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5.111 Principles of Chemical Science  
Fall 2008

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## 5.111 Lecture Summary #22

Acid/Base Equilibrium Continued (Chapters 10 and 11)

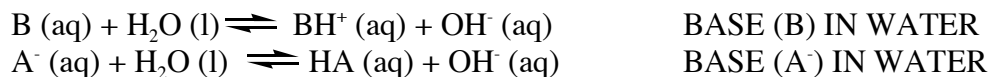
Topics: Equilibrium involving weak bases, pH of salt solutions, and buffers

From Wednesday's handout

2. Base in water

$$\text{Base ionization constant } K_b = \frac{[\text{NH}_4^+][\text{OH}^-]}{[\text{NH}_3]}$$

$K_b$  is  $1.8 \times 10^{-5}$  at  $25^\circ\text{C}$ . This small value tells us that only a small amount of  $\text{NH}_3$  is present as  $\text{NH}_4^+$ . A strong base reacts essentially completely to give  $\text{OH}^-(\text{aq})$  when put in water.  $\text{NH}_3$  is not a strong base. It is a moderately weak base.

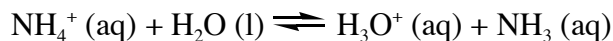


$$\text{p}K_b = -\log K_b$$

larger  $K_b$ , stronger baselarger  $\text{p}K_b$ , weaker base3. Conjugate acids and bases

The stronger the acid, the weaker its conjugate base.

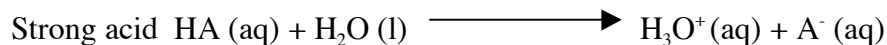
The stronger the base, the weaker its conjugate acid.

Consider conjugate acid-base pair  $\text{NH}_3$  and  $\text{NH}_4^+$ :Multiply  $K$ 's together and get:

$$K_a \times K_b = \frac{[\text{NH}_3][\text{H}_3\text{O}^+]}{[\text{NH}_4^+]} \times \frac{[\text{NH}_4^+][\text{OH}^-]}{[\text{NH}_3]} = [\text{H}_3\text{O}^+][\text{OH}^-]$$

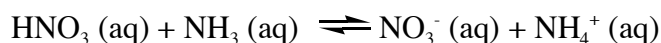
$$K_a \times K_b = K_w$$

$$\log K_a + \log K_b = \log K_w \quad \text{or} \quad \text{p}K_a + \text{p}K_b = \text{p}K_w = 14.00$$



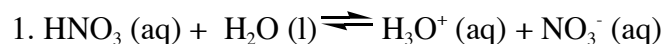
#### 4. Relative strengths of acids

Is  $\text{HNO}_3$  or  $\text{NH}_4^+$  a stronger acid? Will the reaction lie far to the right or left?

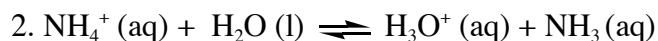


$$K = \frac{[\text{NO}_3^-][\text{NH}_4^+]}{[\text{HNO}_3][\text{NH}_3]}$$

consider each acid separately:



$$K_a (\text{HNO}_3) = \frac{[\text{H}_3\text{O}^+][\text{NO}_3^-]}{[\text{HNO}_3]} = 20.$$



$$K_a (\text{NH}_4^+) = \frac{[\text{H}_3\text{O}^+][\text{NH}_3]}{[\text{NH}_4^+]} = 5.6 \times 10^{-10}$$

Subtract equation 2 from 1 and divide the corresponding equilibrium constants.

$$K = \frac{K_a (\text{HNO}_3)}{K_a (\text{NH}_4^+)} = \frac{\frac{[\text{H}_3\text{O}^+][\text{NO}_3^-]}{[\text{HNO}_3]}}{\frac{[\text{H}_3\text{O}^+][\text{NH}_3]}{[\text{NH}_4^+]}} = \frac{[\text{NO}_3^-][\text{NH}_4^+]}{[\text{HNO}_3][\text{NH}_3]} = \frac{20.}{5.6 \times 10^{-10}} = 3.6 \times 10^{10}$$

Reaction lies far to the \_\_\_\_\_.  $\text{HNO}_3$  is a \_\_\_\_\_ than  $\text{NH}_4^+$ .

