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[TP] The pH of pure water is **different at different temperatures**. This means that as temperature changes ...

- 0% 1. the relative amounts of $\text{H}_3\text{O}^+(\text{aq})$ and $\text{OH}^-(\text{aq})$ in pure water change
- 0% 2. water become more acidic
- 0% 3. water becomes more basic
- 100% 4. None of the above
- 0% 5. Not sure

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Lecture 16 CH131 Summer 1 2021
Thursday, June 24, 2021

- Complete: The pH of water
- **Class evaluation**
- Weak acids and strong acids
- Titration: Reaction of weak acid with strong base
- **Next lecture: Begin ch17:** Electron transfer reactions and electrochemistry.

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What is an acid?

An acid makes $[\text{H}_3\text{O}^+] > [\text{OH}^-]$.

An **acid HA** reacts with water as

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

Since K_w is fixed (at a given temperature), the **increase in $[\text{H}_3\text{O}^+]$** means there is a **decrease in pH** and a corresponding **decrease in $[\text{OH}^-]$** .

$$\text{H}_2\text{O}(\text{l}) + \text{H}_2\text{O}(\text{l}) \rightleftharpoons \text{H}_3\text{O}^+(\text{aq}) + \text{OH}^-(\text{aq}) \quad K = K_w = [\text{H}_3\text{O}^+][\text{OH}^-]$$

$$K_w / [\text{H}_3\text{O}^+] = [\text{OH}^-]$$

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What is a base?

A base makes $[\text{H}_3\text{O}^+] < [\text{OH}^-]$.

A **base B** reacts with water as

$$\text{B}(\text{aq}) + \text{H}_2\text{O}(\text{l}) \rightleftharpoons \text{BH}^+(\text{aq}) + \text{OH}^-(\text{aq})$$

Since K_w is fixed (at a given temperature), the **increase in $[\text{OH}^-]$** means there is a corresponding **decrease in $[\text{H}_3\text{O}^+]$** and so **increase in pH**.

$$[\text{H}_3\text{O}^+] = \frac{K_w}{[\text{OH}^-]}$$

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What is a base?

Hydroxides, when dissolved in water, also make $[H_3O^+] < [OH^-]$.

For example,

$$NaOH(s) \rightarrow Na^+(aq) + OH^-(aq)$$

Since K_w is fixed (at a given temperature), the **increase in $[OH^-]$** means there is a corresponding **decrease in $[H_3O^+]$** and so **increase in pH**.

$$\begin{cases} B(aq) + H_2O(l) \rightleftharpoons BH^+(aq) + OH^-(aq) \\ HA(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + A^-(aq) \end{cases}$$

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[TP] The pH of pure water is **different at different temperatures**. This means that as temperature changes ...

/// 0% 1. ~~the relative amounts of $H_3O^+(aq)$ and $OH^-(aq)$ in pure water change~~
 0% 2. ~~water become more acidic~~
 0% 3. ~~water becomes more basic~~
 100% 4. None of the above
 0% 5. Not sure

50°C $[H_3O^+] = 10^{-6.63}$
 $pH = 6.63$
 $H_2O(l) + H_2O(l) \rightleftharpoons H_3O^+(aq) + OH^-(aq)$
 $[H_3O^+] = [OH^-]$

Acidic = "pH < 7"
 Basic = "pH > 7"
 True only at 25°C for which $K_w = 1.00 \times 10^{-14}$
 $[H_3O^+] = [OH^-] = 1.00 \times 10^{-7}$ 780610

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Online course evaluation

- bu.campuslabs.com/courseeval of lecture and discussion
- Use BU login and Kerberos password
- Anonymous and seen by instructors only after grades submitted
- Comments in text fields **especially valued and encouraged**.
- Please try to answer all questions
- When done, please close your browser

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Strong acids

$$HA(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + A^-(aq)$$

A **strong acid** reacts with water,
 $HA(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + A^-(aq)$,
 with essentially **100% yield**. //

$$K = K_a = \frac{[H_3O^+][A^-]}{[HA]}$$

$K_a \gg 1$
 $K_a = 1 \times 10^5$

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Strong acids //

This means its equilibrium constant,
 $K_a = \frac{[H_3O^+][A^-]}{[HA]} \gg 1$

Assume 25°C
 $K_w = 1.00 \times 10^{-14}$
 $[H_3O^+] = [OH^-] = 1.00 \times 10^{-7}$

and that $[H_3O^+]$ is the same as the molarity of the strong acid solution.
 For example, $c_0 = 0.10 M$, $K_a = 1.0 \times 10^5$, $[H_3O^+] = 0.1 M$.

	HA(aq)	H ₃ O ⁺ (aq)	A ⁻
I	0.10	1.00 × 10 ⁻⁷	0
C	-x	+x	+x
E	0.10 - x ≈ 0	1.00 × 10 ⁻⁷ + x ≈ 0.10	x 0.10

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Weak acids

A weak acid reacts with water,
 $HA(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + A^-(aq)$,
 with yield much less than 100%.

