

### Lecture 16 CH131 Summer 1

Wednesday, June 19, 2019

- Pure strong acid
- Pure weak acid
- Partially neutralized weak acid.
- Exactly neutralized weak acid.
- Neutralized weak acid with excess base.
- Practice with titration.

Next lecture: Ch16: Solubility equilibria

Please bring laptop or tablet for online evaluation

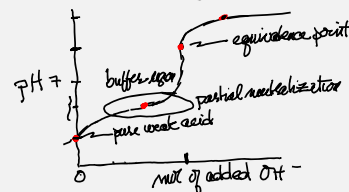


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### Solving acid and base equilibria

- Pure strong acid  $K_a \gg 1$   $HA(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + A^-(aq)$
- Pure weak acid  $K_a \ll 1$
- Partially neutralized weak acid  $HA(aq) + OH^-(aq) \rightarrow H_2O(l) + A^-(aq)$
- Exactly neutralized weak acid  $A^-(aq) + H_2O(l) \rightleftharpoons HA(aq) + OH^-(aq)$
- Neutralized weak acid with excess base



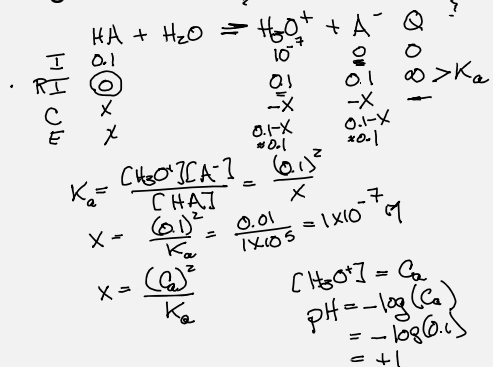
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### Pure strong acid

$C_a = 0.1$ ,  $25^\circ C$ ,  $K_a = 1 \times 10^5$



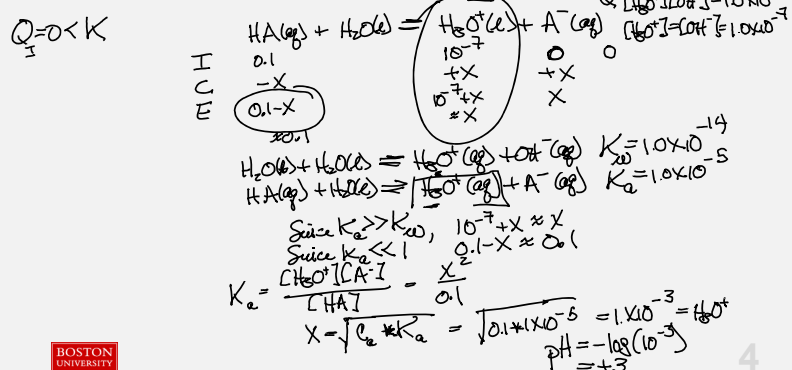
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### Pure weak acid

$C_a = 0.1 M$ ,  $K_a = 1 \times 10^{-5}$



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$c_a = 0.05M$ ,  $K_a = 3 \times 10^{-8}$ ,  $[H_3O^+]$

	HA	$H_3O^+$	$A^-$
I	0.05	$10^{-7}$	0
C	-x	+x	+x
E	0.05	x	x

$$K_a = \frac{x^2}{0.05} = 3 \times 10^{-8}$$

$$x = \sqrt{15 \times 10^{-10}}$$

$$= 3.9 \times 10^{-5}$$

pH = 4.41  
 yield =  $100\% \times \frac{3.9 \times 10^{-5}}{6 \times 10^{-2}} = 0.07\%$

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Dissolve 0.17 mole in 1 L, measure pH = 3.71.  
 What is  $K_a$  of the acid.

$$[H_3O^+] = 10^{-pH} = 10^{-3.71}$$

$$= \sqrt{c_a K_a} = 10^{-pH}$$

$$c_a K_a = 10^{-2 \times pH}$$

$$K_a = \frac{10^{-2 \times pH}}{c_a}$$

$$= \frac{10^{-2 \times 3.71}}{0.17} = 2.24 \times 10^{-7}$$

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### Weak acid $K_a$ values

We can get the numerical value of  $K_a$  by analyzing the acid equilibrium.