Types of acid-base problems

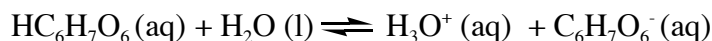
1. weak acid in water
2. weak base in water  $\leftarrow$  salt in water
3. strong acid in water
4. strong base in water
5. buffer

Equilibrium involving weak acids

Example: Vitamin C (ascorbic acid,  $\text{HC}_6\text{H}_7\text{O}_6$ ) has a  $K_a$  of  $8.0 \times 10^{-5}$ . Calculate the pH of a solution made by dissolving 500. mg in 100. mL of water.

$$0.500 \text{ g} \times 1 \text{ mol}/176.126 \text{ g} = 2.84 \times 10^{-3} \text{ mol}$$

$$2.84 \times 10^{-3} \text{ mol}/0.100 \text{ L} = 0.0284 \text{ M}$$



	$\text{HC}_6\text{H}_7\text{O}_6$	$\text{H}_3\text{O}^+$	$\text{C}_6\text{H}_7\text{O}_6^-$
initial molarity	0.0284	0	0
change in molarity	-x	+x	+x
equilibrium molarity	0.0284 - x	+x	+x

$$K_a = 8.0 \times 10^{-5} = \frac{[\text{H}_3\text{O}^+][\text{C}_6\text{H}_7\text{O}_6^-]}{[\text{HC}_6\text{H}_7\text{O}_6]} = \frac{x^2}{0.0284 - x}$$

If  $x \ll 0.0284$ , then  $(0.0284 - x) \approx 0.0284$ .

$$K_a = 8.0 \times 10^{-5} = \frac{x^2}{0.0284}$$

$$x = 0.00151 \text{ (really 2 sf, but carry extra)}$$

Check assumption. Is  $0.0284 - 0.00151 \approx 0.0284$ ?

You can use assumption if  $x$  is less than 5% of the value in question.

Here  $(0.00151/0.0284) \times 100\% = 5.3\%$  (more than 5%), so must use the quadratic equation.

Using quadratic eq,  $x = 0.00147$  (really 2 sf)

$$\text{pH} = -\log [1.47 \times 10^{-3}] = 2.83$$

Equilibrium involving weak bases

Example:  $\text{NH}_3(\text{aq}) + \text{H}_2\text{O}(\text{l}) \rightleftharpoons \text{NH}_4^+(\text{aq}) + \text{OH}^-(\text{aq})$   $K_b$  is  $1.8 \times 10^{-5}$  at  $25^\circ\text{C}$ .

Calculate the pH of a 0.15 M  $\text{NH}_3$  solution at  $25^\circ\text{C}$ .

initial molarity	$\text{NH}_3(\text{aq})$	$\rightleftharpoons$	$\text{NH}_4^+(\text{aq})$	+	$\text{OH}^-(\text{aq})$
change in molarity	0.15		0		0
equilibrium molarity					

base  
ionization  
constant

Using assumption,  $x =$

Check assumption (calculate percentage protonated)

$\text{pOH} = -\log [\text{OH}^-] =$

$\text{pH} =$

pH of salt solutions

A salt is formed by the neutralization of an acid by a base. The pH of salt in water is not always neutral.

Salts that contain the conjugate acids of weak bases produce acidic aqueous solutions; so do salts that contain small, highly charged metal cations (e.g.  $\text{Fe}^{3+}$ ). (Note: all Group 1 and 2 metals (e.g.  $\text{Li}^+$ ,  $\text{Ca}^{+2}$ ) and all metal cations with charge +1 (e.g.  $\text{Ag}^{+1}$ ) are neutral.) Salts that contain the conjugate bases of weak acids produce basic aqueous solution.

For the following solutions, predict the pH as acidic, neutral, or basic

1)  $\text{NH}_4\text{Cl}$  (aq)

$\text{NH}_4^+$  Is  $\text{NH}_4^+$  a conjugate acid of a weak base?

Is  $\text{NH}_3$  a weak base?

$\text{Cl}^-$  Is  $\text{Cl}^-$  a conjugate base of a weak acid?

Is  $\text{HCl}$  a weak acid?

