

### 15.1 - 15.2 - Common Ions & Buffers



### The Common Ion Effect

This section deals with the interactions of weak acids and their salts.

By Le Chatelier's principle, equilibrium shifts when ion concentration changes occur.

This is called the Common Ion Effect, and an example follows.

### Common Ion Example

1. What is the pH of a 1.0 M solution of HF?
2. What is the new pH when the solution has 1.0 M NaF added to it?

### Common Ion Answer 1

1. What is the pH of a 1.0 M solution of HF?

Major species are: HF and H<sub>2</sub>O.

The reaction is:  $HF \rightleftharpoons H^+ + F^-$

This is solved using the process seen in 14.5 and the equilibrium expression:

$$K_a = \frac{[H^+][F^-]}{[HF]} \Rightarrow \frac{(x)(x)}{1.00 - x} \approx \frac{(x)(x)}{1.00}$$

$$7.2E-4 \approx x^2 \quad \Rightarrow \quad x \approx \sqrt{7.2E-4} = \boxed{2.7E-2M}$$

Then:

$$pH = -\log[H^+] = -\log 2.7E-2 = \boxed{1.57}$$

### Common Ion Answer 2

2. What is the new pH when the solution has 1.0 M NaF added to it?

Major species now are: HF, F<sup>-</sup>, Na<sup>+</sup>, and H<sub>2</sub>O.

The important species are F<sup>-</sup> and HF, since Na<sup>+</sup> has neither basic or acidic properties, and H<sub>2</sub>O is a very weak acid (or base).

We can use the same reaction and equilibrium expression as before, but we must adjust the concentrations thusly, then solve for [H<sup>+</sup>]:

Initial (M)	Equilibrium (M)
[HF] <sub>0</sub> = 1.0	[HF] = 1.0 - x
[F <sup>-</sup> ] <sub>0</sub> = 1.0	[F <sup>-</sup> ] = 1.0 + x
[H <sup>+</sup> ] <sub>0</sub> = 0	[H <sup>+</sup> ] = x

### Common Ion Answer 2 (Cont.)

Using the usual process for weak acids at high concentration and our data:

$$K_a = \frac{[H^+][F^-]}{[HF]} \Rightarrow \frac{(x)(1.0 + x)}{1.00 - x} \approx \frac{(x)(1.0)}{1.00}$$

$$x \approx 7.2E-4M$$

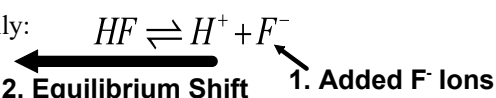
Lastly:

$$pH = -\log[H^+] = -\log 7.2E-4 = \boxed{3.14}$$

### Common Ion Example Discussion

In the second example, with NaF,  $[H^+]$  was much less due to the common ion effect.

Consider what was going on: with proportionally more fluoride ions, the  $H^+$  which would have been free otherwise, were given more opportunities to form HF, thus raising pH.

Pictorially:  $HF \rightleftharpoons H^+ + F^-$   


Essentially, a basic salt was added, and that basicity reacted with the acid, partially neutralizing it.

We will be looking at acid-base titration in 15.3.

### Buffered Solutions

The most important application of acid-base solutions with a common ion is for buffering.

A buffered solution is one that resists a change in pH when either hydrogen or hydroxide ions are added.

For a real-world example, our blood contains buffering components that resist swings in pH that could adversely affect us. It is the delicate balance between carbonic acid ( $H_2CO_3$ ) and the bicarbonate ion ( $HCO_3^-$ ) that keeps our blood in the pH range of 7.35 and 7.45.

A pH lower than 6.8 or higher than 7.8 can lead to death!

### Henderson-Hasselbach Equation

Problem 2 was an example of a buffered solution, in that a weak acid was coupled with its salt.

A mathematical expression exists, which sidesteps some of the computational process seen so far: The Henderson-Hasselbach (H & H) equation.

