

$$CH_3COO^- + H^+ \qquad CH_3COOH$$

➤ The reaction says that the acetate ion in the buffer will react with the added strong acid, and the moles of acetate will decrease and the moles of acetic acid will increase. How much will the decrease and increase be? It is equal to the amount of strong acid added.

➤ We can now write the Henderson–Hasselbalch equation and account for the decrease in moles of acetate and increase in moles of acetic acid:

$$pH = pK_a + \log \frac{(\text{moles } A^- - \text{moles } H^+ \text{added})}{(\text{moles } HA + \text{moles } H^+ \text{added})}$$

$$pH = 4.76 + \log \frac{(0.00500 - 0.00300)}{(0.0100 + 0.00300)}$$

$$pH = 4.22$$

➢ This approach also works in reverse, when you add a strong base to a buffer. In this case, the pH of the buffer will increase, and the relevant chemical reaction is:

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

$$CH_3COOH + OH^- \qquad H_2O + CH_3COO^-$$

➢ This time the moles of acetic acid will decrease and the moles of acetate will increase.

➢ The Henderson–Hasselbalch equation can be written in the following form to solve for the pH:

$$pH = pKa + \log \frac{(\text{moles } A^- + \text{moles } OH^- \text{ added})}{(\text{moles } HA - \text{moles } OH^- \text{ added})}$$

Example 7.14

Calculate the volume of concentrated ammonia and the weight of ammonium chloride you would have to take to prepare 100 mL of a buffer at pH 10.00 if the final concentration of salt is to be 0.200 M. The molarity of concentrated ammonia is 14.8 M.

Solution

$$g = M \times L \times f.wt$$
$$g\ NH_4Cl = 0.2 \times (100/1000) \times 53.5 = 1.07\ g$$

We want 100 mL of 0.200 M NH_4Cl. Therefore, mmol NH_4Cl = 0.200 mmol/mL × 100 mL = 20.0 mmol

$$mg\ NH_4Cl = 20.0\ mmol \times 53.5\ mg/mmol = 1.07 \times 10^3 mg$$

Therefore, we need 1.07 g NH_4Cl. We calculate the concentration of NH_3 by

$$pH = pK_a + \log \frac{[\text{proton acceptor}]}{[\text{proton donor}]}$$

$$= (14.00 - pK_b) + \log \frac{[NH_3]}{[NH_4^+]}$$

$$10.0 = (14.00 - 4.76) + \log \frac{[NH_3]}{0.200\ mmol/mL}$$

$$\log \frac{[\text{NH}_3]}{0.200 \text{ mmol/mL}} = 0.76$$

$$\frac{[\text{NH}_3]}{0.200 \text{ mmol/mL}} = 10^{0.76} = 5.8$$

$$[\text{NH}_3] = (0.200)(5.8) = 1.1_6 \text{ mmol/mL}$$

The molarity of concentrated ammonia is 14.8 M. Therefore, remember, $C_1 V_1 = C_2 V_2$,

$$100 \text{ mL} \times 1.1_6 \text{ mmol/mL} = 14.8 \text{ mmol/mL} \times \text{mL NH}_3$$

$$\text{mL NH}_3 = 7.8 \text{ mL}$$

Questions

1. Explain the difference between a strong electrolyte and a weak electrolyte.

1. What is the Bronsted acid–base theory? What is the Lewis acid–base theory?

1. What is a conjugate acid? Conjugate base?

A **conjugate acid** is formed when a base accepts a proton.

A **conjugate base** is formed when an acid loses a proton. For example, acetate ion is the conjugate base of acetic acid. Similarly, ammonium ion is the conjugate acid of the base ammonia.

Questions

1. Explain the difference between a strong electrolyte and a weak electrolyte.
2. What is the Bronsted acid–base theory? What is the Lewis acid–base theory?
3. What is a conjugate acid? Conjugate base?
4. Write the ionization reaction of aniline, $C_6H_5NH_2$, in glacial acetic acid, and identify the conjugate acid of aniline. Write the ionization reaction of phenol, C_6H_5OH, in ethylene diamine, $NH_2CH_2CH_2NH_2$, and identify the conjugate base of phenol.

$$C_6H_5NH_2 + CH_3COOH \qquad C_6H_5NH_3^+ + CH_3COO^-$$

conjugate acid

$$2C_6H_5OH + NH_2CH_2CH_2NH_2 \qquad 2C_6H_5O^- + NH_3^+\text{-}CH_2CH_2\text{-}NH_3^+$$

conjugate base

5. What are Good Buffers?

Problems

Problem 1

The pH of an acetic acid solution is 3.26. What is the concentration of acetic acid and what is the percent acid ionized?

Solution

$$CH_3COOH = CH_3COO^- + H^+$$

At equilibrium $\quad C$-x $\qquad\qquad$ x $\qquad$ x

$[H^+] = 10^{-pH}$

$$[H^+] = [OAc^-] = 10^{-3.26} = 10^{.74} \times 10^{-4} = 5.5 \times 10^{-4} \underline{M}$$

$$(5.5 \times 10^{-4})^2/[HOAc] = 1.75 \times 10^{-5}$$
$\qquad$ $K_a = [H^+] [CH_3COO^-] / [CH_3COOH]$

$$[HOAc] = 1.7_3 \times 10^{-2} \underline{M} \quad (neglecting\ [H^+]\ in\ the\ denominator).$$

$$\%\ ionized = [(5.5 \times 10^{-4})/(1.7_3 \times 10^{-2})] \times 100\% = 3.2\%$$

% ionized = $[H^+]$ / $[CH_3COOH]$ x 100

Problem 2

The pH of a 0.20 M solution of a primary amine, RNH_2, is 8.42. What is the pK_b of the amine?

