

# Chpt 17 Additional Aspects of Aqueous Equilibria

# [ Additional Aspects ]

- We have discussed in detail the determination of concentrations of products and reactants in chemical equilibrium
- Particular attention was paid to acid-base equilibria, and the determination of pH for various solutions
- We will now focus on additional aspects of aqueous equilibria
  
- Emphasis will be placed on the quantitative aspects of these equilibria using methods developed in our earlier treatment of equilibrium processes

# Common Ion Effect

- The dissociation of a weak electrolyte will decrease when a strong electrolyte having a common ion with the weak electrolyte is added to the solution

- Example: For the reaction



what is the effect of adding  $\text{NH}_4\text{Cl}$ , a strong electrolyte, to the solution?

# Hemoglobin

- Hemoglobin is responsible for the transport of O<sub>2</sub> around the body. The uptake and release of O<sub>2</sub> by hemoglobin can be represented by the following equilibrium.



What is the effect on the capacity of hemoglobin to transport oxygen in the body when undergoing an episode of acidosis (an decrease in blood pH)?

- A – increased
- B – decreased
- C – no change
- D – not enough information

# pH of a Solution Having a Common Ion I

- Example: What is the pH of a 0.16 M nitrous acid,  $\text{HNO}_2$ , solution containing 0.10 M  $\text{KNO}_2$ ?

	$\text{HNO}_2(\text{aq})$	$\text{H}^+(\text{aq})$	$\text{NO}_2^-(\text{aq})$
Initial			
Change			
Equilibrium			

# [ H<sup>+</sup> as a Common Ion I ]

- Example: What is the pH of a 0.16 M HNO<sub>2</sub> solution to which 0.10 M HNO<sub>3</sub> is added?

	HNO <sub>2</sub> (aq)	H <sup>+</sup> (aq)	NO <sub>2</sub> <sup>-</sup> (aq)
Initial			
Change			
Equilibrium			

- A – 1.0                      B – 2.0
- C – 13.0                    D – 8.0
- E – not enough information

# [ $K_a$ ]

- What is the  $K_a$  of propionic acid if the pH of a solution formed by the addition of 0.06 M  $KC_3H_5O_2$  and 0.085 M  $HC_3H_5O_2$  is 4.73?
- A –  $1.0 * 10^{-5}$
- B –  $1.3 * 10^{-5}$
- C –  $2.6 * 10^{-5}$
- D –  $3.6 * 10^{-4}$
- E – not enough information

# [ Buffered Solutions ]

- A buffered solution is one that maintains a (relatively) constant pH against the addition of strong acid or base
  
- We will look first at the preparation of buffered solutions from a weak acid and the salt of its conjugate base
- We will then investigate the buffering action of the solution following addition of strong acid



# Buffer pH

- Example: What is the pH of a buffer prepared from 0.16 M nitrous acid and 0.16 M potassium nitrite?



	$\text{HNO}_2(\text{aq})$	$\text{H}^+(\text{aq})$	$\text{NO}_2^-(\text{aq})$
Initial			
Change			
Equilibrium			

# Buffer and Acid Addition

- If the  $[H^+]$  is small compared to  $[HNO_2]$  and  $[NO_2^-]$ , the small changes to these concentrations can be ignored and

- The addition of a strong acid to a buffer solution will increase the  $H^+$  concentration and shift the equilibrium to the left
- For the  $HNO_2/KNO_2$  buffer



- First the consumption of the additional  $H^+$  ions is considered. Then one recalculates the equilibrium condition for the buffer solution to determine the pH

# Acid + Buffer I

- Example: Calculate the pH of a buffer solution prepared from 0.16 M  $\text{HNO}_2$  and 0.16 M  $\text{KNO}_2$  after addition of 0.04 M  $\text{HNO}_3$ .

