Lecture 24

Buffers

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-Any acid-conjugate base pair or base-conjugate acid pair from Tables 14.2, 14.3, and 14.4 can make a buffer solution.

Values for K_a for Some Common Monoprotic Acids

Table 14.2 ▶ Values of K_a for Some Common Monoprotic Acids

Formula	Name	Value of K_a*
HSO_4^-	Hydrogen sulfate ion	1.2×10^{-2}
$HClO_2$	Chlorous acid	1.2×10^{-2}
$HC_2H_2ClO_2$	Monochloracetic acid	1.35×10^{-3}
HF	Hydrofluoric acid	7.2×10^{-4}
HNO_2	Nitrous acid	4.0×10^{-4}
$HC_2H_3O_2$	Acetic acid	1.8×10^{-5}
$[Al(H_2O)_6]^{3+}$	Hydrated aluminum(III) ion	1.4×10^{-5}
$HOCl$	Hypochlorous acid	3.5×10^{-8}
HCN	Hydrocyanic acid	6.2×10^{-10}
NH_4^+	Ammonium ion	5.6×10^{-10}
HOC_6H_5	Phenol	1.6×10^{-10}

↑ Increasing acid strength

Example K_a reaction for HNO_2, $K_a = 4.0 \times 10^{-4}$:

$$HNO_2(aq) + H_2O(l) \leftrightarrow H_3O^+(aq) + NO_2^-(aq)$$

or: $$HNO_2(aq) \leftrightarrow H^+(aq) + NO_2^-(aq)$$

Buffer Examples (p. 96)

0.10 *M* $HC_2H_3O_2$ + 0.20 *M* $NaC_2H_3O_2$

0.50 *M* HCN + 0.50 *M* KCN

Values for K_b for Some Common Weak Bases

Table 14.3 ▶ Values of K_b for Some Common Weak Bases

Name	Formula	Conjugate Acid	K_b
Ammonia	NH_3	NH_4^+	1.8×10^{-5}
Methylamine	CH_3NH_2	$CH_3NH_3^+$	4.38×10^{-4}
Ethylamine	$C_2H_5NH_2$	$C_2H_5NH_3^+$	5.6×10^{-4}
Aniline	$C_6H_5NH_2$	$C_6H_5NH_3^+$	3.8×10^{-10}
Pyridine	C_5H_5N	$C_5H_5NH^+$	1.7×10^{-9}

Example K_b reaction for C_5H_5N, $K_b = 1.7 \times 10^{-9}$:

$$C_5H_5N(aq) + H_2O(l) \leftrightarrow OH^-(aq) + C_5H_5NH^+(aq)$$

Buffer Examples (p. 96)

0.10 *M* $HC_2H_3O_2$ + 0.20 *M* $NaC_2H_3O_2$

0.50 *M* HCN + 0.50 *M* KCN

0.26 *M* NH_4Cl + 0.26 *M* NH_3

1.0 *M* $C_5H_5NHNO_3$ + 0.75 *M* C_5H_5N

Stepwise Dissociation Constants for Several Common Polyprotic Acids

Table 14.4 ▶ Stepwise Dissociation Constants for Several Common Polyprotic Acids

Name	Formula	K_{a_1}	K_{a_2}	K_{a_3}
Phosphoric acid	H_3PO_4	7.5×10^{-3}	6.2×10^{-8}	4.8×10^{-13}
Arsenic acid	H_3AsO_4	5×10^{-3}	8×10^{-8}	6×10^{-10}
Carbonic acid	H_2CO_3	4.3×10^{-7}	5.6×10^{-11}	
Sulfuric acid	H_2SO_4	Large	1.2×10^{-2}	
Sulfurous acid	H_2SO_3	1.5×10^{-2}	1.0×10^{-7}	
Hydrosulfuric acid*	H_2S	1.0×10^{-7}	$\sim 10^{-19}$	
Oxalic acid	$H_2C_2O_4$	6.5×10^{-2}	6.1×10^{-5}	
Ascorbic acid (vitamin C)	$H_2C_6H_6O_6$	7.9×10^{-5}	1.6×10^{-12}	

$$H_2CO_3 \leftrightarrow HCO_3^- + H^+ \qquad K_{a1} = 4.3 \times 10^{-7}$$

$$HCO_3^- \leftrightarrow CO_3^{2-} + H^+ \qquad K_{a2} = 5.6 \times 10^{-11}$$

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Results of Buffer Calculations

Solution	**pH**	**pH after 0.10 mol NaOH added**	**pH after 0.20 mol HCl added**
H_2O			
0.50 *M* HF + 0.50 *M* NaF (1.0 L)			

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More Buffer Calculations (#1, p. 98)

What concentration of $NaNO_2$ is necessary to buffer a 0.050 *M* HNO_2 solution at pH = 3.00?

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

Buffer = HNO_2 + NO_2^-; K_a for HNO_2 = 4.0×10^{-4}

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

Buffer = HNO_2 + NO_2^-; K_a for HNO_2 = 4.0×10^{-4}

When pH = pK_a or $[H^+] = K_a$, [base] = [acid].

When pH < pK_a or $[H^+] > K_a$, [acid] > [base].