	HA(aq)	$H_3O^+(aq)$	$A^-(aq)$	Q
Initial	$c_a$	$10^{-7}$	0	0
Change	-x	+x	+x	
Equilibrium	$c_a - x$	$10^{-7} + x$	x	$K_a$
Approximate	$\approx c_a$	$\approx x$	x	$K_a$

With these simplifications, the acid equilibrium constant is ...

$$K_a = \frac{[H_3O^+][A^-]}{[HA]} = \frac{x^2}{c_a} = \frac{(10^{-pH})^2}{c_a}$$

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### Weak acid $K_a$ values

We can get the numerical value of  $K_a$  by analyzing the acid equilibrium.

	HA(aq)	$H_3O^+(aq)$	$A^-(aq)$	Q
Initial	$c_a$	$10^{-7}$	0	0
Change	-x	+x	+x	
Equilibrium	$c_a - x$	$10^{-7} + x$	x	$K_a$
Approximate	$\approx c_a$	$\approx x$	x	$K_a$

For example, if  $c_a = 0.10$  and pH = 4, then ...

$$K_a = \frac{(10^{-pH})^2}{c_a} = \frac{(10^{-4.0})^2}{0.10} = 1.0 \times 10^{-7}$$

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## Solving acid and base equilibria

- Pure strong acid
- Pure weak acid
- Partially neutralized weak acid
- Exactly neutralized weak acid
- Neutralized weak acid with excess base

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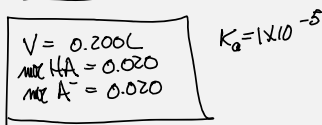
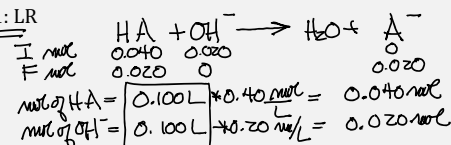
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Step 2:  $[\text{H}_3\text{O}^+]$  when “too little” base added

$V_b = 100$  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,  $K_a = 1.0 \times 10^{-5}$

Step 1: LR

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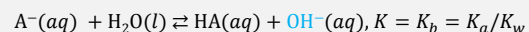
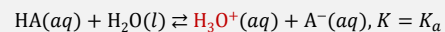
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Step 2:  $[\text{H}_3\text{O}^+]$  when “too little” base added

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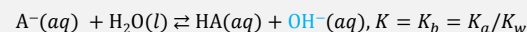
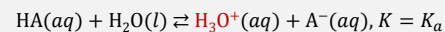
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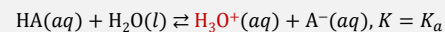
Step 2:  $[\text{H}_3\text{O}^+]$  when “too little” base added

After “too little” base is added there is present both some acid, HA, and its conjugate base,  $\text{A}^-$ . This means there are **two possible ways the system can come to equilibrium**,



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

Say  $K_a = 1.0 \times 10^{-5} \gg K_b = K_a/K_w = 10^{-14} / (1.0 \times 10^{-5}) = 1.0 \times 10^{-9}$ , use ...

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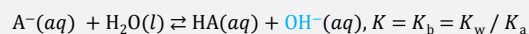
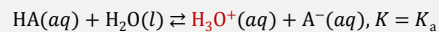
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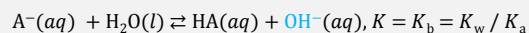
Step 2:  $[H_3O^+]$  when "too little" base added

After "too little" base is added there is present both some acid, HA, and its conjugate base,  $A^-$ . This means there are **two possible ways the system can come to equilibrium**,



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

Say  $K_a = 1.0 \times 10^{-9} \ll K_b = K_w / K_a = 10^{-14} / (1.0 \times 10^{-9}) = 1.0 \times 10^{-5}$ , use ...



