

## Monoprotic Acid/Base Equilibria

### Strong acids and bases:

What is the pH of 0.10 M HCl? How do you calculate it? Why?

Concentration (F)	pH
0.10 ( $10^{-1}$ )	
0.01 ( $10^{-2}$ )	
0.001 ( $10^{-3}$ )	
0.0001 ( $10^{-4}$ )	
0.00001 ( $10^{-5}$ )	
0.000001 ( $10^{-6}$ )	
0.0000001 ( $10^{-7}$ )	
0.00000001 ( $10^{-8}$ )	

Based on our typical method for calculating pH, at  $10^{-8}$  M HCl, pH is greater than 7.00, does this make sense?

Where have we gone wrong?

1

## Monoprotic Acid/Base Equilibria

We have to consider autoprotolysis of water:



Charge Balance:

Mass Balance:

So:

2

## Autoprotolysis

**Question:** When do we have to be concerned with autoprotolysis?

**Answer:** When the (strong) acid or base concentration is around  $K_w^{1/2}$  ( $\sim 10^{-6}$  to  $10^{-8}$  F).

Why not just when the concentration is  $< 10^{-6}$  F?

Lets look back at our strong acid calculation (charge balance)

$$[\text{OH}^-] = [\text{H}^+] - [\text{Strong Acid}]$$

as [Strong Acid] gets smaller and smaller,  $[\text{OH}^-]$  approaches  $[\text{H}^+]$

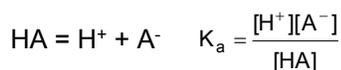
So, for extremely low strong acid or base concentration ( $< 10^{-8}$  F),  
pH = 7.00

**Problem:** What is the pOH, and pH of a  $2.48 \times 10^{-7}$  F solution of NaOH?

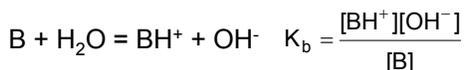
3

## Weak Acids and Bases: Quick Review

Acid Dissociation:



Base Hydrolysis:



For any conjugate acid base pair

$$K_a K_b = K_w$$

What is the pH of a solution prepared by dissolving 0.10 moles of acetic acid in 1.00 L solution? This is tougher than it sounds!

4

## pH of a Weak Acid Solution

What is the pH of a solution prepared by dissolving 0.10 moles of acetic acid in 1.00 L solution? This is tougher than it sounds!



Charge Balance:

$$[\text{H}^+] = [\text{OH}^-] + [\text{OAc}^-]$$

Mass Balance:

$$[\text{HOAc}] + [\text{OAc}^-] = 0.10 \text{ F}$$

Four unknowns, four equations, time to solve.

We end up with a third order equation! What to do?!?

5

## pH of a Weak Acid Solution

Let's make a simplifying approximation.

- Since HOAc is a much stronger acid than H<sub>2</sub>O (look at the K<sub>a</sub>'s), the overwhelming majority of the protons in solution will come from the dissociation of HOAc
- Every time a proton (H<sup>+</sup>) is liberated, an acetate (OAc<sup>-</sup>) is liberated as well
- So, [H<sup>+</sup>] ≈ [OAc<sup>-</sup>], and therefore, [OH<sup>-</sup>] << [OAc<sup>-</sup>]

What does that do for us?

6

## pH of a Weak Acid Solution

We can make this simplifying assumption ( $[H^+] \approx [A^-]$ ) for any weak acid equilibrium (**as long as we verify it at the end**) this will always lead to the following equation:

$$K_a = \frac{[H^+][A^-]}{[HA]} = \frac{x^2}{F-x}$$

where  $x = [H^+]$ .

7

## pH of a Weak Acid Solution

This equation can be solved using the quadratic formula, BUT:

In some instances, we can make things easier yet:

- Remember, HA is a weak acid, so it only dissociates slightly (the  $K_a$  equilibrium lies to the left b/c  $K_a \ll 1$ )
- So, [HA] at equilibrium will not vary much from its initial value, as long its initial concentration (F) isn't extremely dilute.
- This allows us to approximate F-x as F, the equation now becomes:

$$K_a = \frac{x^2}{F} \quad \text{or} \quad x = \sqrt{K_a F}$$

- This approximation is usually good as long as  $K_a < 0.01F$ \*\*\*\*

8

## Fraction of Dissociation

Just how much (what fraction) HA dissociates? It depends on a couple of things:

1.

2.

To calculate fraction of dissociation,  $\alpha$ , for a monoprotic weak acid:

This reduces to:

9

## pH of a Weak Base Solution

The process is basically the same.



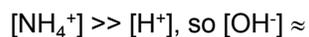
What is the pH of 0.025 F ammonia?

Equilibrium Constants:

Charge Balance:

Mass Balance:

Simplifying assumption:



Simplified solution:

What is the fraction of association of ammonia under these conditions?

10

## Conjugate Acid-Base Pairs and Buffers

Items to remember about conjugate acid-base pairs:

- The conjugate acid of a weak base is a weak acid and the conjugate base of a weak acid is a weak base.
- For any conjugate acid-base pair,  $K_a K_b = K_w$ , where  $K_a$  is the acid dissociation constant for the weak acid, and  $K_b$  is the base hydrolysis constant for the conjugate base.
- Therefore, the conjugate base of a moderately weak acid is a stronger base than the conjugate of a very weak acid:

$$\text{If } K_{a1} > K_{a2}, K_{b1} < K_{b2}$$

**Buffers:** What is a buffer?

Why would you ever need a buffer?

How does a buffer work?

11

## Buffer pH and the Henderson-Hasselbach Equation

H-H Relates pH to relative equilibrium concentrations of acid and conjugate base in solution.

$$K_a = \frac{[H^+][A^-]}{[HA]}$$

12

## Buffer pH and the Henderson-Hasselbach Equation

We use the H-H equation to predict pH using non-equilibrium concentrations. How can we get by not accounting for dissociation?

To a first approximation, the pH of a buffer is essentially independent of dilution. Why?

What you mix isn't exactly what you get, Why?

- Activity and ionic strength considerations
- Concentrations of HA and A<sup>-</sup> may not be equal to their formalities
- Dilute solutions, extreme pH

**Critical Consideration: How would you prepare a buffer solution?**

13

## Buffer Behavior and Selection

**Buffer Capacity:**

$$\beta = \frac{dC_b}{dpH} = -\frac{dC_a}{dpH}$$

- Buffer capacity is a maximum when pH = pK<sub>a</sub>
- Best to choose a buffer system whose pK<sub>a</sub> is within ±1 pH unit of your desired pH (b/c capacity diminishes greatly outside this range).

**PROBLEMS:**

1. Calculate the pH of a solution prepared by mixing 0.010 mol of acetic acid with 0.010 mol of sodium acetate in 1.0 L solution.
2. Calculate the new pH of this buffer after the addition of 15 mL of 0.100 F NaOH.
3. Would you expect a larger or smaller pH change if the buffer had been prepared from 0.10 mol HOAc and 0.10 mol NaOAc? Verify your prediction with a calculation.

14