

Lecture 17 CH102 A2 (MWF 11:15 am) Spring 2018

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[TP] At 25 °C the  $pK_a = -\log(K_a)$  of a certain acid is 4.17. A solution is made by combining 0.314 mol of HA and 0.314 mol of NaA in a total volume of 716 mL. What is the pH of the resulting solution?

- 14% 1. 1.78  
 14% 2. 2.19  
 14% 3. 3.14  
 14% 4. 4.17  
 14% 5. 5.78  
 14% 6. 7.00  
 14% 7. Something else



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## Lecture 17 CH102 A2 (MWF 11:15 am)

Wednesday, February 28, 2018

- $pK_a = -\log(K_a)$ .
- Titration: What happens when some  $OH^-$  is added to an acid
- $[H_3O^+]$  when “too little” base added

Next:  $[H_3O^+]$  when “just enough” base added.  $[H_3O^+]$  when “too much” base added; Practice: Too little, just enough, too much?;  $[H_3O^+]$  when different amounts of “not enough” base added



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$$pK_a = -\log(K_a)$$

Since  $K_a = [H_3O^+][A^-] / [HA]$  we can express the hydronium ion concentration as  $[H_3O^+] = K_a [HA] / [A^-]$

From this we can express pH as

$$pH = -\log(K_a) + \log([A^-] / [HA])$$



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$$pK_a = -\log(K_a)$$

Since  $K_a = [H_3O^+][A^-] / [HA]$  we can express the hydronium ion concentration as  $[H_3O^+] = K_a [HA] / [A^-]$

From this we can express pH as

$$pH = -\log(K_a) + \log([A^-] / [HA])$$

$$= pK_a + \log([A^-] / [HA])$$

where  $pK_a$  is defined as  $pK_a = -\log(K_a)$



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$$\text{p}K_a = -\log(K_a)$$

An important application of

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

is that ...

if **equal amounts** of weak acid and its conjugate base are combined, then

$$\text{pH} = \text{p}K_a + \log(1) = \text{p}K_a$$

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1. 1.78
2. 2.19
3. 3.14
4. 4.17
5. 5.78
6. 7.00
7. Something else

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$$\text{p}K_a = -\log(K_a)$$

Since  $\text{pH} = \text{p}K_a + \log\left(\frac{[\text{A}^-]}{[\text{HA}]}\right)$ , when **equal amounts** of acid and its conjugate base are combined in solution (an **equimolar solution**), the pH will be  $\text{p}K_a$ .

So, a way to measure  $K_a$  is to make an **equimolar solution** and measure its pH, for then

$$K_a = 10^{-\text{pH}}$$

Very useful to remember!

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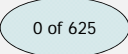

Titration: What happens when **some**  $\text{OH}^-$  is added to an acid?

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**[Quiz]** An acid has  $K_a = 1.0 \times 10^{-7}$  at 25 °C. The hydronium concentration of a  $c_a = 0.40$  M solution of this acid solution is  $[\text{H}_3\text{O}^+] = 2.0 \times 10^{-4}$ . After adding **some** 0.20 M  $\text{OH}^-$ ,  $[\text{H}_3\text{O}^+]$  **must be** ...

1. smaller than  $2.0 \times 10^{-4}$
2. less than  $1.0 \times 10^{-7}$  (basic)
3. equal to  $1.0 \times 10^{-7}$  (neutral)
4. greater than  $1.0 \times 10^{-7}$  (acidic)
5. More information needed

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### Add “some” $\text{OH}^-$ to an acid

When **some**  $\text{OH}^-$  solution is added to an HA solution, **some** HA will be converted to conjugate base,  $\text{A}^-$ .

Therefore,  $[\text{HA}]$  **will be less**, the equilibrium

$$\text{HA}(aq) + \text{H}_2\text{O}(l) \rightleftharpoons \text{H}_3\text{O}^+(aq) + \text{A}^-(aq)$$

will **shift toward reactants**, and so, by Le Chatelier,  $[\text{H}_3\text{O}^+]$  must **decrease**.

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### Add “some” $\text{OH}^-$ to an acid

When **some**  $\text{OH}^-$  solution is added to an HA solution, **some** HA will be converted to conjugate base  $\text{A}^-$ , and so  $[\text{H}_3\text{O}^+]$  must **decrease**.

There are **two steps** to find the new value of  $[\text{H}_3\text{O}^+]$ .