First we consider consumption of the acid

$$[\text{HNO}_3] = 0.04 \text{ M}$$

	$\text{NO}_2^-(\text{aq})$	$\text{H}^+(\text{aq})$	$\text{HNO}_2(\text{aq})$
Initial	0.16	0.04	0.16
Change			
Final			

and then consider the equilibrium

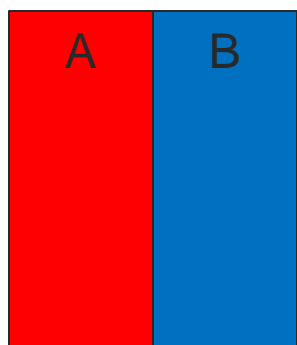
	$\text{HNO}_2(\text{aq})$	$\text{H}^+(\text{aq})$	$\text{NO}_2^-(\text{aq})$
Initial			
Change			
Equilibrium			

# [ Base + Buffer I ]

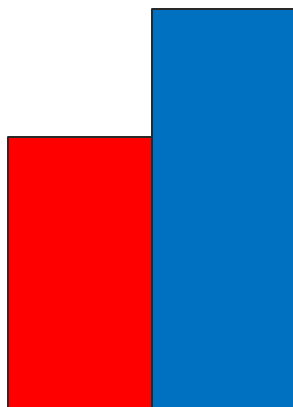
- Example: Calculate the pH of a buffer solution prepared from 0.16 M  $\text{HNO}_2$  and 0.16 M  $\text{KNO}_2$  after addition of 0.04 M NaOH.
- A – 0.92
- B – 1.39
- C – 2.13
- D – 3.57
- E – not enough information

# Buffer Concentrations

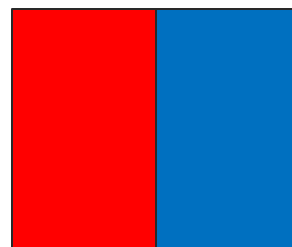
- The picture at left shows the concentration of a weak acid and its conjugate base in a buffer solution.
- Which of the three pictures represents a situation that cannot arise from the addition of a strong acid or base?



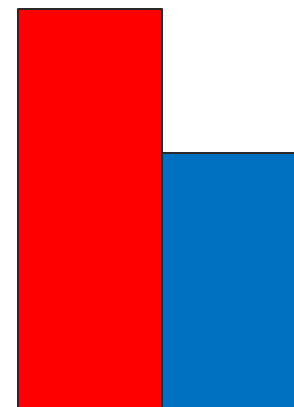
A



B



C



# Buffer Capacity

- The magnitude of the pH change will depend on the initial concentrations of buffer solution.
- The Henderson-Hasselbalch equation
- The [base] and [acid] are those after the strong acid/base is consumed. A larger initial concentration of acid and base in the buffer will more effectively resist pH change.
- When [base]=[acid] in the buffer, the buffer will work equally well against addition of a strong acid or base.

# [ Blood as a Buffer ]

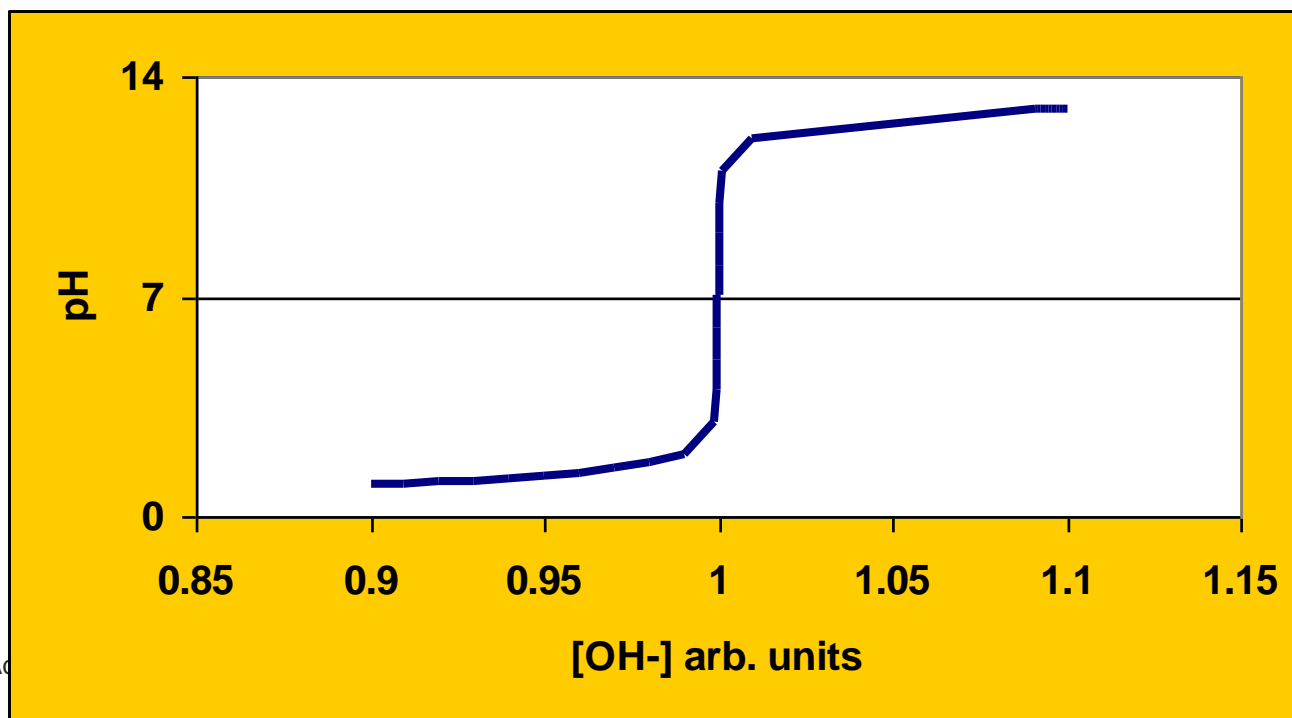
- Blood is a buffered solution maintained by the  $\text{H}_2\text{CO}_3/\text{HCO}_3^-$  conjugate acid-base pair. What is the relative concentration of  $\text{HCO}_3^-$  to  $\text{H}_2\text{CO}_3$  in normal blood at a pH of 7.4?  $\text{pK}_{a1} = 6.1$ ,  $\text{pK}_{a2} = 10.3$