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Weak acids

This means its equilibrium constant,
 $K_a = \frac{[H_3O^+][A^-]}{[HA]} \ll 1$

and therefore that $[H_3O^+]$ must be determined by solving the ICE table.

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Weak acids

25°C
 For example, at 25°C, $c_0 = 0.1 M$, $K_a = 1 \times 10^{-5}$, $[H_3O^+] = 0.001 M$.

	HA(aq)	H ₃ O ⁺ (aq)	A ⁻ (aq)
I	0.1	1.00 × 10 ⁻⁷	0
C	-x	+x	+x
E	0.1 - x ≈ 0.1	1.00 × 10 ⁻⁷ + x x	x

Because $K_a \ll 1$, hardly any reacts, so $0.1 - x \approx 0.1$
 Because $K_a \gg K_w$, x is big compare to 1.00×10^{-7}

$K_w = 1.00 \times 10^{-14}$: $H_2O(l) + H_2O(l) \rightleftharpoons H_3O^+(aq) + OH^-(aq)$
 $K_a = 1.00 \times 10^{-5}$: $HA(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + A^-(aq)$

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	HA	H ₃ O ⁺	A ⁻	
I	0.1	1.00 × 10 ⁻⁷	0	
C	-x	+x	+x	
E	0.1 - x ≈ 0.1	1.00 × 10 ⁻⁷ + x ≈ x	x	

$K_a = 1 \times 10^{-5}$

$$K_a = \frac{[H_3O^+][A^-]}{[HA]} = \frac{(1.00 \times 10^{-7} + x)(x)}{(0.1 - x)} \approx \frac{x^2}{0.1}$$

$$x = \sqrt{0.1 \times K_a} = \sqrt{0.1 \times 10^{-5}} = 1 \times 10^{-3}$$

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"Titrating" a weak acid

An important problem is determining [H₃O⁺] as a result of adding strong base to a weak acid.

There are **two steps**.

First, let the added base react with the acid present 100% as a limiting reagent problem.

Then, use the ICE table to solve the weak acid equilibrium.

③ Add just enough OH⁻ what is [H₃O⁺]
what is [H₂O⁺]
④ Add too much OH⁻ what is [H₃O⁺]
? [H₃O⁺] is 100% equivalence point
No post-equivalence.

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"Titrating" a weak acid: Incomplete neutralization

$V_b = 100. \text{ mL}$ of $c_b = 0.20 \text{ M}$ of OH⁻ is combined with $V_a = 100. \text{ mL}$ of $c_a = 0.40 \text{ M}$ of HA, $K_a = 1.0 \times 10^{-5}$ at 25°C.

① LR: OH⁻ + HA → H₂O + A⁻ $K_a \gg K_b$

I	0.020	0.040	0
F	0	0.020	0

② ICE: HA + H₂O ⇌ H₃O⁺ + A⁻

I	0.020	1.00 × 10 ⁻⁷	0.020
C	-x	+x	+x
E	0.010 - x ≈ 0.010	1.00 × 10 ⁻⁷ + x ≈ x	0.010 + x

$$K_a = \frac{(1.00 \times 10^{-7} + x)(0.010 + x)}{(0.010 - x)} = \frac{x \times 0.010}{0.010} = x$$

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"Titrating" a weak acid: Incomplete neutralization

$V_b = 100. \text{ mL}$ of $c_b = 0.20 \text{ M}$ of OH⁻ is combined with $V_a = 100. \text{ mL}$ of $c_a = 0.40 \text{ M}$ of HA, $K_a = 1.0 \times 10^{-5}$ at 25°C.

	HA(aq)	H ₃ O ⁺ (aq)	A ⁻ (aq)	Q
Initial	0.10	10 ⁻⁷	0.10	10 ⁻⁷ < K _a
Change				
Equilibrium				
Approximate				

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"Titrating" a weak acid: Incomplete neutralization

$V_b = 100. \text{ mL}$ of $c_b = 0.20 \text{ M}$ of OH^- is combined with $V_a = 100. \text{ mL}$ of $c_a = 0.40 \text{ M}$ of HA , $K_a = 1.0 \times 10^{-5}$ at 25°C .

	$\text{HA}(aq)$	$\text{H}_3\text{O}^+(aq)$	$\text{A}^-(aq)$	Q
Initial	0.10	10^{-7}	0.10	$10^{-7} < K_a$
Change	$-x$	$+x$	$+x$	
Equilibrium	$0.10 - x$	$10^{-7} + x$	$0.10 + x$	1.0×10^{-5}
Approximate	≈ 0.10	$\approx x$	≈ 0.10	1.0×10^{-5}

$[\text{H}_3\text{O}^+] = x = \frac{K_a[\text{HA}]}{[\text{A}^-]} = \frac{1.0 \times 10^{-5} \times 0.10}{0.10} = 1.0 \times 10^{-5} //$

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"Titrating" a weak acid: Neutralization / equivalence - //

$V_b = 100. \text{ mL}$ of $c_b = 0.40 \text{ M}$ of OH^- is combined with $V_a = 100. \text{ mL}$ of $c_a = 0.40 \text{ M}$ of HA , $K_a = 1.0 \times 10^{-6}$ and $K_b = K_w / K_a = 1.0 \times 10^{-8}$ at 25°C //

