Chapter 14

Principles of Neutralization Titrations

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Standard Solutions

- The standard reagents used in acid/base titrations are ALWAYS strong acids or bases: HCl, HClO₄, H₂SO₄, NaOH and KOH.
- Standard acids are prepared by diluting of concentrated acids.
- HNO₃ is not used as a standard acid.
- Weak acids and bases are NEVER used as standard reagents—they react incompletely with analytes.

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Acid-Base Indicators

HIn(aq) $H^+(aq)+In^-(aq)$ (acid color) (base color) (base color)

$$K_a = \frac{\lfloor H^+ \rfloor \lfloor In^- \rfloor}{\lfloor HIn \rfloor} \Longrightarrow \frac{K_a}{\lfloor H^+ \rfloor} = \frac{\lfloor In^- \rfloor}{\lfloor HIn \rfloor}$$

Add a few drops of the phenolphthalein indicator to a acidic solution (pH = 1):

 $\frac{K_a}{[H^+]} = \frac{1 \times 10^{-8}}{1 \times 10^{-1}} = \frac{[In^-]}{[HIn]} = \frac{1}{10,000,000}$

The ratio shows that the predominant form of the indicator is HIn, resulting in an acid color solution.





HIn(aq) \longrightarrow H⁺(aq)+In⁻(aq) (acid color) (base color)

As OH⁻ is added to this solution, [H⁺] decreases and the equilibrium shift to right, changing HIn to In⁻. A color change from colorless or slightly red to reddish purple will occur.

For most indicators, **about 1/10 of the initial form must be converted to the other form** before a new color is apparent.

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Indicator pH Range: $pK_a \pm 1$

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

For a acid solution

$$pH = pK_a + \log\left(\frac{1}{10}\right) = pK_a - 1$$

For a basic solution

$$pH = pK_a + \log\left(\frac{10}{1}\right) = pK_a + 1$$





TABLE 14-1 Some Important Acid/Base Indicators Common Name Transition Range, pH Color Change[†] Indicator Type‡ pKa* 1.2 - 2.8Thymol blue 1.658 R-Y 8.0-9.6 8.96§ Y–B Methyl yellow 2.9-4.0 R-Y 2 Methyl orange 3.1-4.4 3.46§ R–O 2 3.8 - 5.4Y-B Bromocresol green 4.668 1 Methyl red 4.2-6.3 5.00§ R-Y 2 Bromocresol purple 5.2-6.8 6.12§ Y–P Bromothymol blue 6.2-7.6 7.10§ Y-B Phenol red 6.8-8.4 7.81§ Y-R Cresol purple 7.6-9.2 Y-P Phenolphthalein 8.3-10.0 C-R Thymolphthalein 9.3-10.5 C–B Alizarin yellow GG 10-12 C-Y 2

*At ionic strength of 0.1.

The blue; C = colorless; O = orange; P = purple; R = red; Y = yellow. (1) Acid type: HIn + 420 \rightleftharpoons H₃O⁺ + In⁻; (2) Base type: In + H₂O \rightleftharpoons InH⁺ + OH⁻. §For the reaction InH⁺ + H₂O \rightleftharpoons H₃O⁺ + In.

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Titration Errors with Acid-Base Indicators

• Systematic (determinate) Errors: Difference between the color change of indicator and the equivalence point.

--blank titration correction

• Personal (Indeterminate) Errors: Uncertainty of color change (± 0.5 to ± 1 pH; best ± 0.1 pH), Insensitivity of eyes to color change. Colorless \rightarrow Red/Red \rightarrow colorless? --use reference color solution

Titrations and pH Curves

- The equivalence point is defined by stoichiometry, not by the pH.
- The pH value at equivalence point is affected by the acid strength or base strength.
- The strength of a weak acid or weak base have significantly effect on the shape of pH curves.

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Determine the Equivalence Point of an Acid-Base Titration

- Use a pH meter to monitor the pH and then plot a titration curve.
- Use an acid-base indicator, which marks the endpoint of a titration by changing color.

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Titration of Strong Acids and Strong Bases

- HCl + NaOH \Leftrightarrow NaCl + H₂O HCl \rightarrow H⁺ + Cl⁻
 - NaOH → Na⁺ + OH⁻

 $H_2O \Leftrightarrow H^+ + OH^-$

- In HCI: [H⁺] = *c*_{HCI} + [OH⁻] ≈ *c*_{HCI}
- In NaOH: [OH⁻] = c_{NaOH} + [H⁺] $\approx c_{\text{NaOH}}$
- Equivalent point: pH = 7

Titrating a Strong Acid with a Strong Base

- Ex. 14-1 Generate the hypothetical titration curve for the titration of 50 mL of 0.0500 M HCl with 0.1000 M NaOH.
- How many mL of 0.1000 M NaOH are needed to complete the reaction? (to reach the equivalent point?