- A – 0.05
- B – 20
- C – 10
- D – 0.001
- E – not enough information

# Strong Acid - Strong Base Titrations

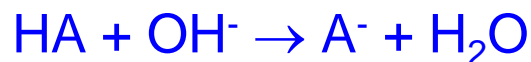
- Titration curves can reveal the equivalence point (equal acid and base concentrations) of an acid base reaction
- The titration of a strong acid solution with a strong base results in the following titration curve





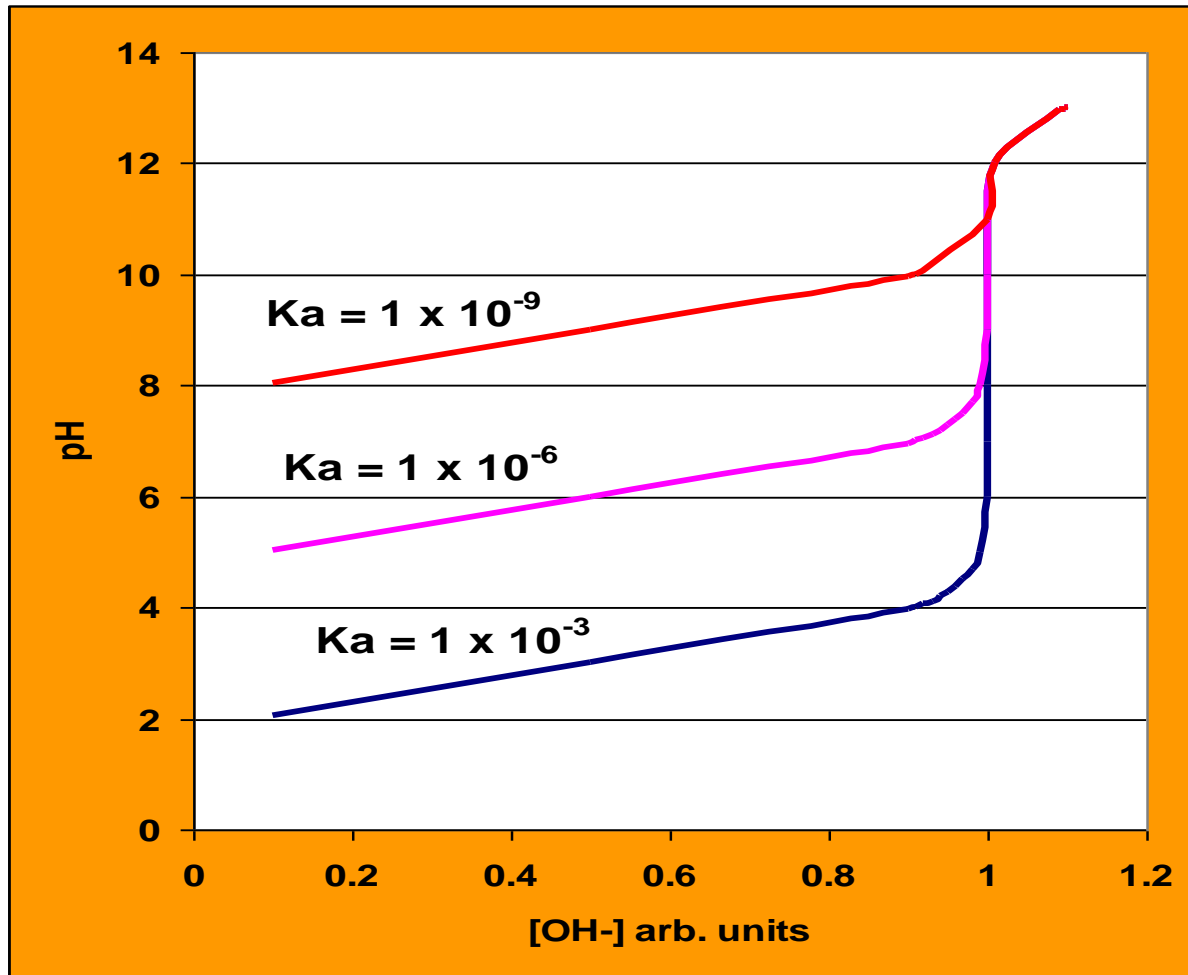