① LR: $\text{OH}^- + \text{HA} \xrightarrow{100\%} \text{H}_2\text{O} + \text{A}^-$
 // I 0.040 0.040
 F 0 0.040

② ICE: $\text{A}^-(aq) + \text{H}_2\text{O}(l) \rightleftharpoons \text{HA}(aq) + \text{OH}^-(aq)$ $K_b = \frac{K_w}{K_a}$
 I 0.040 0.200
 C $-x$ $+x$ $+x$
 E $0.040 - x$ $0.200 + x$ $0.040 + x$

1) $\text{A}^- + \text{H}_2\text{O} \rightleftharpoons \text{HA} + \text{H}_2\text{O}$ $K = 1/K_a$
 2) $\text{H}_2\text{O} + \text{H}_2\text{O} \rightleftharpoons \text{H}_3\text{O}^+ + \text{OH}^-$ $K_2 = K_w$

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"Titrating" a weak acid: Neutralization

$V_b = 100. \text{ mL}$ of $c_b = 0.40 \text{ M}$ of OH^- is combined with $V_a = 100. \text{ mL}$ of $c_a = 0.40 \text{ M}$ of HA , $K_a = 1.0 \times 10^{-6}$ and $K_b = K_w / K_a = 1.0 \times 10^{-8}$ at 25°C .

	$\text{A}^-(aq)$	$\text{HA}(aq)$	$\text{OH}^-(aq)$	Q
Initial	0.040/0.200	0	1.0×10^{-7}	0
Change	$-x$	$+x$	$+x$	
Equilibrium	$0.20 - x$	x	$1.0 \times 10^{-7} + x$	
Approximate	≈ 0.20	x	x	

$K_b = 1.0 \times 10^{-8} = \frac{[\text{HA}][\text{OH}^-]}{[\text{A}^-]} = \frac{x^2}{0.20}$
 $x = \sqrt{0.20 \times 1.0 \times 10^{-8}} = 1.4 \times 10^{-5}$

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"Titrating" a weak acid: Neutralization

$V_b = 100. \text{ mL}$ of $c_b = 0.40 \text{ M}$ of OH^- is combined with $V_a = 100. \text{ mL}$ of $c_a = 0.40 \text{ M}$ of HA , $K_a = 1.0 \times 10^{-6}$ and $K_b = K_w / K_a = 1.0 \times 10^{-8}$ at 25°C .

	$\text{A}^-(aq)$	$\text{HA}(aq)$	$\text{OH}^-(aq)$	Q
Initial	0.20	0	10^{-7}	0
Change	$-x$	$+x$	$+x$	
Equilibrium	$0.20 - x$	x	$10^{-7} + x$	1.0×10^{-8}
Approximate	≈ 0.20	x	$\approx x$	1.0×10^{-8}

$[\text{OH}^-] = x = (K_b \times [\text{A}^-])^{1/2} = (1.0 \times 10^{-8} \times 0.20)^{1/2} = 4.5 \times 10^{-5}$
 $[\text{H}_3\text{O}^+] = K_w / [\text{OH}^-] = (1.0 \times 10^{-14}) / (4.5 \times 10^{-5}) = 2.2 \times 10^{-10}$

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“Titrating” a weak acid: Excess base // Too much OH^-

$V_b = 200.$ mL of $c_b = 0.30$ M of OH^- is combined with $V_a = 200.$ mL of $c_a = 0.20$ M of HA, $K_a = 1.0 \times 10^{-6}$ and $K_b = 1.0 \times 10^{-8}$ at 25°C .

① LR: $\text{OH}^- + \text{HA} \xrightarrow{100\%} \text{H}_2\text{O} + \text{A}^-$

I	0.060	0.040		0
F	0.020			0.040

② ICE: $\text{A}^- + \text{H}_2\text{O} \rightleftharpoons \text{HA} + \text{OH}^-$

I	0.040	0	0.020	0.100
C	-x	+x	+x	
E	0.10-x	x	0.050+x	
	≈ 0.10		≈ 0.050	

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“Titrating” a weak acid: Excess base

$V_b = 200.$ mL of $c_b = 0.30$ M of OH^- is combined with $V_a = 200.$ mL of $c_a = 0.20$ M of HA, $K_a = 1.0 \times 10^{-6}$ and $K_b = 1.0 \times 10^{-8}$ at 25°C .

	$\text{A}^- (\text{aq})$	$\text{HA} (\text{aq})$	$\text{OH}^- (\text{aq})$	Q
Initial	0.040	0	0.020	0
Change	-x	+x	+x	
Equilibrium	0.040-x	x	0.020+x	
Approximate	≈ 0.040		≈ 0.020	

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“Titrating” a weak acid: Excess base

$V_b = 200.$ mL of $c_b = 0.30$ M of OH^- is combined with $V_a = 200.$ mL of $c_a = 0.20$ M of HA, $K_a = 1.0 \times 10^{-6}$ and $K_b = 1.0 \times 10^{-8}$ at 25°C .

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