 $(C_1V_1)_{HCI} = (C_2V_2)_{NaOH}$ V₂ = (0.0500x50)/0.1000 = 25 mL, pH = 7.0

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Calculating pH During a SA-SB Titration
Initial pH: For a strong acid, which is completely dissociated, pH = -log [H₃O⁺].

- **pH before the equivalence point:** Subtract the number of moles of H₃O⁺ reacted from the concentration originally present; divide by the total volume to obtain [H₃O⁺]; determine pH.
- **pH at the equivalence point:** The solution contains only Na⁺, Cl⁻, and H₂O, and is therefore neutral, so $[H_3O^+] = 1.0 \times 10^{-7}$; pH = 7.00.
- **pH after the equivalence point:** Subtract the number of moles of H₃O⁺ reacted from the total number of moles of OH⁻ added to obtain the number of moles of OH⁻ in excess; divide by the total volume to obtain [OH⁻]; determine pOH and pH.

Initial Point	
Before any base is	added, the solution is 0.0500 M in H_3O^+ , and
1	$pH = -\log[H_3O^+] = -\log 0.0500 = 1.30$
After Addition of The hydronium ion the base and dilution	¹ 10.00 mL of Reagent n concentration is decreased as a result of both reaction with on. So the analytical concentration of HCl is
	no. mmol HCl remaining after addition of NaOH
$c_{\rm HCl} =$	total volume soln
	original no. mmol HCl - no. mmol NaOH added
=	total volume soln
	$(50.00 \text{ mL} \times 0.0500 \text{ M}) - (10.00 \text{ mL} \times 0.1000 \text{ M})$
	50.00 mL + 10.00 mL
	$(2.500 \text{ mmol} - 1.000 \text{ mmol}) = 2.500 \times 10^{-2} \text{ M}$
-	60.00 mL
	$[H_3O^+] = 2.500 \times 10^{-2} M$
and	$pH = -\log[H_3O^+] = -\log(2.500 \times 10^{-2}) = 1.60$



At the equival- centrations of equality into the	ence point, neither HCl nor NaOH is in excess, and so the con hydronium and hydroxide ions must be equal. Substituting thi the ion-product constant for water yields
[H	$[0^+] = \sqrt{K_{\rm w}} = \sqrt{1.00 \times 10^{-14}} = 1.00 \times 10^{-7} \mathrm{M}$
	$pH = -\log(1.00 \times 10^{-7}) = 7.00$
After Addition	n of 25.10 mL of Reagent ow contains an excess of NaOH, and we can write
After Addition	n of 25.10 mL of Reagent ow contains an excess of NaOH, and we can write no. mmol NaOH added – original no. mmol HCI
After Addition The solution no C _{NaOH}	n of 25.10 mL of Reagent w contains an excess of NaOH, and we can write $= \frac{\text{no. mmol NaOH added - original no. mmol HCI}}{\text{total volume soln}}$ $= 1000000000000000000000000000000000000$
After Addition The solution n C _{NaOH}	$= \frac{\text{no. mmol NaOH added} - \text{original no. mmol HCl}}{\frac{\text{total volume soln}}{25.10 \times 0.100 - 50.00 \times 0.0500}} = 1.33 \times 10^{-4} \text{ M}$
After Addition The solution n c_{NaOH} and the equilib	$= \frac{\text{no. mmol NaOH added - original no. mmol HCl}}{\frac{\text{no. mmol NaOH added - original no. mmol HCl}}{\frac{\text{total volume soln}}{1}} = \frac{25.10 \times 0.100 - 50.00 \times 0.0500}{75.10} = 1.33 \times 10^{-4} \text{ M}}$ rium concentration of hydroxide ion is
After Addition The solution n C_{NaOH} and the equilib	$= \frac{\text{no. mmol NaOH added - original no. mmol HCl}}{\text{total volume soln}}$ $= \frac{25.10 \times 0.100 - 50.00 \times 0.0500}{75.10} = 1.33 \times 10^{-4} \text{ M}$ rium concentration of hydroxide ion is
After Addition The solution n C_{NaOH} and the equilib	$r of 25.10 \text{ mL of Reagent}$ $= \frac{\text{no. mmol NaOH added - original no. mmol HCl}}{\text{total volume soln}}$ $= \frac{25.10 \times 0.100 - 50.00 \times 0.0500}{75.10} = 1.33 \times 10^{-4} \text{ M}$ $[OH^-] = c_{\text{NaOH}} = 1.33 \times 10^{-4} \text{ M}$

	pH = 14.00 - 3.88 = 10.12			
Changes in pH during the Titration of a Strong Acid with a Strong Base				
	рН			
Volume of NaOH, mL	50.00 mL of 0.0500 M HCl with 0.100 M NaOH	50.00 mL of 0.000500 M HC with 0.00100 M NaOH		
0.00	1.30	3.30		
10.00	1.60	3.60		
20.00	2.15	4.15		
24.00	2.87	4.87		
24.90	3.87	5.87		
25.00	7.00	7.00		
25.10	10.12	8.12		
26.00	11.12	9.12		
30.00	11.80	9.80		