# Strong Base - Weak Acid Titrations

- When a strong base is added to a weak acid solution, the initial response is to consume the strong base



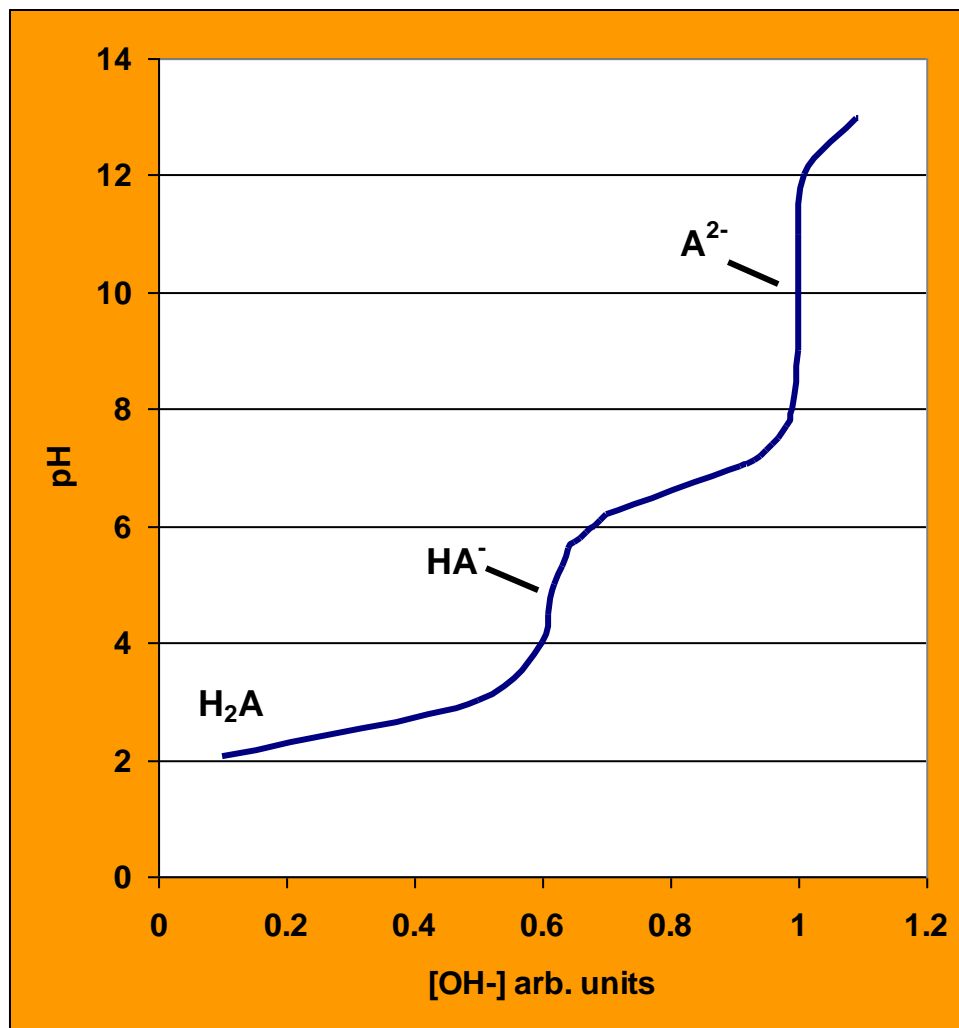
- This reaction is NOT an equilibrium reaction. The reaction will proceed to completion
- The pH will rise more rapidly before the equivalence point
- The pH at the equivalence point **WILL NOT BE 7.0**
- Once the weak acid is consumed, the concentration of excess base will determine the solution pH