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

**Henderson-Hasselbach Equation**

A derivation and proof of this follows, but functionally the equation compares amounts of acid and salt, and solves directly for the pH of a buffered solution.

Note: H & H is an approximation of pH (like earlier calculations), in that the amount of dissociated weak acid has been considered to be zero.

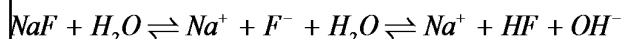
### 3. Revisiting Problem Two

The previous problem involved 1.0 molar solutions of HF (weak acid) and NaF (basic salt).

To understand H & H completely (and not just use it mindlessly) it's important to realize which chemical is the base, and which is the acid.

This understanding will help you get through problems focusing on bases (with acid salts), where  $K_a$  might not be known immediately.

In this problem, the reaction of the basic salt NaF with water contributes to fluoride concentration, and in solution,  $F^-$  is a conjugate base (joins with  $H^+$ ):



### 3. Revisiting Problem Two

Use H & H to solve the previous problem.

$$pH = pK_a + \log \left( \frac{[base]}{[acid]} \right) \Rightarrow pK_a + \log \left( \frac{[F^-]}{[HF]} \right)$$

$$pH = -\log 7.2E-4 + \log \left( \frac{1.0M}{1.0M} \right) = \boxed{3.14}$$

### H & H Proof

This begins with a general acid's dissociation:



Followed by the equilibrium expression:

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

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

Finally, logarithmic manipulation:

$$-\log[H^+] = -\log K_a - \log \left( \frac{[HA]}{[A^-]} \right)$$

$$pH = pK_a + \log \left( \frac{[A^-]}{[HA]} \right)$$

#### 4. Acetate Example

A buffered solution contains 0.50 M acetic acid,  $\text{CH}_3\text{COOH}$  ( $K_a = 1.8 \times 10^{-5}$ ), and 0.40 M sodium acetate ( $\text{NaCH}_3\text{COO}$ ). What is the solution's pH?

Species?  $\text{CH}_3\text{COOH}$     $\text{Na}^+$     $\text{CH}_3\text{COO}^-$     $\text{H}_2\text{O}$   
                     Weak Acid    Neither            Conjugate    Very Weak  
                                     Acid nor            Base            Acid or Base  
   Base

Using H & H:

$$pH = pK_a + \log\left(\frac{[\text{base}]}{[\text{acid}]}\right) \Rightarrow pK_a + \log\left(\frac{[\text{CH}_3\text{COO}^-]}{[\text{HCH}_3\text{COOH}]}\right)$$

$$pH = -\log 1.8 \times 10^{-5} + \log\left(\frac{0.40 \text{ M}}{0.50 \text{ M}}\right) = \boxed{4.64}$$

#### pH Changes in Buffered Solutions

5. From the previous example, what does the pH become if 0.010 moles of solid NaOH are added to 1.0 L of the buffered solution?

6. What would the pH be if the NaOH were merely added to water to make 1.0 L of solution?

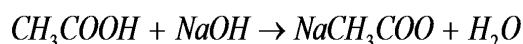
#### 5. pH Change Solution (Slide 1)

First, realize that the NaOH reacts with the acetic acid, and as a strong base it does so completely (the  $\text{OH}^-$  ions glom onto the  $\text{H}^+$  ions).

Species:  $\text{CH}_3\text{COOH}$ ,  $\text{Na}^+$ ,  $\text{CH}_3\text{COO}^-$ ,  $\text{OH}^-$ ,  $\text{H}_2\text{O}$

Note: after the reaction, the  $\text{OH}^-$  is used up.

We start with a balanced reaction:



#### 5. pH Change Solution (Slide 2)

Then, stoichiometry to calculate species amounts:

Initial NaOH = 0.010 mol,

Initial  $\text{HCH}_3\text{COOH}$ :  $1.0 \text{ L} \cdot \frac{0.50 \text{ mol}}{1.0 \text{ L}} = 0.50 \text{ mol CH}_3\text{COOH}$

The reaction will consume all 0.010 moles of NaOH, and reduce the amount of acid by 0.010 moles.