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Step 2:  $[H_3O^+]$  when "too little" base added

$V_b = 110$  mL of  $c_b = 0.20$  M of  $OH^-$  is combined with  $V_a = 100$  mL of  $c_a = 0.40$  M of HA,  $K_a = 1.0 \times 10^{-5}$

Step 1:  $HA + OH^- \rightarrow H_2O + A^-$   $V = 0.210L$

I / mol	0.040 mol	0.020 mol	0	0
F / mol	0.018	0	0.022	0.022

Step 2:  $HA + H_2O \rightleftharpoons H_3O^+ + A^-$

I	0.018 M		$10^{-7}$	0.022 M
C	-x		+x	+x
E	$\approx 0.018 M$		x	$\approx 0.022 M$

$$K_a = \frac{x \cdot 0.022 M}{0.018 M} = 1.0 \times 10^{-5}$$

$$x = K_a \cdot \frac{0.018}{0.022} = 8.18 \times 10^{-6} \approx 8.2 \times 10^{-6}$$

$5.1$



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Step 2:  $[H_3O^+]$  when "too little" base added

$V_b = 100$  mL of  $c_b = 0.20$  M of  $OH^-$  is combined with  $V_a = 100$  mL of  $c_a = 0.40$  M of HA,  $K_a = 1.0 \times 10^{-5}$

	HA(aq)	$H_3O^+(aq)$	$A^-(aq)$	Q
Initial	0.10	$10^{-7}$	0.10	$10^{-7} < K_a$
Change	-x	+x	+x	
Equilibrium	$0.10 - x$	$10^{-7} + x$	$10^{-7} + x$	$1.0 \times 10^{-5}$
Approximate	$\approx 0.10$	$\approx x$	$\approx 0.10$	$1.0 \times 10^{-5}$

$$[H_3O^+] = x = \frac{K_a[HA]}{[A^-]} = \frac{1.0 \times 10^{-5} \times 0.10}{0.10} = 1.0 \times 10^{-5}$$



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## Solving acid and base equilibria

- Pure strong acid
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- **Exactly neutralized weak acid**
- Neutralized weak acid with excess base



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### Step 2: [H<sub>3</sub>O<sup>+</sup>] when "just enough" base added

V<sub>b</sub> = 100. mL of c<sub>b</sub> = 0.40 M of OH<sup>-</sup> is combined with V<sub>a</sub> = 100. mL of c<sub>a</sub> = 0.40 M of HA, K<sub>a</sub> = 1.0 × 10<sup>-6</sup> and K<sub>b</sub> = K<sub>w</sub> / K<sub>a</sub> = 1.0 × 10<sup>-8</sup>

Step 1: I notes HA + OH<sup>-</sup> → H<sub>2</sub>O + A<sup>-</sup> [A<sup>-</sup>] = 0.040 mol / 0.200 L = 0.200 mol/L  
 F notes 0 0

Step 2: A<sup>-</sup>(aq) + H<sub>2</sub>O(l) ⇌ HA(aq) + OH<sup>-</sup>(aq) K<sub>b</sub> = K<sub>w</sub> / K<sub>a</sub>

H<sub>2</sub>O(l) + H<sub>2</sub>O(l) ⇌ H<sub>3</sub>O<sup>+</sup>(aq) + OH<sup>-</sup>(aq) K<sub>w</sub>  
 H<sub>3</sub>O<sup>+</sup>(aq) + A<sup>-</sup>(aq) ⇌ HA(aq) + H<sub>2</sub>O(l) 1/K<sub>a</sub>

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### Step 2: [H<sub>3</sub>O<sup>+</sup>] when "just enough" base added

V<sub>b</sub> = 100. mL of c<sub>b</sub> = 0.40 M of OH<sup>-</sup> is combined with V<sub>a</sub> = 100. mL of c<sub>a</sub> = 0.40 M of HA, K<sub>a</sub> = 1.0 × 10<sup>-6</sup> and K<sub>b</sub> = K<sub>w</sub> / K<sub>a</sub> = 1.0 × 10<sup>-8</sup>

	A <sup>-</sup> (aq)	HA(aq)	OH <sup>-</sup> (aq)	Q
Initial	0.20	0	10 <sup>-7</sup>	0
Change	-x	+x	+x	
Equilibrium	0.20 - x	x	10 <sup>-7</sup> + x	1.0 × 10 <sup>-8</sup>
Approximate	≈ 0.20	x	≈ x	1.0 × 10 <sup>-8</sup>

[OH<sup>-</sup>] = x = (K<sub>b</sub> × [A<sup>-</sup>])<sup>1/2</sup> = (1.0 × 10<sup>-8</sup> × 0.20)<sup>1/2</sup> = 4.5 × 10<sup>-5</sup>

