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Topic 8.5: Acid-Base Titrations

Revision Notes · AP Chemistry

UNIT 8 · ACIDS AND BASES

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The Setup: Analyte, Titrant, and Two Points That Differ

A titration adds a solution of known concentration, the titrant, from a burette into a measured volume of the analyte, while the pH is recorded. Plotting pH against volume added gives the titration curve, which is most of this topic.

The equivalence point is the stoichiometric moment: the moles of titrant added are exactly what the balanced equation demands. For HCl + NaOH the ratio is 1:1; for a diprotic acid neutralized completely it is 2:1.

The endpoint is the volume at which the indicator actually changes color: an experimental signal, not a stoichiometric fact. A well run titration places it within a drop of the equivalence point.

Four Regions, One Rule: Moles First

Every curve divides into the same four regions: the analyte alone before any titrant is added; leftover analyte beside product before equivalence; a steep swing around equivalence, where the analyte runs out; and excess titrant past equivalence, setting the pH.

Strong Acid with Strong Base

The analyte is fully ionized from the start, so 0.100 mol L^{-1} HCl opens at pH 1.00. As NaOH is added, H_3O^+ is consumed mole for mole; before equivalence the pH comes from the leftover H_3O^+ over the total volume.

At equivalence nothing remains but Na^+, Cl^- and water: neither ion reacts with water, the salt is neutral, and the pH is 7.00 at 25 °C. Past equivalence, excess OH^- over the total volume sets the pH.

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The steep section: titrating 25.0 mL of 0.100 mol L^{-1} HCl, the pH is 3.70 after 24.9 mL of 0.100 mol L^{-1} NaOH and 10.30 after 25.1 mL, a swing of more than six units for 0.2 mL.

Weak Acid with Strong Base

A weak acid starts higher, because only a fraction of it is ionized: 0.100 mol L^{-1} CH_3COOH opens at pH 2.88, not 1.00. Its curve climbs gently through a long buffer region, where added OH^- converts HA into A^- and both members stand together under the ratio behavior of Topic 8.4.

Half-equivalence. At half the equivalence volume, exactly half the acid has been converted, so [HA] = [A^-] and pH = pKa. Read the pH there and you have the pKa, hence the Ka.

At equivalence every HA has become A^-, and A^- is a weak base:

$CH_3COO^- + H_2O \rightleftharpoons CH_3COOH + OH^-$

$K_b = K_w / K_a$

The hydrolysis produces OH^-, so the equivalence pH sits above 7. Its size depends on [A^-]: initial moles over total volume, analyte plus titrant. Past equivalence, excess OH^- takes over.

Weak Base with Strong Acid: The Mirror Image

Titrating NH_3 with HCl is the mirror image. The initial pH is set by the weak base equilibrium; through the buffer region NH_3 and NH_4^+ stand together, and at half-equivalence pOH = pKb, here 4.74, giving pH 9.26.

At equivalence all the NH_3 has become NH_4^+, a weak acid with $K_a = K_w / K_b = 5.6 \times 10^{-10}$, so the pH falls below 7. Past equivalence, excess H_3O^+ sets the pH.

Indicators: Put the Color Change Inside the Steep Section

An indicator changes color over a range of about two pH units. It works only if that range falls inside the steep section, so the color flips within a drop of equivalence.

For strong acid with strong base the steep section spans many units, so methyl orange (pH 3 to 4) and phenolphthalein (pH 8 to 10) both fit. For a weak acid with a strong base the steep section sits on the basic side and phenolphthalein is the fit; methyl orange would change color early, inside the buffer region, long before equivalence. For a weak base with a strong acid the steep section is acidic and methyl orange fits; phenolphthalein fades during the buffer region, again too early.

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Polyprotic Acids: One Equivalence Point per Proton

A polyprotic acid gives up its protons one step at a time:

$H_2A \rightarrow HA^- \rightarrow A^{2-}$

and its curve shows one equivalence point per dissociable proton. Fully neutralizing one mole of H_2A takes two moles of OH^-, so 25.0 mL of 0.100 mol L^{-1} H_2A needs 50.0 mL of 0.100 mol L^{-1} NaOH to reach the second equivalence point. If the two Ka values lie close together, the two steep rises merge.