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What is the solution pH after addition of 40.00 and 50.00 mL of 0.1000 M NaOH into 50 mL of 0.05000 M HCI?

When 40.00 mL of NaOH added: [OH⁻] = (0.1000x40.00 - 0.05000x50)/(40 + 50) = 0.0166 M pOH = -log[OH⁻] = 1.78, pH = 14 - pOH = 12.22

When 50.00 mL of NaOH added: [OH⁻] = (0.1000x50.00 – 0.05000x50)/(50 + 50) = 0.025 M pOH = -log[OH⁻] = 1.60, pH = 14 – pOH = 12. 40











From charge-balance equation to simplified calculation $CBE: [H_{3}O^{+}] + [Na^{+}] = [OH^{-}] + [CI^{-}]$ (1) Before quivalence point, $[OH^{-}] \ll [CI^{-}]$, so $[H_{3}O^{+}] \approx [CI^{-}] - [Na^{+}]$ $[H_{3}O^{+}] = \frac{V_{HC}C_{HCI}}{V_{NaOH} + V_{HCI}} - \frac{V_{MaOH}C_{MaOH}}{V_{NaOH} + V_{HCI}} = \frac{V_{HCI}C_{HCI} - V_{MaOH}C_{MaOH}}{V_{MaOH} + V_{HCI}}$ (2) At the equivalence point, $[CI^{-}] = [Na^{+}], [H_{3}O^{+}] = [OH^{-}]$ $[H_{3}O^{+}] = \sqrt{K_{w}}$ (3) Beyond the equivalence point, $[H_{3}O^{+}] \ll [Na^{+}]$ $[OH^{-}] \approx [Na^{+}] - [CI^{-}]$ $[OH^{-}] = \frac{V_{NaOH}C_{MaOH}}{V_{NaOH} + V_{HCI}} - \frac{V_{HCI}C_{HCI}}{V_{NaOH} + V_{HCI}} = \frac{V_{MaOH}C_{NaOH} - V_{HCI}C_{HCI}}{V_{NaOH} + V_{HCI}}$









Titrations of Weak Acid with

Strong Bases In weak acid - strong base titrations (or weak base - strong acid) the pH before and at the equivalence point depends on the acid (base) concentrations and

 $K_a (K_b)$.

 $\Delta pH/\Delta vol$ at the equivalence points of weak acid (base) – strong base (acid) are smaller than for strong acid – strong base titrations.





added and will have reacted with the same number of moles of acid. ∴ moles acid remaining = {(M_a x V_o)/1000 - (M_b x V_t)/1000} in (V_o + V_t) mL. & moles of acetate produced = (M_b x V_t)/1000 also in (V_o + V_t) mL.

Thus the solution will contain both acetic acid and its conjugate base acetate, that is a buffer will have been created with $\{(M_a \; x \; V_o)/1000 - (M_b \; x \; V_l)/1000\} \text{ moles of acetic acid and}$

 $(M_b \times V_t)/1000$ moles of acetate both in $(V_o + V_t)$ mL of solution.

$$\begin{split} & \text{Moles CH}_3\text{COOH in } (V_o + V_l) \text{ mL} = \{(M_a \times V_o)/1000 - (M_b \times V_l)/1000\} \\ & \therefore \text{ [CH}_3\text{COOH]} = \{(M_a \times V_o)/1000 - (M_b \times V_l)/1000\}/(V_o + V_l) \times 1000 \\ & = \{(M_a \times V_o) - (M_b \times V_l)/(V_o + V_l) \text{ mol/L}, \text{ & similarly} \\ \text{ [CH}_3\text{COO]} = (M_b \times V_l)/(V_o + V_l) \text{ mol/L}. \end{split}$$

























Chapter 14 Summary

- Using standard solutions
- Uses and properties of acid-base indicators
- Various types of acid-base titrations of strong and weak acids and bases
- The effect of reagent concentration on the shapes of titration curves
- Calculation and construction of titration curves
- Effect of equilibrium constants on the shapes of titration curves
- Using derivative plots to determine equivalence points

Indicator pH range: pK_a +/- 1

<mark>рК_w</mark> = pH + pOH