**Step 1:** Assume HA and the added  $\text{OH}^-$  react 100%, as a **limiting reagent** problem.

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### Add “some” $\text{OH}^-$ to an acid

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There are **two steps** to find the new value of  $[\text{H}_3\text{O}^+]$ .

**Step 1:** Assume HA and the added  $\text{OH}^-$  react 100%, as a **limiting reagent** problem.

**Step 2:** Use the results of step 1 to re-solve the equilibrium.

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## Add “some” OH<sup>-</sup> to an acid

When **some** OH<sup>-</sup> solution is added to an HA solution, **some** HA will be converted to conjugate base A<sup>-</sup>, and so [H<sub>3</sub>O<sup>+</sup>] must **decrease**.

There are **two steps** to find the new value of [H<sub>3</sub>O<sup>+</sup>].

**Step 1:** Assume HA and the added OH<sup>-</sup> react 100%, as a **limiting reagent** problem.

**Step 2:** Use the results of step 1 to re-solve the equilibrium.

To begin, let's learn about the **results of step 1**.



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## Step 1: HA + OH<sup>-</sup> limiting reagent reaction

There are three possible results of **step 1**.

“**Too little**” base: If fewer moles of OH<sup>-</sup> are added than the moles of acid present, then **only some** of the acid HA will be converted to conjugate base A<sup>-</sup>, consuming **all** of the added OH<sup>-</sup>.



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## Step 1: HA + OH<sup>-</sup> limiting reagent reaction

There are three possible results of **step 1**.

“**Just enough**” base: If the moles of OH<sup>-</sup> added is the same as the moles of acid present, then **all** of the acid HA will be converted to conjugate base A<sup>-</sup>, consuming **all** of the added OH<sup>-</sup>.



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## Step 1: HA + OH<sup>-</sup> limiting reagent reaction

There are three possible results of **step 1**.

“**Too much**” base: If the moles of OH<sup>-</sup> added is more than the moles of acid present, then **all** of the acid HA will be converted to conjugate base A<sup>-</sup> and **unused OH<sup>-</sup>** will be **left over**.



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[TP]  $V_b = 100.$  mL of  $c_b = 0.40$  M of  $\text{OH}^-$  is combined with  $V_a = 100.$  mL of  $c_a = 0.40$  M of HA. The result is ...

- 0% 1. "too little"  $\text{OH}^-$   
 0% 2. "just enough"  $\text{OH}^-$   
 0% 3. "too much"  $\text{OH}^-$   
 0% 4. Further information needed



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[Quiz]  $V_b = 100.$  mL of  $c_b = 0.20$  M of  $\text{OH}^-$  is combined with  $V_a = 100.$  mL of  $c_a = 0.40$  M of HA. The result is ...

- 0% 1. "too little"  $\text{OH}^-$   
 0% 2. "just enough"  $\text{OH}^-$   
 0% 3. "too much"  $\text{OH}^-$   
 0% 4. Further information needed



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### Add "some" $\text{OH}^-$ to an acid

There are two steps to find the new value of  $[\text{H}_3\text{O}^+]$ .

Step 1: Assume the acid HA and the added  $\text{OH}^-$  react 100%, as a **limiting reagent problem** (ignoring equilibrium!).

Step 2: Based on whether we have added "too little", "just enough", or "too much"  $\text{OH}^-$ , we use the results of step 1 to **re-calculate the equilibrium** concentration of  $[\text{H}_3\text{O}^+]$ .



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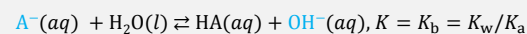
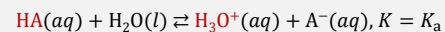
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### Step 2: $[\text{H}_3\text{O}^+]$ when "too little" base added

After "too little" base is added, there are present both some acid, HA, and its conjugate base,  $\text{A}^-$ .

This means there are **two possible ways the system can come to equilibrium**,



One will result in an **acidic solution**, and the other will result in a **basic solution**.

Which one to use?



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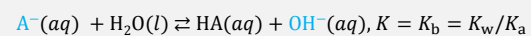
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## Step 2: $[\text{H}_3\text{O}^+]$ when “too little” base added

After “too little” base is added, there are present both some acid, HA, and its conjugate base,  $\text{A}^-$ .

This means there are **two possible ways the system can come to equilibrium**,



One will result in an **acidic solution**, and the other will result in a **basic solution**.

Use the one that has **the larger  $K$**  !



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