CHEM210 – Analytical Chemistry

#### Buffers

A buffer is a solution that resists changes in pH. The pH of a buffer changes very little when small amounts of a strong acid or strong base are added to the buffer.

A buffer consists of approximately equal amounts of a conjugate weak acid/weak base pair in equilibrium with each other. Strong acids and their conjugate bases don’t produce a buffer since strong acid ionization is complete: there is no equilibrium!

##### Acidic Buffers

In an acidic buffer both the weak acid and conjugate base are present initially in roughly equal concentrations. The equilibrium is

HA → H+ + A–

weak acid conjugate base

For a weak acid,  so . Thus : this is the *Henderson-Hasselbalch equation*.

These equations are useful for estimating the pH of a buffer. When [A-] = [HA], it follows that Ka = [H+] and pH = pKa.

# Acidic Buffer Example: Acetic acid (HC2H3O2), sodium acetate (NaC2H3O2)

NaC2H3O2 is a soluble salt that dissolves in water to give Na+ and C2H3O2- ions. Na+ ions are neutral spectator ions, so can be ignored. The C2H3O2- ions provide the conjugate base for the buffer. The buffer equilibrium is

HC2H3O2  → H+ + C2H3O2–

acetic acid acetate ion

For acetic acid, *Ka*(HC2H3O2) = 1.8 x 10-5 so p*Ka* = -log10*Ka* = 4.74. Thus when [HC2H3O2] = [C2H3O2–], pH = p*Ka* = 4.74.

##### Basic Buffers

In a basic buffer both the weak base and conjugate acid are present initially in roughly equal concentrations. The equilibrium is

B + H2O → BH+ + OH–

weak base conjugate acid

For a weak base,  so  = . Thus . Since p*Ka* = 14.00 – p*Kb*, . This is once again the *Henderson-Hasselbalch equation*.

These equations are useful for estimating the pH of a buffer. When [BH+] = [B], *Kb* = [OH–]. Consequently, pOH = p*Kb* for the buffer. It follows that pH = 14.00 – p*Kb* = p*Ka*(BH+)for the buffer.

# Basic Buffer Example: Ammonia (NH3), ammonium chloride (NH4Cl)

NH4Cl is a soluble salt that dissolves in water to give NH4+ and Cl– ions. Cl– ions are neutral spectator ions, so can be ignored. The NH4+ ions provide the conjugate acid for the buffer. The buffer equilibrium is

NH3 + H2O → OH– + NH4+

ammonia ammonium ion

For ammonia, *Kb*(NH3) = 1.8 x 10-5  so p*Kb* = -log10*Kb* = 4.74. Thus when [NH3] = [NH4+], pOH = 4.74 and pH = p*Ka*(NH4+)= 14.00 – 4.74 = 9.26.

# ***Neutral Buffers***

Neutral buffers have a pH close to 7.00. A good example is a NaH2PO4/Na2HPO4 buffer. Since Na+ ions are neutral spectator ions, this is a dihydrogen phosphate/hydrogen phosphate (H2PO4–/HPO42–) buffer. The buffer equilibrium is

H2PO4– → H+ + HPO42–

dihydrogen phosphate ion hydrogen phosphate ion

Here = 6.2 x 10–8. If [H2PO4-] = [HPO42-], *Ka* = [H+] and pH = pKa = 7.21.

***Response of a Buffer to the Addition of a Strong Acid or a Strong Base***

Added Acid. When a small amount of a strong acid such as HCl is added to a buffer, the H+ from the acid reacts with the *basic part* of the buffer to give more of the *acidic part* of the buffer. The reaction is assumed to go 100%. The new concentration of the *acidic part* of the buffer (increased from the initial value) and the new concentration of the *basic part* of the buffer (decreased from the initial value) are then used to calculate the pH of the buffer.

Added Base. When a small amount of a strong base is added to a buffer, the OH– reacts with the *acidic part* of the buffer to give more of the *basic part* of the buffer. The reaction is assumed to go 100%. The new concentration of the *acidic part* of the buffer (decreased from the initial value) and the new concentration of the *basic part* of the buffer (increased from the initial value) are then used to calculate the pH of the buffer.

**Questions**

1. What is a buffer?

2. Write the Henderson-Hasselbalch equation for a weak acid.

3. Write the Henderson-Hasselbalch equation for a weak base.

4. Explain what happens when a small amount of a strong acid is added to a buffer.

5. Explain what happens when a small amount of a strong base is added to a buffer.

4. How many grams of sodium fluoride should be added to 500.mL of a .02M hydrofluoric acid

solution to create a buffer of pH = 3.16?

Assume the change in volume is negligible.

5. Determine the final pH of a buffer system in which 50.0mL of 1.2M HCl is added to 500.mL

of a buffer solution that is 1.0M acetic acid and 1.0M sodium acetate. What would the final pH

have been if the HCl had been added to 500.mL of pure water instead? (You will need to look up

the Ka for acetic acid)

6. Calculate the pH of a buffer solution prepared by adding 20.5g of CH3COOH and 17.8g of CH3COONa to enough water to make 5.00x102mL of solution. (You will need to look up

the Ka for acetic acid)

7. Calculate the pH of a buffer system composed of .05M hydrofluoric acid and .07M

potassium fluoride solution. Is this system better at buffering acids or bases?

Ka for HF is 7.1x10-4