2)  $\text{NaCH}_3\text{CO}_2$ (aq)

3) General rule for compound  $\text{XY}$

$\text{X}^+$  Is  $\text{X}^+$  a conjugate acid of a weak base? If yes, then acidic; If no, neutral

$\text{Y}^-$  Is  $\text{Y}^-$  a conjugate base of a weak acid? If yes, then basic; If no, neutral

Overall: acidic+neutral=acidic; basic+neutral=basic;neutral+neutral=neutral

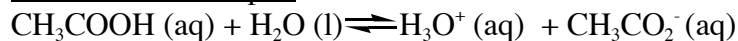
### Buffers

A **buffer** solution is any solution that maintains an approximately constant pH despite small additions of acid and base.

An **acid buffer**: consists of a weak acid and its conjugate base supplied as a salt. It buffers on the acidic side of neutral.

A **base buffer**: consists of a weak base and its conjugate acid supplied as a salt. It buffers on the basic side of neutral.

**Acid Buffer Example:** Mix acetic acid with an acetate salt and get dynamic equilibrium:

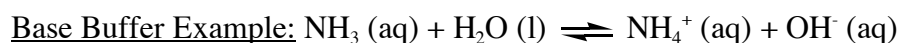


What happens if strong acid is added to a solution containing approximately equal amounts of  $\text{CH}_3\text{CO}_2^-$  and  $\text{CH}_3\text{COOH}$ ? The newly formed  $\text{H}_3\text{O}^+$  ions transfer hydrogen ions (protons) to  $\text{CH}_3\text{CO}_2^-$  generating  $\text{CH}_3\text{COOH}$  and  $\text{H}_2\text{O}$  molecules (back reaction). The added  $\text{H}_3\text{O}^+$  ions are effectively removed and the pH stays constant.

If  $\text{OH}^-$  base is added, the base removes a proton from  $\text{CH}_3\text{COOH}$  to form  $\text{H}_2\text{O}$  and  $\text{CH}_3\text{CO}_2^-$  molecules. The added  $\text{OH}^-$  ions are effectively removed and the pH stays constant.

**Acid buffer action:** The weak acid, HA, transfers protons to  $\text{OH}^-$  ions supplied by strong base. The conjugate base,  $\text{A}^-$ , of the weak acid accepts protons from the  $\text{H}_3\text{O}^+$  ions supplied by a strong acid.

A strong acid and the salt of its conjugate base don't make a good buffer. Why?



When strong acid is added,  $\text{NH}_3$  accepts protons from incoming acid to make  $\text{NH}_4^+$ . When strong base is added,  $\text{NH}_4^+$  donates a proton to form  $\text{NH}_3$  and  $\text{H}_2\text{O}$ . pH remains the same.

**Base buffer action:** The weak base, B, accepts protons supplied by strong acid. The conjugate acid,  $\text{BH}^+$ , of the weak base transfers protons to the  $\text{OH}^-$  ions supplied by a strong base.

A buffer is a mixture of weak conjugate acids and bases that stabilize the pH of a solution by providing a source or sink for protons.

**Sample Buffer Problem:** Suppose 1.00 mol of  $\text{HCOOH}$  and 0.500 mol of  $\text{NaHCOO}$  are added to water and diluted to 1.0 L. Calculate the pH. ( $K_a = 1.77 \times 10^{-4}$ )

	$\text{HCOOH} + \text{H}_2\text{O}$	$\rightleftharpoons$	$\text{H}_3\text{O}^+$	+	$\text{HCOO}^-$
initial molarity	1.00		0		0.500
change in molarity	-x		+x		+x
equilibrium molarity	1.00 - x		+x		0.500 + x

$$K_a = 1.77 \times 10^{-4} =$$

Using approximation that  $x$  is small compared to 1.00 and 0.500,  $x =$

Check assumption

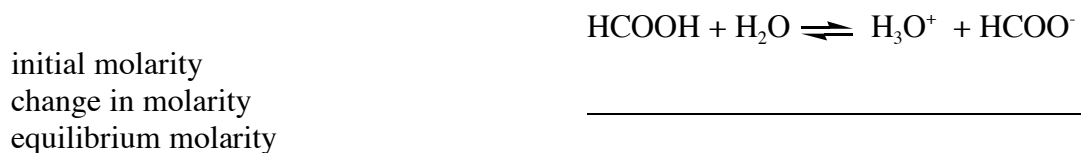
pH =

Now - what if 0.100 mol of a strong acid (HCl) had been included in the 1.0 L solution.