Worked Examples

Example 1: Three points on a strong acid curve. 50.0 mL of 0.100 mol L^{-1} HCl is titrated with 0.100 mol L^{-1} NaOH, starting with 0.00500 mol of H_3O^+. After 30.0 mL of NaOH, 0.00300 mol of OH^- has been added, leaving 0.00200 mol of H_3O^+ in 80.0 mL: $[H_3O^+]$ = 0.0250 mol L^{-1} and pH = 1.60. Equivalence comes at 50.0 mL, pH 7.00. After 60.0 mL the titrant is in excess by 0.00100 mol of OH^- in 110 mL: $[OH^-] = 9.09 \times 10^{-3}$ mol L^{-1}, pOH = 2.04, pH = 11.96.

Example 2: The weak acid curve, point by point. 25.0 mL of 0.100 mol L^{-1} CH_3COOH ($K_a = 1.8 \times 10^{-5}$) is titrated with 0.100 mol L^{-1} NaOH. Initially the acid's own equilibrium rules: the quadratic gives $[H_3O^+] = 1.33 \times 10^{-3}$ mol L^{-1} and pH = 2.88 (the square root approximation gives 2.87, since ionization is only 1.3 percent). Half-equivalence arrives at 12.5 mL with pH = pKa = 4.74. Equivalence arrives at 25.0 mL, where $[CH_3COO^-]$ = 0.00250 mol / 0.0500 L = 0.0500 mol L^{-1}; with $K_b = 5.6 \times 10^{-10}$, $[OH^-] = 5.3 \times 10^{-6}$ mol L^{-1}, pOH = 5.28 and pH = 8.72.

Example 3: Three-quarters neutralized. 25.0 mL of 0.100 mol L^{-1} CH_3COOH is titrated with 0.100 mol L^{-1} NaOH. Equivalence needs 25.0 mL, so after 18.8 mL three-quarters of the acid has become acetate: $[A^-] / [HA] = 3$, and pH = 4.74 + log 3 = 4.74 + 0.48 = 5.22.

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Example 4: The weak base curve, point by point. 25.0 mL of 0.100 mol L^{-1} NH_3 (Kb = 1.8 × 10^{-5}) is titrated with 0.100 mol L^{-1} HCl. Half-equivalence arrives at 12.5 mL with pOH = pKb = 4.74, so pH = 9.26. Equivalence arrives at 25.0 mL, where $[NH_4^+]$ = 0.00250 mol / 0.0500 L = 0.0500 mol L^{-1}; with Ka = 5.6 × 10^{-10}, $[H_3O^+]$ = 5.3 × 10^{-6} mol L^{-1} and pH = 5.28, below 7.

Traps That Cost Marks in Topic 8.5

"The endpoint is the equivalence point." The endpoint is where the color changes; the equivalence point is the mole condition. They coincide only with the right indicator.

"Equivalence means pH 7." Only when both partners are strong: CH_3COO^- pushes the pH above 7, NH_4^+ pulls it below.

Forgetting that the titrant dilutes the flask. At equivalence the conjugate base is not 0.100 mol L^{-1}: its moles spread through analyte plus titrant volume. Post-mixing concentrations always need the total volume.

Using Ka where Kb belongs. At a weak acid titration's equivalence point the species present is A^-, which hydrolyzes with Kb = Kw / Ka. The acid's own Ka describes a solution that no longer exists.

Reading half-equivalence as equivalence. Half the equivalence volume is the buffer midpoint, where pH = pKa and half the analyte is still unreacted.

Stopping a diprotic titration at one equivalent. One mole of OH^- per mole of H_2A reaches only the first equivalence point, leaving HA^-.

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Key Relationships to Remember

- Equivalence point: moles of titrant exactly match the equation's demand; endpoint: the indicator's color change
- Strong acid with strong base: pH 7.00 at equivalence; before it, leftover H_3O^+ over total volume; after it, excess OH^- over total volume
- Weak acid with strong base: buffer region before equivalence; at half-equivalence pH = pKa; at equivalence A^- hydrolyzes with Kb = Kw / Ka and pH > 7
- Weak base with strong acid: mirror image; at half-equivalence pOH = pKb; at equivalence BH^+ hydrolyzes with Ka = Kw / Kb and pH < 7
- A curve hands you the constant: pH at half the equivalence volume is the pKa
- Indicator rule: the color change range must fall inside the steep section around the equivalence point
- Polyprotic acids: one equivalence point per dissociable proton
- Everywhere on the curve: compare moles first, then choose the calculation the region demands

Continue Revising

Topic 8.5 Quiz: Acid-Base Titrations

Topic 8.5 Worksheet

Unit 8: All Topics

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