# Weak Acid Titration Curve



# [ Polyprotic Acid Titration Curve ]

- If a weak acid contains more than one ionizable H ion, the titration with a strong base ( $\text{OH}^-$ ) will occur in a series of steps

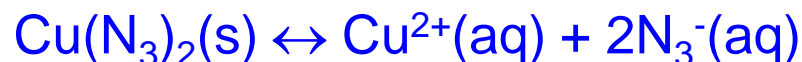


# Titration

- You have two beakers with the indicated concentrations. Which of the following statements are true?
  - 1 – a larger volume of NaOH (aq) is needed to reach the equivalence point in the titration of beaker A
  - 2 – the pH at the equivalence point in beaker B will be lower than the pH at the equivalence point in beaker A
  - 3 – The pH at the start of the titration will be the same
  - 4 – the titration curves will be essentially the same after passing the equivalence point
- A – 2, 3
- B – 2, 4
- C – 1, 4
- D – 4
- E – 1, 2, 4

# Solubility Product Constant

- A saturated solution contains undissolved solute in contact with the solution. An equilibrium expression can be written for the dissolution process



- $K_{\text{sp}}$  is the solubility product constant, and provides a means for determining the solubility of a given substance
- We will discuss the solubility of slightly soluble salts in solution, and factors which affect the solubility

# Solubility Determination

- Example:  $K_{sp} = 6.3 \times 10^{-10}$  for  $\text{Cu}(\text{N}_3)_2$ . What is the solubility of  $\text{Cu}(\text{N}_3)_2$  in water in grams per liter?

	$\text{Cu}(\text{N}_3)_2(\text{s})$	$\text{Cu}^{2+}(\text{aq})$	$2\text{N}_3^-(\text{aq})$
Initial			
Change			
Equilibrium			

# Solubility and a Common Ion I

- Example: What is the solubility (in g/L) of  $\text{Cu}(\text{N}_3)_2$  in water containing 0.01M  $\text{Cu}(\text{NO}_3)_2$ ?

	$\text{Cu}(\text{N}_3)_2(\text{s})$	$\text{Cu}^{2+}(\text{aq})$	$2\text{N}_3^-(\text{aq})$
Initial			
Change			
Equilibrium			

# Solubility and pH I

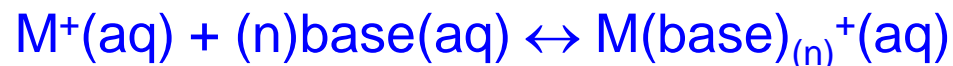
- Example:  $K_{sp} = 1.5 \times 10^{-20}$  for  $\text{Ce}(\text{OH})_3$ . What is the molar solubility of this salt in a solution containing 0.10 M NaOH?

	$\text{Ce}(\text{OH})_3(\text{s})$	$\text{Ce}^{3+}(\text{aq})$	$3\text{OH}^{-}(\text{aq})$
Initial			
Change			
Equilibrium			



# [ Complex Ion Formation ]

- Metal ions can act as Lewis acids towards water molecules and Lewis bases (which are electron pair donors)
- This interaction can strongly affect the solubility of metal ions
- The formation of a complex ion, which is a combination of the metal ion and Lewis base, will proceed by the equilibrium



- $K_f$  is called the formation constant (a selected list of formation constants are available in the book)

# Example of Complex Formation I

- Example: Determine the concentration of  $\text{Cr}^{3+}$  ion when 0.010 mol  $\text{Cr}(\text{NO}_3)_3$  is added to one liter of solution buffered to  $\text{pH} = 10.0$

	$\text{Cr}^{3+}(\text{aq})$	$4\text{OH}^{-}(\text{aq})$	$\text{Cr}(\text{OH})_4^{-}(\text{aq})$
Initial			
Change			
Equilibrium			