[H<sub>3</sub>O<sup>+</sup>] = K<sub>w</sub> / [OH<sup>-</sup>] = (1.0 × 10<sup>-14</sup>) / (4.5 × 10<sup>-5</sup>) = 2.2 × 10<sup>-10</sup>

pH = -log(2.2 × 10<sup>-10</sup>) = 9.66

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### Solving acid and base equilibria

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### Step 2: [H<sub>3</sub>O<sup>+</sup>] when "too much" base added

V<sub>b</sub> = 200. mL of c<sub>b</sub> = 0.30 M of OH<sup>-</sup> is combined with V<sub>a</sub> = 200. mL of c<sub>a</sub> = 0.20 M of HA, K<sub>a</sub> = 1.0 × 10<sup>-6</sup> and K<sub>b</sub> = 1.0 × 10<sup>-8</sup>

Step 1: I mol HA + OH<sup>-</sup> → H<sub>2</sub>O + A<sup>-</sup> V = 0.400 L  
 F mol 0.040 0.060 0

Step 2: I mol A<sup>-</sup> + H<sub>2</sub>O ⇌ HA + OH<sup>-</sup> K<sub>b</sub> = K<sub>w</sub> / K<sub>a</sub> = 1.0 × 10<sup>-8</sup>  
 F mol 0.040 0 0.020 / 0.400

C -x +x  
 E ≈ 0.040 / 0.400 x

[OH<sup>-</sup>] = 0.020 / 0.400  
 [H<sub>3</sub>O<sup>+</sup>] = 1.0 × 10<sup>-14</sup> / (0.020 / 0.400) = 2.0 × 10<sup>-13</sup>  
 pH = 12.7

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

$V_b = 200.$  mL of  $c_b = 0.30$  M of  $\text{OH}^-$  is combined with  $V_a = 200.$  mL of  $c_a = 0.20$  M of HA,  $K_a = 1.0 \times 10^{-6}$  and  $K_b = 1.0 \times 10^{-8}$

	$\text{A}^- (\text{aq})$	$\text{HA} (\text{aq})$	$\text{OH}^- (\text{aq})$	$Q$
Initial	0.10	0	0.050	0
Change	$-x$	$+x$	$+x$	
Equilibrium	$0.10 - x$	$x$	$0.050 + x$	$1.0 \times 10^{-8}$
Approximate	$\approx 0.10$	$x$	$\approx 0.050$	$1.0 \times 10^{-8}$

$[\text{OH}^-] = 0.050$  (easy!)

$[\text{H}_3\text{O}^+] = K_w / [\text{OH}^-] = (1.0 \times 10^{-14}) / (0.050) = 2.0 \times 10^{-13}$

$[\text{HA}] = x = K_b [\text{A}^-] / [\text{OH}^-] = 1.0 \times 10^{-8} \times 0.10 / 0.050 = 2.0 \times 10^{-8}$  (tiny!)

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### Solving acid and base equilibria

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### Practice with titration: Pure weak acid

0.200 L of 0.100 M HA,  $K_a = 1.0 \times 10^{-4}$  at 25 °C:  $[\text{H}_3\text{O}^+] = 3.2 \times 10^{-3}$

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### Practice with titration: “Too little” $\text{OH}^-$

→ 0.200 L of 0.100 M HA,  $K_a = 1.0 \times 10^{-4}$  at 25 °C and 0.100 L of 0.050 M NaOH solution:  $[\text{H}_3\text{O}^+] = 3.0 \times 10^{-4}$

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### Practice with titration: “Just enough” OH<sup>-</sup>

0.200 L of 0.100 M HA,  $K_a = 1.0 \times 10^{-4}$  at 25 °C

and 0.400 L of 0.050 M NaOH solution:  $[H_3O^+] = 5.5 \times 10^{-9}$



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### Practice with titration: “Too much” OH<sup>-</sup>

0.200 L of 0.100 M HA,  $K_a = 1.0 \times 10^{-4}$  at 25 °C

and 0.500 L of 0.050 M NaOH solution:  $[H_3O^+] = 1.4 \times 10^{-12}$



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