Solution

$$RNH_2 + H_2O = RNH_3^+ + OH^-$$

At equilibrium   0.2 - x   x   x
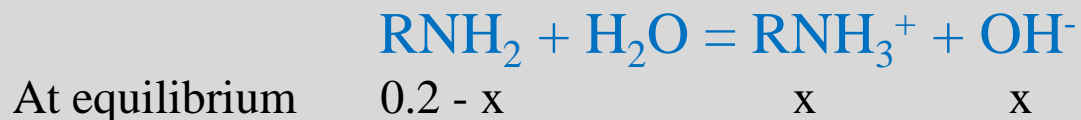
$$K_b = [RNH_3^+]\,[OH^-] / [RNH_2]$$

pH + pOH = 14

$$pOH = 14.00 - 8.42 = 5.58$$

$$[OH^-] = [RNH_3^+] = 10^{-5.58} = 10^{.42} \times 10^{-6} = 2.6 \times 10^{-6}\ \underline{M}$$

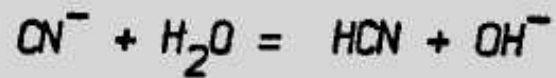$$K_b = (2.6 \times 10^{-6})^2/(0.20) = 3.4 \times 10^{-11}$$

$$pK_b = -\log 3.4 \times 10^{-11} = 10.47$$

$pKp = -\log [kp]$

Problem 3

Calculate the pH of a 0.010 M solution of NaCN. (Ka of HCN = 1.4×10^{-5})

Solution

NaCN   Na$^+$ + CN$^-$

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

$$CN^- + H_2O = HCN + OH^-$$

0.010-x   x   x

$$[HCN][OH^-]/[CN^-] = K_b = K_w/K_a = 1.0 \times 10^{-14}/7.2 \times 10^{-10} = 1.4 \times 10^{-5}$$

$C_{CN^-} > 100\ K_b$. ∴ neglect x compared to 0.010 $\underline{M}$ and use Equation 6.32.

$$[OH^-] = \sqrt{K_b \cdot C_A^-} = \sqrt{(1.4 \times 10^{-5})(0.010)} = 3.7 \times 10^{-4}\ \underline{M}$$

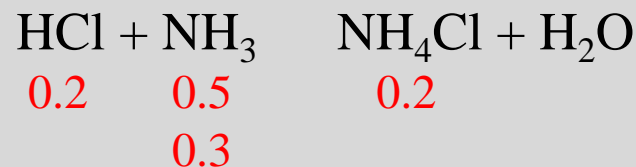pOH = 3.43; pH = 14.00 − 3.43 = 10.57

Problem 4

Calculate the pH of a solution prepared by mixing 5.0mL of 0.10 M NH_3 with 10.0 mL of 0.020 M HCl. (K_b for NH_3 = 1.75 x 10^{-5}).

Solution

$$HCl + NH_3 \quad NH_4Cl + H_2O$$

$$0.2 \quad 0.5 \quad\quad 0.2$$

$$0.3$$

mmole = M x mL

mmol NH_3 = 0.10 x 5.0 = 0.50 mmol

mmol HCl = 0.020 x 10.0 = 0.20 mmol

mmol NH_4^+ formed = 0.20 mmol

mmol excess NH_3 = 0.50 - 0.20 = 0.30 mmol

pH = pKa + log [proton acceptor]/[proton donor] = (pK_w–pK_b) + log [NH_3]/[NH_4^+]

= (14.00 - 4.76) + log (0.30)/(0.20) = 9.24 + 0.18 = 9.42

Or, from Equation 6.58;,

pOH = 4.76 + log ([NH_4^+]/[NH_3] = 4.76 + log (0.20.0.30) = 4.58

pH = 14.00 - 4.58 = 9.42

Problem 5 An acetic acid–sodium acetate buffer of pH 5.00 is 0.100 *M* in NaOAc. Calculate the pH after the addition of 10 mL of 0.1 M NaOH to 100 mL of the buffer. (K$_a$ for CH$_3$COOH = 1.75 x 10^{-5}).

Solution

$$pH = pK_a + \log \frac{[A^-]}{[HA]}$$

$$pK_a = -\log K_a$$

5.00 = 4.76 + log (0.100/[HOAc])

[HOAc] = 0.058 M

mmol HOAc = 0.058 M x 100 mL = 5.8 mmol

mmol NaOAc = 0.100 M x 100 mL = 10.0 mmol

mmol NaOH added = 0.10 M x 10 mL = 1.0 mmol

After adding NaOH:

$$NaOH + CH_3COOH \quad CH_3COONa$$

$$1.0 \qquad\quad 1.0 \qquad\qquad 1.0$$

mmol NaOAc = 10.0 + 1.0 = 11.0

mmol HOAc = 5.8 - 1.0 = 4.8

pH = 4.76 + log (11.0/4.8) = 5.12

The pH increases by 5.12 - 5.00 = 0.12