The reaction also increase the acetate ion by the same amount.

Final  $\text{HCH}_3\text{COOH}$ :  $0.50 \text{ mol} - 0.010 \text{ mol} = 0.49 \text{ mol}$

Final  $\text{CH}_3\text{COO}^-$ :  $0.40 \text{ mol} + 0.010 \text{ mol} = 0.41 \text{ mol}$

#### 5. pH Change Solution (Slide 3)

Finally we calculate pH using H & H:

$$pH = pK_a + \log\left(\frac{[\text{base}]}{[\text{acid}]}\right) \Rightarrow pK_a + \log\left(\frac{[\text{CH}_3\text{COO}^-]}{[\text{HCH}_3\text{COOH}]}\right)$$

$$pH = -\log 1.8 \times 10^{-5} + \log\left(\frac{0.41 \text{ M}}{0.49 \text{ M}}\right) = \boxed{4.66}$$

pH goes up slightly.

#### 6. pH of 0.010 M NaOH Answer

Calculate pOH first:

$$pOH = -\log[0.010] = 2.00$$

Then subtract that from 14 to get pH:

$$pH = 14.00 - 2.00 = 12.00$$

This is WAY higher than if it were added to the buffered solution.

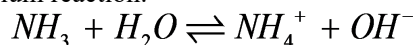
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### 7. Base! How low can you go?

A buffered solution contains 0.25 M  $\text{NH}_3$  ( $K_b = 1.8 \times 10^{-5}$ ) and 0.40 M  $\text{NH}_4\text{Cl}$ . Calculate the pH.

Major species:  $\text{NH}_3$ ,  $\text{H}_2\text{O}$ , and  $\text{NH}_4^+$ ,  $\text{Cl}^-$ .

Equilibrium reaction:



Notice: we've got the  $K_b$ , and need  $K_a$  to use H & H.

$$K_a \cdot K_b = K_w = 1.0 \times 10^{-14}$$

$$K_a = \frac{1.0 \times 10^{-14}}{1.8 \times 10^{-5}} = 5.6 \times 10^{-10}$$

Now for H & H:

$$\text{pH} = \text{p}K_a + \log\left(\frac{[\text{NH}_3]}{[\text{NH}_4^+]}\right)$$

$$\text{pH} = -\log 5.6 \times 10^{-10} + \log\left(\frac{0.25 \text{ M}}{0.40 \text{ M}}\right) = \boxed{9.04}$$

### 8. Adding Strong Acid.

What does the pH become when 0.10 mole of gaseous HCl (to minimize volumetric effects) is added to the previous problem?

First, balanced reaction:  $\text{HCl} + \text{NH}_3 \rightarrow \text{NH}_4^+ + \text{Cl}^-$

Next: molar amounts/stoichiometry:

0.10 mol HCl reduces the amount of  $\text{NH}_3$  in solution: 0.25 M  $\text{NH}_3$  - 0.10 M HCl = 0.15 M  $\text{NH}_3$ .

$[\text{NH}_4^+]$  increases: 0.40 M + 0.10 M = 0.50 M  $\text{NH}_4^+$ .

Finally, H & H:

$$\text{pH} = \text{p}K_a + \log\left(\frac{[\text{NH}_3]}{[\text{NH}_4^+]}\right)$$

$$\text{pH} = -\log 5.6 \times 10^{-10} + \log\left(\frac{0.15 \text{ M}}{0.50 \text{ M}}\right) = \boxed{8.73}$$

In water alone, 0.10 M HCl has a pH of 1. Way less!

### Homework

Preview 15.3 - 15.5

15.1-15.2 Problems in your Booklet

Due: Next Class