Because 0.100 mol of HCl reacts with equal number of moles of  $\text{HCOO}^-$  to form equal moles of HCOOH:

For  $\text{HCOO}^-$ ,  $0.500 \text{ mol} - 0.100 \text{ mol} = 0.400 \text{ mol}$       $[\text{HCOO}^-] = 0.400 \text{ mol}/1.0 \text{ L} = 0.400 \text{ M}$

For HCOOH,  $1.00 \text{ mol} + 0.100 \text{ mol} = 1.10 \text{ mol}$       $[\text{HCOOH}] = 1.10 \text{ mol}/1.0 \text{ L} = 1.10 \text{ M}$



$$K_a = 1.77 \times 10^{-4} =$$

Using approximation that  $x$  is small compared to 1.10 and 0.40,  $x =$

Check assumption (5% rule)

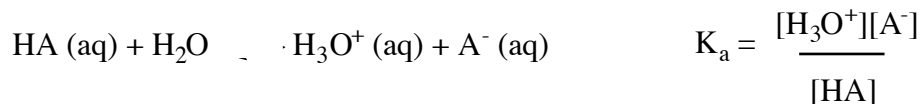
pH = 3.31

So addition of 0.10 mol of strong acid only changed pH from 3.45 to 3.31



### Designing a Buffer

One must consider the relationship between the ratio of [HA] to [A<sup>-</sup>], pK<sub>a</sub>, and pH in designing a buffer.



Rearrange: 
$$[\text{H}_3\text{O}^+] = K_a \times \frac{[\text{HA}]}{[\text{A}^-]}$$

Take logarithms of both sides: 
$$\log [\text{H}_3\text{O}^+] = \log K_a + \log \frac{[\text{HA}]}{[\text{A}^-]}$$

Multiply by (-): 
$$-\log [\text{H}_3\text{O}^+] = -\log K_a - \log \frac{[\text{HA}]}{[\text{A}^-]}$$

That is: 
$$\text{pH} = \text{p}K_a - \log \left( \frac{[\text{HA}]}{[\text{A}^-]} \right)_{\text{eq}}$$

The values of [HA] and [A<sup>-</sup>] in the equation are at equilibrium. However, a weak acid HA typically loses only a tiny fraction of its protons, so [HA] is negligibly different from the molarity of the acid used to prepare the buffer. Likewise, only a tiny fraction of the weakly basic anions of A<sup>-</sup> accept protons, so [A<sup>-</sup>] is negligibly different from the molarity of the base used to prepare the buffer.

So 
$$\text{pH} \cong \text{p}K_a - \log \left( \frac{[\text{HA}]_0}{[\text{A}^-]_0} \right) \quad \text{Henderson-Hasselbalch Equation}$$

↙  
initial

This assumption is valid when [H<sub>3</sub>O<sup>+</sup>] is small compared to [HA] and [A<sup>-</sup>] (i.e. less than 5%).

Example: Design a buffer system with pH 4.60.

Acetic acid is suitable with a  $pK_a$  of 4.75

A buffer solution is most effective in the range of  $pK_a \pm 1$

$$pH = pK_a - \log \frac{[CH_3COOH]_0}{[CH_3COO^-]_0}$$

$$\log \frac{[CH_3COOH]_0}{[CH_3COO^-]_0} = pK_a - pH = 4.75 - 4.60 = 0.15$$

$$\frac{[CH_3COOH]_0}{[CH_3COO^-]_0} = 10^{0.15} = 1.4$$

The ratio is more important than the amounts used. However, the amounts do affect the capacity of the buffer to resist changes in pH. Higher concentrations = more resistance to change.

If you use too low concentrations, the Henderson-Hasselbalch equation won't be valid.

For pH 4.60,  $[H_3O^+]$  is  $2.5 \times 10^{-5}$ .

$$\frac{2.5 \times 10^{-5}}{[HA] \text{ or } [A^-]} \times 100\% < 5\%$$



need concentration  $> 5.0 \times 10^{-4} M$