When pH > pK_a or $[H^+] < K_a$, [base] > [acid].

Lecture Question (p. 98.75)

Consider a buffer consisting of $HONH_2$ and $HONH_3Cl$. Which of the following statements is false? Assume K_a for $HONH_3^+ = 1 \times 10^{-8}$.

a. If NaOH were added to this buffer, the $[HONH_3^+]$ would decrease.

b. If $[HONH_2] = [HONH_3^+]$ in this buffer, pH = 8.0.

c. Adding more $HONH_2$ to the initial buffer will increase the pH.

d. If $[HONH_3^+] > [HONH_2]$ in this buffer, the $[H^+]$ of the solution will be larger than the K_a value.

e. If $[HONH_3^+] < [HONH_2]$ in this buffer, the pH of the solution will be smaller than the pK_a value.

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e. If $[HONH_3^+] < [HONH_2]$ in this buffer, the pH of the solution will be smaller than the pK_a value.

Best Buffer (p. 96)

The two characteristics of a best buffer are:

1. large concentrations of weak acid and conjugate base make for a better buffer than small concentrations.
2. equal concentrations of weak acid and conjugate base make for a best buffer.

Best Buffer (cont) – p. 96

When [weak acid] = [conjugate base] in a best buffer:

$$pH = pK_a + \log\frac{[\text{base}]}{[\text{acid}]} = pK_a + \log(1.0)$$

Best Buffer (cont) – p. 96

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A best buffer has a pH value close to its $\mathrm{pK_a}$ value (pH ≈ $\mathrm{pK_a}$ for a best buffer).

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More Buffer Calculations (#2, p. 98)

Which of the following combinations will be best to buffer a solution at pH = 9.5?

a. $HC_2H_3O_2$ ($K_a = 1.8 \times 10^{-5}$) + $NaC_2H_3O_2$

b. NaH_2PO_4 ($K_a = 6.2 \times 10^{-8}$) + Na_2HPO_4

c. $NH_4Cl + NH_3$ ($K_b = 1.8 \times 10^{-5}$)

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$pK_a = -\log(1.8 \times 10^{-5}) = 4.74$

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$pK_a = -\log(1.0 \times 10^{-14}/1.8 \times 10^{-5}) = 9.26$

Lecture Question (p. 98.75)

Given: K_b for $NH_3 \approx 1 \times 10^{-5}$ and K_b for $C_5H_5N \approx 1 \times 10^{-9}$. Which of the following weak base-conjugate acid pairs should be used to form the best buffer at pH = 5.0.

a. $NH_3 + NH_4^+$

b. $NH_3 + C_5H_5NH^+$

c. $C_5H_5N + C_5H_5NH^+$

d. $C_5H_5N + NH_4^+$

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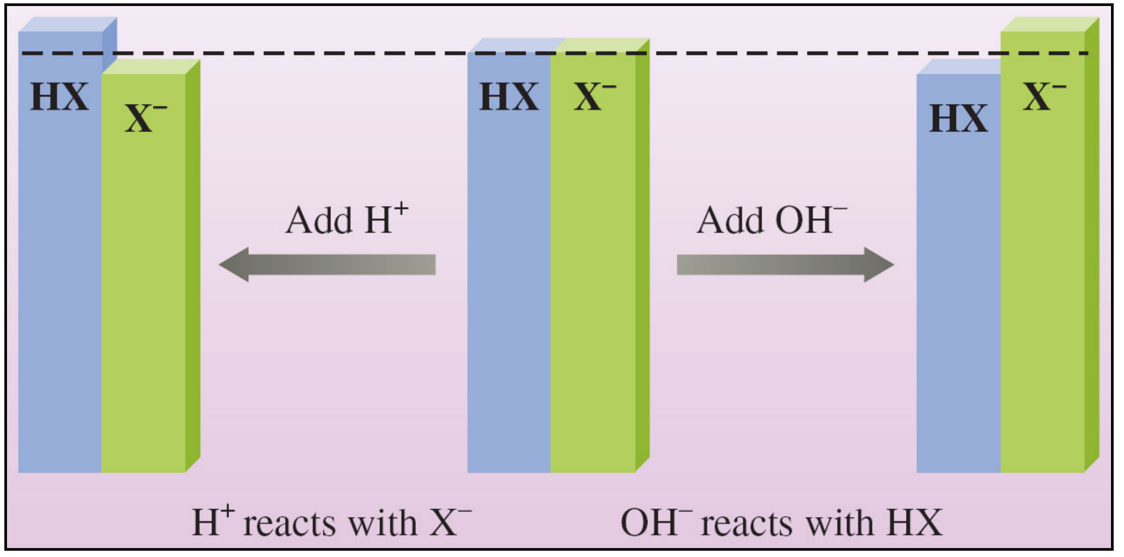
b. $NH_3 + C_5H_5NH^+$

c. $C_5H_5N + C_5H_5NH^+$

d. $C_5H_5N + NH_4^+$

Effect of Added H^+ or OH^- on Buffered System



Added H^+ or OH^- does change [base] and [acid]. But the ratio of [base]/[acid] doesn't change much, so pH doesn't change much when H^+ or OH^- is added.